Derivatization of the crude oil by dissolution in anhydrous ether and treatment with hydrogen chloride yielded 0.694 g (57.5%) of aniline hydrochloride, mp 196–198° (lit.[33] 198°). Mixture melting point determination gave no depression.

In a second identical experiment the aniline (54%) was isolated and characterized as its benzanilide derivative. The oil described above was treated with benzoyl chloride in pyridine to give 1.07 g, mp 161–163° (lit.[33] 163°).

(33) I. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, 1953.

# Proton Nuclear Magnetic Resonance Spectra of Arylmethyl Systems[1]

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The proton nmr spectra of a number of arylmethyl derivatives $ArCH_2X$, where ArH is an alternant aromatic hydrocarbon, have been measured. The differences in chemical shift of the methylene protons appear to be due primarily to ring current effects rather than hyperconjugation.

Since the early days of nmr spectroscopy, much attention has been paid to the factors affecting the chemical shifts of protons attached to atoms in aromatic rings.[3,4] As a result of extensive experimental and theoretical studies, a reasonably consistent picture of such chemical shifts has emerged. This satisfactory situation does not, however, extend to side-chain protons in, *e.g.*, methyl derivatives of such systems, and there has been controversy in such cases concerning the possible role of hyperconjugation.

Fraser and his collaborators[5] measured the nmr spectra of a number of *para*-disubstituted benzene derivatives $XC_6H_4CH_2Y$ and correlated the chemical shifts of the methylene protons using the Hammett relation; they concluded from these correlations that the differences were due to the effect of the substituent X on hyperconjugative interactions between methylene and the ring. On the other hand, Ouellette and van Leuwen[6] interpreted the chemical shifts of methyl in monomethyl derivatives of benzene, naphthalene, anthracene, phenanthrene, and benzo[a]anthracene in terms of diamagnetic shielding of the methyl protons by aromatic ring currents; they did not consider the possible role of hyperconjugation, and the monomethyl derivatives of benzo[c]phenanthrene showed deviations which they attributed to interference with ring currents due to nonplanarity of the molecule.

The work of Fraser, *et al.*,[5] is not conclusive because substituents containing heteroatoms can exert long-range magnetic shielding effects;[7] the correlation with the Hammett relation could therefore have been fortuitous, particularly in view of the small number of compounds studied in some of their series and the scat-

ter of the Hammett plots. It is also possible that the effects of substituents on ring current could roughly follow the Hammett relation; this possibility cannot be excluded on the basis of their results since these referred only to one ring system.

If, on the other hand, hyperconjugation in compounds of the type $ArCH_3$ is important, one would expect it to vary with the nature of the aryl group. The variations observed by Ouellette and van Leuwen[6] could then have been due to this rather than to magnetic shielding, the correspondence with the latter being due to coicidence. As a rough measure of the conjugation between Ar and $CH_3$ in $ArCH_3$, one may take the corresponding interaction between Ar and $CH_2$ in the odd AH (alternant hydrocarbon) $ArCH_2$; this in turn is given approximately by the NBMO (nonbonding MO) coefficient ($a_{or}$) at the position in Ar adjacent to methylene.[8]

Figure 1 shows a plot of the chemical shifts reported by Ouellette and van Leuwen[6] against $a_{or}$; there is clearly a reasonable linear relation between the two quantities and the scatter could well be due to the crudity of this procedure for estimating the hyperconjugative interactions in $ArCH_3$. Only four points deviate significantly from the line and these are all for compounds where the methyl is severely hindered, *viz.*, 4-methylphenanthrene (A), 1-methylbenz[a]anthracene (B), 12-methylbenz[a]anthracene (C), and 1-methylbenzo[c]phenanthrene (D). There is evidence that steric compression may lead to significant chemical shifts.[9]

It is particularly striking that the points for the remaining five methylbenzo[c]phenanthrenes behave normally in the plot of Figure 1; Ouellette and van Leuwen[6] were forced to neglect them since the observed chemical shifts deviated from their relation calculated on the basis of magnetic shielding by ring currents. They attributed the discrepancy to the known nonplanarity of benzo[c]phenanthrene; this, however, seems unconvincing since the angular distortions of the individual rings are too small to influence the $\pi$ MO's significantly, since the total strain

(1) This work was supported by the Air Force Office of Scientific Research, Grant No. AF-AFOSR-1050-67.

(2) NASA Trainee, 1965–1968.

(3) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(4) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965.

