

Crystal Structures and Phase Transitions of 3-Chloro-2,2-bis(chloromethyl)propionic Acid-1 and 1,3-Dichloro-2,2-dimethylpropane*

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The crystal structure of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 was determined from single crystal data. The compound crystallizes in the acentric monoclinic space group $P2_1$. Lattice constants at $T = 304$ K are $a = 6.961(1)$ Å, $b = 9.979(2)$ Å, $c = 12.0569(3)$ Å, $\beta = 94.01(2)^\circ$. Structure refinement on 1736 independent reflections yielded $R = 0.041$. Two molecules are interconnected by hydrogen bridges to form dimers. Thermal analysis and temperature dependent X-ray and IR-measurements gave no indication of a phase transition in the range 150 K $< T < 384$ K. An order-disorder phase transition was detected for 1,3-dichloro-2,2-dimethylpropane at $T_{I \rightarrow II} = 194.3$ K, with a plastic cubic phase in the range 194.3 K $< T < 259.1$ K. The lattice constant in space group $Fm\bar{3}m$ is $a = 9.24$ Å at 220 K with a thermal expansion coefficient $\alpha_{(200\text{ K})} = 2.6769 \times 10^{-4}$ K $^{-1}$. The entropy at the melting point $T_m = 259.1$ K and at the solid-solid phase transition $T_{I \rightarrow II} = 194.3$ K is rather low giving strong evidence of a plastic phase. Powder X-ray diffraction pattern in the ordered phase at $T = 160$ K gave indication of monoclinic symmetry with $a = 12.27$ Å, $b = 10.86$ Å, $c = 10.68$ Å, $\beta = 111.8^\circ$. Temperature dependent infrared measurements revealed the conformation of the molecule.

Key words: ODIC phases, order-disorder, thermoanalysis, crystal structure, pivalic acid.

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

Posvećeno gospodinu profesoru Borisu Kamenaru prigodom njegovog 70. rođendana.

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INTRODUCTION

In the studies of order-disorder phase transitions in molecular crystals, two derivatives of propane were investigated by X-ray diffraction, thermal analysis and infrared spectroscopy. Order-disorder phase transitions are often closely connected with a rather compact form of the molecules. Therefore, spherical or elliptical molecules with mainly hydrogen atoms on the surface are potential candidates for formation of the so-called plastic phases. Classical cases for the formation of plastic crystals are methane CH_4 or adamantane $\text{C}_4(\text{CH}_2)_6$. Following the definition of Timmermans,¹ a plastic phase is characterized by two transitions. One is T_m , the melting point, the other $T_{\text{I} \rightarrow \text{II}}$, the order-disorder transition. In the generally accepted nomenclature, phase I is the plastic phase below the melt whereas ordered phases obtain subsequent numbers as order increases with decreasing temperature. The thermodynamic criterion for the existence of a plastic phase is a low entropy of melting. The entropy at the order-disorder transition is, however, relatively high.

Due to the absence of orientational order of the molecule and the long-range order of their centres, high symmetry (cubic or hexagonal) is found in phase I. Modifications observed at lower temperature crystallize in space groups of lower symmetry.

Pivalic acid (2,2-dimethylpropionic acid-1) is one of the classical examples of a molecular plastic crystal.¹ In order to examine the influence of substituents on the existence of plastic phases, we modified the geometry of the molecules and their potential intermolecular binding forces. Therefore, especially chlorine and hydroxyl groups were introduced. In a previous contribution, we reported on the plastic phase of β, β' -dichloropivalic acid (3-chloro-2-chloromethyl-2-methylpropionic acid-1).² A detailed study of β -chloropivalic acid (3-chloro-2,2-dimethyl-propionic acid-1) is under preparation. Here, we present the results for β, β', β'' -trichloropivalic acid-1 (3-chloro-2,2-bis(chloromethyl)propionic acid-1), abbreviated as **1**.

Closely related to propionic acid-1 are the derivatives of propane. A plastic phase for 2-chloromethyl-1,3-dichloro-2-methylpropane has been described whereas no disordered phase was detected for 2,2-bis(bromomethyl)-1,3-propanediol.³ Here, we report our investigation of 1,3-dichloro-2,2-dimethylpropane, abbreviated as **2** (Figure 1).

