

Low Resolution Microwave Spectra (LRMW) of 1,3-Dichloroacetone, a Conformational Study

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LRMW spectra of 1,3-dichloroacetone (C₂H₄Cl₂O), its perdeuterio- and ¹⁸O-species were obtained and analyzed. The observed low intensity of the bands and the (B+C) values are consistent with the presence of one conformer, which is either *O-cis,trans*, *O-cis,skew* or *O-gauche,skew*(-), probably in rather low concentration. No other conformers were observed, and a microwave investigation at high resolution was unsuccessful.

1,3-Dichloroacetone, *sym* dichloroacetone (DCA) was shown by X-ray diffraction¹ to have the *O-cis,cis* conformation in the crystal phase, see Fig. 1.

Infrared data² showed that two or three conformers of DCA exist in the liquid, in solution and in the gas phase, but the separate conformers were not conclusively assigned.

Parallel to a reinvestigation of the vibrational spectra of DCA and its perdeuterio species³ it was decided to obtain the microwave spectra and try to find one or more of the conformers in the gas phase. Such independent data would be helpful in the rather complicated vibrational analysis.

EXPERIMENTAL

Compounds. The H₄ sample of 1,3-dichloroacetone was a Fluka *purum* product, which was distilled before use.

The D₄ sample was made by exchange with (CD₂)₂CO,⁴ as described in Ref. 3, and isolated by single plate distillation. Mass spectra showed the D enrichment to be ca. 93 %, consistent with the LRMW result.

The ¹⁸O sample was prepared by exchange of 250 mg 1,3-dichloroacetone and 100 μl 90 % enriched H₂¹⁸O in a high vacuum system. The

exchange time was 48 h and the temperature 20–22 °C, except that the mixture was heated twice to 45 °C for ½ h to melt dichloroacetone. 220 mg enriched 1,3-dichloroacetone was isolated by single plate distillation. Mass spectra showed the ¹⁸O enrichment to be ca. 47 %, consistent with the LRMW result.

Spectrometer. The LRMW spectra were measured on a Hewlett-Packard Model 8460A MRR spectrometer, at -10 °C in the region 18–40 GHz (in Göteborg) and at room temperature in the region 26.5–40 GHz (in Copenhagen), with a sample pressure between 50 and 80 mTorr. Several Stark voltages were used and the measurements were made at 1000–1400 V (2000–2800 V/cm) at sweep rates of 10 to 2 MHz/s.

LRMW spectra.⁵ The three isotopic samples of DCA gave a total of six similar type I spectra,⁶ *i.e.* *a*-type *R*-bands. The bands were of rather low intensity, but quite narrow, 150–170 MHz, and could be measured to ±10 MHz. No other band types⁶ were observed. The relative intensity of the bands of the ³⁵Cl₂, ³⁵Cl³⁷Cl, and ³⁷Cl₂ species was expected to be 9:6:1, which was confirmed for the two most abundant species; but no ³⁷Cl₂ bands could be assigned. The bands of the ³⁵Cl(1)³⁷Cl(3) and ³⁷Cl(1)³⁵Cl(3) species were neither split nor broader than the ³⁵Cl₂ bands. The two chlorine atoms must therefore be either symmetrically equivalent or the two chlorine positions in DCA must have very similar coordinates, see below.

The following (B+C) values were obtained from the relation (ν MHz)/(*J*+1): 2038.2, 1990.7, 1992.2, 1947.0, 2024.4, and 1977.6 (all ±0.5) MHz for the parent (C₂H₄³⁵Cl₂¹⁶O), and the ³⁷Cl, D₄, D₄³⁷Cl, ¹⁸O, and ¹⁸O³⁷Cl species, respectively.

MODEL CONSIDERATIONS

Little is known of the exact geometry of halogenated acetones and their conformation