(5) R. R. Fraser, C. Reyes-Zamara, and R. B. Swingle, *Can. J. Chem.*, 46, 1595 (1968).

(6) R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, 34, 62 (1969).

(7) See M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, 89, 390 (1967), and references cited there.

(8) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

(9) See *e.g.*, F. A. Davis and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 90, 3511 (1968), and references cited there.

TABLE I
CHEMICAL SHIFTS[a] OF SIDE-CHAIN PROTONS IN ArCH₂X SYSTEMS

| | \(\overbrace{\text{—OH}^b\text{—}}\) | | \(\overbrace{\text{—Cl—}}\) | | \(\overbrace{\text{—Br—}}\) | | \(\overbrace{\text{—I—}}\) | | \(\overbrace{\text{—OTS—}}\) | | \(\overbrace{\text{—H—}}\) | |
| Ar | $\tau$ | $\Delta_\phi$ | $\tau$ | $\Delta_\phi$ | $\tau$ | $\Delta_\phi$ | $\tau$ | $\Delta_\phi$ | $\tau$ | $\Delta_\phi$ | $\tau$ | $\Delta_\phi$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenyl (a) | 5.37 | 0.00 | 5.45[c] | 0.00 | 5.57 | 0.00 | 5.58 | 0.00 | 4.92 | 0.00 | 7.68 | 0.00 |
| 2-Naphthyl (b) | 5.18 | 0.19 | 5.27 | 0.18 | 5.38 | 0.19 | 5.42 | 0.16 | 4.77 | 0.15 | 7.54 | 0.14 |
| 2-Phenanthryl (c) | 5.12 | 0.25 | 5.27 | 0.18 | 5.31 | 0.26 | | | 4.72 | 0.20 | 7.45[d] | 0.23 |
| 3-Phenanthryl (d) | 5.07 | 0.30 | | | 5.28 | 0.29 | | | 4.65 | 0.27 | 7.40[d] | 0.28 |
| 3-Perylenyl (e) | 4.96 | 0.41[e] | | | | | | | | | 7.42 | 0.26 |
| 2-Pyrenyl (f) | 4.88 | 0.49 | | | | | | | 4.52 | 0.40 | 7.18 | 0.50 |
| 1-Naphthyl (g) | 4.88 | 0.49 | 4.97 | 0.48 | 5.07 | 0.50 | 5.13 | 0.45 | 4.47 | 0.45 | 7.32 | 0.36 |
| 9-Phenanthryl (h) | 4.83 | 0.54 | | | 5.03 | 0.54 | | | 4.43 | 0.49 | 7.31[d] | 0.37 |
| 1-Anthryl (i) | 4.74 | 0.63 | | | 4.90 | 0.67 | | | | | | |
| 1-Pyrenyl (j) | 4.67 | 0.70 | | | 4.82 | 0.75 | | | | | 7.20[f] | 0.48 |
| 9-Anthryl (k) | 4.37 | 1.00 | 4.42 | 1.03 | 4.53 | 1.04 | | | | | 7.03[c] | 0.65 |

[a] Chemical shifts relative to TMS; concentration 30 mg/0.3 ml in DCCl₃ unless otherwise specified; spectra measured with Varian A-60A. [b] Concentration = $2.78 \times 10^{-4}$ mol in 0.3 ml of CDCl₃ + 0.2 ml of acetone-$d_6$. [c] The Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa. [d] K. D. Bartle and J. A. S. Smith, *Spectrochim Acta*, **23A**, 1689 (1967). [e] Very dilute; spectrum measured on Varian HA-100. [f] Measured in CS₂: E. Clar, B. A. McAndrews, and M. Zander, *Tetrahedron*, **23**, 985 (1967).
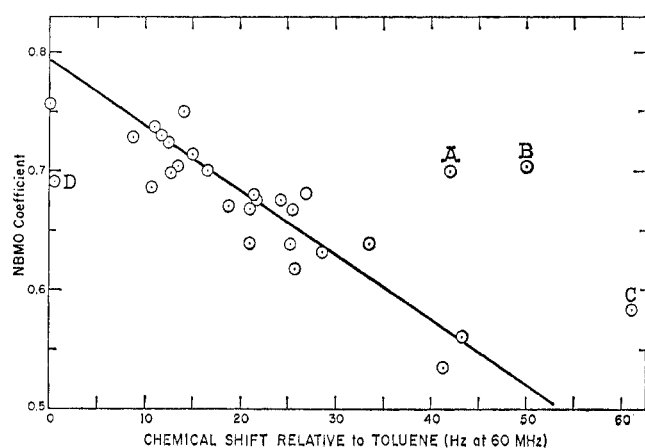


