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Natural Abundance ^{13}C Magnetic Resonance of Oriented 1,3,5-Trichlorobenzene

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Abstract—The natural abundance ^{13}C magnetic resonance spectrum of oriented 1,3,5-trichlorobenzene is reported. The geometrical data calculated from the anisotropic ^{13}C—H-couplings are not in agreement with the assumption that there is no influence of isotopic substitution on the orientation and no anisotropy in the indirect couplings.

1. Introduction

Structural analysis of partially oriented molecules by nuclear magnetic resonance has been confined, until now, mainly to nuclei of high sensitivity and high natural abundance, i.e. proton and fluorine-19.(1) However, in organic molecules, the positions of carbon nuclei may be more interesting. So far, only a few measurements including ^{13}C—H-direct coupling constants have been reported.(2–8) In this work, it is shown that, with the NMR equipment available at present, it is possible to obtain natural abundance ^{13}C magnetic resonance spectra of oriented molecules which are not obscured by strong lines as may be the case with ^{13}C satellites in proton resonance.

2. Experimental

About 15% (w/w) of 1,3,5-trichlorobenzene was dissolved in one part MeO—Ph—CH=N—Ph—OCOPr(9) and one part

$$C_5H_{11}COO—Ph—COO—Ph—OEt.^{(10)}$$

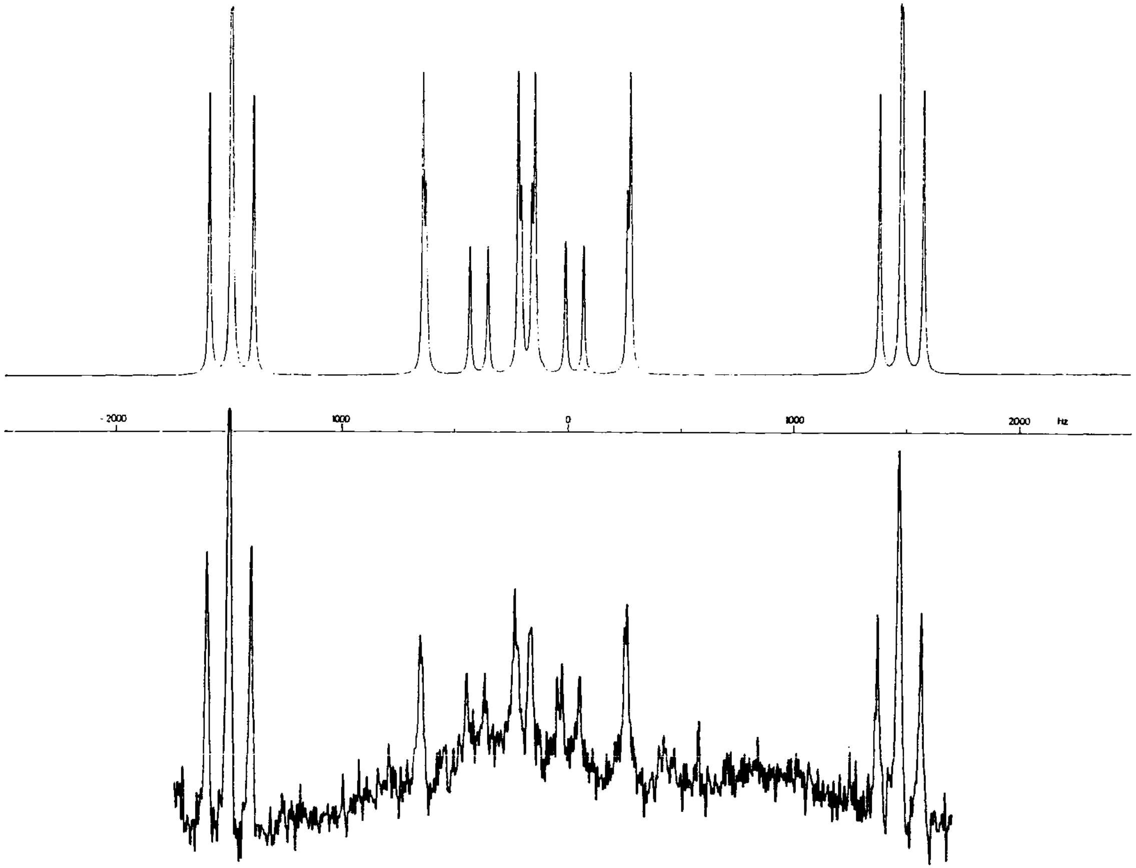

Figure 1. ^{13}C spectrum of oriented 1,3,5-trichlorobenzene.

