Phase Diagram, ^{35}Cl NQR, and Crystal Structure of 1-Chloro-2-methyl-2-chloromethylpropionic Acid (β, β'-Dichloropivalic Acid), Phase II

Roman Strauß[2], Shi-qi Dou[1], Hartmut Fuess[2], and Alarich Weiss[1]

[1] Institut für Physikalische Chemie, [2] Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstr. 20, D-64287 Darmstadt, Germany

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Dedicated to W. Müller-Warmuth on the occasion of his 65th birthday

The phase diagram and the ^{35}Cl NQR spectrum of $(ClH_2C)_2(CH_3)C-COOH$ have been studied in the temperature range $77 \leq T/K \leq$ melting point (343.8 K). On heating no phase transition appears. The cooling cycle shows strong undercooling of the melt, a phase transition at $T_{m \to I} = 319.9$ K and a transition from the orientationally disordered phase I to the ordered phase II at $T_{I \to II} = 297.2$ K.

The ^{35}Cl NQR spectrum is a doublet with negative temperature coefficients within the temperature range covered, showing no phase transition in the heating cycle. At 77 K (298 K) the frequencies are in MHz: $\nu_1 = 34.830$ (34.140); $\nu_2 = 34.018$ (33.258).

The ordered solid crystallizes in the space group Pbca, $Z = 8$, $a = 1019.7$ (3) pm, $b = 1146.3$ (3) pm, $c = 1293.8$ (3) pm. Phase I (plastic phase) is cubic face centered, $a = 911$ pm, $Z = 4$.

Introduction

In the group of tetrahedral molecules, derived from methane by various substituents, many compounds exist which form an orientationally disordered, plastic phase between the ordered crystalline solid phase and the melt. An interesting member of this group is 2,2-dimethylpropionic acid (pivalic acid), which has an orientationally disordered plastic phase as observed by Timmermans [1]. The ordered structure is triclinic, and dimers are the structure determining intermolecular bonds in the ordered phase [2]. The melting point of the compound is 308.5–308.9 K, and the cubic plastic phase I [3] changes into an ordered arrangement of the molecules, phase II, at 279.9 K. Extensive work has been done to explore the nature of this phase transition. Literature is found in [4]. We are interested in the role hydrogen bonds play in solids for the transition from an ordered state to an orientationally disordered phase. A contribution to this problem is the present study of the phase diagram and the crystal structure of 1-chloro-2-methyl-2-chloromethylpropionic acid (β, β'-dichloropivalic acid). One may assume that the substitution of a chlorine atom into two of the methyl groups of pivalic acid will lower the pK_a and strengthen the hydrogen bond. However, the shape of the molecule is changed as well, and this will affect the thermodynamic behaviour of the molecule in the solid, too.

Experimental

Commercial β, β'-dichloropivalic acid (Aldrich, 99%), in the following named sample (a), was purified by sublimation, sample (b), or by recrystallisation from n-hexane, sample (c). DTA-DSC was performed with a homemade equipment. Samples (b) and (c) behave identically in the thermodynamic, X-ray, and NQR experiments, whereas (a) differs remarkably from (b) and (c). The melting point is only little influenced by the purification procedures and in good agreement with the literature value (71 °C [5]). In Fig. 1 we show the DTA results for (b) and (c). In these experiments we have cooled the very pure samples at different speeds dT/dt (6.25 K/min to 0.07 K/min) from 10 K above the melting point (≈ 353 K) down to about 273 K. The transition temperatures $T_{m \to I}$ and $T_{I \to II}$ change very little with speed.

Sample (a) behaves completely different. The undercooling of the melt is much less pronounced, the transition is directly from melt to phase II, $T_{m \to II} = 337$ K,

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Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-64287 Darmstadt.

