Conformational Analysis. XIV. Conformations of Methyl-, Ethyl-, and Isopropylarenes[1,2]

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Abstract: The chemical shifts of the methyl protons of methylarenes, the methylene protons of ethylarenes, and methine protons of isopropylarenes have been determined in dilute solution of carbon tetrachloride at 34°. The aryl groups employed were phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 2-phenanthryl, 3-phenanthryl, and 9-phenanthryl. From the observation that the sensitivity of the chemical shift of the α-protons of the alkyl groups to changes in the aryl group increases in the order methyl < methylene < methine, the conformation of the alkyl groups can be qualitatively predicted. Quantitative correlations of the chemical shifts with relative anisotropic contributions of the aromatic ring are examined as a function of the molecular parameters of bond angles, bond lengths, and dihedral angles. From these correlations it is shown that the preferred conformation of the α-carbon is one in which a carbon–hydrogen bond is coplanar with the aromatic ring. In 2-naphthyl-type compounds two isoenergetic in-plane conformations in nonequivalent magnetic deshielding environments are populated whereas in 1-naphthyl-type compounds only the conformation with a carbon–hydrogen coplanar with the aromatic ring and syn to the peri position is populated.

In an earlier paper[4] we illustrated that the chemical shifts of methylarenes in dimethyl sulfoxide-d_6 could be successfully explained on the basis of the anisotropy resulting from circulating interatomic currents.[5,6] The chemical shifts of 29 compounds were correlated by a single function ΣIR^{-3} where I is the relative ring current of a designated ring and R is the distance separating the center of that ring and a point chosen to represent the three protons of the methyl group. The reference point chosen for the methyl group was a projection on the carbon–carbon bond line extension of the locus of points describing the protons of a conformationally free methyl group. At that time there was little reason to undertake a more complex analysis involving specifically located protons in individual conformations. Indeed it was qualitatively assessed that any decrease in the distance separating one methyl proton from a distant ring as a result of rotation of the methyl group would be compensated for by an increase in the distance for the remaining methyl protons. Therefore the reference point chosen was regarded as a valid representation of the average of the three protons of the methyl group. However, it was pointed out that for ring substituents lacking the symmetry of the methyl group the approach will be inadequate.

A correlation of the chemical shifts in hertz at 60 MHz of methyl groups of methylarenes *vs.* ΣIR^{-3} was established by eq 1. The equation represents an adaptation of the McConnell[7] equation in which I is proportional to $\Delta\chi$ and the $(1 - 3\cos^2\theta)$ term is neglected. Since the point chosen as representative of the methyl group is in a plane containing the plane of the aromatic ring the $|1 - 3\cos^2\theta|$ term was equal to 2 and incorporated in the slope of the correlation line. Thus correlation lines employing $\Sigma IR^{-3}(1 - 3\cos^2\theta)$ will have slopes of approximately one-half that given in eq 1. The exact ratio will be other than a simple factor of $^1/_2$, for the $1 - 3\cos^2\theta$ terms in the summation term are never two but rather always less than two.

$$\delta(\text{Hz}) = 1002.4\sum IR^{-3} + 112.8 \qquad (1)$$

The very existence of ring currents has been questioned[8] as they are based on an incorrect nongage invariant Langevin–Pavili formula for diamagnetism. In more exact quantum mechanic arguments the ring currents do not appear. However, counterviewpoints have appeared[9] and it has been well argued that it would be unwise to discard a model which works so well in explaining the large shifts of protons located inside and above aromatic rings in a variety of compounds. From a phenomological point of view the concept of ring currents is easily visualized and physically intuitively correct. Our interest in this phenomenon is to extend the utility of the point dipole approximation and to examine the possibility of employing the anisotropy of aromatic ring as a probe for the conformation of side chains.

Results and Discussion

The chemical shifts of the methyl protons of methylarenes, the methylene protons of ethylarenes, and the methine protons of isopropylarenes[10,11] are given in Table I. Each resonance was determined for a solution of concentration not greater than 5% in CCl_4 at a temperature of 34°. Both 60-MHz and 100-MHz

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[1] The authors acknowledge a grant from the National Science Foundation in support of this research.

[2] Paper XIII: R. J. Ouellette and B. G. Van Leuwen, *Tetrahedron*, 25, 819 (1969).

