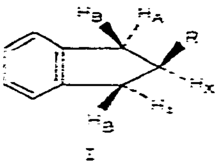
THE NMR SPECTRA OF SOME 2-SUBSTITUTED INDANES AND THEIR TRICARBONYLCHROMIUM COMPLEXES

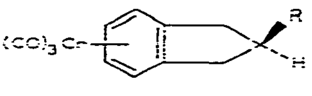
W. R. JACKSON, C. H. McMULLEN, R. SPRATT AND P. BLADON
Departments of Chemistry, Queen's University, Belfast (Northern Ireland) and University of Strathclyde, Glasgow (Scotland)

(Received April 13th, 1965)

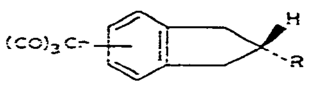
2-Substituted indanes are A_2B_2X systems but since $J_{AA'}$, $J_{AB'}$ and $J_{BB'}$ are all nearly zero the A_2B_2 part of the spectrum can be treated as $(AB)_2$[1]. The AB part of the spectrum consists of two quartets which were well separated when the spectra were determined at 100 Mcps and which occurred *ca.* 7.0 τ. The X proton is split into nine lines in the ideal case as in 2-indanol and its acetate. In all other cases the X proton was not resolved as its τ value became equal to that of the aromatic protons (in the acetate complexes) or to the AB protons (in methyl 2-indanecarboxylate and its complexes) whilst in the alcohol complexes further coupling with the hydroxylic proton gave an unresolved multiplet. The differences in the chemical shifts of the individual protons were large compared with their coupling constants and a first order analysis of the spectra $(AB)_2X$ was used. This approach has been justified in similar systems[2,3] and coupling constants obtained from spectra at different field strengths (40 and 100 Mcps) did not vary by more than 1 cps. The chemical shifts and coupling constants are recorded in Table 1. 2-Indanol and its acetate have J_{AX} *ca.* 6 and J_{BX} *ca.* 3.5. These values are similar to those reported for 2-aminoindane[3] and are consistent with a non-planar five-membered ring. The Karplus equations[4] may not be applicable to the indane ring system[3] but a $\cos^2\theta$ dependence of J(vicinal protons) with θ (dihedral angle) may still be approximately correct. If this is the case the distortion of the C_2 atoms from non-planarity must be in the direction that makes the substituent R adopt a *pseudo*-equatorial position and the proton H_X a *pseudo*-axial one (see IV).



I



II



III

Thus $\angle BX - \angle AX = 120°$. Distortion in the other sense (so that $\angle AX + \angle BX = 120°$) seems to be precluded by expectation of much smaller coupling constants even if an increased factor in the $a\cos^2\theta$ term were used, as has been suggested for six-membered ring compounds[5]. Distortion in the postulated sense would make the B (*trans* to X) protons lie more out of the plane of the benzene ring and the A (*cis* to X) protons lie more in the plane. The A protons would thus be deshielded while the B protons much less so, or even shielded by the ring current[6]. This explanation contrasts

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 2-MONOSUBSTITUTED INDANE DERIVATIVES AND FOR 2-BROMO-1-INDANONE

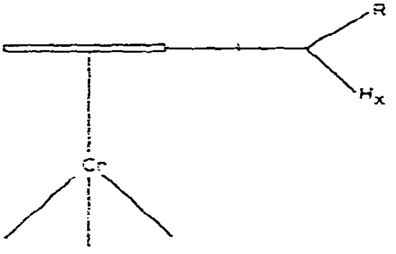
Indanes	H_A	H_B	H_X	*Other hydrogens*
2-Indanol (I, R = OH)	q 325 (6.3, 16.8) [6, 16]	q 281 (3.8, 16.8) [4, 16]	n 461	OH s 229 H Arom m *ca.* 735
trans-Complex (III, R = OH)	q 305 (6.5, 14.8)	q 282 (6.5, 14.8)	m *ca.* 480	OH (3.3) d 193 H Arom m *ca.* 540
cis-Complex (II, R = OH)	q 285 (1.3, 17) [2, 16.5]	q 320 (6, 17) [6, 16.5]	m *ca.* 460	OH (9) d 232 H Arom m *ca.* 540
2-Acetoxyindane (I, R = OAc)	q 338 (5.8, 17) [5.5, 17]	q 300 (3.4, 17) [4, 17]	n 558	CH_3CO s 203 H Arom m *ca.* 730
trans-Complex (III, R = OAc)	q 320 (7.2, 16) [7.4, 16]	q 286 (6.75, 16) [7.4, 16]	m *ca.* 530	CH_3CO s 205 H Arom m *ca.* 530
cis-Complex (II, R = OAc)	q 290 (1, 17) [2, 17.5]	q 321 (6, 17) [5, 17.5]	m *ca.* 530	CH_3CO s 209 H Arom m *ca.* 530
Methyl 2-indanecarboxylate (I, R = CO_2Me)	m *ca.* 335	m *ca.* 335	m *ca.* 335	CH_3OCO s 370 H Arom m *ca.* 730
trans-Complex (III, R = CO_2Me)	m 305–360	m 305–360	m 305–360	CH_3OCO s 376 H Arom m *ca.* 545
cis-Complex (II, R = CO_2Me)	m 300–360	m 300–360	m 300–360	CH_3OCO s 380 H Arom m *ca.* 550
2-Bromo-1-indanone	q 384 (7.3, 18.5)	q 342 (3.5, 18.5)	q 465	H Arom m *ca.* 730

