93. *The Long-range Proton–Proton Couplings in Indene and Benzofuran.*

By J. A. Elvidge and R. G. Foster.

The proton magnetic resonance spectra of the monomethylindenes (four of which are new) show that there is a strong, small coupling (*J* 0·7 c./sec.) between the approximately *trans*-disposed 3- and 7-proton, as there is also in benzofuran (*J* 0·9 c./sec.).

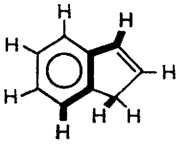
The proton magnetic resonance of indene (I) has recently been analysed, with the aid of a decoupling technique, by Elleman and Manatt.[1] These workers noted that, besides the expected couplings within the 5-membered ring, the olefinic 3-proton was coupled, with $J \approx 0.5$ c./sec., to a benzenoid proton. This, they suggested in the summary of their paper, was the 4-proton, although in the text they specified the 5-proton (presumably a typographical error). They further noted a long-range coupling of similar magnitude between the 1-methylene protons and a benzenoid proton, which they suggested was the 7-proton.

We had measured the proton resonance spectra of some monomethylindenes, in continuation of our studies on aromaticity,[2] and so had definitive data to hand.

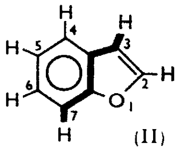
Our spectra show that the origin of the two long-range couplings in question is the 7-proton. The 4(or 5)-proton is not involved.

Similarly, in benzofuran (II), the 3-proton is coupled to that in the 7-position.

Indene Spectra.—In the spectrum of 7-methylindene at 60 Mc./sec. there are two sharp double triplets in the olefinic region, with line widths (at half-height) of 0·6 c./sec. for the lines of the lower-field multiplet arising from the 3-proton and of 1 c./sec. for the lines of the 2-proton multiplet. The assignments follow from the spectra of 2- and 3-methylindene. The methylene signal of 7-methylindene appears as a clean triplet (*i.e.*, it is an overlapping double doublet) with line width 1·6 c./sec. Consequently there are no long-range couplings of appreciable magnitude (⩾0·5 c./sec.) in this compound. 4-, 5-, and



(I)



(II)

---

[1] Elleman and Manatt, *J. Chem. Phys.*, 1962, **36**, 2346.

[2] Elvidge and Jackman, *J.*, 1961. 859.

6-Methylindene, however, like indene itself, show ragged methylene signals of appreciably greater line width (2·3, 4·1, 2·2, 3·4 c./sec., respectively) indicative of further coupling: this must then be to the 7-proton. Furthermore, in the spectra of the last four compounds, the 3-proton signal shows fine splitting, each line of the double triplet being split sharply into two. So again there must be coupling to the 7-proton. The second-order splitting gives $J_{3,7} = 0{\cdot}7$ c./sec. in each case. [None of the 2-proton signals (double triplets) shows fine splitting and the line widths are all 0·6 c./sec.]

Benzofuran Spectra.—In the spectrum of benzofuran, the high- and the low-field olefinic-proton signals appear as a double doublet and as a doublet. That these arise from the 3- and the 2-proton, respectively, was deduced from the spectrum of 3-methylbenzofuran. In the spectrum of 7-methylbenzofuran, both of the olefinic-proton signals appear as sharp doublets. Therefore, there must be coupling in benzofuran between the 3- and the 7-proton. The second-order splitting of the 3-proton signal gives $J_{3,7} = 0{\cdot}9$ c./sec.

The 1,7-coupling in indene recalls that between the protons of a methyl group and an *o*-proton, which is often observable in the spectra of methyl-substituted aromatic compounds. The appreciable 3,7-coupling in indene (I) and in benzofuran (II) is more exceptional. This occurs over five bonds and must result from their favourable "*trans*"-arrangement.[3]

The Table lists the observed proton magnetic resonance data and the results of our first-order analyses. It is unfortunate that an accurate value for $J_{1,7}$ cannot be extracted directly from the indene spectra.

