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SPIN-SPIN COUPLING BETWEEN BENZYLIC AND RING PROTONS

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In general, coupling between benzylic protons and ring protons in substituted aromatic compounds is considered to be negligible, the NMR signals assigned to the benzylic methyl, freely-rotating benzylic methylene and benzylic methine protons being usually described as "sharp" singlets. However, a number of authors have reported splitting of the methyl resonances in toluene derivatives and ascribed it to coupling with the ring protons. Hoffman[1] showed that the splitting of the methyl signals in a number of *ortho*-substituted toluenes depends on the nature of the substituents and Tiers, Bovey and Shapiro[2] proved that the multiplicity of the methyl resonance in 2,2'-dimethyldiphenylether is due to long-range coupling and not to restricted rotation, as previously reported[3,4].

Long-range coupling has also been reported between the aldehydic and ring protons in some substituted benzaldehydes[5,6,7], and systematic

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[1] R.A. Hoffman, *Mol. Phys.* *1*, 326 (1958).

[2] G.V.D. Tiers, F.A. Bovey and B.L. Shapiro, *J. Chem. Phys.* *37*, 1564 (1962).

[3] H. Shimizu, S. Fujiwara and Y. Morino, *J. Chem. Phys.* *34*, 1467 (1961).

[4] *Idem.*, *ibid.* *37*, 1565 (1962).

[5] Dora G. de Kowalewski and V.J. Kowalewski, *Anal. Assoc. Quim. Argentina* *48*, 157 (1960).

[6] *Idem.*, *J. Chem. Phys.* *37*, 1009 (1962).

[7] G.V.D. Tiers and D.R. Hotchkiss, *J. Phys. Chem.* *66*, 560 (1962).

studies[7] showed that the ring protons involved are *five bonds away from the aldehydic protons* and that the phenomenon can be observed only in the case of certain substituted benzaldehyde derivatives. Similar observations were made concerning some heterocyclic aldehydes[8,9,10].

We now wish to report evidence showing that, in a representative number of examples, *the coupling between benzylic protons bound to an sp^3 carbon and ring protons, in para-disubstituted benzenes, occurs principally across four bonds*.

The aromatic protons of *para*-disubstituted benzene derivatives give rise to an A_2B_2 pattern in their NMR spectra, which because of its relative simplicity, has been the subject of a number of investigations[11,12]. We have observed (Table I) that, in a number of *para*-disubstituted benzenes where one of the substituents is an sp^3 carbon atom carrying one, two, or three hydrogens, *the portion of the A_2B_2 pattern assigned to the pair of ring protons ortho to the methyl, methylene, or methine substituent is conspicuously broadened*.

Figure 1 shows an example of this effect, which we interpret as due to long-range coupling between the benzylic protons and the ring protons in the *ortho* position to the benzylic substituent, i.e. across four bonds. The possibility of *less strong* coupling to the *meta* position (i.e. across five bonds.) cannot, of course, be excluded by our evidence.

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[8] J.B. Leane and R.E. Richards, *Trans. Farad. Soc.* **55**, 518 (1959).

[9] R.A. Hoffman and S. Gronowitz, *Arkiv. Kemi.* **16**, 563 (1960).

[10] R.J. Abraham and H.J. Bernstein, *Canad. J. Chem.* **39**, 905 (1961).

[11] H. Suhr, *Z. Electrochem.* **66**, 466 (1962) and references therein.

[12] P.F. Cox, *J. Amer. Chem.* Soc. **85**, 380 (1963) and references therein.