s = singlet; d = doublet; n = nine lines (tripe triplets); q = quartet; m = unresolved multiplet; ( ) coupling constant in cps from 100 Mcps spectrum; [ ] coupling constant from 40 Mcps spectrum. Chemical shifts are in cps downfield from TMS measured at 100 cps for ease of comparison with previous work[3,7]. Agreement between coupling constants at 40 and 100 is reasonable, bearing in mind the instability of the compounds which precluded prolonged detailed examination under scale expansion facilities.

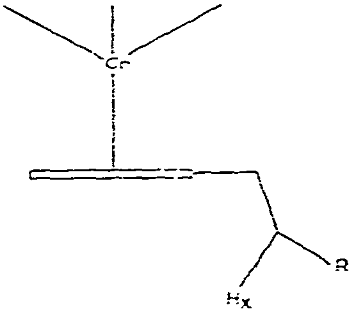
with a recent interpretation of the spectrum of 2-thioacetoxyindane[7] where the non-planarity of the five-membered ring was not considered. The B protons *cis* to the thioacetoxy group were considered to be preferentially deshielded by the carbonyl group. Such deshielding is very long range compared to that of the benzene ring and could not be used to explain the spectra of 2-hydroxy- and 2-aminoindanes. Long-range shielding associated with diamagnetic shielding of the carbon–carbon bonds α, β to the A and B protons and the exocyclic carbon–oxygen bond[8] may also contribute towards the difference in chemical shift between A and B protons.

trans-Tricarbonyl(2-indanol)chromium (III, R = OH) and its acetate (III, R = OAc) both have J_{AX}' and J_{BX}' 6 which would suggest that the ring is becoming more planar (see V). The A protons though are now more out of the plane of the benzene ring than in the parent ligands are now *cis* to the carbonyl chromium residue and could be expected to be deshielded by the group. The chemical shift of these protons thus remains similar to that in the parent ligands.

IV



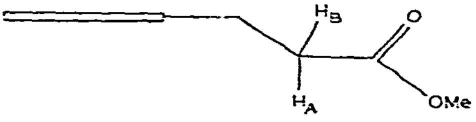
V



VI

If this suggestion is correct then in the corresponding *cis* compounds (II, R = OH, OAc) the B protons are now the ones at lower fields. Thus J_{AX} *ca.* 1 and J_{BX} *ca.* 6. These J values are consistent with further distortion of the ring in the same sense as in the parent ligand, *i.e.* as $\angle$ AX approaches 60° (where $\cos^2\theta = 0.25$). BX approaches 180° ($\cos^2\theta = 1$) and the preferred conformation of the molecule can be represented as in (VI). The infrared spectra of dilute solutions of the *cis*-alcohol compound (II, R = OH) showed intramolecular hydrogen bonding between the hydroxyl group and the chromium carbonyl residue[9]. The coupling constants from the NMR spectrum of this compound do not exclude the possibility of such a conformation in which C_2 must be displaced towards the chromium carbonyl residue but if a $\cos^2\theta$ dependence holds it does not seem to be a highly probable one. The concentrated solutions used in NMR spectroscopy encourage intermolecular hydrogen bonding and it appears probable that conformations with intramolecularly bonded hydroxyl groups do not significantly contribute to the overall structure in these solutions.

The spectra of methyl 2-indanecarboxylate (I, R = CO_2Me) and its *cis-* and *trans*-tricarbonylchromium complexes (II and III, R = CO_2Me) could not be analysed as the absorptions of all five A_2B_2X protons were superimposed. The five protons in the parent ester appeared as a distorted triplet from 6.7–6.9 τ which indicated that the chemical shifts of the A and B protons must have become nearly equivalent. This would be compatable with the ester adopting the conformation (VII) with the ester group staggered to the non-planar ring.