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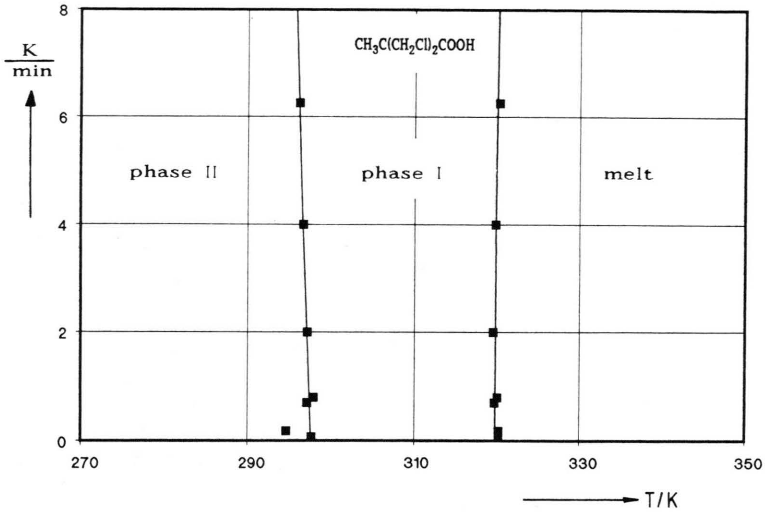

Fig. 1. Phase transition temperatures of β,β'-dichloropivalic acid as function of the cooling speed in the DTA experiment.

Table 1. Thermodynamic data of $(ClH_2C)_2(CH_3)CCOOH$. The data are given for the commercial sample (99%) (a), and for the samples purified by recrystallisation from n-hexane (c) and by sublimation (b). (b) and (c) are identical in their phase diagram. Temperatures are given in K, enthalpies ΔH in $kJ \cdot mol^{-1}$, entropies ΔS in $J \cdot mol^{-1} \cdot K^{-1}$.

Sample	$T_{II \to m}$	$\Delta H_{II \to m}$	$\Delta S_{II \to m}$	$\Delta S_{II \to m}/R$	$T_{m \to II}$	$\Delta H_{m \to II}$	$\Delta S_{m \to II}$	$\Delta S_{m \to II}/R$
(a)	343.4	22.27	63.94	7.69	336.9	18.95		
(b, c)	343.8	21.89	62.90	7.57			56.47	6.79
Sample	$T_{m \to I}$	$\Delta H_{m \to I}$	$\Delta S_{m \to I}$	$\Delta S_{m \to I}/R$	$T_{I \to II}$	$\Delta H_{I \to II}$	$\Delta S_{I \to II}$	$\Delta S_{I \to II}/R$
(b, c)	319.7	3.44	10.77	1.30	297.2	19.39	65.79	7.91

and no phase I appears. In Table 1 we have collected the thermodynamic data obtained from DTA and DSC.

For the structure determination small crystals, crystallized from benzene, were selected and the X-ray diffraction intensities were measured with a 4-circle goniometer. After appropriate corrections for absorption and Lorentz-polarisation factor the structure, including the position of the hydrogen atoms of the OH group, was determined by direct methods [6]. The hydrogen positions in the bonds, C–H, were fixed in length to 96 pm (CH_3-group) and 97 pm (CH_2Cl group), respectively.

The ^{35}Cl NQR spectra were registered with a spectrometer working in the superregenerative mode. Temperatures of the NQR sample were produced by a heated/cooled stream of nitrogen gas and by liquid nitrogen at 77 K. Temperature was measured by a copper-constantan thermocouple to ± 0.5 K. Frequencies were determined with a frequency counter to ± 5 kHz, the accuracy being limited by the width of the resonance lines. The line width is 18–19 kHz at 77 K, increasing from 297 K on up to 40 kHz at 339 K.

Results and Discussion

Thermodynamics

The phase diagram of the title compound depends on the purity of the sample. We were unable to determine the impurity in the 99% sample (a). However we know that it does not influence the NQR, which is quite a sensitive indicator for impurities dissolved in a solid. Heating the crystalline compound from 77 K in the DTA equipment, no phase transition is visible up to the melting point $T_m = 343.8$ K, independent of the history of the sample (a), (b), and (c). In the cooling cycle the sample behaves differently according to its purification. The 99% pure sample undercools by $\Delta T_m \approx 6$ K quite strongly, but this being not unusual, and at 336.9 K it crystallizes to the ordered phase II.

The purified samples (b) and (c) undercool strongly, $\Delta T_m \approx 24$ K, transforming to an orientationally disordered plastic phase I at $T_{m \to I} = 319.7$ K. At $T_{I \to II} = 297.2$ K the transformation to the ordered phase II occurs. Both temperatures are mean values found from the experiments shown in Figure 1. The cooling cycle of (b) was repeated with different speeds dT/dt; only very little dependence on $T_{m \to I}$ and $T_{I \to II}$ is found, as Fig. 1 shows. In Table 1 we have collected the thermodynamic data of the samples. The enthalpy of formation of the orientationally disordered phase from the melt is low, $\Delta H_{m \to I} = -3.44$ kJ mol^{-1}, and the reduced entropy, $\Delta S_{m \to I}/R = 1.30$, lies in the range one expects for the reduced melting entropy of a plastic crystal.

