Supervisor: Dr. Reginald H. Mitchell

ABSTRACT

The existence of the reactive intermediate *trans*-10b,10c-dimethyl-10b,10c-dihydropyr-1-yne, **57**, generated via dehydrobromination, was proved by trapping with N,N-diethyl-1,3-butadienylamine, furan and a series of isoannelated furans. Comparison of **57** with benzyne, **1**, was implemented using the results of MMX/PCMODEL calculations.

A fast route to annelated dihydropyrenes was developed via the reactive intermediate **57**. Through this route, five annelated dihydropyrenes, namely, *trans*-14b,14c-dimethyl-14b,14c-dihydronaphtho[2,1,8-*qra*]naphthacene, **204**, *trans*-16b,16c-dimethyl-16b,16c-dihydrobenzo[a]naphtho[2,1,8-*fgh*]naphthacene, **206a**, *trans*-16b,16c-dimethyl-16b,16c-dihydrobenzo[a]naphtho[2,1,8-*hij*]naphthacene, **206b**, *trans*-14b,14c,18b,18c-tetramethyl-14b,14c,18b,18c-tetrahydrodinaphtho[2,1,8-*uva*; 2,1,8-*jkl*]pentacene, **224a**, and *trans*-15b,15c,18b,18c-tetramethyl-15b,15c,18b,18c-tetrahydrodinaphtho[2,1,8-*uva*; 2,1,8-*pon*]pentacene, **224b**, and one bridged oxa[17]annulene, namely, *trans*-11b,11c-dimethyl-11b,11c-dihydropyreno[1,2-*c*]furan, **222**, were synthesized.

Metal complexation of the benzo[a]dihydropyrene **95** was investigated. This led to the first two metal dihydropyrene complexes, namely, [7,8,9,10,10a,10b-η^6]-*trans*-12b,12c-dimethyl-12b,12c-dihydrobenzo[a]pyrenechromium(0)-tricarbonyl, **239**, and [1,2,3,3a-η^4]-*trans*-12b,12c-dimethyl-12b,12c-dihydrobenzo[a]pyreneiron(0)tricarbonyl, **209**. The delocalization effects due to complexation were studied.

Combining the results of the newly synthesized annelated dihydropyrenes with previously obtained ones, a series of correlations between theoretical calculations and experimental results, such as bond order vs. chemical

shift, bond order vs. coupling constant, and ring current vs. chemical shift were devised.

The *ortho*-metalation of dihydropyrene derivatives and synthesis of 1-bromo-2-fluoro-dihydropyrene were attempted. This led to two new dihydropyrene derivatives, namely, trimethylacetamino-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, **99**, and 2-diethylcarbamyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, **109**, and two new cyclophane derivatives, namely, *syn*-5-bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, **131a**, and *anti*-5-bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, **131b**.

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Table of Contents

APPENDIX

The completed results of π-SCF and PCMODEL/MMX calculations of the compounds mentioned in this thesis are available on request at the following address:

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List of Figures

List of Tables

List of Abbreviations

BuLi	butyllithium
^{13}C nmr	carbon-13 nuclear magnetic resonance
DIBAL	diisobutylaluminium hydride
DMF	dimethylformamide
Et	ethyl
EtOH	ethanol
IR	infrared
^{1}H nmr	proton nuclear magnetic resonance
br	broad
s	singlet
d	doublet
t	triplet
dd	doublet of doublets
m	multiplet
ppm	parts per million
Me	methyl
MeOH	Methanol
mp	melting point
MS	mass spectrum
CI	chemical ionization
EI	electron impact
Ph	phenyl
THF	tetrahydrofuran
UV	ultraviolet

Acknowledgement

I would like to express my sincere thanks to Dr. R. H. Mitchell for his encouragement and guidance through this project.

I am indebted to my colleagues and friends, especially V. Iyer, for their suggestions and supports, without which this work would not have been completed.

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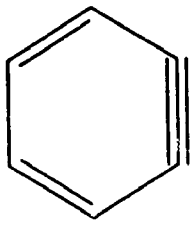
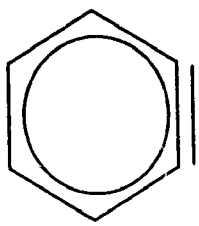
CHAPTER ONE GENERAL INTRODUCTION

1.1 Arynes:

Arynes are aromatic compounds with two adjacent ring hydrogen atoms removed and contain a formal C-C triple bond. Benzyne, **1**, is the simplest and best known member of the series. It is a highly reactive species because of the exceedingly strained triple bond. The study of this reactive intermediate has been one of the most fruitful and exciting areas of chemical research. Benzyne has been mostly described as two structures **1a** and **1b**, the most common being **1a**, from which the 'yne' nomenclature is derived. Although the molecule does not contain the full triple bond shown in **1a**, the structure and the name are useful as a means of depicting and dealing with arynes as a class because its chemistry is in many respects like that of a highly reactive alkyne.

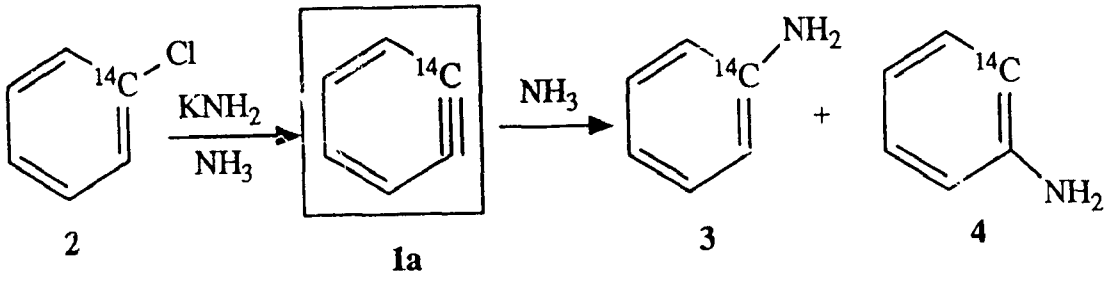


1a



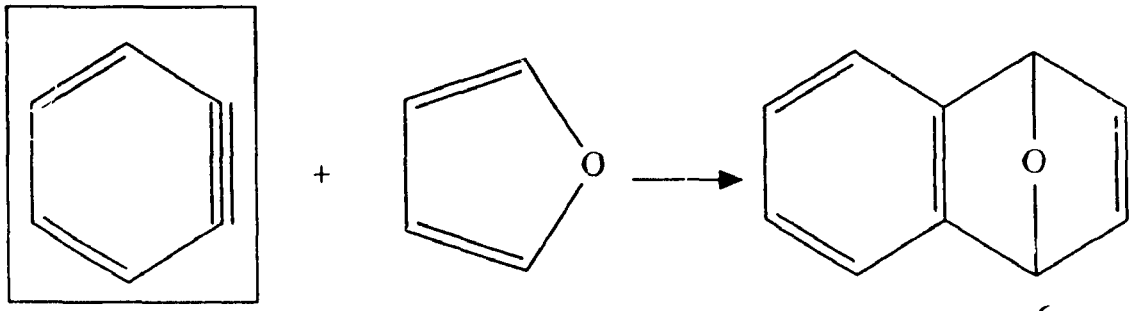
1b

Historically, benzyne was first postulated to explain unexpected experimental results. The first proof for the existence of benzyne was given by the ^{14}C labeling experiment indicated below[1]:



2 1a 3 4

Amination of chlorobenzene with potassium amide in liquid ammonia leads to equal amounts of [1-^{14}C]-aniline, **3**, and [2-^{14}C]-aniline, **4**, a result which demonstrated that a symmetrical intermediate, i.e., benzyne, had been present. This was also confirmed by Wittig[2] by trapping benzyne with a diene in a Diels-Alder reaction, e.g., with furan, **5**.

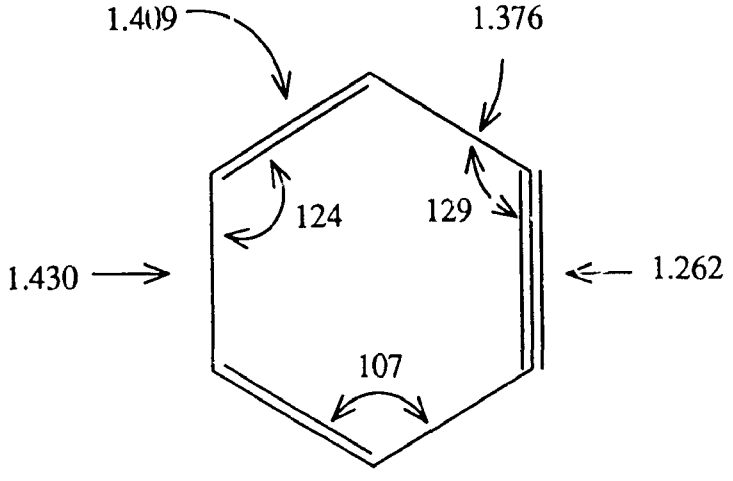


1a 5 6

More recently[3], benzyne has been directly observed in the matrix photolysis of phthaloyl peroxide at 8K. Calculations (MMX/PCMODEL2[4]) predict that benzyne has a short (acetylenic) C1-C2 bond and large 1-2-3 and 6-1-2 bond angles (Figure 1)[4]. These results are supported by reactivity data and the IR spectrum[5], which shows a C-C triple bond absorption at 2085 cm^{-1}.

A short general survey of the generation and reactions of arynes will be presented before their application to our system is discussed.

Figure 1. Bond lengths and angles of benzyne



Distance in Å, Angles in degrees

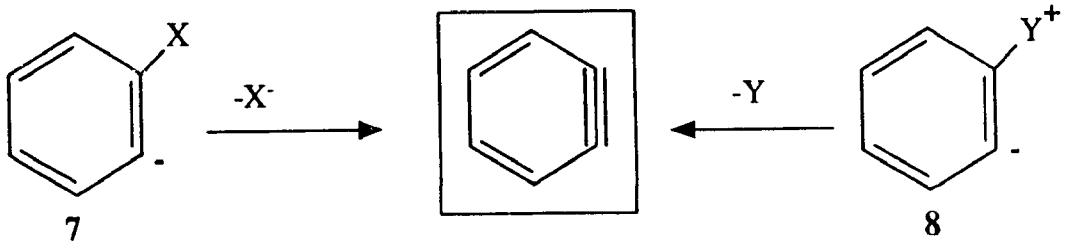
1a

1.1.1 Generation:

The most convenient and common method to generate an aryne is by dehydrohalogenation of a haloaromatic compound using a strong base. This however imposes severe limitations on the reactions which can be studied, since the generated aryne is often rapidly consumed by reaction with the base, rather than reacting with any added reagent. Therefore, much effort has been made to generate arynes using non-basic and mild reaction conditions.

Routes to arynes can be summarized into two main categories: (i) the elimination of an aryl anion with an adjacent leaving group (Scheme 1), and (ii) the fragmentation of a cyclic system ortho-fused to the arene ring (Scheme 2).

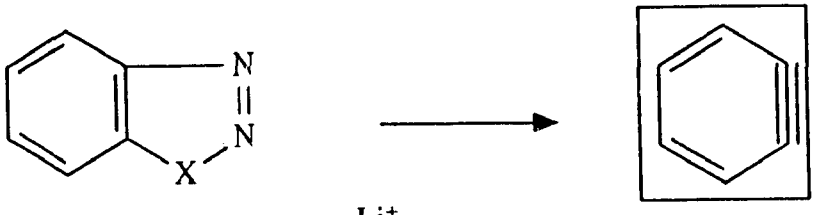
Scheme 1



7 8

X = halogen, OPh, OTs, ClO_3 ; Y = N_2 , NR_3, SR_2, IR.

Scheme 2



1a

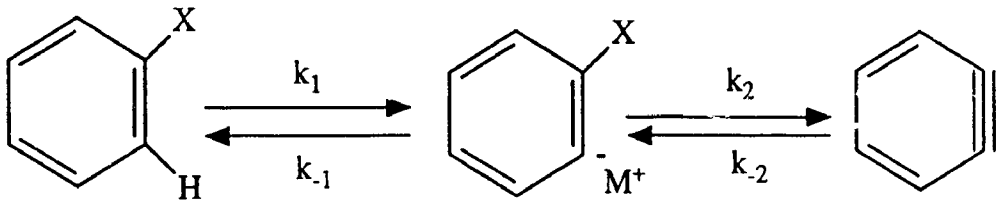
X = NNH_2 , Li^+ $^-N\text{-}N\text{-}N_2NHTs$, or SO_2

9 10 11

(i) Dehydrohalogenation

Because halogenoarenes are easily accessible, halides are the most commonly used anionic leaving group (Scheme 3).

Scheme 3



12 **13** **1a**

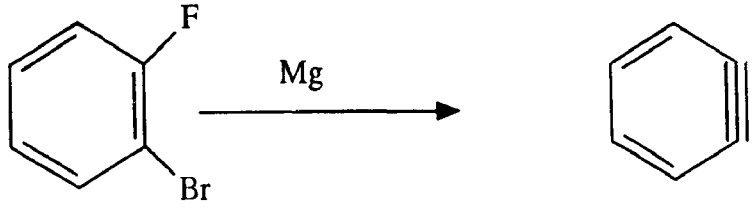
X = halogen

A variety of bases has been used to accomplish the metallation step (k_1) in scheme 3; the weaker the base the higher is the temperature required. For example, chlorobenzene is converted to phenol with aqueous sodium hydroxide at *ca.* 250°C, while the stronger potassium t-butoxide only requires *ca.* 150°C[6]. The metallic amides, such as sodium amide and lithium piperidide, are now more often used because they are strong, convenient to prepare, and can be used over a wide temperature range. It has been found that the reaction can be catalyzed by increasing the cation solvation with free amines, such as piperidine and N,N,N',N'-tetramethylethylenediamine[7]. Lithium tetramethylpiperidide renders better yields of products in both aryne-diene and aryne-nucleophile reactions[8].

Apart from base strength, the acidity of the proton to

be abstracted also plays an important role in the rate of metallation (k_1). Substituent inductive effects, both of the ortho halogen and of other ring substituents, are straightforward, i.e., electron donating substituents should retard the rate of metallation; electron withdrawing groups speed it, e.g., fluorobenzene metallates faster than the other halobenzenes[9].

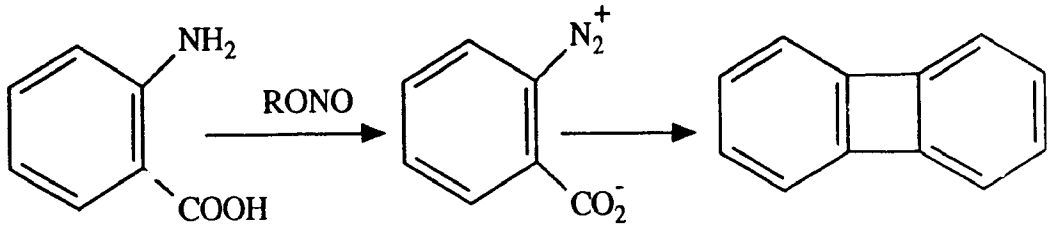
The rate of halide loss step (k_2) also depends on many factors, particularly on the nature of the halogen, the metal, the solvent, and other ring substituents. the rate found is in the expected order: I>Br>Cl>F. However, the same order is found for the reverse (k_{-2}) reaction, so that the net effect k_2/k_{-2} of bromide is larger than iodide, chloride and fluoride[10]. Substituents which are able to stabilize the anion, reduce k_2 and vice versa[10]. The effect of the metal is also important, e.g., on passing from lithium to magnesium, the stability of the intermediate **13** increases but the rate of halide loss is in reversed order, F>Cl>Br[10].



14

Many methods which involve aryl anions have been developed to synthesize arynes[10]. An important example was discovered by Wittig[11] and synthesizes benzyne by metal-halogen exchange of an o-dihalogenobenzene, e.g., 14, with either lithium amalgam or magnesium.

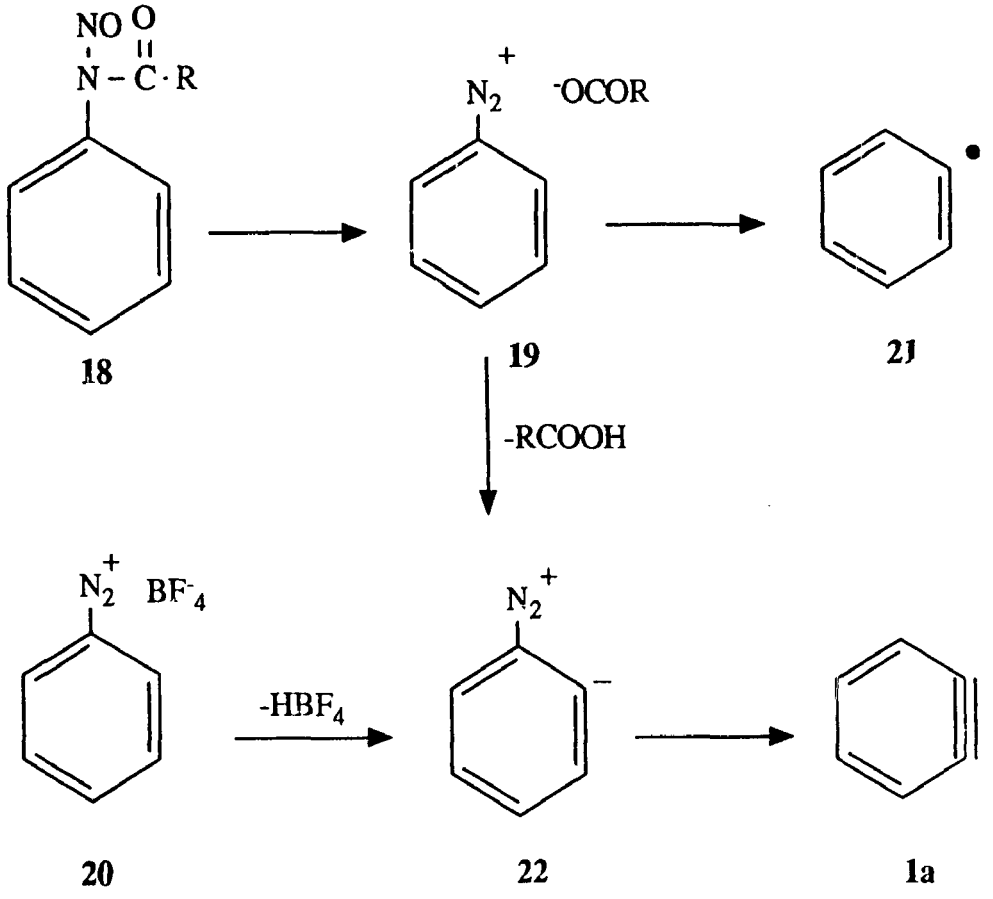
Aprotic diazotization of anthranilic acid, **15**, has also been developed as one of the major synthetic routes to benzyne since its discovery in 1960 by Stiles[12]. The intermediate benzenediazonium-2-carboxylate, **16**, is explosively unstable, but if it is kept wet with the solvent, and isolated at $0^{o}C$, it provides a clean source of benzyne for reactions on a small scale[13]. A major advantage of this reaction is the absence of a strongly basic reaction environment. Biphenylene, **17**, has been synthesized readily by refluxing **16** in 1,2-dichloroethane[13].



15 **16** **17**

It has been found that certain N-nitroso-anilides **18**, when decomposed in solution form arynes via the corresponding rearranged diazonium acetates **19**. This

reaction is in competition with the well known route to aryl radicals, **21**[14]. Benzyne has been formed from diazonium salts **19** and **20** using a mild base such as potassium acetate. It can then be trapped in good yield with trapping reagents[15]. However, biphenylene, **17**, can not be obtained through this route.



(ii) Fragmentation of cyclic systems:

There are a large number of ring systems known which give arynes photochemically or thermally. The severity of the conditions varies from low temperature to flash vacuum pyrolysis at 1000°C and obviously depends on the stability

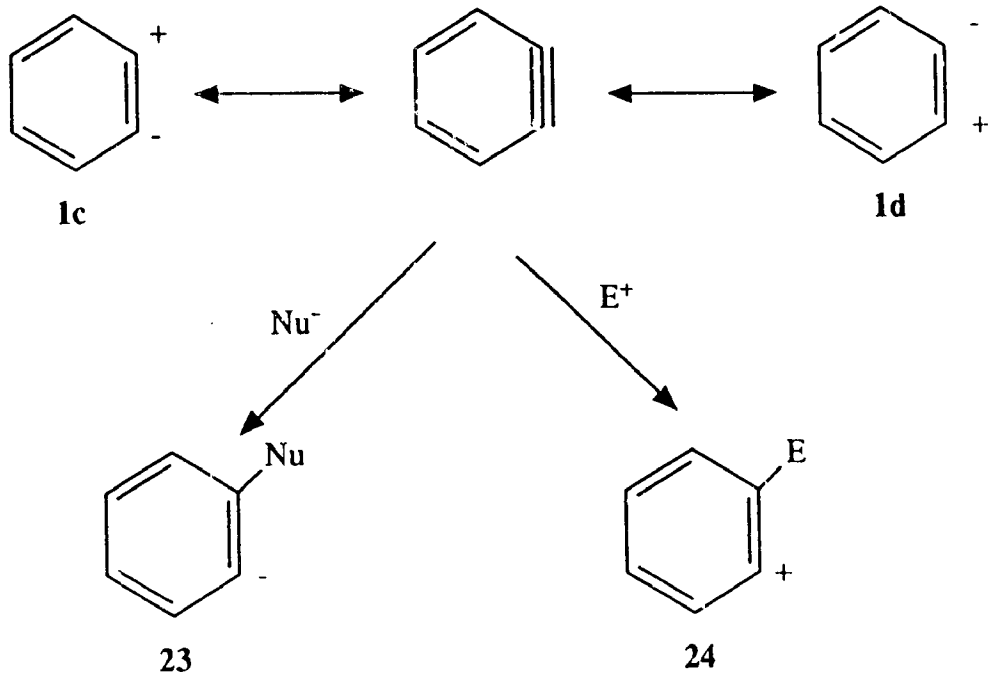
of the cyclic system[10]. Some of these reactions have been used in organic syntheses, e.g., 1-aminobenzotriazole, **9**, which is stable and safe for storage, gives benzyne in excellent yield under oxidative conditions, even at -80°C[16]. This reaction has been used in the generation of substituted arynes, naphthalynes and phenanthryne and has produced biphenylene in the best yield[16].

The highly unstable lithium salt **10**, decomposes rapidly at or below room temperature to give benzyne. This dimerizes to biphenylene in the absence of a trapping reagent, or gives up to 65% of the trapped product[17]. 1,2,3-Benzothiadiazole-1,1-dioxide, **11**, decomposes thermally at 20°C, or photochemically at -50°C, to nitrogen, sulfur dioxide and benzyne. The latter has been trapped with dienes in up to 54% yield[18]. A disadvantage of this route is that the substituted starting materials are not easily accessible.

1.1.2 Reactions:

Arynes are bifunctional reactive intermediates which can form two new bonds in a reaction. Comparison of arynes with carbenes and 1,3-dipoles, indicates that the two newly formed bonds are on adjacent atoms in benzyne, on the same carbon atom in carbenes, and are three atoms apart in 1,3-dipoles.

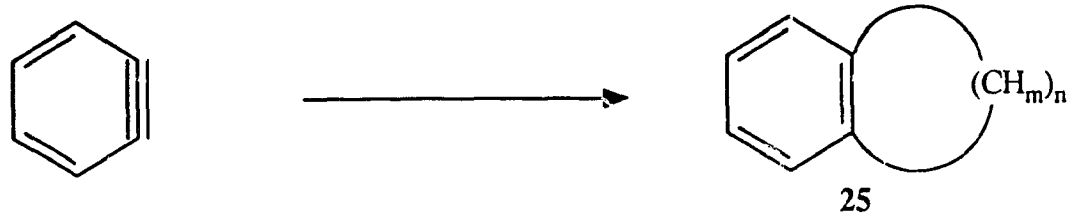
The triple bond in an aryne is easily polarized to the ionic structures **1c** and **1d** by an approaching ion or dipole. Therefore they are highly reactive towards polar additions, i.e., either nucleophilic additions to give **23** or electrophilic additions to give **24**.



$Nu^- = H^-$, RNH^-, RO^-, Ar^-; $E^+ = Br^+ (Br_2)$, $I^+ (I_2$ or ICl)

An important application of benzyne in organic synthesis is to produce a variety of benzocyclic systems **25** through cycloadditions. The lowest example of the series represented by **25** is benzocyclopropenes **27**, which is stable at room temperature[19], but has not yet been synthesized

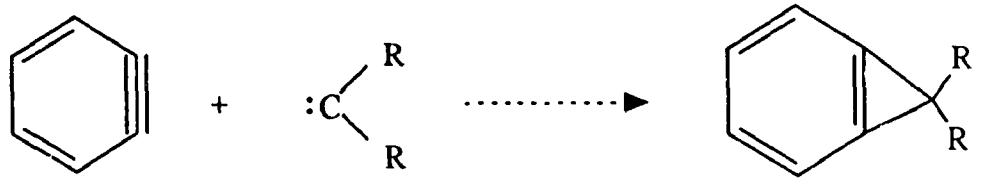
through addition of benzyne to a carbene, **26**. This route should be possible if the two short-lived intermediates could be generated at the same time in high concentration.



25

m = 1 or 2

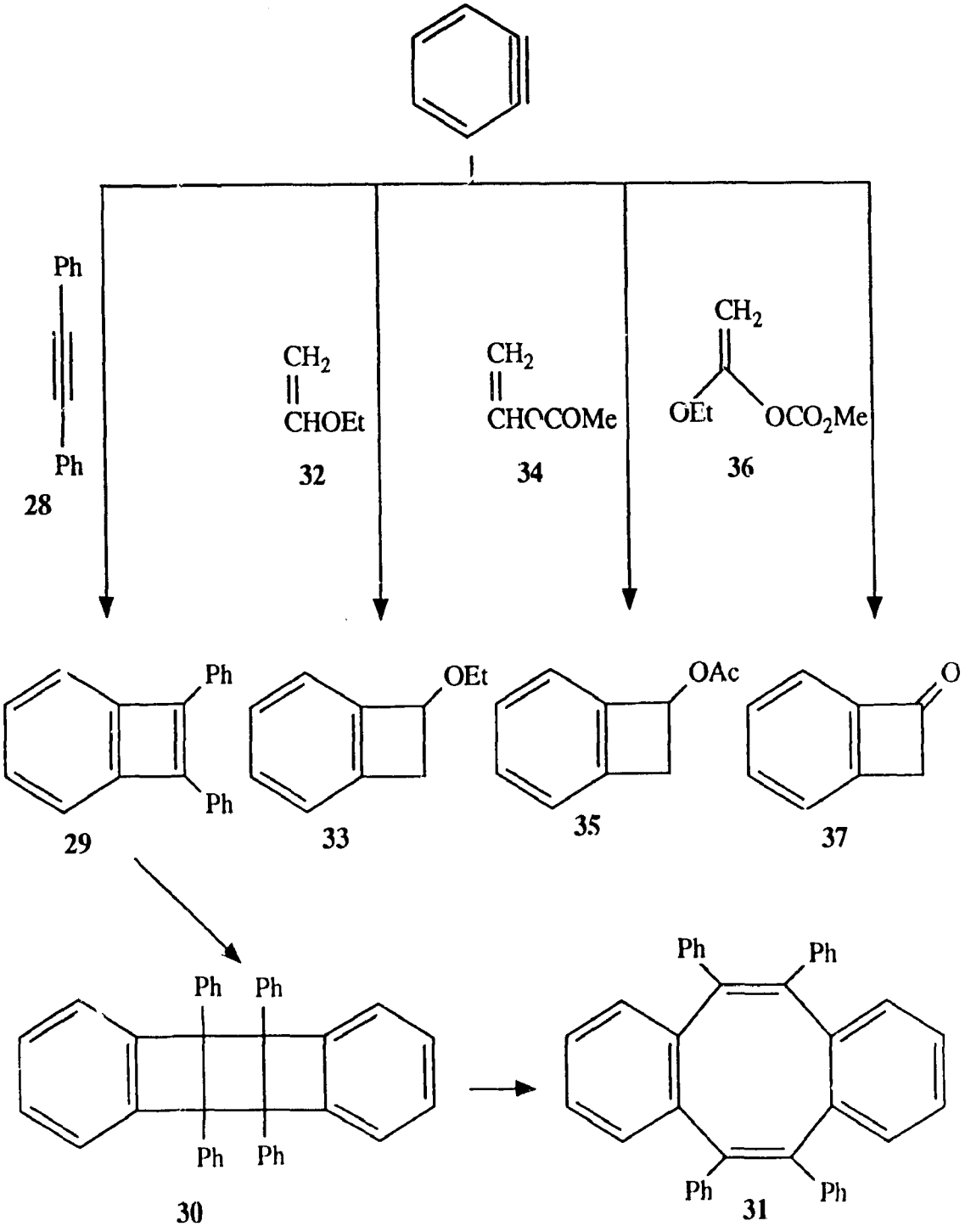
n = 1, 2, 3, or 4



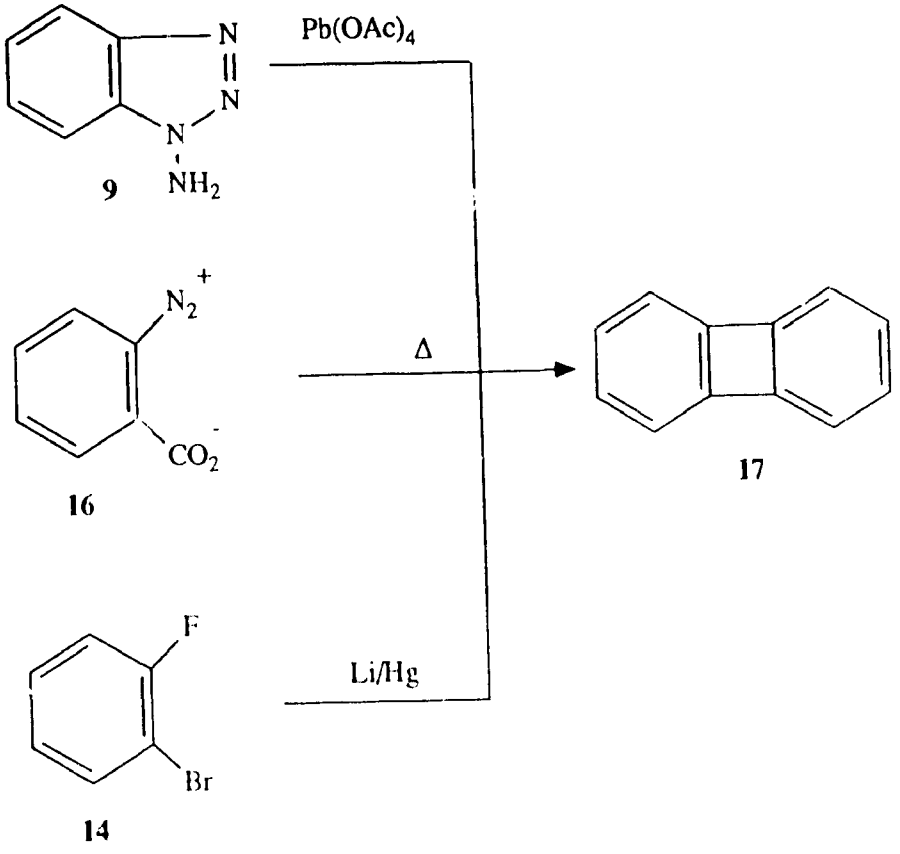
26 **27**

Arynes can undergo [2+2] additions to give four-membered ring compounds in a similar manner to alkynes. When an acetylene is added, the product benzocyclobutadiene is not stable, and gives further addition products, e.g., the formation of tetraphenyl-dibenzocyclooctatetraene, **31**, presumably arises through the diphenylbenzocyclobutadiene **29**, which dimerizes to **30** and finally isomerizes to **31**. Arynes have also been trapped by alkenes, leading to benzocyclobutenes. Electron-rich alkenes give better yields of the products than normal

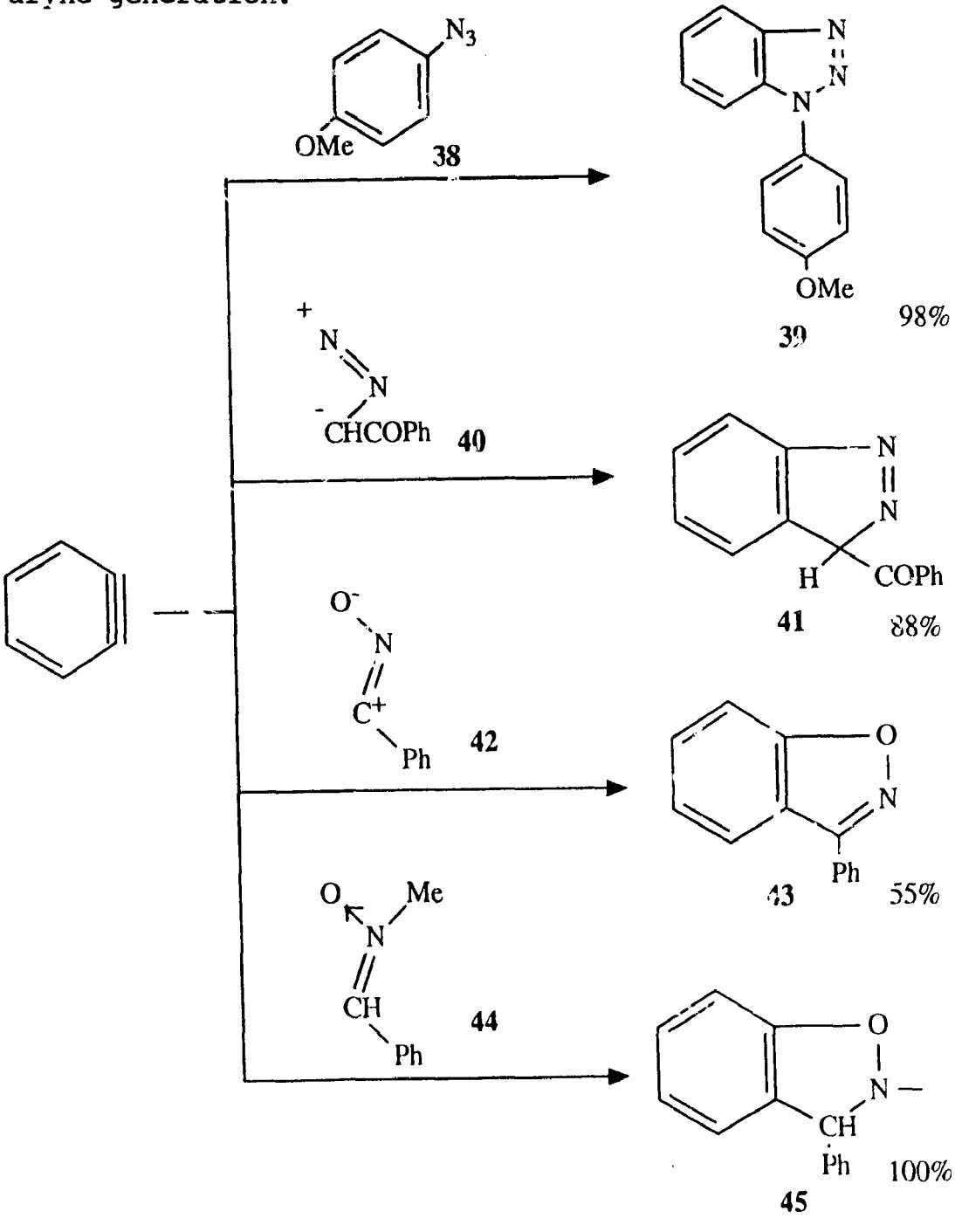
ones. For example, the benzocyclobutene derivatives, **33**, **35**, and **37**, were obtained in up to 45% yield[21].



Dimerization of benzyne only gives biphenylene, **17**, in detectable yield when the local concentration of benzyne is high and that of other species which might react with benzyne is low. Thus, oxidation of 1-aminobenzotriazole, **9**, with lead tetraacetate, matches those conditions well, and gives biphenylene, in *ca.* 90% yield[16]. Thermal decomposition of benzenediazonium-2-carboxylate, **16**, yields 25-30% of biphenylene on a preparatory scale[13]. Sizeable yields of biphenylene are also obtained from o-dihalogenobenzenes and certain metals. Dimerization of benzyne occurs near the metal surface where the concentrations of benzyne are reasonably high[11]. These three methods have been widely used in syntheses of biphenylene.

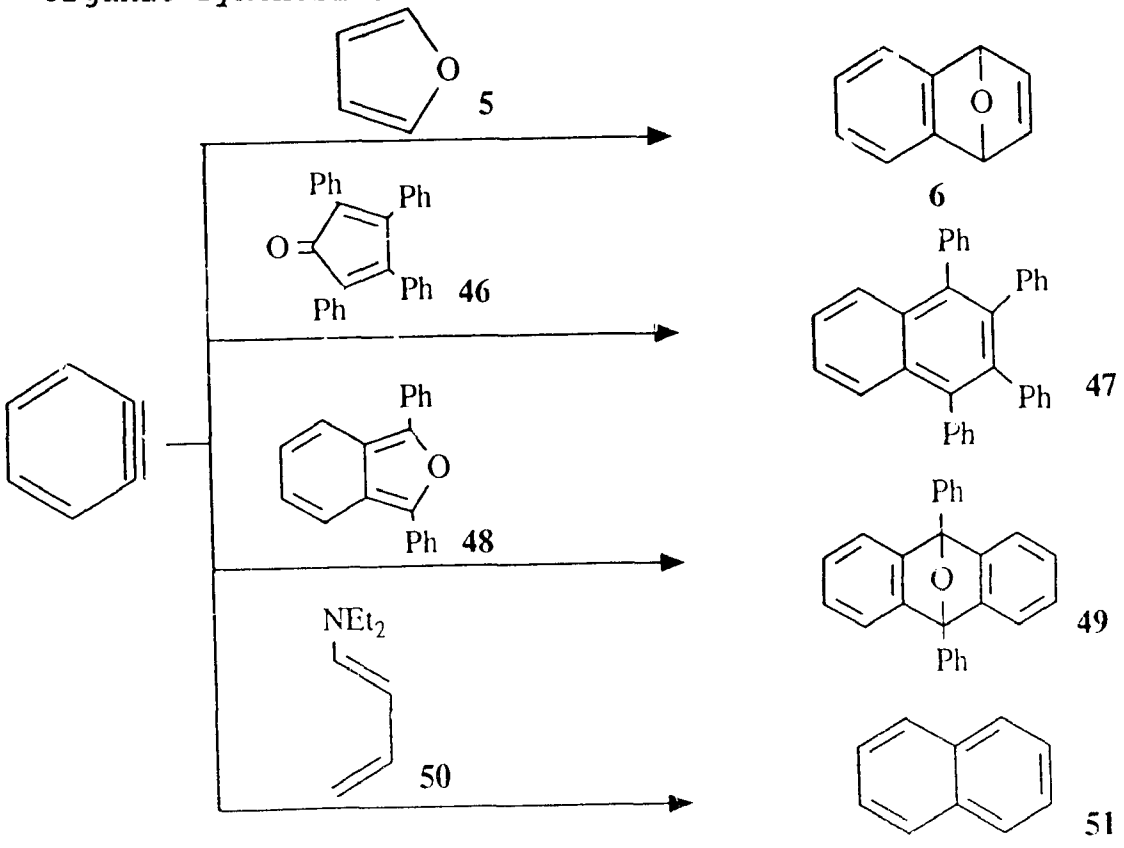


1,3-Dipolar cycloadditions, of arynes are very versatile and useful reactions, particularly in the synthesis of heterocyclic compounds. The limitation of this reaction is that the 1,3-dipolar species must be sufficiently stable under the conditions necessary for aryne generation.



As an illustration of this, benzyne reacts with a series of azides to give benzotriazole derivatives, in which the highest yield was obtained with electron-rich azides, such as 4-methoxyphenylazide, **38**[10]. Similarly, 3-benzoylindazole, **41**, was obtained in 88% yield from benzyne and benzoyldiazomethane, **40**[22]. It is also found that benzyne can be trapped with benzonitrile oxide, **42**, to give 3-phenylbenzisoxazole, **43**, in a yield of 55%[22]. Interestingly, a quantitative yield of the benzisoxazole **45** was achieved by [2+3]-cycloaddition of benzyne with benzylidene methylamine-N-oxide, **44**[20].

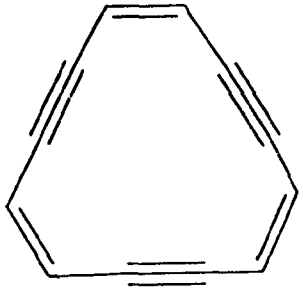
The Diels-Alder reaction, [2+4]-cycloaddition of arynes has been most intensively studied and widely used in organic synthesis.



It also has been used to prove the intermediary nature of arynes by trapping them with a series of dienes such as furan, **5**, tetracyclone, **46**, diphenylisobenzofuran, **48**, and N,N-diethyl-1,3-butadienylamine, **50**. This reaction provides a convenient route to numerous compounds which are difficult to prepare by other means. This reaction has been extensively reviewed by Hoffmann[10].

1.2 Annulynes

Many large ring dehydroannulenes (or annulynes) such as **52** and **53**, have been synthesized as stable species[23a].



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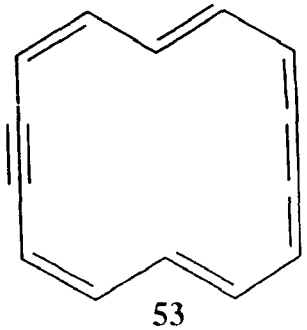
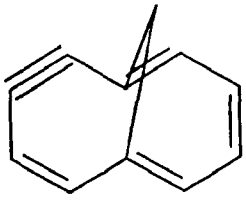
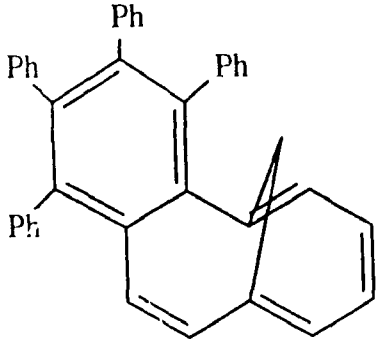


53



54



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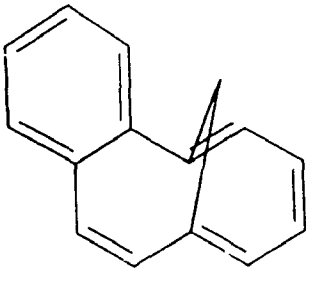

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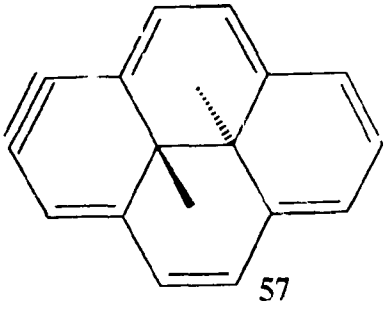

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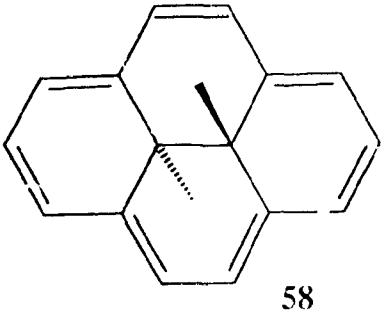


58

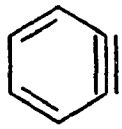
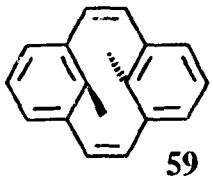
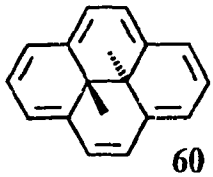
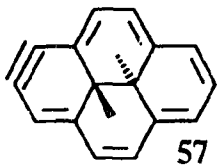
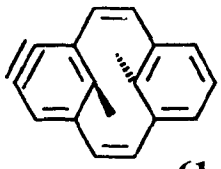
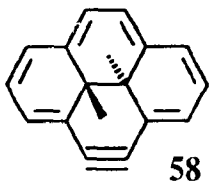
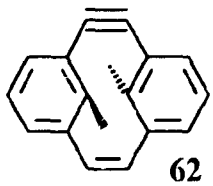
The acetylenic unit removes internal hydrogens and hence transannular steric interactions caused by the planar geometry and introduces rigidity to the ring skeleton. In these cases the large ring can accommodate the acetylenic bond without the molecule being strained. As an overall result, these compounds do not show characteristic aryne reactivity, e.g., easy cycloadditions, but are stable enough for study of their aromaticity.

To the best of our knowledge, only one large ring annulyne **54** is known as a reactive species. This has been trapped with tetracyclone, **46**, and diethylaminobutadiene, **50**, to give the products **55** and **56** in 30% and 20% yields, respectively[23b]. It is thus of interest to investigate the existence of the dihydropyrynes **57** and **58**.

The species **57** and **58** might be as reactive as benzyne, and would probably be difficult to characterize physically. To intuitively understand the essence of these species, therefore, we implemented PCMODEL2/MMX[4] calculations on **57, 58** and related species **59, 60, 61** and **62**. Some of these results are shown in Table 1.

After examining the bond angles and bond lengths, we found the compounds **57, 58, 61** and **62** have similarly predicted in-plane distortions to benzyne. Taking **57** as an example, the bond length calculated for the dehydro bond is 1.23Å, being much shorter than a normal bond in **60** (1.40Å) but definitely longer than the triple bond in the

Table 1. Selected results of PCMODEL/MMX[4] calculations

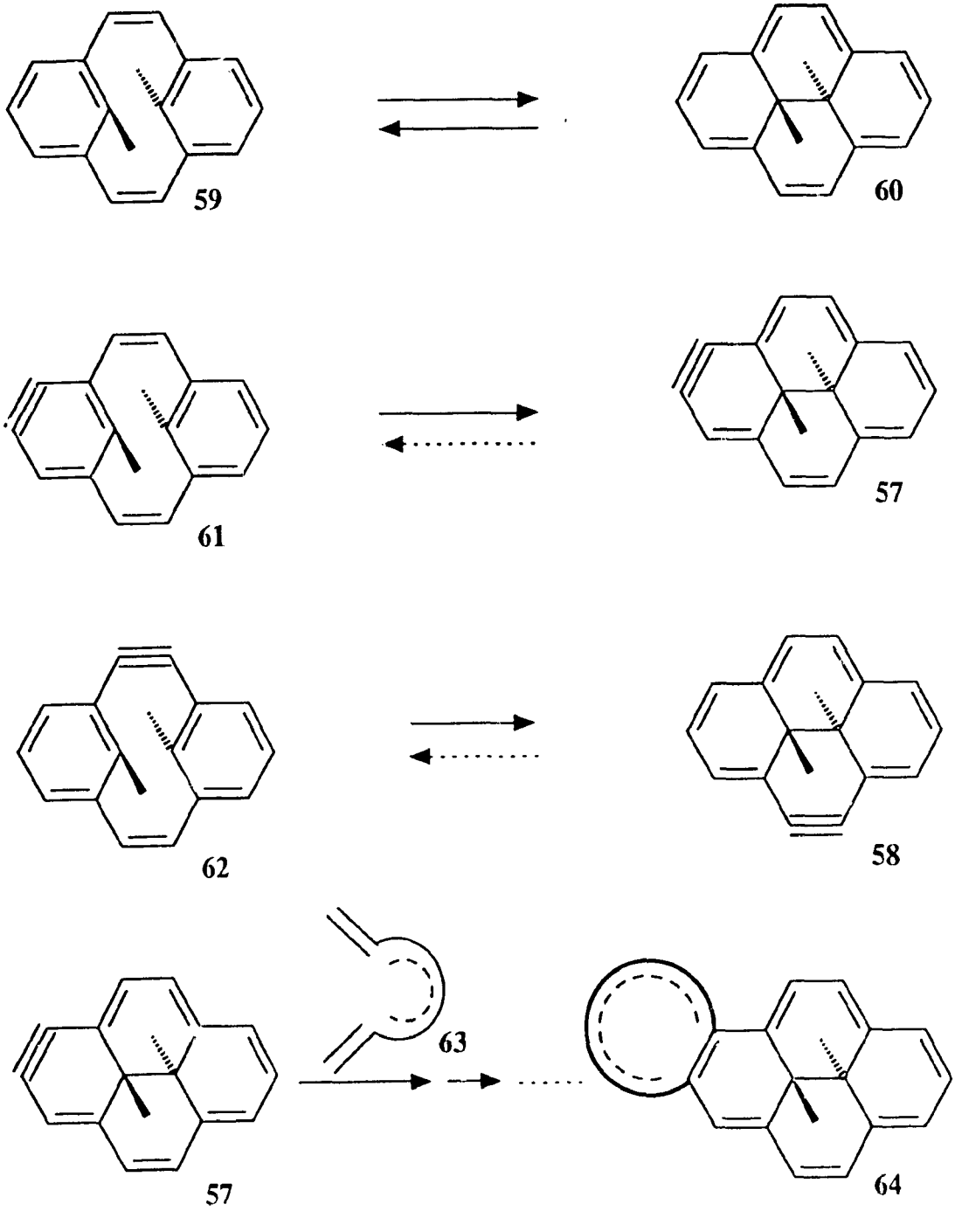
compound	C≡C bond length (Å)	SE (kcal/mol)	ΔH_f (kcal/mol)
		9	19
 **1a**	1.26	37	106
 **59**		70	89
 **60**		26	101
 **57**	1.23	56	181
 **61**	1.26	97	174
 **58**	1.23	59	182
 **62**	1.22	78	154

dehydroannulene **53**, which was found to be 1.200Å by X-ray analysis[24], the same as the value determined for a regular acetylenic triple bond. The difference in length of 0.03Å between the dehydro-bond of compounds **57** and **53** is probably due to the fact that the triple bond in **53** can be shortened without increasing strain, whereas any further shortening of the dehydro-bond in **57** is immediately opposed by increasing strain.

It is interesting to note that the compounds **57**, **58**, **61**, **62**, and benzyne have the same magnitude of strain energy difference (ΔSE kcal/mol) as well as heat of formation difference ($\Delta\Delta H_f$ kcal/mol) between the parent compound and the dehydro-compound, i.e. ΔSE=28 and $\Delta\Delta H_f$=87 for benzene and benzyne, ΔSE=30 and $\Delta\Delta H_f$=80 for **60** and **57**, ΔSE=33 and $\Delta\Delta H_f$=81 for **60** and **58**, and ΔSE=27 and $\Delta\Delta H_f$=85 for **59** and **61**, with the exception of ΔSE=8 and $\Delta\Delta H_f$=65 for **59** and **62**.

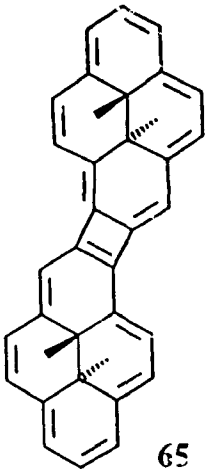
The photochemical or thermal valence isomerization of the cyclophanediene **59** to dihydropyrene **60** is a key step in the synthesis of **60**. However, we expect the compound **57** will be more favored in the equilibrium with **61** than **60** is relative to **59**, since the heat of formation differences indicate that the annulyne **57** is more stable relative to **61** by about 5 kcal/mol, than **60** is relative to **59**. In the case of **62** and **58**, on the other hand, the equilibrium may not lie on the side of **58**, since the annulyne **62** is now more

stable relative to **58** by about 6 kcal/mol, than **59** is relative to **60**. This implies that a cycloadduct of **62** may be observed in the cycloaddition under mild conditions. We have recently isolated solid **59** and it is relatively stable below 0 °C. Hence, it may be possible to observe trapped adducts of **62**.

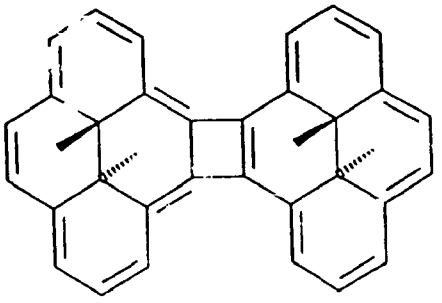


By comparison of the strain energy differences between the above pairs, the annulynes **57**, **58** and **61** should be as reactive as benzyne. Thus all the reactions of benzyne discussed previously should be shown by the dihydropyrynes **57**, **58** and by **61**. This should give us access to interesting and novel compounds which are very difficult to synthesize by other routes. For example, reaction of **57** with a diene like **63**, should give an annelated dihydropyrene **64**.

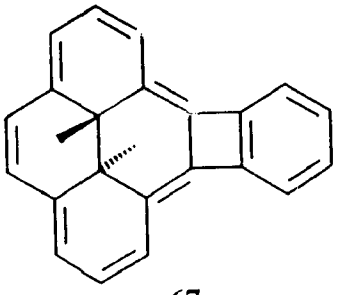
A further possibility is the dimerization of **57** or **58**, and their cross coupling with benzyne to give analogues of biphenylene, such as **65**, **66**, **67** and **68**, respectively. The localization due to the four membered ring in these compounds can then be studied using the dihydropyrene nucleus as the ring current probe[25].



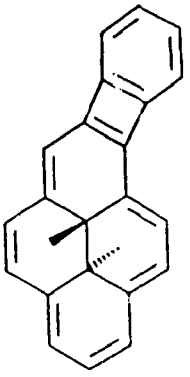
65



66

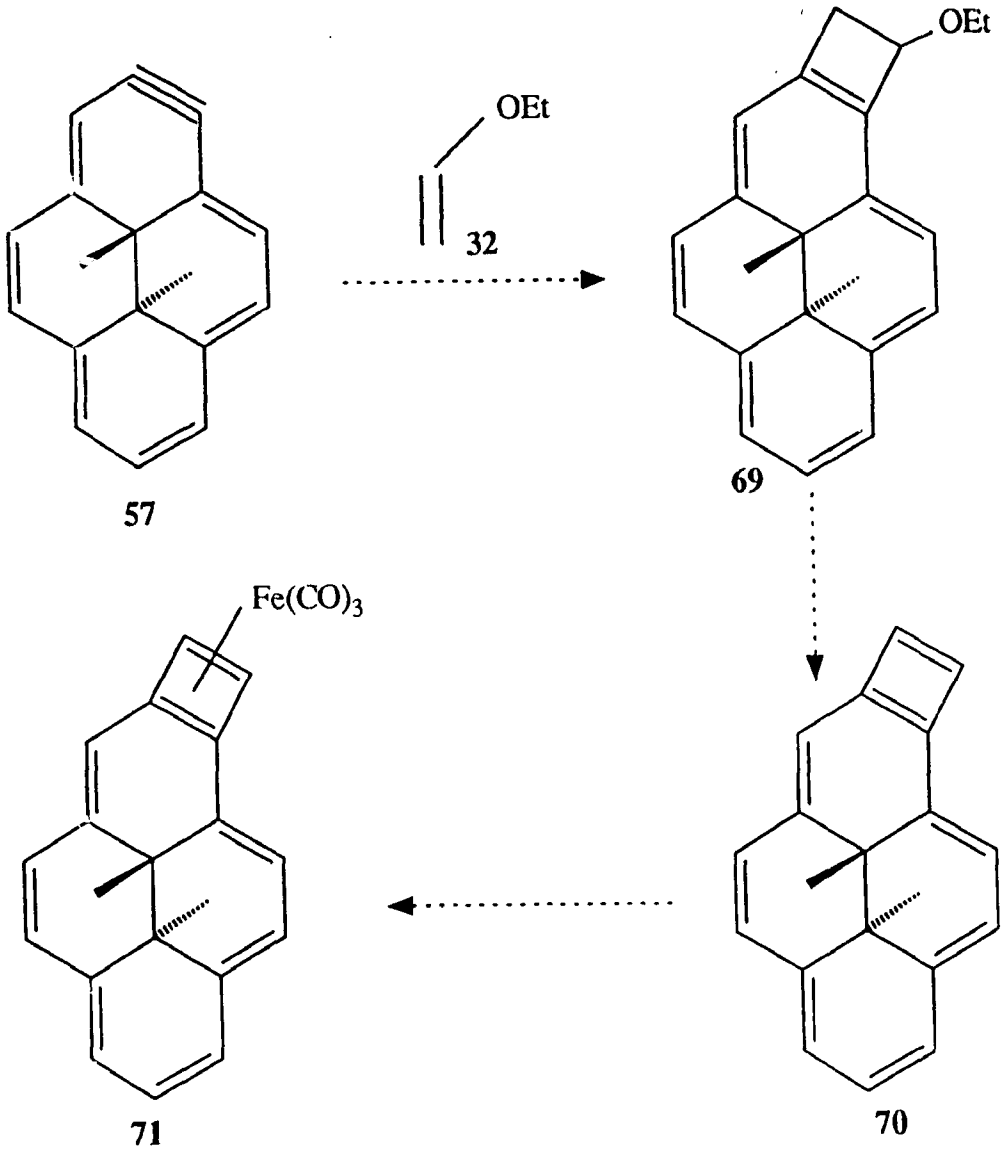


67

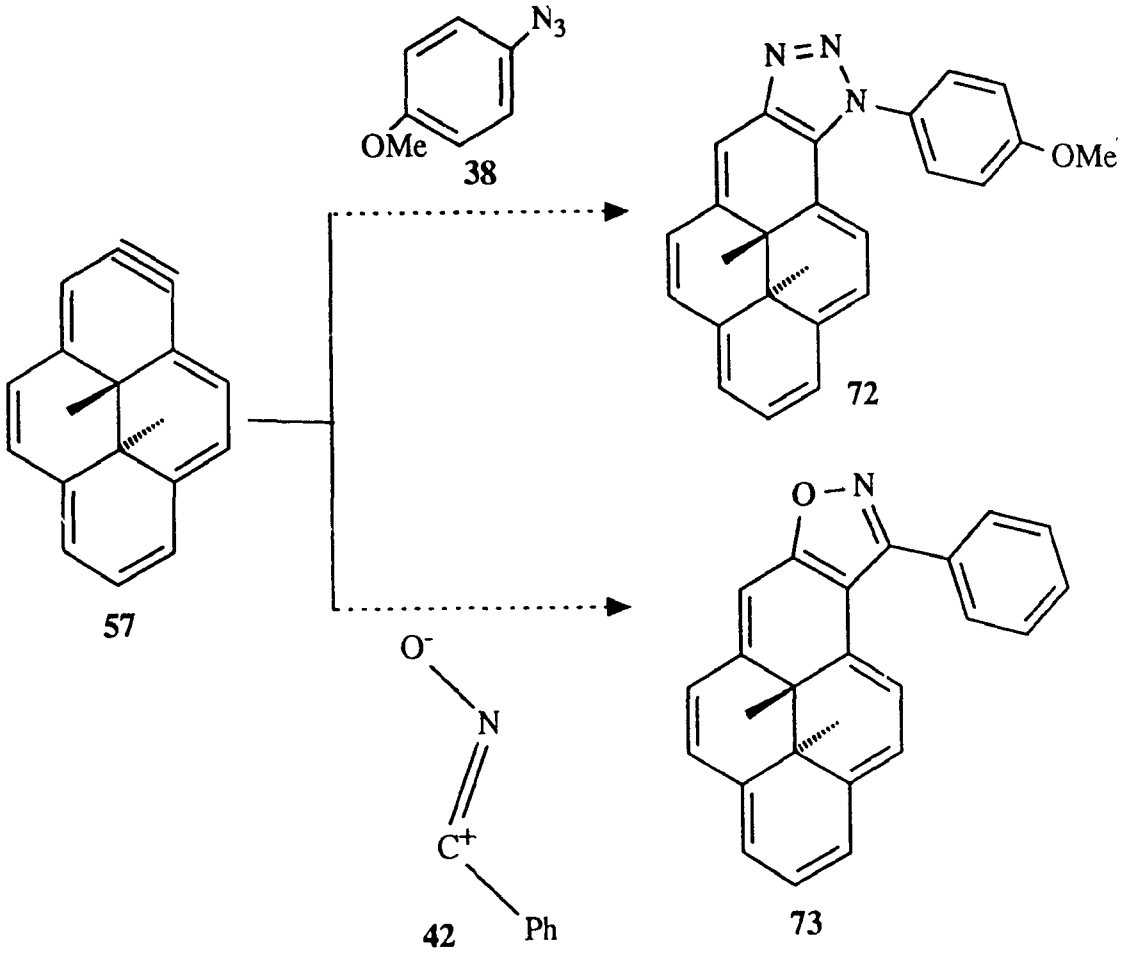


68

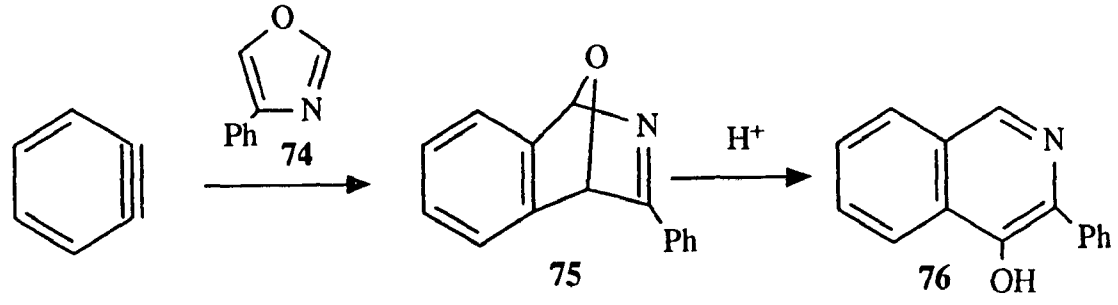
Similarly, [2+2] addition of **57** with electron rich alkenes, such as **32**, should give **69** which should subsequently be convertible to **70** and trapped with $Fe_2(CO)_9$ to yield **71**. In this compound the aromaticity of tricarbonyl cyclobutadiene iron moiety could be evaluated.

