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INTER-RING COUPLING IN 1,8-DIMETHYLNAPHTHALENE

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The existence of inter-ring coupling can be seen quite clearly in the NMR spectrum of 1,8-dimethylnaphthalene. When the benzylic coupling constants of this compound were determined[1], spectra of the aromatic region recorded while decoupling from the methyl group (100 MHz; CCl_4; 72°C) exhibited fine splitting which was not reproduced in those calculated by a computer technique[2]. Since the spectra were calculated from the chemical shifts and intra-ring coupling constants of the aromatic protons[1], the observable difference could only be due to neglect of inter-ring coupling. Comparison of the expanded, observed absorptions of protons 4 and 5 (Fig.1) with the computed trace (Fig.2) illustrates these effects.

1,8-DIMETHYLNAPHTHALENE; ABSORPTIONS OF PROTONS 4 AND 5

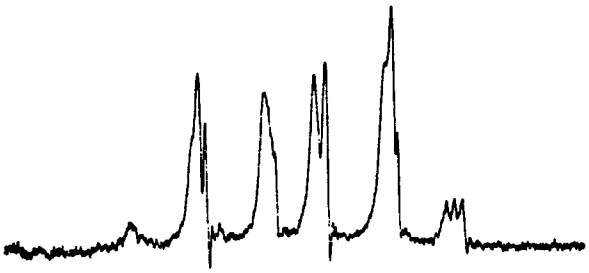

FIG.1 Observed spectrum

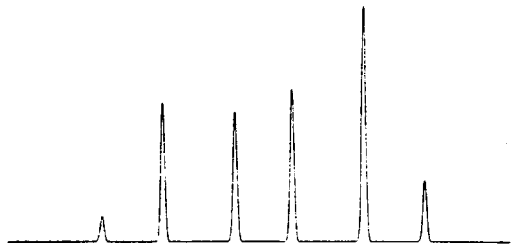

FIG.2 Calculated spectrum excluding inter-ring coupling constants

For the determination of the benzylic coupling constants the effects of inter-ring couplings had been ignored as a first approximation; in view of their possible influence on the methyl absorption it became necessary to establish their magnitude and signs. At that stage such coupling constants had apparently not been investigated systematically, although certain isolated values, e.g. J_{27} and J_{28} in naphthalene, had been determined[3]. Because of the strongly coupled aromatic protons it was considered essential to include all possible coupling constants in the present analysis of the six spin system. Intuitively selected inter-ring coupling values were therefore introduced into calculation and varied in both sign and magnitude; the appropriate chemical shifts and intra-ring J values were kept constant[1]. The spectrum reproduced in Fig.1 was chosen as the initial experimental standard for comparison with the calculated traces because the absorptions of protons 4 and 5, in addition to being well removed from those of other protons, were found to be surprisingly sensitive to changes in the inter-ring coupling values. The parameters recorded in the Table (1st row) provided the best match for the experimental spectrum, and the resulting Calcomp trace for protons 4 and 5 is reproduced in Fig.3; these J values gave equally satisfactory results for the other aromatic absorptions.

TABLE (J values expressed in Hz)

Compound	J_{25}, J_{47}	J_{26}, J_{37}	J_{27}	J_{35}, J_{46}	J_{36}	J_{45}
1,8-Dimethylnaphthalene	-0.17	+0.20	+0.13	+0.20	+0.13	-0.55
Naphthalene[4]	-0.10	+0.25	+0.10	+0.23	+0.10	-0.45

During the final stages of this investigation the corresponding coupling constants of naphthalene (see Table) were determined by Crecely and Goldstein in a carefully executed full analysis of the molecule[4]. The question now arises whether the slight differences between these values and those of dimethylnaphthalene are genuine. Accordingly, the inter-ring J values of dimethylnaphthalene were substituted by those of naphthalene in the previous calculation, and the result was the trace shown in Fig.4. This differs in the magnitude of the fine splitting from both Fig.3 and the experimental spectrum Fig.1, thereby illustrating the sensitivity of the method as well as proving that the parameters are genuinely different in the two compounds. Methyl groups, therefore, have a small but definite effect on inter-ring coupling.

1,8-DIMETHYLNAPHTHALENE; ABSORPTIONS OF PROTONS 4 AND 5

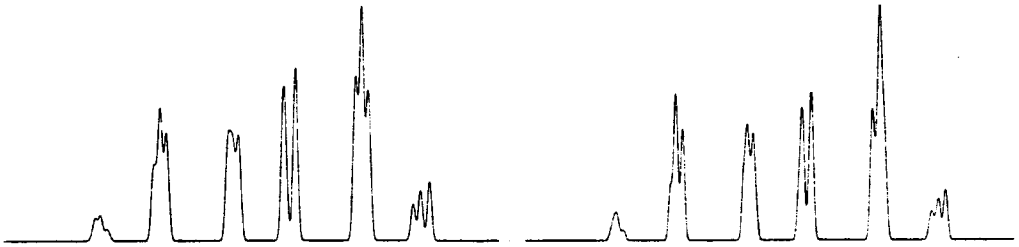

FIG.3 Calculated spectrum including inter-ring coupling constants

FIG.4 Calculated spectrum substituting inter-ring coupling constants of naphthalene

The signs of the inter-ring coupling constants (relative to positive intra-ring J values) are interesting. Calculations for π-electron contributions to long range coupling predict a negative coupling constant between protons with an even number of intervening bonds, and a positive value for those separated by an odd number of bonds. It is, therefore, surprising to find positive values for J_{27} and J_{36}; it is noteworthy that the comparable coupling constants in naphthalene were also found to be positive[4]. These observations may be relevant in assessing the mechanism of long range inter-ring coupling - a subject in which there is increasing activity and interest.

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