X-ray Diffraction

Phase I was studied by powder diffractometry (CuK_α radiation) at $T = 308$ K. Only one diffraction line is observed at $2\Theta = 16.84°$. Annealing the sample over 24 hours did not improve the crystallization of the plastic phase I. Indexing the line as (111), a lattice constant of 910.9 (10) pm results. With $\varrho_{\text{calc.}} = 1.502$ kg m^{-3} found for the ordered phase, see Table 2,

Table 2. Crystal data and experimental conditions for the structure determination of 1-chloro-2-methyl-2-chloromethylpropionic acid, $(ClH_2C)_2(CH_3)CCOOH$. $C_5H_8Cl_2O_2$. $M = 171.03$. Diffractometer: Stoe-Stadi4; wavelength: 71.069 pm (MoK_α); monochromator: Graphite (002); scan: $2\vartheta/\omega$.

Crystal size (mm)^3	$0.80 \times 0.42 \times 0.30$
Temperature/K	299 (2)
Absorption coeff./m^{-1}	713
Θ-range for data collec.	$3.10 \leq \Theta/° \leq 25.00$
Index range	$0 \leq h \leq 12$, $-13 \leq k \leq 13$, $0 \leq l \leq 15$
Lattice constants/pm	$a = 1019.7$ (3) $b = 1146.3$ (3) $c = 1293.8$ (3)
$V \cdot 10^{-6}/(\text{pm})^3$	1512.3 (7)
Space group	D_{2h}^{15}-Pbca
Formula units Z/cell	8
$\varrho_{\text{calc.}}/(\text{Mg} \cdot \text{m}^{-3})$	1.502 (1)
F (000)	704
Reflections collect.	2858
Symmetry indep.	1333
$[R_{\text{int}}]$	0.0265
Data	1332
Restraints/Parameters	0/84
Goodness-of fit on F^2	1.055
Final R ($I > 2\sigma(I)$)	$R_1 = 0.0352$, $wR_2 = 0.0913$
R (all data)	$R_1 = 0.0407$, $wR_2 = 0.0973$
Largest diff. peak, hole/ (10^{-6} e (pm)$^{-3}$)	0.319, -0.335
Max., Min. Transm.	0.799, 0.664
Extinction coeff.	0.0000 (14)
Point positions	All atoms in 8c