This mixture exhibits an equilibrium between a nematic and an isotropic liquid phase, depending on temperature, the isotropic phase containing more solute. At 30 °C about 90% (v/v) is nematic. The spectra were taken at ambient temperature of about 26 °C.

The ^{13}C spectrum is shown together with the computed spectrum in Fig. 1. It was obtained on a Bruker HFX-90/18 spectrometer operating at a frequency of 22.63 MHz in the Fourier Transform mode. The measurement was performed on a 10 mm non-spinning sample containing a 3 mm D_2O capillary for field stabilization. 86 000 pulses of 40 μ sec width were applied with a repetition frequency of 0.4 seconds. The free induction decay was recorded on 4 *k* addresses of a Fabritek 1074 signal averager and then Fourier transformed on a Digital Equipment PDP-8L Computer.

The outer triplets are due to molecules containing ^{13}C neighbouring H; the center multiplet is due to molecules containing ^{13}C neighbouring Cl. A line width of 10 Hz was used in the calculated spectrum. Actually, it is smaller in the centre, and larger in the outer part. Five of these spectra were evaluated to get the direct couplings shown in Table 1. The error in the measurement of the line positions is estimated to 1.5 Hz.

TABLE 1

Coupling nuclei	12	14	15	24	25
J	1.8	172.5	-0.5	5.3	-0.2
D(^{1}H)	-106.0 ±0.4	-1570.9 ±0.3	-211.2 ±0.3	-53.6 ±0.4	-37.4 ±0.8
D(^{13}C)	(-106.0)$^{(a)}$	-1571.0 ±0.5	-211.1 ±0.4	-53.4 ±0.4	-36.3 ±0.8
r	(4.278)$^{(b)}$	1.099 ±0.002	2.146 ±0.004	3.391 ±0.013	3.842 ±0.033
x	—	1.371 ±0.002	—	1.397 ±0.016	—
y	—	—	1.406$^{(c)}$ ±0.052	—	1.372 ±0.033

(a) value taken from ^{1}H resonance.

(b) $r_{12} = z\sqrt{3}$.

(c) large error is due to the fact that $\sphericalangle 152$ is close to 90°.

As the analysis of the ^{13}C spectrum does not furnish accurate values of D_{12} (for numbering of the nuclei see Fig. 2) in addition proton resonance measurements were done of the ^{13}C satellites on a Varian HR 100 with the usual side-band technique. The standard deviation in the line positions, calculated from at least ten spectra, was 1.5 Hz. The line width was 7 to 8 Hz. Because of a temperature difference between the ^{13}C and the ^{1}H measurements, the direct couplings obtained from ^{1}H resonance were corrected for the same D_{14} as in ^{13}C resonance (see Sec. 4).

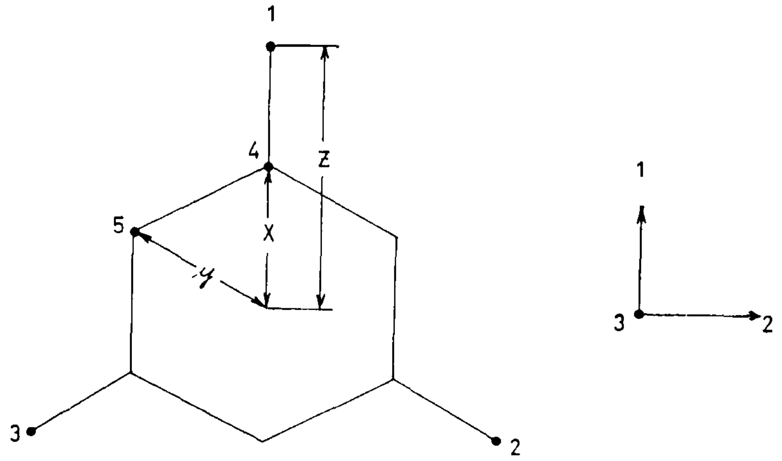

Figure 2. Numbering of nuclei and coordinates in 1,3,5-trichlorobenzene.

