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Preliminary communication

The nuclear magnetic resonance of π-cyclopentadienyltungsten hydride in a nematic phase: further evidence for pseudo-rotation and pseudo-symmetry

M.C. McIVOR
Imperial Chemical Industries Ltd., Petrochemical and polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire (Great Britain)

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The application of NMR of partially oriented molecules to structural problems in organometallic chemistry has hitherto received comparatively little attention[2,3], the main reasons are twofold. Firstly, many organometallic compounds are unstable in the solvents and the relatively high temperatures of the experiment (40–100°) and secondly, few molecules of potential interest are sufficiently symmetrical to yield structural information by this technique[1]. The recent introduction of liquid crystalline materials which are nematic at room temperature reduces the first difficulty somewhat, but careful selection of the compound to be studied is still necessary.

The complex π-$C_5H_5W(CO_3)H$ (I) has been studied in a partially oriented state by dissolving it in the liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-n-butyl aniline (MBBA).

The 220 MHz NMR spectrum (Fig.1) consists of two symmetrical multiplets consistent with an AX_5 system. The hydride region is upfield 12.9 ppm from the aryl resonance and shows the 1/5/10/10/5/1 sextet expected from coupling to the five equivalent cyclopentadienyl ring protons. With spectral accumulation this multiplet was found to be

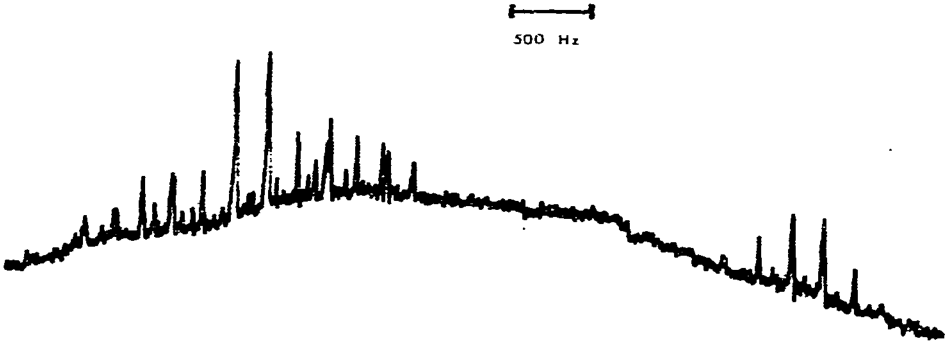

Fig.1. 220 MHz spectrum of *N*-(*p*-methoxybenzylidene)-*p*-n-butyl aniline.

superimposed on another of lower intensity assignable to the 14% of hydride protons involved in $^{183}W-^{1}H$ couplings. Spectral analysis using a modified version[4] of the computer programme LAOCN II gave values for the dipolar (*D*) and isotropic (*J*) coupling constants as shown in Table 1 and Fig.2.

TABLE 1

Parameter	Value	Parameter	Value
D_A	+ 204.5 Hz	J_A	+ 3.0 Hz
D_B	+ 48.3 Hz	J_B	+ 0.8 Hz
D_C	+ 81.3 Hz	J_C	0 Hz
D_D	+ 81.7 Hz	J_D	+ 36.7 Hz
D_E	~ 7 Hz	J_E	0 Hz
r_A/r_C	0.735	r_A/r_B	0.618

In examining the structural implications of this data it is convenient to begin by considering an axially symmetric structure as in Fig.2. in which the W–H bond lies along the symmetry axis of the cyclopentadienyl ring. For such a symmetrical molecule, the expressions for the dipolar couplings are all proportional to a single orientation parameter S_{33}, which can be eliminated to give in this case the ratios:

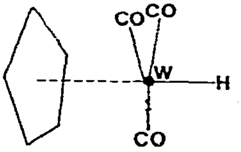

Fig.2.

$$\frac{D_B}{D_A} = \left\{ \frac{r_A}{r_B} \right\}^3 \quad (1)$$

and

$$\frac{D_C}{D_A} = \left\{ \frac{r_A}{r_C} \right\}^3 \cdot (3\cos^2 \phi - 1) \quad (2)$$

where ϕ is the semi-angle of the cone defined by the six protons.