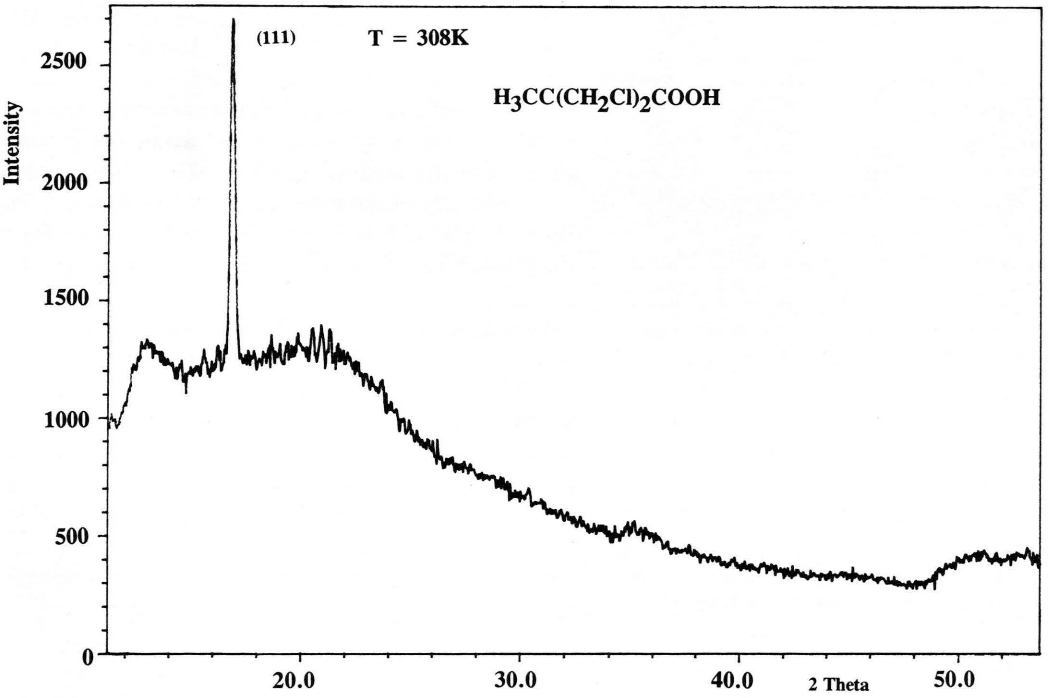

Fig. 2. X-ray powder diffraction diagram of β,β'-dichloropivalic acid, phase I (plastic phase). $T = 308$ K, sample (c), $CuK\alpha$-radiation.

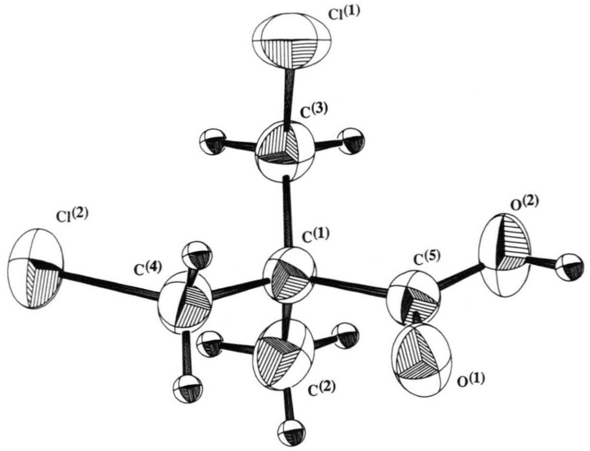

Fig. 3. The molecule $(ClH_2C)_2(CH_3)CCOOH$, numbering of the atoms and thermal ellipsoids; the ellipsoids are at 50% probability level (293 K), hydrogen atoms are drawn as spheres of arbitrary size.

Table 3. Atomic coordinates ($\times 10^4$) and displacement parameters for 1-chloro-2-methyl-2-chloromethyl-propionic acid. The anisotropic displacement factor is of the form $T = \exp[-2\pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hk\,a^* b^* U_{12} + 2hl\,a^* c^* U_{13} + 2kl\,b^* c^* U_{23}]$. U_{eq} is defined as 1/3 of the trace of the orthogonalized tensor U_{ij}. The U_{ij} and U_{eq} are given in $(pm)^2$.

Atom	x	y	z	U_{eq}
$C^{(1)}$	0277(2)	2678(2)	3820(2)	400(5)
$C^{(2)}$	−0775(3)	3508(2)	4257(2)	607(7)
$H^{(1,C2)}$	−0673(11)	4266(5)	3953(10)	728
$H^{(2,C2)}$	−0678(11)	3565(12)	4993(3)	728
$H^{(3,C2)}$	−1630(3)	3209(8)	4096(11)	728
$C^{(3)}$	0035(2)	2540(2)	2664(2)	488(5)
$H^{(1,C3)}$	0079(2)	3300(2)	2336(2)	585
$H^{(2,C3)}$	−0839(2)	2231(2)	2555(2)	585
$C^{(4)}$	1658(2)	3113(2)	4066(2)	468(5)
$H^{(1,C4)}$	2288(2)	2518(2)	3872(2)	561
$H^{(2,C4)}$	1734(2)	3238(2)	4805(2)	561
$C^{(5)}$	0128(2)	1501(2)	4363(2)	388(5)
$Cl^{(C3)}$	1209(1)	1588(1)	2072(1)	649(3)
$Cl^{(C4)}$	2046(1)	4439(1)	3408(1)	714(3)
$O^{(1,C5)}$	0880(2)	1204(1)	5049(1)	556(4)
$O^{(2,C5)}$	−0857(2)	0884(2)	4060(2)	637(5)
$H^{(02)}$	−0836(30)	0243(28)	4369(23)	765

