

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF
MODEL HYDROAROMATIC HYDROCARBONS AND SOLVENTS

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INTRODUCTION

In recent years, a great deal of attention has been directed towards coal as an alternate source of gaseous and liquid fuels and chemicals which are currently derived from petroleum. Liquefaction of coal by catalytic hydrogenation was demonstrated by Bergius as early as 1912.⁽¹⁾ Subsequently other methods for coal liquefaction have been attempted and the kinetics of hydrogenation studied.⁽²⁾ Coal can also be liquefied by hydrogen donor molecules, such as tetralin⁽³⁾ and octahydrophenanthrene.⁽⁴⁾ The initial reactions are thermal cleavage of carbon-carbon or carbon-oxygen bonds, resulting in free radicals. In the absence of hydrogen, free radicals polymerize producing high molecular weight solids. But if hydrogen donor molecules are present, the free radicals are stabilized resulting in low molecular weight liquids or gases. Tetralin is an efficient hydrogen donor molecule but many other structures can function in a similar manner.

Many coal liquefaction processes are currently in developmental stages - both catalytic and noncatalytic. These processes use coal-derived (anthracene oil) or petroleum-derived (decant oil) solvents. To enhance coal dissolution, they may be prehydrogenated or hydrogenated *in-situ* and the hydroaromatic hydrocarbons thereby formed partake in the formation of low molecular weight compounds from coal. An important aspect of coal liquefaction processes is therefore a basic understanding of the structure of the hydroaromatic molecules. Information is needed on the types that are present in aromatic solvents, the structures that are produced upon hydrogenation, their reactivity and the amount of "transferrable" hydrogen they may contain. The *modus operandi* that has succeeded in petroleum chemistry is separation of a complex mixture into simpler fractions, followed by their compositional analysis by spectroscopic techniques. The same method has been adopted here with promising results. The best spectroscopic technique capable of solving the problems posed above is carbon-13 NMR spectroscopy. However, because of the relative novelty of this technique, very little spectral information is available on hydroaromatic hydrocarbons and therefore a necessity arose to develop our own. This paper is a discussion of spectra and spectra-structure correlation of model hydroaromatic hydrocarbons, related compounds and fractions from partially hydrogenated condensed aromatic hydrocarbons.

RESULTS AND DISCUSSION

I Spectral Assignments in Model Compounds

The numbering scheme and structures for the sixteen compounds studied are presented in Figure 1. Assignments of resonance positions were accomplished by several techniques. As a starting point for making the assignments, resonances of quaternary aromatic centers⁽⁵⁾ were separated from those due to carbons directly bonded to hydrogens, by examining the off-resonance spectrum in which the former retain their singlet structure. Furthermore, there are differences in the relative

sensitivity and the shieldings between these two types of carbon atoms. Quaternary carbons, under normal instrumental conditions, do not attain the full nuclear Overhauser enhancement and therefore their resonances appear with reduced intensity and they are deshielded more than the protonated carbons. Also, empirical chemical shift additivity correlation and known information on model compounds were used in assigning values to a given carbon atom.

The results for tetralin (I) in CDCl_3 are in good agreement with those reported for neat tetralin,⁽⁶⁾ but our values are about 1 ppm upfield from those in neat tetralin, probably due to solvent effect. The contribution of the phenyl group along an alkyl chain is to shift the shielding of the α -carbon by +23.0 ppm, the β -carbon by +9.5 ppm and the γ -carbon by ca. -2 ppm. This information along with the results for tetralin is utilized in assigning values to carbon atoms in 2(ar)-butyltetralin (II). The contribution of the aromatic ring of this molecule along the butyl chain is almost identical to that observed in n-butylbenzene. The effect of the chain on the saturated ring is marginal. The shieldings of C-6 and C-7 are unchanged, but a doublet, differing by 0.4 ppm in chemical shift, is observed around 29 ppm. An upfield shift of 0.4 ppm is similar in magnitude to the δ -effect observed in substituted cyclohexanes. Therefore the line at 29.1 ppm is assigned to C-8 and the line at 29.5 ppm to C-5. Naturally, more pronounced effects have to be expected on the shieldings of aromatic carbon atoms. It is evident from the reduced NOE that resonances at 139.8, 136.6 and 134.1 ppm are due to three quaternary centers in the molecule. Butyl substitution decreases the C-2 shielding by +14.0 ppm and increases the C-4a shielding by -3.0 ppm. The latter is the familiar "para" effect. So C-2 is given the value 139.8 ppm and C-4a 134.1 ppm. The rest of the assignments are in Table I.

