

Notizen

NMR Spectrum of Oriented 2-chloroethanol

D. Pumpernik and A. Azman

Chemical Institute Boris Kidrič, University of Ljubljana,
Ljubljana, Yugoslavia(Z. Naturforsch. **29a**, 527–528 [1974];
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Various spectroscopic methods predict that an intramolecular hydrogen bonding¹ 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

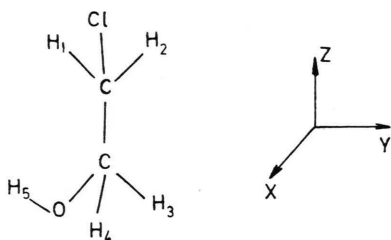


Fig. 1. Scheme of 2-chloroethanol.

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 modified² LAOCOONOR program. Two sets of coupling constants can be deduced that equally well reproduce the experimental data:

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 constants³ 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 inappropriate.

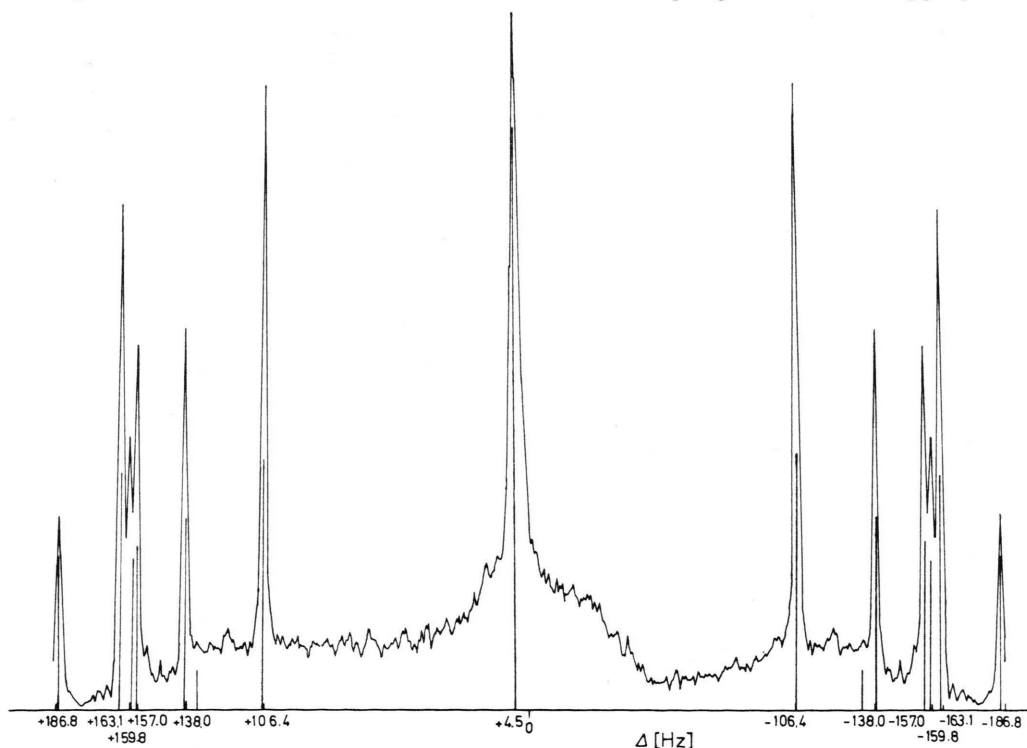


Fig. 2. Observed (curve) and calculated (lines) spectrum.

Reprint requests to Dr. A. Azman, Chemical Institute, Boris Kidrič, University of Ljubljana, Murnikova 6, Ljubljana, Yugoslavia.



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

<i>ij</i>	12	13	14	15	23	24	25	34	35	45
<i>I_{ij}</i> ^a	0.0	13.8	13.8	0.0	13.8	13.8	0.0	0.0	0.0	0.0
<i>D_{ij}</i> ^a	983.2	-103.2	-166.0	0.0	-166.0	-103.2	0.0	977.5	0.0	0.0
<i>I_{ij}</i> ^b	0.0	-10.5	-10.5	0.0	-10.5	-10.5	0.0	0.0	0.0	0.0
<i>D_{ij}</i> ^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):

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

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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¹ R. G. Azrak and E. B. Wilson, J. Chem. Phys. **52**, 5299 [1970].

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.