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$C^{(1)}$	431(10)	350(10)	418(10)	009(8)	016(8)	063(8)
$C^{(2)}$	607(14)	461(13)	753(17)	081(11)	167(13)	92(11)
$C^{(3)}$	521(11)	484(11)	458(12)	002(10)	−065(10)	113(9)
$C^{(4)}$	502(11)	444(11)	456(12)	−100(10)	009(10)	077(9)
$C^{(5)}$	397(10)	363(10)	403(11)	−002(8)	014(9)	031(8)
$Cl^{(C3)}$	848(5)	640(4)	458(4)	063(3)	045(3)	−062(3)
$Cl^{(C4)}$	799(5)	525(4)	816(5)	−227(3)	078(3)	137(3)
$O^{(1,C5)}$	655(10)	454(9)	560(9)	−104(7)	−210(8)	150(7)
$O^{(2,C5)}$	647(10)	515(9)	750(12)	−205(8)	−248(9)	264(9)

$Z = 4.003$ results. If one takes the observed reflection as (110) and the density of the ordered phases, the lattice constant is 747 pm and $Z = 2.178$. Therefore we assume a face centered cubic lattice, space group Fm3m, for phase I of the title compound, with $a = 911$ pm, $Z = 4$. This compares well with the lattice constant of the plastic phase of pivalic acid which is 882 pm [7]. The widening of the lattice of the title compound compared to pivalic acid is due to the replacement of H by Cl in two of the methyl groups of $(CH_3)_3CCOOH$. The highest symmetry would be Fm3m. The X-ray powder diagram of the plastic phase I is shown in Figure 2.

At room temperature the crystal structure of β,β'-dichloropivalic acid is orthorhombic, Pbca, $Z = 8$, $a = 1019.7\,(3)$ pm, $b = 1146.3\,(3)$ pm, $c = 1293.8\,(3)$ pm. Table 2 gives crystal data of the compound and the experimental conditions for the structure determination. In Fig. 3 a molecule is drawn with the ellipsoids of thermal motion and the numbering of the atoms used throughout the paper. Table 3 lists the coordinates of atoms in the unit cell and the temperature factors U_{eq}, U_{ij}. The intramolecular (bond) distances and angles are given in Table 4, and in Table 5 we list the intermolecular distances found within the sum of van der Waals radii [6, 7] of neighboring atoms. Figure 1 shows the projection of the unit cell along [100] onto the bc plane. The interesting feature of the crystal structure is the hydrogen bond $C{-}O{-}H \cdots O{=}C$, which one, of course, expects for a carboxylic acid and which also determines the structure of the ordered phase of pivalic acid $(CH_3)_3CCOOH$. The intramolecular geometry of the molecule shows no unusual features. The bond lengths $d(C{-}C)$ are 152.6 pm (except $d(C^{(1)}{-}C^{(2)})$, which is 154 pm), the distances $d(C{-}Cl)$

Table 4. Intramolecular distances d (in pm) and intramolecular angles (in °) for 1-chloromethyl-2-methyl-2-chloromethyl-propionic acid.

Connection	d/pm	Connection	Angle/°
$C^{(1)}{-}C^{(2)}$	154.2(3)	$C^{(2)}{-}C^{(1)}{-}C^{(3)}$	108.1(2)
$C^{(1)}{-}C^{(3)}$	152.4(3)	$C^{(2)}{-}C^{(1)}{-}C^{(4)}$	111.3(2)
$C^{(1)}{-}C^{(4)}$	152.8(3)	$C^{(2)}{-}C^{(1)}{-}C^{(5)}$	107.9(2)
$C^{(1)}{-}C^{(5)}$	152.8(3)	$C^{(3)}{-}C^{(1)}{-}C^{(4)}$	112.8(2)
$Cl^{(C3)}{-}C^{(3)}$	179.1(2)	$C^{(3)}{-}C^{(1)}{-}C^{(5)}$	110.2(2)
$Cl^{(C4)}{-}C^{(4)}$	178.7(2)	$C^{(4)}{-}C^{(1)}{-}C^{(5)}$	106.5(2)
$C^{(5)}{-}O^{(1,C5)}$	122.2(2)	$O^{(1,C5)}{-}C^{(5)}{-}O^{(2,C5)}$	123.8(2)
$C^{(5)}{-}O^{(2,C5)}$	129.0(3)	$O^{(1,C5)}{-}C^{(5)}{-}C^{(1)}$	121.2(2)
$O^{(2,C5)}{-}H^{(02)}$	084.0(30)	$O^{(2,C5)}{-}C^{(5)}{-}C^{(1)}$	115.0(2)
		$Cl^{(C3)}{-}C^{(3)}{-}C^{(1)}$	112.0(2)
		$Cl^{(C4)}{-}C^{(4)}{-}C^{(1)}$	112.5(2)
		$C^{(5)}{-}O^{(2,C5)}{-}H^{(02)}$	109.0(20)