3. Indirect Couplings

The indirect couplings J_{12}, J_{14} and J_{24} were taken from measurements in isotropic solvents. The signs of coupling constants of these types are generally agreed to be positive. J_{14} was determined to be 172.2 Hz in $CBrCl_3$(11) and in $CDCl_3$.(12) Our own measurements gave 172.3 Hz in CCl_4 and 172.7 Hz in C_6D_6. Similarly, J_{12} and J_{24} did not show a significant solvent dependence.

J_{15} and J_{25} are too small to be observed in the proton spectra. So J_{15} was estimated to -0.5 Hz according to a correlation between $^{1}J_{CH}$ and $^{2}J_{CH}$.(13) J_{25}, like J_{12}, is similar to the allylic four-bond coupling, for which theoretical treatments were given by Barfield.(14,15)

It was found in the INDO-MO-treatment(15) that in a planar fragment a cisoid coupling (corresponding to J_{25}) should be 2.8 Hz more negative than a transoid coupling (corresponding to J_{12}).

However, comparison with experimental data shows that, while transoid couplings are reproduced very nicely by the theory, cisoid couplings come out, on an average, 0.4 Hz too negative. Therefore it is estimated that J_{25}, if both coupling nuclei were protons, should be about $J_{12} - 2.4 = -0.6$ Hz. A corresponding H—C-coupling of about -0.2 Hz is obtained from the H—H-coupling by multiplication with

$$\gamma_C \cdot \varphi_0^2(C)/\gamma_H \cdot \varphi_0^2(H).^{(16)}$$

That this procedure yields roughly the correct magnitude has been shown for various CH-couplings.(17)

4. Direct Couplings

The spectra were analysed with the LAOCOON II programme(18) modified for direct couplings according to the procedure of Diehl *et al.*(19) The degree of orientation was postulated to be independent of ^{13}C substitution.

Therefore, D_{12} was taken directly from ^{1}H resonance as one third of the splitting in the intense triplet due to molecules containing no ^{13}C. To correct for the same degree of orientation as in the ^{13}C resonance measurement, this value was multiplied by $D_{14}(^{13}C)/D_{14}(^1H)$, where $D_{14}(^{13}C) = 1570.4$ Hz was obtained from ^{13}C resonance by iteration on D_{12}, D_{14} and D_{24}. In the following steps of the analysis, the corrected value of D_{12} (106.0 Hz) was fixed and sets of δ_4, D_{14}, D_{24} and δ_5, D_{15}, D_{25} were varied. The new value of D_{14} thus obtained differs only a few tenths of a hertz from the first one. To get comparable values, all direct couplings from ^{1}H resonance were multiplied by the same factor $D_{14}(^{13}C)/D_{14}(^1H)$ and are shown along with the ^{13}C values in Table 1.

The $D(^1H)$ values in the table result from averaged line positions from ten or more spectra. The $D(^{13}C)$ values are averaged from the evaluations of five computer read-outs. The standard deviation of the spectral fit was 0.7 Hz for the ^{1}H spectra and 1.3 Hz for the ^{13}C spectra in most cases.

The errors quoted in the table are the probable errors calculated by LAOCOON II. They were checked according to Diehl *et al.*,(20) but this yielded smaller errors in all cases.

5. Internuclear Distances

From the direct couplings, relations of internuclear distances may be calculated.(1) To start, z (see Fig. 2) was set to 2.470 Å, which is the sum of $r_{CH} = 1.083$ Å and $r_{CC} = 1.387$ Å from an X-ray analysis(21) and slightly lower than the ortho H—H-distance $r_{HH} = 2.481$ Å in benzene.(22)

Z and D_{12} yield the degree of orientation $S_{11} = 0.0691 \pm 0.0003$ (for the ^{13}C resonance experiment). From S_{11} and the average of $D(^1H)$ and $D(^{13}C)$ the corresponding internuclear distances were calculated. Now, it was assumed the molecule has D_{3h} symmetry. With the resulting geometrical relations x from $D_{14}(\equiv x_{14})$ and from $D_{24}(\equiv x_{24})$ and y from $D_{15}(\equiv y_{15})$ and from $D_{25}(\equiv y_{25})$ (see Fig. 2) was calculated to check the consistency of the measurements and the validity of the basic assumptions. All these distances are presented in Table 1. The errors quoted are the sums of the errors due to the errors in the two direct couplings used in the calculation of each distance. No vibrational corrections were applied, as this in general does not lead to a better agreement with molecular geometries obtained from other methods than NMR.(23)