Assignment of values to carbons in 2(ar)-n-butyl-8-n-hexyl tetralin (III) is attempted, considering (I) and (II) as models. The contribution of a cyclohexyl ring along an alkyl chain can be derived from the results published by Adams and Lindeman⁽⁹⁾ and are similar but not identical to those of a phenyl ring; α -carbon is deshielded by ca. +24 ppm, β -carbon by ca. +4 ppm, and the γ -carbon is shielded by -2 ppm, compared to the parent alkane. The contribution of the hexyl chain to the ring carbons can be ascertained from the results on saturate hydrocarbons⁽⁹⁾ and alkyl benzenes. C-8a, due to the hexyl group on C-8, experiences a deshielding β -effect and a shielding γ -effect. These combined effects would place its chemical shift 4 ppm downfield from the corresponding value in tetralin or butyltetralin and so the value 141.2 ppm is assigned to C-8a. There appears to be γ -effect on C-1, similar in magnitude to that observed, for example, in n-butylbenzene: an upfield shift of 0.5 ppm. C-2, C-3, C-4 and C-4a are unperturbed. A normal alkyl chain, longer than C_4 , decreases the shielding of substituted carbon by ca. +9 ppm and so one of the lines around 37 ppm is due to C-8. β -effect of lesser magnitude would place the resonance of C-7 around 27 ppm. C-5 is least perturbed and so its chemical shift value would be 29.5 ppm. Recalling the α , β , and γ effects of a cyclohexyl ring along the alkyl chain and remembering that the chain is n-hexyl, the chemical shift values to be expected for α , β , and γ carbons to the ring in the hexyl chain are respectively about 37, 27, and 29 ppm. This mutual interaction has resulted in three pairs of closely spaced lines and sorting them out is indeed a problem. The chemical shift value of C-5 in (II) and (III) can be expected to be identical. So the value 29.5 ppm is assigned to C-5 and 29.7 to C-8 γ . In the off-resonance experiment the line at 37.2 is split into doublet, while the line at 37.7 into a triplet. So the former is assigned to C-8 and the latter to C-8 α . The distinction that has been made between C-7 and C-8 β is arbitrary. We have so far accounted for all the lines except the one at 20.1 ppm, which has to be associated with C-6. The upfield dis-

placement of C-6 (3.5 ppm) relative to that observed in (II) indicates a γ relationship between the hexyl chain and C-6. All the four carbon atoms in the saturated ring of tetralin are not coplanar with the aromatic ring. A 'half-chair' and 'half-boat' conformations are possible.⁽¹⁰⁾ We think that the carbon atoms 6 and 7 are above the plane⁽⁸⁾ of the aromatic ring and consequently C-6 experiences an upfield γ steric shift.

Chemical shift values for carbons in three gem substituted tetralins are given in Table I. The assignment of chemical shift values in 8,8-dimethyltetralin is facilitated by careful intensity measurement and the decoupling characteristics of signals. There are two interesting changes relative to tetralin; 16.2 and 4.3 ppm downfield shifts of C-7 and C-8, respectively, which is analogous to the shifts observed in 1,1-dimethylcyclohexane.⁽¹¹⁾ In 8,8-diethyltetralin (V), C-8 is further deshielded while the effect of ethyl substitution is the upfield displacement of C-7. Downfield displacement of C-8 is due to β -effect while the upfield displacement of C-7 is due to ' γ ' relationship between the methyl carbon of ethyl group and the C-7 position. This trend is noticed in the transition from methylcyclohexane to ethylcyclohexane.⁽⁹⁾ In 8,8-dibutyltetralin (VI), the shielding of C-8 is slightly increased, while curiously enough, the shielding of C-7 is decreased by +1.3 ppm. We have not understood these effects. The other changes are qualitatively similar to those observed in substituted cyclohexanes.^(8,11)