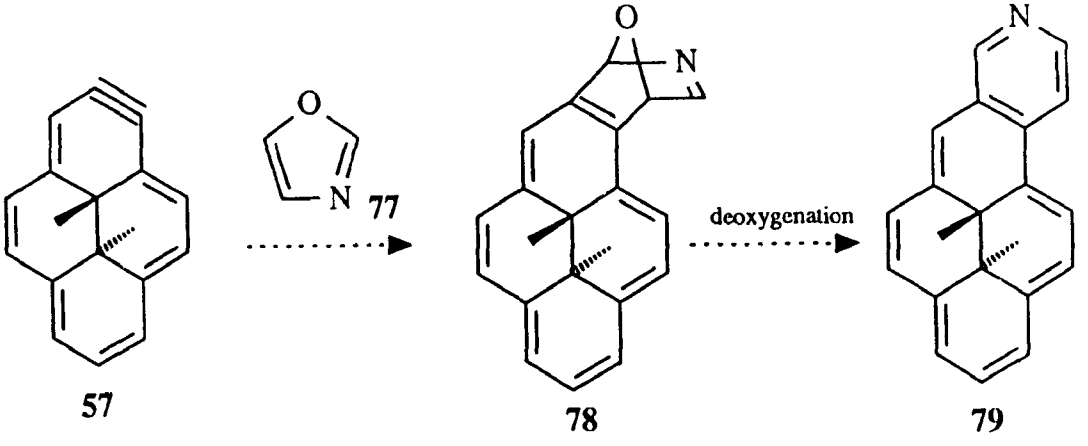


Through [2+3]-additions of **57**, a series of five membered heterocycles, such as **72** and **73**, might be obtained so that the aromaticity of these five membered rings may be probed.

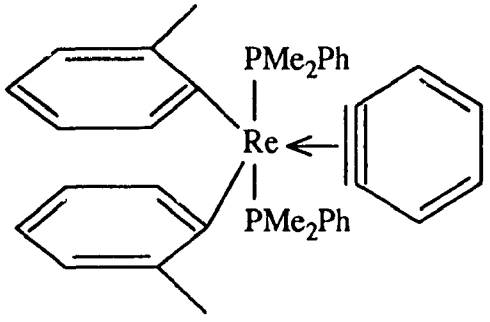


Recently, the reaction of benzyne and 4-phenyloxazole, **74**, was reported[26]. The adduct **75** was readily converted to 3-phenylisoquinolin-4-ol, **76**, under acidic conditions. Compound **79** might thus be accessible through the addition of **57** to oxazole, **77**, and subsequent deoxygenation of **78**.

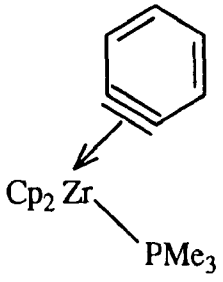




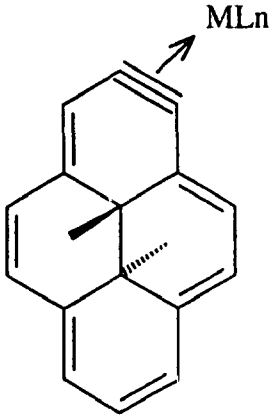
It is known that benzyne can form complexes with transition metals. The benzyne moiety in these compounds is stable enough to allow X-ray determination of the structure, e.g., the rhenium complex **80**[27] and zirconium complex **81**[28]. It will be interesting to investigate syntheses of metal complexes of **57** and **58**, such as **82**, in which any delocalization change in the dihydropyrene moiety can be probed by nmr.



80



81



82

The foregoing discussion has indicated that potential for reaction of **57** and **58** is great. In the first instance we directed our research efforts to investigate the preparation and reactions of **57**, since this seemed more accessible.

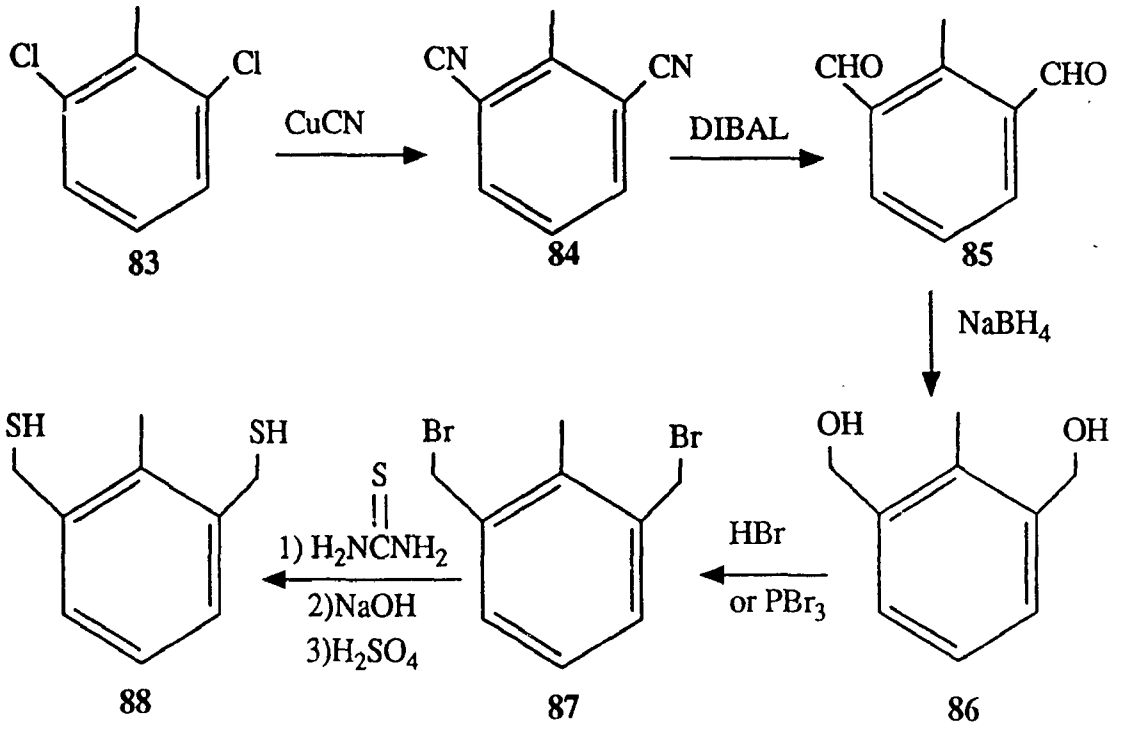
CHAPTER 2 SYNTHESES

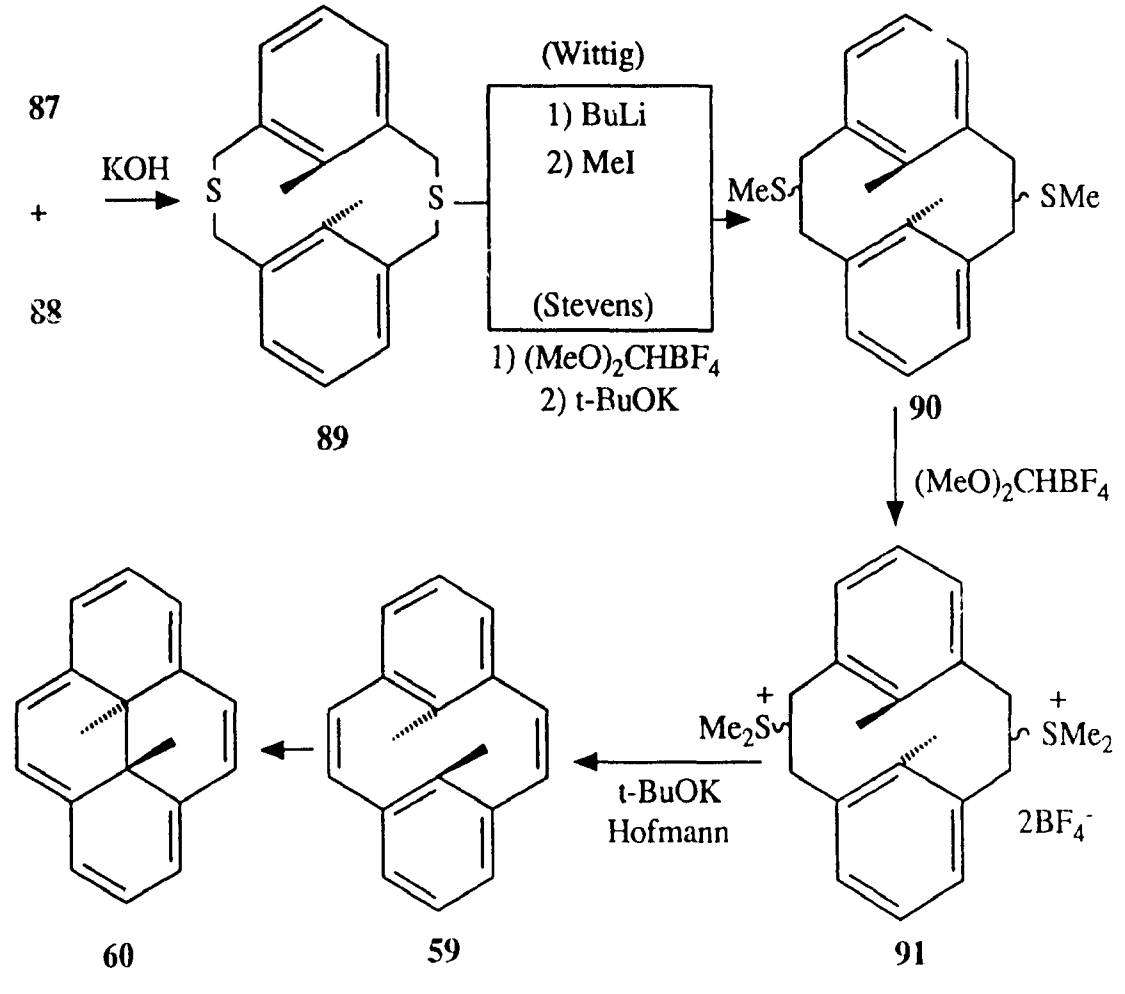
In the previous chapter, we have described a variety of methods to generate arynes. Unfortunately, not all of the methods can be applied to prepare the dihydropyryne **57**, because the starting materials are not easily accessible . In consideration of this limitation we implemented the following syntheses:

2.1 Synthesis of the starting material -- dihydropyrene 60

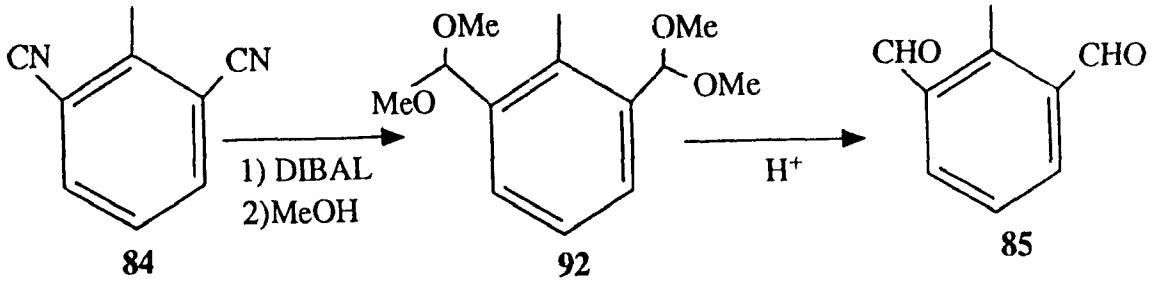
Although the dihydropyrene **60** was first reported by Boekelheide[29a] in 1964, the newer synthetic route developed by Boekelheide and Mitchell[29b] involves less steps and gives higher overall yield, and was used throughout the project.

The commercially available 2,6-dichlorotoluene, **83**, was converted into 2,6-dicyanotoluene, **84**, in about 60% yield with cuprous cyanide. The reduction of **84** with diisobutylaluminum hydride (DIBAL) gave the dialdehyde **85** in 99% yield. The further reduction of the dialdehyde with $NaBH_4$ produced the diol **86** in 95% yield. The diol was converted in 95% yield into the dibromide **87** which was further converted to the dithiol **88** in 90% yield.


Cl
Cl
CuCN
CN
CN
DIBAL
CHO
CHO
83
84
85
NaBH4
SH
SH
Br
Br
OH
OH
S
1) H2NCNH2
2)NaOH
3)H2SO4
HBr
or PBr3
88
87
86


87
+
88
KOH
S
S
(Wittig)
1) BuLi
2) MeI
(Stevens)
1) (MeO)2CHBF4
2) t-BuOK
89
MeS
SMe
90
(MeO)2CHBF4
Me2S
+
SMe2
+
2BF4-
t-BuOK
Hofmann
91
59
60

A solution of dibromide **87** and dithiol **88** in THF was added slowly into a solution of KOH in EtOH/H_2O (4 : 1) with vigorous stirring. This gave the major isomer, *anti*-dithiacyclophane **89** in 60% yield[29c]. Methylation of **89** with dimethoxycarbonium fluoroborate gave the corresponding bis(sulfonium)salt in 95% yield. Subjection of the salt to Stevens rearrangement led to the ring contracted cyclophane **90**, isolated as a mixture of isomers, in about 90% yield. Finally dihydropyrene **60** was obtained in 80% yield by further methylation of the mixture of isomers **90** and sequential Hofmann elimination with t-BuOK in THF at reflux temperature. It was discovered that the pure diene **59** could be isolated when the Hofmann elimination was carried out at room temperature.



84 **92** **85**

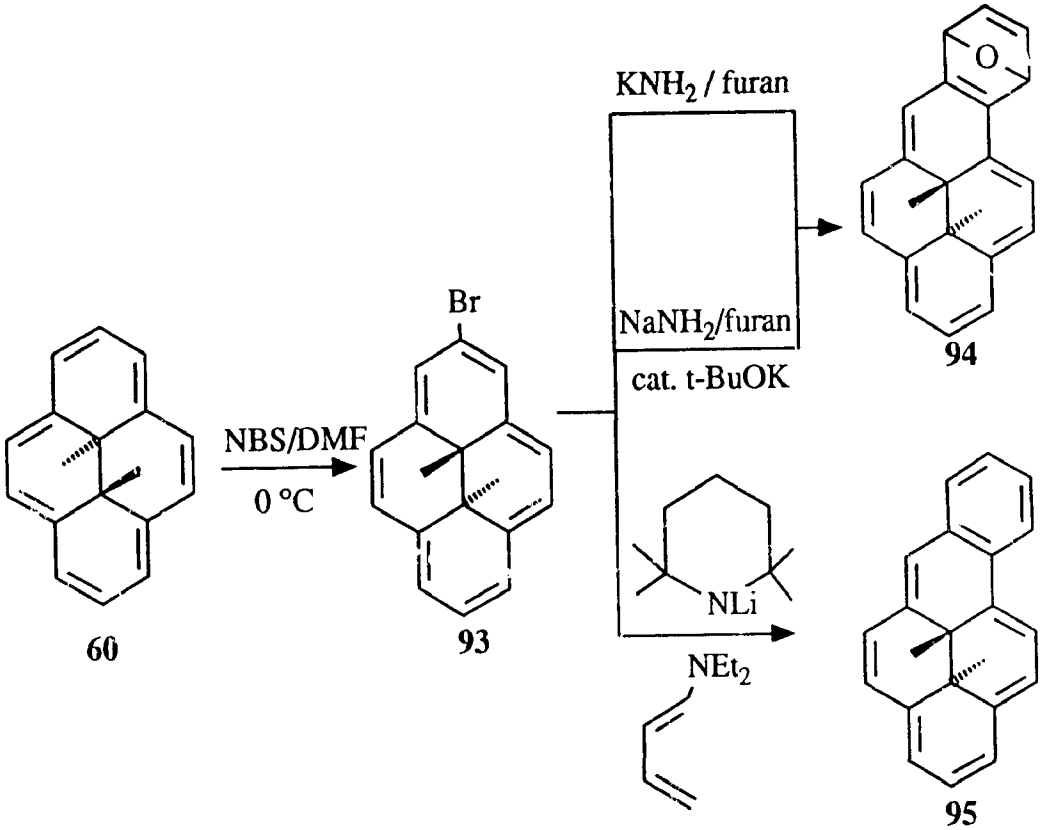
During the reduction of the nitrile **84**, we observed that the diacetal **92** was formed when MeOH was added to destroy the excess hydride. Therefore it is necessary to acidify and warm up the reaction mixture in the final work-up step to yield the dialdehyde.

2.2 Routes to the aryne 57

2.2.1 Dehydrohalogenation:

Dehydrohalogenation of haloarenes to arynes is one of the most convenient reactions to prepare arynes because of the ease of accessiblity of the haloarenes.

Mitchell[30] has reported that the bromodihydropyrene **93** can be obtained in high yield from **60** using NBS in DMF. We found that the reaction time can be shortened such that the reaction was complete as soon as the addition of NBS in DMF was finished. Fast addition of NBS in DMF leads to a small amount of polybromodihydropyrene.



The dehydrobromination of **93** was next tried under a variety of different conditions, and the aryne **57** was immediately trapped as the furan adduct **94**. This adduct was obtained either with KNH_2/furan or $NaNH_2$ /furan in equal yield. Hence commercially available $NaNH_2$ was used as the base for the dehydrobromination throughout the project. In the absence of any catalyst, the reaction of **93** with $NaNH_2$ was slow, usually 48 hr was necessary. It has been reported that alkoxides can activate $NaNH_2$ and catalyze the reaction; indeed $NaNH_2$/t-BuONa is known as Caubere's 'complex base'[31]. We found that a catalytic amount of t-BuOK shortened the reaction time from 48 hr to 2-3 hr. Generally, the dehydrohalogenation of haloarenes was carried out in THF at reflux temperature, however, the reaction of the bromodihydropyrene **93** gave higher yield (60%) at room temperature than at reflux temperature (*ca.* 10%), where decomposition occurred.

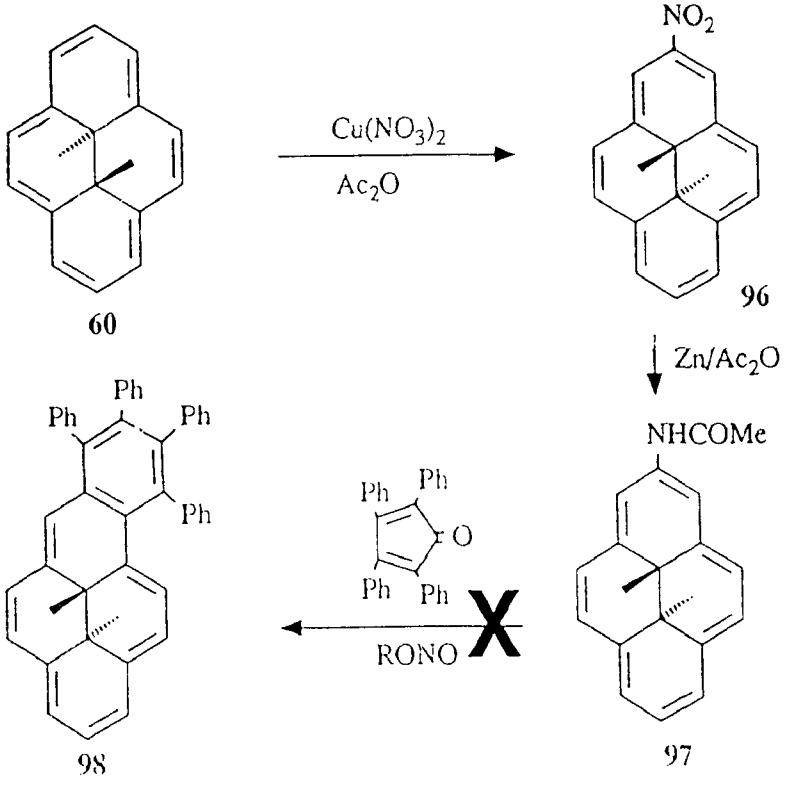
The aryne **57** could also be trapped by N,N-diethyl-1,3-butadienylamine to give the known benzoannulene **95**. In this case, the aryne was generated by the action of the strong and highly sterically hindered base lithium tetramethylpiperidide, which also caused in situ elimination of diethylamine. The yield of **95** was very low and N,N-diethyl-1,3-butadienylamine is difficult to prepare and not very stable, and so this reaction was not further used to prepare **95**. Nevertheless, the existence of reactive

intermediate dihydropyryne **57** has been confirmed by its Diels-Alder reaction with a cyclic diene (furan) and an acyclic diene (N,N-diethyl-1,3-butadienylamine). In all of these reactions, no adduct of cyclophanediene **61** could be observed. This is consistent with the fact that dihydropyrenes are generally found to be more stable than cyclophanedienes.

A disadvantage of dehydrohalogenation is the strongly basic conditions employed. These limit the choice of trapping reagents and products to those that are stable to base. We therefore now investigated milder preparative methods to generate **57**.

2.2.2 Elimination of a diazonium salt:

The electrophilic substitution of dihydropyrene **60** has



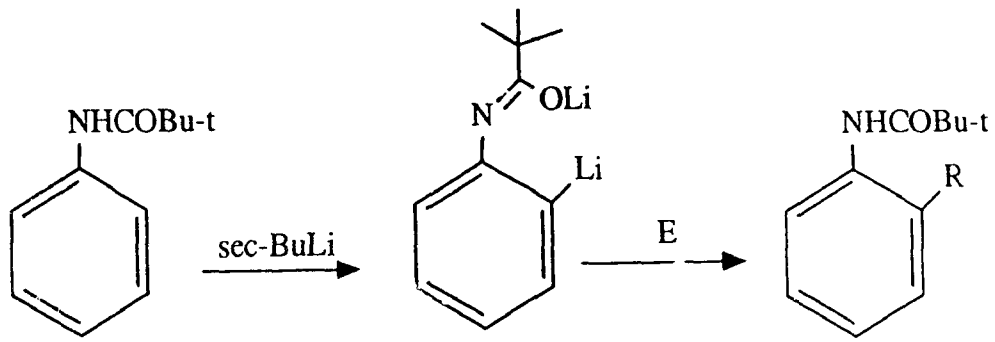
been studied by Boekelheide[33]. The 2-acetamido-dihydropyrene, **97**, can be obtained by nitration followed by reduction. Reaction of **97** with pentyl nitrite and tetraphenylcyclopentadienone, using the method of Cadogan[14] did not give any expected product **98** and lead to no recovered starting material **97**.

2.2.3 Attempted ortho metallation of derivatives of the dihydropyrene 60:

Arynes can be generated efficiently by the decomposition of benzenediazonium-2-carboxylates under mild conditions, in either the presence of benzyne traps to give adducts in high yield, or in the absence of the traps to dimerize into biphenylenes. Such a reaction of **57** would lead to the novel compound **65**. The key step in this sequence is the preparation of an ortho substituted dihydropyrene **100**. Gschwend[34] has described a method to convert N-pivaloylanilines, **103**, into their *o*-lithio derivatives, **104**, which react with a variety of electrophiles to give *o*-substituted derivatives, **105**, in very good yield.

We thus attempted the synthesis of **100**. The compound **99** was readily prepared by the reduction of **96** with zinc in pivaloylanhydride. Unfortunately, further reaction of **99** with BuLi and subsequently CO_2 did not give any of the expected product **100**, but led to partially recovered

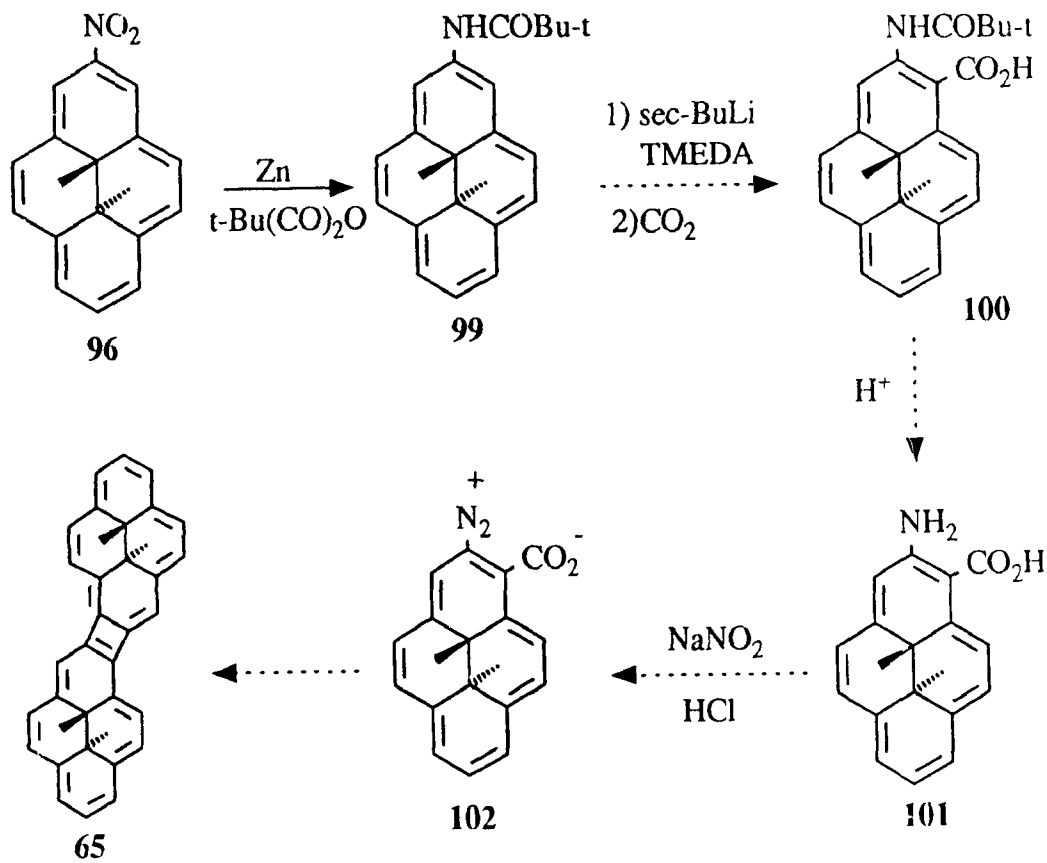
starting material, and addition of butyl group to dihydropyrene (indicated by the mass spectrum). This failure may be because of easy addition to the dihydropyrene nucleus, and perhaps to accomplish the *ortho*-lithiation, a more powerful directing group should be used.



103 **104** **105**

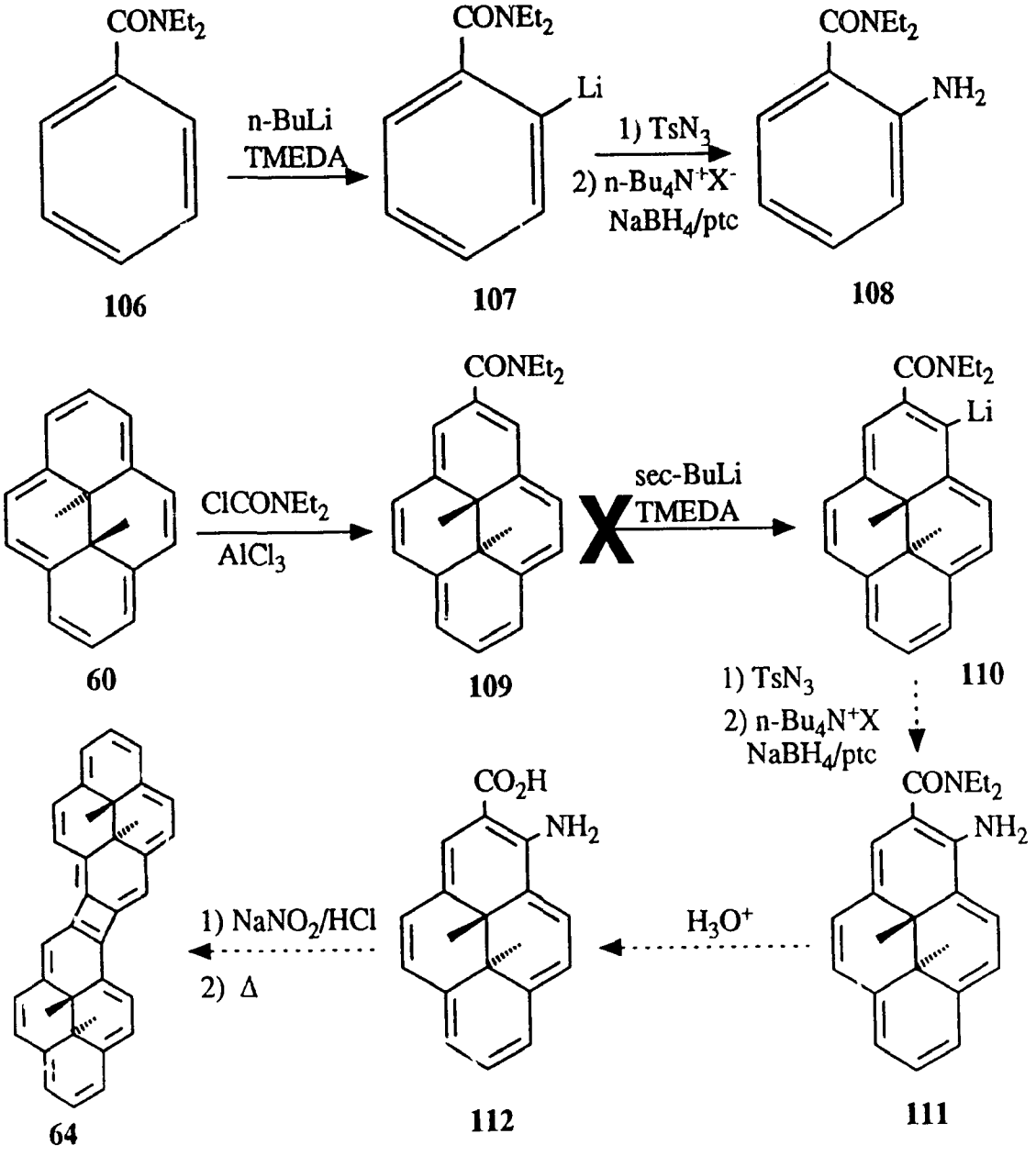
$E = (CH_3S)_2$, $R = SCH_3$, yield: 78%

E= DMF, R = CHO, yield: 53%



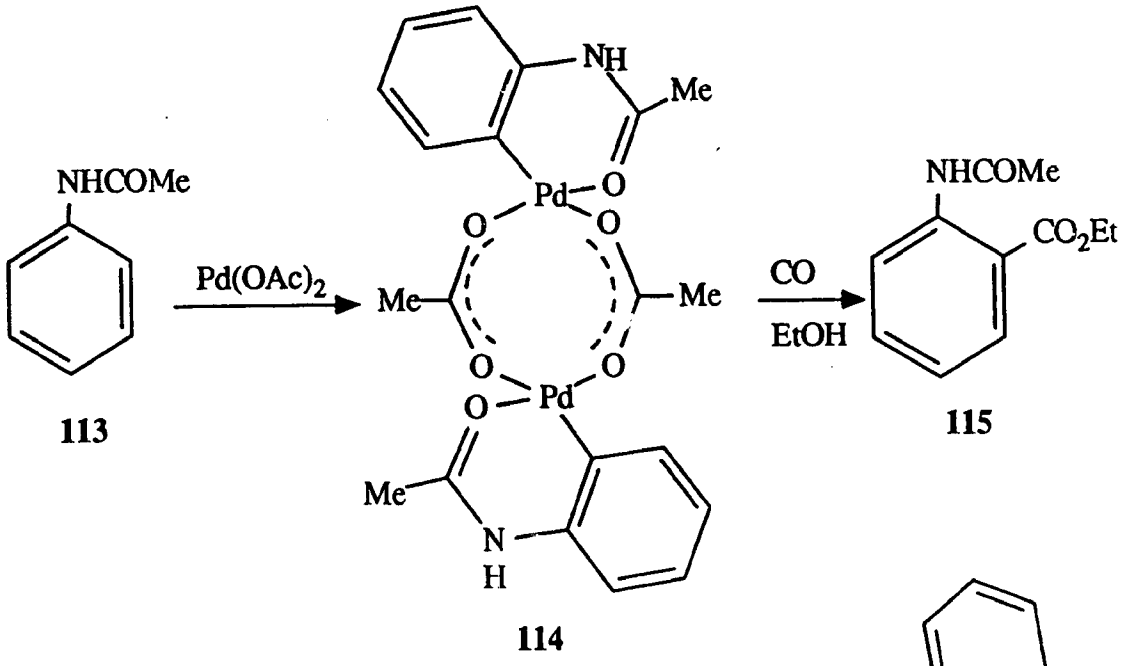
96 **99** **100** **101** **102** **65**

It is well documented that N,N-diethylbenzamide **106** can be readily *ortho*-lithiated on treatment with sec-BuLi/TMEDA or even n-BuLi/TMEDA at -78 °C. The lithiated species reacts with tosyl azide followed by sequential reduction

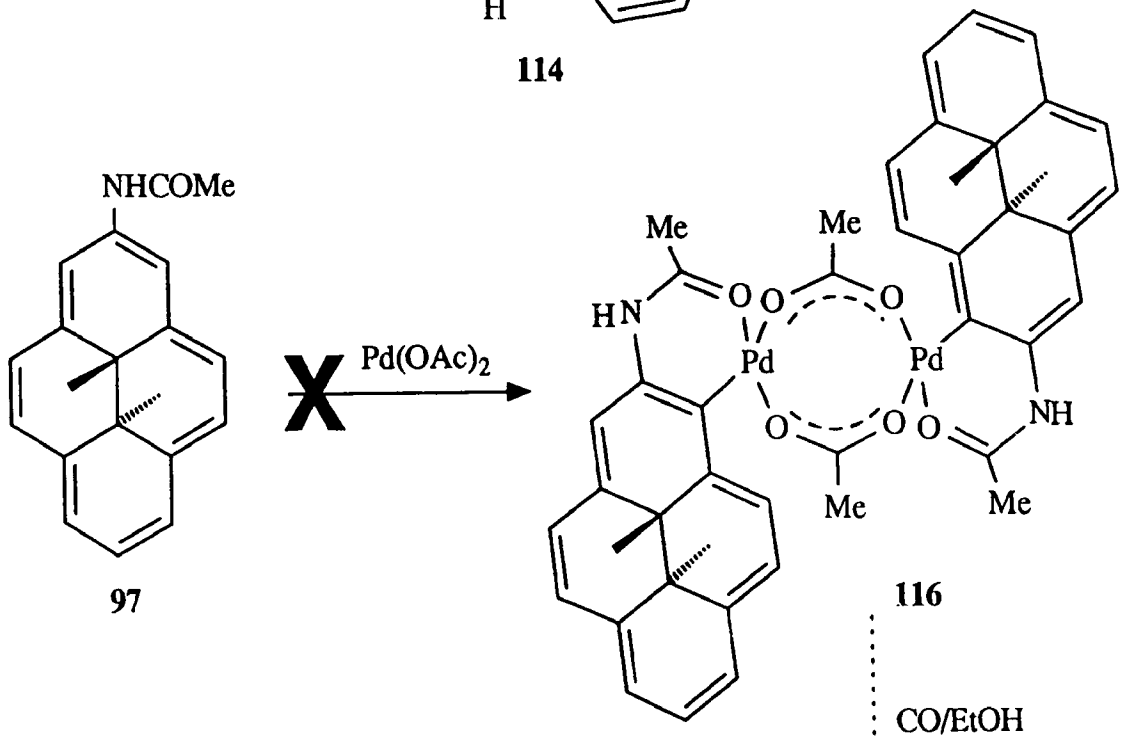


with $NaBH_4$[35] in the presence of phase transfer catalyst or with Ni-Al/KOH[36] to give the anthranilamide **108**. Thus the synthesis of an isomer of **101**, namely **112** was attempted. Friedel-Crafts reaction of diethylcarbamyl chloride with dihydropyrene **60** in the presence of catalyst $AlCl_3$ gave **109**. Disappointingly, compound **109** failed to lithiate under various conditions reported in the literature[37].

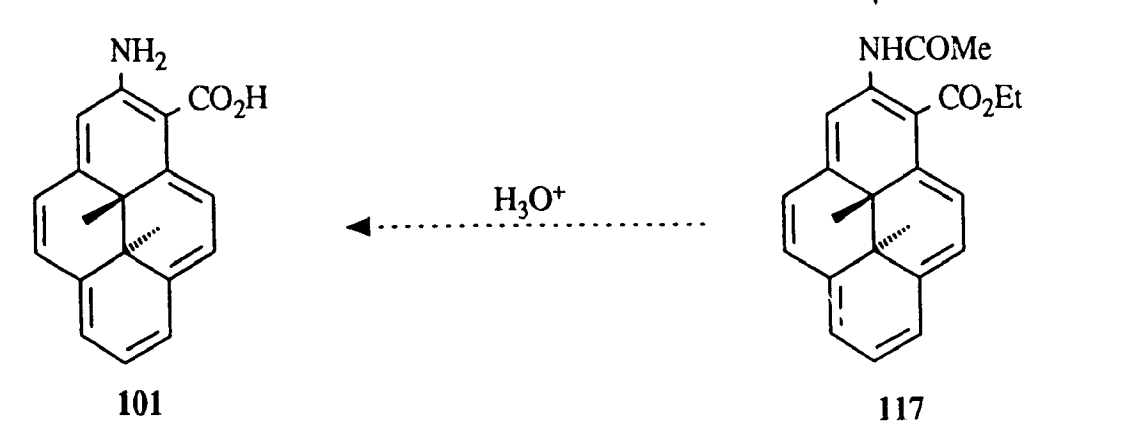
It has been reported that the aromatic amides can be *ortho*-functionalized via cyclopalladation complexes[38]. An interesting example is the reaction of acetanilide **113** with palladium acetate to give an ortho-palladated complex **114**, which reacts with carbon monoxide to produce the N-acylanthranilic ester **115**. The yields in these reactions are very high. Hence we tried the amide **97** in a similar reaction to obtain the product **117**, which in turn should yield **101**. Unfortunately, our efforts were not crowned with success. Mostly starting material was recovered, and a small amount of unidentifiable product was isolated. So far we do not understand why the *ortho* metallation of the dihydropyrene derivatives **99**, **109**, and **97** failed.



113 **114** **115**

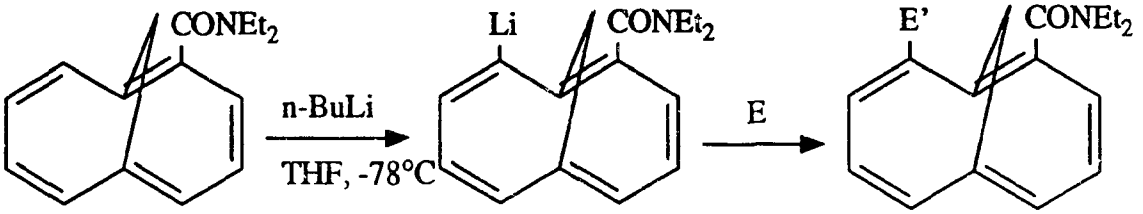


97 **116**



117 **101**

It is, however, interesting to note that lithiation of N,N-diethyl-1,6-methano[10]annulene-2-carboxamide,**118**, with BuLi followed by quenching with different electrophiles yields 2,10-disubstituted-1,6-methano[10]annulenes, **120**, and not 2,3-disubstituted compounds[39].



118 **119** **120**

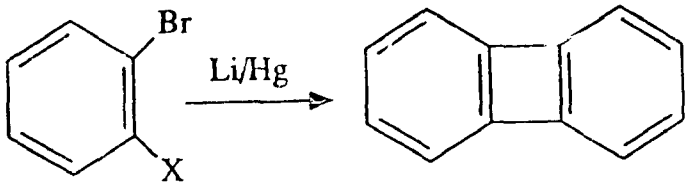
E = $ClCO_2Me$, CH_3I, CO_2, DMF.

E' = $-CO_2Me$, $-CH_3$, $-CO_2H$, -CHO.

2.2.4 Attempted synthesis of an *o*-dihalodihydropyrene

The failure in the ortho directed metallation strategy of dihydropyrene derivatives led us to consider the ortho functionalization at an early stage in the synthesis of an *o*-disubstituted dihydropyrene , i.e., at the dithiacyclophane stage or before the coupling reaction to dithiacyclophane **89**. In particular, the *o*-dihalo-dihydropyrene **123** caught our attention first since it could be a precursor to dihydropyryne **57**. It is well documented that biphenylene **17** and triphenylene **122** have been isolated in a number of reactions of o-dihalobenzene with metals[40].

For example, in the reaction of o-bromofluorobenzene with lithium amalgam, a 24% yield of biphenylene has been reported, together with 3% of triphenylene[11]. However, o-bromoiodobenzene with lithium produced biphenylene, **17**, in 12% yield and triphenylene, **122**, in 55% yield[41]. Attractively, haloarenes should not be affected by the reactions used in the dihydropyrene synthesis such as the methylation and Hofmann elimination[45]. Thus we next attempted the synthesis of the *o*-bromofluorodihydropyrene **123**. This might further lead to **65** and **124** which have a number of possible isomers.

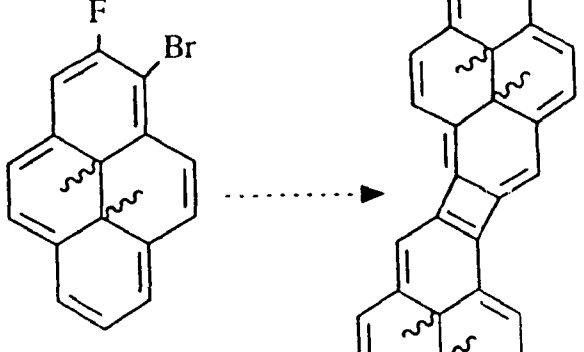


14 X = F
121 X = I

17

+

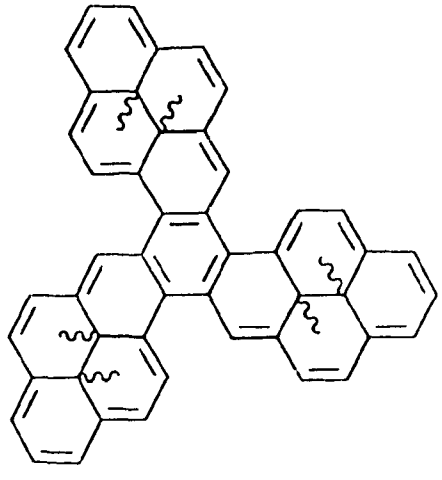
122



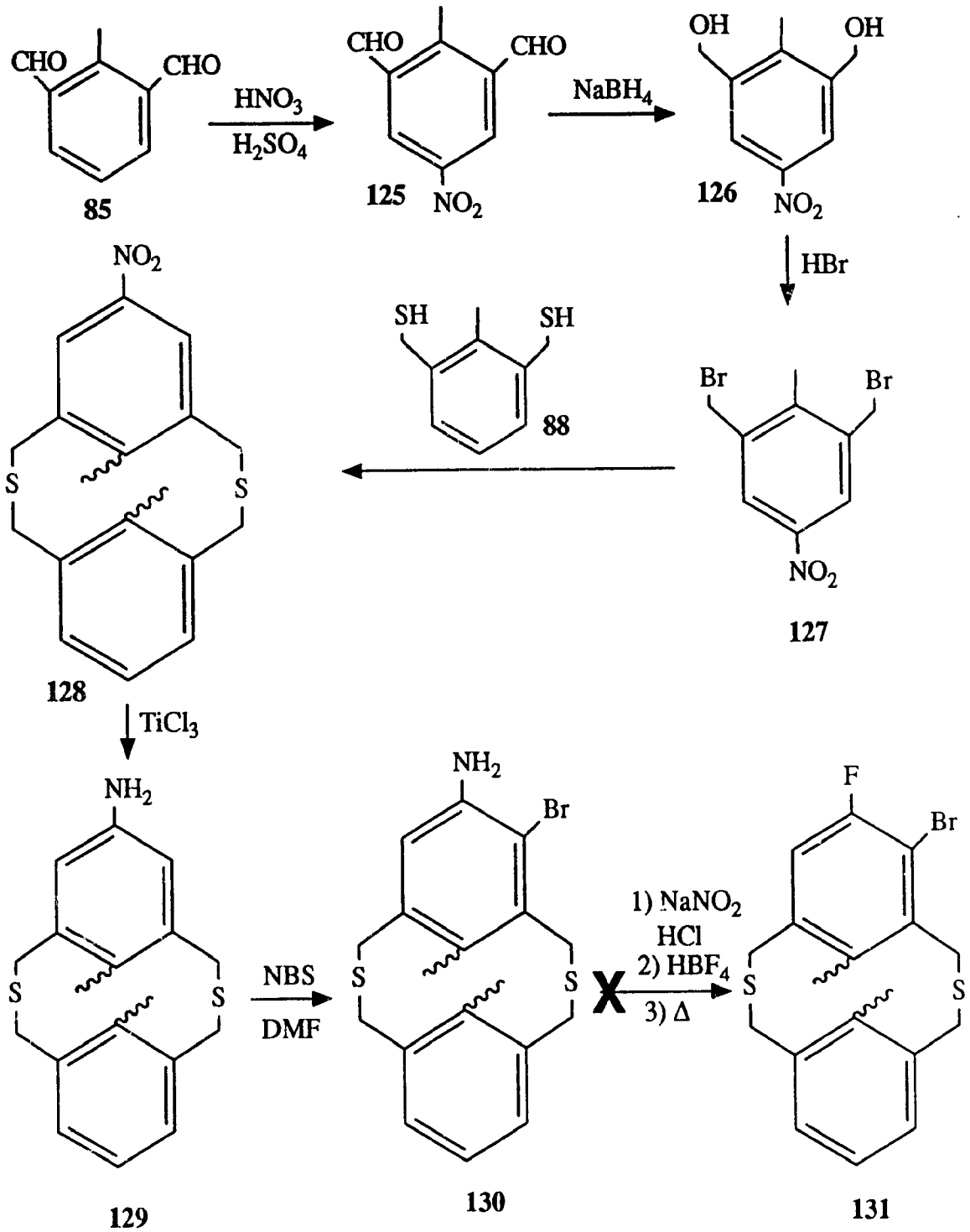
123

65

+

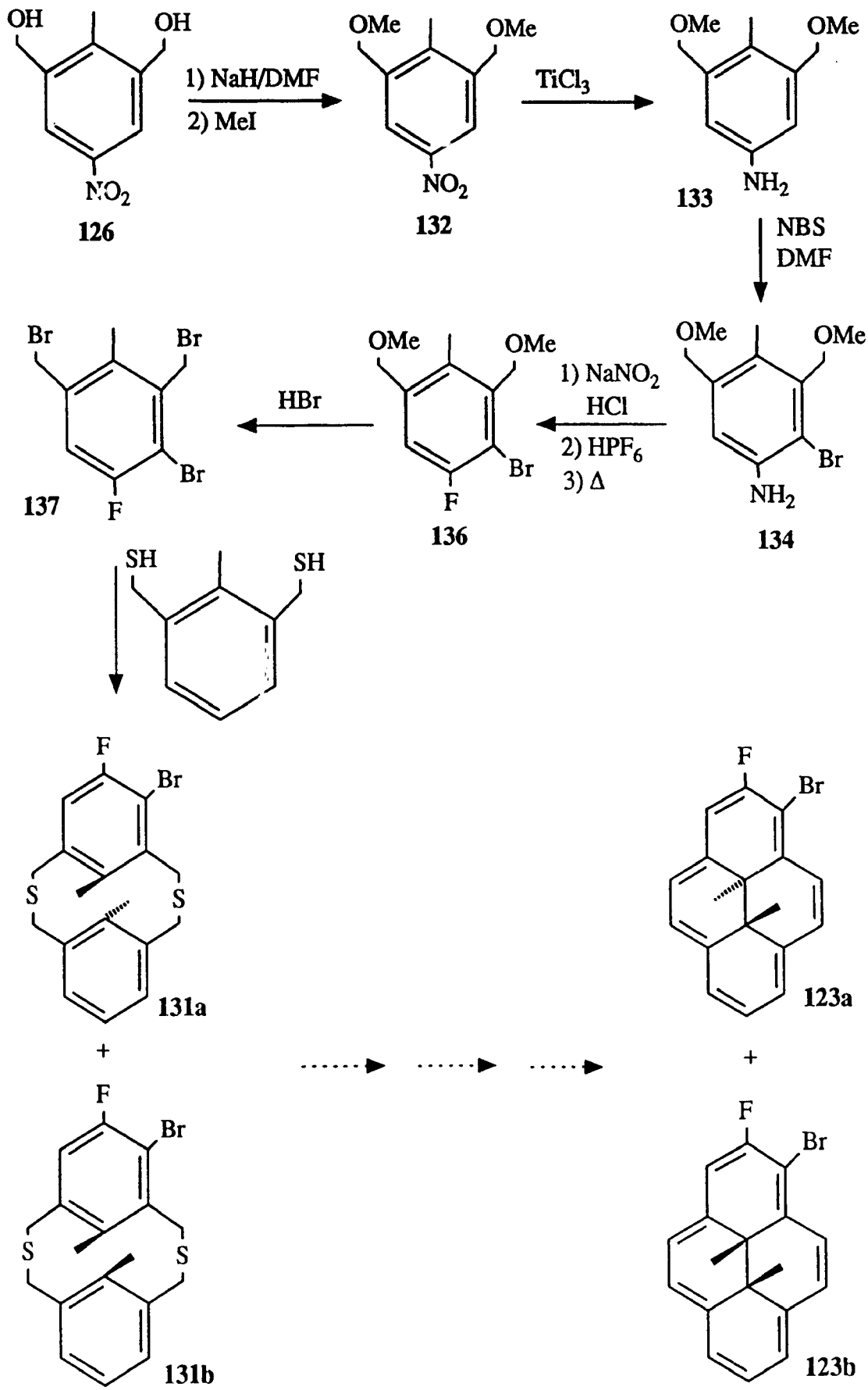


124

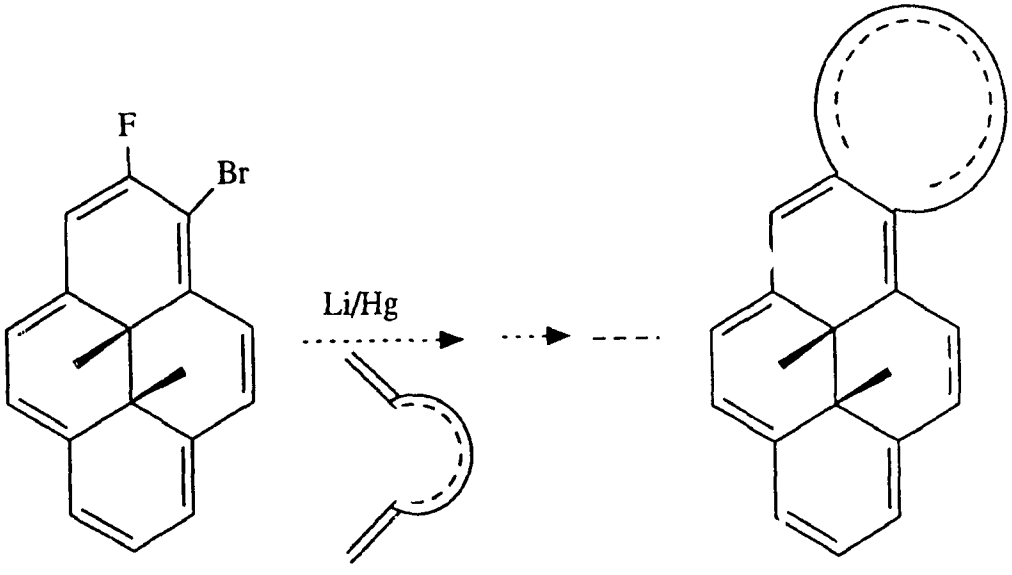

CHO
CHO
85
HNO3
H2SO4
CHO
CHO
125
NO2
NaBH4
OH
OH
126
NO2
HBr
Br
Br
NO2
127
SH
SH
88
NO2
S
S
128
TiCl3
NH2
S
S
129
NBS
DMF
NH2
Br
S
S
130
1) NaNO2
HCl
2) HBF4
3) Δ
F
Br
S
S
131

The nitrodithiacyclophane **128** was prepared following the literature procedure[42]. Reduction of **128** with $TiCl_3$ produced the amino compound **129** in quantitative yield. Reaction of **129** with NBS/DMF[30] gave the expected product **130** in 50% yield. However the compound **130** on the treatment with $NaNO_2$/HCl, followed with HBF_4, gave a solid which was not able to be decomposed to give the desired o-bromofluoro compound **131**. This solid was not soluble in water, NaOH solution, DMF or other organic solvents and did not show the diazonium band in its IR spectrum. Thus we attempted a different route in which the *o*-dihalo compound would be obtained before the dithiacyclophane stage.

The diol **126** was protected in 93% yield to give **132** by methylation with NaH in DMF followed by addition of excess MeI. Reduction of **132** with $TiCl_3$ gave the amino compound **133** in 86% yield. Reaction of the amino compound with NBS/DMF produced the monobromide **134** in 66% yield and a small amount of dibromide **135**. The best conditions for conversion of of **134** to **136**, consisted of preparing the diazonium hexafluorophosphate salt from **134** and decomposing it in di-(*n*-butyl)ether at 150 ^{o}C. Thus the *o*-bromofluoro compound **136** was obtained under these conditions in 22% yield, accompanied by a large amount of polymer.

