

LONG RANGE SPIN-SPIN COUPLING AND
THE MILLS-NIXON EFFECT*

P. Madhavan Nair and G. Gopakumar[†]
National Chemical Laboratory, Poona (India)

(Received 11 February 1964)

ALTHOUGH long range spin-spin coupling between benzylic and ring protons (hereafter referred to merely as "benzylic coupling") in aromatic compounds has been investigated by a number of workers¹, there has so far been no attempt to study the variation of this coupling with changes in π electron distribution. We wish to report here the results of such a study on some methyl substituted aromatic compounds. What prompted us most to undertake it was the realization that it would furnish the background in which a reconsideration of the old and unsettled question of the Mills-Nixon Effect² may be made.

As has been pointed out by Dewar³ the theoretical treatment of McConnell⁴ for the π -contribution to the coupling between aromatic protons may be applied to the case of

*Presented at a symposium on "Physical Methods in Structure Determination" held at the National Chemical Laboratory (December 1963) under the auspices of the Chemical Research Committee of the CSIR (India).

[†]CSIR Junior Research Fellow.

benzylic coupling if one of the Q terms of the equation* for the coupling constant is substituted with the hyperfine splitting constant for the fragment $.C - X$, where X is the benzylic carbon atom bearing protons. This means that benzylic coupling should be proportional to the square of the π bond order between the aromatic carbon atoms involved. For all the compounds used in this study X is a freely rotating methyl group.

The data describing the nature of the methyl signals of the 60 Mc PMR spectra[†] of a number of methyl substituted aromatic compounds are presented in Table 1. In most of the cases where clear splitting is observed, the signals display fine structure and only the largest coupling is readily estimated. In the monomethyl derivatives, the π -electron distribution may be assumed, as a first approximation, to be nearly the same as in the parent compounds. The methyl signals of these compounds are clearly split in all cases where an aromatic C-C bond connecting the methyl group to an ortho proton has a large mobile bond order (p). The

*The constant J for the coupling between protons attached to carbon atoms N and N' is given by the expression, $J_{NN'}^{\pi} = (\beta Q)^2 p_{NN'}^2 / h \Delta E$, where $p_{NN'}$ is the mobile bond order between carbon atoms N and N' , and ΔE is an average electronic excitation energy. Q is the isotropic hyperfine splitting constant and β the Bohr magneton.

†The PMR spectra were obtained in carbon tetrachloride or $CDCl_3$ solution on an A-60 spectrometer.

Table 1

No.	Compound	Splitting of Me signal (+ve or -ve).	Largest coupling in cps (approx.)	Band width in cps.
1	2-Methylnaphthalene	+	0.7	2.0
2	1-Methylnaphthalene	+	0.7	
3	1,2-Dimethylnaphthalene	-		2.2
4	1-Methyl-7-isopropyl-naphthalene	-		1.4
5	1-Methyl-6-isopropyl-naphthalene	-		1.4
6	1,6-Dimethyl-4-ethyl-naphthalene	-(1) +(6)	0.4	1.5 1.9
7	2-Methylanthracene	+	0.8	2.6
8	1-Bromo-2-methyl-naphthalene.	-		1.2
9	1-Deutero-2-methyl-naphthalene.	-		1.2
10	2-Methylbenzanthrone	+	0.5	2.0
11	4- " "	+	0.6	1.9
12	10- " "	-		2.0

methyl signals of 2-methylnaphthalene, 1-bromo-2-methylnaphthalene, 1-deutero-2-methylnaphthalene and 2-methylanthracene are shown in FIG.1 (A,B,C and D respectively). As may be expected from theory, the splitting observed for 2-methylnaphthalene disappears on substitution of the 1-position with bromine or deuterium and the methyl band width is reduced. The well known difference in the p values for the 1-2 bonds of naphthalene and anthracene is reflected in the observed splittings (0.7 and 0.8 cps