6. Discussion

If all previous assumptions are valid, on ground of purely geometrical arguments, one would expect $x_{14} = x_{24}$ and $y_{15} = y_{25}$ and a slight difference between x and y due to deviation of the carbon skeleton from hexagonal symmetry. This is clearly not the case and it is found that the two values in both cases are different and their average comes very close to the X-ray value.

There are two possible reasons for these discrepancies:

1. Different orientational behaviour for the three kinds of molecules (no ^{13}C, ^{13}C neighbouring H, ^{13}C neighbouring Cl). For monodeuterobenzene, an isotopic influence of this kind was found by Diehl *et al.*(20)

2. Anisotropies in the indirect couplings. Recently, these anisotropies have been subject of much discussion.(6,23–26) It does not seem reasonable, however, to try a decision on these possibilities on the basis of the values presented in this work, because the inaccuracies of the measurements are too large for a safe conclusion.

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REFERENCES

1. For a review, see Diehl, P. and Khetrapal, C. L., in " NMR-Basic Principles and Progress ", Vol. 1, Springer-Verlag, Berlin 1970.
2. Snyder, L. C. and Meiboom, S., *J. Chem. Phys.* **47,** 1480 (1967).
3. Spiesecke, H., *Z. Naturforsch.* **23a,** 467 (1968).
4. Englert, G. and Saupe, A., *Mol. Cryst. and Liq. Cryst.* **8,** 233 (1969).
5. Meiboom, S. and Snyder, L. C., *J. Chem. Phys.* **52,** 3857 (1970).
6. Krugh, T. R. and Bernheim, R. A., *J. Chem. Phys.* **52,** 4942 (1970).
7. Spiesecke, H., in " Liquid Crystals and Ordered Fluids " 123, Plenum Press 1970.
8. Morishima, I., Mizuno, A. and Yonezawa, T., *J. Amer. Chem. Soc.* **93,** 1520 (1971).
9. Kelker, H. and Scheurle, B., J. Phys. (Suppl. Colloq. C 4), **30,** C4 104 (1969).
10. Kelker, H. and Scheurle, B., private communication.
11. Hutton, H. M., Reynolds, W. F. and Schaefer, T., *Can. J. Chem.* **40,** 1758 (1962).
12. Freeman, R., *J. Chem. Phys.* **43,** 3087 (1965).
13. Sackmann, E. and Dreeskamp, H., *Spectrochimica Acta* **21,** 2005 (1965).
14. Barfield, M., *J. Chem. Phys.* **41,** 3825 (1964).
15. Barfield, M., *J. Amer. Chem. Soc.* **93,** 1066 (1971).
16. Dreeskamp, H., *Z. Naturforsch.* **19a,** 139 (1964).
17. Schumann, C. and Dreeskamp, H., *J. Magn. Res.* **3,** 204 (1970).
18. Castellano, S. and Bothner-By, A. A., *J. Chem. Phys.* **41,** 3863 (1964).
19. Diehl, P., Khetrapal, C. L. and Kellerhals, H. P., *Mol. Phys.* **15,** 333 (1968).
20. Diehl, P. and Khetrapal, C. L., *Can. J. Chem.* **47,** 1411 (1969).
21. Milledge, H. J. and Pant, L. M., *Acta Cryst.* **13,** 285 (1960).
22. Langseth, A. and Stoicheff, B. P., *Can. J. Phys.* **34,** 350 (1956).
23. Bulthuis, J. and MacLean, C., *J. Magn. Res.* **4,** 148 (1971).
24. Buckingham, A. D. and Love, I., *J. Magn. Res.* **2,** 338 (1970).
25. Buckingham, A. D. and Dunn, M. B., *Mol. Phys.* **19,** 721 (1970).
26. Spiesecke, H. and Saupe, A., *Mol. Cryst. and Liq. Cryst.* **6,** 287 (1970).