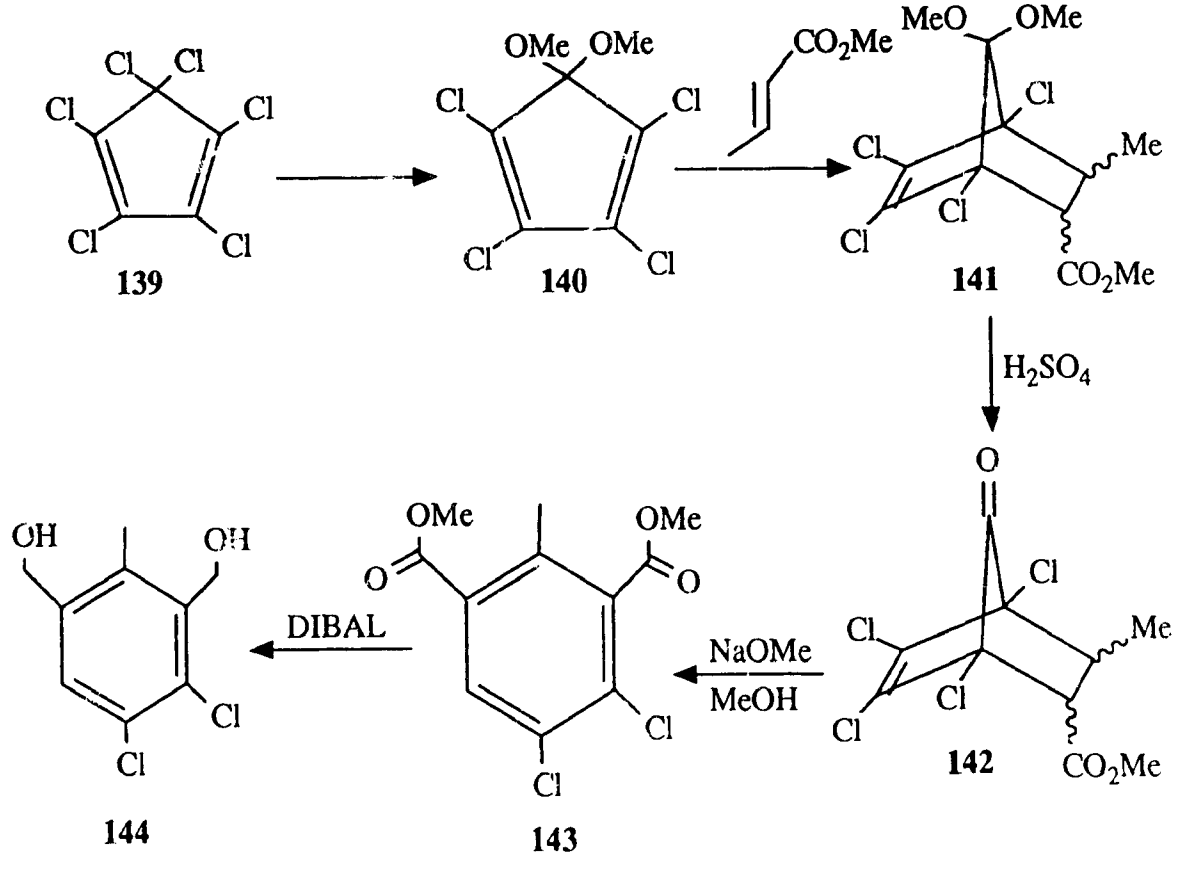

OH
OH
NO2
126
1) NaH/DMF
2) MeI
OMe
OMe
NO2
132
TiCl3
OMe
OMe
NH2
133
NBS
DMF
OMe
OMe
Br
NH2
134
1) NaNO2
HCl
2) HPF6
3) Δ
OMe
OMe
Br
F
136
HBr
Br
Br
Br
F
137
SH
SH
F
Br
S
S
131a
+
F
Br
S
S
131b
F
Br
123a
+
F
Br
123b

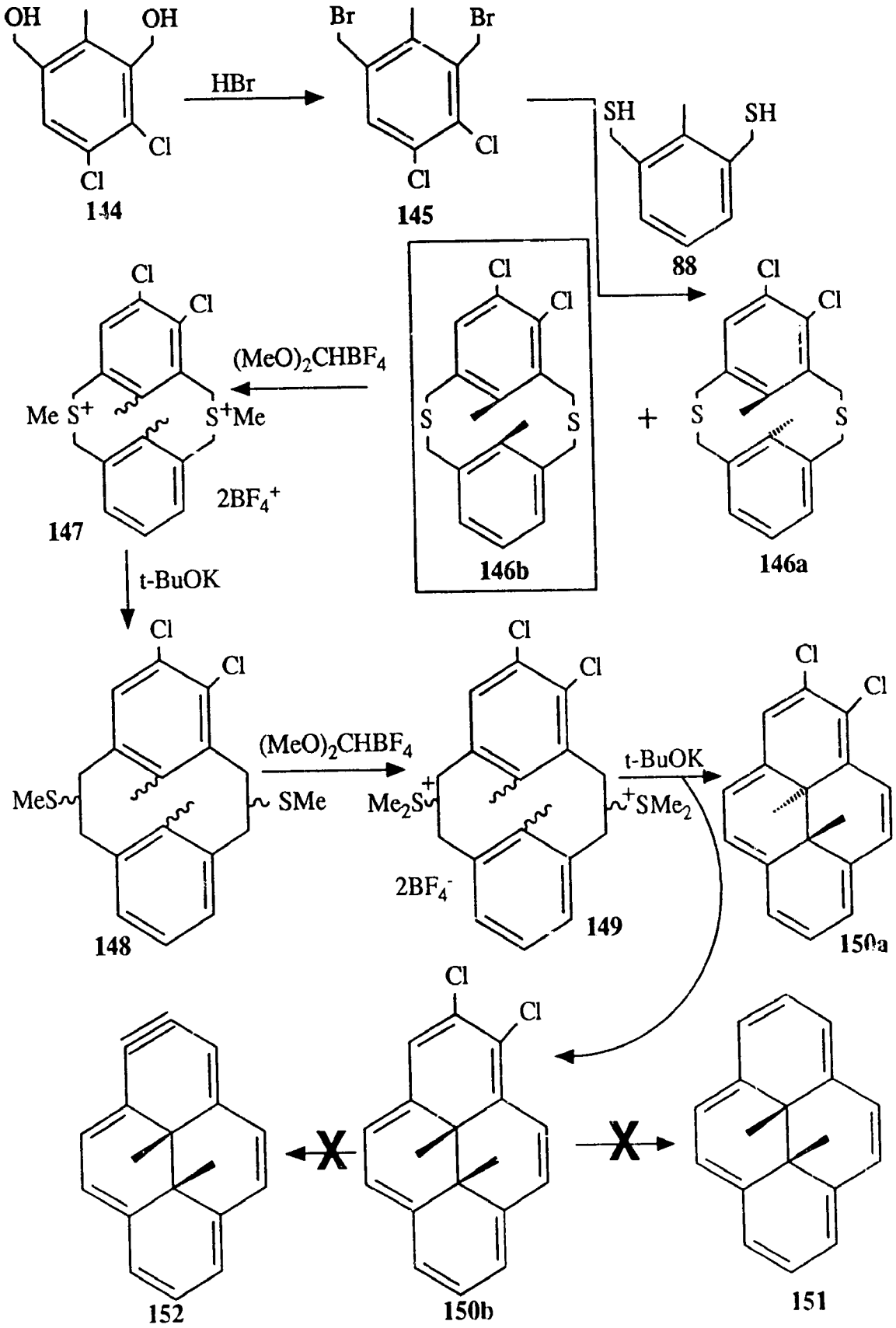
Reaction of diether **136** with HBr (48%) in the presence of catalytic amount of concentrated H_2SO_4 for 3 hr at 100°C gave bromide **137** in a quantitative yield, from which with dithiol **88** was obtained the *anti*- and *syn*-dithiacyclophanes **131a** and **131b** in a 1:1 ratio in a total yield of 34%. Note that as has been observed previously[42], electron withdrawing halogens present in the coupling increase the *syn* : *anti* ratio to 1 : 1 from 1: 7 in the unsubstituted case. This might make possible the study of annelated *syn*-dihydropyrenes, **138**, via the *syn*-dihydropyryne. This route has not yet been explored further, but **123a** might be a useful precursor to **65** and hence should be further investigated when time permits.



123b **138**

A synthesis of the *o*-dichlorodihydropyrene **150** has been previously reported by Mitchell[45]. This starts from the readily available hexachlorocyclopentadiene, **139**, and methyl crotonate. The coupling reaction of dibromide **145** and dithiol **88** proceeded in excellent yield (96%), and gave 61% of the *syn*-dithiacyclophane **146b** and 35% of the *anti*-isomer **146a**. After separation, pure *syn*-isomer **146b** was taken through a Stevens rearrangement-Hofmann elimination sequence to give syn-dihydropyrene **150b** and anti-isomer **150a** in a ratio of 1.5:1. However, removal of the two chlorine substituents to form syn-dihydropyrene **151** and dechlorination to generate the corresponding *syn*-dihydropyryne **152** were not successful.




OH
OH
Cl
Cl
144
HBr
Br
Br
Cl
Cl
145
SH
SH
88
Cl
Cl
(MeO)2CHBF4
Me S+
S+Me
2BF4+
147
t-BuOK
S
S
146b
+
146a
148
(MeO)2CHBF4
MeS
SMe
Me2S+
+SMe2
2BF4-
149
t-BuOK
150a
150b
152
151

CHAPTER 3 RESULTS AND DISCUSSION

3.1 Criteria for aromaticity

It is remarkable that more than 75% of the seven million chemical substances so far characterized are "aromatic" compounds[46]. These have stimulated chemists' and physicists' enthusiasm for extensive study in the theoretical and experimental aspects of this topic. However, the term "aromaticity" has been much disputed and is currently one of the most controversial in chemistry. However we believe that the term "aromaticity" should be retained because a) it has firmly established itself and has gained wide acceptance in all branches of chemistry; b) it had and has provided a vehicle for a fruitful interaction between theoretical and experimental chemists; c) it inspires us to the synthesis of novel non-natural compounds and the generation of new theoretical concepts.

Classification of compounds as aromatic or non-aromatic can be achieved by two approaches, i.e., either by choosing theoretical parameters as theoretical criteria, or experimental results as experimental criteria. Many theoretical criteria have been suggested for determining the aromaticity of a compound, e.g., the resonance energy per π electron (REPEs) for a number of systems calculated by Dewar and Gleicher[47] using the Pople-Pariser-Parr (PPP)

method and by Hess and Schaad[48] using the HMO method; the absolute hardness and relative hardness derived by Zhou and Parr[49]. The advantage of theoretical criteria is that they can be applied to compounds which have not yet been prepared, or are too reactive to be determined experimentally. The drawback is that those criteria are always uncertain because assumptions are made to solve the equations. Therefore, experimental results are needed to verify and prove the calculations. If Schrödinger's equation were soluble for any molecule, so that all the properties of the molecule could be deduced from the solutions, we experimental chemists would miss the fun of doing experiments. Another problem with theoretical criteria that we face is our inability to understand the basis of the theoretical calculations and this leads to confusion about the ideas of aromaticity. Thus experimental criteria are necessary to define aromaticity and deepen our comprehension of the term "aromaticity".

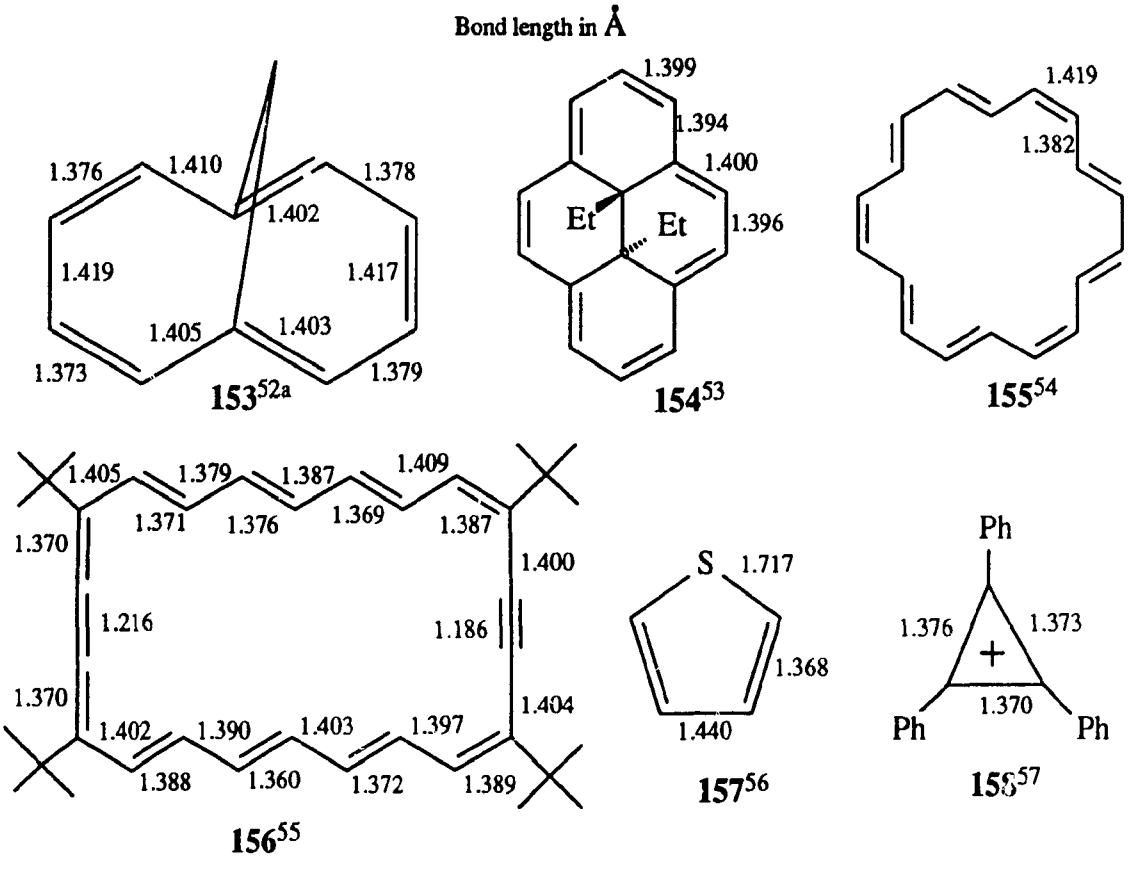
There are a variety of experimental results which can be used as criteria for aromaticity but only three of them have been satisfactorily and widely used. They deserve to be briefly discussed here.

3.1.1 Bond length

In 1959, Albert[50] suggested that in a cyclic

conjugated molecule the greater the equalization of the C-C bond lengths throughout the molecule, the more aromatic it is. One refinement[51] of this criterion is that the compound is aromatic if the lengths of its C-C bonds are between 1.36 and 1.43 Å. Using this criterion, we do not hesitate to claim that 1,6-methano[10]annulene **153**, diethyldihydropyrene **154**, [18]annulene **155** and triphenylcyclopropenium perchlorate **158** are all aromatic. However, a problem arises in the dehydroannulene **156** and the thiophene **157** which would not be considered aromatic according to this criterion.

Figure 2. Bond lengths of annulenes



The second refinement [58] of Albert's criterion takes the mean square deviations of the C-C bond lengths as a measure of aromaticity. The aromaticity constant, A, is defined by the equation:

$$A = 1 - \frac{225\,\Sigma(d_{rs} - \bar{d})^2}{n\,\bar{d}^2}$$

where $d_{(rs)}$ is the length of the rs bond and $\bar{d}$ is the mean bond length of the n periphery bonds which are unequivalent in the molecule. The results of some compounds are listed in Table 2.

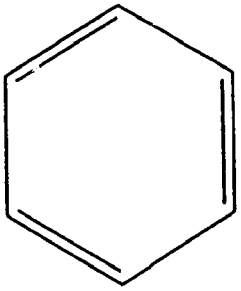
Table 2. Aromaticity constants based on bond lengths

molecule	aromatic constant (A)
1,6-methano[10]annulene **153**	0.97
diethyldihydropyrene **154**	1.00
[18]annulene **155**	0.96
tetra-t-butyl-bisdehydro[22]annulene **156**	0.40
thiophene **157**	0.85
triphenylcyclopropenyl pechlorate **158**	1.00

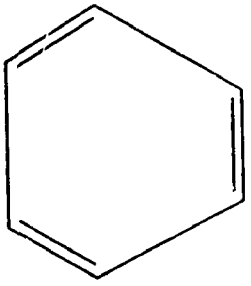
In a heterocyclic system, the hetero atom-carbon bonds are excluded in the calculations. It is obvious that the aromatic constant A of benzene is 1 and it is zero when the periphery bond length of a molecule alternates between 1.33 and 1.52 Å which are approximately C=C (sp^2-sp^2) bond length and C-C (sp^3-sp^3) bond length, respectively. The greatest difficulty with this criterion is that the bond lengths of most compounds are not known.

3.1.2 Resonance energy derived from thermochemical data

There have been two general methods to determine the amount of stabilization that results from aromatic delocalization, namely resonance energy, which is essentially the difference between the energy of the real molecule and that of hypothetical model molecule. Taking benzene as an example, if the calculated energy of the structure **160** was same as the experimental value within experimental deviation, then structure **160** would well represent benzene. On the other hand, if the experimental energy of benzene is greatly different from the calculated energy of the structure **160**, the structure **160** would be a poor representation of the real molecule. This energy difference may be attributed to the resonance structure **159**.



159



160

One method is to use the heat of atomization of a compound. For example, a very simple calculation of the heat of atomization for cyclohexatriene **160** would be to sum the bond energies of six C-H, three C-C and three C=C bonds. Then we can derive the resonance energy of benzene

either as (a) 46.7 kcal/mol by taking the bond energy of ethylene as the double bond in the calculation or as (b) 35.3 kcal/mol by taking the bond energy of a cis-disubstituted ethylene double bond in the calculation. The results are shown in Table 3.

Table 3. Simple calculations of the resonance energy (RE) of benzene (kcal/mol)

	C-H	C-C	C=C	$\Delta H_a°$(160)	$\Delta H_a°$(159)	RE
cal.(a):	6(98.5)	3(83.1)	3(143.7)	1271.4	1318.1	46.7
cal.(b):	6(98.5)	3(83.1)	3(147.5)	1282.8	1318.1	35.3

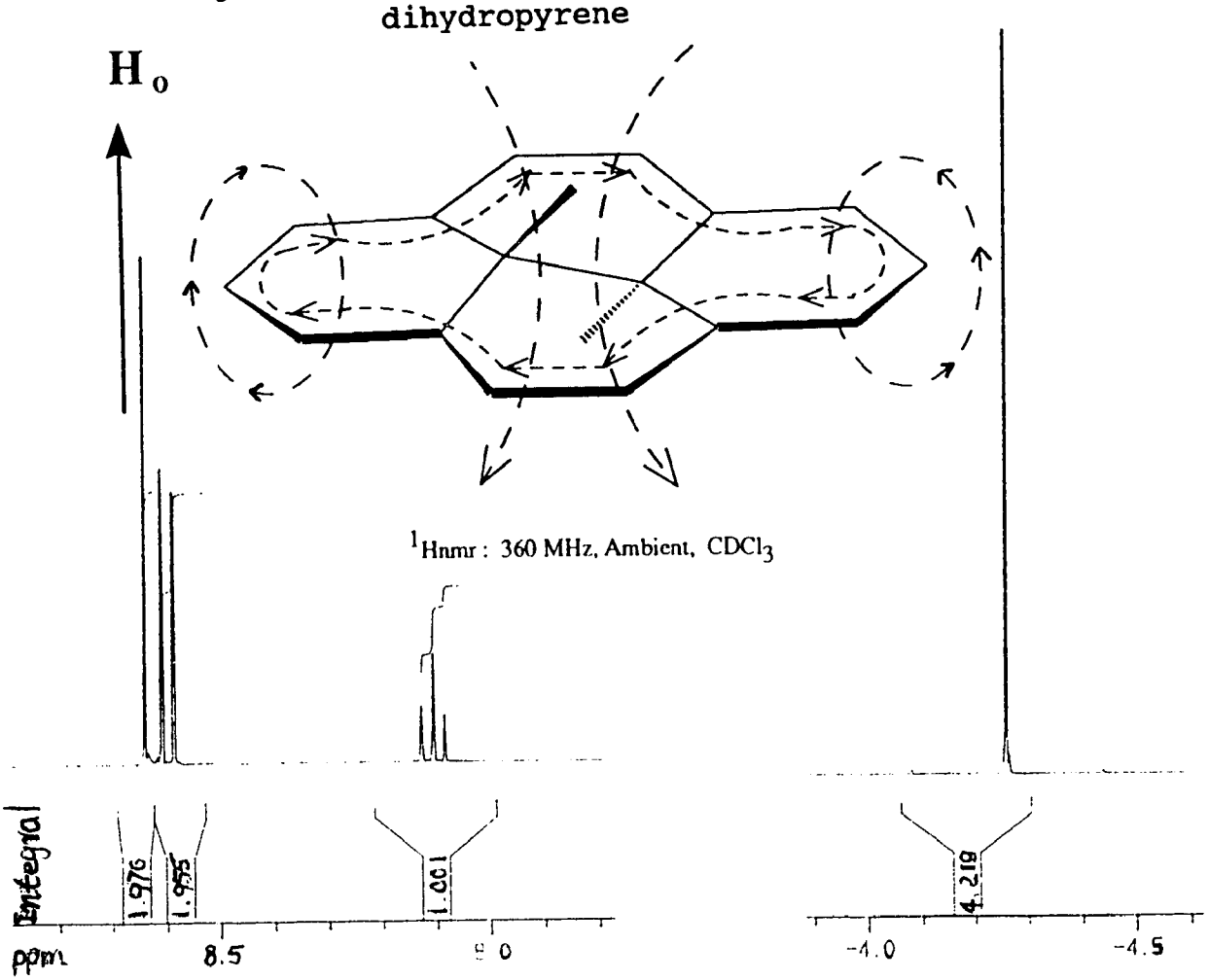
Another method is to use hydrogenation data. For example, the heat of hydrogenation for cyclohexatriene **160** can be calculated as 85.8 kcal/mol by multiplying that of cyclohexene by 3, i.e., 3 X 28.6 = 85.8 kcal/mol. Comparison of this value with the actual heat of hydrogenation of benzene (49.8 kcal/mol) immediately gives the resonance energy of benzene as 36 kcal/mol.

The difficulty with this criterion is that the thermochemical data of a fictitious model structure can not be obtained with certainty and accuracy. Furthermore, the resonance energy could be easily swamped by steric, strain, and or electronic interactions which are not considered in the calculation.

3.1.3 Nuclear magnetic resonance spectroscopy

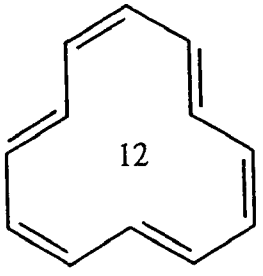
The ^{1}Hnmr spectra of molecules are very easily studied, so they have been widely used as criteria of aromaticity. The ring current model has been introduced to explain the unique chemical shifts of aromatic compounds. It predicts that if the protons are inside or above the ring of an aromatic compound, they should be shielded, in contrast to this, the peripheral protons would be deshielded. This has been proved by synthesis of many annulenes. One excellent example is the dihydropyrene **60** whose ^{1}Hnmr spectrum and ring current model are shown in Figure 3.

Figure 3. Ring current model and ^{1}H nmr spectrum of dihydropyrene



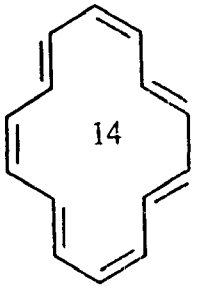
Annulenes can be classified into three types, namely, annulenes, dehydroannulenes and bridged annulenes. Some of their examples are shown in Figure 4, 5, and 6, respectively.

Figure 4: Annulenes



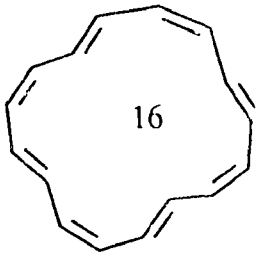
δ = 7.83 (3H)
5.88 (9H)
at -170°C

161[60]



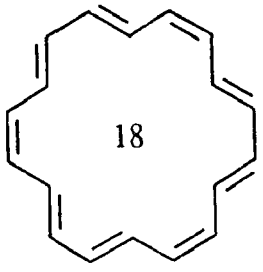
δ = 7.6 (10H)
0.0 (4H)
at -160°C

162[61]



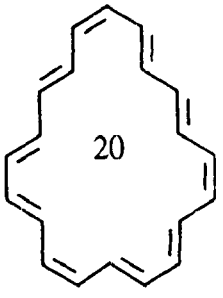
δ = 10.4 (4H)
5.4 (12H)
at -120°C

163[62]



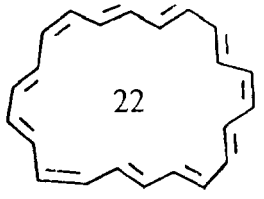
δ = 9.28 (12H)
-2.99 (6H)
at -60°C

155[63]



δ = 13.9 - 10.9
6.6 - 4.1
at -105°C

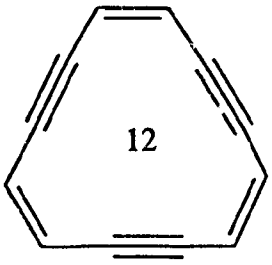
164[64]



δ = 9.65 - 9.3
-0.4 - -1.2
at -90°C

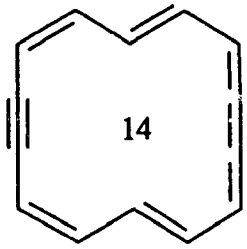
165[65]

Figure 5: Dehydroannulenes



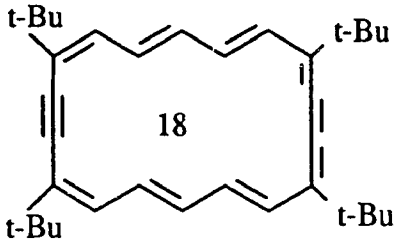
δ = 4.42

52[66]



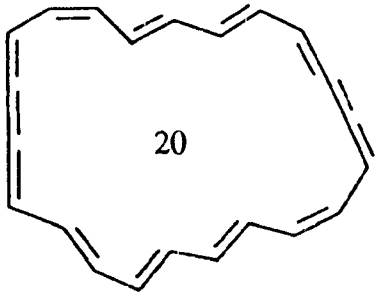
δ = 8.54 (8H)
-5.48 (2H)

53[69]



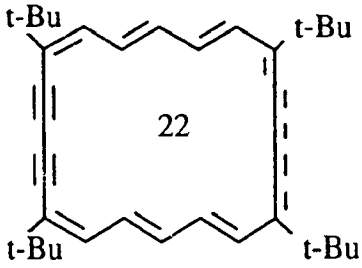
δ = 9.87 (6H)
-3.42 (4H)

166[67]



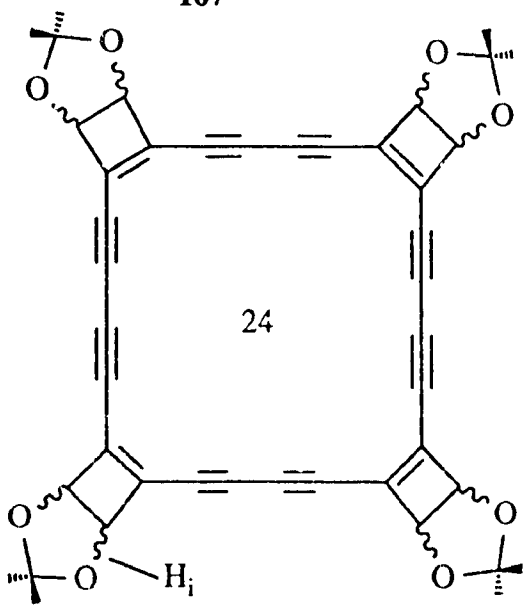
δ = 11.60, 10.45 (4H)
5.60, 5.07 (12H)
at -80°C

167[68]



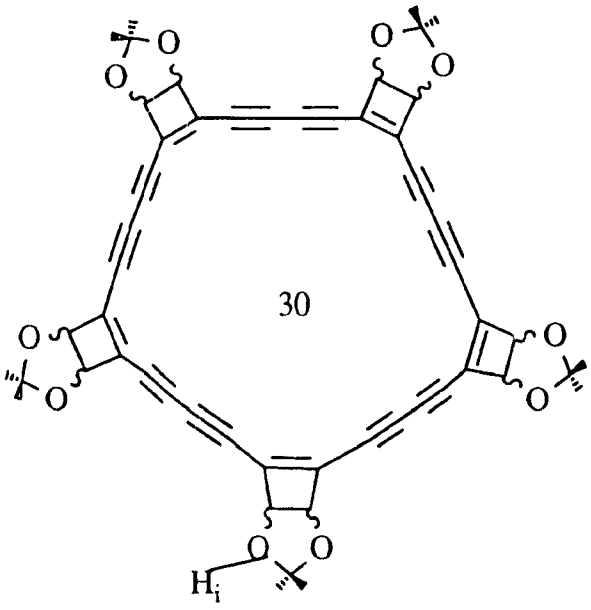
δ = 10.40, 9.91 (6H)
-3.70 (4H)

168[55]



δ_i = 5.28 (23°C)

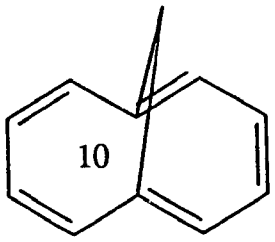
169[70]



δ = 4.95 (23°C)

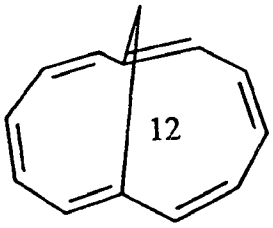
170[70]

Figure 6: Bridged Annulenes



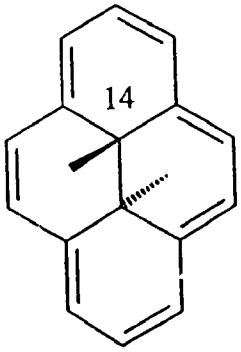
δ = 7.5 - 6.8 (8H)
-0.5 (2H)

153[52a]



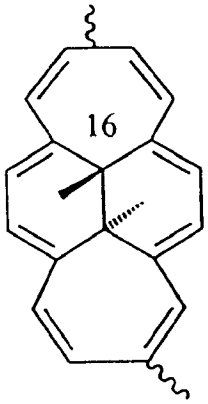
δ = 6.0 (2H)
5.5, 5.2 (10H)

171[71]



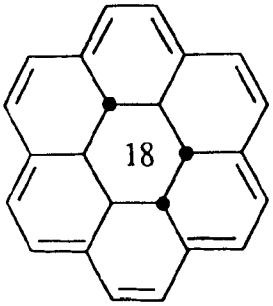
δ = 8.64, 8.60, 8.11 (10H)
-4.26 (6H)

60[72]



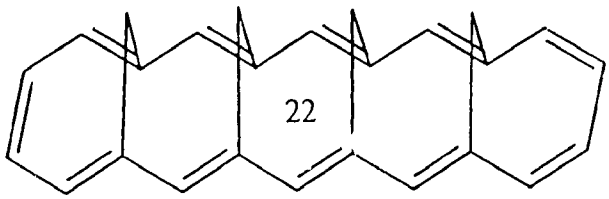
δ = 4.81 (6H)
4.0 (10H)

172[73]



δ = 9.55 - 9.50 (12H)
-6.54 - -7.96 (6H)

173[74]



δ = 7.8 - 6.5 (14H)
2.1, 1.2, 0.3 (8H)

174[75]

In [4n]annulenes, such as compounds **161** and **164**, the inner and outer protons resonate in the opposite direction from what we might be expected based on the ring current model. This has been attributed to a paramagnetic ring current[76]. In quantum-mechanical theories of the ring current effect, the ring current depends on two terms, namely, σ_1 from first-order perturbation theory and σ_2 from second-order perturbation theory. With [4n+2]annulenes, σ_1 dominates. However, [4n]annulenes have an exceedingly low-lying excited state, in which the difference in energy between the HOMO and the LUMO is small. This small difference in energy will lead to a very large σ_2 which will more than compensate σ_1. The result is a reversed direction of the ring current. Secondly, we noticed that the ^{1}Hnmr spectra of most annulenes and some dehydroannulenes, but not the bridged annulenes, were studied at low temperatures to obtain unambiguous information of the ring current effects. The reason for this, is that at higher temperatures, different conformers interchange more rapidly than the time scale of the ^{1}Hnmr experiment so that a very poorly resolved or a simple spectrum was observed. For example, in the case of [18]annulene **155**, at 110 ^{o}C, only a single peak was observed at δ 5.45, showing nothing about the ring current effect; at 20 ^{o}C, two broad peaks were seen at δ 8.94 and -2.0. However, at -60 ^{o}C, two multiplets were exhibited at

δ 9.28 and -2.99, indicating a strong ring current effect.

It deserves mention that very recently Houk and coworkers[70] reported that cyclobutene annelation increases the stability of macrocycles. This stabilization has been attributed to a reduction of conformational flexibility of the annulene perimeters as a result of the small ring fusion. For example, the annelated [24]dehydroannulene **169** is a planar paratropic annulene in striking contrast to its parent dehydro[24]annulene, an atropic and nonplanar compound.

Garratt[77] has suggested that we should use the terms "paratropic" for a system with a paramagnetic ring current shielding in the ^{1}Hnmr spectrum, e.g., [12]annulene, **161**, and "diatropic" for systems with a diamagnetic ring current shielding, e.g., the bridged [14]annulene, dihydropyrene **60**, and "atropic" for systems with no ring current effect. Usually paratropic systems are antiaromatic, diatropic systems aromatic, and atropic systems are nonaromatic. These three terms have been widely accepted by chemists.

Up to this point, the chemical shifts predicted by the ring current model work very well qualitatively to classify compounds into three classes, i.e., aromatic, antiaromatic and nonaromatic. However, it is very difficult to use a chemical shift caused by a ring current effect to measure the aromaticity quantitatively, because of the complications in establishing a relationship between the

chemical shift and ring current. Haddon[78] has however developed a relationship for annulenes using the Biot-Savart law for the calculation of the spatial magnetic fields. The ring current (RC) is calculated from the n observational equations:

$$RCCS_i = RC \times RCGF_i \qquad i = 1, 2, 3, \ldots n$$

where n is the number of distinct chemical shifts observed for a given molecule. $RCCS_i$(ppm) = MCS (δ) - OCS_i(δ), in which $RCCS_i$ is ring current chemical shift of proton i, MCS is model chemical shift (6.129 ppm for annulenic protons), OCS_i is observed chemical shift of proton i, $RCGF_i$ is a ring current geometric factor. Some of his results are shown in Table 4.

Table 4. Calculated ring current (RC) and aromatic character (k)

compound	RC ($x10^3$) (CGS)	Aromatic Character (k)
benzene	-1.1861	1
[10]annulene **153**	-0.7622	0.768
[12]annulene **161**	-0.2137	0.582
[14]annulene **60**	-1.5495	1.000
[16]annulene **163**	0.6288	0.729
[18]annulene **155**	-1.2043	0.837
[24]annulene	0.8862	0.805

In all cases, the direction of ring current effect is predicted correctly, i.e, a negative ring current is diatropic and a positive is paratropic, as also are the individual ring current intensities deduced from a statistical comparison with experimental ^{1}Hnmr chemical shifts. Moreover, a set of aromatic character k values[79] has been derived as a measure of aromaticity, which is based on the HMO theory with allowance for simple bond alternation. The method is briefly described as follows. When an annulene has alternately longer and shorter bond length, the resonance intergral between adjacent P_{π} orbitals are no longer expected to be equal to the non-alternating value β (usually taken from benzene, which has a bond length of 1.397 Å).In this case, two resonance intergrals (β_1 and β_2) are now required to describe the π-electron properties of the molecule, i.e.:

$$RC = f(\beta_1,\beta_2) \text{ ---------- (1)}$$

If the resonance intergrals are assumed as:

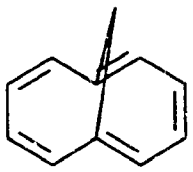
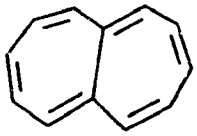
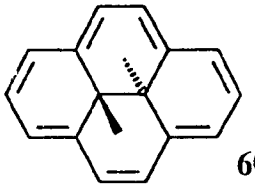
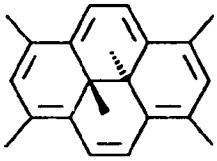
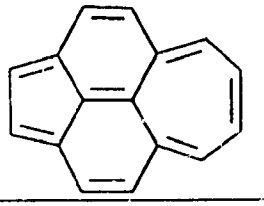
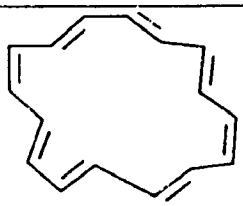
$$\beta_1 = k\beta,\ \beta_2 = \beta\ (k \leq 1)$$

This gives

$$RC = f(k\beta,\beta) \text{ ----------(2)}$$

The RC of a variety of annulenes has been calculated previously. To derive k, β has to be parameterized, e.g., benzene, as the perfect [6]annulene, obviously may be assigned a k value of unity. Using the benzene RC, β would be readily estimated from equation (2). Thus, substituting

Table 5. Dimagnetic exaltation data[80b]

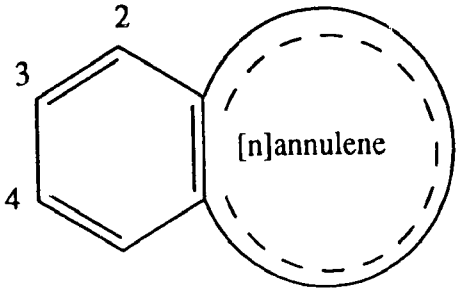
compound	dimagnetic exaltation (Λ X 10^6) (cm^3 mol^{-1})
 **153**	36.8
 **176**	-6
 **60**	81
 **177**	72
 **178**	53
 **179**	-5

RC of an annulene into equation (2), it would be possible to derive the aromatic character k. Very interestingly, using dihydropyrene **60** rather than benzene to parameterize β renders much smaller errors in calculating the aromatic character k of a series of annulenes.

^{1}Hnmr techniques have also been used to measure diamagnetic susceptibility exaltation which is a well documented criterion of aromaticity[80]. Some of these results are shown in Table 5. Very recently, a similar method has been reported for measuring the relative ring current effects of aromatic compounds[81].

Another feature of ^{1}Hnmr experiments is that coupling constants can be obtained. It has been suggested that the size of the $^{3}J_{HCCH}$ coupling constant of vicinal protons should be a measure of aromaticity[82]. Günther et al have demonstrated that the π-electronic structure of an annulene can be studied by examining the vicinal coupling constants of the benzene nucleus in the corresponding benzo[n]annulene. He proposed a quantitative index, named the "alternance parameter", Q, as the quotient of the bond orders ($P_{u,v}$) of the 2,3 and 3,4 bonds of the six-membered ring in the benzo[n]annulene **184**, i.e., $Q=P_{2,3}/P_{3,4}$. The bond orders, $P_{2,3}$ and $P_{3,4}$, can be calculated theoretically or determined experimentally from the measured $^{3}J_{u,v}$ values by using equation **3** based on the π-SCF bond order data and coupling constants in benzene, naphthalene, and

anthracene[83a]. Some results of this method are given in Table 6. The corrected Q values were obtained using equation 3, in which $^3J_{uv}$ was corrected for steric effects by subtracting a phenanthrene type (0.30 Hz) or naphthalene type (0.08Hz) correction from the corresponding experimental value.



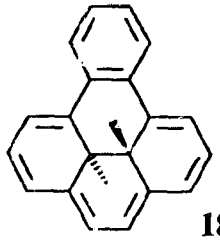
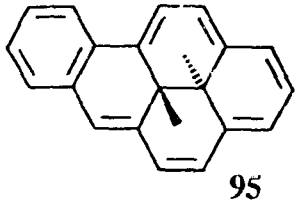
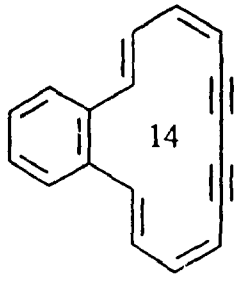
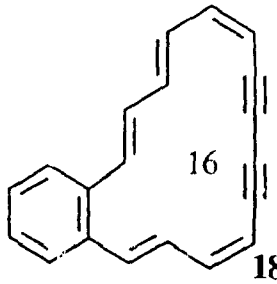
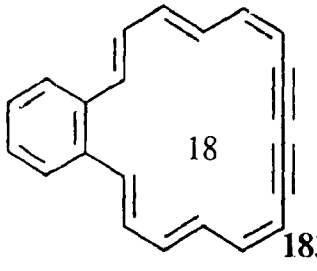
184

$$P_{u,v}(SCF) = 0.104\ ^3J_{u,v} - 0.120 \quad \text{--------} \quad (3)$$

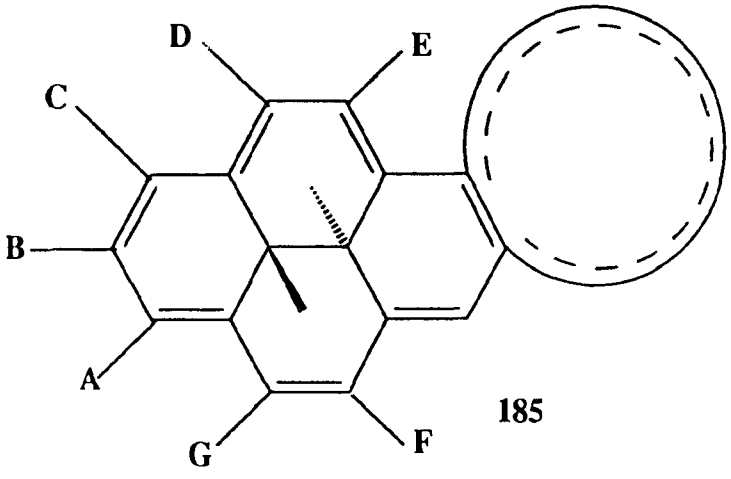
Similar to the chemical shift measurement of the ring current effects and to that of the diamagnetic susceptibility, Günther's Q-value leads to classification of [n]annulenes into three classes: (1) delocalized $4n\pi$ systems ($Q<1.04$); (2) delocalized $(4n+2)\pi$ systems ($Q>1.10$); and (3) localized π systems ($Q=1.04$ to 1.10).

In comparison with the chemical shift measurement of the ring current model, the coupling constant measurement of Q-values is less sensitive to the solvent and neighboring group effects. On the other hand, the coupling constants are more largely affected by geometrical factors, such as bond and dihedral angles. Also in many cases, some of the four protons on the six-ring are degenerate in the

Table 6. Günther's alternance parameters

compound	$Q_{(SCF)}$	Q_{Exp}	Q_{Exp}(corrected)
 **180**	1.146[84]	1.230	1.178
 **95**	1.162[32] 1.165	1.261 1.216	1.207 1.202
 **181**	1.143[83d]	1.171	1.139
 **182**	1.016[83d]	1.033 1.021	0.986
 **183**	1.080[83d]	1.160	1.108

^{1}Hnmr spectrum, or appear as an ABCD system without enough observed lines for analysis. Under such complications, the coupling constants are not analyzable.



185

We intend to use the dihydropyrene ring to probe the aromaticity of rings which are fused to the dihydropyrene. We are interested in this project for several reasons: (1) Dihydropyrene is an almost planar, rigid skeleton so that it acts as a perfect [14] annulene; (2) It has more than one probe to index the π-electronic structure of either the dihydropyrene ring or the annelating ring in structure **185**. The peripheral protons A, B, C, D, and G, and internal methyl protons are little affected by annelating ring so that their chemical shift can be directly used to measure the delocalization effects in both rings. Similarly, the coupling constants J_{AB}, J_{BC}, J_{DE} and J_{FG} can be used. (3) The ^{1}Hnmr analysis of a dihydropyrene moiety is very simple. Similar to the spectrum in Figure 3, for structure **185**, the chemical shifts of the internal methyl protons are

trivial to measure, and the protons A, B, and C should approximately appear as an ABM system; in addition, the protons D, E, and F, G would be two AB systems, respectively. Hence, a ^{1}Hnmr analysis of the dihydropyrene moiety in those compounds can be readily carried out.

3.1.4 Summary

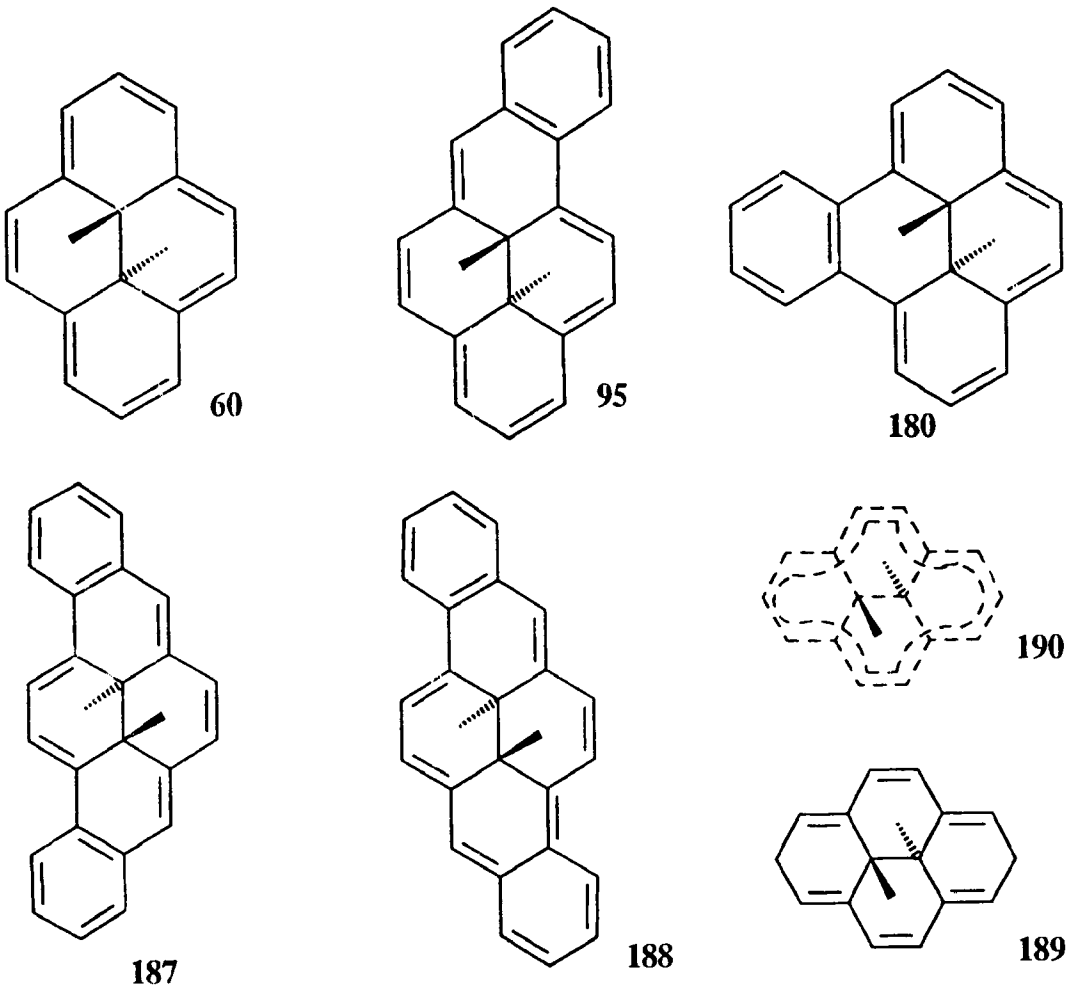
In the foregoing material, we have discussed the three main criteria for the aromaticity of a molecule. The first is the bond length which gives a clear guide to whether the molecule is aromatic. The second is the resonance energy. The third is the ^{1}Hnmr spectra in which the chemical shift and coupling constants give some measure of the aromaticity. It seems that the ^{1}Hnmr spectrum is the easiest to use and requires the least amount of material, moreover, it gives more information. The studies of benzoannulenes are especially suited to using ^{1}Hnmr techniques for the investigation of aromaticity of these compounds.

3.2 Annelated dihydropyrenes

In 1982, Mitchell and coworkers[85] published a series of papers under the title "Toward the understanding of benzannelated annulenes", where the effects of bond

localization in the macrocyclic ring on the reduction of diatropicity and the role of Kekulé structures in differentiation of benzoannulenes were discussed. Using the compounds **60, 95, 180, 187, 188** and **189**, they derived

Figure 7. Dihydropyrenes



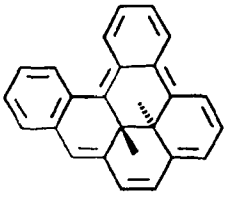
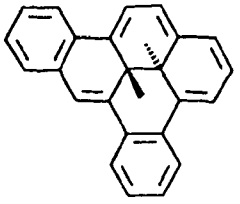
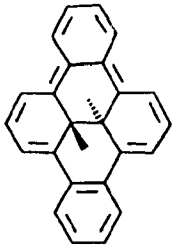
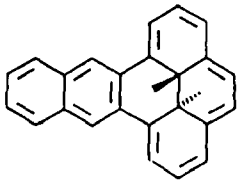
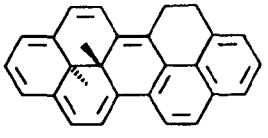
empirically for benzodihydropyrenes a linear relationship (equation 4) between the chemical shift shielding ($\Delta\delta$=0.97-δ) of the internal methyl protons relative to the model

compound **189** (δ=0.97), and the average deviation ($\Delta r = m^{-1}\Sigma|P_u-0.642|$) of the π-SCF bond orders (P_u) of the macrocyclic ring from the fictitious Hückel [14]annulene **190** value of 0.642.

$$\Delta\delta = 5.533 - 0.02752\Delta r \quad \text{---------- (4)}$$

(correlation coefficient p = 0.9902)

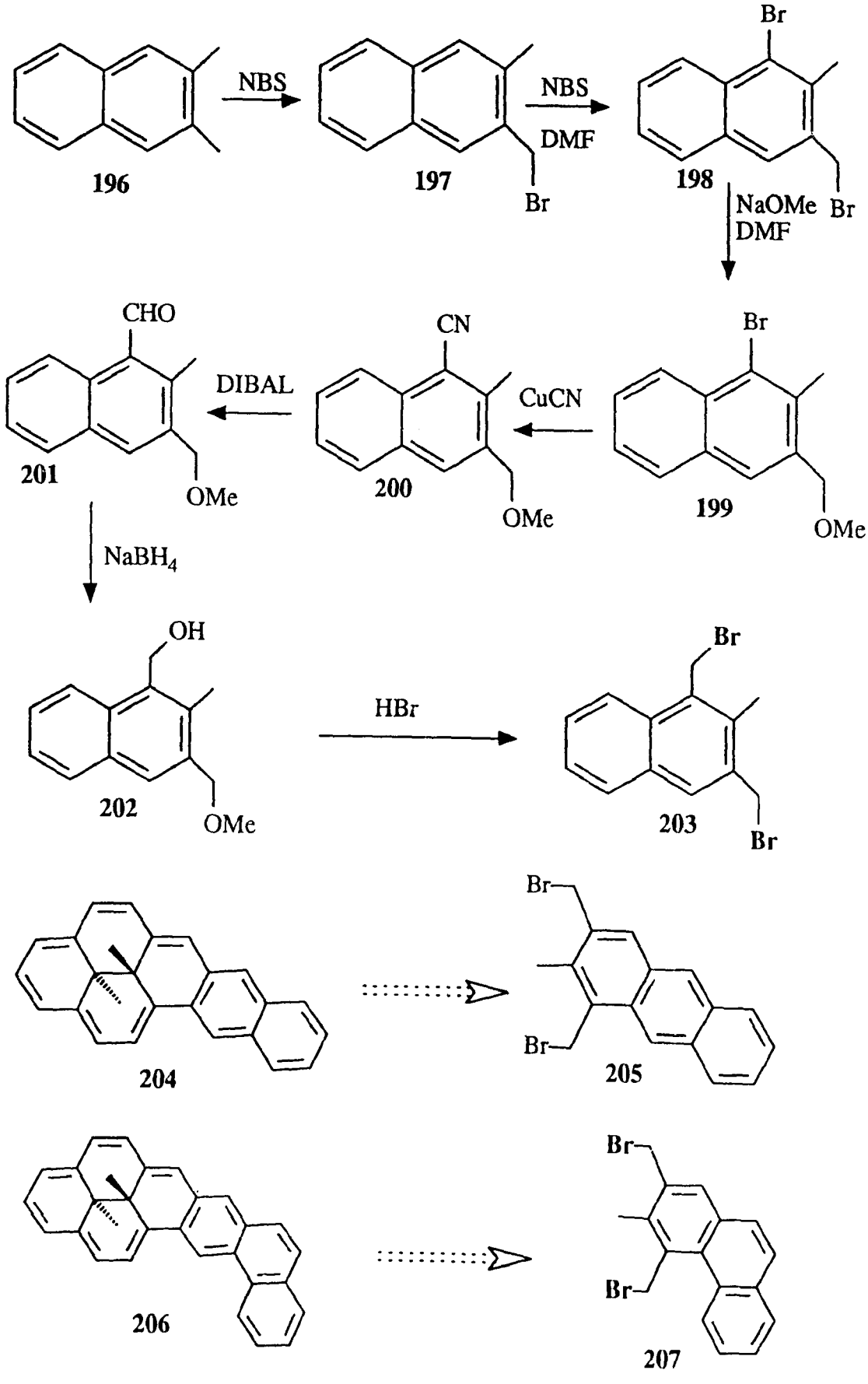
Table 7. Calculated and observed methyl chemical shift (δ_{Me})

compound	δ_{calc} (Mitchell)	δ_{calc}(Vogler)	$\delta_{Exp.}$
 **191**	-3.43	-3.69 -3.62	.....
 **192**	0.10	-0.35 -0.40	.....
 **193**	-3.31	-3.85	.....
 **194**	-1.25	.....	-0.74
 **195**	-2.75	.....	-2.78

Armed with this equation, they have predicted the chemical shifts of the internal methyl protons for many benzodihydropyrenes. As well, Vogler[86] has calculated the chemical shifts of some benzoannelated [14]annulenes by means of semi-empirical quantum chemical procedures. Some of the results from both methods and from experiments are listed in Table 7.

3.2.1 Syntheses

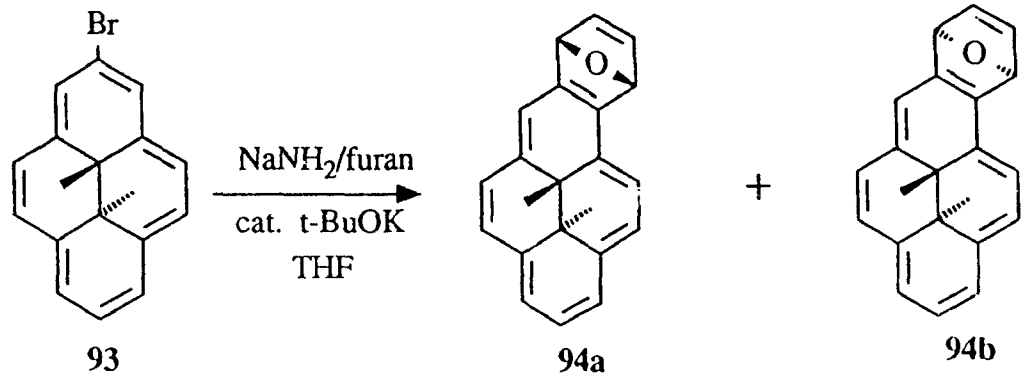
Most syntheses of benzodihydropyrenes have been achieved using the very faithful sequence developed by Boekelheide and Mitchell, which we discussed previously in detail (see page 26). Thus for benzodihydropyrenes **95**, **180**, **187**, and **188**, the same dibromide **203** was involved and the syntheses were basically achieved through (1) Wittig rearrangement followed by methylation of the bis-thiolate anion or methylation of the dithiacyclophane followed by Stevens rearrangement, (2) conversion of the bis(S-methyl)derivative into the bis(dimethylsulfonium)salts, and (3) Hofmann elimination followed by valence isomerization of the cyclophanedienes into the benzodihydropyrenes. The beauty of this sequence is that a single precursor dibromide **203** leads to four benzodihydropyrenes **95**, **180**, **187**, and **188**. However, a suitable dibromide synthesis can be quite time consuming, e.g. the dibromide **203** was


NBS
NBS
DMF
NaOMe
DMF
DIBAL
CuCN
NaBH4
HBr
196
197
198
199
200
201
202
203
204
205
206
207
Br
CN
CHO
OH
OMe

prepared in overall yield of 18% through seven steps. In the cases of the naphtho[a]dihydropyrene **204** and the phenanthro[a]dihydropyrene **206**, the corresponding dibromides **205** and **207** have no obvious syntheses. Therefore we decided to investigate an alternative approach to these novel compounds that might make use of a single common intermediate, aryne **57**.

In chapter 1, we indicated that our objective is to generate the dihydropyryne **57** and to use it to synthesize a variety of annelated dihydropyrenes. In this approach, dihydropyrene **60** is a starting material, which can be readily synthesized (see chapter 2). However after the unsuccessful attempts to ortho-metallate dihydropyrene, we decided to go back to the dehydrobromination of the easily accessible bromide **93** to easily access the aryne.

Initially, the furan adducts **94** were obtained in very low yield (13%). Further investigations indicated that a higher yield (62%) could be achieved under conditions of room temperature, the presence of a catalytic amount of t-BuOK, five equivalents of $NaNH_2$, and a large excess of furan. The ^{1}Hnmr spectrum of the product showed that the isomers **94a** and **94b** were formed in an approximate 1:1 ratio. The isolation of one of the isomers was achieved using a combination of chromatography and fractional recrystallization. However which isomer this was is too hazardous to assign by ^{1}Hnmr alone (Figure 8).


Br
NaNH2/furan
cat. t-BuOK
THF
O
O

93 94a 94b

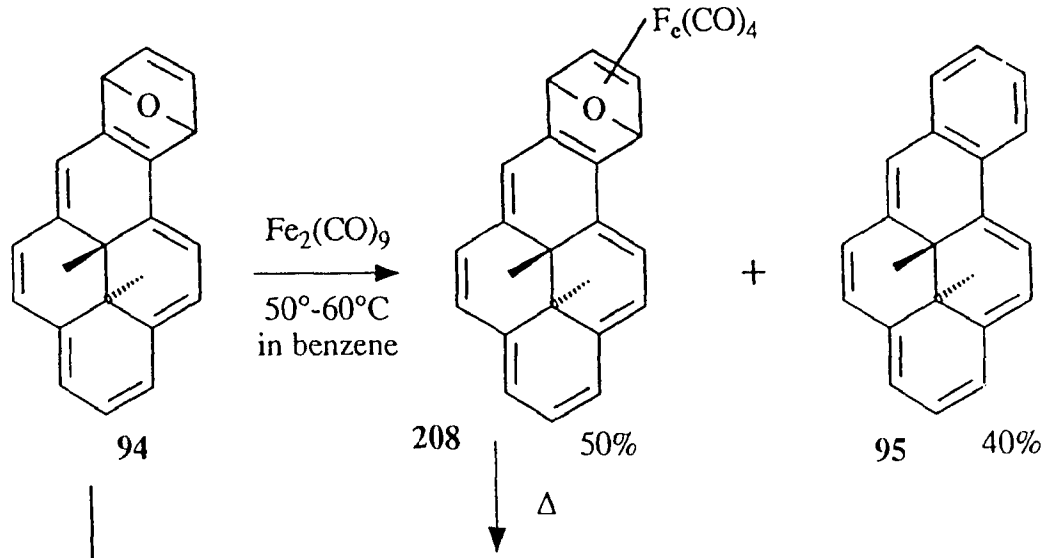

O
Fe(CO)4
O
Fe2(CO)9
50°-60°C
in benzene
208
50%
95
40%
94
Δ
Fe2(CO)9
reflux in benzene
95
Fe(CO)3
209

Figure 8. ^{1}H nmr spectrum of 94

(^{1}Hnmr: 250 MHz, $CDCl_3$, Amb.)