respectively) for their 2-methyl derivatives. The couplings

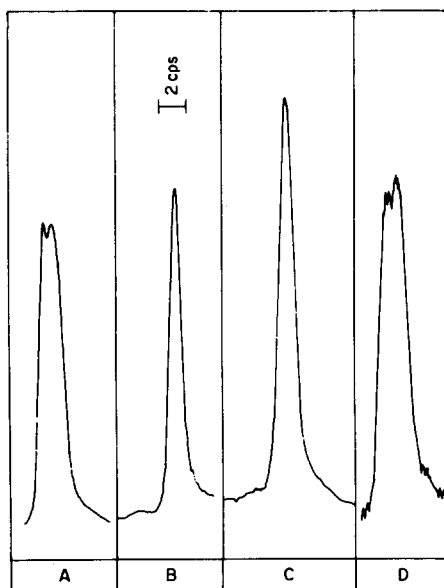
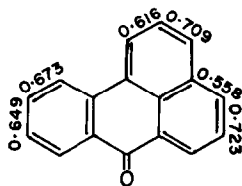


FIG.1

to the 3-positions are weaker and not well resolved. 1-Methylnaphthalene also shows a similar methyl spectrum although the band shape is somewhat different. The α -methyl signals of 1-methyl-7-isopropylnaphthalene, its 1,6 isomer and 1,6-dimethyl-4-ethylnaphthalene are not so readily resolved, although the band width and shape indicate appreciable coupling to the ortho protons. The splitting of the β -methyl group of the last mentioned compound is only 0.4 cps. The additional substitution seems to have changed the π -electron distribution appreciably. In agreement with

expectation, the methyl signals of 1,2-dimethylnaphthalene are not split; but the band widths for both are increased and not decreased. This is attributable to the long range coupling between the methyl protons themselves.

The case of the three methylbenzanthrones studied provides a clear illustration of the bond order dependence of benzylic coupling. The molecular orbital calculations of Goodwin⁵ give the following bond orders for benzanthrone.



The methyl spectra of 4-, 10- and 2-methylbenzanthrones are shown in FIG.2 (A,B and C respectively). Whereas the first of these compounds gives a clean doublet methyl absorption with a coupling of 0.6 cps, the second gives an unsplit signal. The behaviour of the third is intermediate and the corresponding coupling is about 0.5 cps. It is readily seen that the nature of the methyl signals reflects the different extents of "fixation" or localization of the π bonds in the three rings.

From the foregoing discussion the following conclusion may be drawn regarding the NMR absorption of a methyl group on an aromatic ring having protons in both ortho positions. When it is flanked by bonds whose p values are comparatively small and not very different from

each other, no splitting is expected for its resonance

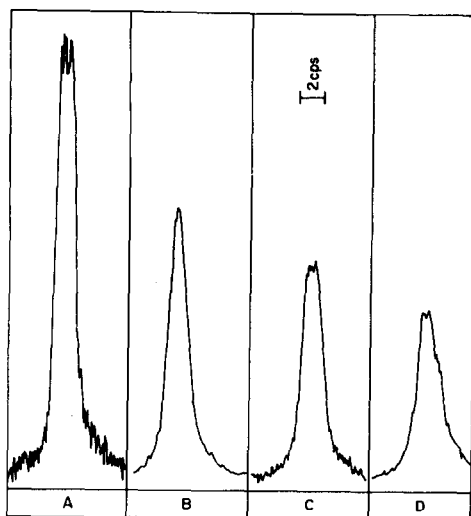


FIG.2

under the conditions of resolution obtaining. On the other hand, when there is considerable difference between the p values or when the p values are both quite large (as is indicated in the case of *mesitylene*^{1a}), clear splitting should be obtainable. However, since the magnitudes of the splitting lie close to the limit of resolution of the instrument used, slight distortions of the signal often make it unobservable and the absence of splitting cannot, by itself, be taken to imply absence of appreciable benzylic coupling.