VII

The B protons, with less aromatic deshielding, could be expected to be preferentially deshielded by the carbonyl group and absorb at a similar field strength to the A protons.

Finally the relative signs of the coupling constants for vicinal and geminal hydrogens in the indane ring system were determined. The spin-decoupling method[5,10] cannot readily be applied to an A_2B_2X system and 2-bromo-1-indanone whose spectrum is of the ABX type with three widely separated quartets at 100 Mcps was used. Selective irradiation of the branches of the A and B quartets and observation of the appearance of the decoupled multiplet, lead to unambiguous assignment of like signs of coupling constants for vicinal hydrogens opposite to that for the geminal hydrogens, as was to be expected from previous work[5,11].

EXPERIMENTAL

The indane compounds have been previously described[9]. 2-Bromo-1-indanone, m.p. 36–37°, was obtained by the method of House *et al.*[12].

NMR spectra and double irradiation experiments

Solutions 5–10% (w/v) were prepared in deuterochloroform containing 0.5% tetramethylsilane as internal standard. Spectra were determined using a Perkin Elmer R.10 spectrometer at 40 Mcps and on a Varian H.R.100 spectrometer at 100 Mcps. Line positions were calibrated by the sideband technique.

TABLE 2

DOUBLE IRRADIATION OF 2-BROMO-1-INDANONE

Proton and lines irradiated	*Decoupling frequencies* ($\omega_2 - \omega_1$)	*Lines collapsed*
B (1 and 2)	133.8	11, 12
B (3 and 4)	115	9, 10
A (5 and 6)	87.8	10, 12
A (7 and 8)	69.8	9, 11

[*] The lines are numbered in the order of descending field strength.

The decoupling technique as applied to 2-bromo-1-indanone was similar to that described previously[5,13]. Spectra were observed in the first 2 kHz high field sideband (ω_1) and additional field modulation at a variable frequency (ω_2) was made available for selective nuclear saturation. The HX quartet always regained its shape when ($\omega_2 - \omega_1$) was increased beyond the optimum coupling value.

SUMMARY

The NMR spectra of 2-indanol and its acetate indicate that the cyclopentane ring is non-planar and that the substituent group adopts a *pseudo*-equatorial position. The cyclopentene ring in *cis*-tricarbonyl(2-indanol)chromium (II, R = OH) and its acetate (II, R = OAc) appears to be even more distorted but almost planar in the corresponding *trans*-compounds. No evidence could be found for strong intramolecular hydrogen bonds in the *cis*-alcohol compound. The spectra of methyl 2-indanecarboxylate and its carbonylchromium complexes are also discussed. Relative signs of coupling constants in the five-membered ring have been determined.

REFERENCES

1 B. Gestblom, R. A. Hoffman and S. Rodmar, *Acta Chem. Scand.*, 18 (1964) 1222.
2 D. H. Williams and N. S. Bhacca, *J. Am. Chem. Soc.*, 86 (1964) 2742.
3 W. E. Rosen, L. Dorfman and M. P. Linfield, *J. Org. Chem.*, 29 (1964) 1723.
4 M. Karplus, *J. Am. Chem. Soc.*, 85 (1963) 2870; *J. Chem. Phys.*, 30 (1959) 11.
5 R. U. Lemieux and J. W. Lown, *Can. J. Chem.*, 42 (1964) 893.
6 L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, London, 1959, p. 125.
7 A. A. Oswald, K. Griesbaum and W. Naegele, *J. Am. Chem. Soc.*, 86 (1964) 3791.
8 Ref. 6, p. 117.
9 W. R. Jackson and C. H. McMullen, *J. Chem. Soc.*, (1965) 1170.
10 R. Freeman and D. H. Shiffen, *Mol. Phys.*, 4 (1961) 321.
11 R. R. Fraser, R. U. Lemieux and J. D. Stevens, *J. Am. Chem. Soc.*, 83 (1961) 3901; F. A. L. Anet, *J. Am. Chem. Soc.*, 84 (1962) 3767; B. D. Nageswara Rao, J. D. Baldeschweiler and J. I. Musher, *J. Chem. Phys.*, 37 (1962) 2480.
12 H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, *J. Am. Chem. Soc.*, 82 (1960) 1452.
13 L. F. Johnson, *Technical Information Bulletin*, Vol. III, No. 3, Varian Associates.