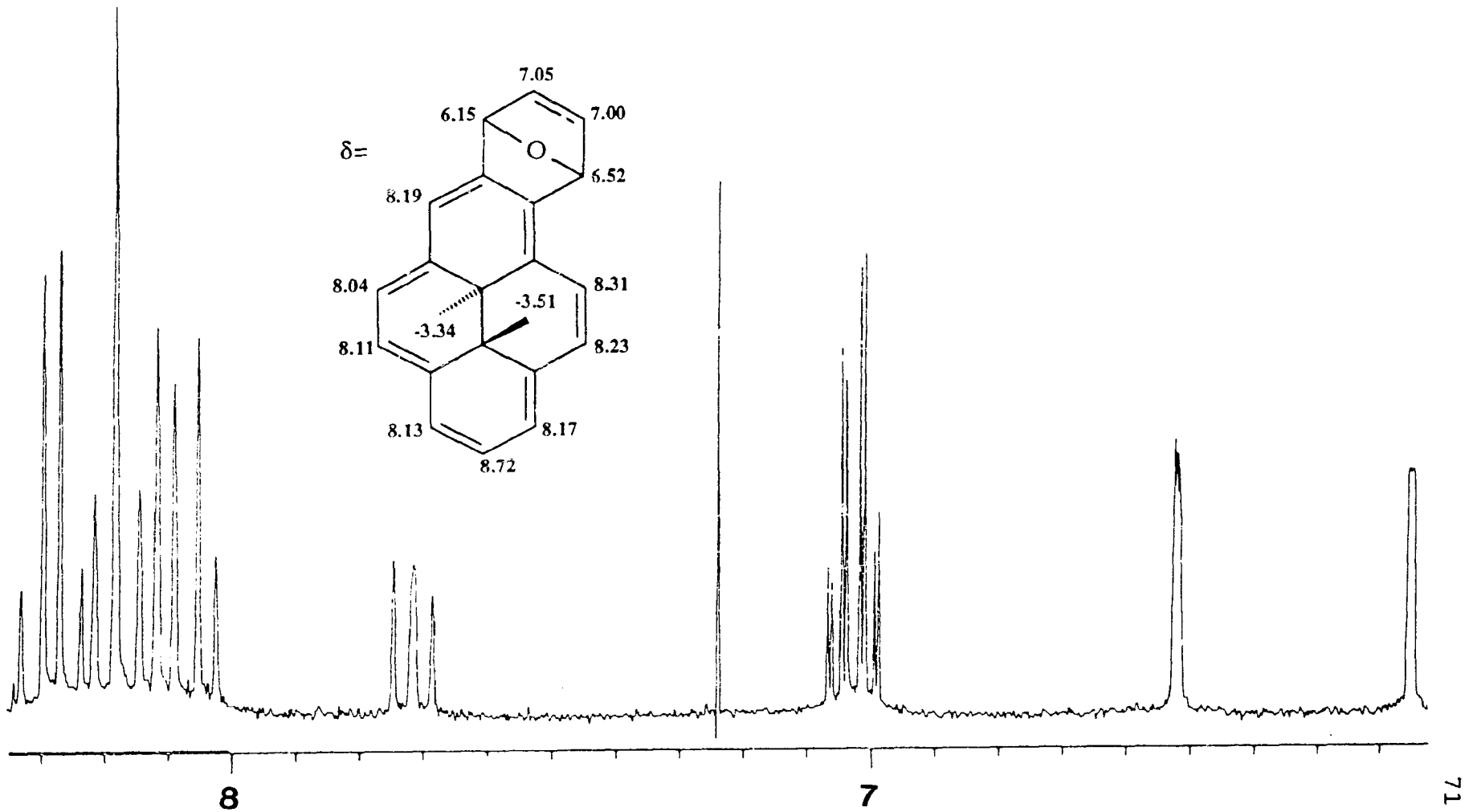
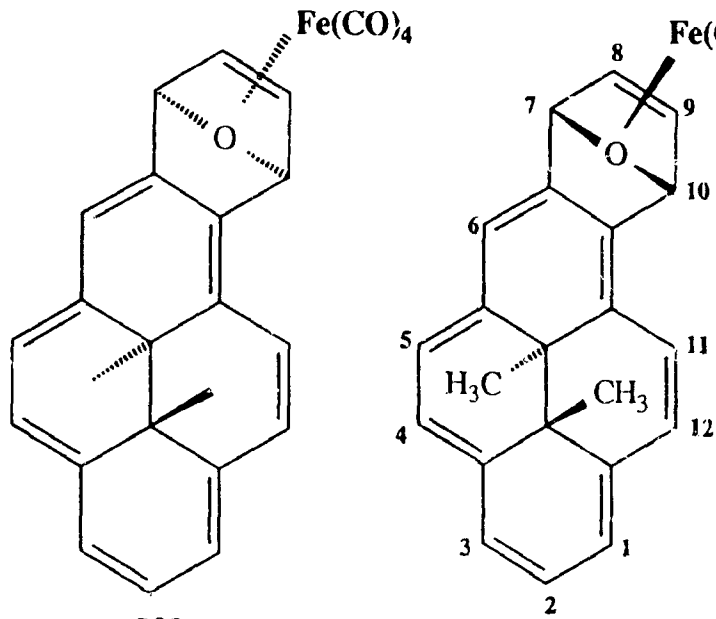
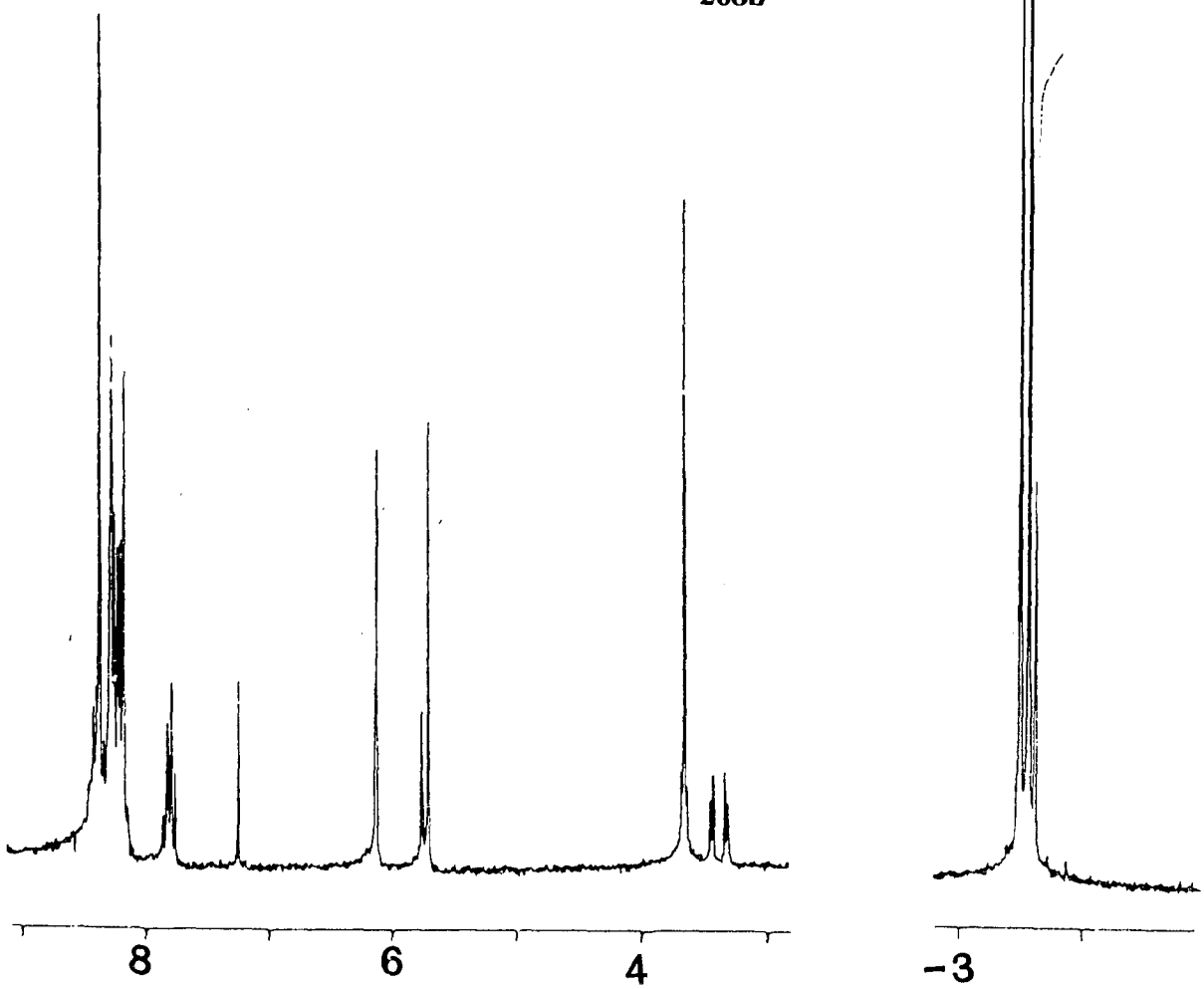


Figure 9. ^{1}H nmr spectrum of **208**

(^{1}Hnmr: 250 MHz, $CDCl_3$, Amb.)



208a **208b**



The deoxygenation of the adducts **94a** and **94b** was carried out using $Fe_2(CO)_9$[88], which proved to be very rewarding for us. The intermediate complex **208** was moderately stable so that it could be isolated as a crystalline solid. As expected[89], the ^{1}Hnmr spectrum (Figure 9) showed that only a pair of isomers (**Fe** *cis* to **O**)**208a** and **208b** were obtained when the mixture of **94a** and **94b** was used as the starting material. In other words, **94a** selectively gave **208a** and **94b** gave **208b**. In the ^{1}Hnmr spectrum of the mixture, the chemical shifts of the dihydropyrene moiety protons appeared as two multiplets at δ 8.30 for protons 1, 3, 4, 5, 6, 11, and 12, and δ 7.80 for proton 2. The four singlets at δ 6.14, 6.13, 5.76, and 5.71 are due to the bridgehead protons 7 and 10 in the two isomers **208a** and **208b**, and the two ABs at δ 3.65/3.64 with J_{AB}=5.8Hz and δ 3.43/3.31 with J_{AB}=5.1Hz are due to protons 8 and 9. There are three peaks at δ -3.51, -3.58, and -3.63 due to the internal methyl protons and the intergrations indicate that the ratio of two isomers is about 2:1. In the free ligand **94**, the vinyl protons resonate at δ 7.05/7.00. The upfield shift of *ca* 3.5 ppm in the vinyl protons 8 and 9 in going from **94** to **208** proves that the bonding is formed between the vinyl π-bond and the iron, since upfield shifts of *ca*. 3 ppm have been observed for a number of similar complexes[89]. In refluxing benzene the complexes **208** gave benzodihydropyrene **95** quantitatively. As well

benzodihydropyrene could be produced in 90% yield when the deoxygenation of the adducts **94** was achieved by refluxing the solution in benzene in the presence of one equivalent of $Fe_2(CO)_9$ without isolation of the complexes **208**. By doing this very excitingly, we discovered that a small amount of complex **209** was also formed when an excess amount of $Fe_2(CO)_9$ was used. This interesting complex will be discussed later.

Previously, the benzo[a]dihydropyrene **95** was synthesized through a 16-step route in an overall yield of *ca.* 4.7% by our group[32]. However, in this new route, it is obtained in 12 steps in an overall yield of *ca.* 19%. These results encouraged us to investigate the syntheses of other annelated dihydropyrenes, such as the naphtho[a]dihydropyrene **204** and the phenanthrodihydropyrene **206**.

The two compounds **204** and **206** were chosen because of the accessibility of the required trapping reagents, **212** and **218**. Starting from phthalide, **210**, the 1-methoxy-phthalan **211** was obtained in almost quantitative yield using a one-pot reaction modified from the literature[90]. Then, a resonably stable solution of isobenzofuran, **212**, was prepared on treatment of **211** with $NaNH_2$ in THF. The subsequent addition of bromodihydropyrene **93** and $NaNH_2$ gave the expected adducts **213** in *ca.* 42% yield. Not surprisingly two isomers **213a** and **213b** were formed. One of the isomers

was purified by fractional recrystallization, and its ^{1}Hnmr spectrum is shown in Figure 10. Finally, deoxygenation of **213** with $Fe_2(CO)_9$ gave the naphtho[a]dihydropyrene **204** in 70% yield together with a small amount of its complex, presumably **214**.

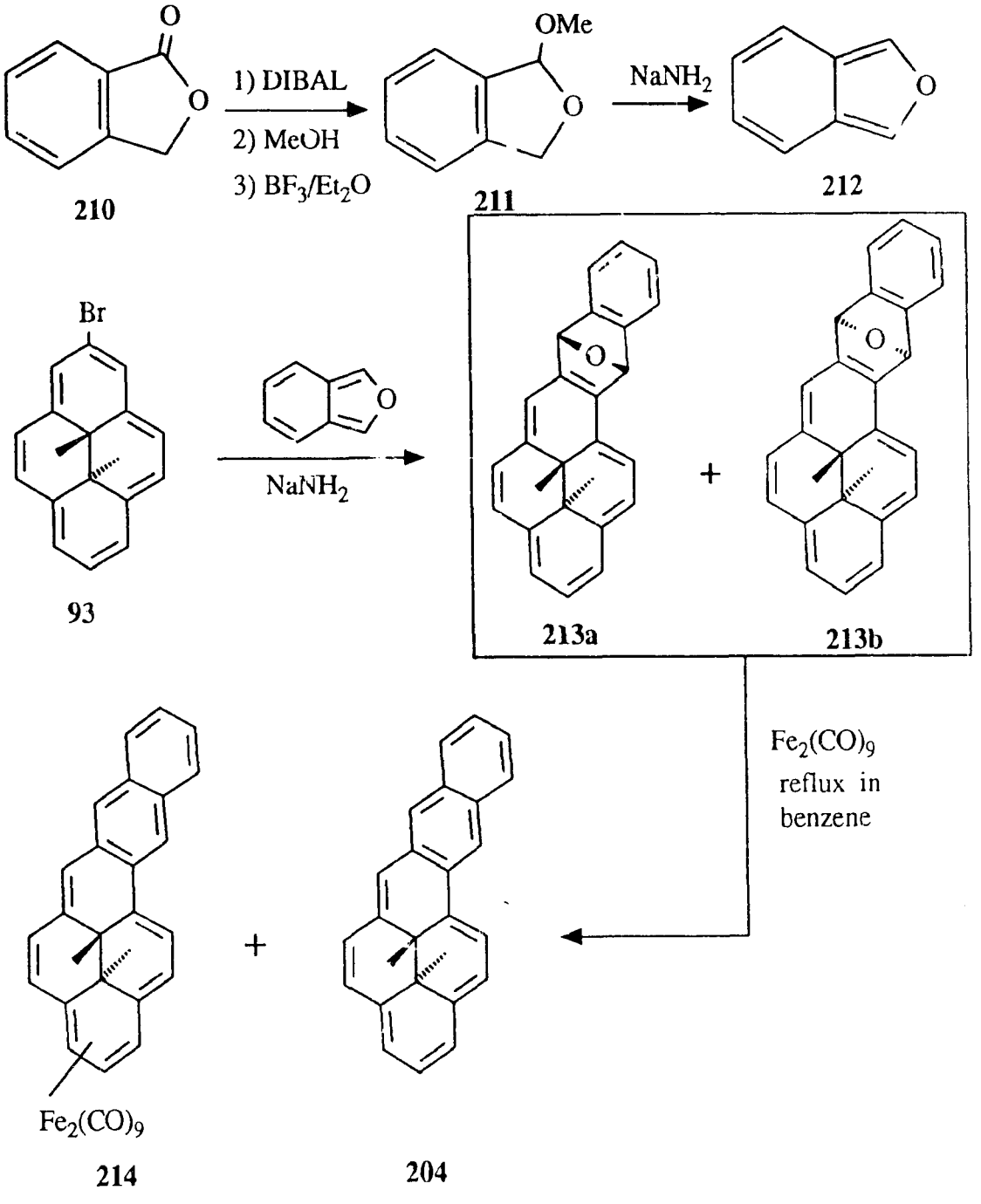


Figure 10. ^{1}H nmr spectrum of **213**

(^{1}Hnmr: 250 MHz, $CDCl_3$, Amb.)

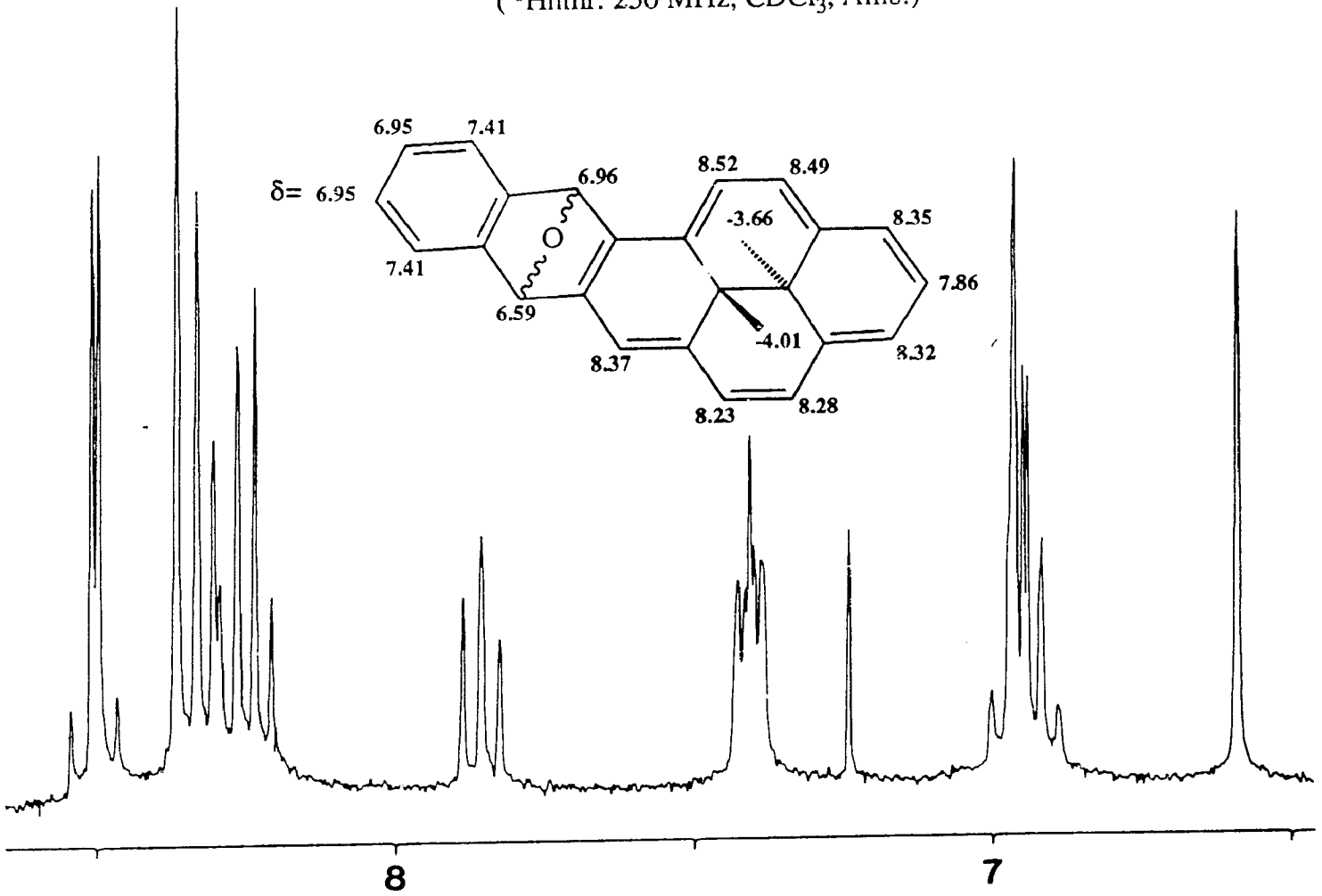


Figure 11. ^{1}H nmr spectrum of **204**

(^{1}Hnmr: 360 MHz, $CDCl_3$, Amb. δ, *J*)

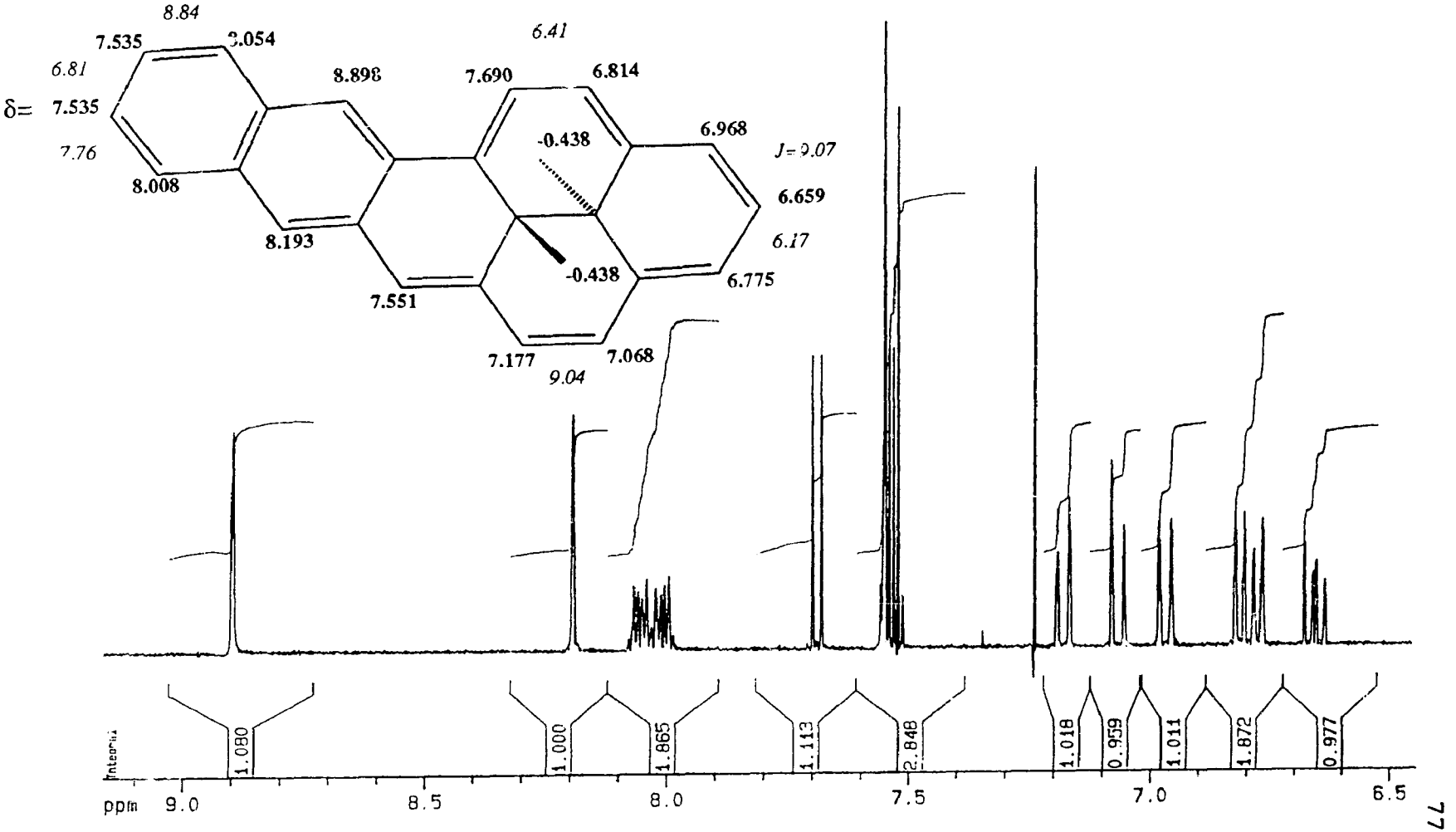
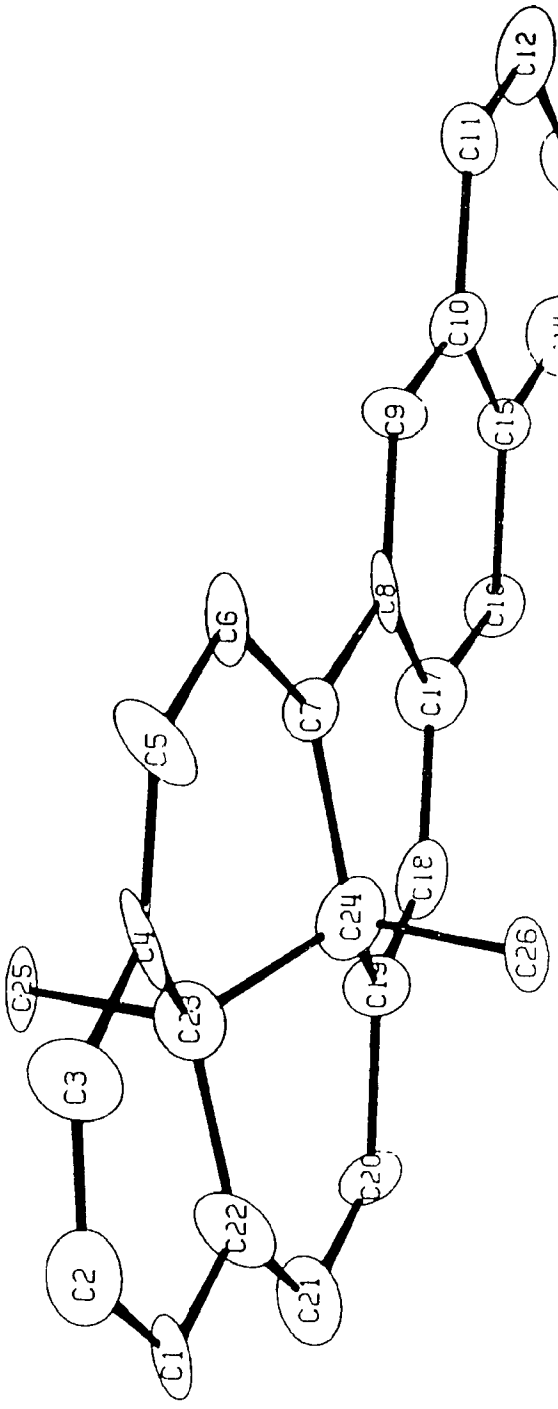


Figure 12. Ortep plot of **204**

Ortep plot of **204**: X-ray structure determination clearly indicated the carbon skeleton, but would not complete using a least square refinement to give the hydrogen atoms. Th crystal system was orthorhombic, space group Pccn (No. 56), with a=24.392Å, b=23.785Å, c=6.140Å.



Naphthannulene **204** is a relatively stable, dark red, crystalline compound, mp 182-183°C, which disolves readily in most organic solvents. Its ^{1}Hnmr spectrum and preliminary x-ray results are shown in Figure 11 and 12, respectively.

Starting from 1-bromonaphthalene **215**, naphtho[1,2-c]furan, **218**, was prepared through a modified method from the literature[31b]. Reaction of the furan **218** with bromodihydropyrene **93** and $NaNH_2$ yielded 47% of a mixture of the four isomers **219a, 219b, 219c,** and **219d**, which are indicated by the resonances of the internal methyl protons between *ca.* -3 and -4 ppm in the ^{1}Hnmr spectrum. Attempted separation of these isomers failed. Therefore, they were used directly in next step where deoxygenation with $Fe_2(CO)_9$ yielded 44% of a red crystalline solid, **206**. Surprisingly, the ^{1}Hnmr spectrum showed that two isomers were formed in a ratio of 4.5:1, which, presumably, is due to better complexation of one isomer with $Fe_2(CO)_9$.

After recrystalization, the major isomer was obtained pure as a stable dark red crystalline compound, mp 209-210°C. Its structure was readily assigned as **206a** on the basis of it having the most deshielded proton 14 at 9.90 ppm in its ^{1}Hnmr spectrum (Figure 13). This assignment was confirmed later by the preliminary x-ray studies (Figure 14).

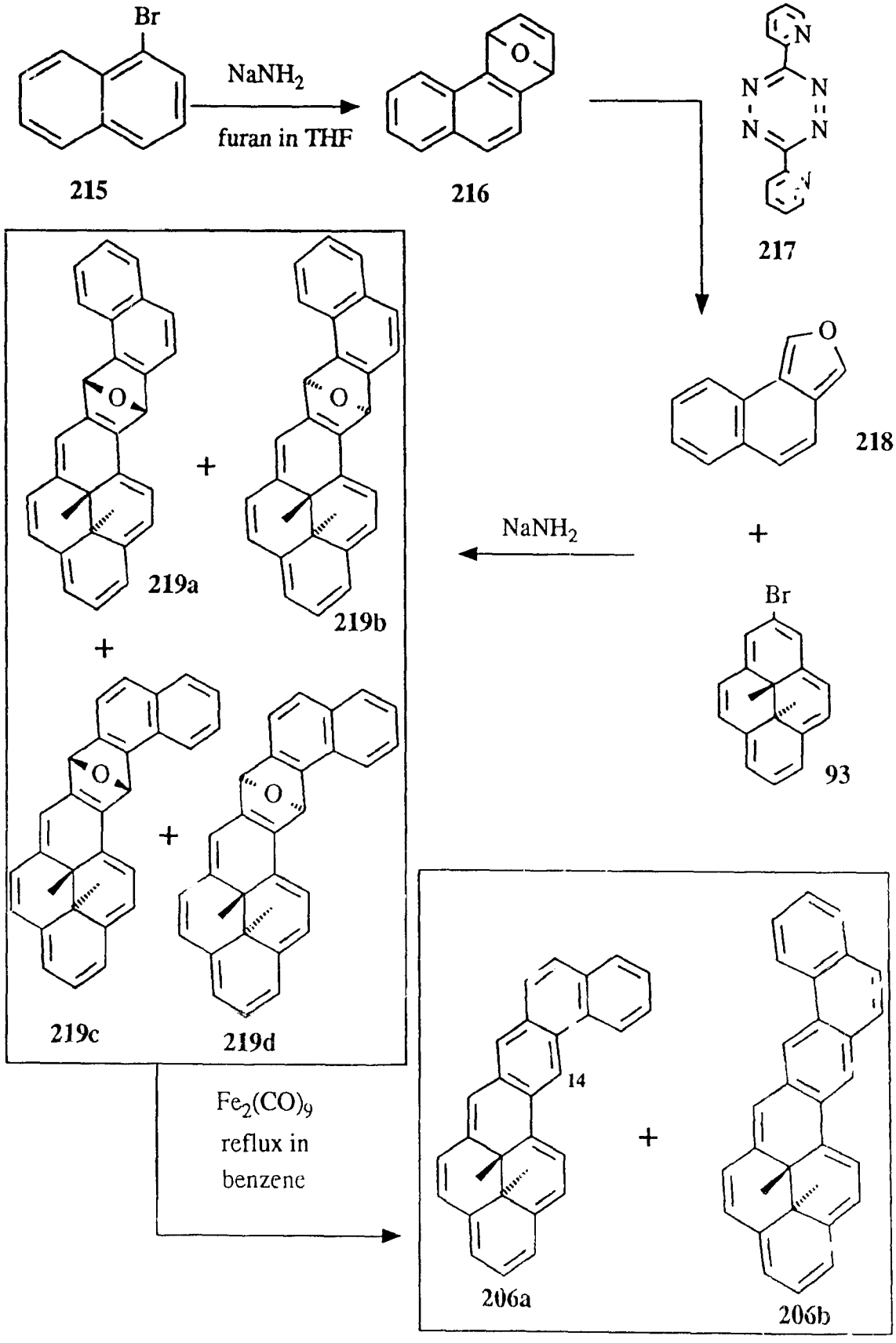

Br
NaNH2
furan in THF
O
N
N
N
N
N
215
216
217
O
218
+
Br
93
NaNH2
O
O
219a
219b
+
O
O
219c
219d
+
Fe2(CO)9
reflux in
benzene
14
206a
+
206b

Figure 13. ^{1}H nmr spectrum of **206a**

(^{1}Hnmr: 360 MHz, $CDCl_3$, Amb. δ, *J*)

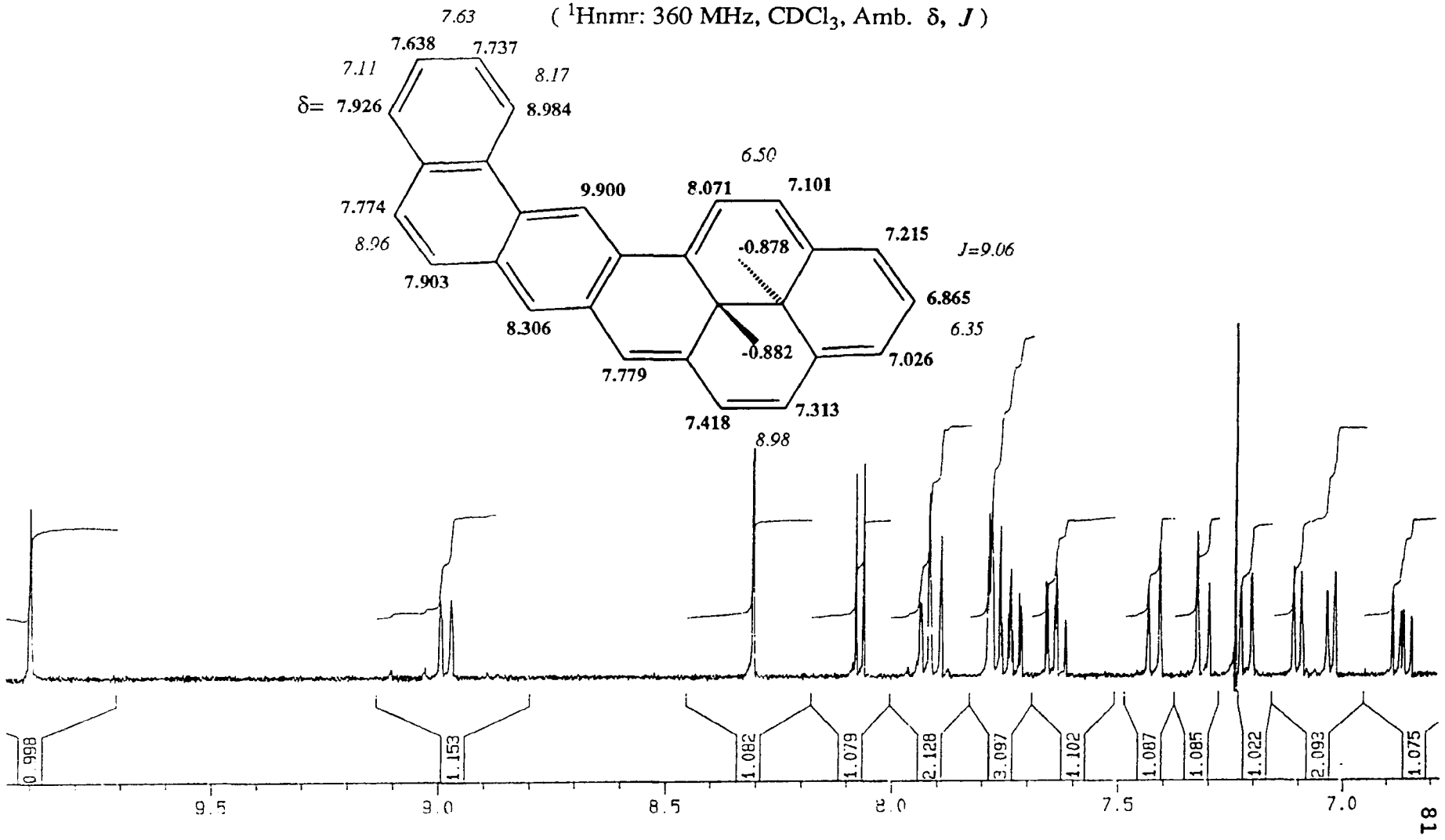
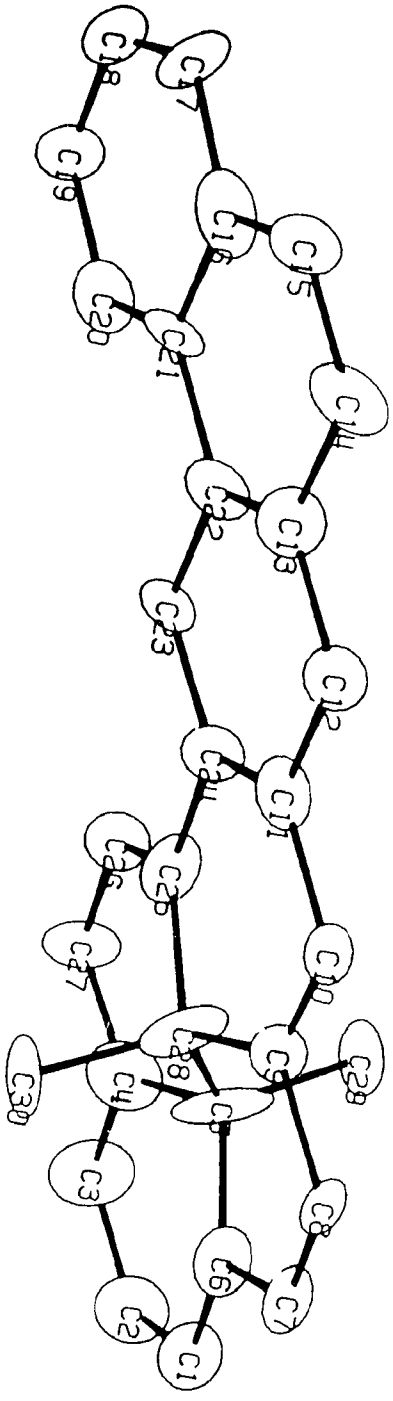


Figure 14. Ortep plot of **206a**

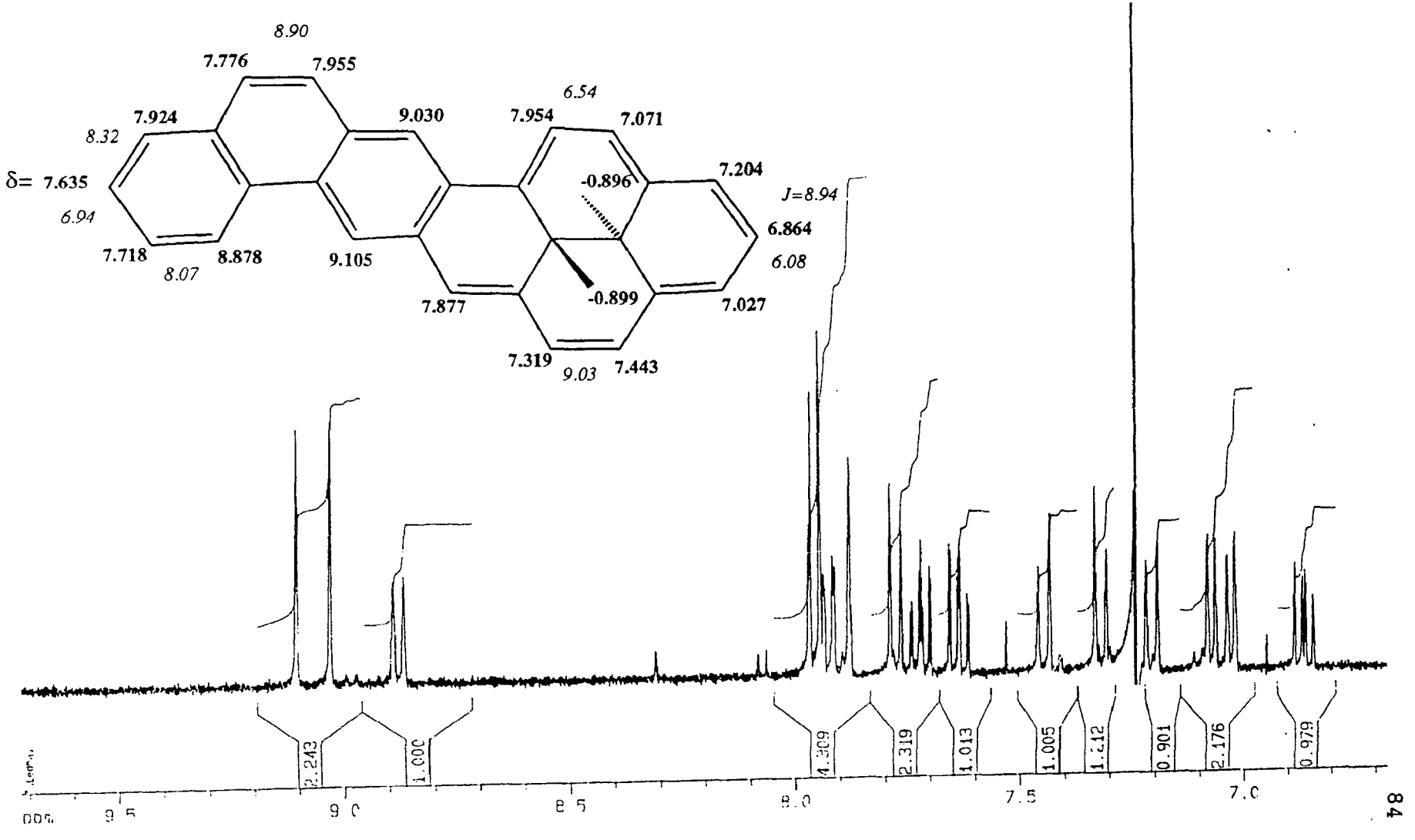
Ortep plot of **206**: X-ray structure determination clearly indicated the carbon skeleton, but would not complete using a least square refinement to give the hydrogen atoms (R=0.13). Th crystal system was tetragonal, space group $P4_2/n$ (No. 86), with a=17.311Å, b=17.304Å, c=13.606Å.



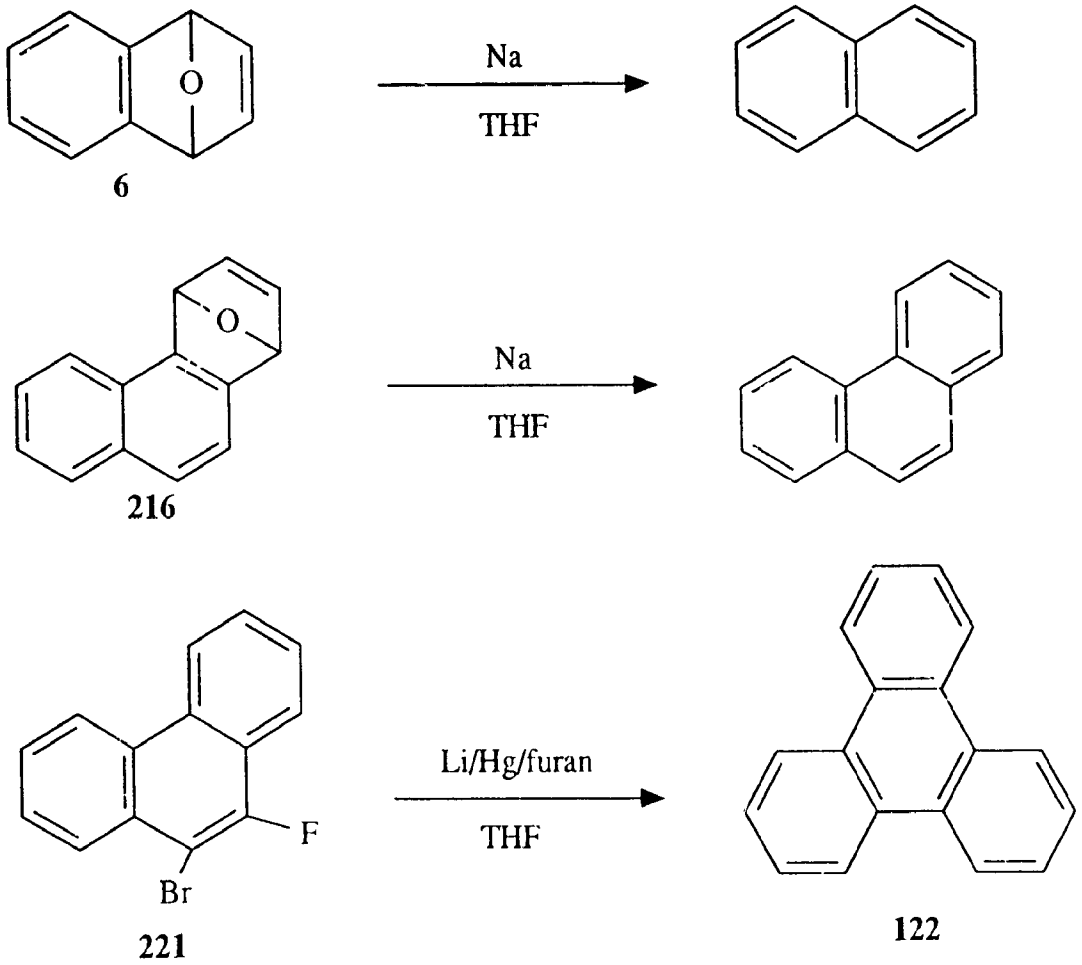
An interesting discovery was that some of the deoxygenated products, namely benzodihydropyrene **95**, naphtho-dihydropyrene **204** and phenanthrodihydropyrene **206** were occasionally formed during the preparation of their corresponding adducts **94, 213**, and **219**, respectively. For example, on one occasion, a large amount of deoxygenated product phenanthrodihydropyrene **206** was obtained in attempting to prepare the adduct **219** when a large excess $NaNH_2$ was used. This fortunate result yielded **206a** and **206b** in a ratio of 1:1, permitting the isomer **206b** to be purified in a characterizable amount. The chromatography of this 1:1 mixture was carried out on silica gel using light petroleum ether as eluant. The red band on the column was collected in three fractions, front, central and rear portion, respectively. The ^{1}Hnmr spectrum of each portion showed that the rear portion contained the highest concentration of isomer **206b**. On recrystalization of this fraction from heptane, two kinds of crystals were formed: cubes and needles. These were readily separated by hand. The needles proved to be isomer **206b** by ^{1}Hnmr spectroscopy (Figure 15)and the cubes **206a**.

Figure 15. ^{1}H nmr spectrum of **206b**

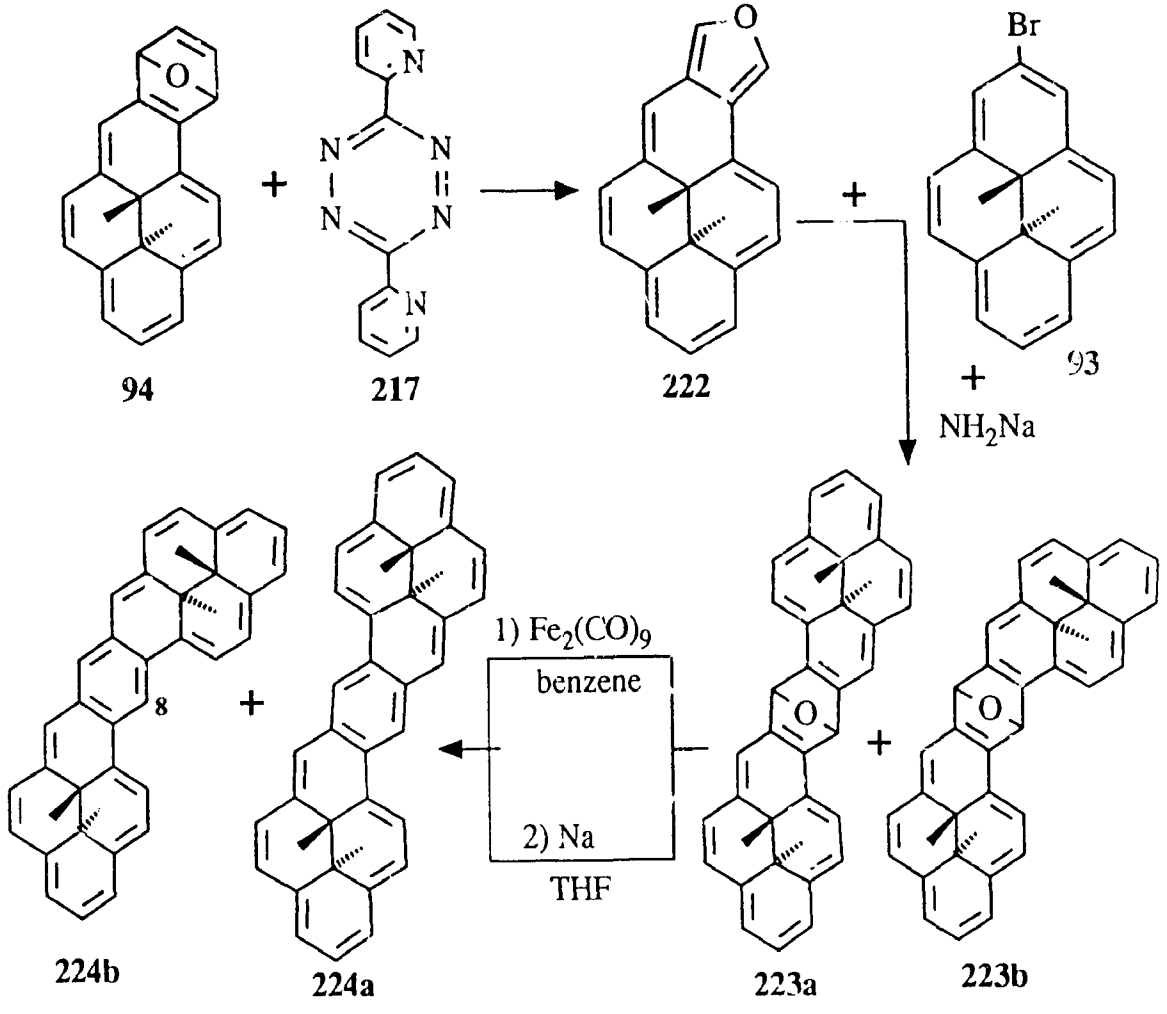
(^{1}Hnmr: 360 MHz, $CDCl_3$, Amb. δ, ***J***)



Deoxygenation with $NaNH_2$ is unusual and has not been reported, although it occurs with a tertiary amine under irradiation[91a]. Sodium metal itself does react with **6** and **216** which give naphthalene and phenanthrene in 47% and 39% yield respectively. As well, Wittig and coworkers[91b] have reported a very similar reaction in which triphenylene **122** was formed in 70% yield from the dihalophenanthrene **221** on treatment with Li/Hg in the presence of furan. Free sodium present in commercial sodium amide, while possible seems somewhat unlikely. At this point, we can not propose a definitive mechanism for deoxygenation caused by $NaNH_2$.



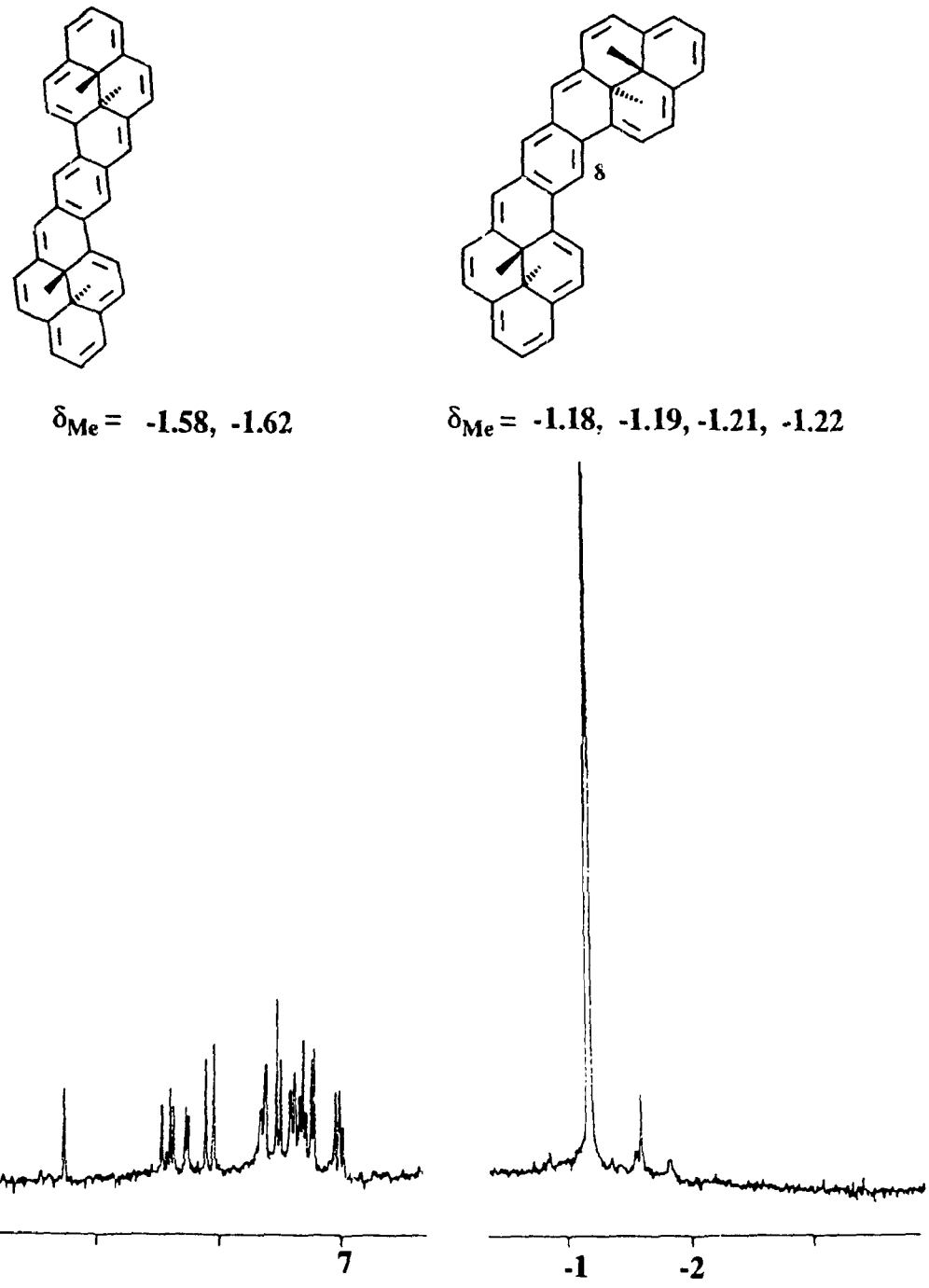
Following the successful syntheses of the annelated dihydropyrenes **95**, **204**, and **206**, we directed our research efforts to the synthesis of the novel compound **224** using the strategy discussed above. Reaction of the endoxide **94** with the tetrazine **217** gave the very interesting dihydropyreno[1,2-c]furan **222** which could be used as benzyne trapping reagent and whose properties will be discussed later. In this particular case, two equivalents of the bromide **93** relative to the furan **222** were used in the dehyrohalogenation reaction because of the easier



accessibility of the bromide **93** than the furan **222**. In the adducts **223**, the dihydropyryne **57** and furan **222** could be fused in two directions: linear **223a** and angular **223b**. A maximum of sixteen possible stereoisomers could be formed by consideration of the arrangements of internal methyl groups and the bridge oxygen. That several were formed was indicated by many peaks for the internal methyl protons between δ *ca.* -3.5 and -5.0 in the ^{1}Hnmr spectrum of the adducts **223**. The formation of so many isomers discouraged us to attempt any separation, and the mixture was used directly in next step. Firstly, deoxygenation with $Fe_2(CO)_9$ gave the product **224** in very low yield. The compound **224** was obtained as a red crystalline solid, which decomposed quickly either on chromatography over silica gel or in $CDCl_3$. Presumably, the low yield in the deoxygenation with $Fe_2(CO)_9$ was due either to the decomposition at the high temperature which is required for deoxygenation, or the complexation of the product formed with $Fe_2(CO)_9$. To improve the yield, the deoxygenation was carried out with sodium in THF at room temperature, which we discovered earlier in this project. This proved to be better for this particular reaction and give a higher yield (47%) of the desired product **224** than reaction with $Fe_2(CO)_9$. Unfortunately, the low stability of the compound **224** prevented us obtaining it in a pure state and characterizing it completely. Nevertheless, its mass

spectrum (CI) gave a molecular ion at m/e 487 (MH^+) and its ^{1}Hnmr spectrum exhibited all the expected resonances (Figure 16).

Figure 16. ^{1}H nmr spectrum of **224** (^{1}H nmr: 250 MHz, THF, Amb.)

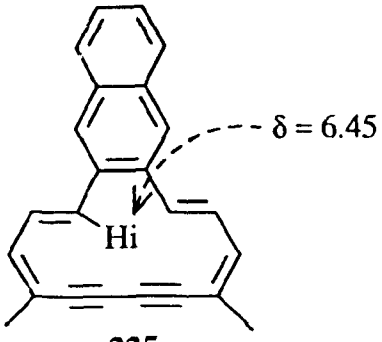


Interestingly the ^{1}Hnmr spectrum showed that the deoxygenation with $Fe_2(CO)_9$ produced isomers **224a** as major product while with sodium, **224b** was the major product. These were easily assigned by the greater chemical shift of the deshielded proton 8 at *ca.* δ 10 in **224b**, and the more deshielded internal methyl protons, which are located closer to the second dihydropyrene ring, so that they are more deshielded than in **224a**. The ^{1}Hnmr spectrum of the mixture has two groups of high field chemical shifts centered at *ca.* -1.20 for **224b** and *ca.* -1.60 for **224a**, respectively. Figure 16 shows the ^{1}Hnmr spectrum for the product mixture obtained from the deoxygenation with sodium in THF.

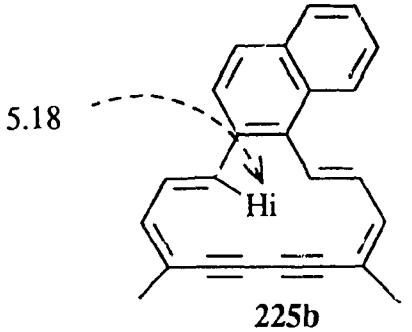
3.2.2 Comparisons

Few higher annelated [n]annulenes have been reported in the literature, due probably to the difficulties in their synthesis. The [2,3]- and [1,2]-naphtho[14]annulenes **225a** and **225b** were obtained by Sondheimer and coworkers[92].