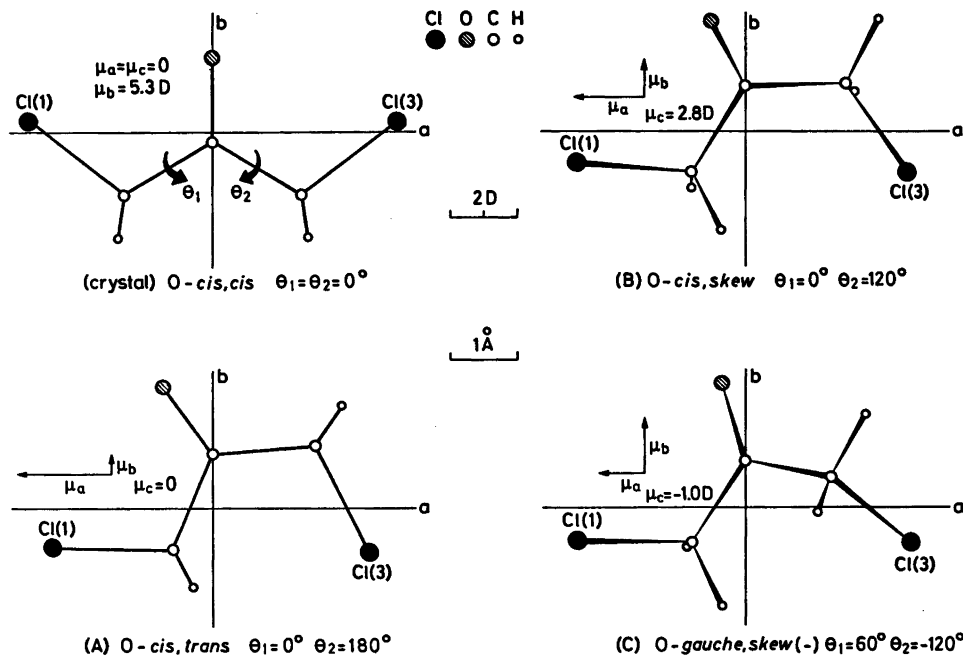


Fig. 1. Some of the possible conformers of 1,3-dichloroacetone and definition of the dihedral angles θ_1 and θ_2 .

Table 1. Geometrically possible conformers of 1,3-³⁵Cl₂-acetone, their point group symmetry and model values of B+C (MHz), κ , μ_a (D), μ_{total} (D), and Cl,Cl distance (Å). The dihedral angles θ_1 and θ_2 (degrees) are defined in Fig. 1.

θ_1^a	θ_2	Point group ^b	B+C	κ	μ_a	μ_{total}	Cl,Cl	Consistent with LRMW
0	0	C_{2v}^b	(1700)	-0.98	(0)	5.3	5.4	—
0	60	C_1	(1800)	-0.99	(0.7)	4.8	5.3	—
0	120	C_1	2000	-0.94	2.1	3.6	4.9	(B), Fig. 1
0	180	C_s^{ab}	2100	-0.88	2.8	2.9	4.7	(A), Fig. 1
60	60	C_s^{bc}	2100	-0.95	(0)	4.9	4.6	—
60	120	C_1	(2500)	-0.7	1.7	4.0	4.0	—
60	-120	C_1	2000	-0.93	1.4	2.3	4.9	(C), Fig. 1
60	180	C_1	(2400)	-0.7	2.3	2.5	4.2	—
120	120	C_s^{bc}		(+0.9)	(0)	3.3	(2.9)	—
120	180	C_1		(+0.8)	(0.4)	1.7	(2.9)	—
180	180	C_{2v}^a		(-0.4)	1.1	1.1	(2.0)	—
60	-60	C_s^b	(1750)	-0.99	(0)	3.7	5.4	—
120	-120	C_s^b	(2600)	(-0.6)	(0)	0.5	4.1	—
Estimated model uncertainty			± 150			± 0.5	± 0.2	

^a Models with (θ_1, θ_2) and $(-\theta_1, -\theta_2)$ are mirror images and give the same rotational constants etc.
^b a, b, c are the principal inertial axes.

in the gas phase. A recent microwave paper on 1,3-difluoroacetone⁷ showed that the intensity of the observed spectrum is consistent with a 20–30 % content of the *O-cis, trans* conformer, whereas the spectrum of other conformer(s) could not be assigned, probably due to small dipole moment(s).

Several models were tried in an attempt to assign the LRMW results to one conformer of DCA. The κ correction of $(B+C)$ to $B_0 + C_0$,⁸ which is less than 0.5 % (or 10 MHz) when $\kappa < -0.8$, has been ignored throughout the calculations, since we consider the model uncertainty on $B+C$ to be about 150 MHz or 5–10 %. The experimental uncertainty ± 0.5 MHz is much less than either of these.

A summary of the model calculations is given in Table 1. Bond lengths and bond angles were assumed to be close to the microwave results for acetone⁹ and ethyl chloride¹⁰ and the X-ray results for DCA.¹ The two dihedral angles $\theta_1 = \text{Cl}(1)\text{C}(1)\text{C}(2)\text{O}$ and $\theta_2 = \text{Cl}(3)\text{C}(3)\text{C}(2)\text{O}$ were given values of 0, ± 60 , ± 120 , or 180° , referred to as *O-cis*, *O-gauche*(\pm), *O-skew*(\pm), or *O-trans*, with θ positive when Cl is above the CCC plane, see Fig. 1. The dipole moments and their components were estimated for each model by vectorial addition of partial dipole moments 2.9 and 2.0 D along the bonds $\text{C}=\text{O}$ ($+\rightarrow-$) and $\text{C}-\text{Cl}$ ($+\rightarrow-$), respectively.