EXPERIMENTAL

Starting material for the synthesis of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 was pentaerythrole, which was heated together with pyridine to 340 K. Thio-

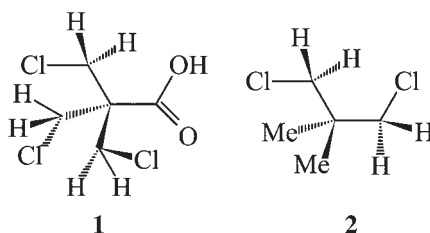


Figure 1. Scheme of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (**1**) and 1,3-dichloro-2,2-dimethylpropane (**2**).

nylchloride was added under stirring. The solution was stirred for about twelve hours at 390 K – 400 K under reflux. After complete reaction (absence of SO_2) cold water was added first and then toluene. The product (pentaerythritole trichlorhydrin) was then in a solution of toluene. Oxidation to the acid was achieved by nitric acid. Several steps of purification and crystallization were added and finally crystalline needles were obtained. The preparation followed a method by Lynch for analogous propene derivatives.⁴ The 1,3-dichloro-2,2-dimethylpropane **2** was from ICN Biochemicals (99%). It was treated by fractional distillation.

Differential thermal analysis was performed by a SETARAM DSC 121. The X-ray powder diffraction were carried out in transmission on a STOE-STADI-P diffractometer and a position sensitive detector (aperture 6°) with $\text{Co-K}\alpha_1$ ($\lambda = 1.78897 \text{ \AA}$) for **1** and $\text{Cu-K}\alpha_1$ ($\lambda = 1.5405 \text{ \AA}$) for **2**.

The single crystal study on an ENRAF-NONIUS CAD4 diffractometer with $\text{Mo-K}\alpha$ ($\lambda = 0.71093 \text{ \AA}$) was carried out at room temperature.* Relevant data are summarized in Table I. The structure was solved after the usual corrections by direct methods with SHELXS-86 and refined by SHELXL-93 ($R = 0.041$). The infrared studies were performed with a Perkin Elmer FT-IR 1750 in a KBr-pellet. For temperature dependent experiments, a furnace from Graseby Specac was used.

RESULTS

The thermodynamic data are presented in Table II. No plastic phase has been found for **1** and the value of $\Delta S/R$ is considerably higher than the value of 2.5, which is an approximate thumb rule for the existence of a plastic phase. No other transition has been observed in the range $153 \text{ K} < T < 300 \text{ K}$. Both the low melting entropy ($\Delta S_{\text{I} \rightarrow \text{M}} = 6.0 \text{ J mol}^{-1} \text{ K}^{-1}$) and the reduced entropy $\Delta S/R = 0.7$ indicate a plastic phase I for compound **2**. In Table II only values for a rate of 1 K min^{-1} for heating and cooling are given and a

* Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Supplementary data are available from the IUCr electronic archives (CSD Reference No. 410373).

TABLE I

Crystal data and structure refinement of 3-chloro-2,2-bis(chloro-methyl)propionic acid-1

Identification code	1	
Empirical formula	$C_5H_7Cl_3O_2$	
Formula weight	205.46	
Temperature	304(2) K	
Wavelength (Mo-K α)	0.71093 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 6.9610(10)$ Å	$\alpha = 90^\circ$
	$b = 9.979(2)$ Å	$\beta = 94.01(2)^\circ$
	$c = 12.059(3)$ Å	$\gamma = 90^\circ$
Volume	$835.6(3)$ Å ³	
<i>Z</i>	4	
Density (calculated)	1.633 Mg/m ³	
Absorption coefficient	1.034 mm ⁻¹	
<i>F</i> (000)	416	
Crystal size	0.50 x 0.08 x 0.08 mm	
Theta range for data collection	1.69 to 25.95°	
Index ranges	$-8 \leq h \leq 1, -12 \leq k \leq 0, -14 \leq l \leq 14$	
Reflections collected	1899	
Independent reflections	1736 [$R_{int} = 0.0288$]	
Absorption correction	Empiric psi-scan	
Max. and min. transmission	0.998 and 0.928	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1735 / 1 / 187	
Goodness-of-fit on F^2	1.02	
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0403, wR_2 = 0.0862$	
<i>R</i> indices (all data)	$R_1 = 0.1100, wR_2 = 0.1073$	
Absolute structure parameter	0.1(2)	
Largest diff. peak and hole	0.322 and -0.281 e Å ⁻³	

pronounced hysteresis is observed. An average value of $T_M = 259.1$ K for the melting point was derived. The temperature $T_{I \rightarrow II} = 194.3$ K is the value for the order-disorder transition. The $\Delta S/R$ values averaged over all observations are 0.74 for I \rightarrow II. The DSC measurement is displayed in Figure 2. The order-disorder transition is characterized by two maxima, thus indicating a second partially ordered phase.