[3] Sinclair Oil Fellow, 1967–1968.

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[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, London, 1965, p 142.

[7] H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

[8] J. I. Musher, *ibid.*, 46, 1219 (1967).

[9] J. M. Gaidis and R. West, *ibid.*, 216, 1218 (1967).

[10] The values for the 2-, 3-, and 9-ethylphenanthrenes reported by Bartle and Smith[11] are acceptably close to our values.

[11] K. D. Bartle and J. A. S. Smith, *Spectrochim. Acta*, 23, 1689 (1967).

Table I. Chemical Shifts of Alkylarenes[a]

No.	Aryl	Alkyl CH_3	CH_2CH_3	$CH(CH_3)_2$
1	Phenyl	2.37	2.55	2.86
2	1-Naphthyl	2.68	2.91	3.70
3	2-Naphthyl	2.52	2.68	3.02
4	1-Anthryl	2.80	3.07	3.85
5	2-Anthryl	2.55	2.78	3.09
6	2-Phenanthryl	2.56	2.76	3.08
7	3-Phenanthryl	2.60	2.79	3.12
8	9-Phenanthryl	2.72	3.02	3.70

[a] In parts per million downfield from TMS.

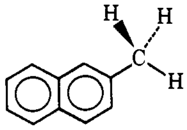
instruments of Varian Associates were utilized. In the case of the 60-MHz spectra, the chemical shifts were determined by side banding with a Hewlett-Packard 202A low-frequency function generator counted by a Hewlett-Packard 522B electronic counter. For the 100-MHz spectra the instrument was operated in HA mode locked on internal TMS and the shifts obtained by direct display. In contrast to our earlier work in the field we now report chemical shifts in parts per million downfield from TMS. Thus earlier slopes and intercepts derived from data in hertz on a 60-MHz instrument must be divided by 60 for comparison with the present work.

An examination of the data for the three series of compounds reveals that the change in the chemical shift caused by changes in the aryl group increase in the order methyl < ethyl < isopropyl. In addition the changes are greatest for aryl groups of the α-naphthyl type as compared to the β-naphthyl type. The trends can be qualitatively interpreted by preferred conformations in which the protons of the methylarenes are replaced by methyl groups in such a manner as to leave the remaining protons closer to the plane of the aromatic ring on a time average basis. Furthermore the large change observed for compounds of the α-naphthyl type suggests that the protons remaining on the α-carbon after methyl substitution reside in positions syn to the peri position of adjoining rings.

In order to assess the conformational features of alkylarenes in a quantitative manner a computer program was designed to locate specifically the individual protons attached to the α-carbon and to determine the distances separating those protons from the centers of each aromatic ring. In addition θ was also determined for each *R* vector and the rings. The input variables which allow for these calculations are the dimensions of the aromatic rings, the C–C and C–H bond lengths, the CCH bond angle and the dihedral angle between the C–H bond and the plane of the aromatic ring. Although a variety of bond lengths were examined, it was decided that a C–C bond length of 1.52 Å and a C–H bond length of 1.09 Å were reasonable choices for all compounds. While variations in anisotropic contributions to the chemical shift of the α-protons were noted for changes of 0.01 Å, in the bond length it was clear that variations in the CCH bond angle and more dramatically in the dihedral angles gave rise to more substantial changes in anisotropic contributions. Accordingly the program was simplified to account for only changes in the CCH bond angle and dihedral angle. Rotation of a single proton which was located in a plane containing the aromatic ring anti to additional aromatic rings and designated as a 0° dihedral angle, was carried out in 15° increment and in a clockwise fashion toward the adjacent aromatic ring. The ΣIR^{-3} $(1 - 3\cos^2\theta)$ function was determined for the proton and averaged with the functions for the other protons contained on the α-carbon but located at other dihedral angles dictated by molecular geometry to obtain an output corresponding to a time average value of all protons which could interchange positions to yield the identical conformation. Since the program only gave families of values for single conformations at specific dihedral angles it was necessary to consider isoenergetic conformers of nonequal magnetic contributions which when mixed by a time averaging process would give an average ΣIR^{-3} $(1 - 3\cos^2\theta)$ term. For example, the two conformations of 2-methylnaphthalene designated **1** and **2** should be of nearly equal energy and their ΣIR^{-3} $(1 - 3\cos^2\theta)$ terms, which in turn are composites of a time average of the three constituent protons, must be averaged. Therefore two in-plane conformations for all β-naphthyl-type compounds were averaged. Although it is less clear *a priori* that the same should be done for α-naphthyl-type compounds, the resulting values fit the same correlation lines as for β-naphthyl-type compounds. Independent of the dihedral angle, the correlation lines for mixtures of isoenergetic conformers such as outlined above for CCH angles of 111° were identical. The symmetry of the methyl group must account for this serendipitous occurrence. The ΣIR^{-3} $(1 - 3\cos^2\theta)$ terms for the methyl groups are given in Table II. The correlation shown in Figure 1 is given by eq 2 whose correlation coefficient is 0.995.[12,13] The identity of correlation lines independent of the con-