Figure 1.—Plot of chemical shifts of the methyl protons in ArCH₃ vs. NBMO coefficients ($a_{or}$) at the methylene carbon in ArCH₂.

energy seems to be only about 7 kcal/mol,[10] and since similar strain effects occur in A, B, and C, the points which followed the relation derived by Ouellette and van Leuwen. Their results therefore certainly do not establish unequivocally that the variations in chemical shift of the methyl groups in ArCH₃ are due to magnetic shielding rather than hyperconjugation.

In the course of another investigation[11] we had occasion to prepare a number of compounds of the type ArCH₂X where ArH is an alternant aromatic hydrocarbon. As has been pointed out previously,[3] the use of such groups avoids complications due to polar effects since alternant hydrocarbons are nonpolar; any differences in chemical shifts between different members of a given series of compounds ArCH₂X, X being constant, must therefore be due solely to the effects of ring currents and/or of hyperconjugation.

## Experimental Section

Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Melting points were determined with a Thomas–Hoover melting point apparatus and are uncorrected, and nmr spectra were measured with a Varian A-60 spectrometer except in cases indicated where a Varian HA-100 spectrometer was used.

(10) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).
(11) M. D. Bentley and M. J. S. Dewar, work in course of publication.

**3-Hydroxymethylperylene.**—3-Formylperylene (20 g) was added to a stirred solution of sodium borohydride (0.15 g) in tetrahydrofuran (100 ml) and the mixture refluxed for 2 hr. Half the solvent was distilled and the residue poured onto a mixture of crushed ice (300 g) and concentrated hydrochloric acid (300 ml). The resulting solid was collected and crystallized several times from benzene, giving 3-hydroxymethylperylene as a pale yellow powder, mp 175° dec.

*Anal.* Calcd for C₂₁H₁₄O: C, 89.34; H, 5.00. Found: C, 89.11; H, 5.19.

The remaining compounds were prepared according to methods described in the literature. Their melting points and other physical properties agreed with those previously recorded. Full details will be found in a thesis by one of us.[12]

## Results and Discussion

Table I lists the chemical shifts for the side-chain protons for the compounds investigated by us. For each group X in ArCH₂X, the first column gives the chemical shift of the side-chain protons on the $\tau$ scale while the second column shows their values ($\Delta_\phi$) relative to the benzyl derivative, PhCH₂X. The chemical shifts for the methyl derivatives (X = H) show a reasonable correspondence with those of Ouellette and van Leuwen, given that they used a different solvent (DMSO).

The most interesting feature of the data in Table I is the remarkable constancy of the $\Delta_\phi$ values from series to series for a given aryl group. For the two most extensive series, the arylmethyl bromides and the arylcarbinols, the $\Delta_\phi$ values are almost identical even though the spectra were obtained in different solvents. A further conclusion is that although the $\Delta_\phi$ values are reasonably constant for a given aryl in the ArCH₂X (X ≠ H) series, they are consistently smaller in the ArCH₃ series; thus $\Delta_\phi$ ranges from 0 for benzyl bromide to 1.04 ppm for 9-anthrylmethyl bromide, whereas the corresponding change in the methyl series amounts to only 0.65 ppm.

One obvious explanation of these results would be based on the magnetic shielding effect of aromatic ring currents; indeed, the chemical shifts in Table I run approximately parallel to those observed[4] for protons attached to corresponding positions in the ring. The latter must of course be due essentially to the magnetic effects of ring currents since there can be no resonance interactions between such a hydrogen atom and the

(12) M. D. Bentley, Ph.D. Dissertation, The University of Texas, 1968.

ring. It is, however, difficult to explain on this basis the difference between arylmethyl derivatives $ArCH_2X$ (X ≠ H) and the corresponding arylmethanes, for the magnetic environment of the side-chain protons is very much the same in both cases.