Results for 9,10-dihydrophenanthrene (VII) and sym-octahydrophenanthrene (VIII) in $CDCl_3$ are similar to those reported by Retcofsky and Friedel⁽⁶⁾ in neat liquid. But C-1, C-2 and C-3 in (VII) and C-4a and C-10a in (VIII) are not identical as suggested by their results. The carbon chemical shifts in (I) and (VIII) have been calculated by them by considering these structures as being benzene ring in which pairs of adjacent hydrogens are progressively replaced with six-membered hydroaromatic rings and equating them to appropriate multi-methyl substituted benzene. This scheme has provided values for the chemical shifts of aromatic carbons, agreeing well with the observed results. It remains to be seen whether this method is applicable to other molecules considered here. For example, is it possible to predict the shielding of aromatic carbons in 1,2,3,4-tetrahydrophenanthrene knowing the values for carbons in 1,2-dimethylnaphthalene? Several dimethylnaphthalenes have been studied by carbon NMR,⁽¹²⁾ but no detailed information is yet available on 1,2-dimethylnaphthalene. Spectral information on a variety of multi-methyl substituted naphthalenes may facilitate assignment of values to carbons in partially hydrogenated pyrenes also. In the absence of such information, assignment of chemical shifts to appropriate carbon atoms in structures (VII) to (XVI) is accomplished by comparing the results with those of parent aromatic compound, among themselves and by other considerations.

In (X), the shieldings of carbons in positions 4b, 5, 6, 7 and 8 should be comparable to those in the corresponding positions of phenanthrene. So the lines at 122.7, 125.5, 125.6, 128.1 and 131.2 are associated respectively with C-5, C-6, C-7, C-8 and C-4b. To select values for other carbons, the molecule is considered as perturbed phenanthrene. The effect of saturated carbons is most pronounced at positions 10, 4a and 10a. A deshielding of +1.5 ppm is reasonable for C-10 and so the line at 128.3 ppm is assigned to it. The shieldings of C-4a and C-10a are expected to decrease by about +2 ppm and they are assigned the values 132.7 and 133.9 ppm, respectively. These assignments leave us with two lines, one at 132.2 ppm and the other at 124.5 ppm. For obvious reasons, the former has to associate with C-8a and by the process of elimination, the latter with C-9. C-9 is shielded due to the para effect, which raises the question why C-8a is not experiencing a similar para

effect. An examination of chemical shift of carbons in 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN), relative to naphthalene⁽¹²⁾ provides a satisfactory answer, although qualitative. C-4 experiences a shielding para effect in 1-MN, while it is deshielded in 2-MN. C-4a experiences similar effects, but the magnitudes of these effects are not identical at these two centers. The combined effect of methyl substitutions at positions 1 and 2 is an upfield shift at C-4 and no change at C-4a. C-4 and C-4a in 12-DMN corresponds to C-9 and C-8a respectively in (X). The calculation of chemical shift values for carbons in 12-DMN, starting from 1-MN and 2-MN, although unorthodox without the knowledge of steric effect due to substitutions ortho to each other, has provided some information on the shieldings of C-9 and C-8a due to hydrogenation of one of the terminal rings in phenanthrene. Our assignments are further substantiated by the spectrum of octahydrophenanthrene (VIII) relative to 1,2,3,4-tetrahydrophenanthrene. The spectrum of VIII has three lines of equal intensity in the region where aromatic carbons absorb. The line at the lowest field is assigned to C-8a and C-10a and the line at 134.0 ppm to C-4a and C-4b. The combined effect of two saturate rings on the quaternary carbons results in the merging of lines due to C-4a and C-4b to a singlet, with a similar effect on C-10a and C-8a. The effect of a saturated ring on C-10 in (X) is a decrease in shielding by +1.4 ppm and on C-9, an increase in shielding by -2.4 ppm, compared to phenanthrene. C-9 and C-10 are subjected to similar changes by the other saturated ring in (VIII). C-10 is shielded by about the same magnitude and the shielding of C-9 is decreased by +2.0 ppm. The combined effect of increase and decrease in shielding, due to the successive hydrogenation of the outer two rings in phenanthrene, results in the same resonance frequency for C-9 and C-10.