Preparation of Monomethylindenes.—Unambiguous preparations of 5- and 7-methylindene were achieved by cyclising the known β-*p*- and β-*o*-tolylpropionic acids with hydrogen fluoride to the indan-1-ones, reducing these with lithium aluminium hydride to the indan-1-ols, and then effecting acid-catalysed dehydration. The last process has been shown not to cause isomerisation.[4] The cyclisation of β-*m*-tolylpropionic acid gave a mixture of two indanones, necessarily the 5- and the 7-methyl compound. These were separated well on a column of alumina, the latter being eluted first, as expected. The 7-methylindanone and the derived 4-methylindene showed C–H deformation frequencies close to those for 2,6-dimethylacetophenone and 1,2,3-trimethylbenzene, respectively. Similar agreement was found between the indanone eluted second and 2,4-dimethylacetophenone, and between the derived 6-methylindene and 1,2,4-trimethylbenzene. Further support for the assignments of structure came from proton magnetic resonance measurements. Thus the first-eluted indanone had τ_{Me} 7·43 as compared with τ_{Me} 7·57 for the second, which indicated that the methyl substituent in the first was adjacent to carbonyl and deshielded by it. In agreement with this interpretation, the two indanols

Line positions in c./sec. (and τ), and coupling constants, *J*.*

(10% solutions in CCl_4, containing 0·5% of $SiMe_4$.)

	$1\text{-}H_2$	2-H	3-H	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,7}$
Indene	198·5 (6·69)	388·4 (3·53)	4·114 (3·14)	1·95	1·95	5·8	0·7
2-Me- ,, ...	188·5 (6·85)		382·5 (3·63)				
3-Me- ,, ...	193·2 (6·78)	364·1 (3·93)					
4-Me- ,, ...	198·0 (6·70)	391·3 (3·48)	420·3 (3·00)	1·95	1·95	5·7	0·7
5-Me- ,, ...	196·0 (6·73)	390·2 (3·49)	410·2 (3·16)	1·90	1·90	5·5	0·7
6-Me- ,, ...	195·5 (6·74)	381·3 (3·65)	405·8 (3·24)	1·90	1·90	5·7	0·7
7-Me- ,, ...	189·0 (6·85)	389·9 (3·50)	412·4 (3·13)	1·95	1·85	5·8	
Benzofuran ...		450·8 (2·49)	398·0 (3·37)			2·15	0·9
7-Me- ,, ...		449·1 (2·52)	397·1 (3·38)			2·2	

* The calibration of the Varian A 60 spectrometer was checked. The sweep rate was 0·2 c. per sec. per sec. and the scale 0·2 c. per sec. per mm.

---

[3] Davis and Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 2252; Davis, Lutz, and Roberts, *ibid.*, 1961, **83**, 246.

[4] Koelsch and Schneiderbauer, *J. Amer. Chem. Soc.*, 1943, **65**, 2311.

obtained on reduction had almost identical methyl group resonance, at τ 7·66 and 7·68, respectively.

Experimental.—5- *and* 7-*Methylindan*-1-*one* (cf. ref. 5). β-*m*-Tolylpropionic acid[6] (12·5 g.) was kept with hydrogen fluoride (400 c.c.) in a Polythene bottle for 24 hr., and the solution then allowed to evaporate. An excess of saturated aqueous sodium acetate was added, mixture was steam-distilled, and the distillate cooled in ice. Chromatography of the solid (7·5 g.), m. p. *ca.* 32°, in 1 : 1 chloroform–hexane on a column (65 × 4 cm.) of alumina (Spence's type H), collection of fractions and evaporation, afforded (i) a solid (1·5 g.), m. p. 52—55°, (ii) a mixture (0·5 g.), and (iii) a solid (3·8 g.), m. p. 50—70°. Sublimation of fraction (i) at 40—45°/10^{-5} mm. gave 7-methylindanone, m. p. 54—55° (Found: C, 81·9; H, 6·8. Calc. for $C_9H_{10}O$: C, 82·1; H, 6·9%), τ_{Me} (in CCl_4) 7·43, $\lambda_{max.}$ (in EtOH) 248, 297 mμ ($10^{-3}\varepsilon$ 12·5, 2·5), $\nu_{max.}$ (Nujol mull) 778 cm.$^{-1}$. 2,6-Dimethylacetophenone has $\nu_{max.}$ 775 cm.$^{-1}$. Crystallisation of fraction (iii) from light petroleum (b. p. 40—60°) gave plates of 5-methylindanone, m. p. 70—71° (Found: C, 82·1; H, 6·9%), τ_{Me} (in CCl_4) 7·57, $\lambda_{max.}$ (in EtOH) 253, 287, 293 mμ ($10^{-3}\varepsilon$ 13·1, 3·2, 3·4), $\nu_{max.}$ (Nujol mull) 813 cm.$^{-1}$. 2,4-Dimethylacetophenone has $\nu_{max.}$ 822 cm.$^{-1}$.