$$\delta(\text{ppm}) = 9.22\sum IR^{-3}(1 - 3\cos^2\theta) + 1.95 \quad (2)$$

formation of the methyl group is a fortunate occurrence as it then allows for the unambiguous assignment of a slope of 9.22 which must represent the relationship



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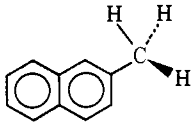

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Table II. Anisotropic Functions for Alkylarenes[a–c]

Aryl	Alkyl CH_3	CH_2CH_3	$CH(CH_3)_2$
Phenyl	0.04516	0.04753	0.05405
1-Naphthyl	0.07917	0.08788	0.11260
2-Naphthyl	0.06128	0.06411	0.07230
1-Anthryl	0.09329	0.10681	0.12530
2-Anthryl	0.06795	0.07053	0.07902
2-Phenanthryl	0.06804	0.07008	0.07875
3-Phenanthryl	0.07052	0.07329	0.08221
9-Phenanthryl	0.08180	0.09635	0.12071

[a] Absolute values. [b] *R* in ångströms. [c] *I* values used in ref 4.

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(13) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," Wiley, New York, N. Y., 1954, p 37.

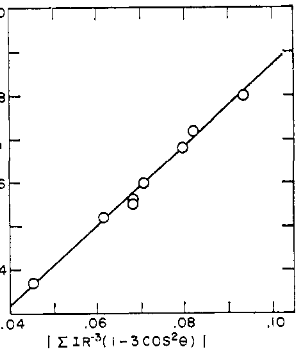


Figure 1. Correlation of anisotropic contribution to methylarenes.

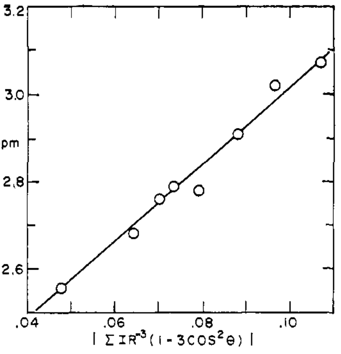


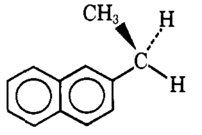
Figure 2. Correlation of anisotropic contributions to ethylarenes.

of the relative anisotropic contributions of the aromatic rings. Therefore this slope must be duplicated for all other ring substituents containing C–H bonds in less symmetric structures if the correct conformation is chosen.

It should be noted that toluene possesses a sixfold rotational barrier of 13.94 cal/mol[14] which would preclude any significance to populational determinations of methylarenes. However, the replacement of a hydrogen by a methyl group to yield ethylbenzene eliminates the sixfold symmetry and the energy barrier is 1.3 kcal/mol.[15] The barrier for isopropylbenzene has not been determined but it should be of comparable magnitude to ethylbenzene and the minimum energy conformation of both compounds is a valid subject for experimental investigation.

While molecular dimensions of ethylbenzene are unavailable it can be reasonably assumed that the C–C and C–H bonds are not significantly different from those used in the calculations for toluene. It is likely, however, that the CCH bond angle is changed. Using the bond angles of propane as an approximation of ethylbenzene we suggest CCC, HCH, and CCH bond angles of 112, 107, and 109.5°, respectively, at the α-carbon.

