Notizen

NMR Spectrum of Oriented 2-chloroethanol

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Various spectroscopic methods predict that an intramolecular hydrogen bonding[1] is operating in 2-chloroethanol. The aim of this work is to report the NMR spectrum of oriented 2-chloroethanol (Figure 1). The nematic phase Merck V was used and the spectrum (Fig. 2) was recorded with a Jeol PS-100 instrument. All information about the coupling of the carboxylic proton (H_5) is lost because of its exchange with the nematic phase. The system has therefore effectively four spins. The spectrum was analysed with a modified[2] LAOCOONOR program. Two sets of coupling constants can be deduced that equally well reproduce the experimental data:

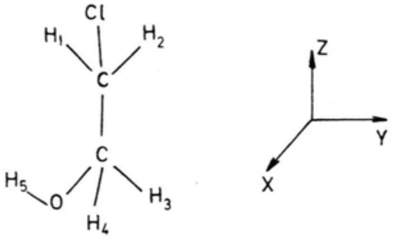

Fig. 1. Scheme of 2-chloroethanol.

a) System of four spins with C_{2v} symmetry. The calculated direct and indirect coupling constants are given in Table 1. The interatomic distances are connected with the coupling constants[3] and the following values are obtained:

$$\frac{r_{34}}{r_{12}} = 1; \quad \frac{r_{13}}{r_{12}} = 2.42 \quad \text{and} \quad \frac{r_{23}}{r_{12}} = 2.62 .$$

The last two values are much higher than the values (1.40 and 1.69) calculated from microwave data. Therefore the analysis with the above described set of coupling constants is unappropriate.

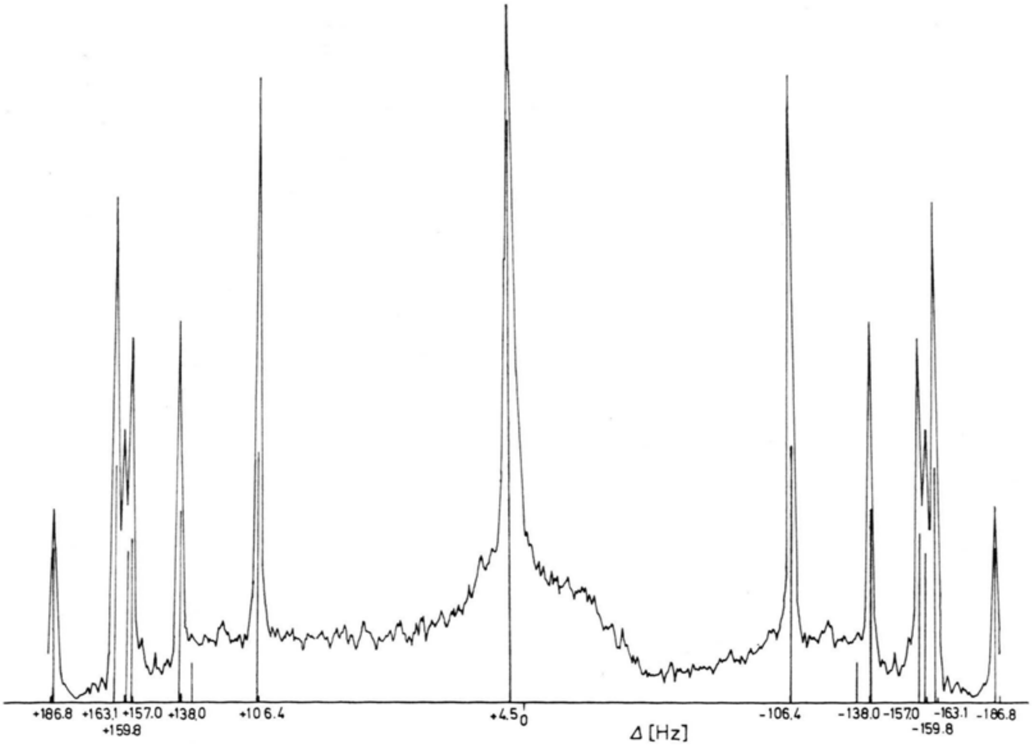

Fig. 2. Observed (curve) and calculated (lines) spectrum.

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Table 1. Direct (D) and indirect (I) coupling constants (Hz).

ij	12	13	14	15	23	24	25	34	35	45
I_{ij} [a]	0.0	13.8	13.8	0.0	13.8	13.8	0.0	0.0	0.0	0.0
D_{ij} [a]	983.2	−103.2	−166.0	0.0	−166.0	−103.2	0.0	977.5	0.0	0.0
I_{ij} [b]	0.0	−10.5	−10.5	0.0	−10.5	−10.5	0.0	0.0	0.0	0.0
D_{ij} [b]	1056.7	−118.0	−118.0	0.0	−118.0	−118.0	0.0	910.4	0.0	0.0

[a, b] See text and Fig. 1 for proton numbering.

b) The second set coupling constants (Table 1) predicts $D_{23} = D_{14} = D_{24} = D_{13}$ or rotation of CH_2Cl group. This set and the geometric parameters from Ref. 1 give the following S matrix elements (X axis is along $H_3 - H_4$):

$$S_{xx} = -3.86 \cdot 10^{-2}; \qquad S_{yy} = -6.14 \cdot 10^{-2}; \qquad S_{zz} = 10.0 \cdot 10^{-2}.$$

The preferential orientation of the molecule is with C-C bond along magnetic field.

In the oriented spectrum of 2-chloroethanol many features observed e. g. in microwave spectroscopy are missed. The carboxylic proton, due to its exchange with the nematic phase, does not stabilize the gauche-gauche form, many rotamers are therefore possible, and in NMR spectrum this is simplified as the rotation of the CH_2Cl group.

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[2] P. Diehl, C. L. Khetrapal and H. P. Kellerhals, Mol. Phys. **15**, 333 [1968].

[3] P. Diehl and C. L. Khetrapal, "NMR Basic Principles and Progress", Vol. 1, pp. 1−97, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin 1969.