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BENZYLIC COUPLING IN 1,8-DIMETHYLNAPHTHALENE

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During an investigation of methyl substituted naphthalenes by n.m.r. it was discovered that the α-methyl absorption was unusually complex. This was quite unexpected in view of the small benzylic coupling and the large chemical shift difference between the aromatic and methyl protons. The largest benzylic coupling constant in 1-methylnaphthalene, measured from the splitting of the methyl absorption, has been reported to be 0.7 Hz.[1] It has now been established that this doublet is, however, asymmetric, which casts doubt on the magnitude of a coupling constant determined from simple measurement. The α-methyl absorptions of 1,6-, 1,7-, and 1,8-dimethylnaphthalene (Fig. 1) show similar asymmetry, while those of the 1,4- and 1,5-isomer are even more complex (100 MHz; CCl_4; 72°C).

G.l.c. analysis established that the compounds were pure; furthermore, spin decoupling proved in each case that the multiplicity of these absorptions is a true function of the molecule since the α-methyl absorption collapsed to a singlet on irradiation of the appropriate aromatic region. A similar result was obtained with 1-methylphenanthrene, where the weak upfield absorption has previously been ascribed to an impurity.[2]

The factors responsible for the distorted intensities of the α-methyl absorption have been determined by computer analysis. To simplify the calculations, the symmetrically substituted 1,8-dimethylnaphthalene was chosen in preference to 1-methylnaphthalene. The aromatic region was analyzed first and was treated as two superimposed ABX systems. Spin decoupling experiments had suggested that the methyl groups were coupled to their ortho, meta, and para protons. Initial parameters for the aromatic protons were therefore calculated from spectra in which these protons had been decoupled from the methyl protons. The final parameters were obtained by a method based on Swalen and Reilly's iterative computer technique[3].

Magnetic Shielding Parameters in Hz from TMS		Spin-Spin Coupling Constants in Hz	
Protons 2 and 7	= 709.6	$J_{2,3} = J_{6,7}$	= 6.8
Protons 3 and 6	= 712.9	$J_{2,4} = J_{5,7}$	= 1.1
Protons 4 and 5	= 751.5	$J_{3,4} = J_{5,6}$	= 9.1

Inter-ring coupling constants were ignored; this was felt to be a valid first approximation since they should not significantly affect the methyl absorption. Their effect can, however, be seen by comparing the experimental spectrum with the calculated trace; work is in progress to obtain their magnitude.

The methyl group was now included in the calculations. Using a magnetic shielding parameter of 287.0 Hz, various feasible combinations of coupling constants from the methyl group to the ortho, meta, and para protons were tried. The signs of the three coupling constants were

also varied, and the experimentally obtained methyl absorption was compared with the calculated trace. An exact match (Figs. 1 and 2) was obtained with the following parameters, relative to the positive signs of the ring proton coupling constants:

J_{H,CH_3}ortho = -0.75 Hz; J_{H,CH_3}meta = +0.40 Hz; J_{H,CH_3}para = -0.65 Hz

A sign reversal of J_{H,CH_3}ortho and J_{H,CH_3}meta did not affect the computed spectrum, but a - + - combination is more likely on theoretical grounds[4]. These coupling constants appear not to have been previously determined in substituted naphthalenes and are similar to J values of toluene derivatives[4,5,6]. Both the peak shape and the splitting of the methyl absorption are dependent on all three coupling constants. Figs. 3, 4, 5 and 6 illustrate this point. Fig. 3 shows the line shape of the methyl absorption computed from the parameters previously calculated for the aromatic protons, and coupling constants of -0.75, +0.35 and -0.45 Hz between the methyl protons and the ortho, meta and para protons respectively. Figs. 4, 5 and 6 show how a change of 0.2 Hz in each of the coupling constants in turn affect the shape and splitting of the peak. Figs. 5 and 6 further illustrate the complexity which long range coupling of this type can produce in the methyl absorption. The more intense peak is itself unsymmetrical and therefore the peak maximum does not coincide with the centre of the band.

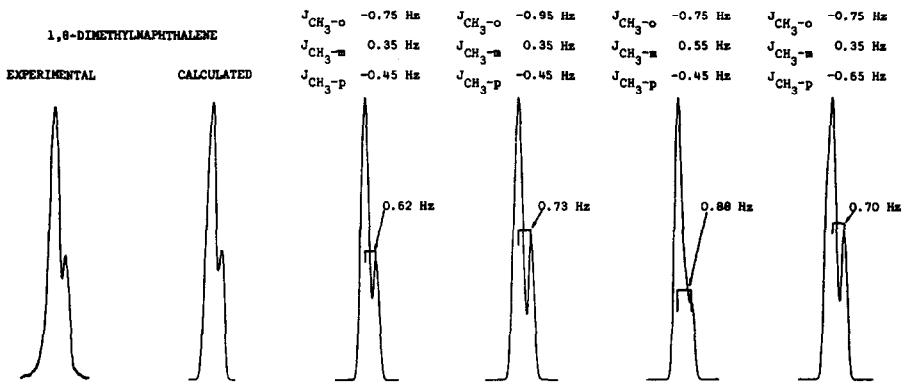

FIG. 1 FIG. 2 FIG. 3 FIG. 4 FIG. 5 FIG. 6

Thus, although measurement of the peak separation may give an approximate J value, it is fundamentally an incorrect method. The increasing use of n.m.r. for the determination of bond orders in polycyclic aromatic systems makes the determination of the true coupling constants essential in order to obtain meaningful results.

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