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THE LOCATION OF DOUBLE BONDS IN METHYL-ACENES

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A considerable number of facts point to the distribution of six π-electrons in three orbitals in any benzenoid ring of which the pair in the lowest orbital is located in a true double bond. This could be mobile or fixed, whilst the other two pairs of π-electrons are delocalized in circular orbitals (1). The presence of a true double bond can be demonstrated by the splitting of the CH_3NMR signal. Thus a fixed double bond like the one in phenanthrene produces a CH_3 doublet with a separation of 1.-Hz (2).

It is an amazing fact that the CH_3 band in the first annellation series in Fig.1 does not show a splitting of this degree. No splitting of the CH_3 signal can be observed in p-xylene, whilst 1.4-dimethylnaphthalene and 1.4-dimethylanthracene show doublets with a separation of 0.2 and 0.3 Hz resp. Decoupling of the aromatic protons, as marked by points, also shows that the degree of coupling is very small and is not consistent with 50% double bond character in the bond adjacent to the CH_3 group. This can be attributed to a fixed double bond as indicated by the formulae for dimethylnaphthalene and dimethylanthracene, or in the case of p-xylene by two equal positions as marked by dashed lines. The other delocalized π- electrons are not symbolized in the formulae.

Quite different results are observed in the second annellation series in Fig.1. The CH_3 band of o-xylene appears as a singlet, decoupling, marked by points, has very little effect. The CH_3 signal in 2.3-dimethylnaphthalene and 2.3-dimethylanthracene forms a doublet with a separation of 0.5 and 0.65 Hz resp. Decoupling has a strong effect. Whilst the double bond in o-xylene can be in three non-adjacent bonds, only half a double bond appears adjacent to the CH_3 groups in the former hydrocarbons, as marked by dashed lines.

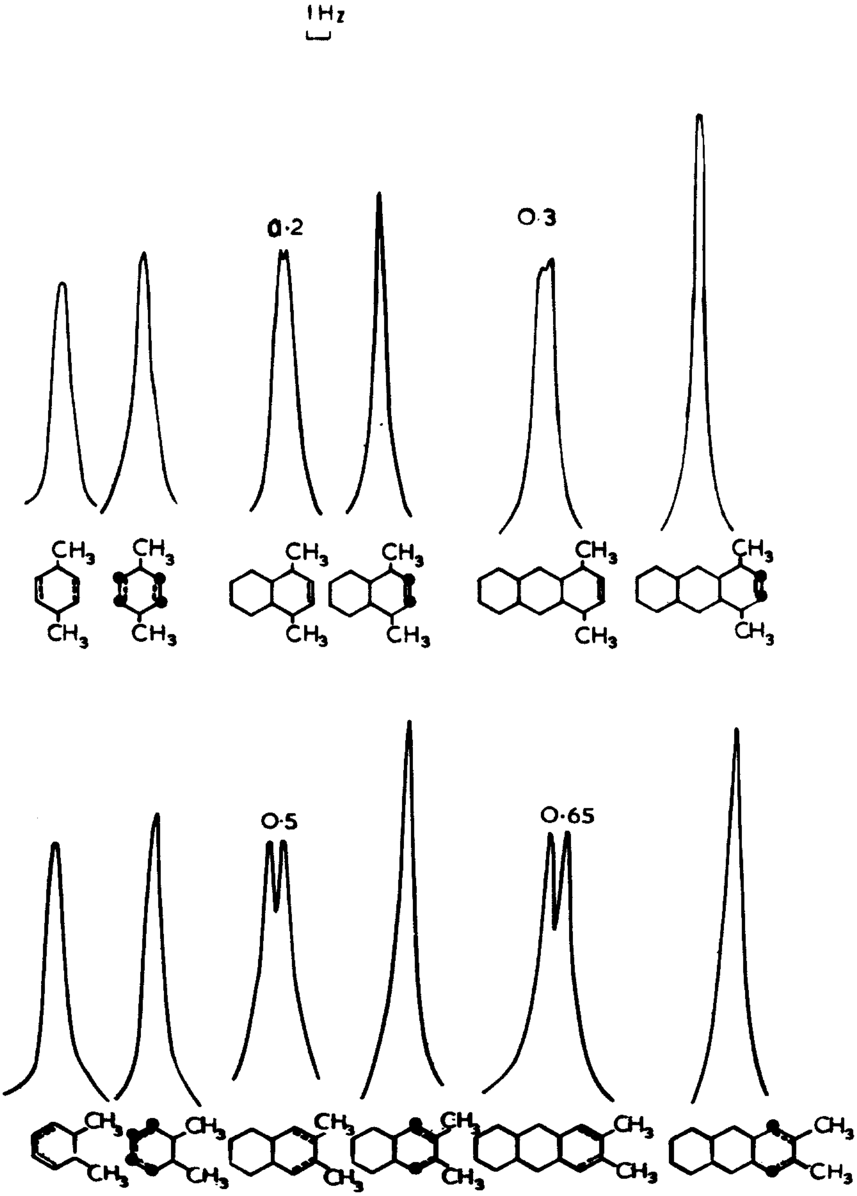
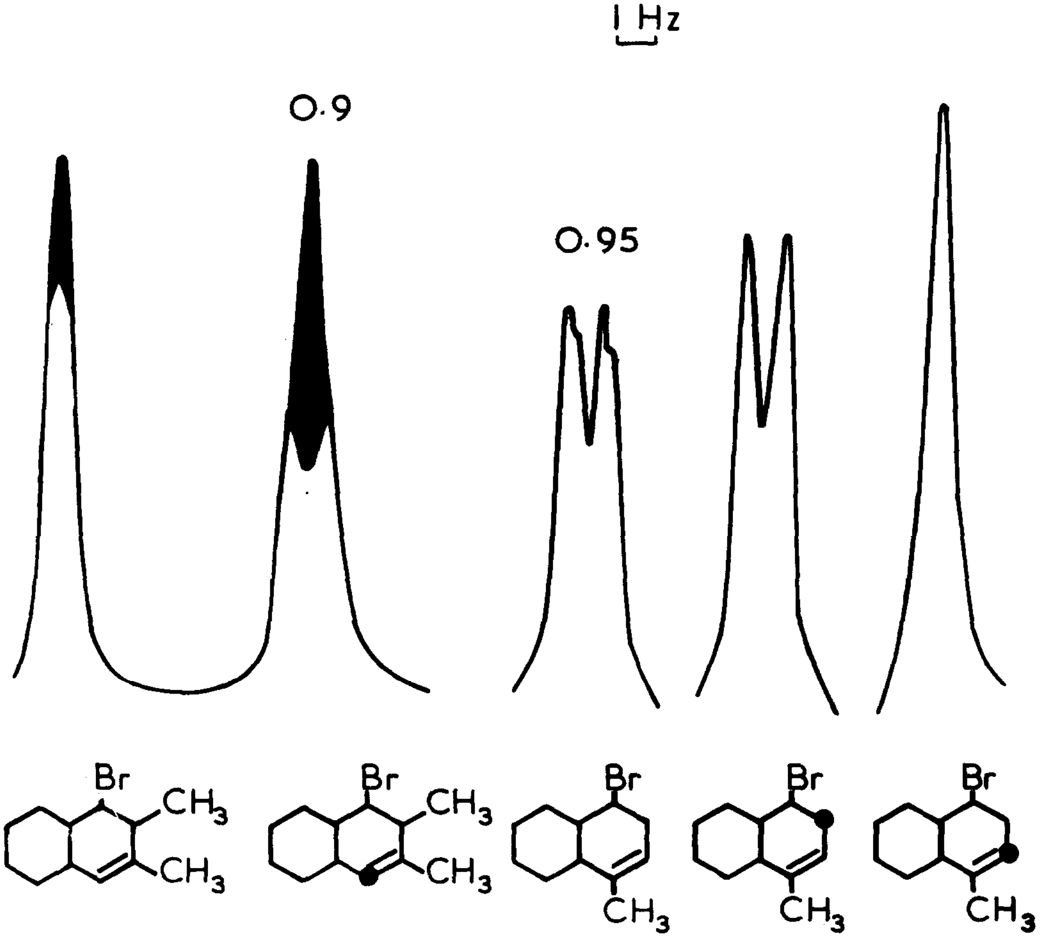