The next interesting pair of compounds in the phenanthrene class are 9,10-dihydrophenanthrene (VII) and its dimethyl derivative (IX). As observed in other molecules in this class, para shielding effect is evident in (IX). But more interesting, this molecule constitutes another example of the recently reported deshielding 'δ' effect, where substantial downfield shifts are found in compounds containing spatially interacting δ function.⁽¹³⁾ In the two partially hydrogenated phenanthrene molecules that we have so far examined, assignment of values to quaternary centers was accomplished by the procedure mentioned earlier, and by using the results on phenanthrene published by Ozubko and co-workers.⁽¹⁴⁾ In (IX), methyl substitution in strategic positions provided an additional handle in selecting values to quaternary carbons. The spectrum of (IX) has three lines with reduced intensity at 141.3, 135.1 and 134.7 ppm, of which the last one is the least intense. Quaternary carbons in position 5 (4) and 8a (10a) have protons in ortho positions, while that in position 4a (4b) is devoid of protons in its immediate vicinity. It is reasonable to expect that relaxation is determined by the ¹³C-H dipole-dipole mechanism and consequently, C-4a should have the longest relaxation time (T₁). Based on this consideration, the line at 134.7 ppm is assigned to C-4a (C-4b). Substantial downfield shift (6.6 ppm) due to 'δ' shielding effect is observed for C-1 in 7,12-dimethylbenz[a]anthracene compared to 7-methylbenz[a]anthracene.⁽¹⁴⁾ A larger downfield shift for C-5 (4) is possible due to mutual 'δ' effect added to the downfield shift due to methyl substitution, compared to C-5 in (VII). So the line at 141.3 ppm is assigned to C-5 (4) and the remaining line at 135.1 ppm to C-8a (10a). The difference in the relaxation times (T₁) between C-4a (4b) and C-8a (10a) surfaced in this molecule due to -CH₃ substitution at C-4 (5), and permitted an unambiguous assignment to quaternary centers, and has also helped us to understand the spectrum of (VII) and other lines in the spectrum of (IX). Carbon chemical shifts in tetralin follow the trend in o-xylene.⁽⁶⁾ So it is reasonable to expect the trend in 9,10-dihydrophenanthrene to be similar to that in 2,2'-dimethylbiphenyl. But no spectral information is available on the latter. Nevertheless, approximate values for the chemical shifts of quaternary

carbons can be calculated from the chemical shift values of carbons in biphenyl.⁽¹⁵⁾ This calculation indicates that the resonance of C-4a (4b) in (VII) should be at a lower field than that of C-8a (10a). Upon -CH₃ substitution in positions 4 and 5, the changes that can be expected are the shieldings of C-8a and C-10a to be practically the same, while those of C-4a and C-4b to be increased by about -2.5 ppm. The latter is a manifestation of γ steric effect. These changes are indeed observed, substantiating the assignment of values to C-8a (10a) and C-4a (4b) in (IX). There are four lines, three of which are closely spaced, in the spectrum of VII corresponding to four protonated aromatic carbons. Methyl substitution separates the three closely spaced lines and the separations have been useful in arriving at further assignments. Methyl substitution decreases the shielding of C-6 and increases that of C-8, leaving the value of C-7 unchanged. The para shielding effect -2.4 ppm is similar in magnitude to that observed in other aromatic structures. The complete assignments are in Table II, along with those for the saturated carbons.

The next class of compounds which have been investigated are pyrenes and partially hydrogenated pyrenes. The spectrum of 3-n-decylpyrene (XI) is included, although it is not a hydroaromatic, to understand the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene, and also to assess the contribution of a multi-nuclear aromatic structure along an alkyl chain. Shieldings at carbons 1,5,6,7,8,9,10,13 and 14 are similar to those for the corresponding carbons of pyrene (XVI). Amidst the group of lines corresponding to aromatic carbons directly bonded to protons, there is a line at 125.0 ppm with reduced intensity, which has to be associated with quaternary centers and we think that it corresponds to the line at 124.5 ppm in the spectrum of pyrene, which is assigned to C-15 and C-16.⁽¹⁶⁾ The theory predicts that C-15 and C-16 should have similar chemical shift to other bridgehead positions. It is reasonable to explain both of these upfield shifts with an anisotropic ring current in the peripheral ring carbons. The line at the lowest field, 137.1 ppm, is assigned to C-3. The shielding of C-2 is likely to be slightly decreased and so the line at 126.3 ppm is assigned to it. The upfield shift of 3.9 ppm at C-4, relative to pyrene is again attributed to a γ steric shift. The remaining two lines are at 128.5 and 129.6 ppm. The shielding of C-11 is expected to increase by about -2.5 ppm due to para effect, and so the line at 128.5 ppm is assigned to it. By default the line at 129.6 ppm is assigned to C-12.