We thought at first that this discrepancy might be due to hyperconjugation, the side-chain protons being deshielded by the resulting transfer of charge from the side-chain protons to the ring. This effect should of course depend critically on the dihedral angle of the CH bond in the side chain relative to the ring, and steric effects could well lead to a greater net interaction in compounds of the type $ArCH_2X$ (X ≠ H) than in $ArCH_3$. An explanation in terms of hyperconjugation also seemed to be supported by the linearity of a plot (Figure 2; points ○) of our chemical shifts against corresponding reactivity numbers (*cf.* Figure 1). However, our calculations of the possible effects of ring current indicated that our results might also be explained in terms of magnetic shielding (*cf.* ref 6); so we devised a crucial experiment to distinguish between the two hypotheses.

Calculations of the magnetic shielding of the methylene protons in 2-hydroxymethylpyrene (I) and 3-hydroxyperylene (II), using the Johnson–Bovey tables[13] together with the procedure of Jonathan, Gordon, and Dailey,[14] indicated that the methylene protons in I should be much more deshielded than those in benzyl alcohol (III), while the methylene protons in II should be deshielded to almost the same extent as those in α-hydroxymethylnaphthalene (IV). On the other hand the NBMO coefficients $a_{or}$ corresponding to I and IV are identical, whereas that for II is much smaller than that for IV. If then hyperconjugation is in fact the dominant factor, the methylene protons in I and III should have similar chemical shifts, while the methylene protons in II should appear well downfield of those in IV. Conversely, if magnetic shielding predominates, the signal for the methylene protons in I should appear downfield from that for III, while the signals for II and IV should be almost identical. In this case the point for I should deviate to the right of the line in Figure 2, and the point for II to the left. Furthermore, the conclusions reached in this way are not made ambiguous by steric effects.

CH₂OH structures labeled I, II, III, IV
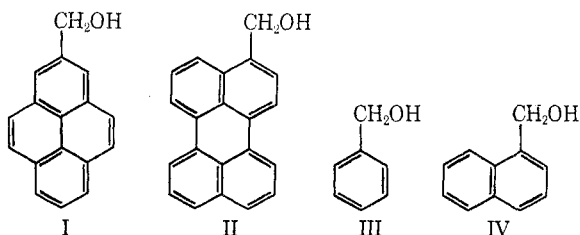
The points for I (□) and II (△) are also plotted in Figure 1; it will be seen that they deviate markedly from the line and in the directions to be expected if the chemical shifts are indeed due primarily to magnetic shielding rather than hyperconjugation.

It is of course possible that some or all of these effects might be functions of the solvent; this, however, seems unlikely.[6] All the spectra, except those of the carbinols, were measured in fairly dilute (6% w/w) sol-
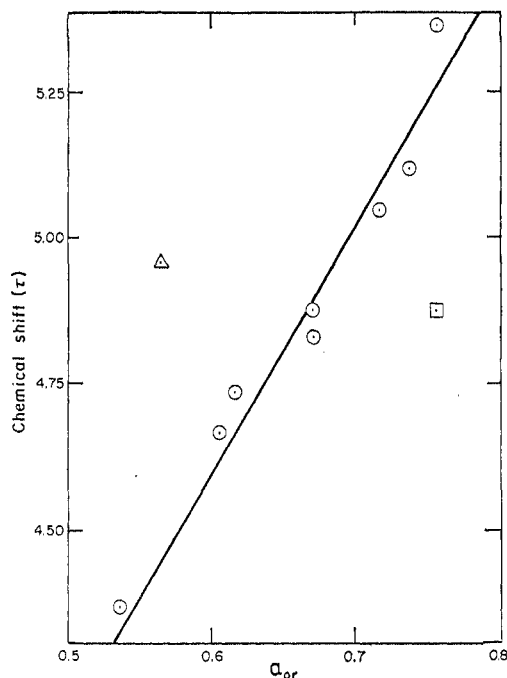


Figure 2.—Plot of $\Delta\phi$ *vs.* $a_{or}$ for arylmethylcarbinols.

ution, and extrapolation to infinite dilution in one typical case (9-bromomethylphenananthrene) led to a change in chemical shift of only 4.5 Hz. Likewise the change in chemical shift for toluene in chloroform-*d* on passing from 6% solution to infinite dilution is only 1.8 Hz.[15] Changes of this magnitude are far too small to account for the differences in Table I. Moreover the $\Delta_\phi$ values for the bromides and carbinols were almost identical, although the former were measured in 6% w/w solution in chloroform-*d* while the latter were measured at constant molar concentration in a different solvent (acetone-*d₆*–chloroform-*d*). It seems unlikely that this could have been due to a coincidence.