Of the thirteen geometrically possible models with different combinations of θ_1 and θ_2 , see Table 1, ten models could be excluded, since they did not fulfil one or more of the

following criteria (i) $1800 \text{ MHz} < B+C < 2300 \text{ MHz}$, (ii) $\kappa < -0.7$, (iii) $\mu_a > 1\text{D}$, and (iv) a Cl,Cl distance $> 3.5 \text{ \AA}$ (twice the van der Waals radius of chlorine). The excluded model values are given in parentheses in Table 1.

Models for three of the conformers, *i.e.* *O-cis,trans*, *O-cis,skew*, and *O-gauche,skew(-)*, fulfil the four criteria, and have $(B+C)$ values rather close to the experimental result given above. Slight variations in bond lengths and angles could bring either of them in perfect agreement with the experimental $(B+C)$.

The experimental values for the relative change in $(B+C)$ by isotopic substitution, $\Delta(B+C)/(B+C)$, are consistent with the same three models (within the model uncertainty), an example is given in Fig. 2.

The low intensity of the LRMW spectra could be explained by a low concentration of the conformer and/or a small a-component of the dipole moment.

INFORMATION FROM ISOTOPIC SPECIES

Although only $(B+C)$ values were observed for DCA and for its isotopic species, $(B'+C')$, some information on the possible structure of DCA can be obtained in the following way.

The change in the two moments of inertia I_b and I_c by isotopic monosubstitution is $\Delta I_b \cong \mu(a^2 + c^2)$ and $\Delta I_c \cong \mu(a^2 + b^2)$, where μ is the reduced mass and a , b , and c are the coordinates.¹¹ This is an approximation, since a slight rotation of the axes has been ignored. The

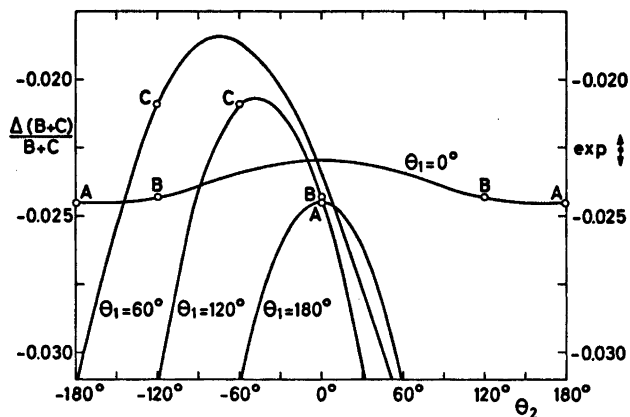


Fig. 2. Relative change in $B+C$, $\Delta(B+C)/(B+C)$, by D_2 substitution in 1,3- $^{35}\text{Cl}_2$ -acetone as a function of the dihedral angles θ_1 and θ_2 .

validity of the approximation was checked with model values. The relative change in $(B+C)$ by substitution is then given by

$$\frac{(B'+C')-(B+C)}{B+C} = \frac{\Delta(B+C)}{B+C} = \frac{-\mu}{B+C} \left\{ \left(\frac{B'}{I_b} + \frac{C'}{I_c} \right) a^2 + \frac{C'}{I_c} b^2 + \frac{B'}{I_b} c^2 \right\}$$

When model values of the factors to the squared coordinates for ^{37}Cl substitution are inserted, we get the following relation between the chlorine a - and b -coordinates for the (A) conformer (where the c -coordinate is assumed to be zero by symmetry, see Fig. 1), $-(4.1a_{\text{Cl}}^2 + 1.6b_{\text{Cl}}^2)10^{-3} = -0.0233 \pm 0.0005$ (exp. value and uncertainty), which gives the correlated coordinates $a_{\text{Cl}} = 2.35 \pm 0.05 \text{ \AA}$ and $b_{\text{Cl}} = 0.6 \pm 0.2 \text{ \AA}$. The coordinate uncertainty includes the estimated model uncertainty in the factors as well as the experimental uncertainty in $\Delta(B+C)/(B+C)$. For the (B) and (C) conformers, see Fig. 1, a similar relation (and the same experimental value) gives the correlated coordinates $a_{\text{Cl}} = 2.42 \pm 0.05 \text{ \AA}$, $b_{\text{Cl}} = 0.5 \pm 0.2 \text{ \AA}$, and $c_{\text{Cl}} < 0.3 \text{ \AA}$. The resulting average chlorine coordinates for the three models are $a_{\text{Cl}} = 2.4 \pm 0.1 \text{ \AA}$, $b_{\text{Cl}} = 0.5 \pm 0.2 \text{ \AA}$, and $c_{\text{Cl}} < 0.3 \text{ \AA}$. This is also an average for the two symmetrically inequivalent but geometrically similar positions in the molecule, since we have only one experimental $(B+C)$ value for the two $^{35}\text{Cl}/^{37}\text{Cl}$ species.