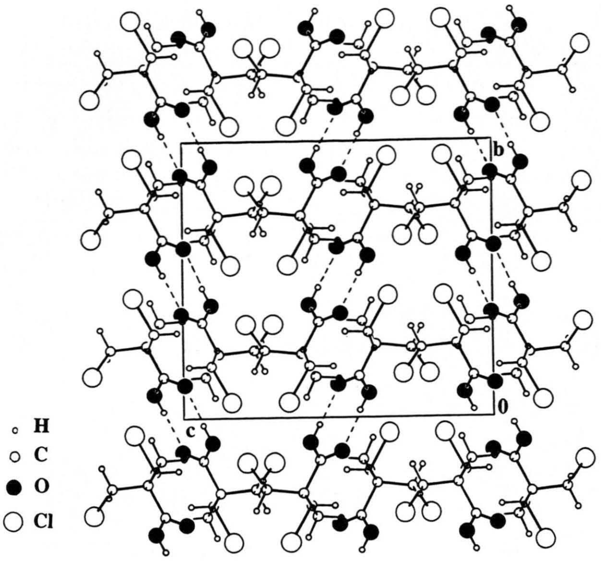

Fig. 4. Projection of the unit cell of 1-chloro-2-methyl-2-chloromethylpropionic acid along [100] onto the bc plane. The oxygen atoms are shown by the filled symbols. Hydrogen bonds are marked by dashed lines.

Table 5. Intermolecular distances *d* (in pm) for 1-chloro-2-methyl-2-chloromethylpropionic acid. Only distances within 360 pm are considered. The following van der Waals radii r_{vdW} (in pm) have been assumed [6, 7]: Cl, 180; O, 170; CH_2, CH_3, 200.

Connection		*d*/pm	Connection	Angle/°
$Cl^{(C4)} \cdots Cl^{(C3)}$	[1]	350	$O^{(2,C5)}{-}H^{(02)} \cdots O^{(1,C5)}$ [5]	174.9(31)
$Cl^{(C4)} \cdots O^{(1,C5)}$	[2]	362		
$O^{(2,C5)} \cdots Cl^{(C2)}$	[3]	343		
$O^{(1,C5)} \cdots CH^{(C2)}$	[4]	354		
$O^{(2,C5)} \cdots O^{(1,C5)}$	[5]	266		
$H^{(02)} \cdots O^{(1,C5)}$	[5]	182		

[1] $Cl^{(C3)}$ ($\frac{1}{2}-x$, $\frac{1}{2}+y$, z); [2] $O^{(1,C5)}$ ($\frac{1}{2}-x$, $\frac{1}{2}+y$, z); [3] ($Cl^{(C2)}$ ($\frac{1}{2}-x$, y, $\frac{1}{2}-z$); [4] $CH^{(2)}$ ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$); [5] $O^{(1,C5)}$ ($-x$, $-y$, $1-z$).

are 179.1 pm and 178.7 pm, and the carbon oxygen distances of the carboxyl group are 122.2 pm for the connection $C^{(5)}{=}O^{(1)}$ and 129.0 pm for the bond $C^{(5)}{-}O^{(2)}$, where $O^{(2)}$ belongs to the hydroxyl group. All intramolecular angles are in the expected range. The scattering around 109° for the angles (C−C−C) and (Cl−C−C) and around 120° for the angles (O−C−C) is not significant, bond angles being weak bond parameters. There are van der Waals interactions between the "paired" molecules (Fig. 4 and Table 5).