TABLE II

Thermodynamic data of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (**1**) and 1,3-dichloro-2,2-dimethylpropane (**2**)

	Transition temperature K	Transition type	Rate K min ⁻¹	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{\Delta S}{\text{J mol}^{-1} \text{K}^{-1}}$	$\Delta S/R$
1	383.9	II→m	1 h	20.9	54.2	6.5
	380.9	m→II	1 c	-21.4	-56.3	-6.8
2	265.1	m→I	1 c	-1.8	-6.7	-0.8
	186.7	I→II,III	1 c	-4.1	-22.3	-2.7
	193.8	III→II	1 h	0.6	3.2	0.4
	198.4	II→I	1 h	3.6	17.9	2.2
	262.2	I→m	1 h	1.6	6.0	0.7

h: heating, c: cooling.

The minus sign indicates an exothermal, the plus sign an endothermal process.

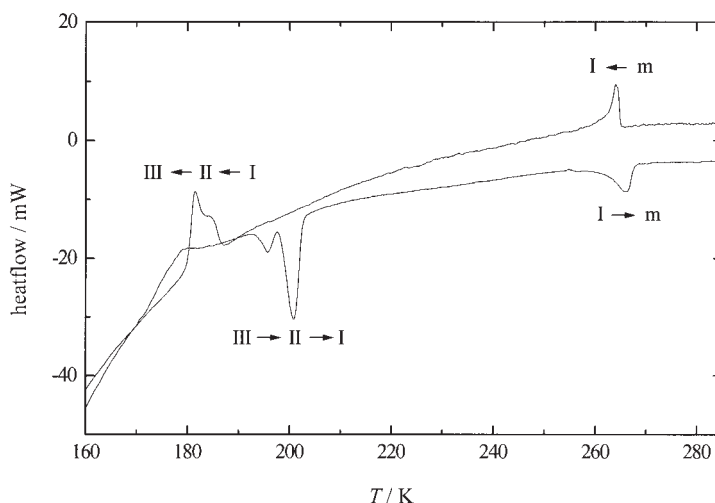


Figure 2. DSC-plot of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (**1**) and 1,3-dichloro-2,2-dimethylpropane (**2**).

Crystal Structure of **1**

The structure of **1** has been solved in the monoclinic space group $P2_1$ (Table III). The asymmetric unit with two molecules is shown in Figure 3, the intermolecular arrangement in Figure 4. Bond lengths and angles (Table IV) in the aliphatic group are within the usual range.

TABLE III
Atomic coordinates ($x, y, z \times 10^4$) and equivalent isotropic displacement parameters ($U_{eq} \times 10^3 / \text{\AA}^2$) for **1**

	x	y	z	U_{eq}
C(1)	7217(10)	6267(8)	9885(6)	36(2)
C(2)	5988(10)	6243(11)	8774(7)	35(2)
C(3)	5403(10)	4820(8)	8526(6)	44(2)
C(4)	4240(9)	7161(8)	8872(5)	43(2)
C(5)	7128(9)	6874(8)	7865(5)	40(2)
C(6)	281(9)	6294(8)	2628(5)	33(2)
C(7)	1380(10)	6273(11)	3785(7)	29(1)
C(8)	2169(10)	7713(7)	3975(5)	38(2)
C(9)	24(10)	5850(8)	4647(5)	40(2)
C(10)	2985(10)	5257(8)	3808(5)	41(2)
O(1)	7558(8)	5249(6)	10397(4)	56(2)
O(2)	7821(9)	7434(6)	10174(5)	50(2)
O(3)	17(8)	7288(5)	2085(4)	48(1)
O(4)	-328(10)	5088(8)	2335(5)	58(2)
Cl(1)	2890(3)	6691(3)	9995(2)	69(1)
Cl(2)	9287(3)	5941(3)	7680(2)	67(1)
Cl(3)	3980(3)	4662(2)	7233(2)	59(1)
Cl(4)	4490(3)	5440(2)	2688(2)	55(1)
Cl(5)	-1939(3)	6968(3)	4741(2)	64(1)
Cl(6)	3268(3)	7910(2)	5340(2)	54(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