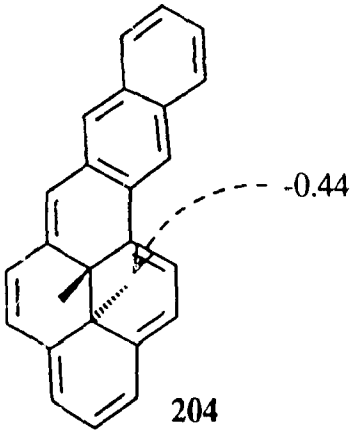
Comparison of **225a** and **225b** can be made with the naphthoannulenes **204** (this project) and **195**[85]. The substantial differences in δ of H_i in **225a** and **225b** and of the internal methyl protons in **204** and **195** indicate that



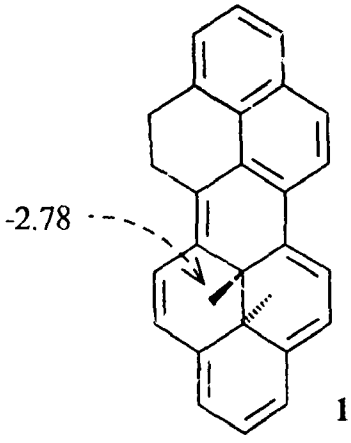
225a



225b

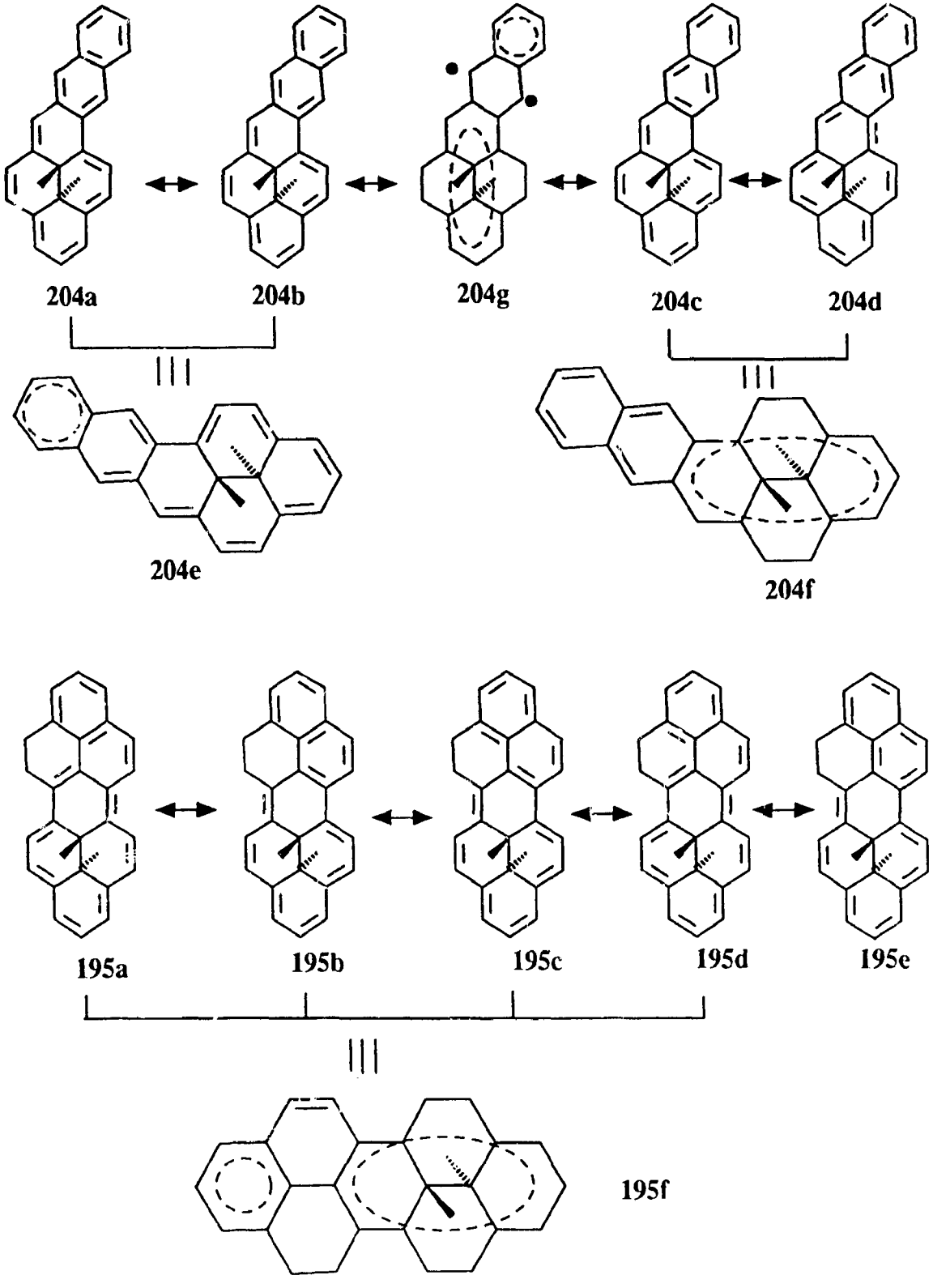


204

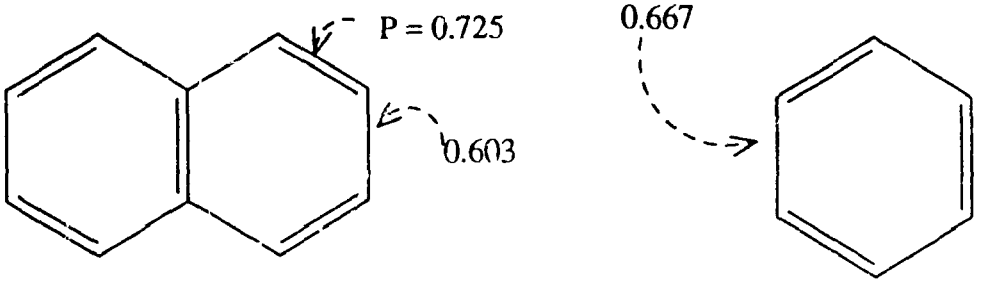


195

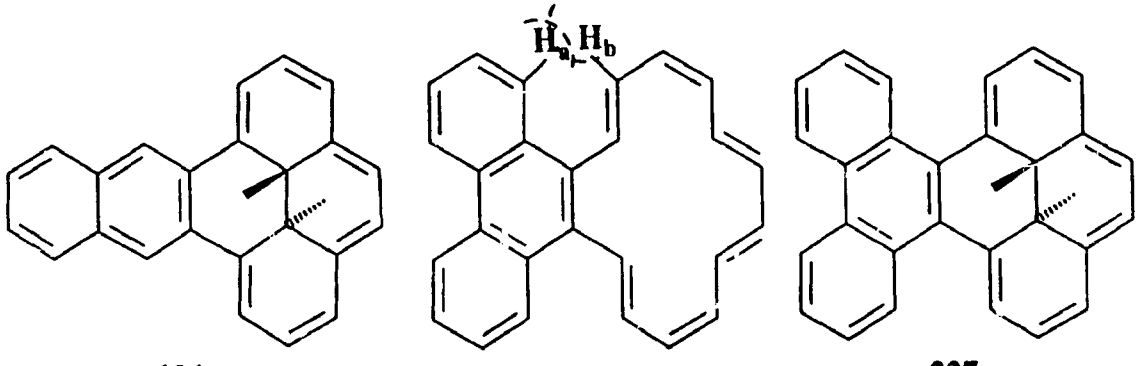
Figure 17. Resonance structure of **204** and **195**



the 14-ring in **225b** and **195** sustains a stronger ring current than that in **225a** and **204** respectively. This leads us to the conclusion that the phenanthrene-like naphtho-fusing in **225b** and **195** is better for the mutual aromaticities of the individual rings than the anthracene-like fusing in **225a** and **204**. Pictorially, this can be understood by examining their Kekulé structures. For example, Figure 17 shows that for the benzene ring to be delocalized in **204e** or for the 14π ring to be delocalized in **204f** the rest of the molecule must be bond fixed. In **195** however both a benzene and the 14π ring can be delocalized at the same time, **195f**. Thus structure **195f** should dominate because of the preservation of two delocalizations, one benzene ring and the macroring, and so the macroring can have a large ring current. In the case of **204** however, both structures **204e** and **204f** contribute, which results in a smaller ring current in the macroring. This result clearly demonstrate the different nature of 1-2 and 2-3 bond shown by other studies, e.g., bond orders[93].



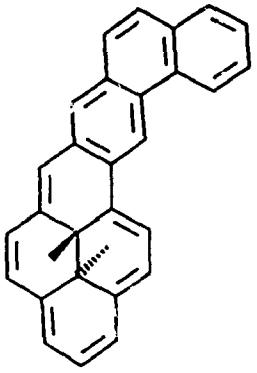
Very recently, Venugopalan[87] has synthesized an isomer of compound **204**, namely **194**. Its internal methyl protons appear at δ -0.74, close in value to those of **204**.



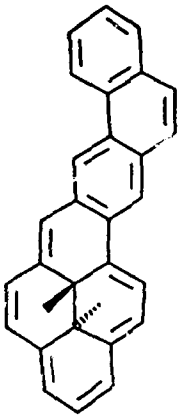
194 226 227

Phenanthro[n]annulenes are rare in the literature. Staab and coworkers[94] have described the 9,10-phenanthro[14]annulene **226**. Its ^{1}Hnmr spectrum indicates that it has an olefinic nonplanar structure for the 14-ring due to strong interactions between H_a and H_b. The 9,10-phenanthrodihydropyrene **227**, reported by Lai[95], clearly demonstrates that fusion in this position retains a high diatropicity in the macroring (the chemical shift of internal methyl protons at -3.32 ppm). However, to the best of our knowledge, no 2,3-phenanthro[14]annulene has been reported. The synthesis of **206a** and **206b** provides the first examples of this system. Comparison of the chemical shifts

of their internal methyl protons (**206** at -0.88 ppm and **227** at -3.32 ppm) shows the difference between fusion at the 2,3- and 9,10-bond.



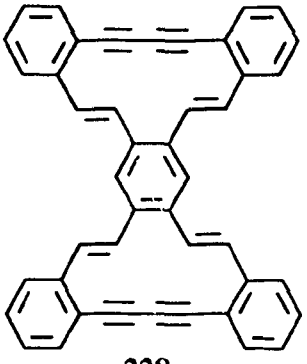
206a



206b

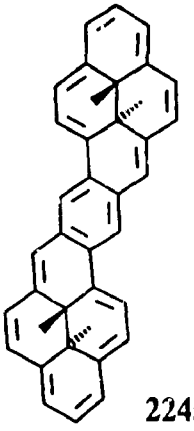
An interesting double [14]annulene **228** was reported to be atropic due presumably to the localization effects of the five benzene rings. However, the pair of double dihydropyrenes **224a** and **224b**, synthesized here, clearly shows that the macrocyclic rings of these are 'diatropic'. The chemical shifts of the internal methyl protons of **224b** are at -1.20 ppm and of **224a** are at -1.60 ppm. Since the methyl groups in **224a** are less deshielded by the second 14-ring than in **224b**, δ values of **224a** should reflect the ring current effect better. Comparison of $\Delta\delta$ values (difference from δ of model **189**) of **224a** with that of the parent dihydropyrene **60** leads us to the conculusion that **224a** shows *ca.* 50% of the ring current in the macroring relative

to that in dihydropyrene **60**. In terms of Kekulé's structures, this result implies that the contributions of structure **224e** and **224f** are negligible and that of **224c** and **224d** are predominant. In each of these predominant structures, there is always one delocalized dihydropyrene ring.

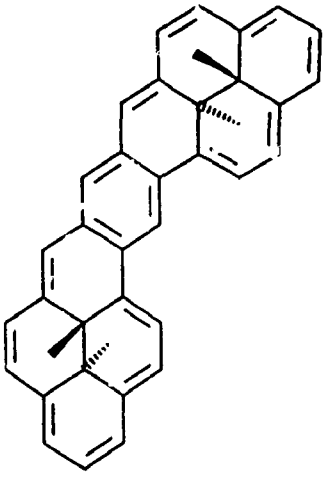


228

$\delta_{Me} = -1.60$

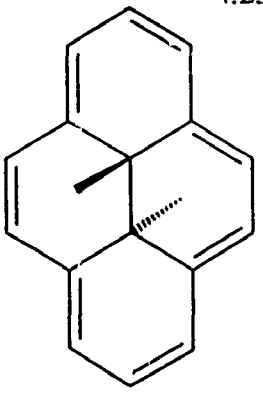


224a



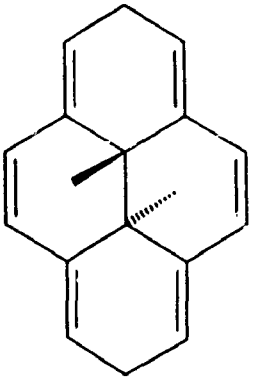
224b

-4.25



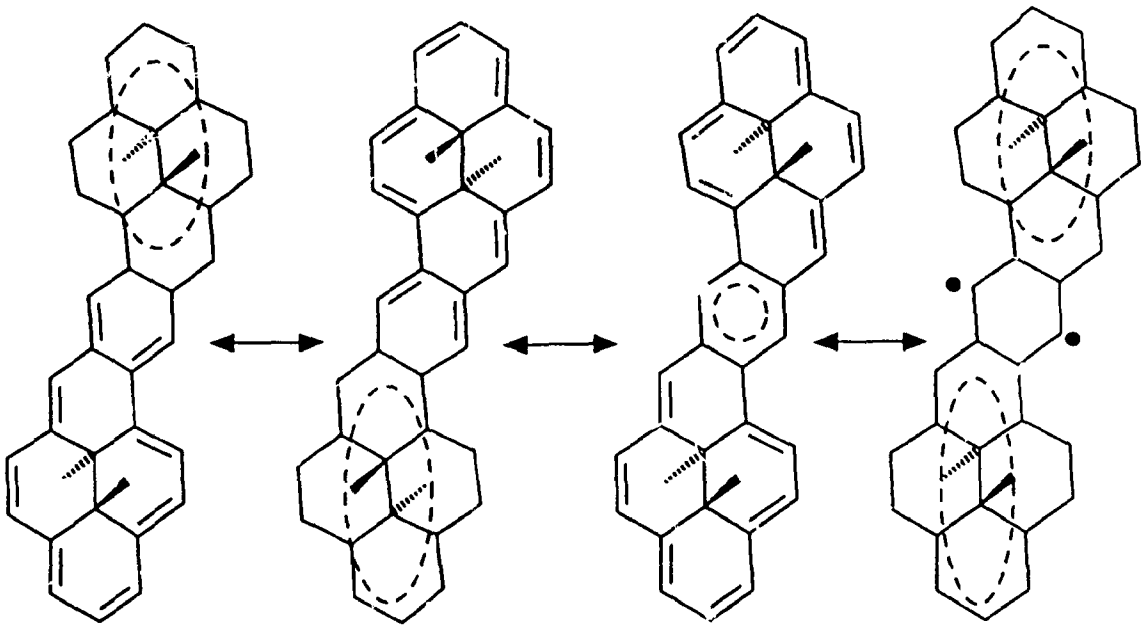
60

+0.97



189

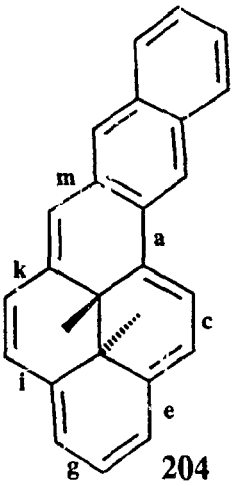
$$RC^{97} = \frac{-1.60 - 0.97}{-4.25 - 0.97} \approx 50\%$$



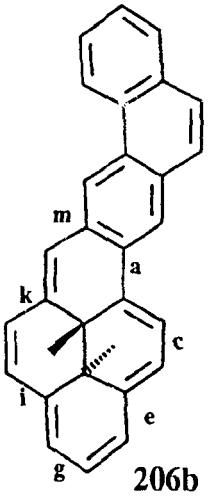
224c 224d 224e 224f

3.2.3 Bond order -- chemical shift correlation

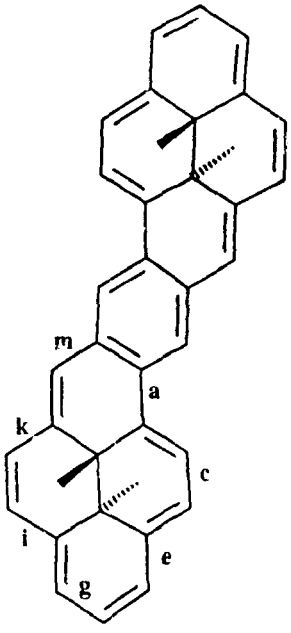
As we discussed earlier, Mitchell and coworkers have evaluated the average deviation of the π-SCF bond order from the Hückel value (0.642) of a perfectly delocalized annulene for each macrocyclic ring in **60, 95, 180, 187,** and **188**, and plotted this against the chemical shift shielding of the internal methyl groups. The result was a straight line plot which gave the correlation (equation 4), and the predictions of chemical shifts for many annelated annulenes. Naphthodihydropyrene **204** was one of these annulenes. Similarly, we made a prediction for compounds **206b** and **224a** (see table 8). The calculated and observed chemical shifts for the compound **204** and **206b** are not very satisfying in relation to the other annelated dihydropyrenes thus far prepared. But they are however, not in bad disagreement, and still provide considerable support for the original hypothesis. A relatively poor prediction also occured for the naphtho[e]dihydropyrene **194**, where the observed value is δ -0.74 and the predicted value is -1.25. It is worthwhile to ponder why the method appears not to work as well in some of these systems. In comparison with the reference compound **189**, the chemical shifts of the internal methyl protons in these compounds are mainly affected by three factors: (1) the macrocyclic ring current, (2) the deshielding effect of the added



204



206b



224a

Table 8. Bond orders ($X10^3$), P_u, and calculations

Bond	P_u		
	204	**206b**	**224a**
a	457	464	470
b	766	761	757
c	529	535	538
d	738	734	731
e	538	542	545
f	733	730	728
g	554	558	560
h	730	726	724
i	532	538	540
j	750	745	742
k	515	521	524
l	774	767	764
m	456	466	471
$\Delta P_u=\Sigma\lvert P_u-642\rvert$	1552	1481	1440
m	13	13	13
$\Delta r=\Delta P_u/m$	119	114	111
δ_{calc}	-1.28	-1.43	-1.52
δ_{found}	-0.44	-0.88	-1.60

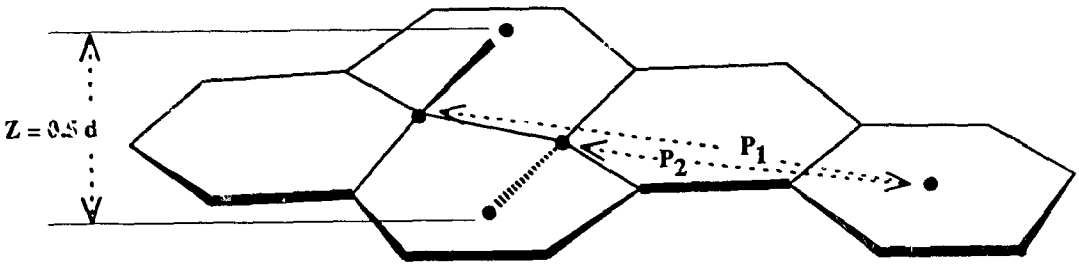
benzannelating rings and (3) local anisotropy changes due to annelation.

The deshielding effect of the added benzannelating rings can be estimated readily from Memory's equation[98]:

$$\Delta\delta = 31.45 \left[\frac{1-P}{(4P^2-6P+3+4Z^2)^{3/2}} + \frac{1}{(4P^2+3+4Z^2)^{3/2}} + \frac{1+P}{(4P^2+6P+3+4Z^2)^{3/2}} \right]$$

where $\Delta\delta$ is the ring current effect (in ppm, negative for deshielding and positive for shielding), Z is the distance of the reference point above the plane of the ring, and P is the in-plane projected distance from the ring center (their units are in units of the C-C bond length of benzene, taken to be 1.40 Å). Since the X-ray structures of our compounds are not available, the geometrical parameters Z and P were estimated using the MMX/PCMODEL2 program[4]. For the sake of simplicity, P was derived as the average distance of three protons and Z was approximated as half the distance between the two methyl carbons (Figure 18).

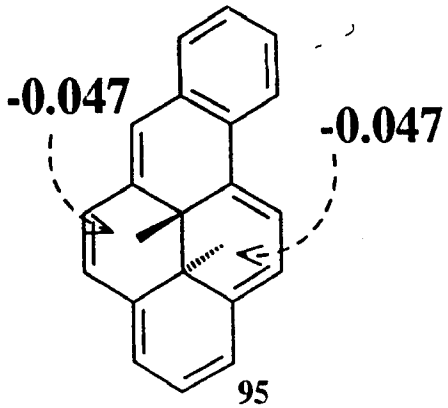
Figure 18. Geometry for Memory's equation



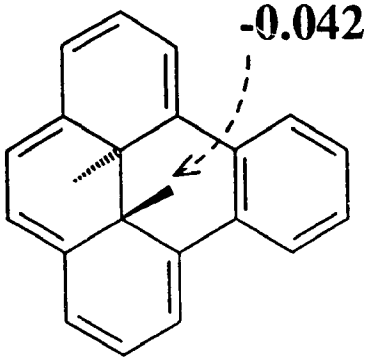
The values for P and Z were then obtained by querying the MMX output structure file in display mode of PCMODEL2. For more than one benzene, the overall effect was taken as the sum of all benzene rings. Some of the results obtained are shown in Figure 19. A negative sign for $\Delta\delta$ indicates a deshielding effect. It ranges from -0.042 to -0.103 ppm, which is very small. This kind of effect thus probably does not introduce large errors in the predictions.

The contribution of the local anisotropy effect is often large and depends to a large extent on the geometry of the molecule. However annelation of dihydropyrene presumably does not change its geometry too much, because of the rigid framework (this is confirmed by MMX calculation), hence the change of the local anisotropy with annelation is very small. This has been shown by Vogler and Mitchell[86] in their theoretical study of geometries and proton chemical shifts of benzannelated [14]annulenes using semi-empirical quantum chemical procedures, where they demonstrated that the chemical

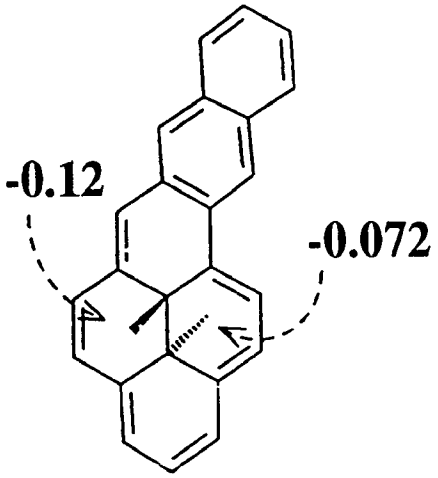
Figure 19. Deshielding calculated from Memory's equation

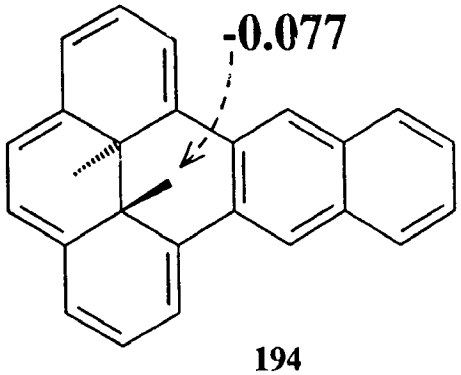


95

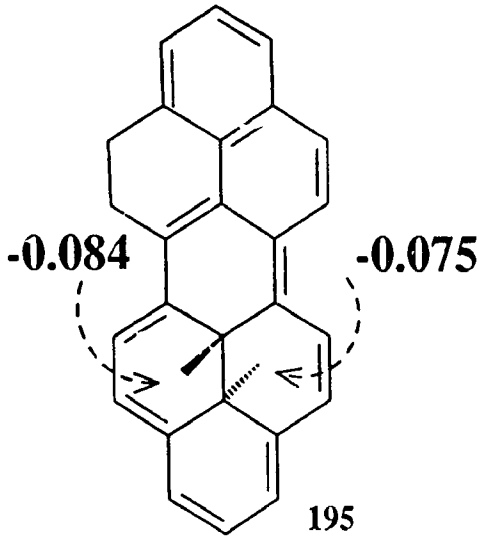


180

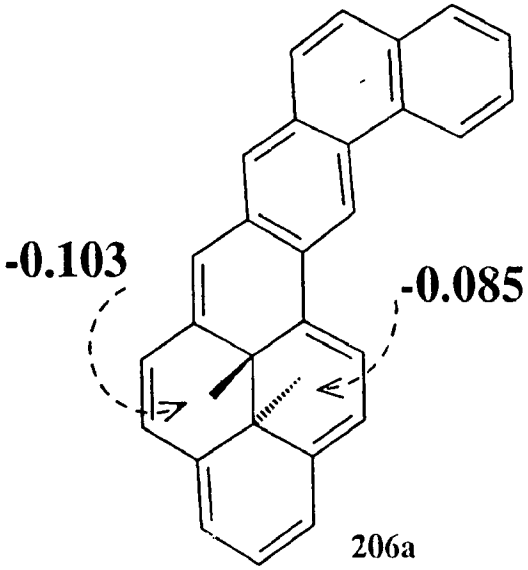




194



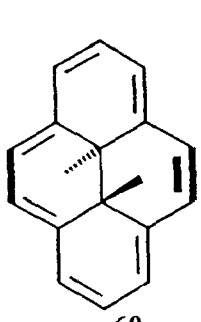
195



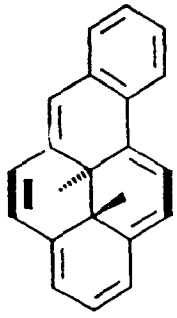
206a

shifts of the internal methyl protons resulted only from the ring current and are in excellent agreement with the experimental chemical shifts. So far, two out of the three possibilities which might cause the experimental results deviate substantially from those predicted by equation 4 have been eliminated. The remaining one relates to the origin of the equation. Careful examination of the procedures used for the calculation shows that the predictions depend upon which bond orders are included. When only the highlighted bonds (Figure 20) are included in the calculation of the mean bond order deviation, plotting δ vs r also gives a linear correlation, equation (5), with a correlation coefficient of 0.99 (see Graph 1).

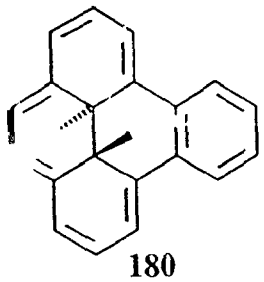
Figure 20. Dihydropyrenes with highlighted bonds



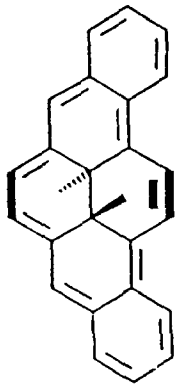
60



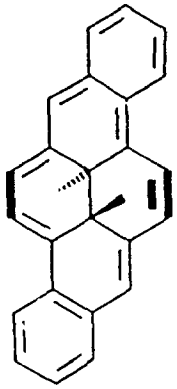
95



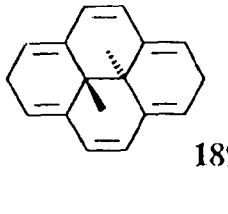
180



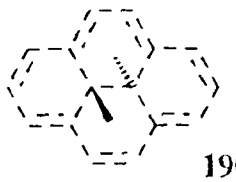
187



188

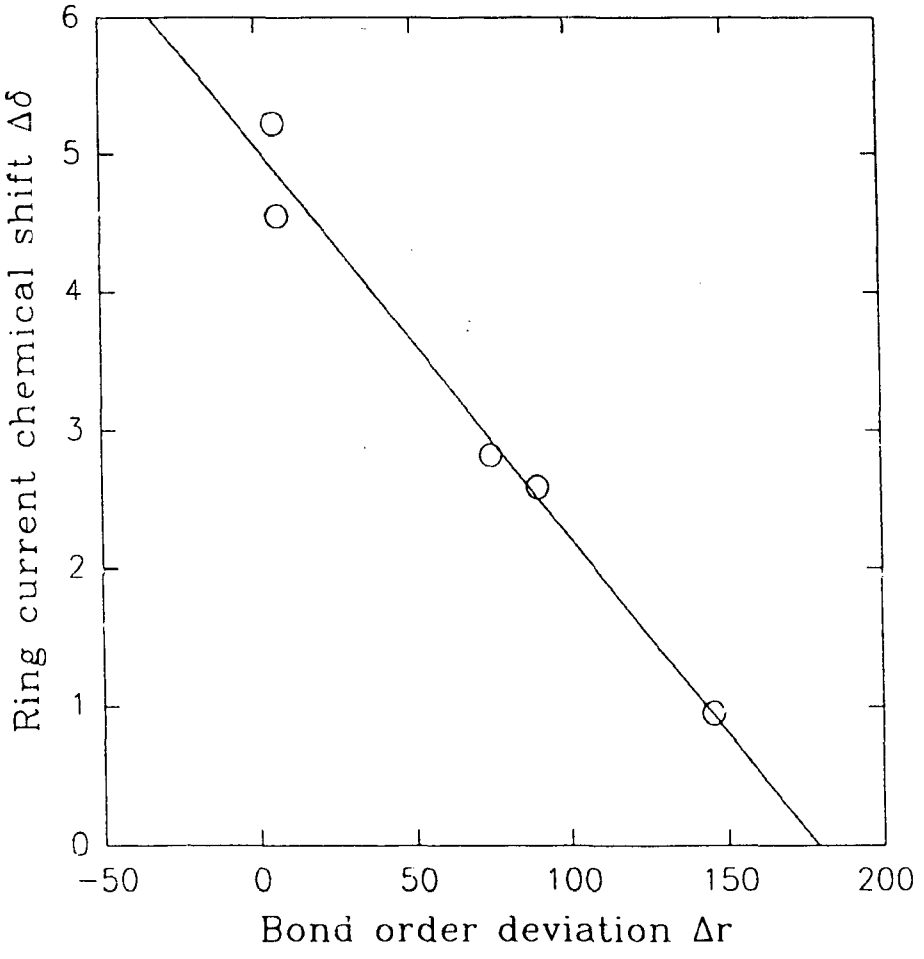


189



190

Graph 1. Bond order vs chemical shift



The graph contains the following data:

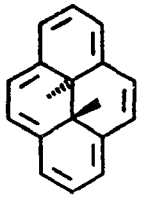
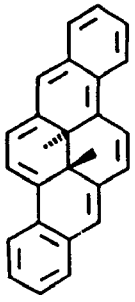
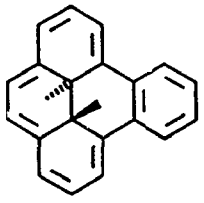
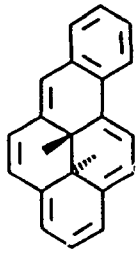
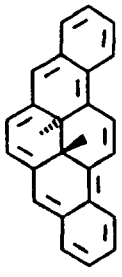
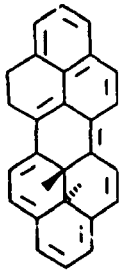
Compound	Δr	Δδ
60	6	5.22
188	7	4.55
180	75	2.82
95	90	2.59
187	145.5	0.95

$$\Delta\delta = -0.0283\Delta r + 5.055 \quad \text{---------(5)}$$

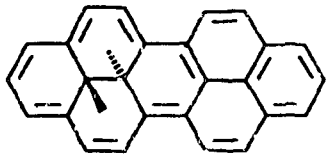
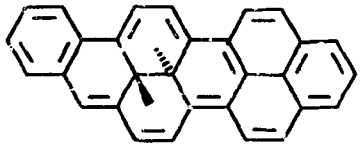
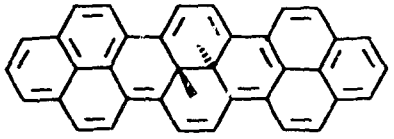
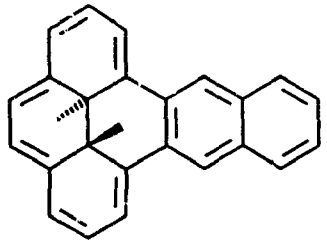
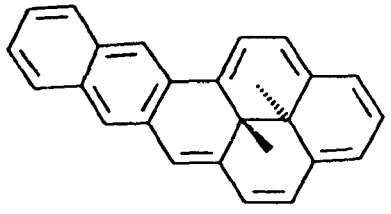
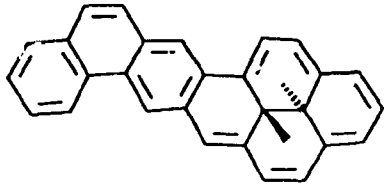
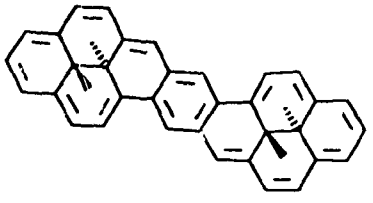
The predictions from this equation and from the original equation, as well as the observed results, are shown in Table 9. Comparison of the data in Table 9 indicates that taking only the highlighted bonds, improves the predictions for some particular compounds, such as the naptho[a]-dihydropyrene **204** and phenanthro[a]-dihydropyrene **206**. The standard deviation of the predictions from observed results shows that the new equation (5) (standard deviation σ=0.340) is better than original equation (4) (σ=0.363). However, the new equation would not be useful for [e,l]annelated systems, since the selected bonds are excluded from the calculation. Generally we have found that the chemical shift predictions from the above equations are of the correct magnitude but sometimes they can lead to up to 0.5 ppm errors due probably to the approximations in π-SCF calculations.

Considering all these facts we may conclude that using the highlighted bond orders slightly changed the original equation in detail, but not in substance. The original equation has thus stood the further test. Unfortunately, due to the indeterminable errors of bond orders, the predictions are not always very satisfactory quantitatively.

Table 9. Predicted and observed internal methyl chemical shift (δ_{Me})

compound	δ'_{Me} (from eq. 4)	$\lvert\delta'_{Me} - \delta_{obs}\rvert$	δ''_{Me} (from eq. 5)	$\lvert\delta''_{Me} - \delta_{Me}\rvert$	δ_{obs}
	-4.42	0.17	-3.92	0.33	-4.25
	-3.22	0.36	-3.89	0.31	-3.58
	-1.80	0.05	-1.96	0.11	-1.85
	-1.86	0.26	-1.54	0.06	-1.60
	+0.04	0.02	+0.03	0.01	+0.02
	-2.75	0.03	-2.40	0.38	-2.78

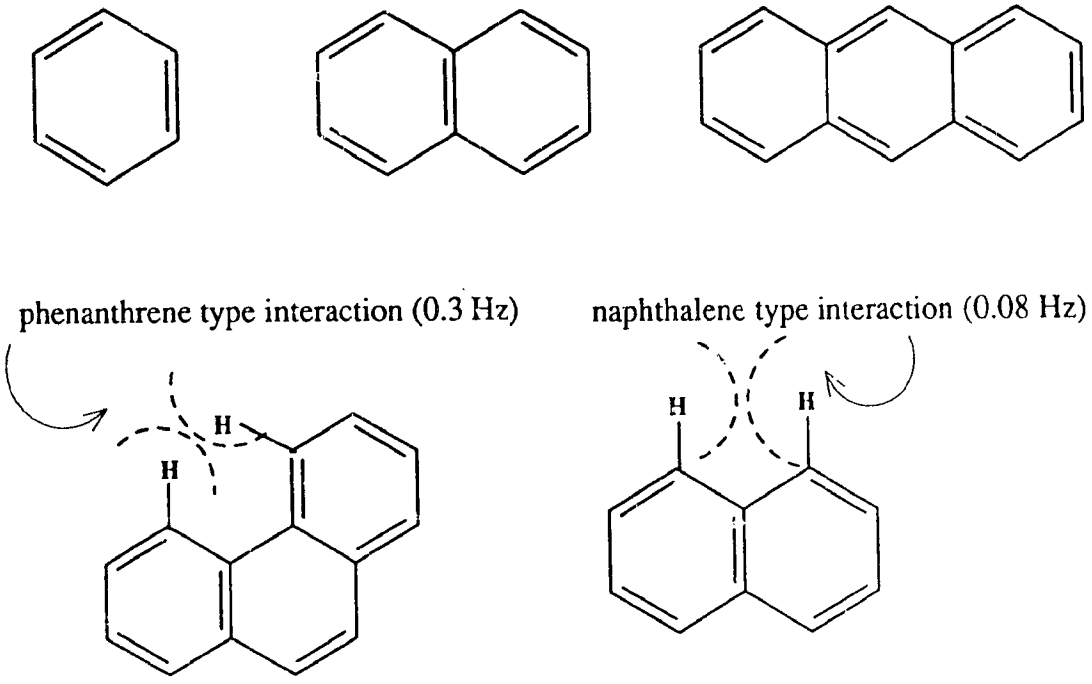
continued from **Table 9:**

	-3.97	0.22 0.31	-3.72	0.47 0.56	-4.19 -4.28
	-1.73	0.38 0.32	-1.56	0.21 0.15	-1.35 -1.41
	-2.99	0.21	-3.04	0.16	-3.20
	-1.25	0.51	-1.37	0.63	-0.74
	-1.28	0.84	-0.94	0.50	-0.44
	-1.44	0.56	-1.11	0.23	-0.88
	-1.51	0.10	-1.20	0.41	-1.61
σ (standard deviation)		**0.363**		**0.340**	

3.2.4 Bond order -- coupling constant correlation

Günther[83] obtained equation (3) using π-SCF bond orders and coupling constants from benzene, naphthalene, and anthracene. He applied this equation to several

Figure 21. Naphthalene and phenanthrene type interaction



$$P_{u,v}\,(SCF) = 0.104\ {}^{3}J_{u,v} - 0.120 \quad \text{---------} \quad (3)$$

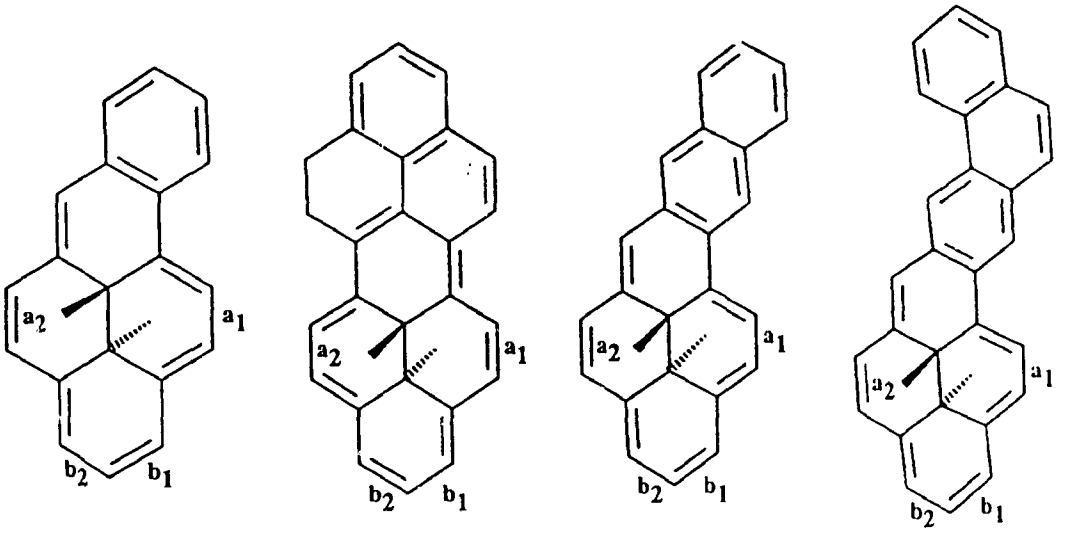
benzannulenes in order to comprehend the changes in delocalization in such compounds. It is known that strain

has only a small effect on vicinal coupling constants in benzocycloalkanes[100], except for compounds such as benzocyclopropene. Thus unless extreme angle deformation is occuring, it is unlikely that strain is affecting ^{3}J values much in the annelated dihydropyrenes. On the other hand, the steric effect around the bay region of phenanthrene or peripositions in naphthalene containing compounds is generally larger and correction is necessary, i.e., to predict coupling constants with equation (3), there should be added to the calculated values 0.08 Hz for each perinaphthalene type interaction and 0.3 Hz for each phenanthrene type interaction (Figure 21).

This inspired us to derive similar equations for the annelated dihydropyrenes, using the compounds **95, 195, 204,** and **206.** In consideration of the different geometries of type a and type b bonds in those compounds (Figure 22), two equations were obtained by plotting (Graph 2a and 2b) π-SCF bond orders against the corresponding coupling constants (after corrections for steric effects, see Table 10).

With these two equations (6) and (7), we can calculate π-SCF bond orders from coupling constants in new annelated dihydropyrenes and perhaps more importantly the coupling constants can be deduced from calculated bond orders so that ^{1}Hnmr analysis of the new annelated dihydropyrene will be simplified.

Figure 22. Dihydropyrenes

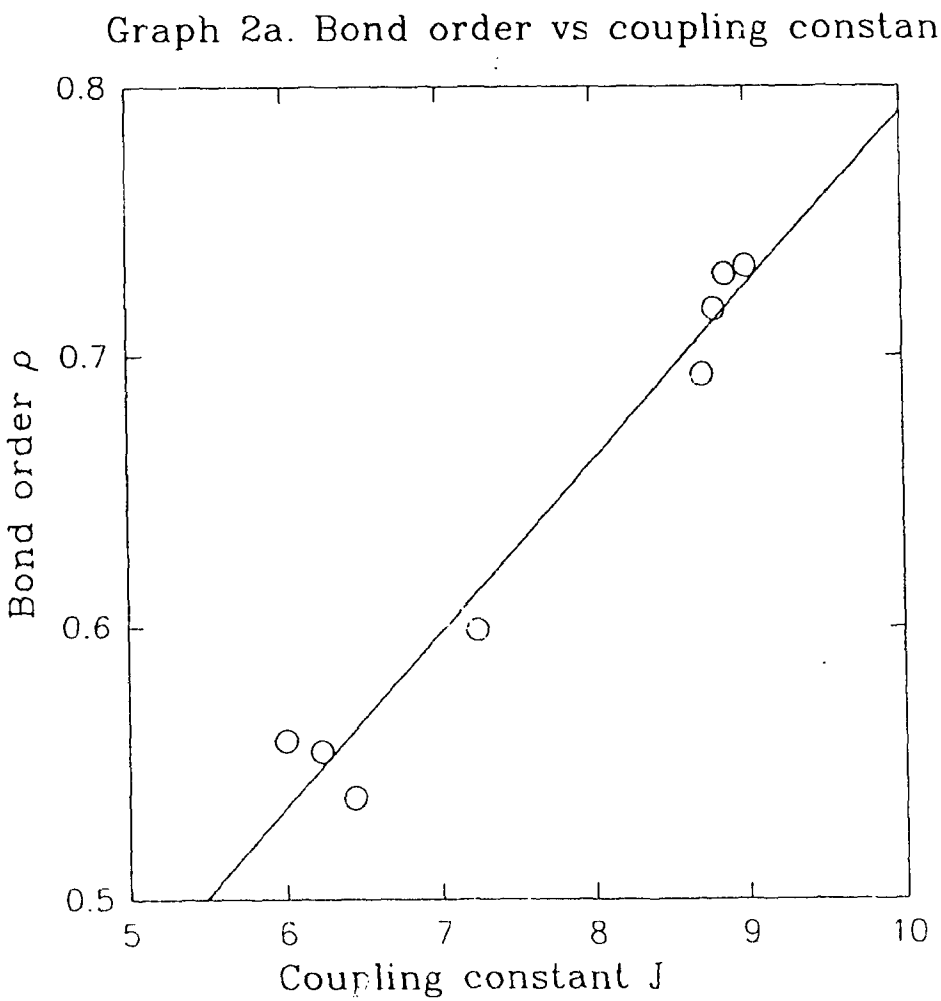


95 195 204 206

Table 10. Coupling constant (J) and π-SCF bond orders (P)

compound	Ja_1	Pa_1	Ja_2	Pa_2	Jb_1	Pb_1	Jb_2	Pb_2
95	6.20	0.552	8.67	0.731	8.79	0.717	6.44	0.573
195	6.94	0.583	8.41	0.702	8.71	0.693	7.24	0.599
204	6.11	0.529	8.92	0.750	9.00	0.733	6.23	0.554
206	6.16	0.535	8.87	0.745	8.86	0.730	6.00	0.558

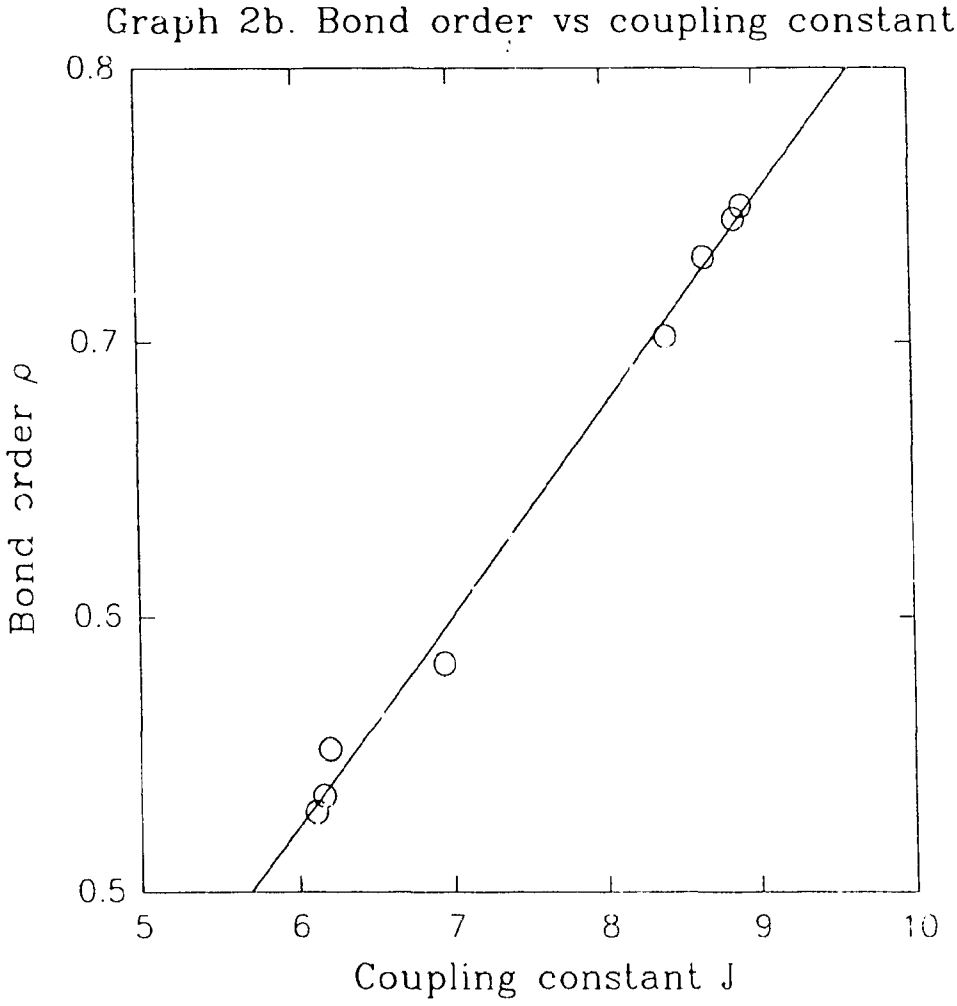
Figure 23a. Graph 2a and equation 6



$$\rho = 0.0643\,J + 0.147 \text{ - - - - - - - - - - - - } (6)$$

(Correlation coefficient: 0.982)

Figure 23b. Graph 2b and equation 7

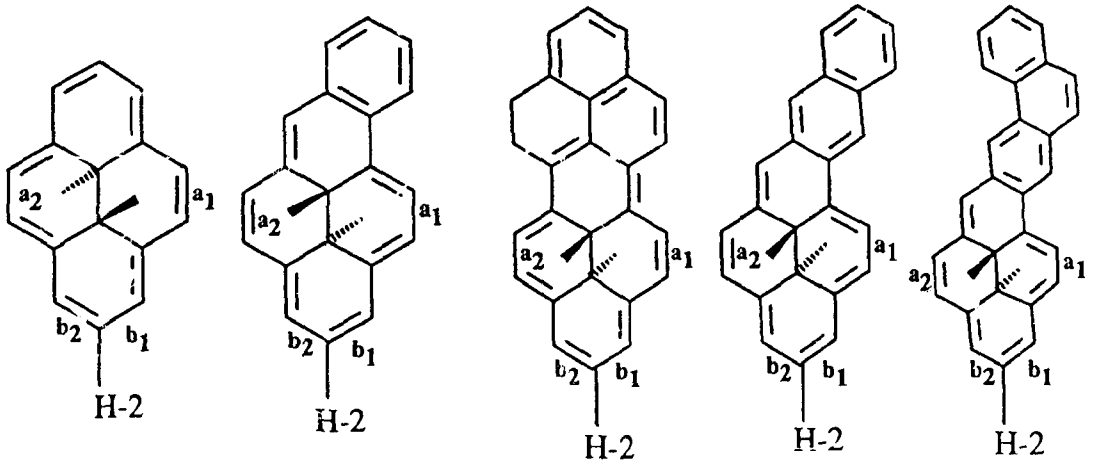


$$\rho = 0.0765\,J + 0.0642 \quad \text{---------- (7)}$$

(Correlation coefficient: 0.997)

3.2.5 Coupling constant -- chemical shift correlation

In the preceeding sections we have derived bond order -- chemical shift and bond order -- coupling constant correlations. It thus seems likely that a coupling constant -- chemical shift correlation also exists. Indeed on plotting (Graph 3a) the ring current shielding change, $\Delta\delta$ (defined as -4.25 - δ, where -4.25 is δ_{Me} for the dihydropyrene **60** and δ is δ_{Me} for the annelated annulene) vs the average coupling constant deviation $\Delta\bar{J}$ (defined in Table 11) a linear correlation equation (8a) is obtained. A somewhat better correlation (Graph 9a) can be obtained using $\sigma_{\Delta J}$, the standard deviation of the coupling constants (see Table 11). This is the first time that the two ^{1}Hnmr parameters, i.e., coupling constant and chemical shift have been correlated, in annelated dihydropyrenes. Similar equations were also derived for the peripheral proton 2 (Graph 3c and 3d, equation 8b and 9b).



60 **95** **195** **204** **206b**

Table 11. J after steric correction and δ_{Me}

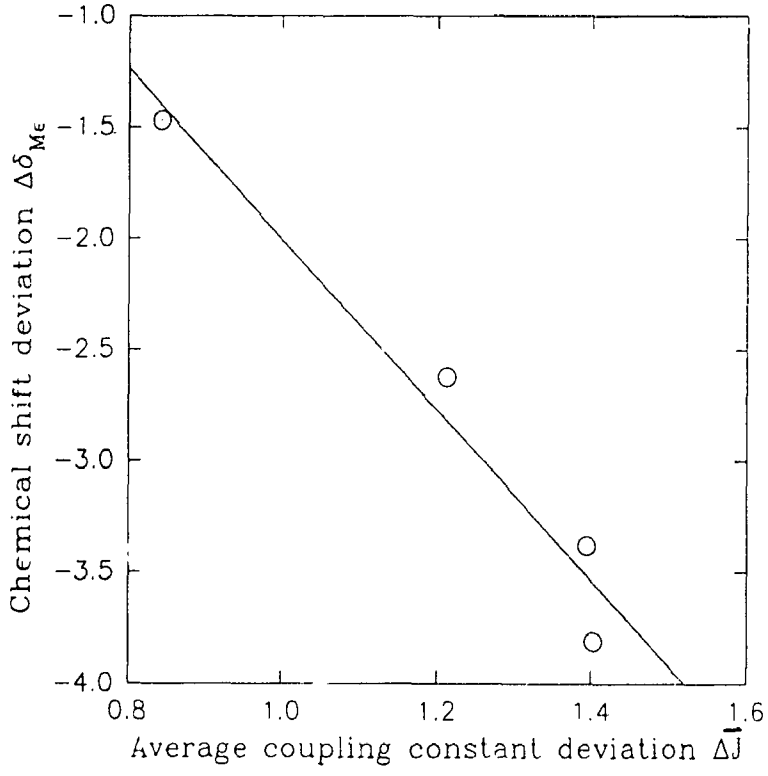
compound	60	95	195	204	206
Ja_1	7.44[a]	6.20	6.94	6.11	6.16
Ja_2	7.44[a]	8.67	8.41	8.92	8.87
Jb_1	7.44	8.79	8.71	9.00	8.86
Jb_2	7.44	6.44	7.24	6.23	6.00
δ_{H-2}	8.11	7.13	7.60	6.66	6.86
δ_{Me}	-4.25	-1.62	-2.78	-0.44	-0.87
ΔJ^b	0	1.205	0.735	1.395	1.393
$\sigma^c_{\Delta J}$	0	1.212	0.843	1.402	1.394
$\Delta\delta_{H-2}$	0	0.98	0.51	1.45	1.25
$\Delta\delta_{Me}$	0	-2.62	-1.47	-3.81	-3.38

a: We assumed Ja = Jb in **60** since Ja is not available.

b: $\Delta J = 1/4\Sigma|J-7.44|$. c: $\sigma_{\Delta J} = [(J-7.44)^2/4]^{1/2}$

Figure 24a. Graph 3a and equation 8a

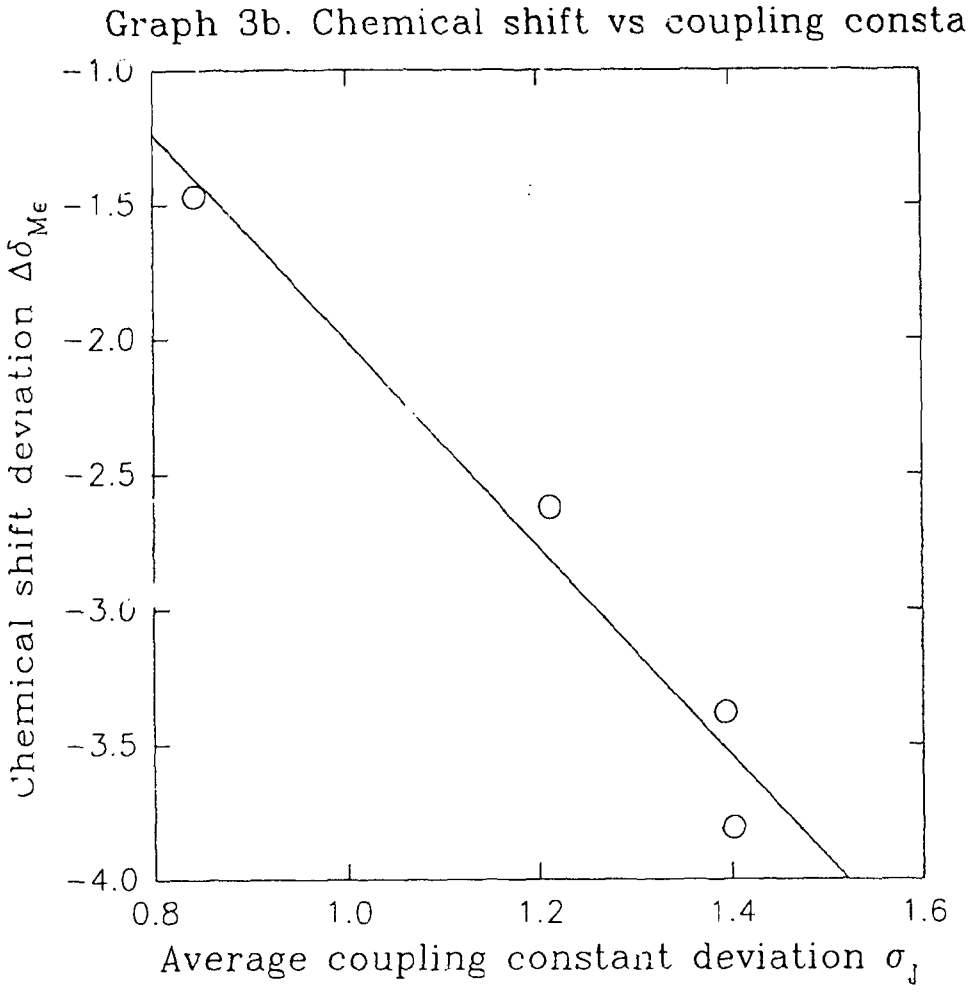
Graph 3a. Chemical shift vs coupling constant



$$\Delta\delta_{Me} = -3.197\,\overline{\Delta J} + 0.959 \quad \text{---------} \quad (8a)$$

(Correlation coefficient: 0.969)

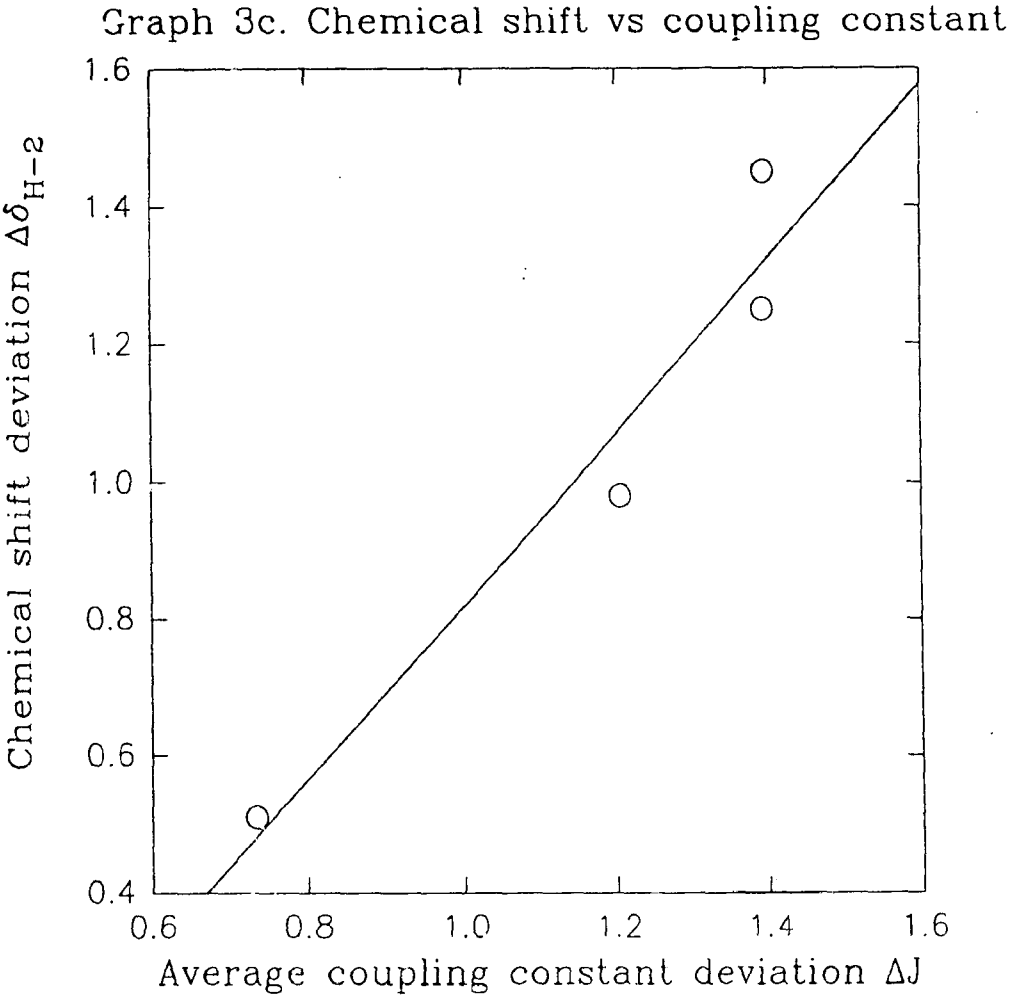
Figure 24b. Graph 3b and equation 9a



$$\Delta\delta_{Me} = -3.838\,\sigma_J + 1.834 \text{ ---------- (9a)}$$

(Correlation coefficient: 0.979)