As expected by the changed symmetry, the methylene protons of ethylarenes experience marked differing anisotropic contributions as a function of dihedral angle. The slopes of correlation lines exceed that of the standard slope determined for methylarenes except for the conformations in which one C–H bond is coplanar with the aromatic ring. In the case of β-naphthyl-type compounds the two in-plane conformations depicted by **3** and **4** are considered isoenergetic and their functions averaged. The individual functions for conformations **3** and **4** are averages of the two methylene protons as they can be interchanged to magnetically equivalent positions by 120° rotations. In the case of α-naphthyl-type compounds the two conformations **5** and **6** are certainly not isoenergetic and in fact are associated with dramatically different anisotropy functions. While populations of as much as 5% **6** can be tolerated within the limitations of the experimental error, progressively increasing the population of **6** and similar conformers in other compounds decreases the correlation coefficient and increases the slope over that of the standard established for methylarenes. In Table II are given the $\Sigma IR^{-3}(1 - 3\cos^2\theta)$ functions for the averaged β-naphthyl-type compounds and the single α-naphthyl-type conformations in which the in-plane hydrogen is syn to the peri position. The correlation line shown in Figure 2 is given by eq 3 with $r = 0.995$.



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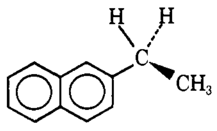

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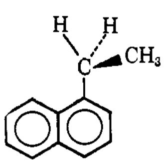

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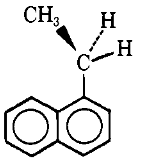

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$$\delta = 9.17\sum IR^{-3}(1 - 3\cos^2\theta) + 2.11 \qquad (3)$$

Attempts to account for the dramatically increased sensitivity of the methine proton chemical shift of isopropylarenes to changes in the aromatic ring were only partially successful. The bond lengths were unchanged from those utilized in the previous two series of compounds. The CCH and CCC bond angles were chosen as 104 and 111° on the basis of the structure of isobutane. It was found that the methine proton must be located coplanar with the aromatic ring in order to account for the large chemical shifts. However, only the β-naphthyl-type compounds can be correlated with a slope equal to the reference slope. The α-naphthyl-type compounds are more deshielded than predicted from the $\Sigma IR^{-3}(1 - 3\cos^2\theta)$ function even for the in-plane conformation with the methine proton syn to the peri position. A correlation line with $r = 0.997$ determined for β-naphthyl-type compounds is shown in Figure 3 and is given by eq 4.

$$\delta = 9.22\sum IR^{-3}(1 - \cos^2\theta) + 2.36 \qquad (4)$$

The significant deviations observed for the three α-naphthyl-type compounds containing isopropyl group might reflect the differential anisotropic contributions of the peri C–H bond.[16] In all β-naphthyl-type com-

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[14] H. D. Rudolph, H. Dreizler, A. Jaeschke, and P. Windling, *Z. Naturforsch. A*, 22, 940 (1967); C. A. Wulff, *J. Chem. Phys.*, 39, 1227 (1963); K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, 65, 803 (1943).

[15] F. G. Brickwedde, M. Moskow, and R. B. Scott, *J. Chem. Phys.*, 12, 547 (1946).

[16] Early workers assumed that $\Delta\chi$ for CH was zero or negligible.[17-19]

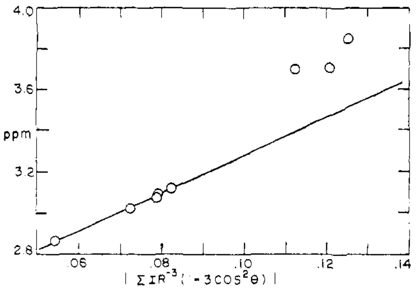
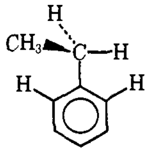
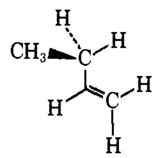


Figure 3. Correlation of anisotropic contributions to isopropylarenes.