Table I : NMR data[13] on some p-disubstituted benzene derivatives

Substance[14]	Chemical shift of ring protons[15] (c/s ex TMS)	
	H_2 and H_6	H_3 and H_5
4-aminotoluene	404.5(b),412.5(b)[16]	375.5,383.5
4-hydroxytoluene	406.5(b),415(b)	390.5,399
4-methoxytoluene	414(b),422.5(b)	395,403.5
4-chlorotoluene	414(b),422.5(b)	424.5,433
4-cyanotoluene	428(b),436.5(b)	444,452.5
4-sodiumcarboxylatetoluene[17]	419.5(b),427.5(b)	463.5,471.5
4-carbethoxytoluene	414.5(b),423(b)	467,475.5
4-carbethoxytoluene d^3	421.5,430	471,479.5
4-carboxytoluene	431.5(b),439.5(b)	476.5,484.5
4-nitrotoluene	437.5(b),446.5(b)	483.5,492.5
4-hydroxybenzylalcohol[17]	425.5(b),434(b)	393.5,402
4-methoxybenzylalcohol	418(b),426.5(b)	394.5,403
4-methoxybenzylchloride	426(b),434.5(b)	399,407.5
4,4'-dimethoxybibenzyl	418.5(b),427(b)	401.5,410
4-nitrophenylaceticacidmethylester	439.5(b),448(b)	479,487.5
4-nitrobenzylcyanide	449.5(b),458(b)	490.5,499
4-methoxybenzaldehydediethylacetal	432(b),440.5(b)	399.5,408
4-methoxy-α-chloroethylbenzene	429.5(b),438(b)	400,408.5
4-nitro-α-bromoethylbenzene	449(b)[18],457.5(b)[18]	481,489.5
4-nitrobenzaldehydedimethylacetal	449.5(b),458(b)	483,491.5
4-nitrobenzaldehydediacetate	458(b),466.5(b)	491,499.5
4-methoxybenzaldehyde	463.5,472	412.5(b),421(b)
4-hydroxybenzaldehyde[19]	460,468.5	413(b),421.5(b)
4-nitrobenzaldehyde	479,487.5	498(b),506.5(b)

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[13] Taken in CCl_4 or $CDCl_3$ solution with TMS as internal reference on a Varian A60 spectrometer. As concentrations varied between 5 and 15 per cent, the values of chemical shift have no general significance and were used only to identify various groups of signals.

[14] All compounds gave m.p.'s or b.p.'s in accord with the literature, and their NMR spectra were in full agreement with their structures.

[15] Frequencies refer to the four principal resonances of the A_2B_2 system. Assignments are based on empirical correlations (cf. L.M. Jackman, "Applications of NMR spectroscopy in Organic Chemistry", p.63. Pergamon Press, London (1959)).

[16] b: Broadened signal, i.e. the resonance is broader (and less high) than the corresponding opposite number in the A_2B_2 system (cf. Fig.1). The broadening was determined on at least six runs, the field being swept in alternate directions.

[17] In D_2O solution, the signal due to H_2O being assumed to lie 285 c/s downfield from TMS.

[18] Broadening barely detectable.

[19] In dimethylsulphoxide with TMS as internal reference.

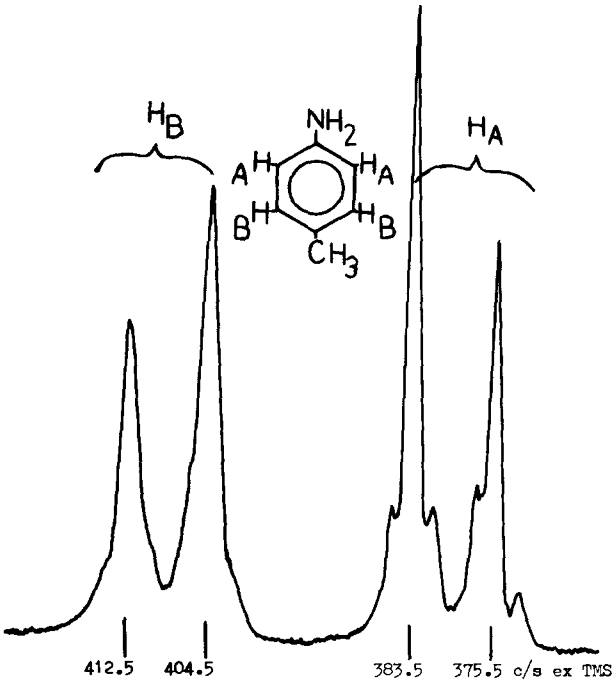

Figure 1. - Portion of 60-MC PMR spectrum of p-toluidine.

It is most unlikely that the observed broadening of one of the two symmetrical portions of the A_2B_2 pattern is due to factors other than spin-spin coupling[20], and we have four independent lines of evidence which indicate that the asymmetric broadening of half of the A_2B_2 pattern is, in fact, due to long-range coupling with benzylic protons, at least with the toluene derivatives. The case for methylene and methine derivatives depends, at present, on analogy with the methyl derivatives.