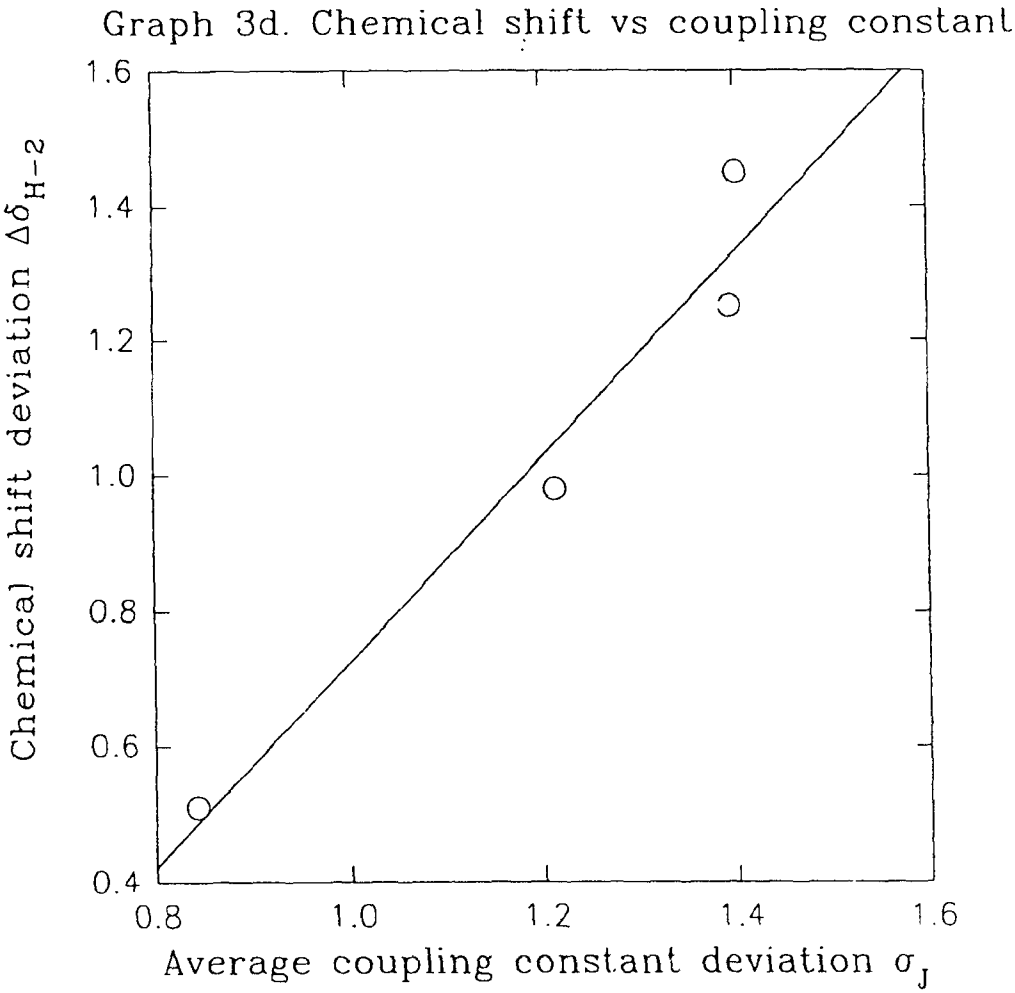
Figure 24c. Graph 3c and equation 8b



$$\Delta\delta_{H\text{-}2} = 1.265\Delta\overline{J} - 0.448 \quad \text{---------} \quad (8b)$$

(Correlation coefficient: 0.967)

Figure 24d. Graph 3d and equation 9b



$$\Delta\delta_{H\text{-}2} = 1.518\sigma_J - 0.793 \quad \text{---------} \quad (9b)$$

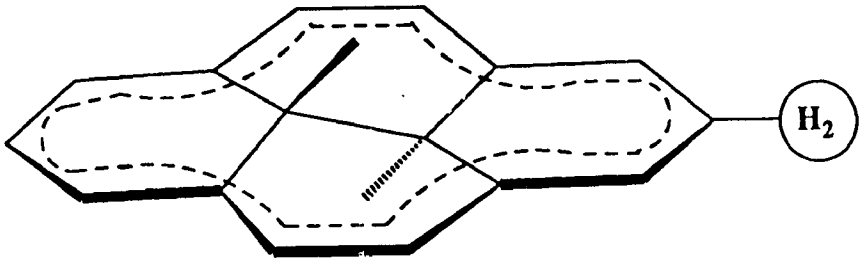
(Correlation coefficient: 0.976)

3.2.6 Ring current -- chemical shift correlation

In section 3.1, we discussed that Haddon[78] has deduced the ring current intensity for a variety of annulenes using the following equation:

$$\mathbf{RCCS = RC \ X \ RCGF} \quad \text{----------(10)}$$

in which the RCGF was calculated on the bases of the Biot-Savart law and the X-ray structure data of the compounds. Let $RCCS_H$ and $RCGF_H$ respectively be the ring current chemical shift and ring current geometry factor for the



proton H-2, and similarly $RCCS_{Me}$ and $RCGF_{Me}$ for the internal methyl protons. Then

$$\mathbf{RCCS_H = RC \ X \ RCGF_H} \quad \text{-------} \ (11)$$

$$\mathbf{RCCS_{Me} = RC \ X \ RCGF_{Me}} \quad \text{------(12)}$$

Dividing equation (12) by (11), we have

$$\frac{\mathbf{RCCS_{Me}}}{\mathbf{RCCS_H}} = \frac{\mathbf{RC \ X \ RCGF_{Me}}}{\mathbf{RC \ X \ RCGF_H}} \quad \text{---------(13)}$$

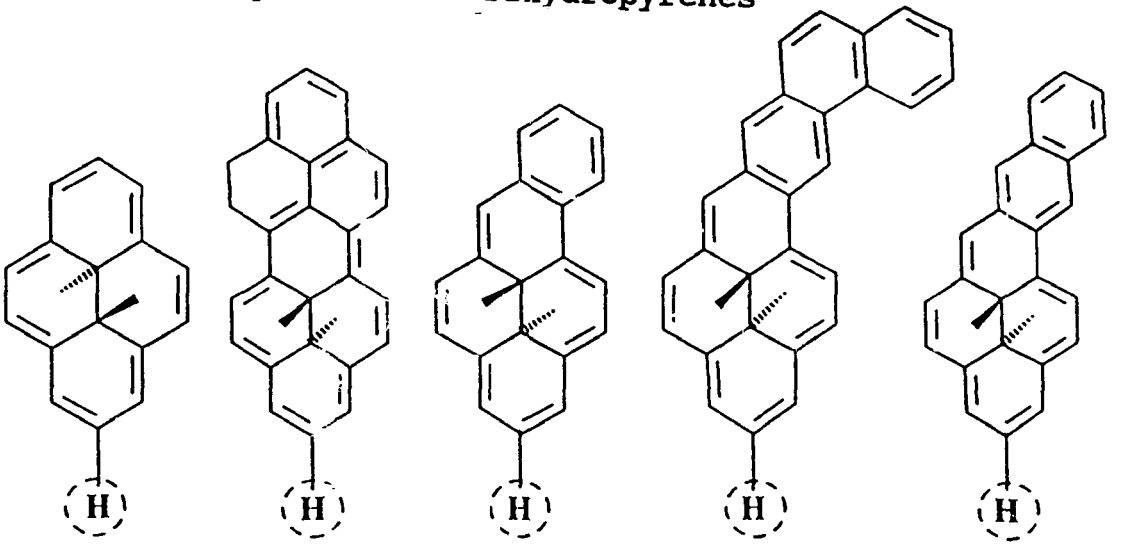
Then rearranging equation (13) gives

$$RCCS_{Me} = \frac{RCGF_{Me}}{RCGF_{H}} X\, RCCS_{H} \quad \text{--- -------(14)}$$

Substituting Haddon's values of RCGF, we get

$$RCCS_{Me} = \frac{-3306.66}{1387.42} X\, RCCS_{H} = -2.38\, RCCS_{H} \quad \text{-----(15)}$$

Figure 25. Dihydropyrenes



60 195 95 206a 204

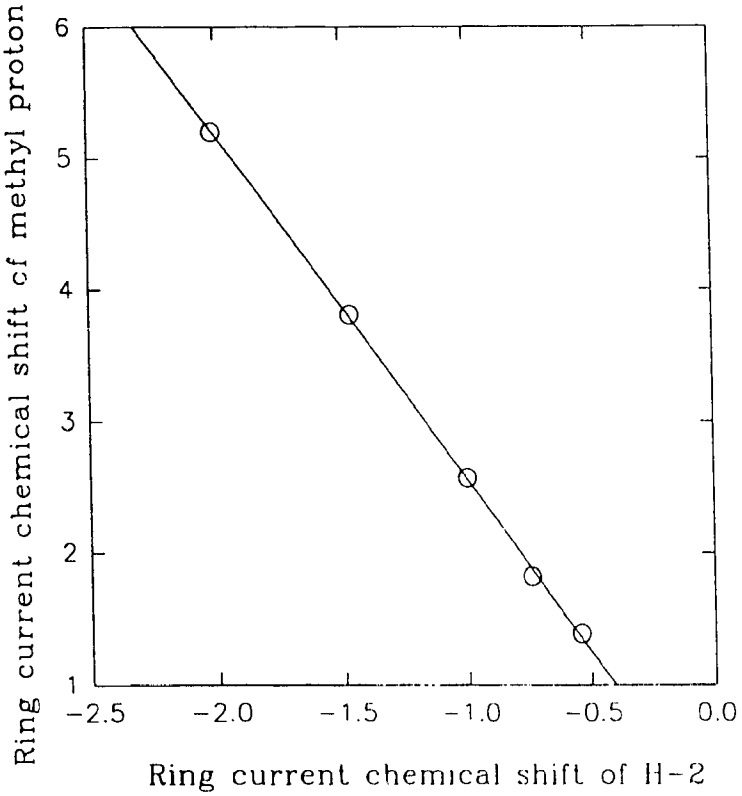
Table 12. Deshielding shift of ring current

compound	60	195	95	206b	204
MCS_H	6.129	6.129	6.129	6.129	6.129
MCS_{Me}	0.95	0.95	0.95	0.95	0.95
OCS_H	8.14	7.60	7.13	6.87	6.66
OCS_{Me}	-4.25	-7.86	-1.63	-0.87	-0.44
$RCCS_H$	-2.01	-1.47	-1.00	-0.74	-0.54
$RCCS_{Me}$	5.20	3.81	2.57	1.82	1.39

MCS: Model Chemical Shift; OCS: Observed Chemical Shift; RCCS: Ring Current Chemical Shift.

Equation 15 suggests that a) it is possible to experimentally obtain the correlation of $RCCS_H$ and $RCCS_{Me}$ by changing the ring current intensity in a series of dihydropyrenes; b) the internal methyl protons should be 2.38 times more sensitive to ring current changes than proton H-2; c) the effect on $RCCS_H$ and $RCCS_{Me}$ due to the RC change is in opposite directions, i.e., deshielding on proton H-2 and shielding on the internal methyl protons. With the availability of new dihydropyrenes from this project, these suggestions have been tested as outlined in using compounds **60, 95, 195, 206a,** and **204** (Figure 25).

Graph 4. Ring current chemical shift correlation



In Table 12, the model chemical shift (MCS) was originally set to be 6.129 for proton H-2 and 0.95 for the internal methyl protons by Haddon[78]. Plotting $RCCS_H$ against $RCCS_{Me}$ (Graph 4), we obtain an extremely well correlated straight line. The least squares fit gave

$$RCCS_{Me} = -2.60 \times RCCS_H - 0.029 \text{ ------(16)}$$

with a correlation coefficient of 0.9998. Such a high correlation coefficient suggests that only one factor which affects the chemical shifts is varied during the course of changing the structure of the annelating ring on the dihydropyrene in these compounds **59, 195, 95, 206a,** and **204.** This factor is the ring current. In consideration of the experimental errors and assumptions in theoretical calculations, the experimental equation (16) is in excellent agreement with the theoretical one (15). Therefore our experimental results have provided strong support for the ring current model.

3.2.7 Summary

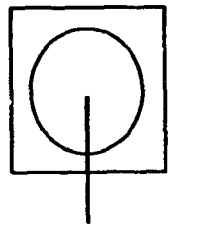
To draw a conclusion we quote one of the critiques[46] addressed to the term "aromaticity" by Labarre: "Chemists and physicists are at present in the middle of a cavern which Plato would not have disavowed; they observe on the walls of the cavern certain shadows resulting from the lighting of an unknown subject (aromaticity) by the

different sources represented by their various chemical or physical techniques of observation: an agreeable odor, an aptitude tc nitration and sulphonation, a ring current, a magneto-optical excess, a diamagnetic anisotropy, a resonance energy, a UV bathochromic effect, and even for some, a mathematical term. The question is: Do these shadows all belong to the same invisible reality? No one is able, at present, to answer such a question". Using the dihydropyrene moiety as a probe and correlating chemical shifts, coupling constants and bond orders with each other, we have enriched the observations of "aromaticity" and proved that the ring current model is a good model for aromaticity studies.

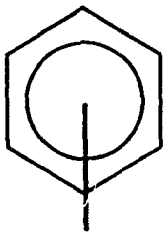
3.3 Dihydropyrene metal complexes:

The synthesis of arene metal complexes has been a fascinating subject in chemistry and metal complexes of condensed aromatic hydrocarbons and heterocycles have been extensively studied[102]. However, large annulene metal complexes are rare in the literature, although small ones such as **232**[103] and **233**[104], have been well documented. Since Vogel reported the first metal-complexed bridged annulenes **234**[105] in 1966, and then **235**[106] and **236**[107] in 1982, no further development has occured in this area, perhaps in

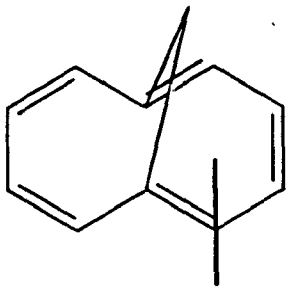
part because of the limited accessibility and stability of large annulenes.



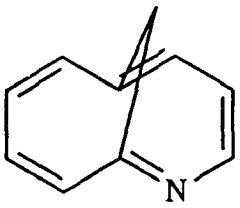
232



233



234



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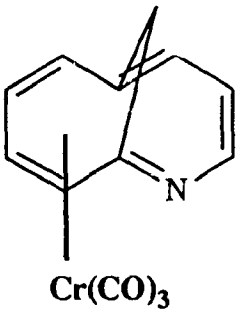

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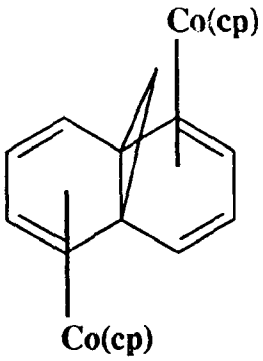
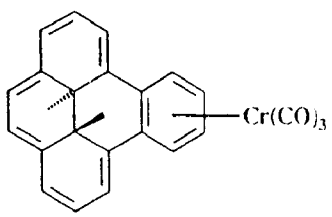


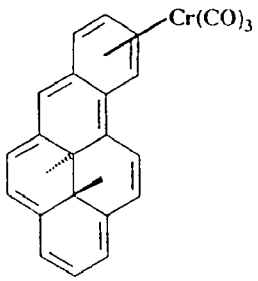
236

The upfield shift of about 2 ppm of the protons in arene chromium tricarbonyl complexes, such as **233**, has prompted much investigation of its origin[109]. Such shifts have been interpreted as a combination of effects including quenching of the ring current, withdrawal of electron density from the ring by the $Cr(CO)_3$ moiety, the magnetic anisotropy of the Cr-ligand bonds, and partial rehybridization of the ring carbon atoms. In the ^{1}Hnmr spectrum[108] of **234**, the bridge methylene protons appear at δ -1.77 and -1.14, considerably upfield from the ligand **153** (δ -0.52). A similar upfield shift is found for the complex **235**, i.e., an upfield shift of 0.42 and 0.66 ppm

corresponding to δ 0.67 and -0.36 in the ligand **237**, to δ 0.15 and -1.02 in the complex. This upfield shift is the sum of effects from the diamagnetic anisotropy of the $Cr(CO)_3$ group and the delocalization change due to the complexation. It is impossible to evaluate each of these effects separately. The synthesis of metal complexed benzannulenes such as **238** or **239**, however, has been of interest for some period of time because the internal methyl groups are far away from the $Cr(CO)_3$ moiety. The effect through space of the $Cr(CO)_3$ should be small and thus any chemical shift change of the methyl protons will mostly reflect a delocalization change in the macrocyclic ring. Unfortunately, because of the difficulty in synthesizing the ligands in large quantity, investigation of metal complexation in such species has been inhibited. Given our success in establishing a more efficient route to annelated dihydropyrenes, a relatively large amount of these compounds is now accessible. Thus, we decided to synthesize their metal complexes and hopefully to make a definitive statement on the bond delocalization present in **233**, as well as an estimate of its effective resonance energy, relative to that of benzene.



238



239

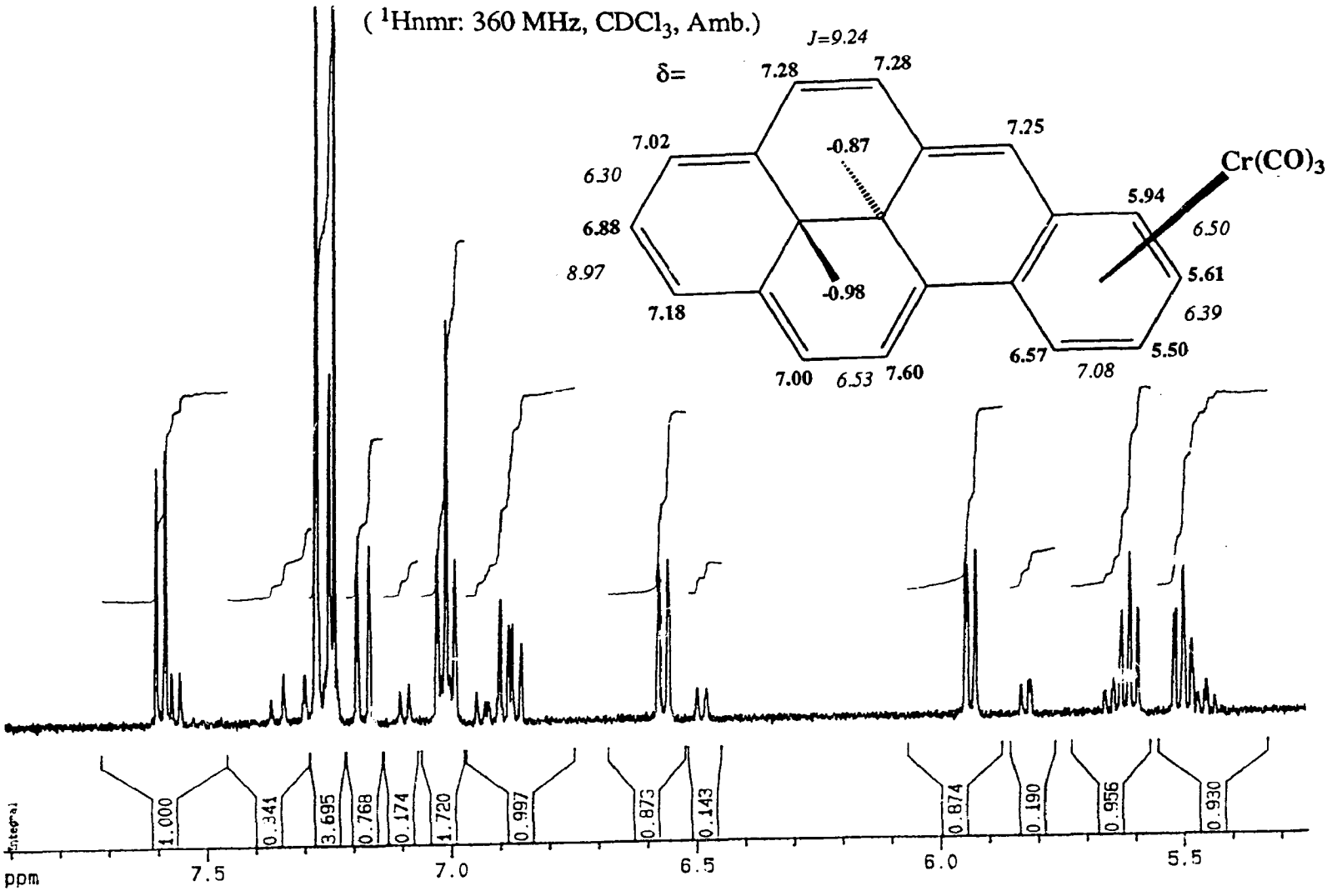
3.3.1 Dihydropyrene tricarbonyl chromium complex

Heating **95** with $Cr(CO)_6$ or $Cr(CO)_3(CH_3CN)_3$ gave no complexed **95**, only decomposition. However, the exchange reaction[110] between **95** and naphthalene chromium tricarbonyl **240** in diethyl ether in the presence of 4 equivalents of THF relative to **240** at 50-60 ^oC, gave a mixture of two isomers, **239a** and **239b**, in a ratio of about 1 : 2.9 and a total yield of 60%. A preliminary X-ray study indicates that **239a** is the major isomer (see Figure 27). By nmr (Figure 26), the minor isomer is assigned the structure **239b**. The chemical shifts found for the internal methyl protons are **239a:** δ -0.87 and -0.98, and for **239b:** δ -0.81 and -1.16. In **239a**, the methyl *syn* to the Cr is assigned the shift -0.87 and the methyl *anti* to the Cr is assigned the shift -0.98. The anisotropy effect of $Cr(CO)_3$ on the internal methyl protons and peripheral protons of the macroring can be estimated using the McGlinchey equation[111], (17).

$$\sigma = 56.34\ X\ \frac{3\cos^2\theta - 1}{R^3} \qquad \text{---------(17)}$$

σ : $Cr(CO)_3$ anisotropic effect (positive for shielding and negative for deshielding)

Figure 26. ^{1}H nmr spectrum of **239**



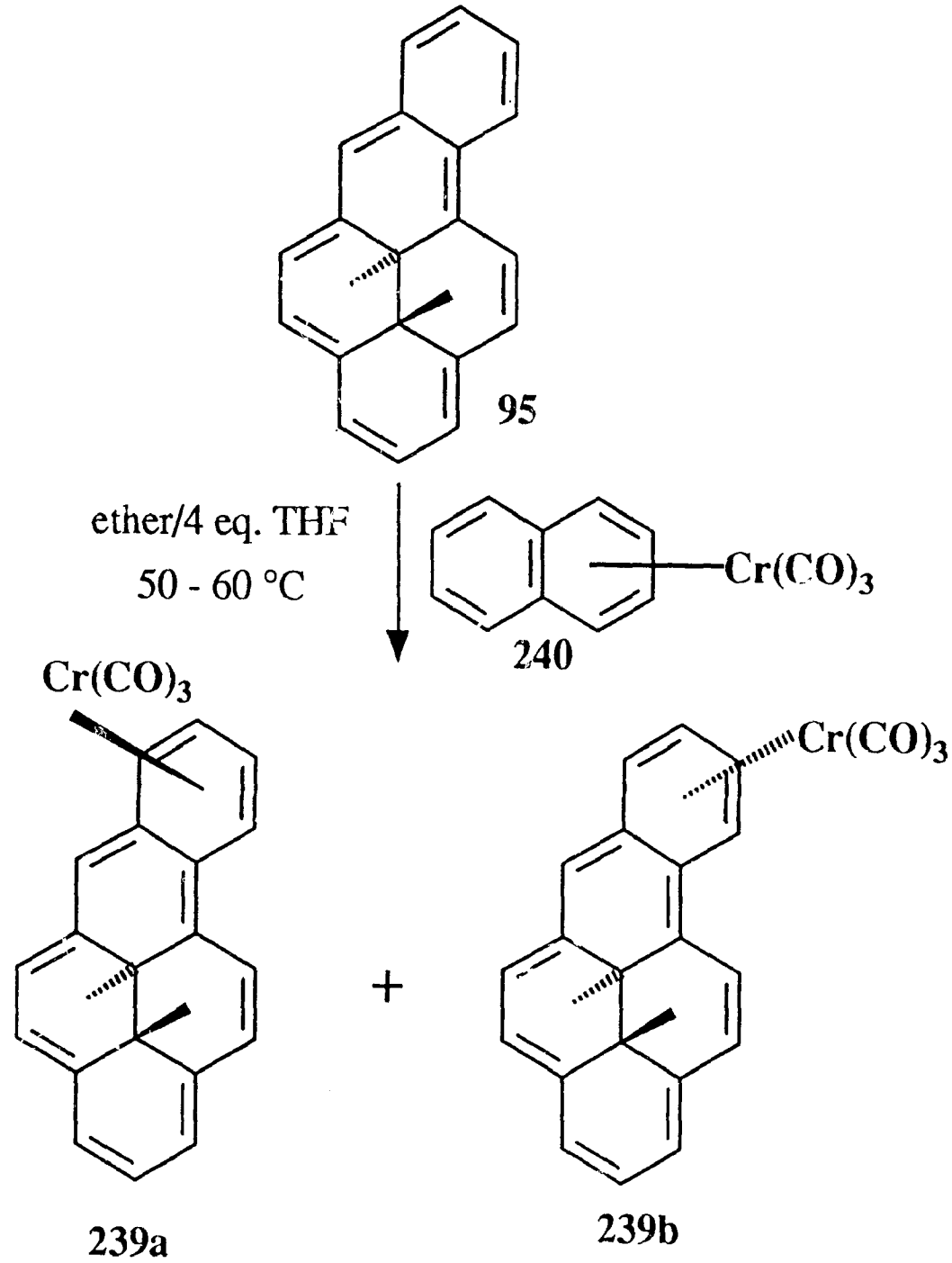
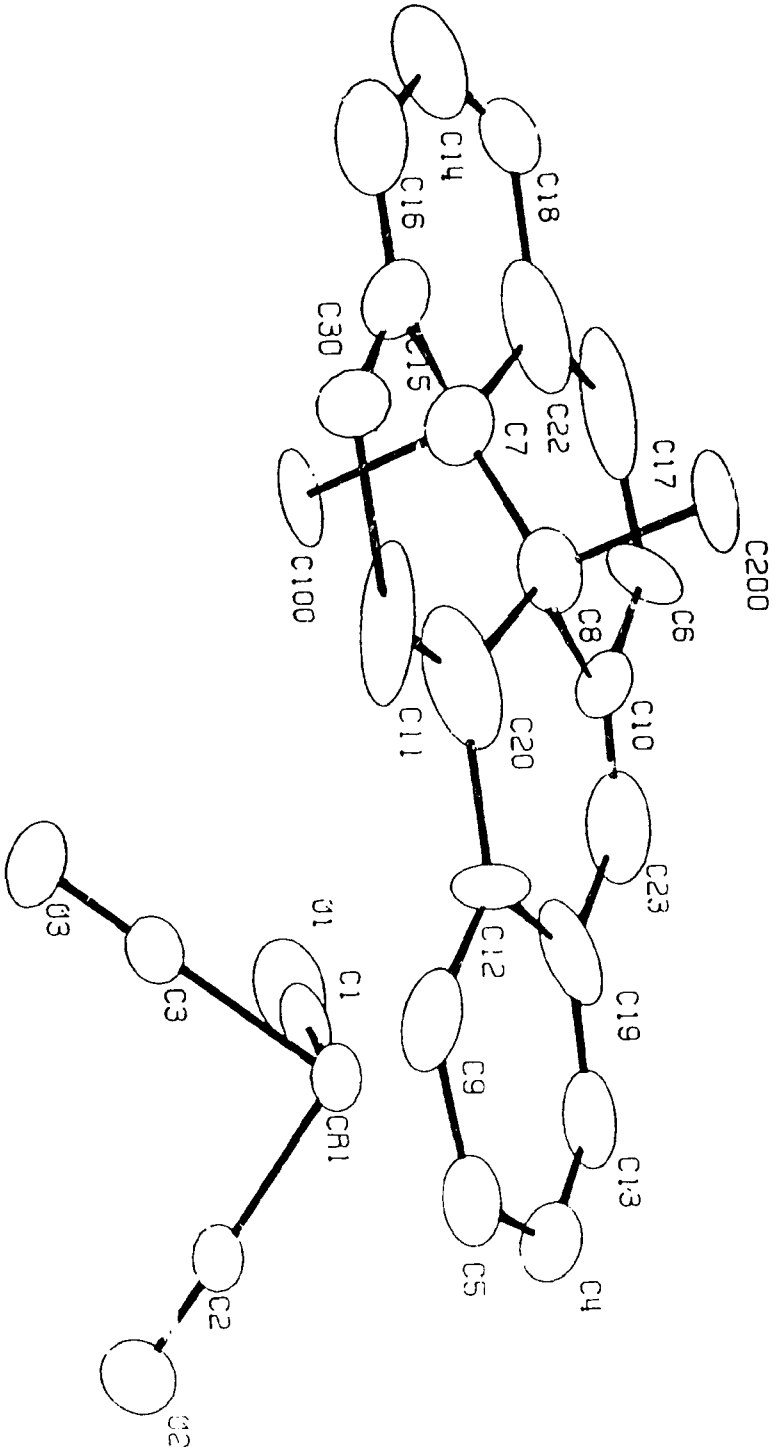

95
ether/4 eq. THF
50 - 60 °C
Cr(CO)3
240
Cr(CO)3
Cr(CO)3
+
239a
239b

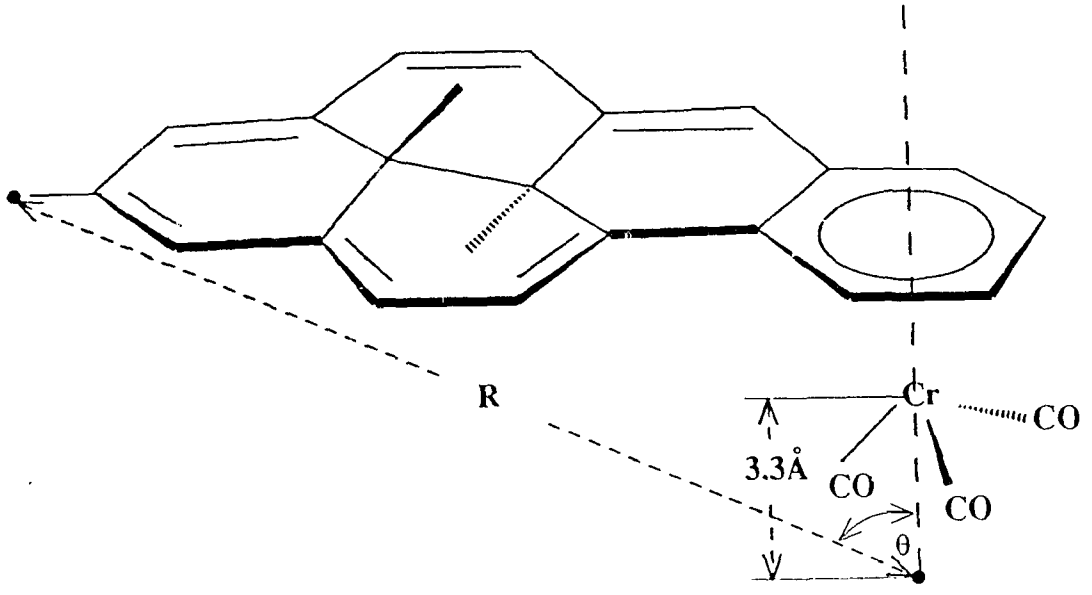
Figure 27. Ortep plot of **239**

Ortep plot of **239**: X-ray structure determination clearly indicated the carbon skeleton, but would not complete using a least square refinement to give the hydrogen atoms (R=0.066). Th crystal system was triclinic, space group P1, with a=14.516Å, b=9.062Å, c=7.772Å.



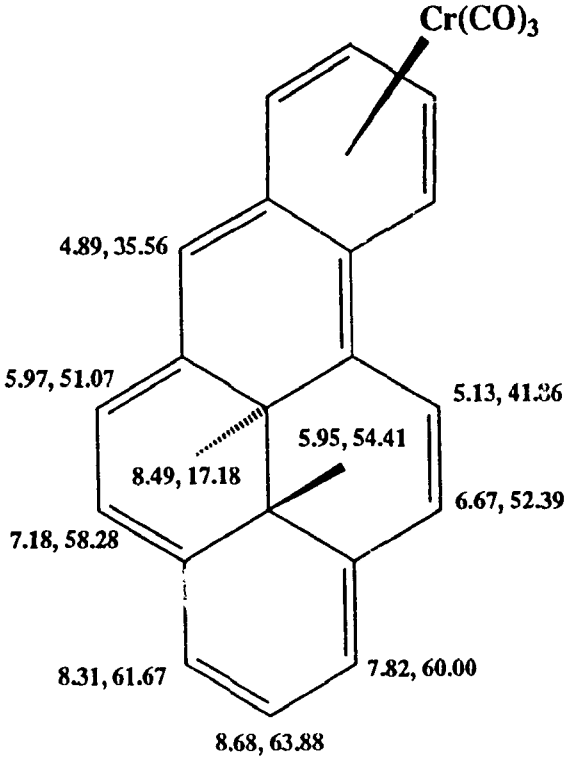
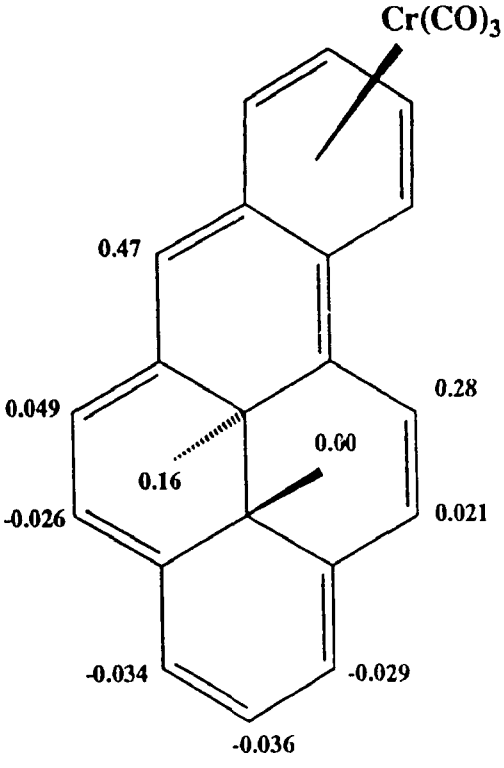
In one of his methods, the three carbonyl groups are considered as a "super-carbonyl" along the C_3 axis. The center of the super-carbonyl is found 3.3Å below Cr atom. R is taken as the distance from this center to the proton under consideration and θ as the angle made by R with the C_3 axis. Using the output geometry of the complex **239b** from PCMODEL2/MMX, we defined R and θ for each proton. This is exemplified with one of the ring protons in Figure 28. The geometries and anisotropy effect on each proton from the McGlinchey equation are given in Table 13.

Figure 28. Illustrator of Geometry for McGlinchey equation



The results show that the calculated $Cr(CO)_3$ anisotropy effects on the remote macrocring protons and internal methyl protons are small enough to be neglected. Earlier, we found that for a series of annelated annulenes the chemical shift of the methyl protons correlates very well with the chemical shift of the distant ring proton H-2 in equation 16. In **239**, H-2 is the most distant proton from $Cr(CO)_3$ center, and thus is hardly affected at all, and

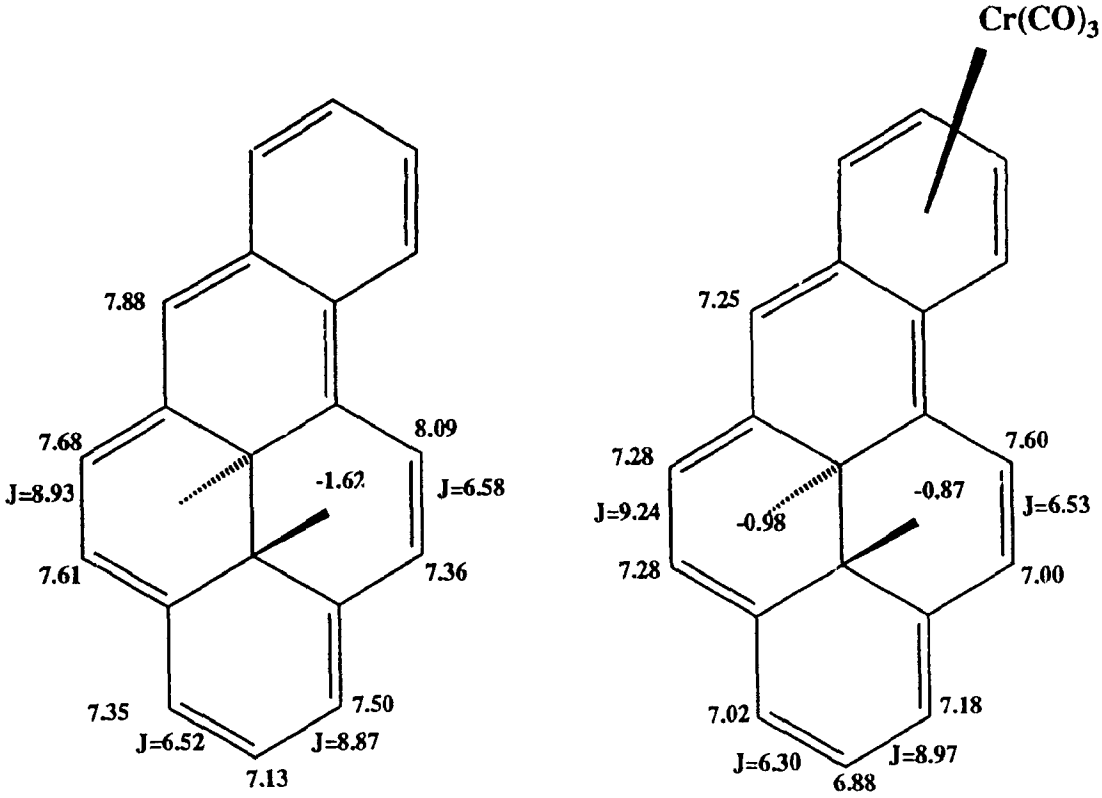
Table 13. Geometry and anisotropic effect

geometry (R, θ), R in Å and θ in °	anisotropic effect (σ in ppm)
	

based on its chemical shift of δ 6.88, we can calculate the expected chemical shift of the methyl protons to be δ: -0.97. Since the found values agree very closely to this, we may conclude that in **239**, the $Cr(CO)_3$ has almost no anisotropy effect on the chemical shifts of the methyl protons and distant macroring protons. Hence, these chemical shifts can be used to probe any π-electronic structure change due to the Cr complexation.

Comparison of the chemical shifts of internal methyl protons and distant peripheral protons suggests that the former are less shielded and latter are more shielded in

Figure 29. Chemical shifts and coupling constants of **95** and **239a**



95 **239a**

the complex **239** than in the ligand **95**. Consider two of the possible reasons: one, due to its electron withdrawing character, the $Cr(CO)_3$ diminishes the ring current; and/or two, due to the complexation, the bond fixation diminishes the ring current. To evaluate the effects from these two arguments, we placed a 1.5 unit positive charge on the center of benzene ring in the free ligand **95** to imitate a Cr atom and calculated the π-SCF bond orders. The results indicate that almost no charge is withdrawn from the dihydropyrene ring but about 0.2 e per carbon atom is from the benzene ring in the molecule. This suggests that any effect from the first argument is negligible. However, the bond orders from π-SCF calculations show that the bond alternation around the macroring has been substantially increased relative to the free ligand. Using the previously discussed equations 4 and 5, we calculated the expected chemical shifts of internal methyl protons. Based on π-SCF bond orders, the predicted δ_{Me} for the complex **239** is -0.62 with equation 5 and -0.82 with the equation 4. Moreover based on bond orders derived from coupling constants with equation 6, the predicted δ_{Me} is -0.92 with equation 5. This good agreement of the predictions with the experimental values (-0.87 and -0.98) suggests that the complex **239** behaves as an annelated dihydropyrene where the complexed benzene is equivalent to an annelating group, but nothing else.

Figure 30. π-SCF results and coupling constants

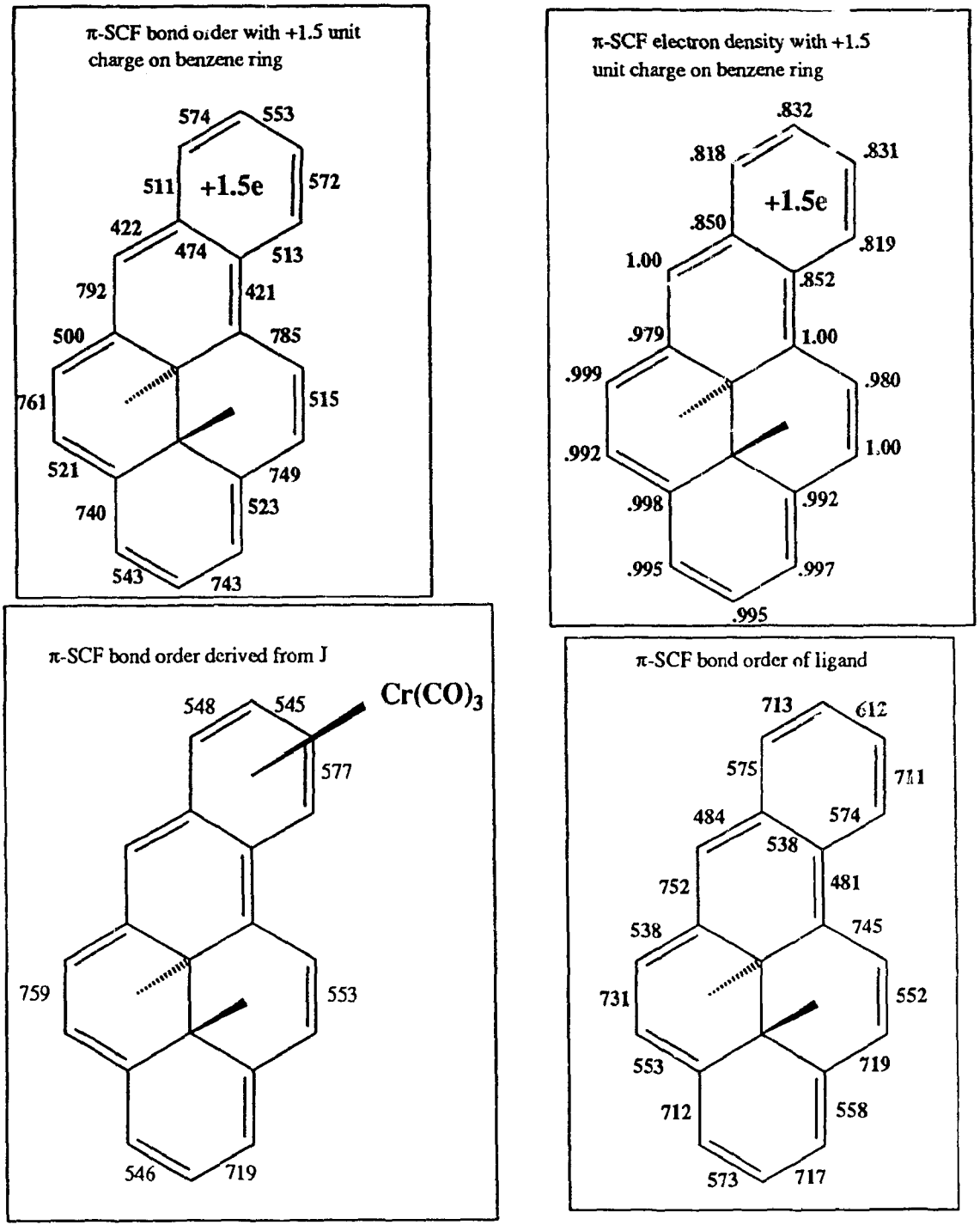


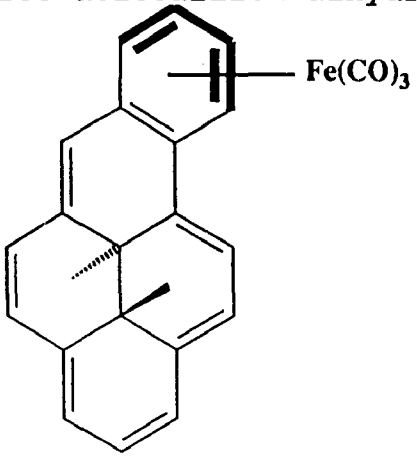
Table 14. δ_{Me} calculated from equations 4 and 5

equation	Δr (πSCF) →	δ_{Me}	Δr (J) →	δ_{Me}
5	123	-0.60	112	-0.92
4	136	-0.82	——	——

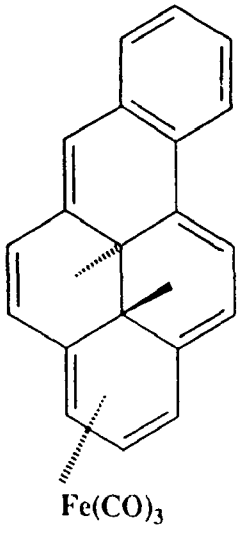
Based on these observations, the complexation effect on delocalization may be evaluated in terms of fixation power of an equivalent annelating ring. This might also be described as the "effective resonance energy". Using the equation developed by Mitchell and Venugopalan[87], we calculated the resonance energy of chromium tricarbonyl benzene as about 1.3 in units of benzene resonance energy, i.e., chromium tricarbonyl benzene would fix the delocalization of dihydropyrene **60** about 1.3 times more than benzene itself.

3.3.2 Benzo[a]dihydropyrene tricarbonyl iron 209

To complement the results from the chromium complex **239**, we thought it would be nice if we could prepare other metal dihydropyrene complexes. In particular, we attempted the synthesis of iron complex **241**, since $Fe(CO)_3$ may bond with a diene moiety of a benzene ring and hence render out of **241** a free delocalized dihydropyrene ring.



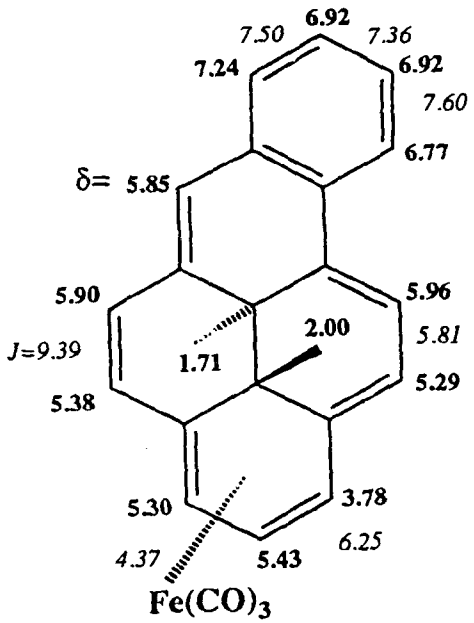
241



209

Figure 31. ^{1}H nmr spectrum of **209**

(^{1}Hnmr: 360 MHz, $CDCl_3$, Amb.)



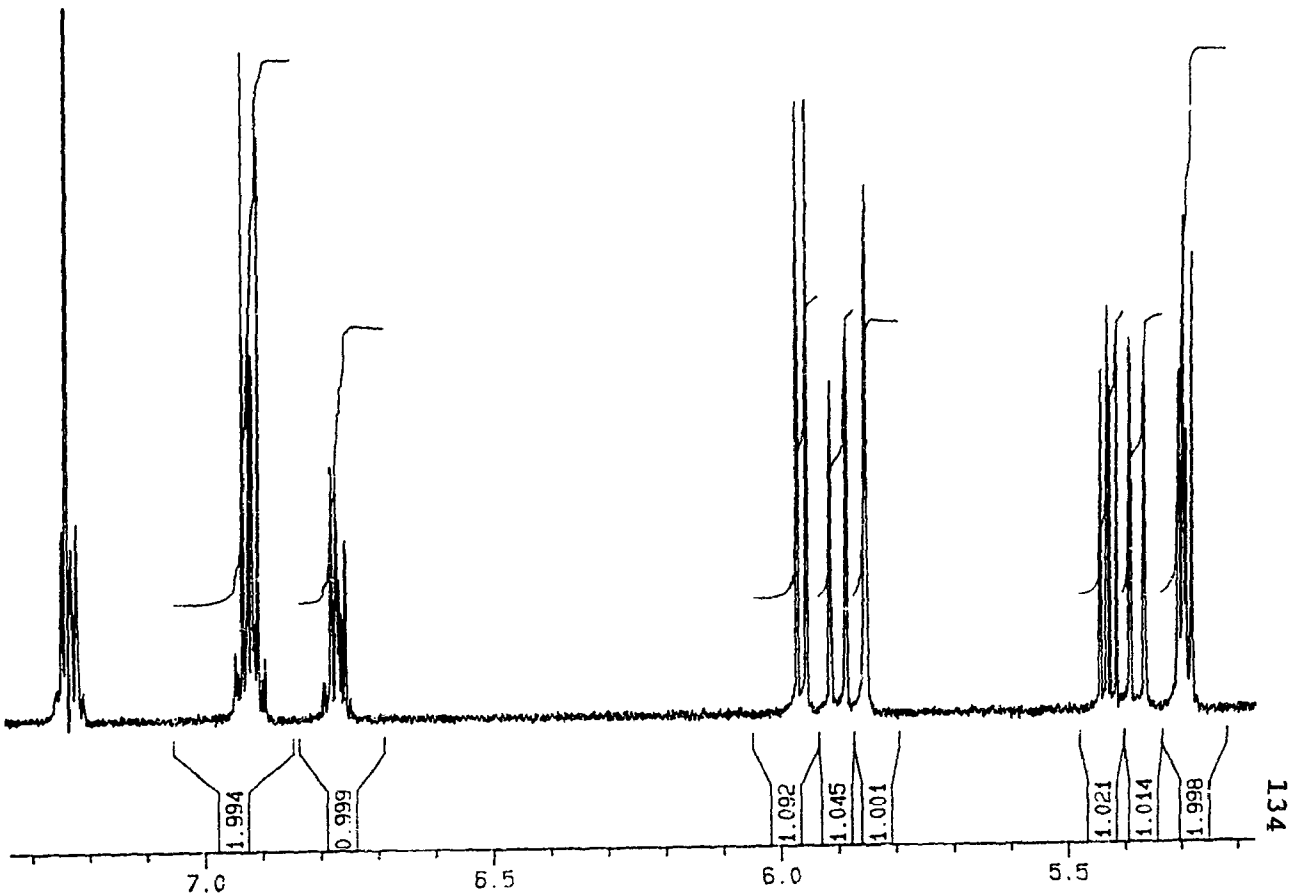


Figure 31a. Simulated and observed partial ^{1}H nmr spectrum of **209**
(Simulated and observed spectra of protons on the benzene ring in **209**: 360 MHz, $CDCl_3$, amb.)

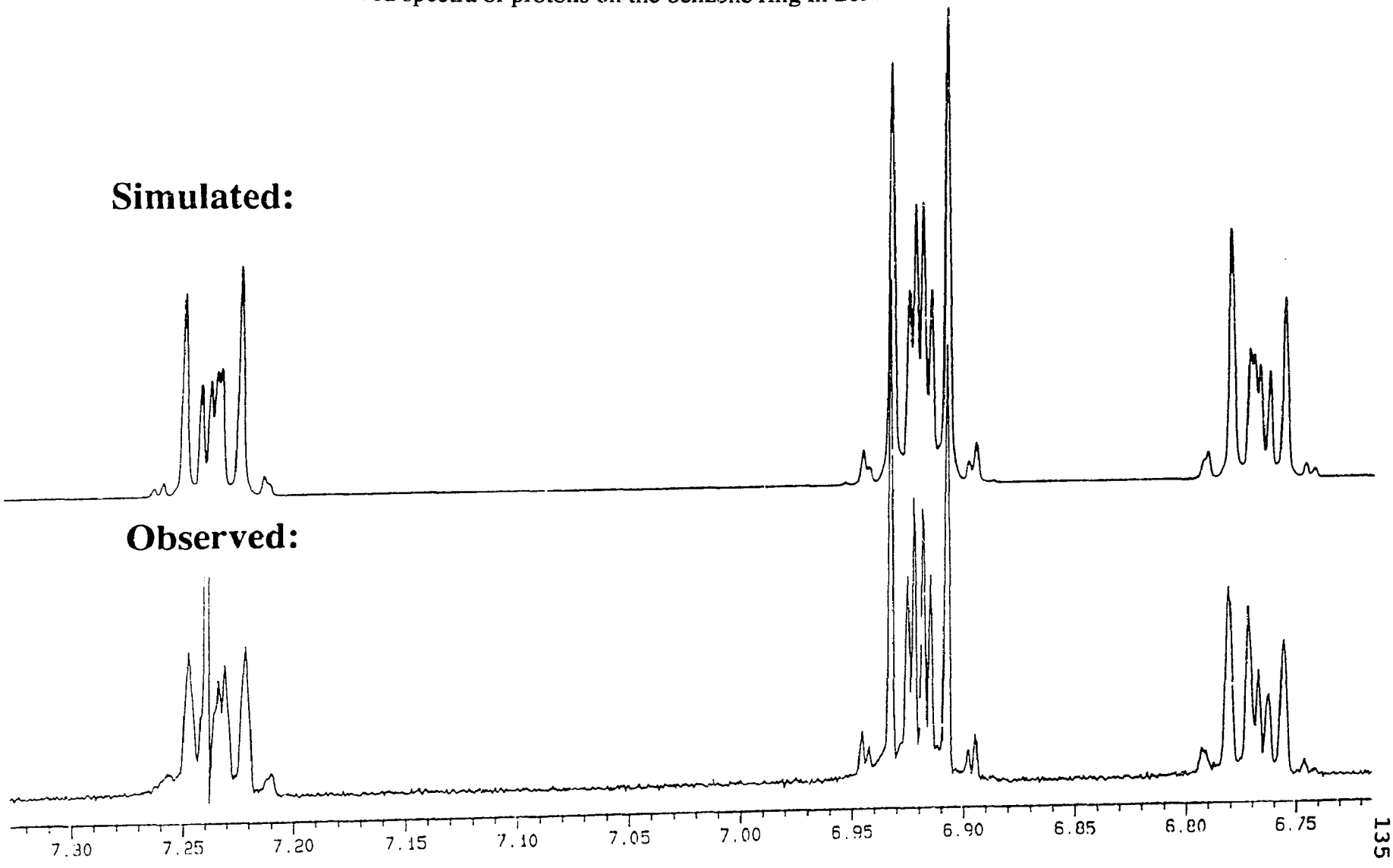
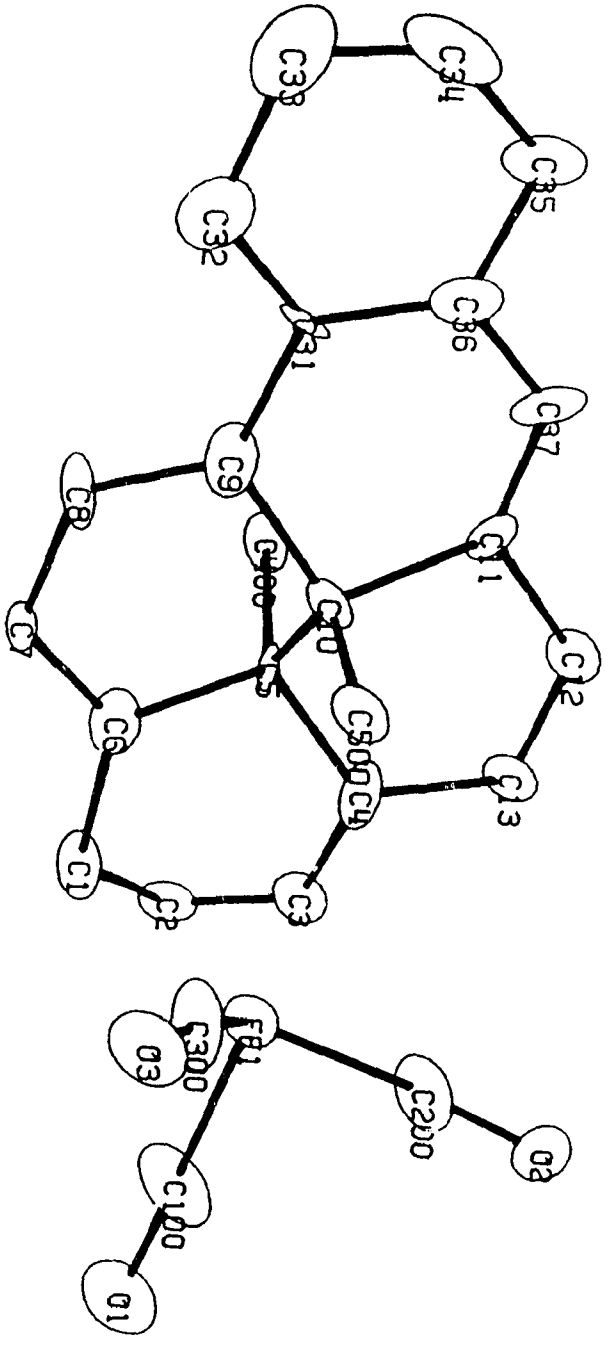


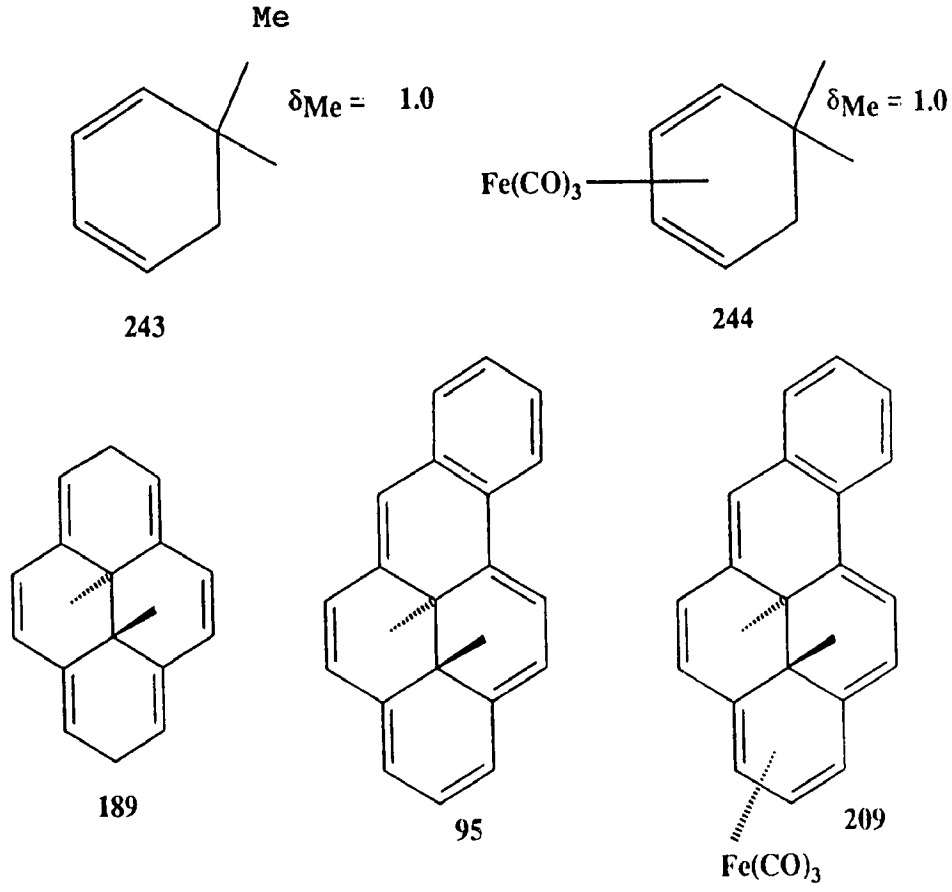
Figure 32. Ortep plot of **209**

Ortep plot of **209**: X-ray structure determination clearly indicated the **C, O, Fe** atoms but would not complete using a least square refinement to give the hydrogen atoms (R=0.16). Th crystal system was monoclinic, space group (C2/C (No. 15), with a=12.052Å, b=7.643Å, c=41.600Å.

