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CONFORMATIONAL ANALYSIS—XIII

POLYCYCLIC ARYLMETHANOLS*[1]

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Abstract—The chemical shifts of both the hydroxyl and methylene protons of polycyclic arylmethanols in DMSO as solvent have been determined. Eleven aryl methanols where the aryl group equals phenyl, naphthyl, phenanthryl and anthryl, have been studied. A good linear correlation of the chemical shifts of the methylene protons and the function ΣIR^{-3} has been established. Compounds of both 1-naphthyl and 2-naphthyl-type structure fall on the same correlation line. However, the correlation of the chemical shifts of the hydroxyl protons with ΣIR^{-3} is poor and indicates that the time average conformation of the compounds is a function of structure.

THE Me proton chemical shifts of methylarenes have been shown to be a function of ΣIR^{-3}, where I is the relative ring current intensity of an aromatic ring, and R is the distance separating the center of the aromatic nucleus and a single reference point chosen to represent the time average position of the Me protons.[1] This approach is remarkably sensitive to small changes in both R and I. Therefore, application of the method previously outlined should allow a determination of a representative time average conformation of a variety of groups which could be attached to the aromatic ring. In effect, the aromatic ring might provide a magnetic map with mobile coordinates which can be used to probe the conformation of groups of low symmetry.

Our previous experience with the conformational features controlling the chemical shifts of the OH protons of benzyl alcohols[2] suggested that the incorporation of the —CH_2OH group at various positions on polycyclic aromatic rings would be an experimentally advantageous approach. The presence of several anisotropic rings would provide a directional probe for orientation which was lacking in our earlier work. Furthermore, the presence of two different types of protons in the CH_2OH group could provide an internal check for any proposed conformational population changes as a function of molecular structure.

RESULTS

All of the compounds utilized in this study were synthesized by known methods and possessed the proper physical constants.[3–9] In addition the NMR spectra served as a further indication of both isomeric and overall purity.

Reproducible chemical shifts of both the OH and methylene protons were obtained at 0·025 mole fraction of the alcohol in DMSO at approximately 40°. All chemical shifts were calculated relative to the 221 Hz low field C_{13} satellite of DMSO as the internal reference. The methylene and OH proton chemical shifts are listed in Table 1.

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The spin system is AB_2, and in most cases the hydroxyl resonance appeared as a four line multiplet instead of the simple triplet expected from first order analysis considerations.[10] The methylene resonance is a doublet, albeit broadened, indicating the nonresolved four line component of the B_2 multiplet. A representative spectrum of the spin system is illustrated in Fig. 1 for 1-anthrylmethanol.

TABLE 1. METHYLENE AND HYDROXYL PROTON CHEMICAL SHIFTS OF ARYLMETHANOLS

Number	Aryl	Methylene Hz[a]	Hydroxyl Hz[a]
1	Phenyl	270·0	307·0
2	1-Naphthyl	298·5	316·0
3	1-(2-methylnaphthyl)	296·5	296·5
4	2-Naphthyl	280·8	317·5
5	2-Phenanthryl	285·5	322·0
6	3-Phenanthryl	288·8	323·5
7	4-Phenanthryl	310·0	342·0
8	9-Phenanthryl	303·5	325·0
9	1-Anthryl	307·5	322·0
10	2-Anthryl	384·5	321·5
11	9-Anthryl	328·8	321·0

[a] At 60 MHz relative to TMS.

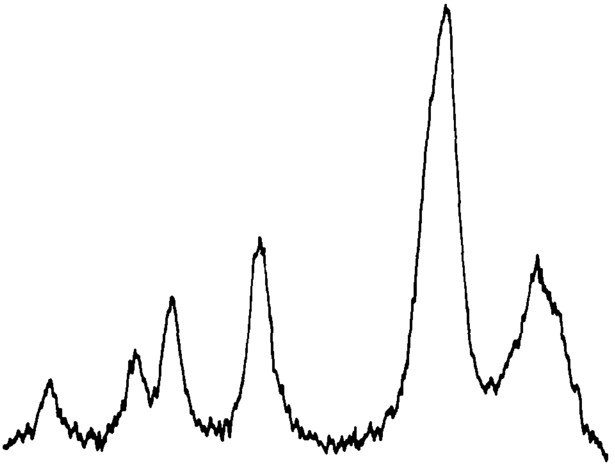


FIG. 1 Hydroxyl and methylene proton resonance spectrum of 1-anthrylmethanol.