Closer examination of Table I shows that the differences in $\Delta_\phi$ between $ArCH_2X$ and $ArCH_3$ are greater the more hindered the aryl group. Thus the differences are negligible for groups of "β-naphthyl" type with both positions *ortho* to the side chain free, are large for groups of "α-naphthyl" type with one *ortho* position blocked by an adjacent ring, and are very large for 9-anthryl where both *ortho* positions are blocked. This suggests very strongly that the differences are conformational in origin, the group X in $ArCH_2X$ being obstructed by adjacent *peri* hydrogens. Steric effects of this kind could influence the side-chain chemical shifts, regardless of whether they are due primarily to hyperconjugation or the effects of aromatic ring currents.

The steric origin of these differences was further supported by studies of the nmr spectra at low temperatures. Thus the methylene protons of 1-naphthylmethyl bromide in acetone–Freon-11 showed a downfield shift of 24 Hz on cooling from 40 to −100°, while the corresponding protons in 2-naphthylmethyl bromide showed only a 12-Hz downfield shift over the same temperature range. This result incidentally indicates that steric effects that force the group X in $ArCH_2X$ out of

(13) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(14) N. Jonathan, S. Gordon, and B. P. Dailey, *ibid.*, **36**, 2443 (1962).

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

the plane of the ring shift the methylene signal downfield, and that similar steric effects are present even in compounds of "β-naphthyl" type.

An attempt was made to calculate the effect of such noncoplanarity on the shielding due to ring current by using the Johnson–Bovey tables[13] and the procedure of Jonathan, Gordon, and Dailey.[14] In the case of the arylmethanes, it was assumed that the methyl groups rotate freely, while in $ArCH_2X$ (X ≠ H) only conformations ranging from those with the C–C–X plane perpendicular to the plane of the ring to those with the C–C–X plane parallel to the plane of the ring, with X *trans* to the *peri* hydrogen, were considered. The results are shown in Table III.

TABLE III

$\Delta_\phi$ VALUES OF SIDE-CHAIN PROTONS IN ArY SYSTEMS

| | Y, | CH₃, | $\overbrace{\qquad\qquad}^{\text{CH}_2\text{X}}$ | |
|---|---|---|---|---|
| Ar | $\Delta_\phi$calcd | $\Delta_\phi$exptl | $\Delta_\phi$calcd | $\Delta_\phi$exptl (X = OH) |
| Phenyl | 0.00 | 0.00 | 0.00 | 0.00 |
| 2-Naphthyl | 0.24 | 0.14 | 0.17 | 0.19 |
| 1-Naphthyl | 0.45 | 0.36 | 0.50 | 0.49 |
| 9-Anthryl | 1.05 | 0.65 | 1.06 | 1.00 |

The calculations clearly do not account for the differences between $ArCH_3$ and $ArCH_2X$; however, it could well be that our procedure is simply too crude, assuming as it does that there is *no* interaction between X and an *ortho* hydrogen. The constancy of the $\Delta_\phi$ values for different derivatives $ArCH_2X$ is certainly easier to explain if the effect is due to magnetic shielding, since hyperconjugation should be influenced by the nature of the group X.

As mentioned above, similar arguments have been used by Fraser, *et al.*,[5] to account for the chemical shifts of the methylene protons in *para*-disubstituted benzenes, $X-C_6H_4-CH_2Y$. They analyzed their results in terms of the Hammett relation, obtaining values of $\rho$ for different groups Y ranging from −0.02 to −0.2 ppm/$\sigma$. The variations in $\rho$ did not show any correlation with the electronegativity of the atom in Y adjacent to the benzyl group, but seemed to correlate roughly with the size of that atom; Fraser, *et al.*, accordingly attributed the variations in $\rho$ to steric effects, the group X restricting rotation about the $C_6H_4-CH_2$ bond.

These conclusions were, however, based on somewhat inadequate data, the number of compounds of a given type often being small and the linearity of the Hammett plots far from convincing. It is perhaps significant that no such effect was observed in the present work in any of the systems studied, although the range of chemical shifts was much greater (1 *vs.* 0.2 ppm) than in the cases reported by Fraser, *et al.*, and although the possible steric effects in many of our compounds were much greater. We suspect that the small differences observed by Fraser, *et al.*, may well have been due to intermolecular association, particularly in cases where highly polar substituents were present. Fraser, *et al.*, do not seem to have extrapolated their results to infinite dilution, and of course solvent effects, and effects of association, would be relatively much more important in the systems studied by them since the substituent chemical shifts were so small.