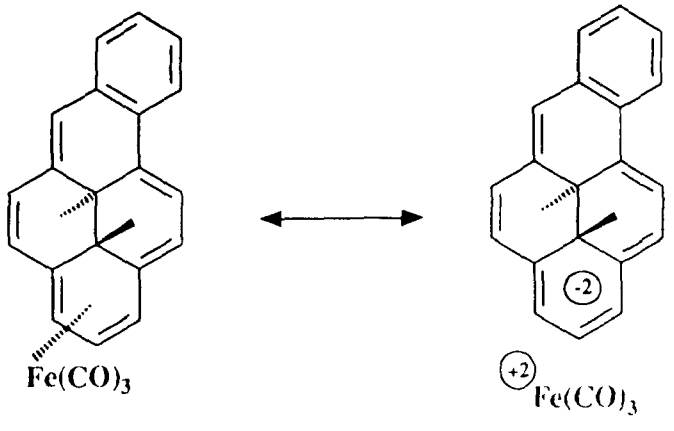


Unfortunately but not uninterestingly, the reaction of **95** with $Fe_2(CO)_9$ gave not **241**, but instead the complex **209** in a 40% yield in refluxing benzene. The ^{1}Hnmr spectrum and a preliminary X-ray structure of **209** are shown in Figure 31 and Figure 32, respectively. Very interestingly, the proton chemical shifts of the two internal methyl groups in the complex **209** appear at lower field (2.00 and 1.71 ppm) even than in the model compound **189** (0.97 ppm)! Two factors can be considered to rationalize such a low field shift: one, an anisotropic effect of the $Fe(CO)_3$ moiety; two, a paratropic ring current present in the macroring. To

Figure 33. δ of ligands and complexes

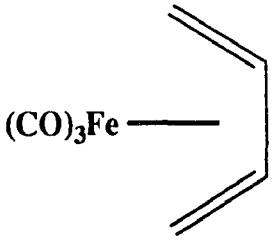


estimate the anisotropic effect of the $Fe(CO)_3$ moiety in the complex **209**, a pair of model compounds **243** and **244** are employed. The geometries of two methyl groups relative to the $Fe(CO)_3$ in **244** are very like that in **209**, hence, very similar anisotropic effects should be expected in these two compounds. Comparison of δ_{Me} in the free ligand **243** with the complex **244** suggest that the anisotropic effects are very small. Therefore, the anisotropic effect in **209** should be neglected. If the $Fe(CO)_3$ moiety in **209** completely fixes the delocalization in the macroring, the difference between **209** and **189** is approximately a benzene ring. Using Memory's equation, the deshielding of this benzene ring in **209** was previously estimated as -0.047 ppm, which is negligible. To rationalize the lower chemical shift ($\Delta\delta$: 1.03, 0.74) of the methyl protons in **209** relative to **189**, we proposed a weak paratropic ring current in the macroring of the complex **209**. This paratropicity is sustained by a hidden 16π-electron system which is formed from the 14-ring plus two electrons back-donated from the Fe center. This may be illustrated by drawing an ionic resonance structure **209a**,

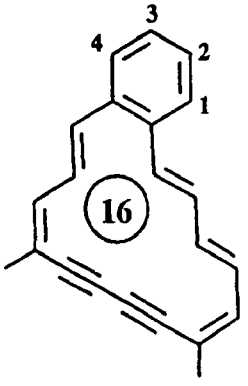


209 209a

in which a dianion of dihydropyrene is present. However, the contribution of this structure **209a** is very small based upon comparison of δ_{Me} of the dihydropyrene dianion **59**$^{2-}$, (downfield shift 21.00+4.25=25.25 ppm relative to the parent) with **209** (downfield shift 2.00+1.62=3.62 ppm). Although no direct evidence has been developed for the 16π-electron paramagnetic ring current proposal, the electron back-donating of iron to a π-ligand is a well-known phenomenon, e.g., the stability of tricarbonyl cyclobutadiene iron, **232**, and the 2C-3C bond shortening in **245** are attributed to electron back-donation from iron. We also observed bond shortening in complex **209** (bond 8-9 is 1.26Å) through a preliminary X-ray study. This is direct evidence for electron back-donating in the complex **209**.



245



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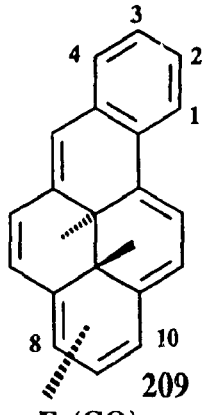


209

Fe(CO)3

Table 15. π-SCF bond order (Pu,v) and Q values

Compound	$P_{1,2}$	$P_{3,4}$	$P_{2,3}$	Q_{exp}	$Q_{\pi\text{-scf}}$
182	0.679	0.671	0.675	0.985, 1.017	1.016
209	0.639	0.658	0.645	0.991, 1.020	----

In order to further confirm the paratropic character of the macroring **209**, we derived the Q index of this compound using the coupling constants $J_{3,4}$=7.48 and $J_{2,3}$=7.36 (after steric correction, $P_{3,4}$=0.658 and $P_{2,3}$=0.645, Q=1.020). The Q value being smaller than 1.04 suggests that the dihydropyrene ring in **209** should be classified as a delocalized 4nπ-system annelated by a benzene ring. The simulated and observed ^{1}Hnmr spectra of the benzene ring are shown in Figure 31a. Table 15 compares Q values for **209** and [16]annulene **182**.

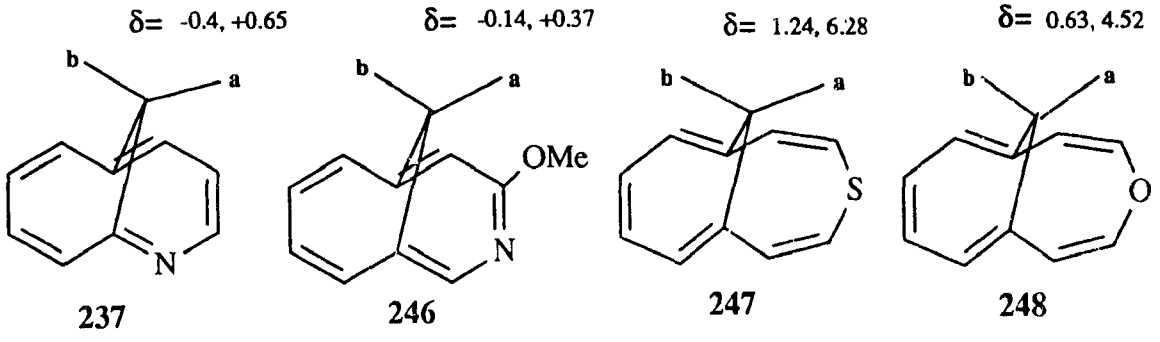
Given the success in preparing **209**, in the future, it may be possible to complex other metals with a dihydropyrene and then probe their electron back-donating ability using the chemical shifts of internal methyl protons of dihydropyrene.

3.4 Bridged heteroannulenes

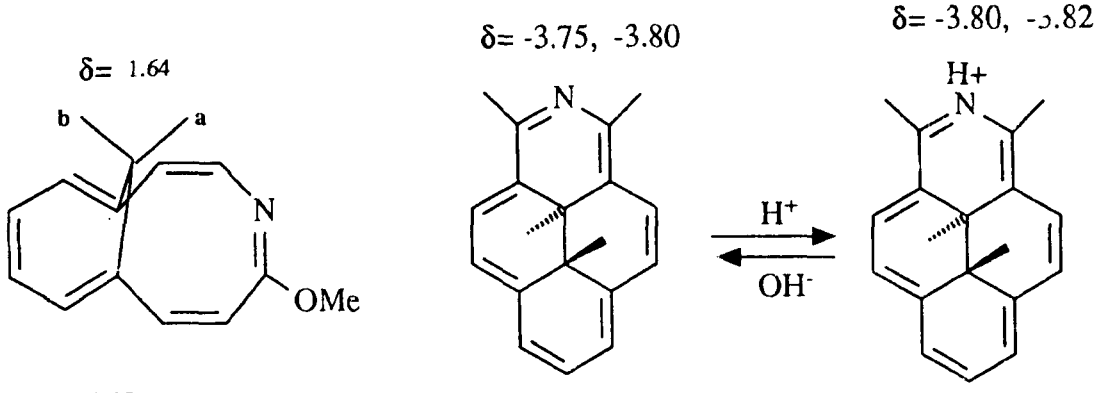
Bridged heteroannulenes have only been prepared recently. The bridging atoms hold the π-atom framework rigidly and avoid different conformations and mobility in the system so that π interactions can be easily probed.

In 1978, Vogel[113] reported the synthesis of 1-aza-2,7-methano[10]annulene, **237**, and as well Vogel[113] and Helmkamp[114] independently obtained 1-aza-10-methoxy-3,8-methano[10]annulene, **246**, the first derivative of 1-aza-

3,8-methano[10]annulene. The high field chemical shifts of protons a and b in these two compounds **237** (δ_a and δ_b: -0.4 and +0.65) and **246** (δ_a and δ_b: -0.14 and +0.37) indicate the diatropicity of these systems. However, 1-thia-4,9-methano[11]annulene, **247**[115], 1-oxa-4,9-methano[11]annulene, **248**[115], and 1-aza-2-methoxy-5,10-methano[12]annulene **249**[116] do not exhibit paratropicity in their ^{1}Hnmr spectra. On the other hand, 2-aza-1,3,15,16-tetramethyl-15,16-dihydropyrene, **250**[117], is strongly diatropic. Interestingly the chemical shifts of the internal methyl protons suggest that the corresponding conjugate acid **251** has a stronger



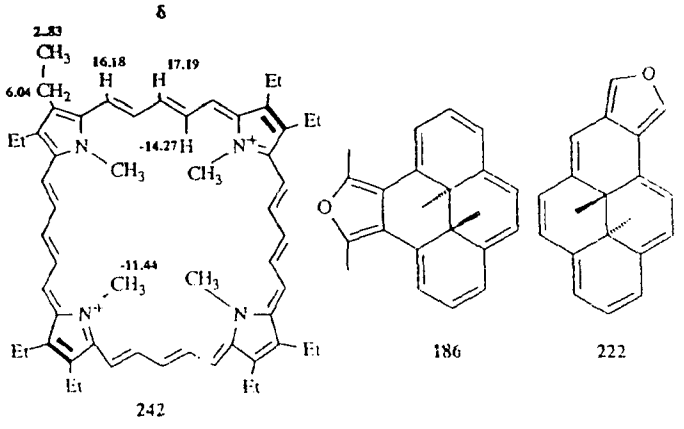
237 246 247 248



249 250 251

diamagnetic ring current than **250**. Another remarkable example with extremely large diatropicity is the [34]porphyrin dibromide **242** which shows the resonances for the most strongly shielded proton at δ -14.27 and deshielded at 17.19 for the protons inside and outside the ring[118a]. Recently, Lai[118b] has reported the synthesis of the furanodihydropyrene **186**. He reported an unexpectedly high field chemical shift of its internal methyl protons of -3.97 ppm.

To confirm whether these were correct, we decided to synthesize the furanodihydropyrene **222**, which should have similar δ_{Me} to **186**. As we discussed earlier, the reaction of endoxide **94** with the tetrazine **217** readily gave **222**. The crude product **222** was purified by careful chromatography to give a red crystalline solid **222** in 78% yield. This red solid was not stable and readily decomposed either in $CDCl_3$ or on silica gel. It is interesting to note that diethyl ether tends to stabilize the compound especially when diethyl ether is used as one component of eluant in a column chromatography process.



242 186 222

Figure 34. ^{1}H nmr spectrum of **222**

(^{1}Hnmr: 250 MHz, $CDCl_3$, Amb.)

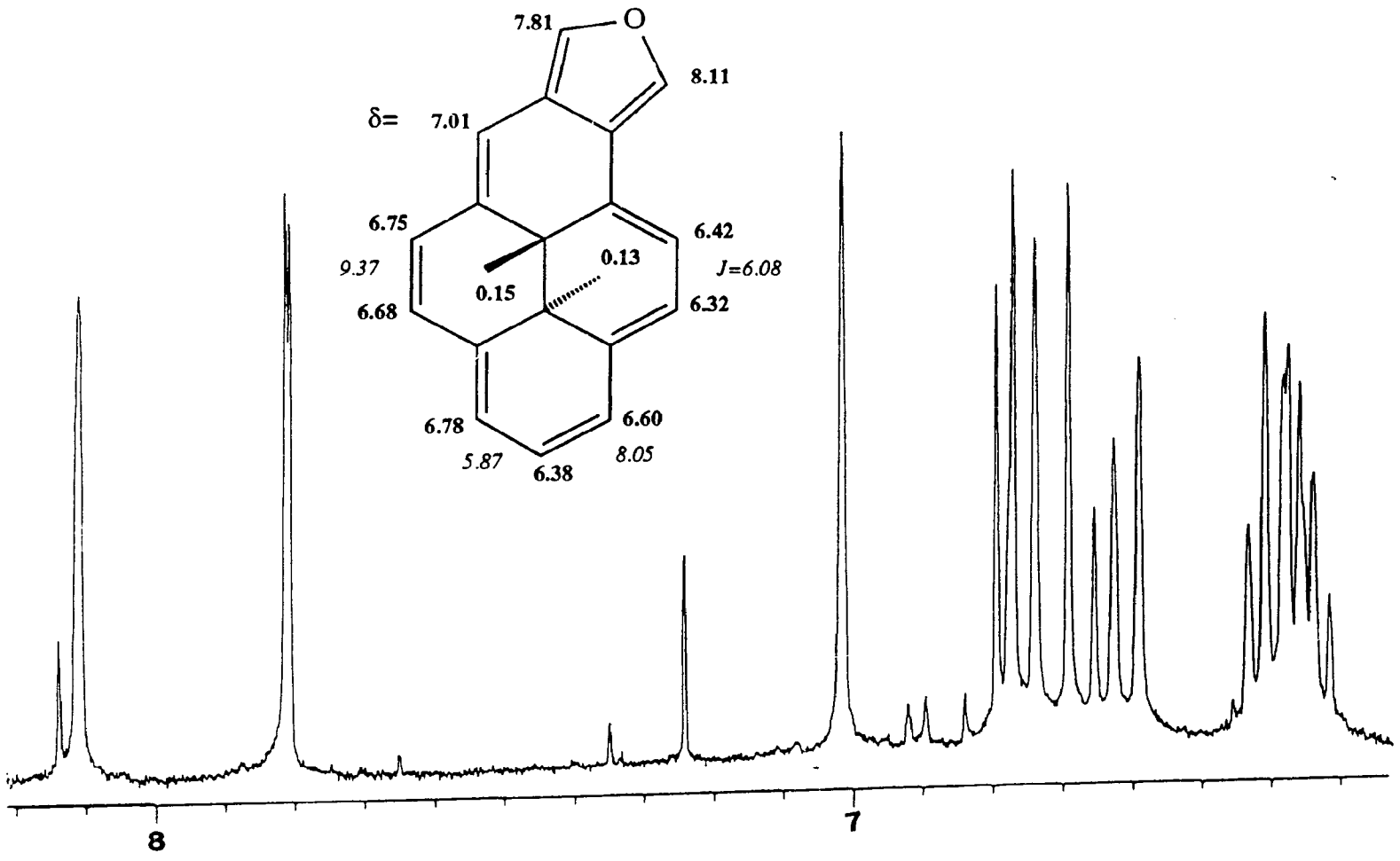


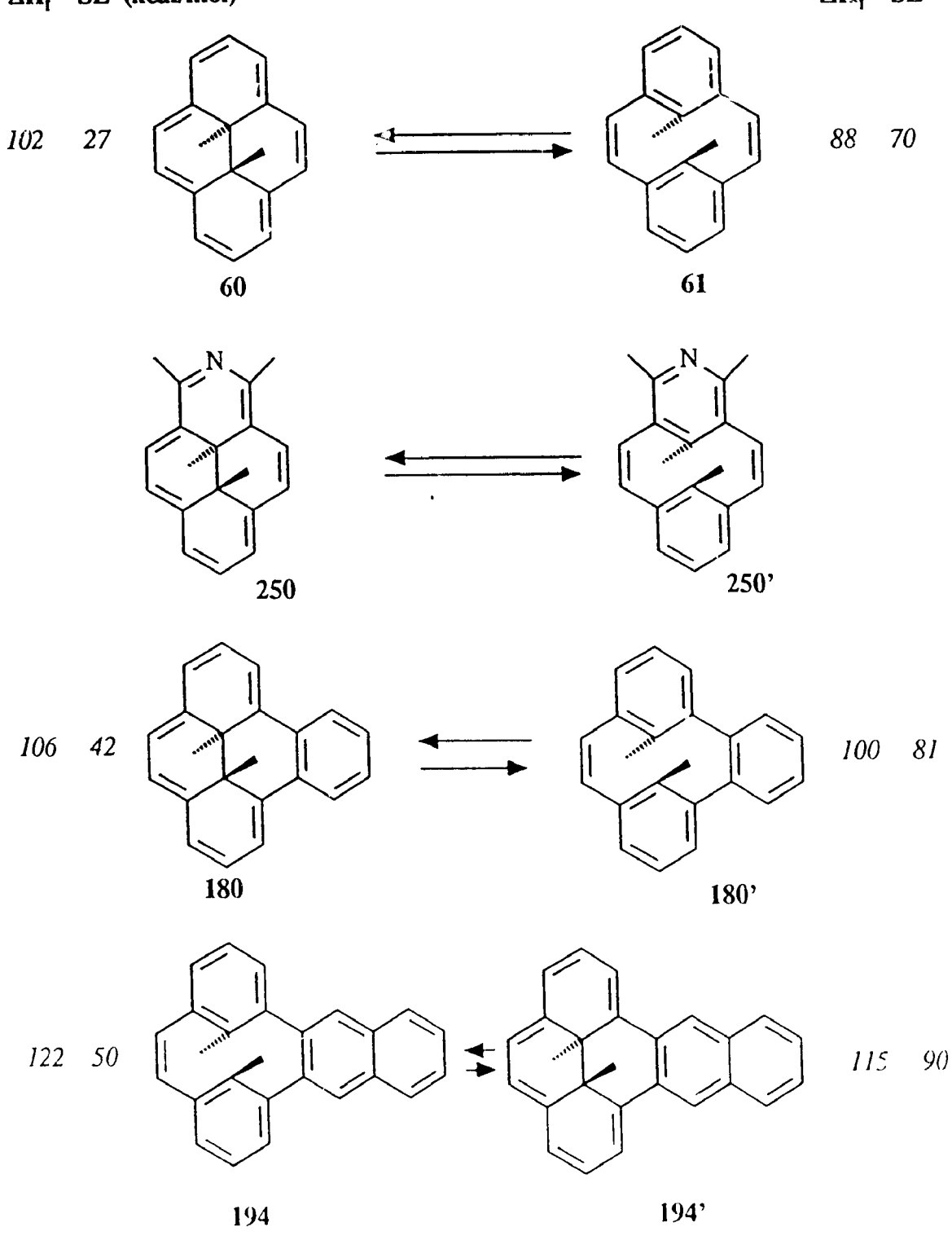
Figure 34 shows the ^{1}Hnmr spectrum of compound **222**. As we expected, the chemical shifts (δ_{Me}=0.15, 0.13) of the internal methyl protons in this compound indicate substantial bond fixation relative to dihydropyrene **60**. Private communication with Dr. Lai indicated that the correct chemical shift for the internal methyl protons for the compound **186** should be 0.63 instead of -3.97. In comparison with δ_{Me} 0.97 of the model compound **189**, there is still a weak diamagnetic ring current in compound **222**. However use of equation 4 or 5 to predict δ_{Me} from calculated bond order suggests that compound **222** is not an annelated dihydropyrene, but that it should be classified as an oxa[17]annulene. This synthesis of the oxa[17]annulene **222** has corrected an error in literature[118] and expanded our chemistry into a new area of bridged heteroannulenes.

3.5 Photoisomerization of dihydropyrene derivatives

It is well known that some dihydropyrene derivatives undergo photochemical valence isomerization to the metacyclophanedienes, e.g., dihydropyrenes **60**, **250**, **180** and **194**. All of these colored compounds can be bleached to the colorless cyclophanedienes by a tungsten lamp fairly rapidly; upon removal from the light, the color returns. However, it has also been reported that when **95**, an isomer

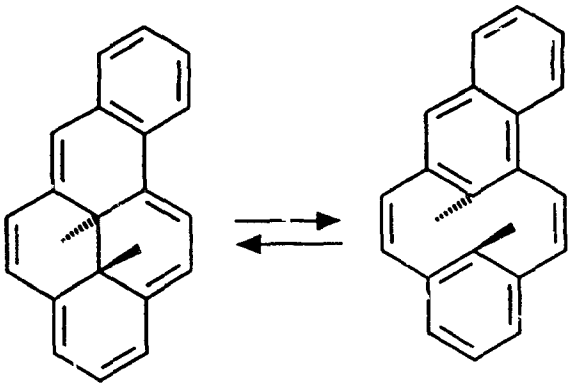
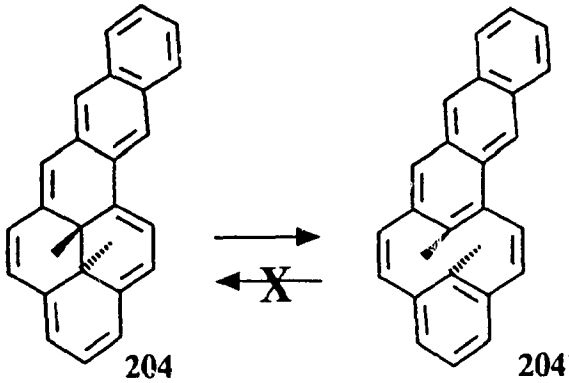
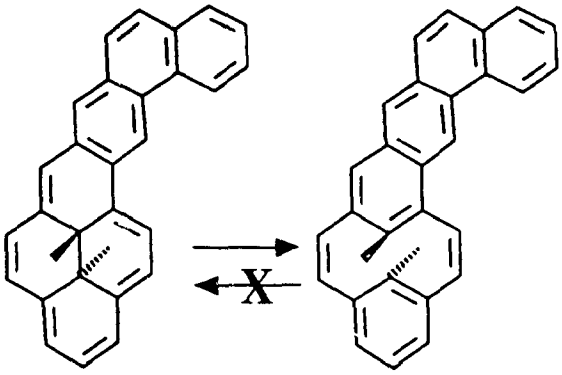
of **180**, was irradiated, no detectable amount of corresponding diene **95'** could be observed. Thus, we thought

Figure 35. Strain energy and heat of formation



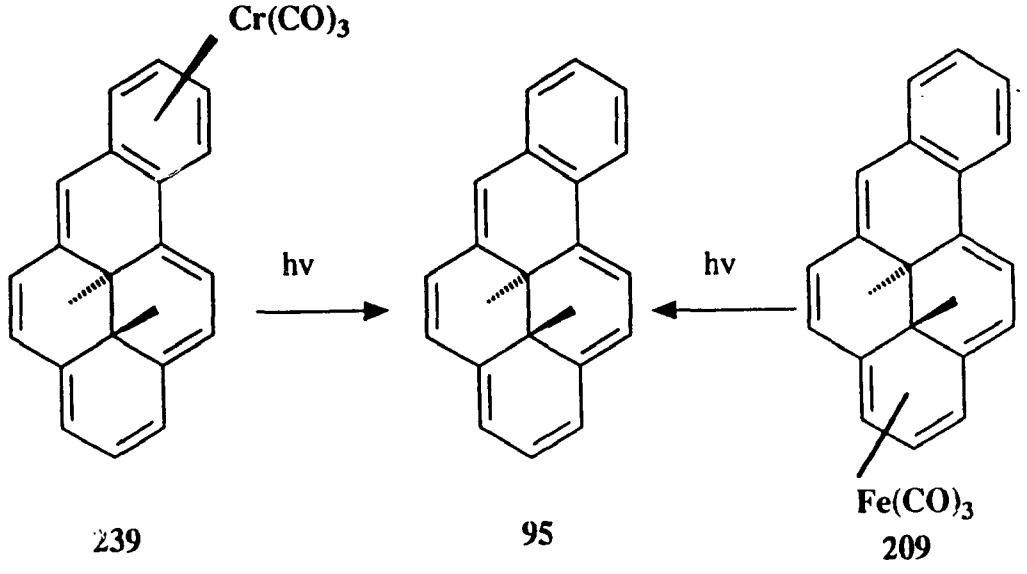
it is worthwhile to investigate the photoisomerization of the stable dihydropyrenes prepared in this project.

Figure 36. Strain energy and heat of formation

ΔH_f	SE (kcal/mol)		ΔH_f	SE
102	*38*	 **95** **95'**	*105*	*81*
118	*47*	 **204** **204'**	*126*	*90*
133	*58*	 **206** **206'**	*141*	*102*

Interestingly all of these [a]annelated dihydropyrenes, **95**, **204** and **206**, are not converted to the corresponding diene forms in any detectable amount. To rationalize these results, we carried out PCMODEL2/MMX calculations on these compounds. The resulting energies, such as heat of formation (ΔH_f) and strain energy (SE), indicate that: (1): [e]annelated dihydropyrenes **180** and **194** are less stable than their corresponding dienes (Figure 35), and vice versa for [a]annelated dihydropyrenes **95**, **204** and **206** (Figure 36); (2): the [a]annelated dihydropyrenes **95** and **204** are more stable than their corresponding [e]annelated isomers in terms of both ΔH_f and SE.

We wondered whether metal complexation might change this, however, irradiation of the metal complexes **239** and **209** only gave the ligand **95**.

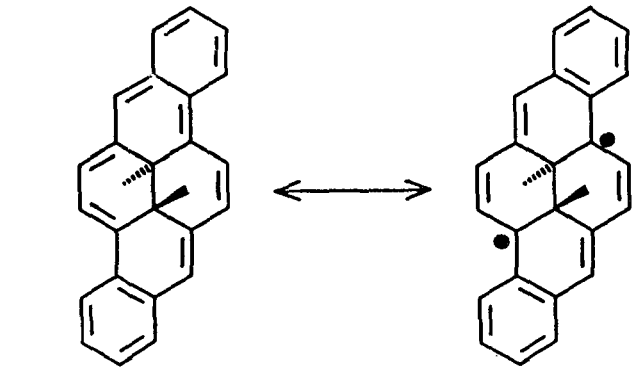


239 95 209

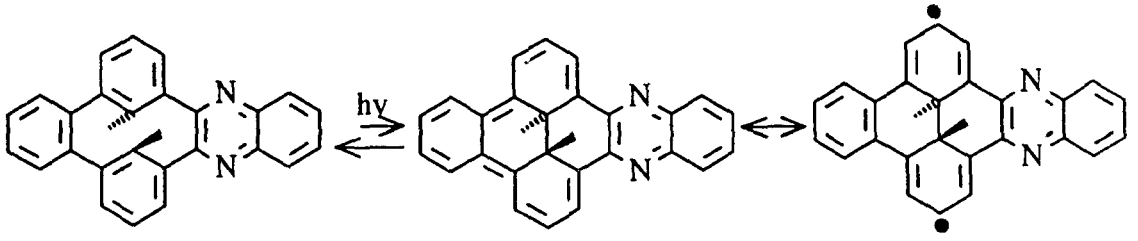
CHAPTER 4 FUTURE WORK

4.1 Diannelated dihydropyrenes

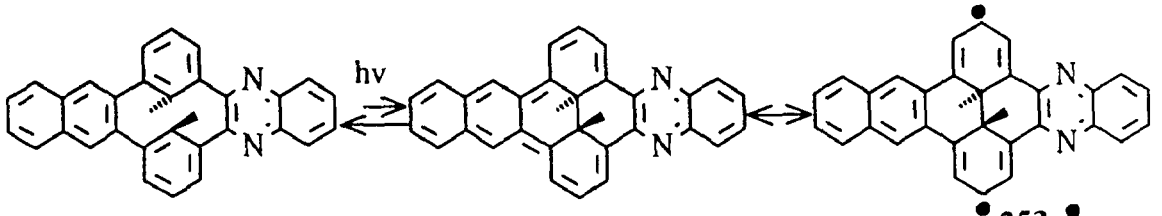
Two diben.. annelated [a,h]- and [a,i]dihydropyrenes **188** and **187** have been reported by Mitchell and coworkers[119].



188 **188•** **187**



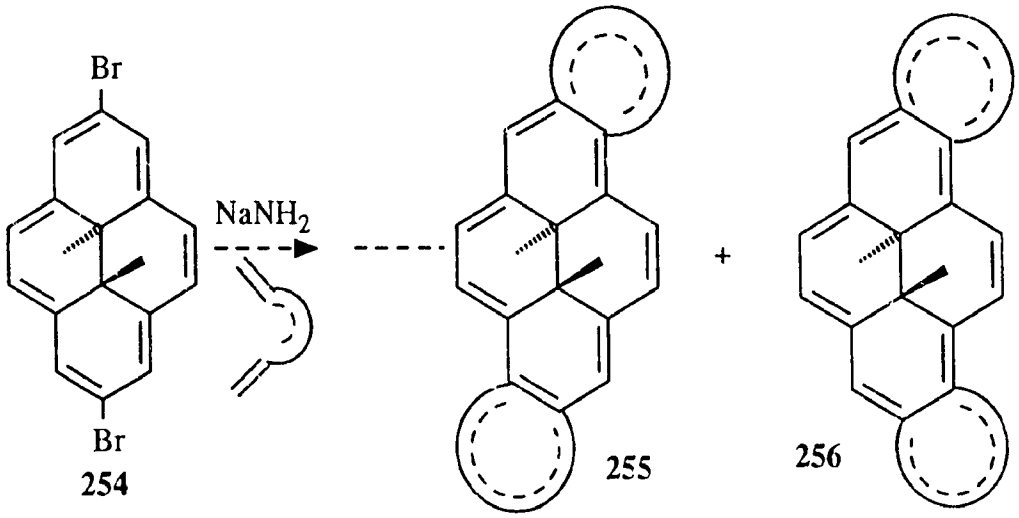
252b **252a** **252a•**



253b **253a** **253a•**

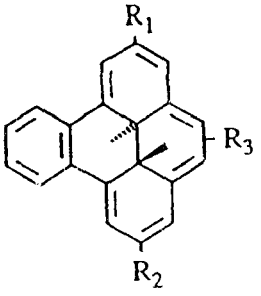
Recently they also reported the observations of biradicaloid diannelated [e,l]dihydropyrenes **252a** and **253a**[120]. The latter two reddish-purple compounds were formed upon irradiation of their corresponding stable cyclophanedienes **252b** and **253b** but gave a nmr spectrum with broad featureless signals. This was rationalized by drawing one of their biradicaloid resonance structures such as **252a**$^{\bullet}$ and **253a**$^{\bullet}$. Similarly the compound **188** also displays radicaloid properties but gives a characterizable ^{1}Hnmr spectrum.

Boekelheide[33] had reported that treatment of dihydropyrene **60** with bromine produced a mixture of polysubstituted bromo compounds, whereas NBS in CCl_4, under free-radical conditions, gave about 19% of the 2,7-dibromide **254**. Apparently, we should next try the synthesis

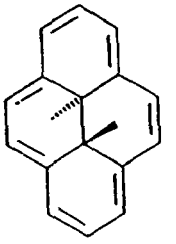


of diannelated dihydropyrenes **255** and **256** through the sequence of dehydrobromination of **254** with trapping reagents followed by deoxygenation.

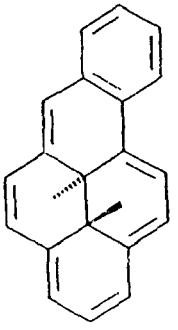
It is known that electrophilic substitution (nitration, acylation) proceeds readily in the macro ring of the benzannelated dihydropyrene **180** to give procucts **257**, **258**, **259**, and **260**, similar to that of the non annelated parent **60**[121]. Interestingly, our preliminary investigations showed that the bromination of **95** with



180: $R_1 = R_2 = R_3 = H$
257: $R_1 = NO_2, R_2 = R_3 = H$
258: $R_1 = R_2 = NO_2, R_3 = H$
259: $R_1 = R_2 = R_3 = NO_2$
260: $R_1 = COCH_3, R_2 = R_3 = H$

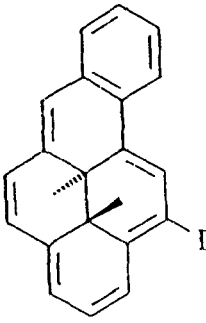


60



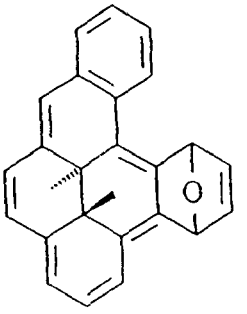
95

NBS
DMF

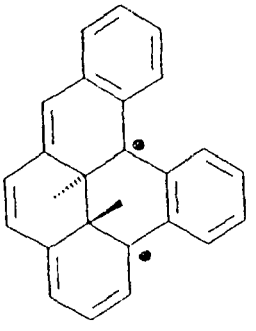


261

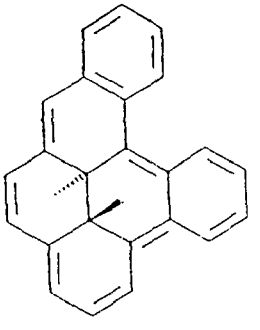
$NaNH_2$
furan



262

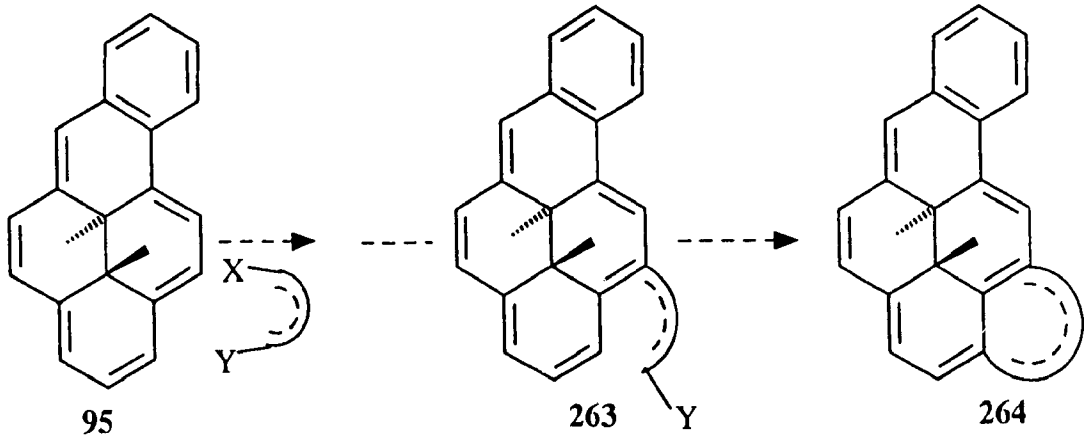


191•



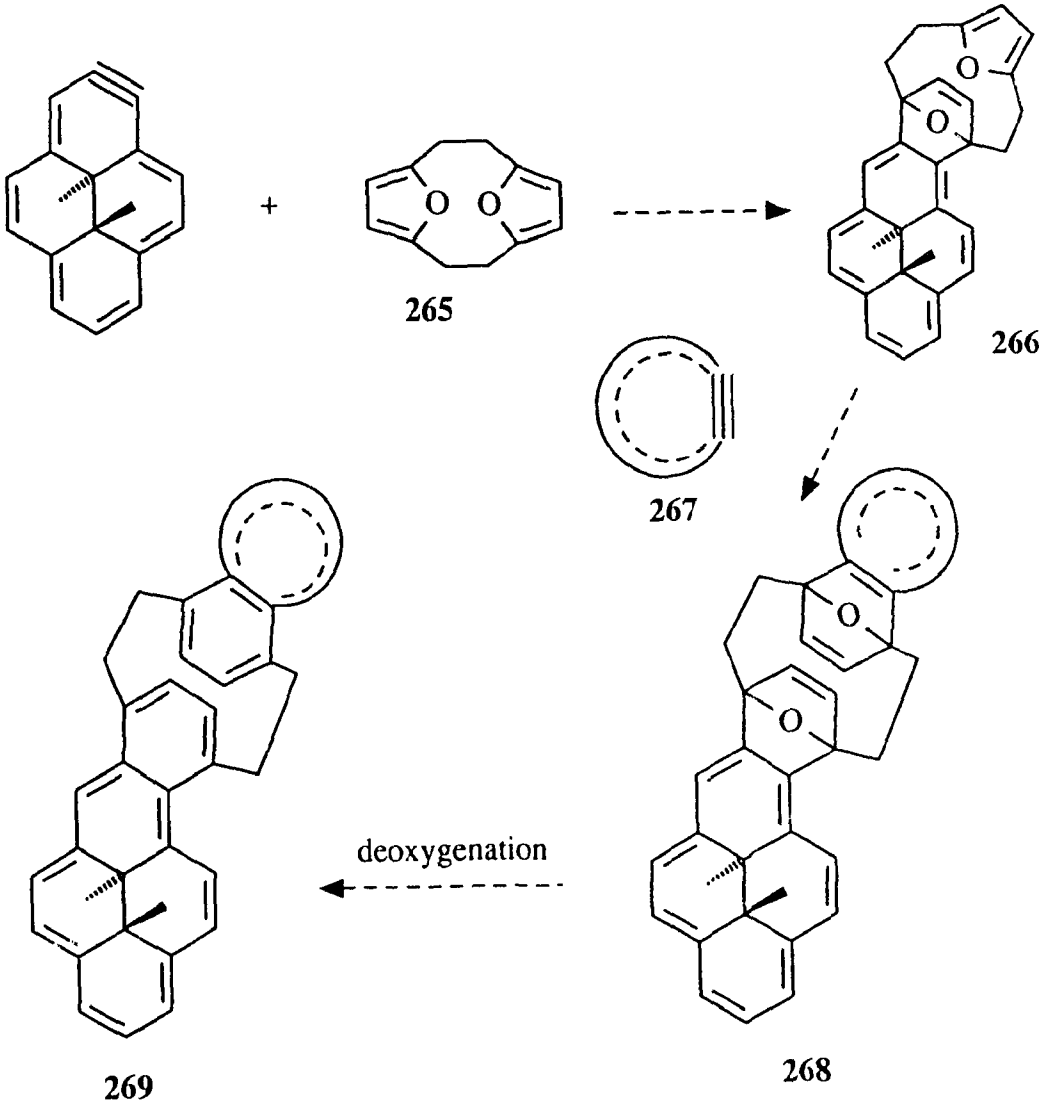
191

NBS/DMF selectively gave the mono bromide **261**. The reaction of this bromide with $NaNH_2$ in the presence of furan gave the adduct **262**. The deoxygenation of **262** with $Fe_2(CO)_9$ in benzene at reflux temperature gave a deep red solid without ^{1}Hnmr signals. This might be due to the radicaloid properties of **191** that were demonstrated by one of the biradicaloid resonance structures **191**$^{\bullet}$. Further investigation are needed to fully characterize the compounds **261** and **262**, and hopefully a cautious deoxygenation of **262** will give the novel compound **191** with enough ^{1}Hnmr signals. Moreover it is possible to access the novel annelated dihydropyrene **264** taking advantage of selective electrophilic substitution of **95**.



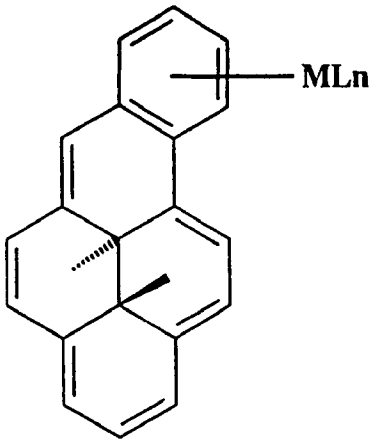
4.2 Novel Cyclophanes

Using the novel trapping reagent **265**[122] we might get the novel cyclophanes **269.**



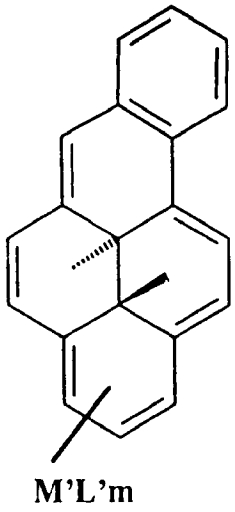
4.3 Metal complexes

To complete a series of study, more metal complexes should be prepared, i.e., **270** and **271**.



M = Mo, W, Ru, Fe,etc.

270

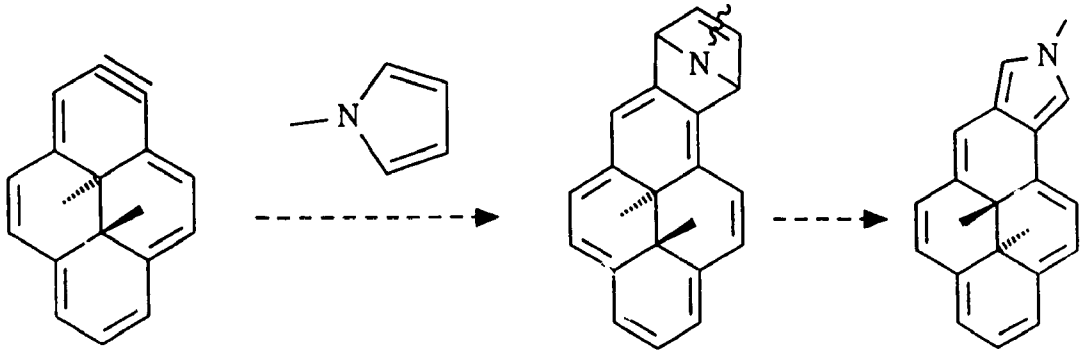


M' = Co, Ni, etc.

271

4.4 Bridged heteroannulenes

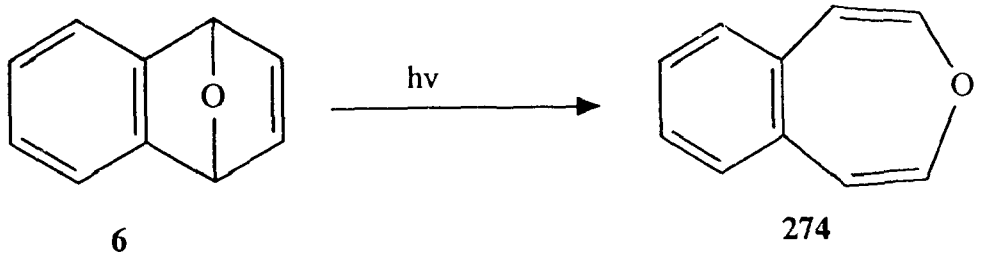
It would be desirable to prepare the aza[17]annulene **273** and compare it with the oxa[17]annulene **222**.



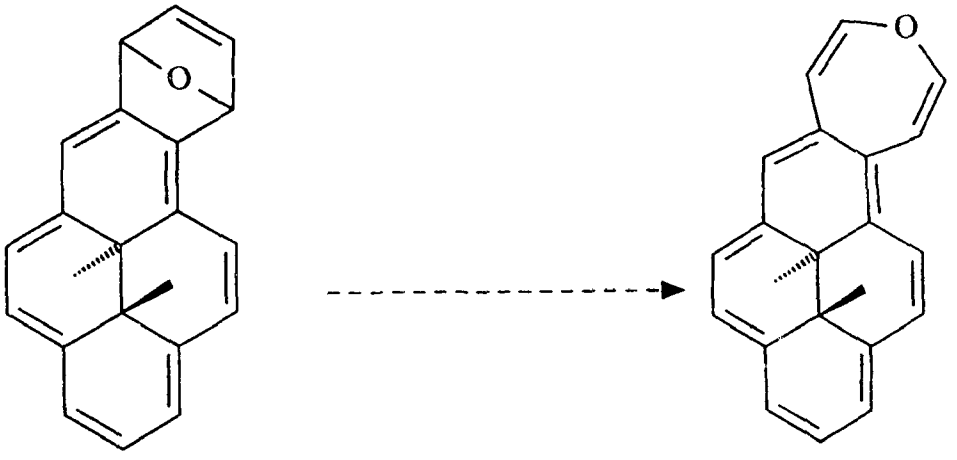
272 **273**

4.5 Reactions of the adduct 94

It is known that 1,4-epoxy-1,4-dihydronaphthalene, **6**, photorearranges to benz[f]oxepin **274**[123]. Thus, it might be possible to access dihydropyreno[f]oxepin **275**.



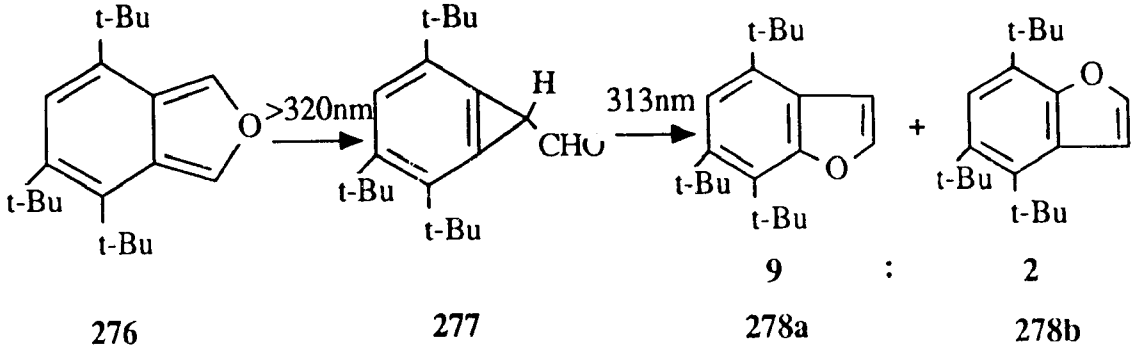
6 **274**



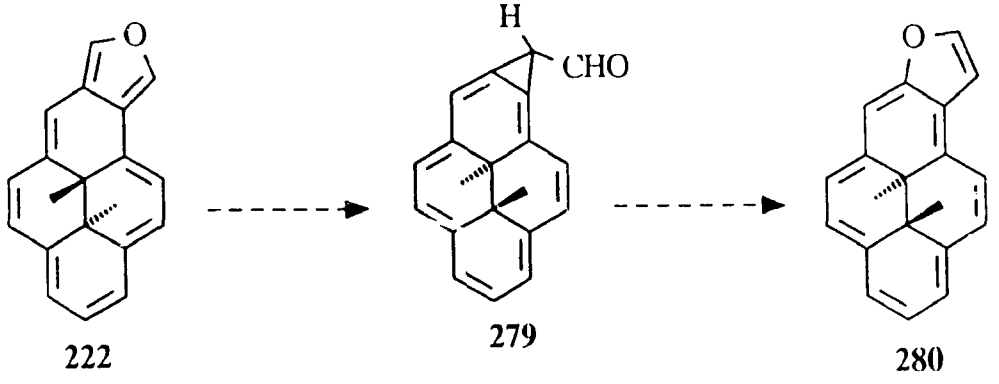
94 **275**

4.6 Reactions of the oxa[17]annulene 222

Recently, it was reported that 4,5,7-tri-t-butylisobenzofuran, **276**, undergoes photolysis to give (3,4,6-tri-t-butylbenzo)-cyclopropene-3-carbaldehyde, **277**, as a primary product. Subsequent irradiation of **277** afforded the mixture of benzofurans **278a** and **278b** in a 9:2 ratio[124]. It will be interesting to know what the fate of **222** is under similar irradiation.

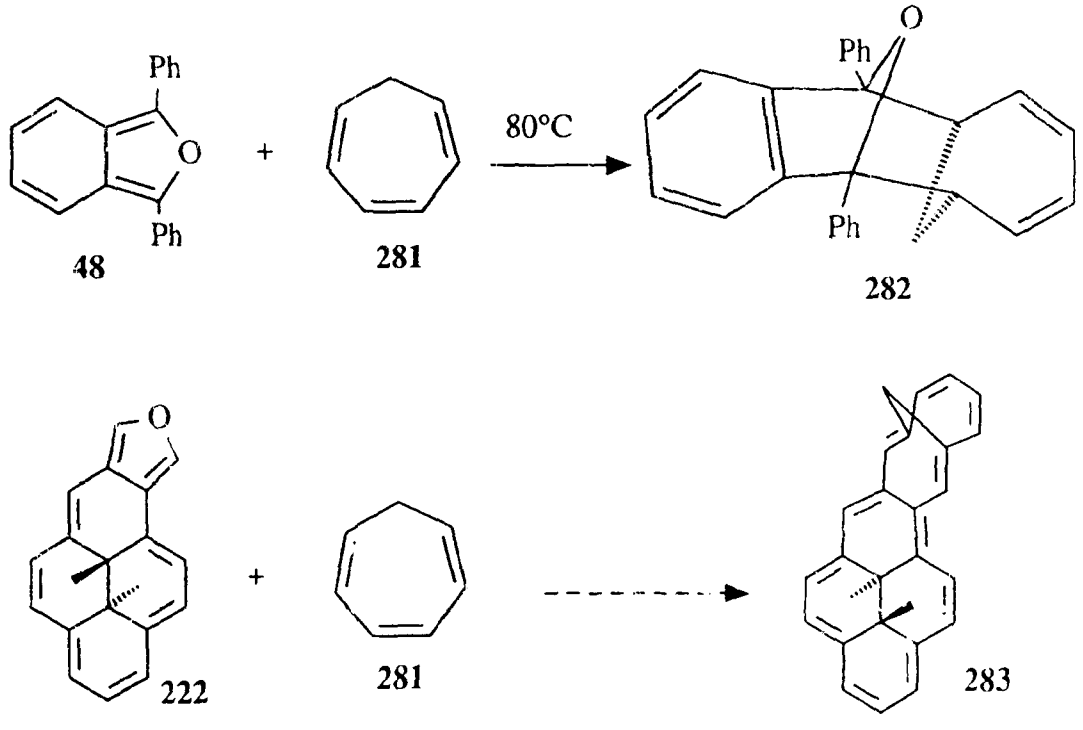


276 277 278a 278b



222 279 280

Another interesting reaction is that thermal cycloaddition of 1,3-diphenylisobenzofuran **48** with cycloheptatriene **281** gives a [6+4] adduct **282**[125]. With **222**, it might be possible to achieve the fusion of Boeklheide's [14]annulene[28] and Vogel's [10]annulene[70] to give the novel compound **283** through above reaction and subsequent deoxygenation.



CHAPTER 4 CONCLUSIONS

The existence of the reactive intermediate dihydropyryne **57** generated via dehydrobromination has been proved by trapping with N,N-diethyl-1,3-butadienylamine and a series of isoannelated furans. Unfortunately, no physical data for **57** has been collected because of its high reactivity and harsh conditions in its formation. However, Comparison of **57** with benzyne was implemented using the results of MMX/PCMODEL calculations.

Using the dihydropyryne **57** as an intermediate, a more efficient route to annelated dihydropyrenes has been developed. Through this route, three types of annelated dihydropyrene and the oxa[17]annulene **222** have been synthesized. This route has high potential and versatility for synthesis of other annelated dihydropyrenes, also for 4- and 5-membered ring annelation as we discussed in Chapter 1.

Larger quantities of the benzo[a]dihydropyrene **95** were obtained than was previously possible, so that metal complexation of **95** was able to be investigated. This led to the first two metal dihydropyrene complexes **239** and **209**. The delocalization effects due to complexation have been studied.

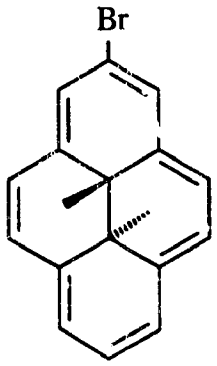
Combining the results of the newly synthesized annelated dihydropyrenes with previously reported ones, a series of correlations between theoretical calculations and

experimental results, such as bond order vs. chemical shift, bond order vs. coupling constant and ring current vs. chemical shift, have been devised. These results show that the major factor involved with the chemical shift and coupling constant changes is a change in bond order brought about by annelation with another aromatic ring. Through space and through bond anisotropic factors are clearly small and do not perturb the results greatly. However any further correlations of the results would need to take into account these small other effects. Nevertheless this work has provided a considerable number of experimental results which support the original hypothesis that the ring current change is the major factor to affect chemical shifts on annelation with another aromatic, and that these ring current changes can be approximately correlated with the changes in bond order predicted by theoretical calculations.

The *ortho*-metallation of dihydropyrene derivatives and synthesis of 1-bromo-2-fluoro-dihydropyrene were attempted. This led to two new dihydropyrene derivatives, namely, trimethylacetamino-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, **99**, and 2-diethylcarbamyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, **109**, and two new cyclophane derivatives, namely, *syn*-5-bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, **131a**, and *anti*-5-bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, **131b**.