DISCUSSION

An examination of the conformation of the methylene protons as a function of rotation about the C—C bond indicates that qualitatively the extent of deshielding of one of the methylene protons by changes in distance and angle from the aromatic ring should increase while that of the other proton should decrease. Therefore the time average chemical shift of the methylene protons should be relatively insensitive to changes in the conformational population of the arylmethanols. Thus the chemical shifts of the methylene group of arylmethanols should be correlated with a single function such as that previously described for the more symmetrical Me group.

The $\Sigma I R^{-3}$ terms used for the Me group in previous work are employed in this study. The distance R is measured from the center of the aromatic rings to a single point at a distance of 0·4 Å beyond the Me-carbon nucleus on a line extension of the C—C bond. This reference point is a projection of the locus of points describing all the possible positions of the methylene protons. Such a reference point has been shown to be sufficiently accurate to represent the protons of a Me group. It is an approximation which still should be valid for the time average position of two protons in compounds having the side chains CH_2X, but not for one proton in CHXY.

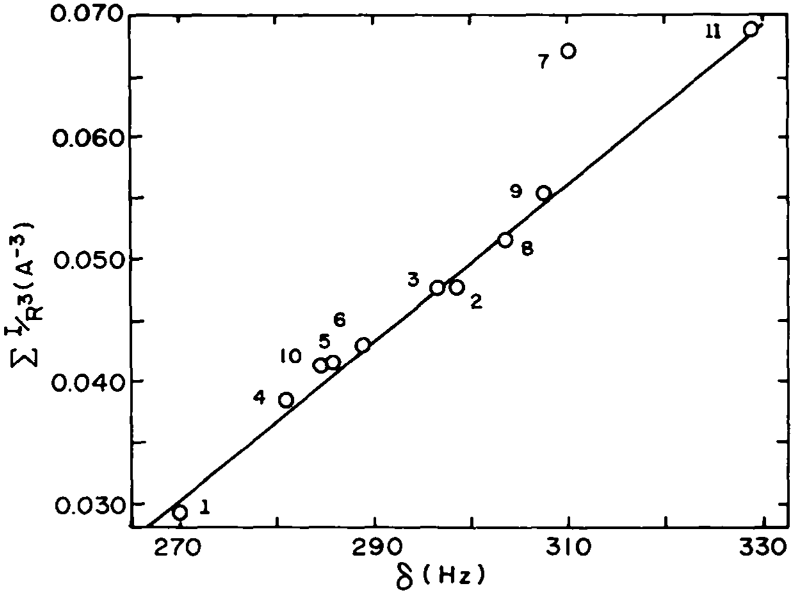
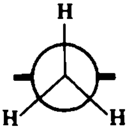


Fig. 2 Correlation of methylene proton resonances with $\Sigma I R^{-3}$.

The chemical shifts of the methylene protons correlate well with $\Sigma I R^{-3}$ as illustrated in Fig. 2. The indicated line suffices to represent compounds of both the 1-naphthyl and 2-naphthyl type structure. Therefore, either the conformational populations of both structural classes are equivalent or there is a compensatory relationship affecting the chemical shifts of the individual methylene protons which constitute the observed time average chemical shift and thus masks populational changes. The latter alternative is the more reasonable in light of the data reported for substituted benzyl alcohols.[2] In addition, the *peri* hydrogen of the 1-naphthyl substituted compounds gives rise to well known differences in the steric environment of the 1-position as compared to the 2-position.

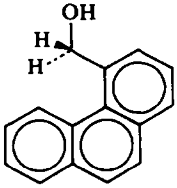
The slope of the correlation line, 1520, for the methylene protons is larger than that for the Me protons, 1002, reported earlier. The direction of this change is qualitatively expected on the basis of preferred rotamers. However, the quantitative aspects of the discussion cannot be advanced without specific knowledge of exact rotamer populations. Due to angular considerations the proton at a 90° dihedral angle with respect to the aromatic ring in the Newman projection will be less deshielded than the other two protons which are more nearly in the plane of the aromatic ring.



Newman projection of toluene.

The preferred conformation of a complexed hydroxyl group would be expected to be that in which the hydroxyl group is at a 90° dihedral angle with respect to the aromatic ring. Therefore the average chemical shift of the three methyl protons of methylarenes will reflect a smaller chemical shift change as the result of anisotropic contributions than will the average of two protons of an arylmethanol near the plane of the ring. The methylene protons then would experience a larger chemical shift dependence on the nearby rings. Since a single average R^{-3} term is used for both methyl and methylene corrections instead of $R^{-3}\,(1-3\cos^2\theta)$ for each individual proton, the apparent slope for the Me compounds is lower than for the hydroxymethyl compounds.