4- and 6-Methylindan-1-one were prepared by analogous cyclisation of β-*o*-[7] and β-*p*-tolylpropionic acid.[6]

Reduction of methylindanones. The ketone (1·85 g.) in ether (50 c.c.) was added to a stirred suspension of lithium aluminium hydride (0·2 g., 10% excess) in ether (80 c.c.) to maintain gentle refluxing. The mixture was then heated under reflux for 1 hr., next cooled in ice, and water was added cautiously. The white solid was dissolved by addition of 10 : 1 aqueous sulphuric acid, and the ethereal layer was separated and combined with ether-extracts of the aqueous layer. After being dried ($MgSO_4$), the ethereal solution was evaporated until the methylindan-1-ol (*ca.* 1·6 g.) crystallised.

7-Methylindan-1-ol had τ_{Me} (in CCl_4) 7·66 and 5-methylindanol 7·68.

Monomethylindenes ($C_{10}H_{10}$ requires C, 92·25; H, 7·75%).

Compound	B. p./mm.	n_D (temp.)	Found (%) C	Found (%) H	Compound	B. p./mm.	n_D (temp.)	Found (%) C	Found (%) H
4-Me	88°/13	1·5669 (26°)	92·1	8·0	7-Me	90°/15	1·5659 (25°)	92·15	7·7
5-Me	92°/20	1·5660 (24°)	92·3	7·8	2-Me[8]	90°/15	1·5629 (27°)	92·2	7·9
6-Me	89°/16	1·5641 (25°)	91·95	8·0	3-Me[8]	89°/17	1·5610 (26°)	92·45	8·0

Dehydration of methylindanols. The alcohol was boiled in benzene (50 c.c.) containing a few crystals of toluene-*p*-sulphonic acid for 30 min. The solution was cooled and shaken vigorously with water, and the aqueous layer was separated and extracted with ether. The ethereal extract was combined with the benzene solution and dried ($MgSO_4$), and the solvents were evaporated. Distillation of the residue under reduced pressure afforded the methylindene. Polymerisation of the 3-methylindene was prevented by addition of a few crystals of quinol and a little anhydrous potassium carbonate before distillation. 4- and 6-Methylindene, as liquid films, showed max. at 775 and 827 cm.$^{-1}$, respectively. 1,2,3- and 1,2,4-Trimethylbenzene respectively show max. at 775 and 815 cm.$^{-1}$.

7-*Methylbenzofuran.* 7-Methylcoumaran-3-one[9] was reduced with lithium aluminium hydride (see above), and the alcohol was dehydrated by repeated distillation to give 7-methylbenzofuran,[10] b. p. 83°/20 mm., n_D^{26} 1·5559 (Found: C, 81·9; H, 6·2. Calc. for C_9H_8O: C, 81·8; H, 6·1%), $\lambda_{max.}$ (in EtOH) 244, 272, 275, 282 mμ ($10^{-3}\varepsilon$ 19·0, 5·7, 5·6, 6·9).[11]

We gratefully acknowledge the use of a Varian A 60 spectrometer, on permanent loan to Professor D. H. R. Barton, F.R.S., from the Wellcome Trustees.

CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[*Received, July* 16*th*, 1962.]

---

[5] Elsner and Parker, *J.*, 1957, 592.
[6] von Miller and Rohde, *Ber.*, 1890, **23**, 1887.
[7] Young, *Ber.*, 1892, **25**, 2102.
[8] Ruzicka and Peyer, *Helv. Chim. Acta*, 1935, **18**, 676.
[9] Higginbotham and Stephen, *J.*, 1920, **117**, 1534.
[10] Stoermer, *Annalen*, 1900, **312**, 237.
[11] Andrisano and Pappalardo, *Gazzetta*, 1953, **83**, 108