Fig. 1. CH$_3$ NMR signals of p-xylene,1.4-dimethylnaphthalene, 1.4-dimethylanthracene, o-xylene, 2.3-dimethylnaphthalene and 2.3-dimethylanthracene at 60 MHz in CS$_2$. Decoupled protons are marked with points.

The correctness of the assumption that one double bond is shared between the two α-β-positions in 2,3 dimethylnaphthalene as shown by the dashed lines in Fig.1, second series, can be demonstrated by the CH_3 bands of 1-bromo-2.3-dimethylnaphthalene, Fig.2. The low field CH_3 band (position 2) is a singlet, little sharpened by decoupling H_4. However, the signal of the high field CH_3 (in position 3) is a doublet with a separation of 0.9 Hz, which is almost double the separation of the doublet in 2.3-dimethylnaphthalene (0.5 Hz). One must assume that the double bond is fixed as shown in Fig. 2. The very different decoupling effects prove the correctness of the assignment of the two CH_3 groups.



Fig, 2. CH_3 NMR signals of 1-bromo-2.3-dimethylnaphthalene and 4-bromo-1-methylnaphthalene in CS_2 at 60 M.Hz. Decoupled protons are marked with points; black area after decoupling.

A shifting of the double bond is also observed in 4-bromo-1-methylnaphthalene (Fig.2) by comparison with 1.4-dimethylnaphthalene (Fig. 1). Whilst the latter shows no double bond adjacent to CH_3, the small splitting of 0.2 Hz, being about the same as between CH_3 and a proton in m-position, there is a very strong separation of 0.95 Hz of the CH_3 doublet recorded in 4-bromo-1-methylnaphthalene (Fig.2). There appears to be a double bond fixation as shown in the formulae. Decoupling of the protons marked with points proves the origin of the o-coupling (0.95) and m-coupling (0.25 Hz).

2.6-Dimethylnaphthalene and 2.7-dimethylanthracene have CH_3 doublets with a separation of 0.6 and 0.9 Hz resp. This is less than in the above Br-derivatives and more than in the 2.3-dimethyl derivatives. It indicates a high but incomplete degree of double bond fixation between CH_3 and 1-position. The above series show a drastic influence of the substituents on the distribution of double bonds by comparison with the parent hydrocarbons. It is difficult to see how bond orders of Kekulé structures can account for this. An improved theory ought to begin with the establishment of more empirical rules from similar series of this kind. NMR spectra of numerous methylnaphthalenes and some methylanthracenes have been published before (3), but the striking effects of substitution and annellation on the CH_3 resonances have not been reported so far.

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