We have sufficient evidence, considered later, to believe that the di-plus triaromatic fraction of hydrogenated pyrene contains symmetric hexahydro and tetrahydropyrenes. Symmetric tetrahydropyrene in pure form has been studied by us and by subtraction, the chemical shift values for carbons in symmetric hexahydropyrene have been obtained. This information is utilized in understanding the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene (XII). In (XV) the chemical shift value for the carbons at positions 4,5,9,10 is 123.4 ppm. Alkyl substitution at C-4 has least effect on C-9 and C-10, and so they are assigned the values 123.5 and 122.5 ppm, respectively. The other line which we believe is due to a protonated aromatic carbon is at 126.1 and is associated with C-5. The shielding is decreased more than expected. Again, the line at the lowest field is assigned to C-4. The anisotropic ring current effect should be less pronounced in this compound compared to pyrene; consequently, the shielding of C-15 and C-16 is expected to be comparable to other bridgehead carbons. However, the NOE is less at these two centers compared to positions 11, 12, 13 and 14. The assignments are given in Table III.

The assignment of values to saturate side-chain and ring carbons is less complicated. The values for the side-chain carbons are given in Table IV, while those for ring carbons are included in Table III. Shifts for side-chain carbons in

(XI) and (XII) should be close and by comparing the spectrum of these two compounds upfield from 35 ppm, the lines due to hydroaromatic carbons are selected and their shielding should be comparable to corresponding carbons in symmetric hexahydropyrene, except for C-3. γ steric shift, observed in other structures, increases its shielding. The chemical shift values for carbons in symmetric tetrahydropyrene are given in Table III. The other compound that we have studied in this class is 1,2,3,9,10,11-hexahydropyrene and its values are also given in Table III.

II Compositional Analysis of Fractions From Hydrogenated Condensed Aromatics

In our studies on induced dissolution of coal by hydrogen donor solvents, several solvents in bulk quantities were prepared. They can be divided into two classes. One, resulting from the hydrogenation of fairly pure aromatic compounds and the second, from the hydrogenation of coal and petroleum-derived oils. The major effort in this study was the separation of the solvent and the reaction products into mono- and di-plus triaromatic fractions⁽¹⁷⁾ and the examination of the fractions by different spectroscopic techniques to understand the reaction mechanism. Carbon-13 spectra of some of the fractions from the hydrogenated phenanthrene and pyrene model solvents are considered here. The composition of the fractions, even after separation, is extremely complex due to unconverted parent aromatic compound or compounds and numerous products resulting from cracking. However, the major contributions to the intensities in the saturate region are from hydroaromatic hydrocarbons, facilitating their recognition in the mixture. The analysis of real solvents is underway and will be discussed in a future publication.

The simplest system is di-plus triaromatic fraction of hydrogenated pyrene. In the region where saturated carbons absorb, three lines are observed at 31.4, 28.3, and 23.3 ppm. Resonance line positions of aromatic carbons are at 135.3, 134.0, 130.6, 130.1, 127.0, 125.9, and 123.4 ppm. From our previous experience, it is obvious that the line at 28.3 ppm is due to the four equivalent saturated carbons of tetrahydropyrene and the other lines associated with this structure are in the spectrum. The line at 31.4 ppm is twice as intense as the line at 23.3 and the one at 123.4 ppm, which does not belong to symmetric tetrahydropyrene, splits into a doublet in the off-resonance experiment. These observations suggest that these three lines in the spectrum are due to symmetric hexahydropyrene and the resonance lines due to quaternary centers are at 134.0 and 130.1 ppm. The structure of this compound is included in Figure 1 and complete assignments in Table III. There is no evidence for the presence of unsymmetric hexahydropyrene, which can be recognized because of bridgehead saturated carbons in the structure. The spectrum of di-plus triaromatic fraction of hydrogenated phenanthrene is also complex. However, if weak lines are ignored and only intense lines are considered, they account for two structures: 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene. The spectrum of the mono-aromatic fraction also has several lines, but intense lines are due to symmetric octahydrophenanthrene. The major hydroaromatic hydrocarbons that are formed on hydrogenation of phenanthrene are 9,10-dihydro-, 1,2,3,4-tetrahydro- and symmetric octahydro-derivatives. But unlike in the case of pyrene, a large number of other products are formed, some of which are due to ring openings.