CHAPTER 6 EXPERIMENTAL SECTION

6.1 Structure index:



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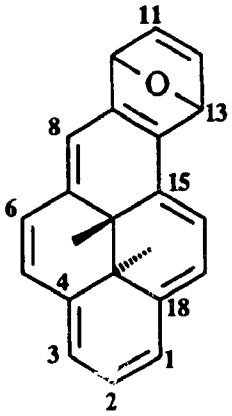

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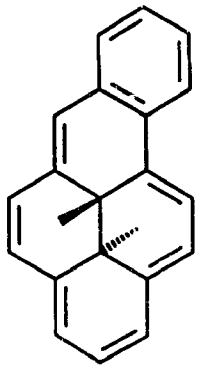

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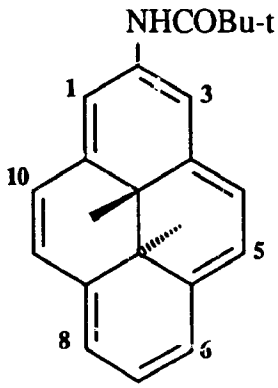

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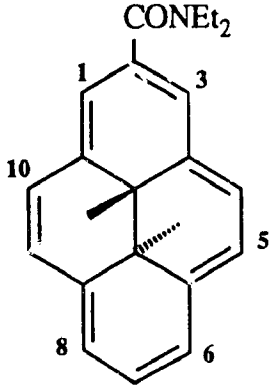

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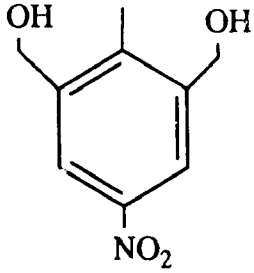

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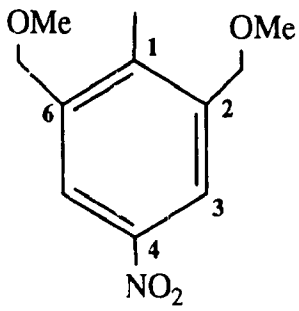

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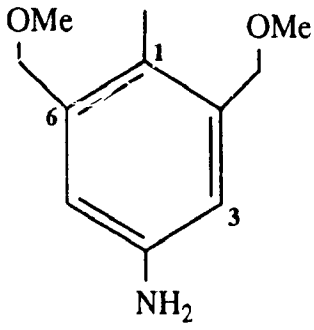

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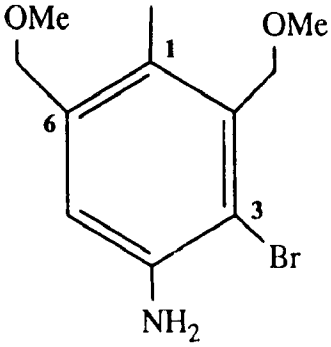

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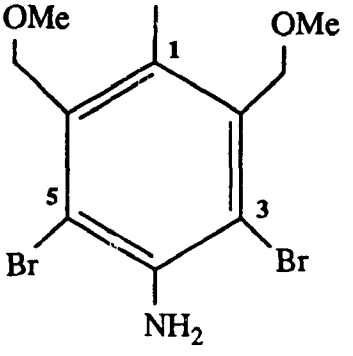

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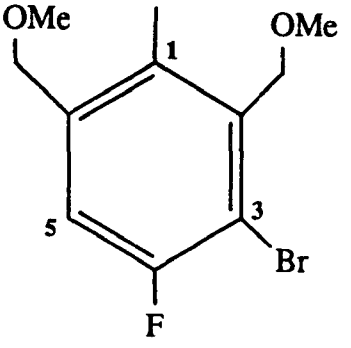

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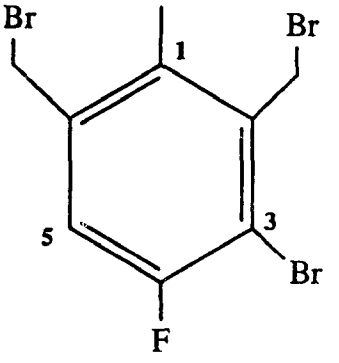

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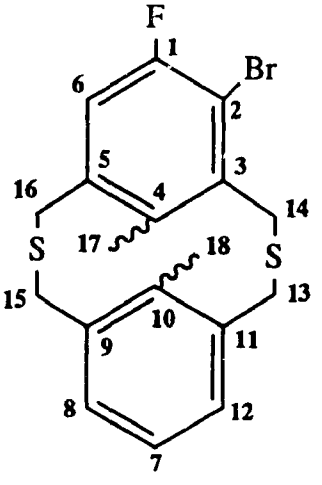

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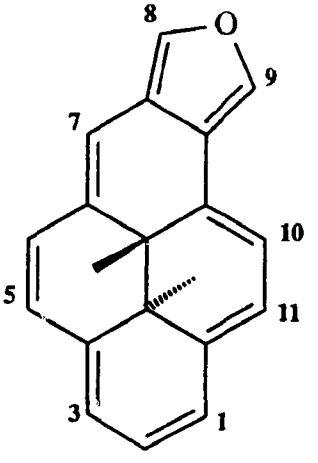

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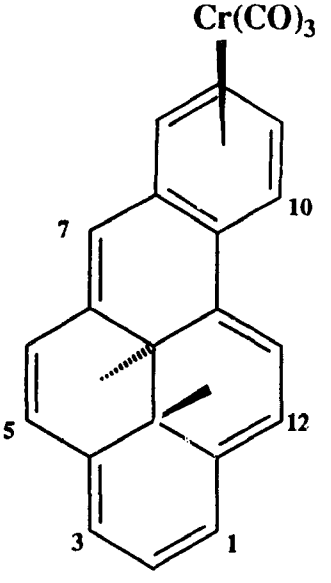

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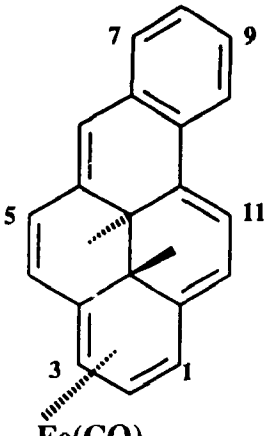

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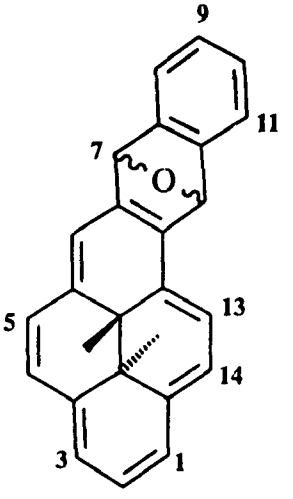

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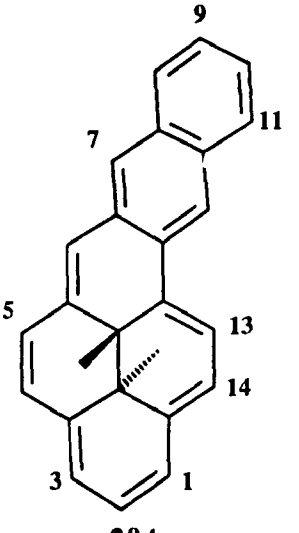

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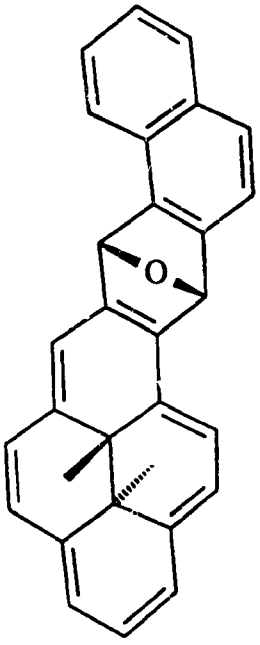

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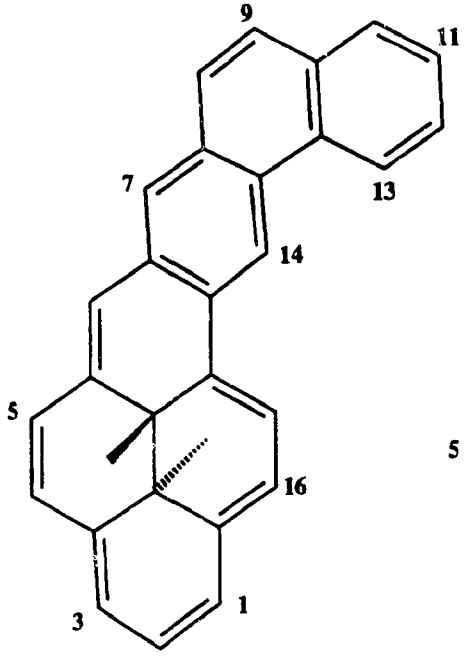

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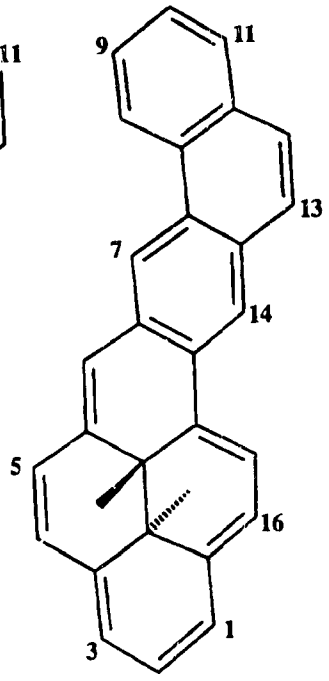

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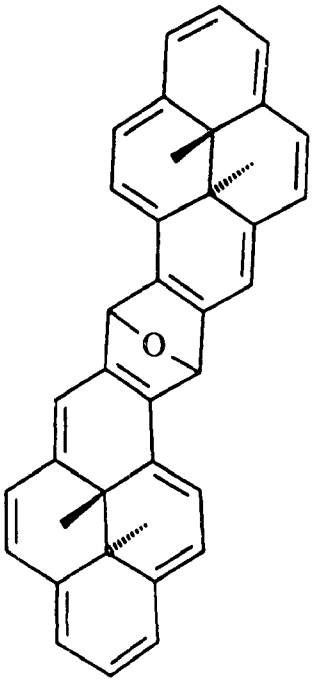

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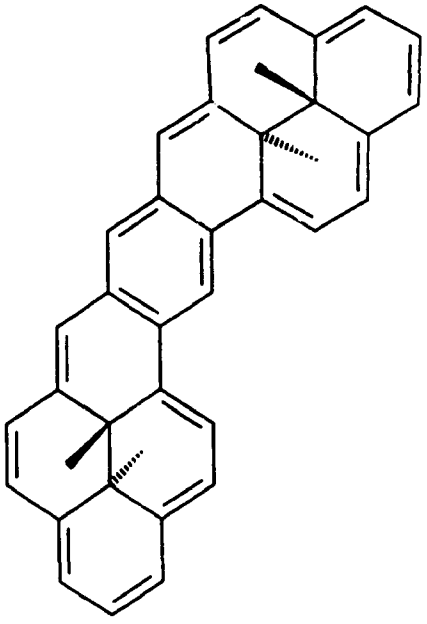

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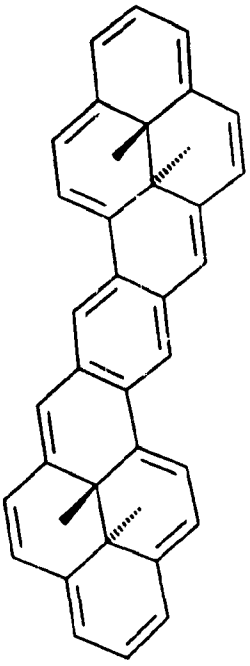

224a

6.2 Instrumentation

Melting points are uncorrected and were determined on a Reichert 7905 melting point apparatus intergrated to an Omega Engineering Model 199 Chromel-alumel thermocouple. Infrared spectra, calibrated with polystyrene, were recorded on a Perkin-Elmer 283 spectrometer. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda-4B spectrophotometer using cyclohexane as solvent. Proton nuclear magnetic resonance spectra of solutions in chloroform-d (unless otherwise specified) were recorded on a Perkin-Elmer R-32 (90 MHz) using tetramethylsilane as internal standard, a Bruker WM 250 (250 MHz) spectrometer or a Bruker AMX 360 (360 MHz) using the solvent deuterium signal as the lock signal at room temperature. Carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker WM 250 (62.9 MHz) spectrometer using solutions in chloroform-d and the peak at 77.0 ppm for calibration. Fluorine-19 nuclear magnetic resonance spectra were recorded on a Bruker WM 250 (235.4 MHz) using $CFCl_3$ as the external standard. Mass spectra were recorded on a Finnigan 3300 gas chromatography-mass spectrometry system using methane as a carrier gas for chemical ionization. Exact mass determinations were done on a Perkin-Elmer Hitachi RMU-6E spectrometer with 70 ev electron impact ionization using perflurokerosene as the standard. Elemental analyses

were performed by Canadian Microanalytical Services Ltd., Vancouver, British Columbia. X-ray diffraction studies (crystallography) were performed by Dr. G. W. Bushnell and Kathy Beveridge on a Picker 4 circle diffractometer automated with a PDP 11/10 computer.

6.3 Experimental procedure

2-Bromo-*trans*-10b,10c-dimethyl-10b.10c-dihydropyrene, 93[30]

A solution of NBS (0.77 g, 4.31 mmol) in DMF (50 mL) was added slowly to a stirred solution of dihydropyrene **60** (1.0 g, 4.31 mmol) in DMF (50 mL) at 0°C. After 5 min, the mixture was poured into ice water and extracted with diethyl ether. The ether layer was washed well with water to remove all DMF, dried, concentrated and preabsorbed on silica gel. The chromatography was then carried out on silica gel using petroleum ether as an eluant. This gave the product monobromide (1.1 g) in 80% yield. A sample was recrystallized from petroleum ether; **mp:** 110-111°C, (lit.[30]: 111-112°C); **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.70 (s, 2, 1- and 3-H), 8.65-8.50 (m, 6, 4-, 5-, 6-, 8-, 9- and 10-H), 8.07 (t, 1, J=9.00, 7-H), -4.07 and -4.08 (s, 3 each).

Trapping of dihydropyryrne 57 with furan to give adduct 94

$NaNH_2$ (63 mg, 1.6 mmol) and t-BuOK (5 mg) were added to a solution of the bromide **93** (100 mg, 0.32 mmol) and furan (1 mL) in THF (5 mL) under nitrogen at room temperature. After the mixture was stirred for 6 hr, a small amount of methanol was added to decompose the excess $NaNH_2$. The solvent was evaporated and the residue was dissolved in diethyl ether and then preabsorbed on silica gel and then chromatographed on silica gel, eluting with 1:10 diethyl ether : petroleum ether. The first fraction after evaporation gave a small amount of dihydropyrene **60**, and bromide **93**. The second fraction gave the adduct (59 mg, 62% yield). A pure sample of an isomer was obtained by fractional recrystallization from dichloromethane and heptane; **mp:** 171-173°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.31, 8.23, (AB, 2, 16- and 17-H, J=8.59), 8.20 (d, 1, 3-H, $J_{2,3}$=8.17), 8.19 (s, 1, 8-H), 8.13 (d, 1, 1-H, $J_{1,2}$=6.99,), 8.11, 8.04 (AB, 2, 5- and 6-H, J=7.02), 7.72 (dd, 1, 2-H), 7.05 (dd, 1, 12-H, $J_{11,12}$=5.55, $J_{12,13}$=1.78), 7.00 (dd, 1, 11-H, $J_{10,11}$=1.72), 6.52 (m, 1, 13-H), 6.15 (m, 1, 10-H), -3.34, -3.51 (-Me); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 142.01, 140.67 (olefin C), 141.46, 137.98, 137.91, 137.14, 128.47, 127.40 (quaternary Ar-C), 125.08, 124.97, 122.95, 122.95, 122.95, 121.98, 119.05, 116.33 (ArCH), 82.94, 80.53 (-OCH-), 33.16, 32.38 (bridge quaternary C), 15.56, 14.89 (-Me); **MS peaks (CI) at m/e (relative intensity):** 281 (38), 282 (12), 283 (17), 298 (69), 299 (100), 327 (6); **MS peaks (EI)**

at m/e (relative intensity): 107 (5), 119 (9), 120 (23), 213 (11), 237 (11), 238 (5), 239 (100), 240 (81), 241 (12), 242 (13), 255 (33), 268 (62), 269 (8), 283 (15), 298 (75); **IR (KBr, major bands, cm^{-1}):** 3000, 2900, 1440, 1350, 1320, 1270, 990, 900, 860, 830, 820, 730, 700, 680, 650; **UV (cyclohexane) λ_{max} nm (ϵ_{max}):** 479 (5360), 454 (4990), 380 (30700), 356 (23800), 339 (83600), 238 (6390), 196 (16770); **Anal. Calcd. for $C_{22}H_{18}O$:** C 88.64, H 6.09; found C 88.01, H 6.29.

***trans*-12b,12c-Dimethyl-12b,12c-dihydrobenzo[a]pyrene, 95**[32]

A) Deoxygenation of the furan adduct 94

A mixture of the adduct **94** (54 mg, 0.18 mmol) and $Fe_2(CO)_9$[88] (79 mg, 0.22 mmol) in benzene (0.5 mL) was stirred magnetically under nitrogen at 50 to 60 °C for 1 hour. After the mixture was cooled to room temperature, it was preabsorped on silica gel and chromatographed on silica gel with petroleum ether as eluant. The first fraction gave 20 mg of benzo[a]dimethyldihydropyrene **95** and second fraction gave the complex **208** (42 mg, 50%). This complex was then refluxed in benzene for 15 min. After chromatography, a quatitative yield of **95** was obtained. A sample of **95** was recrystallized from petroleum ether; **mp:** 116-117°C (lit.[32]: 115-116°C); **^{1}Hnmr (250 MHz, $CDCl_3$) δ:**

8.79-8.70 (m, 1, 10-H, $J_{9,10}$=8.62), 8.09/7.36 (ABq, 2, 11- and 12-H, $J_{11,12}$=6.58), 8.05-7.95 (m, 1, 7-H, $J_{7,8}$=7.73), 7.88 (s, 1, 6-H), 7.68/7.61 (Abq, 2, 4- and 5-H, $J_{4,5}$=8.83), 7.70-7.64 (m, 2, 8- and 9-H, $J_{8,9}$=6.89), 7.50 (d, 1, 1-H, $J_{1,2}$=8.87), 7.35 (d, 1, 3-H, $J_{2,3}$=6.52), 7.13 (dd, 1, 2-H), -1.62 and -1.63 (s, 3 each, internal methyl).

B) Trapping of aryne 57 with N,N-diethyl-1,3-butadienylamine and *in situ* deamination

A solution of bromodihydropyrene **93** (120 mg, 0.39 mmol) in N,N-diethyl-1,3-butadienylamine[126] (2mL) was injected into the mixture of 2,2,6,6-tetramethylpiperidine (0.5 mL, 3 mmol) and n-BuLi (1.4 mL of 1.4 M solution in hexanes, 2 mmol). After this mixture was refluxed for 2 hr, the dark-brown mixture was poured into a mixture of ice and ether. The aqueous layer was removed and the organic layer was washed with diluted HCl and water. After drying and evaporation of the solvent, the residue was passed through a silica gel column eluting with petroleum ether to give 10 mg of **95** (9% yield), identical to the previous samples.

2-Trimethylacetamino-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, 99

To a solution of nitrodihydropyrene **96**[33] (200 mg, 0.72 mmol) in pyvaloyl anhydride (5 mL) there was added zinc dust (1.0 g, 15.2 mmol) and water (0.1 mL). After the mixture was stirred at room temperature for 3 days, dichloromethane was added. Then the remaing zinc dust was removed by filtration and the anhydride was decomposed carefully with ice cold concentrated NH_4OH. The organic layer was dried with Na_2SO_4 and evaporated. The crude product was chromatographed on silica gel with 1:2 diethyl ether : petroleum ether as an eluant to give a green solid (120 mg, 50%). A sample was recrystallized from dichloromethane and cyclohexane as green crystals, **mp:** 190-192°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.87 (s, 2, 1- and 3-H), 8.60-8.50 (m, 6, 4-, 5-, 6-, 8-, 9- and 10-H), 8.11 (br, 1, NH), 7.99 (t, 1, 7-H), $J_{76}=J_{78}=7.68$), 1.49 (s, 9, t-Bu), -4.05 (s, 3), -4.10 (s, 3, internal methyl); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 176.92 (carbonyl), 137.30, 135.54, 133.00 (quaternary aryl c), 124.55, 124.22, 122.19, 122.01, 115.01 (ArCH), 40.05 (quaternary t-Butyl C), 30.05, 29.76 (bridged quaternary C), 27.85 (Me of t-Bu), 14.49, 13.74 (internal methyl); **MS peaks (CI) at m/e (relative intensity):** 83 (47), 84 (5), 85 (4), 316 (8), 331 (38), 332 (100), 360 (12), 373 (4); **MS peaks (EI) at m/e (relative intensity):** 190 (73), 218 (60), 317 (100), 331 (36); **IR (KBr, major bands cm^{-1}):** 3350, 2960, 1650, 1560, 1540, 1500, 1470, 1390, 1370, 1340, 1300, 1190, 870, 810, 660; **UV**

(cyclohexane) λ_{max} **nm** (ϵ_{max})**:** 487 (11600), 385 (28300), 342 (89300), 261 (10500), 235 (10400); **Anal. Calcd. for** $C_{23}H_{25}NO$**:** C 83.34, H 7.60, N 4.23, Found: C 82.96, H 7.85, N 4.44.

2-Diethylcarbamyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, 109

To a solution of dihydropyrene **60** (200 mg, 0.86 mmol) in dichloromethane (20 mL) there was added diethylcarbamyl chloride (2.5 mL, 20 mmol) and followed by the addition of $AlCl_3$ (200 mg, 1.5 mmol). After the mixture was refluxed for 24 hr under nitrogen, the mixture was poured onto ice and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and evaporated. The residue was then chromatographed over silica gel using 1:5 ether : petroleum ether as the eluant and give the product as a green solid (223 mg, 80% yield). A sample was recrystallized from dichloromethane and cyclohexane as green crystals, **mp:** 160-161°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.69-8.57 (m, 8, 1-, 3-, 4-, 5-, 6-, 8-, 9- and 10-H), 8.12 (t, 1, 7-H, $J_{75}=J_{78}=7.71$), 3.67 (br, 4, $-NCH_2-$), 1.21 (br, 6, ethyl $-CH_3$), -4.15 (s, 3), -4.18 (s, 3, internal methyl); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 172.78 (carbonyl), 137.90, 135.58, 130.19 (quaternary aryl C), 124.91, 124.04, 123.90, 123.90 121.65 (ArCH), 43.64 (br, -N-C-), 40.16 (br, -N-C), 30.22,

29.69 (bridged quaternary C), 14.53, 14.20 (internal $-CH_3$), 13.77 (b) and 13.30(br, $-NCH_2CH_3$); **MS peaks (CI) at m/e (relative intensity):** 100 (13), 331 (27), 332 (100), 334 (4), 360 (12), 372 (2); **MS peaks (EI) at m/e (relative intensity):** 72 (50), 100 (100), 201 (66), 202 (23), 215 (40), 216 (14), 229 (20), 243 (34), 316 (42), 317 (9), 331 (31), 332 (9); **IR (KBr, major bands, cm^{-1}):** 2960, 2910, 1615, 1470, 1420, 1370, 1310, 1260, 1245, 1210, 1160, 875, 820, 800, 640; **UV (cyclohexane) λ_{max} nm (ϵ_{max}):** 476 (4300), 380 (18300), 340 (50500), 278 (4060), 200 (15800); **Anal. Calcd. for $C_{23}H_{25}NO$:** C 83.34, H 7.60, O 4.83, N 4.23; found: C 82.68, H 7.80, O 5.21, N 4.21.

2,6-Bis(methoxymethyl)-4-nitrotoluene 132

A solution of 2,6-bis(hydroxymethyl)-4-nitrotoluene[42], **126**, (5 g, 25.1 mmol) in 50 mL of DMF was added dropwise to a stirred mixture of sodium hydride (2.5 g, 80%, 83.3 mmol, washed with pentane three times) and MeI (8 mL) in DMF (50 mL) at 0°C. After four hr a small amount of MeOH was added slowly to decompose the excess NaH. The solvent was then evaporated and the residue was acidified and extracted with diethyl ether three times. The combined organic layer was washed with water three times, dried and evaporated to give a yellow solid (5.3 g, 93% yield). Recrystallization from

diethyl ether and petroleum ether gave white crystals, **mp:** 78-80°C (lit[127], b.p. 180-185°C/12 Torr); **^{1}Hnmr (250 MHz, $CDCl_3$)** δ: 8.13 (s, 2, Ar-H), 4.47 (s, 4, $-CH_2-$), 3.43 (s, 6, $-OCH_3$), 2.27 (s, 3, $ArCH_3$); **^{13}Cnmr (62.9 MHz, $CDCl_3$)** δ: 145.84 (4-C), 142.29 (1-C), 138.42 (2- and 6-C), 122.05 (3- and 5-C), 72.07 ($-CH_2-$), 58.52 ($-OCH_3$), 14.14 ($ArCH_3$); **MS peaks (CI) at m/e (relative intensity):** 226 (100), 254 (14), 266 (2); **MS peaks (EI) at m/e (relative intensity):** 225 (weak), 163 (100), 194 (7), 180 (3); **IR (KBr, major bands, cm^{-1}):** 2900, 1585, 1500, 1450, 1370, 1340, 1310, 1240, 1190, 1100, 950, 890, 800, 750, 730, 650; **Anal. Calcd. for $C_{11}H_{15}NO_4$:** C 58.65, H 6.71, N 6.22; found: C 58.58, H 6.68, N 6.18.

4-Amino-2,6-bis(methoxymethyl)toluene 133

Aqueous $TiCl_3$ solution (154 mL, 20%) was evaporated to dryness on a rotavapor at 95°C with a water pump. After ethanol (100%, 50 mL) was added to the violet residue, the mixture was shaken very well and stirred with a magnetic stirrer. Then a solution of the nitro compound **132** (5 g, 22.2 mmol) in THF (50 mL) was added slowly to the $TiCl_3$/EtOH mixture. After the mixture was stirred overnight the solvent was evaporated. Then the residue was basified with NaOH solution and extracted with diethyl ether three times. The combined organic layer was washed with water,

dried and evaporated to give a light yellow liquid (3.7 g, 86% yield), **b.p.:** 185-186°C/12 Torr[127]; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 6.62 (s, 2, ArH), 4.36 (s, 4, $-CH_2-$) 3.37 (s, 6, $-OCH_3$), 2.12 (s, 3, $-CH_3$); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 143.81 (4-C), 137.19 (2- and 6-C), 124.31 (1-C), 114.31 (3- and 5-C), 73.04 ($-CH_2$), 57.93 (OCH_3), 12.64 ($ArCH_3$); **IR (KBr, major bands, cm^{-1}):** 3450, 3350, 3210, 2980, 2920, 2870, 2810, 2730, 1610, 1470, 1430, 1370, 1350, 1320, 1250, 1190, 1150, 1100, 960, 940, 920, 900, 850; **Exact Mass Calcd. for $C_{11}H_{17}NO_2$:** 195.126; found 195.127.

4-Amino-2,6-bis(methoxymethyl)-3-bromotoluene 134 and 4-amino-2,6-bis(methoxymethyl)3,5-dibromotoluene 135

A solution of NBS (3.5 g, 19.7 mmol) in DMF (80mL) was added dropwise to a solution of the starting material **133** (3.8 g, 19.5 mmol) in DMF (25 mL) with stirring at room temperature. After this mixture was stirred for 4 hr, it was poured into ice water and extracted with diethyl ether. The ether layer was washed with water three times, dried and evaporated to give a yellow solid. This solid was chromatographed on silica gel by eluting with 1:1 ether : petroleum ether. After concentration, the first fraction gave white crystals (0.8 g), which was identified as the dibromide **135; mp:** 134-135°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 4.63 (s, 4, $-CH_2-$), 3.38 (s, 6, $-OCH_3$), 2.41 (s, 1, $-CH_3$),

^{13}Cnmr (62.9 MHz, $CDCl_3$) δ: 140.30 (4-C), 134.96 (2- and 6-C), 129.64 (1-C), 113.36 (3- and 5-C), 72.00 ($-CH_2-$), 58.10 ($-OCH_3$), 15.77 ($-CH_3$); **MS peaks (EI) at m/e (relative intensity):** 351 (53), 353 (100), 355 (48); **IR (KBr, major bands, cm^{-1}):** 3410, 3300, 2960, 2900, 2880, 2860, 2800, 2020, 1595, 1540, 1480, 1450, 1425, 1385, 1370, 1320, 1285, 1240, 1180, 1160, 1090, 980, 935, 795, 750, 680, 640, 605; **Anal. Calcd. for $C_{11}H_{15}O_2Br_2N$:** C 37.42, H 4.28, N 3.97, Br 45.27; found: C 37.58, H 4.34, N 3.97, Br 46.63.

The second fraction gave monobromide **134** as a light yellow solid 2.9 g, 66% yield). Recrystallization from benzene and heptane gave white crystals; **mp:** 79-81°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 6.76 (s, 1, ArH), 4.64 (s, 2, $-CH_2-$), 4.33 (s, 2, $-CH_2-$), 4.02 (br, 2, $-NH_2$), 3.40 (s, 3, -OMe), 3.37 (s, 3, -OMe), 2.24 (s, 3, -Me); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 142.00 (4-C), 136.41 (2-C), 135.41 (6-C), 127.24 (1-C), 115.69 (5-C), 112.74 (3-C), 72.76 ($-CH_2-$), 71.65 ($-CH_2-$), 58.15 (-OMe), 58.06 (-OMe), 14.12 (-Me); **MS peaks (EI) at m/e (relative intensity):** 273 (99), 275 (100); **Anal. Calcd. for $C_{11}H_{16}O_2NBr$:** C 48.19, H 5.88, N 5.11, Br 29.15; found: C 48.37, H 5.70, N 5.07, Br 29.94.

2,6-Bis(methoxymethyl)-3-bromo-4-fluorotoluene 136

A solution of aq. HCl (12N, 5 mL) in water (34 mL) was added with mechanical stirring to amine **134** (5 g, 18.2

mmol) in a 100 mL 3-necked flask equipped with a thermometer. Solution was effected by heating the mixture with a water bath. A solution of $NaNO_2$ (1.51 g, 21.9 mmol) in water (4mL) was added with stirring while the mixture was maintained at -5 to -10°C by means of an acetone/CO_2 bath. At the end of reaction there was an excess of HNO_2, which was detected with starch iodide paper. Cold HPF_6 (4.6 mL) was added in one portion with vigorous stirring to a cold solution of above mixture. Cooling and slow stirring were continued for an additional 30 min and the precipitated diazonium hexafluorophosphate was then collected on a Buchner funnel. The salt was washed on the funnel with cold water (15 mL) and with a solution of methanol (4 mL) in diethyl ether (17 mL). After drying, a white solid (7.18 g, 91% yield) was obtained. This salt was added to hot di-n-butyl ether (400 mL) heated in a oil bath at 150°C. The mixture was stired under nitrogen for 15 min, and after cooling it was extracted with diethyl ether and a solution of $NaHCO_3$. The ether layer was dried and evaporated. The crude product was preabsorbed on silica gel and chromatographed on silica gel using 1:2 ether : petroleum ether as eluant to give a yellow oil. This yellow oil was distilled at 130°C under reduced pressure (0.5 mm) to give a colorless oil. A sample was recrystallized from heptane as needle crystals (1 g, 22% yield); **mp:** 37-38°C; **^{1}Hnmr (250 MHz, $CDCl_3$)** δ: 7.14 (d, 1, ArH, J_{HF}=9.26), 4.68

(s, 2, $-CH_2-$), 4.38 (s, 2, $-CH_2-$), 3.40 (s, 6, -OMe), 2.30 (d, 3, -Me, $^6J_{HF}$=1.08); **^{19}Fnmr (235 MHz, $CDCl_3$) δ:** -111.43 (d, J_{HF}=9.14), **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 157.00 (d, 4-C, $^1J_{CF}$=243.10), 137.97 (d, 6-C, $^3J_{CF}$=6.75), 136.87 (s, 1-C), 133.28 (d, 2-C, $^3J_{CF}$=3.02), 115.26 (d, 5-C, $^2J_{CF}$=23.13), 111.69 (d, 3-C, $^2J_{CF}$=20.17), 72.05 ($-CH_2-$), 70.72 ($-CH_2-$), 58.39 (-OMe), 58.17 (OMe), 14.36 (-Me); **MS peaks (EI) at m/e (relative intensity):** 276 (1), 278 (1); **IR (KBr, major bands, cm^{-1}):** 2900, 1600, 1450, 1380, 1410, 1190, 1130, 1110, 1070, 1030, 980, 950, 880, 800; **Anal. Calcd. for $C_{11}H_{14}O_2FBr$:** C 47.67, H 5.09; found C 47.70, H 5.00.

2,6-Bis(bromomethyl)-3-bromo-4-fluorotoluene 137

The mixture of fluoride **136** (290 mg, 1.05 mmol), 48% HBr (4 mL) and conc. H_2SO_4 (0.5 mL) was stirred at 100°C under nitrogen for 3 hr. Then ice was added to cool the mixture to 0°C. The precipitate was collected by filtration and washed with cold water. The crude product was preabsorbed and chromatographed on silica gel using 1:6 ether : petroleum ether as eluant to give white crystals (392 mg, 100%); **mp:** 87-88°C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 7.07 (d, 1, 5-H, J_{HF}=8.48), 4.70 (s, 2, $-CH_2-$), 4.42 (s, 2, $-CH_2-$), 2.44 (s, 3, -Me); **^{19}Fnmr (235 MHz, $CDCl_3$) δ:** -109.18 (d, J_{HF}=8.43); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 157.10 (d, 4-C, $^1J_{CF}$=245.64), 138.01 (s, 1-C), 137.22 (d, 6-C, $^3J_{CF}$=6.59),

133.84 (s, C-2), 117.55 (d, 5-C, $^{2}J_{CF}$=23.43), 112.97 (d, 3-C, $^{2}J_{CF}$=20.26), 30.74 ($-CH_2-$), 30.56 ($-CH_2-$), 15.03 ($-CH_3-$); **MS peaks (EI) at m/e (relative intensity):** 372 (50), 374 (100), 376 (100), 378 (50); **IR (KBr, major bands, cm^{-1}):** 1590, 1450, 1310, 1210, 1170, 1120, 1020, 940, 890, 870, 740, 680, 620, 600, 550, 510; **Anal. Calcd. for $C_9H_8Br_3F$:** C 28.83 H 2.15; found C 29.18 H 2.26.

Coupling of 137 and 88 to give the *syn* and *anti* isomers 131a and 131b

A: *syn*-5-Bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3,3]metacyclophane, **131a**

The bromide **137** (171 mg, 0.457 mmol) and the dithiol **88** (84 mg, 0.457 mmol) in deoxygenated THF (100 mL) were added dropwise over 6 hr under nitrogen to a deoxygenated solution of potassium hydroxide (102 mg, 1.46 mmol) in water : ethanol (1:5) with stirring. After the mixture had been evaporated to dryness, the residue was extracted with dichloromethane and dilute HCl. The organic layer was dried and concentrated to give a white residue, which was preabsorbed and chromatographed over silica gel using benzene : cyclohexane (1:6) as the eluant. After evaporation, the first fraction gave almost pure *syn* isomer

(8 mg). A sample was recrystallized from dichloromethane and heptane as colorless crystals, **mp:** 189-191°; **^{1}Hnmr (250 MHz, $CDCl_3$)** δ: 6.98-6.68 (m, 3, 7-, 8- and 12-H), 6.38 (d, 1, 6-H, H_{HF}=9.25), 4.7-3.3 (m, 8, 13-, 14-, 15- and 16-H), 2.52 (s, 3, 17-H), 2.50 (s, 3, 18-H); **^{19}Fnmr (235 MHz, $CDCl_3$)** δ: -100.57 (d, J_{HF}=9.05); **^{13}Cnmr (62.9 MHz, $CDCl_3$)** δ: 155.9 (d, 1-C, $^{1}J_{CF}$=242.4), 111.3 (d, 2-C, $^{2}J_{CF}$=20.1), 137.2 (s, 3-C), 133.3 (s, 4-C), 135.3 (s, 5-C), 117.4 (d, 6-C, $^{2}J_{CF}$=23.1), 124.8 (7-C), 130.4 (8-C), 136.5 (9-C), 136.0 (10-C), 136.4 (11-C), 127.61 (12-C), 36.61 (13-C), 36.21 (14-C), 36.73 (15-C), 34.45 (16-C), 17.42 (17-C), 17.51 (18-C); **MS peaks (CI) at m/e (relative intensity):** 397 (4), 399 (4), 425 (weak), 427 (weak); **IR (KBr, major bands, cm^{-1}):** 2930, 1580, 1450, 1380, 1300, 1020, 730, 680; **Anal. Calcd. for $C_{18}H_{18}BrFS_2$:** C 54.41, H 4.57; found: C 53.85, H 4.91.

B: *anti*-5-Bromo-6-fluoro-9,18-dimethyl-2,11-dithia[3,3]metacyclophane, **131b**

The second fraction gave a mixture of *anti* and *syn* (1:1) isomers (40 mg). The third fraction gave almost pure *anti* isomer (13 mg). The overall yield of this reaction is 34%. A sample of the *anti*-isomer was recrystallized from dichloromethane and heptane as colorless crystals, **mp:** 196-198°C; **^{1}Hnmr (250 MHz, $CDCl_3$)** δ: 7.46-7.05 (m, 3, 7-, 8-

and 12-H), 7.23 (d, 1, 6-H, J_{HF}=9.29), 4.20-3.35 (m, 8, 13-, 14-, 15- and 16-H), 1.47 (s, 3, 18-H), 1.26 (d, 3, 17-H, J_{HF}=0.96); **^{19}Fnmr (235 MHz, $CDCl_3$) δ:** -99.84 (d, J_{HF}=9.32); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 156.9 (d, 1-C, $^1J_{HF}$=242.8), 138.8 (3-C), 138.4 (4-C), 137.4 (10-C), 135.8 (9-C), 134.8 (11-C), 133.2 (5-C), 130.5 (12-C), 129.8 (8-C), 125.7 (7-C), 117.5 (d, 6-C, $^2J_{CF}$=23.11), 111.1 (d, 2-C, $^2J_{CF}$=20.2), 32.65 (14-C), 31.76 (15-C), 31.60 (13-C), 29.35 (16-C), 15.28 (17-C), 15.14 (18-C); **MS peaks (CI) at m/e (relative intensity):** 397 (24), 398 (6), 399 (25), 400 (5), 425 (5), 427 (5); **IR (KBr, major bands, cm^{-1}):** 1580, 1450, 1400, 1300, 1200, 1120, 1010, 860, 790, 750, 730, 670; **Anal. Calcd. for $C_{18}H_{18}BrFS_2$:** C 54.41, H 4.57; **found:** C 53.95, H 4.69.

trans-11b,11c-dimethyl-11b,11c-dihydropyreno[1,2-c]furan, 222

3,6-di(pyridin-2'-yl)-s-tetrazine **217**[128] (55 mg, 0.25 mmol) was added to a solution of the adduct **94** (59 mg, 0.20 mmol) in $CHCl_3$ (2 mL) under N_2 at room temperature. Evolution of N_2 bubbles was observed. The mixture was stirred magnetically at 40-50 ^oC for 15 min. Then the mixture was evaporated to dryness using N_2 stream. The residue was disolved using diethyl ether and preabsorbed on silica gel. The mixture was chromatographed on silica gel

using 1 : 10 ether : petane as eluant under N_2 pressure. The first red fraction was collected and on evaporation (without heat) gave **222** (42 mg, 78%), which polymerizes slowly in $CDCl_3$ into a greenish compound at room temperature and is stable in the solid state at -20 °C. **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.11 (s, 1, 8-ArH), 7.81 (d, 1, 7-ArH, $J_{7,8}$=1.38), 7.01 (s, 1, 6-ArH), 6.78 (d, 1, 3-ArH, $J_{2,3}$=5.87), 6.75 and 6.68 (AB, 2, 4-,5-ArH, $J_{4,5}$=9.37), 6.60 (d, 1, 1-ArH, $J_{1,2}$=8.05 Hz), 6.42 (d, 1, 9-ArH, $J_{9,10}$=6.08 Hz), 6.38 (dd, 1, 2-ArH), 6.32 (d, 1, 10-ArH), 0.19 and 0.16 (s,s, 3,3, two internal -CH_3); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 140.90, 140.38, 138.93, 128.81 120.61, 117.14 (quaternary Ar-C), 137.22, 136.96 (ArCH-O-), 127.35, 126.70, 126.49, 123.96, 122.12, 120.95, 116.85, 114.44 (ArCH), 40.46, 40.39 (bridge quaternary C), 19.98, 19.58 (internal -CH_3); **MS peaks (CI) at m/e (relative intensity):** 84 (33), 85 (15), 272 (48), [illegible] (100), 274 (11), 301 (7); **MS peaks (EI) at m/e (relative intensity):** 242 (100), 272 (21); **UV (cyclohexane) λ_{max} nm (ϵ_{max}):** 494 (6850), 343 (61700), 328 (74000), 320 (66500).

[7,8,9,10,10a,10b-η^6]*trans*-12b,12c-dimethyl-12b,12c-dihydrobenzo[a]pyrenechromium(0)tricarbonyl, 239

The mixture of benzo[a]dimethyldihydropyrene **95** (20

mg, 0.071 mmol), naphthalenetricarbonylchromium[129] (30 mg, 0.11 mmol) and THF (35 µl, 0.43 mmol) in diethyl ether (1mL) was stirred magnetically at 50 to 60 ^{o}C overnight. The mixture was preabsorbed on silica gel and chromatographed on silica gel using 1 : 4 dichloromethane : petroleum ether as eluant. The first fraction a gave small amount of starting material **95** and the second fraction gave 20 mg of two isomers of the complex **239** in a ratio of 1 : 2.9 (60% total yield). A sample of **239a** was recrystallized from dichloromethane as deep red crystals, mp 189 - 190 ^{o}C (dec.); **^{1}Hnmr (250 MHz, $CDCl_3$)** δ: 7.60 (d, 1, 11-ArH, $J_{11,12}$=6.53), 7.28 (s, 2, 4-, 5-ArH, $J_{4,5}$=9.24 obtained in benzene), 7.25 (s, 1, 6-ArH), 7.18 (d, 1, 1-ArH, $J_{1,2}$=8.97), 7.02 (d, 1, 3-ArH, $J_{3,2}$=6.30), 7.00 (d, 1, 12-ArH), 6.88 (dd, 1, 2-ArH), 6.57 (d, 1, 10-ArH, $J_{9,10}$=7.08), 5.94 (dd, 1, 7-H, $J_{7,8}$=6.50, J_{79}=0.87), 5.61 (ddd, 1, 8-ArH, $J_{8,9}$=6.39, $J_{8,10}$=0.45), 5.50 (ddd, 1, 9-ArH), -0.87 and -0.98 (s,s, 3,3, two internal CH_3); **^{1}Hnmr (360 MHz, $CDCl_3$)** δ: 7.594 (d, 1, 11-ArH, $J_{11,12}$=6.51), 7.276 (s, 2, 4-, 5-ArH), 7.244 (s, 1, 6-ArH), 7.179 (d, 1, 1-ArH, $J_{1,2}$=9.13), 7.021 (d, 1, 3-ArH, $J_{3,2}$=6.513), 7.002 (d, 1, 12-ArH), 6.882 (dd, 1, 2-ArH), 6.567 (d, 1, 10-ArH, $J_{9,10}$=6.97, $J_{8,10}$=0.948, $J_{7,10}$=-0.02), 5.939 (dd, 1, 7-H, $J_{7,8}$=6.633, J_{79}=1.126), 5.613 (ddd, 1, 8-ArH, $J_{8,9}$=6.00), 5.503 (ddd, 1, 9-ArH), -0.871 and -0.977 (s,s, 3,3, two internal CH_3); **^{13}Cnmr (62.9 MHz, $CDCl_3$)** δ: 232.62 (carbonyl

carbon), 140.75, 140.29, 139.08, 130.47 (quaternary ArC), 128.16, 126.61, 126.03, 125.21, 123.29, 121.10, 120.82, 119.75 (ArCH), 101.51, 98.16 (quaternary ArC-Cr), 91.83, 91.66, 90.65, 88.04 (ArCH-Cr), 37.73, 36.85 (bridge quaternary C), 20.03, 18.37 (internal $-CH_3$); **MS peaks (CI) at m/e (relative intensity):** 283 (2), 332 (1), 333 (1), 335 (38), 336 (13), 337 (2), 361 (2), 363 (17), 364 (5), 415 (2), 416 (4), 418 (69), 419 (100), 420 (35), 415 (2), 416 (4), 418 (69), 419 (100), 420 (35), 421 (8), 433 (weak), 447 (weak); **IR (KBr, major bands):** 1950, 1860, 865, 840, 670, 615 and 530 cm^{-1}; **UV (cyclohexane)** λ_{max} **nm** (ϵ_{max})**:** 434 (14800), 336 (28800), 216 (26300); **Anal. Calcd. for** $C_{25}H_{18}CrO_3$**:** C 71.76, H 4.34; **found** C 71.06, H 4.39. For isomer **239b:** ^{1}**Hnmr (360 MHz,** $CDCl_3$**)** δ**:** 7.563 (d, 1, 11-ArH, $J_{11,12}$=6.55), 7.355/7.287 (AB, 2, 4-, 5-ArH, J_{45}=9.07), 7.244 (s, 1, 6-ArH), 7.010 (d, 1, 1-ArH, $J_{1,2}$=8.05), 7.095 (d, 1, 3-ArH, $J_{3,2}$=6.30), 7.012 (d, 1, 12-ArH), 6.925 (dd, 1, 2-ArH), 6.489 (d, 1, 10-ArH, $J_{9,10}$=6.90, $J_{8,10}$=0.00, $J_{7,10}$=0.00), 5.826 (dd, 1, 7-H, $J_{7,8}$=6.63, J_{79}=1.30), 5.645 (ddd, 1, 8-ArH, $J_{8,9}$=5.70), 5.453 (ddd, 1, 9-ArH), -0.807 and -1.158 (s,s, 3,3, two internal CH_3).

[1,2,3,3a-η^4]*trans*-12b,12c-dimethyl-12b,12c-dihydrobenzo[a]pyreneiron(0)tricarbonyl,209

The mixture of benzo[a]dimethyldihydropyrene **95** (50

mg, 0.18 mmol) and $Fe_2(CO)_9$[130] (262 mg, 0.72 mmol) in benzene (1 mL) was refluxed with magnetical stirring under nitrogen for 1 hr. After the mixture was cooled to room temperature, the residue was chromatographed on silica gel with petroleum ether as eluant. The third fraction gave 30 mg of the complex **209** (40%). A sample was then recrystallized from chloroform and heptane, **mp:** 156 °C (dec.); **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 7.25 (m, 1, 7-H), 6.93 (m, 2, 8- and 9-H), 6.78 (m, 1, 10-H), 5.97 (d, 1, 11-H, $J_{11,12}$=5.91), 5.91 (d, 1, 5-H, $J_{5,4}$=9.36), 5.86 (s, 1, 6-H), 5.43 (dd, 1, 2-H, $J_{1,2}$=6.33, $J_{2,3}$=4.34), 5.39 (d, 1, 4-H), 5.31 (dd, 1, 3-H), 5.30 (d, 1, 12-H), 3.79 (dd, 1, 1-H), 2.01 (s, 3, $-CH_3$), 1.72 (s, 3, $-CH_3$); **^{1}Hnmr (360 MHz, $CDCl_3$) δ:** 7.237 (m, 1, 7-H, $J_{7,8}$=7.50, $J_{7,9}$=1.52, $J_{7,10}$=0.33), 6.921/6.925 (m, 2, 8- and 9-H, $J_{8,9}$=7.36, $J_{8,10}$=1.16), 6.772 (m, 1, 10-H, $J_{9,10}$=7.601), 5.963 (d, 1, 11-H, $J_{11,12}$=5.81), 5.899 (d, 1, 5-H, $J_{5,4}$=9.39), 5.852 (s, 1, 6-H), 5.426 (dd, 1, 2-H, J_{12}=6.25, J_{23}=4.37), 5.377 (d, 1, 4-H), 5.298 (dd, 1, 3-H, J_{13}=1.30), 5.289 (d, 1, 12-H), 3.781 (dd, 1, 1-H), 1.997, 1.713 (-Me); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 211.30 (carbonyl carbons), 143.67, 140.96, 138.37, 134.26, 131.79 (quaternary aryl carbons), 130.84, 128.52, 127.97, 127.76, 127.40, 123.94, 122.52, 117.26, 112.23 (ArCH), 81.17 (quaternary aryl C-Fe), 79.61, 77.49, 67.25 (ArCH-Fe), 43.04, 42.80 (bridged quaternary C), 25.89, 25.16 (internal $-CH_3$); **MS peaks (CI) at m/e**

(relative intensity): 267 (1), 282 (9), 284 (21), 285 (1), 311 (1), 323 (2), 339 (3), 365 (4), 367 (29) 369 (2), 394 (30), 395 (50), 397 (3), 422 (47), 423 (100), 425 (7); **MS peaks (EI) at m/e (relative intensity):** 252 (60), 267 (25), 282 (20), 323 (100), 366 (25), 394 (25), 394 (35), 422 (20); **IR (KBr, major bands):** 2040, 1960, 1345, 880, 820, 740, 600, 550 cm^{-1}; **UV (cyclohexane)** λ_{max} **(**ϵ_{max}**):** 348 (8753), 199 (7804); **Anal. Calcd. for** $C_{25}H_{18}FeO_3$**:** C 71.11, H 4.30; found: C 71.14, H 4.34.

1-Methoxyphthalan 211[90]

Diisobutyl aluminum hydride (50 mmol, 42 mL of 1.2M solution in hexanes) was added dropwise to a solution of phthalide (6.7 g, 50 mmol) in toluene (100 mL) with magnetic stirring at -78°C followed by addition of diethyl ether (50 mL). After the mixture was stirred at -78 °C for 2 hr, MeOH (150 mL) was added, followed by addition of BF_3 etherate (10 mL). The mixture was allowed to warm to room temperature and concentrated. The residue was extracted with ether and NaCl solution. The ether layer was dried and evaporated. After the toluene was removed at the pump, 1-methoxyphthalan was obtained in quantitative yield. **^{1}Hnmr (90 MHz, $CDCl_3$) δ:** 7.25 (m,4), 6.15 (s, 1), 5.25 and 5.00 (AB, 2, J=13), 3.40 (s,3).

Dihydropyrene benzoisofuran adduct 213

$NaNH_2$ (350 mg, 9 mmol) was added to a solution of 1-methoxyphthalan (1.2 g, 8 mmol) in THF (10 mL) under nitrogen at room temperature. After the mixture was stirred for 8 hr, bromodihydropyrene **93** (100 mg, 0.32 mmol) was added. Then the mixture was stirred overnight and poured into small amount of MeOH. The mixture was preabsorbed and chromatographed on silica gel using petroleum ether with increasing concentration of diethyl ether as eluant. The first fraction (green + red) was collected and concentrated. The residue was distilled at low pressure to evaporate off excess 1-methoxyphthalan and benzofuran, then chromatographed on silica gel using petroleum ether as eluant to give 20 mg of naphthodihydropyrene **204** (19%). The second fraction was chromatographed on silica gel with 50 : 1 petroleum ether : diethyl ether as eluant to give 26 mg of the adduct **213** (23%). One major isomer was obtained pure by recrystallization from chloroform and petroleum ether; **mp:** 203-204 ^{o}C; **^{1}Hnmr (250 MHz, $CDCl_3$) δ:** 8.52 and 8.49 (AB, 2, 13-, 14-ArH, $J_{13,14}$=8.47), 8.35 (d, 1, 1-ArH, $J_{1,2}$=8.06), 8.32 (d, 1, 3-ArH, $J_{2,3}$=7.38), 8.28 and 8.23 (AB, 2, 4-, 5-ArH, $J_{4,5}$=7.17), 7.86 (dd, 1, 2-ArH), 7.41 (m, 2) and 6.95 (m, 2) (8-, 9-, 10-, 11-ArH), 6.96 (s, 1, 12-H), 6.59 (s, 1, 7-H), -3.66 (s, 3) and -4.01 (s, 3) (two internal $-CH_3$); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 147.97, 147.45,

141.58, 138.08, 138.08, 137.66, 137.00, 127.12 (quaternary aryl carbons), 125.96, 125.91, 124.77, 124.69, 123.27, 123.12, 122.90, 122.44, 120.11, 119.99, 118.71, 116.01 (ArCH), 83.59, 81.13 (-OCH-), 32.29, 31.34 (bridged quaternary carbons), 14.90, 14.44 (internal $-CH_3$); **MS peaks (CI) at m/e (relative intensity):** 132 (3), 144 (4), 289 (3), 290 (3), 318 (5), 319 (19), 320 (5), 321 (14), 322 (3), 332 (2), 333 (28), 334 (16), 335 (2), 347 (4), 348 (77), 349 (100), 350 (25), 351 (3), 377 (3), 389 (weak); **MS peaks (EI) at m/e (relative intensity):** 130 (14), 131 (17), 147 (43), 144 (100), 289 (33), 318 (28), 333 (16), 348 (10); **IR (KBr, major bands):** 3010, 2960, 2920, 1445, 1360, 1270, 980, 930, 890, 830, 760, 750, 680, 665, 650, 530 cm^{-1}; **UV (cyclohexane)** λ_{max} **(**ϵ_{max}**):** 478 (7483), 383 (38638), 345 (106034), 278 (5621), 243 (9888), 194 nm (42095); **Exact Mass Cald. for** $C_{26}H_{20}O$**:** 348.152; found: 348.158.

trans-14b,14c-dimethyl-14b,14c-dihydronaphtho[2,1,8-*qra*]naphthacene 204

The deairated mixture of $Fe_2(CO)_9$ (27 mg, 0.075 mmol) and the adduct **213** (26 mg, 0.075 mmol) in dry benzene (5mL) was refluxed with magnetic stirring under nitrogen for 5 min. After the mixture was cooled, a small amount of silica gel was added. Then the mixture was evaporated to dryness and chromatographed on silica gel using petroleum

ether as eluant. The first red fraction gave the deoxygenated product (18 mg) in a 70% yield upon evaporation of the solvent. A sample was recrystallized from dichloromethane and heptane; **mp:** 182-183°C; **^{1}Hnmr (360 MHz, $CDCl_3$) δ:** 6.659 (dd, 1, 2-H, J_{12}=9.07, J_{23}=6.17), 6.775 (d, 1, 3-H), 6.968 (d, 1, 1-H), 6.814 (d, 1, 14-H, $J_{13,14}$)=6.41), 7.068 and 7.177 (AB, 2, 4- and 5-H, J_{45}=9.04), 7.535 (m, 2, 9- and 10-H, J_{89}=7.76, $J_{9,10}$=6.81, $J_{9,11}$=0.676, $J_{10,11}$=8.84, $J_{8,10}$=2.02), 7.551 (s, 1, 7-H), 8.008 (m, 1, 8-H, $J_{8,11}$=-0.004), 8.054 (m, 1, 11-H), 8.193 (s, 1, 7-H), 8.898 (s, 1, 12-H), -0.438 (s, 3, -Me), -0.443 (s, 3, -Me); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 141.02, 139.86, 138.33, 134.14, 132.50, 132.00 129.60 127.78 (eight quaternary aryl C), 128.07, 127.44, 126.86, 126.86, 126.17, 126.11, 125.79, 125.59, 124.25, 124.19, 122.11, 122.11, 121.13, 117.51 (ArCH), 38.91, 37.99 (bridged quaternary C), 19.46, 18.57 (internal Me); **MS peaks (CI) at m/e (relative intensity):** 333 (100), 361 (8), 373 (1); **MS peaks (EI) at m/e (relative intensity):** 302 (100), 303 (21), 317 (19), 332 (20), 333 (3); **IR (KBr, major bands, cm^{-1}):** 3040, 3010, 2970, 2920, 1520, 1490, 1440, 1350, 1330, 1090, 1050, 1010, 990, 950, 900, 890, 840, 790, 740, 720, 690, 670, 650, 475; **UV (cyclohexane) λ_{max} nm (ϵ_{max}):** 517 (4350), 394 (27100), 373 (46800), 358 (73400), 343 (61000), 253 (18900), 201 (26600); **Anal. Calcd. for $C_{26}H_{20}$:** C 93.94, H 6.06; found C93.97, H 6.11.

Naphthoisofuran dihydropyrene adduct 219

Tetrazine **217** (205 mg, 0.92 mmol) was added to a solution of 1,4-dihydro-1,4-epoxyphenanthrene, **216**[31b], (160 mg, 0.84 mmol) in chloroform (2 mL) under nitrogen at room temperature. The mixture was magnetically stirred at 40-50 ^{o}C for 15 min and evaporated to dryness in a nitrogen stream at room temperature. The residue was taken up with diethyl ether and preabsorbed on silica gel. After a filtration chromatography on silica gel with 5 : 1 petane : diethyl ether mixture as eluant, the solution was evaporated to dryness without heating and pumped to give light yellow crystals. These crystals were dissolved in THF (5 mL) followed by addition of bromodihydropyrene **93** (100 mg, 0.32 mmol), $NaNH_2$ (66 mg, 1.69 mmol) and a few crystals of t-BuOK under nitrogen at room temperature. The mixture was stirred for 1 - 2 hr, then maleic anhydride (165 mg, 1.68 mmol) was added. After 5 min, the mixture was poured into small amount of MeOH and preabsorbed and chromatographed on silica gel using petroleum ether with increasing concentration of ether as eluants to give a small amount of deoxygenated product and 60 mg (47% yield) of the adduct **219**. Attempted separation of this adduct mixture by chromatography and recrystallization was unsuccessful. Therefore it was used directly in next step.

A mass spectrum (CI) showed peak at M+1=399, M+29=427 and M+41=439).

trans-16b,16c-dimethyl-16b,16c-dihydrobenzo[a]naphtho[2,1,8-_fgh_]naphthacene 206a

and

trans-16b,16c-dimethyl-16b,16c-dihydrobenzo[a]naphtho[2,1,8-_hij_]naphthacene 206b

A deairated mixture of $Fe_2(CO)_9$ (82 mg, 0.23 mmol) and the adducts **219** (60 mg, 0.15 mmol) in benzene (5 mL) was refluxed with magnetic stirring under nitrogen for 5 min. After the mixture was cooled, a small amount of silica gel was added. Then the mixture was evaporated to dryness and chromatographed on silica gel using petroleum ether as eluant. The first red fraction gave a red solid (25 mg, 44% yield). ^{1}Hnmr showed that two isomers of **206a** and **206b** were present in a ratio of 4.5:1. A sample of isomer **206a** was obtained by recrystallization from heptane; **mp:** 209-210 ^{o}C; **^{1}Hnmr (360 MHz, $CDCl_3$) δ:** 9.90 (s, 1, 14-H), 8.98 (d, 1, 13-H, $J_{12,13}$=8.25), 8.30 (s, 1, 7-H), 8.07 and 7.10 (AB, 2, 15-, 16-H, $J_{15,16}$=6.56), 7.77 (s, 1, 6-H), 7.36-7.61 (m, 5 8-,9-, 10-, 11-, 12-H), 7.42, 7.32 (AB, 2, 4-, 5-H, $J_{5,6}$=9.00) 7.22 (d, 1, 1-H, $J_{1,2}$=9.02), 7.03 (d, 1, 3-H, $J_{2,3}$=6.37), 6.87 (dd, 1, 2-H), -0.87 (s, 3, two internal -

CH_3); **^{13}Cnmr (62.9 MHz, $CDCl_3$) δ:** 140.49, 140.49, 139.46, 139.46, 138.19, 134.25, 132.05, 131.35, 130.58, 129.64 (quaternary aryl carbons), 128.75, 127.19, 127.19, 126.73, 126.73, 126.68, 126.28, 125.96, 124.08, 123.80, 122.77, 122.17, 121.18, 117.50, 117.17 (ArCH), 37.86 and 37.20 (bridged quaternary carbons), 18.89 and 18.03 (two internal $-CH_3$); **MS peaks (CI) at m/e (relative intensity):** 383 (52), 384 (100), 385 (18), 412 (weak); **MS peaks (EI) at m/e (relative intensity):** 175 (27), 176 (78), 352 (100), 353 (16), 368 (16), 382 (16); **IR (KBr, major bands) cm^{-1}:** 1370, 905, 835, 810, 750, 650; **UV (cyclohexane) λ_{max} nm (ϵ_{max}):** 511 (5350), 485 (4980), 402 (34400), 369 (84900), 279 (21700), 265 (18300), 223 (19400); **Anal. Calcd. for $C_{30}H_{20}$:** C 94.20, H 5.80; found C 94.69, H 5.75. The accumulated by-product **206** (**206a** and **206b** in 1:1 ratio, from dehydrobromination reaction) was chromatographed on silica gel using petroleum ether as eluant. The rear part of the red band was concentrated. On recrystallization from heptane, two kinds of crystals were formed: cubes and needles. These were readily separated by hand. The needles proved to be isomer **206b** by ^{1}Hnmr spectroscopy; **^{1}Hnmr (360 MHz, $CDCl_3$) δ:** 9.105 (s, 1, 7-H), 9.030 (s, 1, 14-H), 8.878 (dd, 1, 8-H, J_{89}=8.07, $J_{8,10}$=0.45), 7.955 (d, 1, 12-H), 7.954 (d, 1, 15-H), $J_{15,16}$=6.54), 7.071 (d, 1, 16-H), 7.924 (dd, 1, 11-H, $J_{10,11}$=8.318, $J_{9,11}$=0.94), 7.718 (ddd, 1, $J_{9,10}$=6.94), 7.635 (ddd, 10-H), 7.877 (s, 1, 6-H), 7.443

(d, 1, 4-H, J_{45}=9.03), 7.319 (d, 1, 5-H), 7.204 (d, 1, 1-H, J_{12}=8.94), 7.027 (d, 1, 3-H, J_{23}=6.08), 6.864 (dd, 1, 2-H), -0.899, -0.896 (-Me). The cubes were identical to **206a**.

The adduct from dihydropyryne 57 and pyrenoisofuran 222

$NaNH_2$ (70 mg, 1.8 mmol) and a catalytic ammount of t-BuOK was added to a solution of bromodihydropyrene **93** (100 mg, 0.32 mmol) and furanodihydropyrene **222** (50 mg, 0.18 mmol) in THF (5mL) under N_2. After the mixture was stirred for 2 hr at room temperature, a small amount of MeOH was added. The solvent was then evaporated and the residue was preabsorbed and chromatographed on silica gel. using 1:20 ether : petroleum ether mixture as eluant to give 44 mg of the adduct as dark yellow crystalline solids (49% yield); **MS peaks (CI) at m/e (relative intensity):** 504 (95), 503 (100); **^{1}Hnmr (250 MHz, $CDCl_3$)** indicated the product was a mixture of all possible isomers (12 peaks between δ: -3.5 and -5.0). This mixture was used directly in next deoxygenation step.

trans-14b,14c,18b,18c-tetramethyl-14b,14c,18b,18c-tetrahydrodinaphtho[2,1,8-_uva_; 2,1,8-_jkl_]petacene 224a

and

trans-14b,14c,18b,18c-tetramethyl-14b,14c,18b,18c-tetrahydrodinaphtho[2,1,8-_uva_; 2,1,8-_pon_]petacene 224a

A mixture of **223** (10 mg, 0.02 mmol) and sodium (1.8 mg, 0.08 mmol) in THF (2 mL) was stirred under nitrogen at room temperature overnight. The solvent was evaporated with a nitrogen stream at room temperature. The solid residue was disolved with THF-d_8 and filtered through a glass wool plugged pipette directly into an nmr tube under nitrogen. **^{1}Hnmr (250 MHz, THF-d_8)** δ: 5 peaks at -1.18, -1.19, -1.20, and -1.21 corresponding to **224b** type isomers and -1.58 and -1.62 corresponding to **224a** type isomers.. After evaporation of THF-d_8 4.6 mg of red solid were obtained (47% yield). Attempted purification was failed. **MS peaks (CI) at m/e (relative intensity):** 397 (77), 413 (55), 487 (100), 515 (weak).

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