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DOUBLE BOND FIXATION IN METHYLNAPHTHALENE DERIVATIVES

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P. Madhavan Nair and G. Gopakumar (1), from a study of splitting of the methyl group in naphthalene and anthracene derivatives have noted that 2-methylnaphthalene and 2-methylanthracene show a coupling constant of 0.7 and 0.8 Hz respectively for the 2-methyl group. According to these authors the difference in bond orders for the 1,2 bonds of naphthalene and anthracene is reflected in these splittings and this can be explained in terms of Kekule structures. They have pointed out that the couplings of the 2-methyl group to the 3-proton are weaker and are not resolved. E. Clar and C.C. Mackay (2) have used the splitting of the CH_3 NMR signal in methyl-acenes to demonstrate the presence of a "true" double bond. It will, however, be noted that neither P. Madhavan Nair and G. Gopakumar (1) nor E. Clar and C.C. Mackay (2) have mentioned anything about the splitting or otherwise of the protons on the adjacent carbons at the 1 and 3-positions, presumably because chemical shifts of these protons could not be specifically assigned in the relevant NMR spectra. During our work on some naturally occurring naphthols and naphthaquinones (3) we had come across suitable model compounds which lend themselves to a better study of the splitting of the C-2 methyl group and the C-1 and C-3 protons. The study of our compounds I to XI clearly shows both with reference to C-2 methyl and C-1 and C-3 protons that allylic type of coupling takes place across the 1,2 bond but not across the 2,3 bond. Presumably, theoretical calculations leading to the coupling constants for the 1,2 and 2,3 bonds in these systems might confirm this observation.

In 2-methyl-4-hydroxy-5-methoxynaphthalene (I), the methyl group gives a broadened singlet, whereas the C-3 proton gives a clean doublet; the C-1 proton gives a multiplet showing a coupling with the allylic methyl in addition to the meta coupling with the C-3 proton. The same position obtains

TABLE*

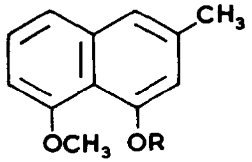
Chemical shifts of methylprotons and protons at C-1 and C-3 positions.

Compound	2-CH_3	1-H	3-H
I	2.38 (s) $J_{\frac{1}{2}}$ width = ca. 0.5 Hz	7.06 (m)	6.74 (d) $J_{1,3}$ = 1.5 Hz
II	2.44 (s) $J_{\frac{1}{2}}$ width = ca. 0.5 Hz	7.17 (m)	6.67 (d) $J_{1,3}$ = 1.5 Hz
III	2.45 (s) $J_{\frac{1}{2}}$ width = ca. 0.5 Hz	7.47 (m)	6.92 (d) $J_{1,3}$ = 1.5 Hz
IV	2.48 (s) $J_{\frac{1}{2}}$ width = ca. 0.5 Hz	7.55 (m)	7.00 (d) $J_{1,3}$ = 1.5 Hz
V	2.37 (d) J = ca. 1 Hz	7.06 (q) J = ca. 1 Hz	—
VI	2.40 (d) J = ca. 1 Hz	7.46 (q) J = ca. 1 Hz	—
VII	2.40 (d) J = ca. 1 Hz	7.31 (q) J = ca. 1 Hz	—
VIII	2.38 (d) J = ca. 1 Hz	7.31 (q) J = ca. 1 Hz	—
IX	2.40 (s)	—	6.72 (s)
X	2.27 (s)	—	6.76 (s)

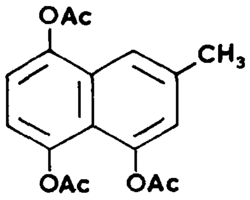
* NMR spectra are recorded in $CDCl_3$ and chemical shifts reported in δ values (in ppm from T.M.S.).

in its methylether (II), its acetyl derivative (III) and 2-methyl-4,5,8-triacetoxy naphthalene (IV).

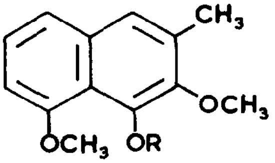
In 2-methyl-4-hydroxy-3,5-dimethoxynaphthalene (V), the methyl group is split into a doublet and the C-1 proton is seen as a clean quartet; (J = ca. 1 Hz). The acetyl derivative (VI) gives a similar spectrum. Similarly



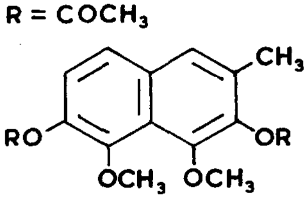
I R = H
II R = CH_3
III R = $COCH_3$



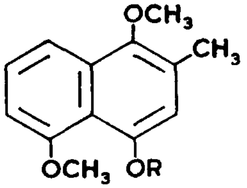
IV



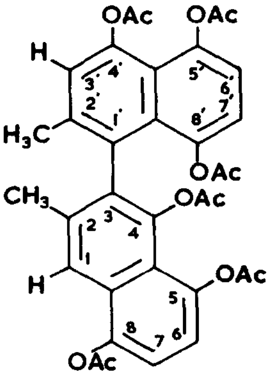
V R = H
VI R = $COCH_3$



VII R = H
VIII R = CH_3



IX R = H
X R = $COCH_3$



XI

2-CH_3	2.19(d) (J = ca. 1 Hz)
1-H	7.75(q) (J = ca. 1 Hz)
2′-CH_3	1.96 or 2.24 (s)
3′-H	7.10 (s)

in 2-methyl-3,6-dihydroxy-4,5-dimethoxynaphthalene (VII) and its dimethylether (VIII), the C-2 methyl is seen as a doublet and the C-1 proton as a quartet, (J = ca. 1 Hz).

In 2-methyl-4-hydroxy-1,5-dimethoxynaphthalene (IX) and its acetyl derivative (X) no allylic coupling across the 2,3-bond can be seen as the methyl and C-3 H both give narrow singlets.

The hexaleucoacetate of isodiospyrin (XI) has C-methyl groups in both the above types of environments (4). The C-2 methyl group is split into a doublet by the peri proton across the 1,2 naphthalenic double bond which is seen as a quartet (J = ca. 1 Hz); there is no proton at C-1' and, therefore, the C-2' methyl is seen only as a singlet though there is a proton on C-3' across the 2'-3' naphthalenic bond.

The chemical shifts of the C-2 methyl and the C-1 and C-3 protons in the above compounds are recapitulated in the table.

The methyl groups in compounds I, II, III and IV have a J value of 0.5 Hz which compares with 0.7 Hz in 2-methylnaphthalene. One could, therefore, infer that substitution at C-4 does not significantly help in increasing bond fixation between C-1 and C-2. However, in (V), (VI), (VII) and (VIII) the J value of the methyl group is 1 Hz which is characteristic of a localized double bond as in 9-methylphenanthrene (5). The same is true for the 2-methyl group of XI. Perhaps, the introduction of a substituent in C-3 helps in a greater localization of the C-1 and C-2 double bond.

Compounds (III), m.p. 142-143°, (VI), m.p. 85° and (X), m.p. 97° have been prepared from their parent compounds (I), (V) and (IX) respectively by acetylation. (VI) and (X) are reported for the first time in literature. Satisfactory analyses have been obtained for these compounds.

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