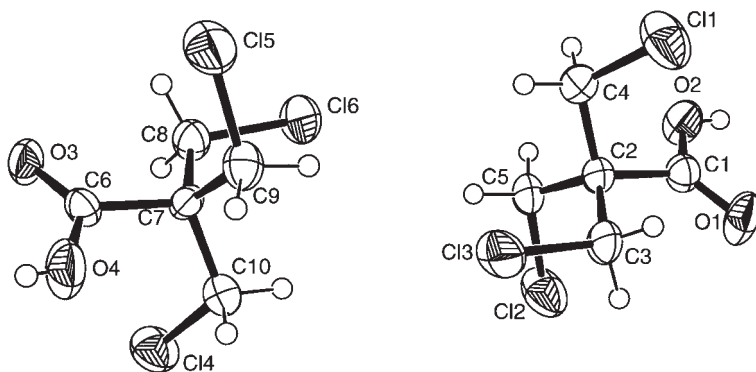


Figure 3. Asymmetric unit of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (**1**).

TABLE IV
Bond lengths /Å and angles /° for **1**

Bond lengths			
C(1)–O(1)	1.204(8)	C(1)–O(2)	1.279(10)
C(1)–C(2)	1.538(10)	C(2)–C(3)	1.501(13)
C(2)–C(5)	1.533(10)	C(2)–C(4)	1.534(10)
C(3)–Cl(3)	1.795(7)	C(4)–Cl(1)	1.765(6)
C(5)–Cl(2)	1.795(7)	C(6)–O(3)	1.195(8)
C(6)–O(4)	1.316(11)	C(6)–C(7)	1.543(10)
C(7)–C(10)	1.507(11)	C(7)–C(9)	1.512(9)
C(7)–C(8)	1.550(13)	C(8)–Cl(6)	1.778(7)
C(9)–Cl(5)	1.774(7)	C(10)–Cl(4)	1.776(6)
O(2)–H(2O)	0.68(8)	O(4)–H(4O)	0.56(10)
Bond angles			
O(1)–C(1)–O(2)	125.4(7)	O(1)–C(1)–C(2)	120.7(8)
O(2)–C(1)–C(2)	113.9(7)	C(3)–C(2)–C(5)	113.1(7)
C(3)–C(2)–C(4)	112.0(6)	C(5)–C(2)–C(4)	105.2(7)
C(3)–C(2)–C(1)	108.4(8)	C(5)–C(2)–C(1)	109.4(6)
C(4)–C(2)–C(1)	108.6(6)	C(2)–C(3)–Cl(3)	112.4(6)
C(2)–C(4)–Cl(1)	111.6(5)	C(2)–C(5)–Cl(2)	110.8(5)
O(3)–C(6)–O(4)	125.2(6)	O(3)–C(6)–C(7)	123.7(7)
O(4)–C(6)–C(7)	111.1(7)	C(10)–C(7)–C(9)	107.3(7)
C(10)–C(7)–C(6)	110.3(7)	C(9)–C(7)–C(6)	109.4(6)
C(10)–C(7)–C(8)	111.5(6)	C(9)–C(7)–C(8)	112.9(7)
C(6)–C(7)–C(8)	105.6(7)	C(7)–C(8)–Cl(6)	111.4(5)
C(7)–C(9)–Cl(5)	112.9(6)	C(7)–C(10)–Cl(4)	113.1(5)

Hydrogen bonds exist between O(2) and O(3) and between O(1) and O(4), both with an O–O distance of 2.6705 Å. The hydrogen atom between O(2) and O(3) was located by difference Fourier synthesis and refined by the method of least squares. All other hydrogen atoms have been calculated and not refined.

An X-ray powder diffraction pattern has been refined by the Rietveld method (Figure 5). The positional parameters of all atoms and the distances and angles agree within standard deviations with the single crystal results.

Temperature dependent X-ray patterns were registered between 303 K and 383 K in a furnace. Data were collected with a position sensitive detector of 40° in 2θ. Positions of four reflections were observed and only a slight

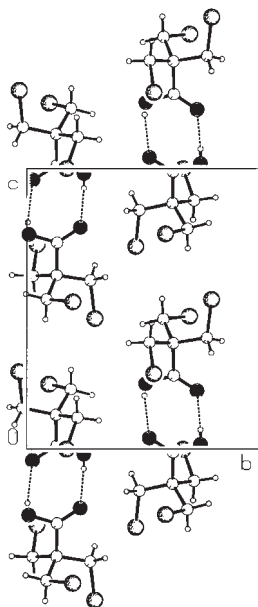


Figure 4. View along [100] of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (1) showing the hydrogen bridged dimers.