There is one serious deviation from the correlation line: the 4-phenanthrylmethanol appears at higher field than predicted on the basis of ΣIR^{-3}. However, 4-methylphenanthrene is known to be nonplanar[11] and· therefore, both the I and R terms used in the calculation are only approximations. 4-Methylphenanthrene also deviates from a similar correlation line for methylarenes, but in this case the deviation is a low field shift. While there is no unambiguous manner in which the deviation in opposite directions can be explained quantitatively, the results are not inconsistent with the nonplanar model. Twisting of the phenanthrene ring skeleton should decrease the ring current of the center ring and increase that of the terminal rings. The population of the conformer of 4-phenanthrylmethanol in which the two methylene protons are proximate to the center ring should be relatively high as compared to other unhindered positions. Therefore, the extent of the deshielding contributions from the center ring, as a result of the relatively low ring current intensity, and from the terminal ring, as a result of twisting which should increase the R germ relative to the calculated value, should decrease in relation to the other arylmethanols examined. For 4-methylphenanthrene there are three protons that contribute to the observed chemical shift. The net result of the third proton of the Me compound compared to the alcohol is a deshielding contribution to the time average chemical shift because of its proximity to the ring containing the Me group.



Suggested preferred conformation of 4-phenanthrylmethanol.

In order to determine whether the OH proton resonance responds to the same structural features as the methylene protons, a $\Sigma I R^{-3}$ versus chemical shift correlation line was sought. Since the exact distribution of conformers that result from rotations about both the C—C and C—O bond is not known, it is necessary to choose an arbitrary reference point for the time average position of the OH proton. It was assumed that the distribution of conformers that result from rotation about the two bonds is statistical. A projection of this time average position onto the line extension of the carbon–carbon bond was used as representative of the distance R. This distance is approximately the same as previously used for the methylarenes and, therefore, the correlation was derived from the same parameters and is shown in Fig. 3.

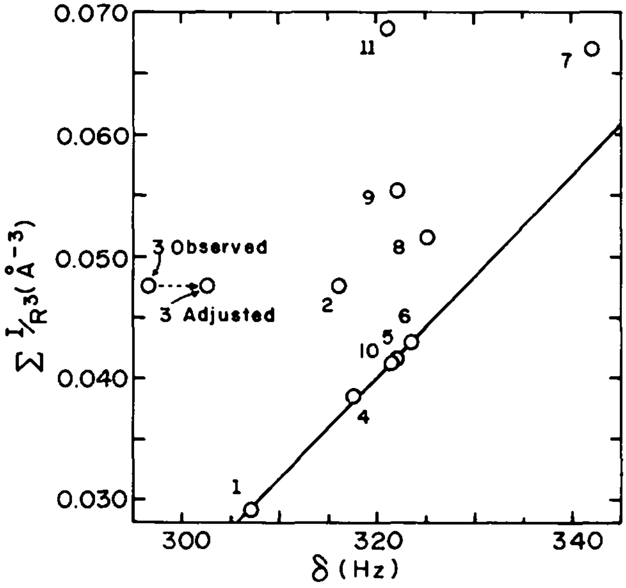
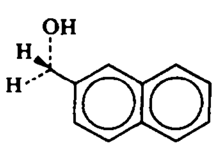
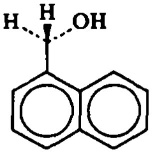


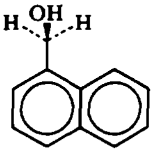
FIG. 3 Correlation of hydroxyl proton resonances with $\Sigma I R^{-3}$.

The chemical shifts of the OH protons of the five arylmethanols, benzyl alcohol, 2-naphthylmethanol, 2 and 3-phenanthrylmethanol and 2-anthylmethanol, are linearly related to $\Sigma I R^{-3}$. Whatever the conformation populations of those compounds, the distributions would be identical and, therefore, the correlation is to be expected. Six compounds which are of the 2-naphthyl substitution type exhibit resonances which do not fit the correlation line for the 2-naphthyl-type compounds. The 1-naphthylmethanol, 9-phenanthrylmethanol and 1-anthrylmethanol, which contain substituents in identical steric environments, do not form even a separate independent correlation line. The scatter of the resonances for the three compounds indicates that their conformational populations cannot be represented properly by the chosen R value. Each resonance indicates that the shielding of the proton is higher than predicted and therefore, on a time average basis, the proton must be located closer to the shielding region of the aromatic ring than is the case for the 2-naphthyl type compounds. This conformational change in population is entirely reasonable. For example, the conformations containing a OH group in the same plane of the aromatic ring should be more highly populated in 2-naphthylmethanol than in 1-naphthylmethanol.