It is accepted that the induced dissolution of coal is by hydrogen transfer from hydroaromatic hydrocarbons and so an effort was made to understand the carbon-13 spectra of model compounds and solvents. In a large scale process, it would be prohibitively expensive to use pure compounds or model solvents as a source of hydrogen. Hydrogenated coal and/or petroleum-derived solvents are attractive

substitutes. We are examining by carbon-13 NMR hydrogenated anthracene and decant oils and have identified several hydroaromatic structures in them. However, to understand the kinetics of hydrogen transfer reaction and thereby further improve the coal solvation process, the results have to be quantified. The cliché that carbon-13 NMR spectroscopy is analytically difficult is no longer true. Work is in progress in our laboratory to overcome some of the problems inherent to quantitative carbon NMR and initial results are gratifying. The composition of hydrogenated and unhydrogenated real solvents, quantification of results will be the subject of future reports.

EXPERIMENTAL

Materials

Compounds I and VII were obtained from Aldrich Chemical Company, Inc. and compound XIII from K and K Laboratories, Inc. Compound X is an API reference material. Compounds IV, V and VIII were specially prepared for us by Oklahoma State University. The rest were drawn from the hydrocarbon bank of Pennsylvania State University. All compounds and solvents were used without purification.

Spectra

Nuclear magnetic resonance spectra of ^{13}C in natural abundance were obtained by the pulsed FT technique at 20 MHz on a Varian CFT-20 spectrometer, which is equipped with 620/L computer with 16K memory. The free induction decays, after a sufficient number of transients have been accumulated, were smoothed with an exponential function and Fourier transformed. Samples were studied in 8 mm OD tubes at a concentration corresponding to about 200 mg in a total volume of 1.4 ml and at a probe temperature of 36°C. The solvent was invariably CDCl_3 . The deuterated solvent was used as a field-frequency lock and chemical shifts are in ppm downfield from internal TMS. The initial spectrum in each case was obtained with proton noise decoupling; later as the situation demanded, off-resonance decoupling and suppressed NOE spectra were obtained to facilitate spectral assignment.

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Table I

 ^{13}C SHIELDINGS FOR RING AND SIDE CHAIN CARBONS IN I-VI (δ^{C} FROM TMS)

Position	Compound					
	I	II	III	IV	V	VI
C-1	129.0	129.0	128.5	126.5	127.0	126.8
C-2	125.4	139.8	139.7	126.0	125.5	125.6
C-3	125.4	125.7	125.6	125.3	125.0	125.0
C-4	129.1	129.0	128.8	129.1	129.0	129.0
C-4a	136.9	134.1	134.0	135.6	137.8	137.4
C-5	29.4	29.5	29.5	30.9	30.8	30.9
C-6	23.4	23.6	20.1	20.0	19.8	20.0
C-7	23.4	23.6	27.6	39.6	30.8	32.1
C-8	29.4	29.1	37.2	33.7	40.1	39.8
C-8a	136.9	136.6	141.2	145.3	143.3	143.9
C-2 α		35.4	35.5			
C-2 β		34.0	34.0			
C-2 γ		22.6	22.5			
C-2 δ		14.0	14.0			
C-8 α			37.7	31.9	34.4	42.7
C-8 β			27.7		8.7	26.6
C-8 γ			29.7			23.7
C-8 δ			32.1			14.1
C-8 ϵ			22.8			
C-8 ζ			14.1			

Table II

 ^{13}C SHIELDINGS FOR RING AND $-\text{CH}_3$ CARBONS IN VII-X (δ^{C} FROM TMS)

Position	Compound			
	VII	VIII	IX	X
C-1	127.2	30.2	124.3	30.3
C-2	126.8	23.8	126.4	23.2
C-3	128.0	23.2	129.0	22.9
C-4	123.6	26.3	141.3	25.5
C-4a	137.1	134.0	134.7	132.7
C-4b	137.1	134.0	134.7	131.2
C-5	123.6	26.3	141.3	122.7
C-6	128.0	23.2	129.0	125.5
C-7	126.8	23.8	126.4	125.6
C-8	127.2	30.2	124.3	128.1
C-8a	134.4	134.8	135.1	132.2
C-9	28.9	126.5	31.5	124.4
C-10	28.9	126.5	31.5	128.3
C-10a	134.4	134.8	135.1	133.9
C-4 α			20.6	
C-5 α			20.6	