(a) The asymmetric broadening of part of the A_2B_2 pattern due to the ring

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[20] J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance", p.28. McGraw-Hill, New York (1959).

protons in toluene derivatives (Table I) was <u>always</u> accompanied by a pronounced broadening of the resonance assigned to the methyl group bound to the aromatic nucleus. This was measured by comparing the line widths at half-height (W_H) of the methyl signals with those assigned to the methyl resonances of either anisole or acetone (introduced into the sample in equivalent molar ratios). This method avoided the necessity of degassing the sample and otherwise relying on achieving minimum line widths[20].

More convincingly, in all three methoxy toluenes, the methyl resonances are considerably broader than the methoxy resonances:

Compound	W_H methyl/W_H methoxy
4-methoxytoluene	2.54 ∓ 0.05
3-methoxytoluene	2.50 ∓ 0.05
2-methoxytoluene	1.98 ∓ 0.05

In contrast, the ratios of half-height widths of the methoxy and carbomethoxy resonances in methyl anisate is 1.02 ∓ 0.05 and of the methoxy and methylketone resonances in p-methoxyacetophenone is 1.15 ∓ 0.05.

The apparently significant difference in these ratios between 2-methoxytoluene on the one hand and the 3- and 4-methoxytoluenes on the other (see above) constitutes supporting evidence for the occurrence of long-range coupling primarily across four bonds. No attempt was made, at that stage, to interpret the fine structure of the methyl resonances, but it is interesting to note that the methyl resonance of toluene itself is broad, indicating long-range coupling with some ring protons, in contrast to the aldehydic proton of benzaldehyde where no long-range coupling was reported[7].

(b) In a number of <u>para</u>-disubstituted benzenes where none of the substituents carries any benzylic protons (e.g. methyl anisate, p-methoxyacetophenone) no asymmetry in the A_2B_2 pattern comparable with that observed in the benzylic compounds (Table I) could be detected. This indicates that any asymmetry in the A_2B_2 system introduced by other factors[20] is negligible for benzene derivatives carrying the range of substituents investigated here.

(c) In a number of para-substituted benzaldehydes (Table I) an asymmetric broadening of the A_2B_2 system was also observed, but here the pair of protons affected is five bonds away from the aldehydic protons, as expected from the established relationships[7].

(d) Table I includes some NMR data on ethyl-p-toluate which had been selectively deuterated[21] in the benzylic portion of the molecule to the extent of 90 per cent of the total hydrogen. In this case, no asymmetry was observed in the resonances assigned to the ring protons. The integrated intensities of the two halves of the A_2B_2 system were identical, showing that the number of protons in the positions ortho and meta to the methyl group remained exactly the same (i.e. no selective deuteration in the ring had taken place).

The different types of long-range coupling in benzaldehydes (across five bonds[7]) and in the presently investigated benzylic derivatives (across four bonds) are of interest. One reason for such differences may have been steric[22,23], the aldehydic protons in benzaldehyde derivatives being in the plane of the benzene ring[24] while those of the methyl groups are necessarily on average out of this plane. However, the NMR spectra of some benzylic methine derivatives (Table I), where the benzylic protons should be on average closer to the plane of the benzene ring, give no indication of long-rang coupling

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[21] C.G. Macdonald and J.S. Shannon, private communication (1963).

[22] D.J. Collins, J.J. Hobbs and S. Sternhell, Tetrahedron Letters 197 (1963).

[23] J.T. Pinhey and S. Sternhell, Tetrahedron Letters, 275 (1963).

[24] K. Yates and R. Steward, Canad. J. Chem. 37, 664 (1959).

across five bonds. With 4-nitro-α-bromoethylbenzene (Table I) there is some qualitative indication of suppression of long-range coupling[22,23].

The most likely reason for the observed differences in long-range coupling behaviour of benzaldehyde and toluene derivatives is, in our opinion, the different state of hybridization of the benzylic carbon in the two series. Investigation of suitably substituted styrenes, hydrazones, etc. should throw light on this problem.

Further aspects of long-range coupling in benzylic systems, including quantitative aspects and the influence of substituents, are under investigation in these laboratories.

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