As a result of such steric considerations it is not unreasonable that a higher percentage of the conformers of 1-naphthylmethanol contain the OH group in closer proximity to the shielding region than is the case for 2-naphthylmethanol. The population of the out of plane conformer of 1-naphthylmethanol can account for the observed increased shielding.



In the same manner, the deviations, of 9-phenanthrylmethanol and 1-anthrylmethanol appear to be in a reasonable direction. In fact, it appears possible to semiquantitatively account for the magnitude of deviation for the three compounds. The magnitude of the deviation·from the correlation line should be a reflection of the ring current intensities of the proximate rings. The OH proton in 1-naphthylmethanol is located on a ring with a relative current intensity of 1·09 and adjacent to a ring whose current intensity is 1·09. The deviation from the correlation line is 14·5 Hz. In the case of 9-phenanthrylmethanol the ring current intensity of the center ring is 0·975 and that of the ring adjacent to the substituent is 1·133. The proximity of the hydroxyl proton to the center ring is reflected in a smaller deviation from the correlation line of 9·5 Hz. In 1-anthrylmethanol the substituent is bound to a ring whose current intensity of 1·085 is nearly identical with 1-naphthylmethanol but is adjacent to a ring whose current intensity of 1·280 is significantly higher. The deviation of 17 Hz for 1-anthrylmethanol is higher than that for 1-naphthylmethanol.

It is important to realize that the relative shielding effect observed does not arise by placing the hydroxyl proton in the shielding region of the aromatic ring but only that it reflects less deshielding by movement away from the area of maximum deshielding in the plane of the ring.

The conformational population of 9-anthrylmethanol and 2-methyl-1-naphthylmethanol should be different from that of 1-naphthyl type compounds. The steric environment at the ring positions of the two compounds results in a higher population of the conformer in which the dihedral angle between the hydroxyl group and the aromatic ring is 90°. The deviation from the 2-naphthyl line for 9-anthrylmethanol is 34 Hz, and for 2-methyl-1-naphthylmethanol is 32 Hz. However, in the case of the latter compound a magnetic contribution of the methyl group should be considered. The observed chemical shift difference between 1-phenylpropan -2-ol and 1-(2-methylphenyl)-propan-2-ol under the same solvent conditions is reported[2] as 6 Hz, the Me derivative appearing at lower field. Adjusting the chemical shift of (2-methyl- 1-

naphthyl)methanol by 6 Hz results in a deviation of 26 Hz. These results are in accord with the postulated conformational preference of the hydroxylmethyl group.

The magnitude of the deviation for 4-phenanthrylmethanol is 10 Hz. Any interpretation of the deviation would be difficult as the molecular variables include both conformational populations and ring distortion.

REFERENCES

[1] Paper XII. Robert J. Ouellette and B. G. VanLeuwen, *J. Org. Chem.* in Press.

[2] R. J. Ouellette, D. L. Marks and D. Miller, *J. Am. Chem. Soc.* **89**, 913 (1967).

[3] P. Fierens, R. Martin and J. Van Rysselberge, *Helv. Chim. Acta* **38**, 2005 (1955).

[4] E. Mosettig and J. Van deKamp, *J. Am. Chem. Soc.* **52**, 3704 (1930).

[5] E. Bamberger and P. Lodter, *Ber. Dtsch. Chem. Ges.* **21**, 256 (1886).

[6] A. Cook, J. Downer and B. Horung, *J. Chem. Soc.* 502 (1941).

[7] E. Bamberger and B. Boltimann, *Ber. Dtsch. Chem. Ges.* **20**, 1115 (1887).

[8] S. Akivama, S. Misumi and M. Nakayawa, *Bull. Chem. Soc. Japan* **35**, 1826 (1962).

[9] A. Streitwieser, Jr. and W. Langworthy, *J. Am. Chem. Soc.* **85**, 1757 (1963).

[10] O. L. Chapman and R. W. King, *Ibid.* **86**, 1256 (1964).

[11] C. Reid, *J. Mol. Spect.* **1**, 18 (1957).