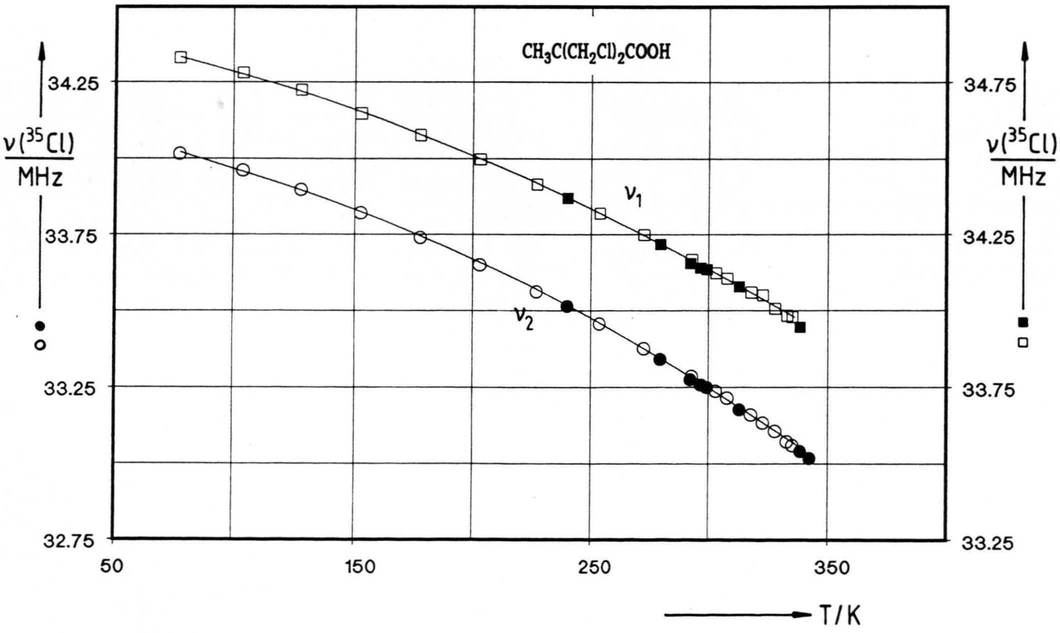

Fig. 5. ^{35}Cl NQR frequencies of the title compound as function of temperature. Open symbols: Sample (a); filled symbols: Sample (c).

Table 6. Coefficients a_i of the power series development (1) for $\nu = f(T)$ of 1-chloro-2-methyl-2-chloromethylpropionic acid and ^{35}Cl NQR frequencies at selected temperatures. The power series approximation is valid for the range $77 \leq T/K \leq 345$.

ν_i	ν/MHz (77 K)	ν/MHz (293 K)	z	$\frac{\sigma}{\text{kHz}}$	$\frac{a_0}{\text{MHz}}$	$\frac{a_{-1}}{\text{MHz} \cdot \text{K}}$	$\frac{a_1 \cdot 10^3}{\text{MHz} \cdot \text{K}^{-1}}$	$\frac{a_2 \cdot 10^6}{\text{MHz} \cdot \text{K}^{-2}}$
ν_1	34.830	34.168	24	5.4	34.9221	1.63070	−1.00362	−5.48534
ν_2	34.018	33.288	25	5.2	34.0589	4.18359	−0.64412	−7.02704

^{35}*Cl Nuclear Quadrupole Resonance*

The ^{35}Cl NQR spectrum is a dublet, in accordance with the crystal structure which reveals two inequivalent chlorine atoms in the molecule. The two resonance frequencies decrease smoothly with increasing temperature in the range $77 \leq T/K \leq 342.5$. There is no difference in the NQR spectrum between sample (a) and samples (b) and (c) within the limits of error. In the cooling cycle the ^{35}Cl NQR lines of sample (a) appear immediately below the transition point $T_{m \to II}$, and for the samples (b) and (c) the temperature at which the NQR spectrum appears is just below $T_{I \to II}$. With increasing temperature line ν_1 fades out around 340 K and line ν_2 around 343 K for samples (a), (b) and (c). Figure 5 shows $\nu(^{35}\text{Cl}) = f(T)$. The functions $\nu = f(T)$ have been rationalized by polynomials according to

$$\nu = \sum a_i T^i, \quad -1 \leq i \leq 2, \tag{1}$$

and the coefficients a_i are given together with frequencies at selected temperatures in Table 6. The decrease of the signal to noise ratio until the signal fades out completely is due to the increase of the line width. The librational motions of the CH_2Cl group are the reason of this, such a fade out being often observed in NQR on compounds with CCl_3–, CCl_2H-, and CH_2Cl groups.

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