Table III

 ^{13}C SHIELDINGS FOR RING CARBONS IN XI-XVI (δ^{C} FROM TMS)

Position	Compound					
	XI	XII	XIII	XIV	XV	XVI
C-1	124.5	30.9	125.8	30.9	31.4	124.8
C-2	126.3	23.2	126.9	22.8	23.3	125.7
C-3	137.1	27.4	125.8	31.1	31.4	124.8
C-4	123.3	135.6	28.2	127.5	123.4	127.2
C-5	127.4	126.1	28.2	124.2	123.4	127.2
C-6	124.6	31.5	125.8	124.3	31.4	124.8
C-7	125.5	23.3	126.9	125.6	23.3	125.7
C-8	124.6	31.5	125.8	125.5	31.4	124.8
C-9	127.0	123.5	28.2	29.9	123.4	127.2
C-10	127.0	122.5	28.2	30.6	123.4	127.2
C-11	128.5	133.5	135.2	37.6	134.0	131.0
C-12	129.6	130.3	135.2	136.0	134.0	131.0
C-13	131.4	133.9	135.2	134.3	134.0	131.0
C-14	130.9	133.8	135.2	131.3	134.0	131.0
C-15	125.0	130.5	130.4	132.2	130.1	124.5
C-16	125.0	129.0	130.4	129.6	130.1	124.5

Table IV

 ^{13}C SHIELDINGS FOR SIDE CHAIN CARBONS IN XI AND XII
($^{\text{C}}$ FROM TMS)

Position	Compound	
	XI	XII
CC-1*	33.5	33.4
CC-2	31.8	31.5
CC-3	29.8	29.9
CC-4	29.6	29.7
CC-5	29.6	29.7
CC-6	29.6	29.7
CC-7	29.3	29.4
CC-8	31.9	31.9
CC-9	22.7	22.7
CC-10	14.1	14.1

* CC-1 is the first carbon α to the ring.

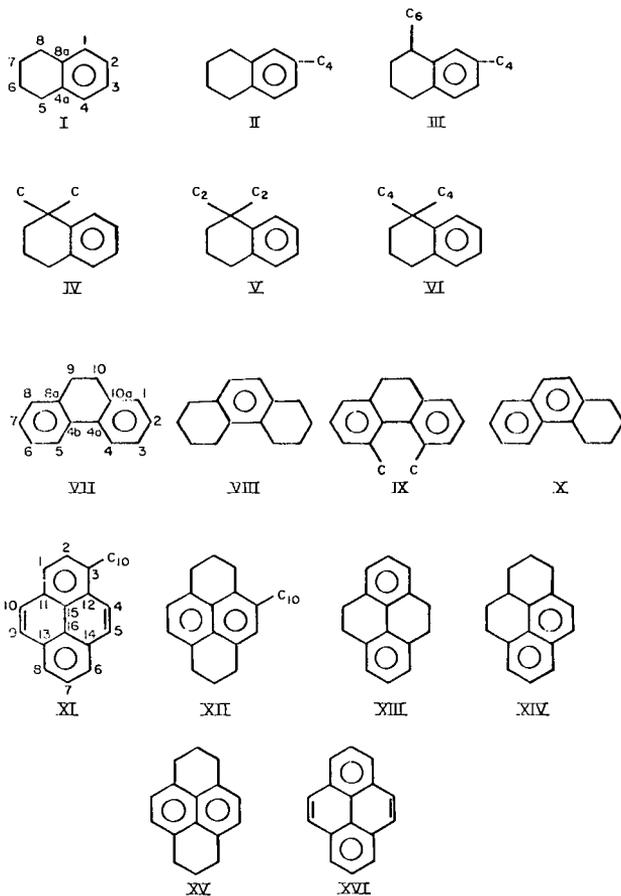


FIGURE 1: NUMBERING SCHEME FOR HYDROAROMATIC HYDROCARBONS