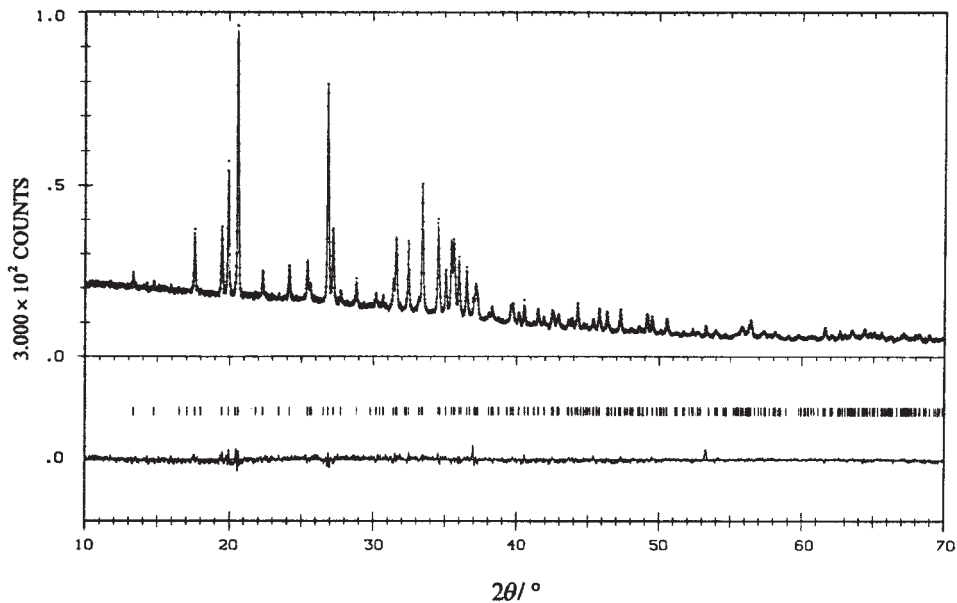


Figure 5. Observed and calculated X-ray powder pattern of 3-chloro-2,2-bis(chloromethyl)propionic acid-1 (1) at room temperature. The difference plot is shown, as well. ($\lambda = 1.78897 \text{ \AA}$.)

change in d -values was detected. No precise determination of lattice constants was feasible but an increase of about 1% was estimated.

Structural Investigation of 2

No single crystals of 1,3-dichloro-2,2-dimethylpropane could be obtained. The powder diffraction pattern exhibited two reflections only in phase I (Figure 6, top). A cubic face centered lattice has been attributed space group $Fm\bar{3}m$. The temperature dependence of the lattice constant was followed in