A re-examination of the question of the fixation of π bonds in indane and tetralin may be made in the light of this conclusion. The methyl spectrum of 5-methylindane, prepared by a route⁶ known to give a pure product, is shown in FIG.2(D). The signal is a doublet with a separation of about 0.5 cps, indicating an appreciable difference between the 4-5 and 5-6 bonds. The fixation can be as postulated by Mills and Nixon or in the opposite sense as has been considered likely from the theoretical study of Longuet-Higgins and Coulson⁷. The second of these alternatives is shown to be correct by the fact that the methyl band widths for 6-deutero-5-methylindane and 5,5'-dimethyl-6,6'-diindanyl are nearly the same as for 5-methylindane (2.2 cps). That the π -electron distributions in indane and tetralin are different is confirmed by chemical shift values. Whereas the 6-protons of both 5-methyl- and 5-acetyl-indanes absorb at higher fields than the 4-protons ($\Delta\delta_{4\rightarrow 6} \approx 0.08$ ppm), the 5- and 7-protons of 6-acetyltetralin have nearly the same chemical shift. The higher shielding at the 6-position in the first two derivatives is apparently a property of the indane ring system. The change from an electron donating to an electron withdrawing substituent does not alter the relative absorption positions of the aromatic protons. In this connection, it is interesting to note that the width of the main band in the absorption spectrum of the aromatic protons of indane is about 3.4 cps,

while the corresponding figures for tetralin and *o*-xylene are only 1.4 and 1.1 cps respectively. The chemical shift difference between the A and B pairs of these A_2B_2 systems is larger for the former than for the latter two. In contrast to the behaviour of 5-methylindane, the resonance of the 6-methyl group of 1,6-dimethyl-4-isopropyltetralin shows no tendency to split. The NMR data are consistent with the accepted notion that there is little or no bond fixation in tetralin.

For indene J_{17} has been reported to be 0.5 cps⁸ while J_{18} for acenaphthene is 1.5 cps³. It would therefore appear that bond fixation of the same type as in indane is present in indene also.

More detailed studies of the Mills-Nixon Effect and also benzylic coupling are in progress.

Acknowledgement - We are very grateful to Prof. K. Venkataraman and Dr. Sukh Dev for their kind interest in and encouragement of this work. Our thanks are also due to Dr. S.C. Bhattacharyya, Dr. C. J. Sanchowala and Mr. J.R. Prahlad for sparing us samples of some of the compounds used in this study, and to the CSIR for the grant of a fellowship to one of us (G.G.).

REFERENCES

- ¹a) R.A. Hoffman, Mol. Phys. 1, 326 (1958)
- b) G.V.D. Tiers, F.A. Bovey and B.L. Shapiro, J.Chem.Phys. 37, 1564 (1962).
- c) H. Shimizu, S. Fujiwara and Y. Morino, J.Chem.Phys. 37, 1565 (1962).
- d) H. Rottendorf and S. Sternhell, Tetrahedron Letters 20, 1289 (1963).
- ²a) G.M. Badger, Quart. Revs.(London) 5, 147 (1951).
- b) G.W. Wheland, "Resonance in Organic Chemistry", J.Wiley and Sons Inc. New York (1955), p.497.
- c) I.M. Hunsberger, H.S. Gutowsky, W. Powell, L. Morin and V. Bandueco, in "Hydrogen Bonding", Hadzi, Pergamon Press London (1959) p.461.
- ³M.J.S. Dewar and R.C. Fahey, J. Amer.Chem.Soc. 85, 2704 (1963).
- ⁴H.M. McConnell, J. Mol. Spectroscopy, 1, 11 (1957).
- ⁵T.H. Goodwin, J. Chem. Soc., 1689 (1955).
- ⁶Sukh Dev, J. Indian Chem. Soc., 32, 403 (1955).
- ⁷H.C. Longuet-Higgins and C.A. Coulson, Trans.Faraday Soc., 42, 756 (1946).
- ⁸a) D.D. Elleman and S.L. Manatt, J.Chem.Phys., 36, 2346 (1962).
- b) J.A. Elvidge and R.G. Foster, J. Chem. Soc., 590 (1963).