The value obtained for r_A/r_B on substituting the experimental data into Eq.(1) is 0.618, a result which merely confirms that the cyclopentadienyl protons form a regular pentagon. When reasonable values for r_A, r_C and ϕ, based on X-ray crystallographic data[5] are substituted in Eq. (2), there is serious disagreement with the observed D_C/D_A, the experimental value being much larger than the predicted one. Furthermore, no reasonable distortion of the assumed structure, by shortening the W–H bond length and by assuming the ring protons to be inclined out of the plane of the ring, is sufficient to bring the predicted ratio close to that observed. The obvious conclusion is that the axially symmetric model is incorrect, and the W–H bond is inclined towards the cyclopentadienyl ring in close analogy to the structure found by Bennett and Mason[6] for π-$C_5H_5Mo(CO)_3C_2H_5$ (II).

For this less symmetrical structure of (I) the theoretical expressions for the dipolar couplings involve five independent orientation parameters (1) and it is no longer possible to obtain an expression for D_C/D_A involving only the geometrical constants of the molecule. Because of the ring "whizzing" which is well known to occur in π-C_5H_5 complexes, D_A and D_B are averaged over all possible configurations within the plane of the ring, and consequently Eq. (2) still holds.

Another consequence of this lower symmetry is that D_C/D_A is expected to depend on the orientation parameters and any change in the orientation conditions, *e.g.* by varying the temperature or the concentration or the solvent, is expected to cause a change in the ratio D_C/D_A. An observation in this work is that for a range of concentrations in MBBA and a temperature variation from 12–30° the ratio changed by less than 1% on either side of its mean and showed no systematic trend. This compares with a systematic change from 8.25 to 10.16 for the analogous ratio in 1,1-dichloroethane when examined under the same conditions. The absence of a marked variation for (I) strongly suggests that, notwithstanding its apparently low symmetry, the molecular orientation is determined, to a good approximation, by a single orientation parameter S_{33}.

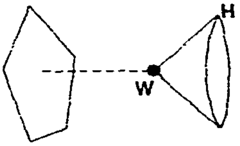

Fig.3.

It is interesting to consider the consequences if we now consider a different model for (I) in which the hydride proton, although lying off the axis of the cyclopentadienyl ring, is in effect uniformly distributed around a circle centred on this axis, perhaps as a result of some rapid orbital motion (Fig.3).

We then have

$$\frac{D_C}{D_A} = r_A^{\ 3} \left\langle \frac{3\cos^2\phi - 1}{r_C^{\ 3}} \right\rangle \qquad (3)$$

where the brackets $\langle\ \rangle$ imply an average over the circumference of the circle around which H moves. A reasonably good approximation to this average is obtained by taking three positions whose dihedral angles relative to a given cyclopentadienyl proton are 0, 120 and 240° respectively. Applying this model to the experimentally observed D_C/D_A, the half-angle of the cone described by the W–H bond was calculated as 53 ± 3°. this may be compared with an analogous angle in (II) of 69.6°, the difference being perhaps a result of the relative bulk of the ethyl ligand compared with the hydrido group.

The model implied in Fig.3 is closely related to the fluxional behaviour proposed by Faller *et al.*[7] to account for the temperature dependence of the isotropic phase NMR spectrum of (I).

It is surprising, however, that the resulting pseudo-rotation in the nematic phase is apparently so rapid as to produce pseudo-symmetry. This would require the pseudo-rotation to be rapid compared with the time for molecular orientation in the nematogen.

There are other possible explanations for the predominance of the S_{33} orientation parameter which involve other orientation parameters being taken into account but fortuitously having near zero values. ^{13}C labelling experiments would allow this theory to be examined and are to be included in a future programme of work which will also include studies of related molecules.

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