pounds such contributions are equal. Furthermore their effect is muted be averaging the several protons of methyl and methylene groups and by averaging isoenergetic contributions. In the case of α-naphthyl-type compounds averaging the protons of the methyl and methylene groups also mutes the differential σ bond anisotropic contributions to chemical shift. However, with the single conformation of 1-isopropylnaphthalene and structurally related compounds the σ bond contribution becomes noticeably important. Indeed the contribution becomes more significant due to the change in the CCH angle in isopropylarenes as compared to methyl and ethylarenes. The distance separating the in-plane methylene proton of 1-ethylnaphthalene and the center of the peri C–H bond is 0.1 Å greater than that for 1-isopropylnaphthalene. The McConnell equation for σ bond contributions cannot be used to evaluate the chemical shift deviation from the correlation line as *R* is not significantly larger than the length of the induced magnetic moment.[7] Modified McConnell equations[25] have been proposed to account for chemical shifts due to closely proximate σ bonds. However, considering the changes in chemical shift which could be induced by bond angle deformations and small dihedral angle changes at such small distances a quantitative treatment of this problem was not attempted.

The finding that a C–H bond prefers to eclipse the plane of the aromatic ring is not unique. In 1-butene the populations of the eclipsed conformations in which either a C–H or a C–CH_3 eclipses the plane of the vinyl group are statistical.[26] However, as the alkyl group in compounds given by $CH_2{=}CHCH_2R$ increase in steric size the conformation in which C–H eclipses the vinyl group predominates over the C–R eclipsed conformation. In alkylarenes the ring system could be considered as an extended version of a vinyl group. However, the bond lengths are not strictly identical. Furthermore in the eclipsed conformation of ethylbenzene the hydrogen and methyl group at 60° dihedral angles with respect to the ring are not





in environments similar to those in 1-butene. Thus the similarities in the structures of 1-butene and ethylbenzene in the eclipsing region are associated with differences elsewhere. Until the calculations for the stabilities of organic molecules are well developed for unsaturated compounds[27,28] an explanation of the observation of this work must be postponed.

Experimental Section

Ethylbenzene, 1-ethylnaphthalene, 2-ethylnaphthalene, and isopropylbenzene were obtained commercially from Chemical Samples Co.

1-Ethylanthracene was prepared by a sequence of reactions consisting of oxidation of benzanthrone[29] to 9,10-anthraquinone-1-carboxylic acid, conversion to anthracene-1-carboxylic acid,[30] addition of methyllithium to yield 1-anthryl methyl ketone,[31] and reduction by the Clemmenson procedure.[32]

2-Ethylanthracene was prepared from 2-ethyl-9,10-anthraquinone by a published procedure.[33]

2-Ethylphenanthrene was prepared by a sequence of reactions consisting of a Friedel–Crafts acetylation of phenanthrene[34] followed by Clemmenson reduction.[35]

3-Ethylphenanthrene was prepared by the same reactions[34,36] as for 2-ethylphenanthrene.

9-Ethylphenanthrene was prepared by the Clemmenson reduction of 9-acetylphenanthrene.[37]

1-Isopropylnaphthalene was prepared by a sequence of reactions involving conversion of 1-naphthoic acid to its ethyl ester, addition of methyl Grignard reagent, dehydration by phosphorus oxychloride, and reduction by hydrogen.[38]

2-Isopropylnaphthalene was prepared,[39] starting from methyl-2-naphthoate, by a sequence of reactions described for 1-isopropylnaphthalene.

1-Isopropylanthracene was prepared by addition of methyl Grignard reagent to 1-anthryl methyl ketone followed by dehydration and reduction.

2-Isopropylanthracene was prepared by a sequence of reactions involving oxidation of methyl-9,10-anthraquinone to 9,10-anthraquinone-2-carboxylic acid,[40] reduction to anthracene-2-carboxylic acid,[41] esterification with ethanol, addition of methyl Grignard reagent, dehydration by phosphorus oxychloride, and reduction.[42]

2-Isopropylphenanthrene was prepared by addition of methyl Grignard reagent to 2-phenanthryl methyl ketone followed by dehydration with phosphorus oxychloride and hydrogenation.[36]

3-Isopropylphenanthrene[43] was prepared by the same method as described for 2-isopropylphenanthrene utilizing 3-phenanthryl methyl ketone as the starting material.

9-Isopropylphenanthrene[43] was prepared by the same method as for 2-isopropylphenanthrene.

However, it has been shown to be in the same order of magnitude for $\Delta\chi$ of CC.[20-24]

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