As seen in Fig. 1, the three conformers (A), (B), and (C) have their chlorine atoms in similar positions, and the result can therefore not be used to discriminate between the conformers. An upper limit to the Cl,Cl distance is $4.8 \pm 0.2 \text{ \AA}$.

For ^{18}O substitution a set of correlated oxygen coordinates derived in a similar way is $a_{\text{O}} = 0.6 \pm 0.2 \text{ \AA}$, $b_{\text{O}} = 1.8 \pm 0.2 \text{ \AA}$, and $c_{\text{O}} < 0.4 \text{ \AA}$. We find again, that this result cannot be used to discriminate between the three conformers.

For D_4 substitution, the relative change in $(B+C)$, $\Delta(B+C)/(B+C)$, was derived exactly for several models, examples are given in Fig. 2. An approximate expression, similar to that given above for monosubstitution, is

$$\frac{\Delta(B+C)}{B+C} = \frac{-\Delta m}{B+C} \times$$

$$\left\{ \left(\frac{B'}{I_b} + \frac{C'}{I_c} \right) \sum_i a_i^2 + \frac{C'}{I_c} \sum_i b_i^2 + \frac{B'}{I_b} \sum_i c_i^2 \right\}$$

where a_i , b_i , and c_i are the hydrogen coordinates, $\Delta m = m_{\text{D}} - m_{\text{H}}$, $\Delta I_b \cong \sum_i \Delta m (a_i^2 + c_i^2)$, and $\Delta I_c \cong \sum_i \Delta m (a_i^2 + b_i^2)$. The approximation is here that the center of mass correction and the rotation of axes are ignored. The validity of the approximation was checked on model values. The expression depends on six hydrogen coordinates for the *O-cis,trans* conformer, where C_s symmetry is assumed, and on twelve coordinates for the two other conformers, which do not have a symmetry plane. This can clearly not be used to determine the hydrogen coordinates or even to restrict their values, but only to confirm that a model is reasonable. The experimental result for the D_4 species, $\Delta(B+C)/(B+C) = -0.0226 \pm 0.0005$, is consistent with model calculations for all three conformers.

DISCUSSION

As seen above the information from the measured isotopic species of 1,3-dichloroacetone can set certain limits on the chlorine and oxygen coordinates, and comparison with model calculations has confirmed the effect of D_4 substitution. (It should be noted that two species (D_4^{37}Cl and $^{18}\text{O}^{37}\text{Cl}$) have not been used explicitly, since they give no independent information. Their $(B+C)$ values are, however, consistent with the derivation above).

The exact expression for conversion of $(B+C)$ to (I_b+I_c) is $k/(B+C) = (I_b+I_c)(1-x^2)/4$, where $x = (B-C)/(B+C) = (I_c-I_b)/(I_c+I_b) = (P_b-P_c)/(2P_a+P_b+P_c)$, $P_a = \sum_i m_i a_i^2$, etc., and k is the usual conversion factor $k = BI = 505\,379.1 \text{ MHz u \AA}^2$.

Taking now the semiquantitative substitution coordinates of the two chlorine atoms and of oxygen and using model coordinates of the hydrogen (and carbon) atoms, we find for the three conformers that the (I_b+I_c) contribution from 2Cl, O, and 4H is 83 ± 3 , 6.5 ± 1 , and 2.5 ± 1 %, respectively, leaving only ca. 8 % to the three carbon atoms.

Since the error in these percentages is rather high, nothing significant can be said of the contribution to (I_b+I_c) , or to $(B+C)$, from the three carbon atoms. High resolution results

are needed to find P_c , which could distinguish between the *O-cis,trans* conformer, where P_c (model) is ca. $3 \text{ u}\text{\AA}^2$, and the other two possibilities, *O-cis,skew* and *O-gauche,skew(-)*, where P_c (model) is about 16 and $20 \text{ u}\text{\AA}^2$, respectively.

Several attempts to obtain a high resolution microwave spectrum of DCA were unsuccessful, which might be explained as follows. For near-prolate molecules ($\kappa \leq -0.9$) it may be difficult to Stark modulate and thus to observe the 2R -branch transitions with low K_{-1} values, as well as to resolve the dense bands of 2R -branch transitions with high K_{-1} values making up the weak LRMW bands observed. The presence of two chlorine isotopes in non-equivalent positions and the expected quadrupole hyperfine structure from these nuclei, together with the supposedly large number of satellite lines from low lying vibrational states adds to the number of lines, and no separate transitions could be assigned.

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