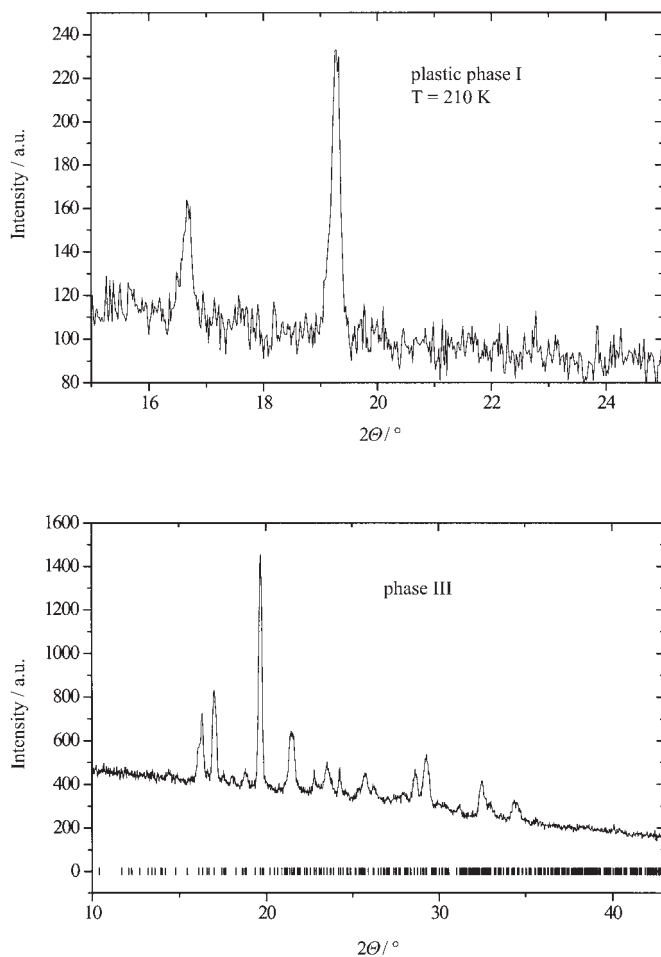


Figure 6. X-ray powder pattern of 1,3-dichloro-2,2-dimethylpropane (**2**). ($\lambda = 1.54056 \text{ \AA}$)
Top: plastic phase I at $T = 210 \text{ K}$.
Bottom: phase III at $T = 160 \text{ K}$, the tics are given for the estimated cell dimensions.

the range $200 \text{ K} < T < 260 \text{ K}$ in intervals of 10 K. An increase from $a = 9.1884 \text{ \AA}$ (200 K) to $a = 9.3409 \text{ \AA}$ (260 K) led to the regression law of

$$\alpha(T)/\text{\AA} = 8.69762 + 0.00246 T/\text{K}$$

and the thermal expansion coefficient

$$\alpha(T) = 1/a_T (\delta a/\delta T)_p$$

where $\alpha(T)$: thermal expansion coefficient at temperature T , and a_T : lattice constant a at temperature T . The value obtained at $T = 200 \text{ K}$ is thus

$$\alpha(200 \text{ K}) = 2.6769 \times 10^{-4} \text{ K}^{-1}.$$

The volume expansion in the plastic range is about 5%.

The powder pattern at 160 K of phase III did produce fairly broad peaks (Figure 6, bottom). Indexation with the program TREOR 90 revealed monoclinic symmetry. The calculated lattice parameters of $a = 12.27$, $b = 10.86$, $c = 10.68 \text{ \AA}$, $\beta = 111.8^\circ$ and $V = 1324.9 \text{ \AA}^3$ propose a possible solution. The pattern furthermore revealed a fairly high background, indicating that the crystallization was far from perfect. All attempts to solve the structure from powder data were hampered by the poor diffraction pattern.

TABLE V
Selected wave numbers ($\tilde{\nu}/\text{cm}^{-1}$) of **2** at different temperatures

Lit.	90 K	GG	AG	273 K	233 K	213 K	193 K	153 K
406	–	v37		?	411	406	409	408
417	–	v36		?	421	417	419	418
492	490	v35		494	494	–	–	–
702	703	v34		703	703	sh	sh	sh
718	716	v17		718	717	716	717	717
876	–		v31	sh	sh	–	–	–
910	910		v29	911	912	909	909	909
984	–		v27	sh	–	–	–	–
1017	1019	v13	v26	1018	1019	1020	1020	1020
1249	1251	v11		1250	1251	1250	1251	1251
1273	1274	v34		1274	1275	1275	1275	1275
1286	1297		v21	sh	sh	?	?	?

A: anti, G: gauche, sh: shoulder.

For comparison, the values given in the literature⁵ are displayed, as well.

Infrared Spectroscopy

Temperature dependent infrared measurements were performed for both compounds **1** and **2** at room temperature and in the region above for **1** and below for **2**.

The infrared spectra of **1** confirmed the absence of any phase transition. The attribution of vibrations to the observed wave numbers was achieved by comparison with literature data.⁵ Infrared measurements on **2** were performed in the liquid and solid phases. The normal modes are known from literature.^{6,7,8} Spectra at different temperatures are displayed in Figure 7.

Four out of nine possible conformers may be distinguished by spectroscopy (Figure 8). The amounts of the various conformers in the gaseous state were determined by Stolevik *et al.*,⁹ who found 56% of all molecules in the GG conformation, 37% in the AG conformation and 7% in AA (G = gauche, A = anti). At 80 K, only the GG conformer was detected in IR experiments.¹⁰ Combined Raman and infrared spectroscopic results indicated the possible existence of a plastic phase between 190 K and 260 K.¹¹ No clear indication about the existence of one or more conformers in phase III could be found in the literature. The difference in energy ΔH (AG–GG) is nearly 4–5 kJ mol⁻¹ and ΔH (GG–AA) approximately 7–8 kJ mol⁻¹.

The spectra were registered between 153 K and 300 K (see Figure 7). The vibrational modes in the region 3000 to 2800 cm⁻¹ are independent of the given conformer, but they sharpen considerably at lower temperature.

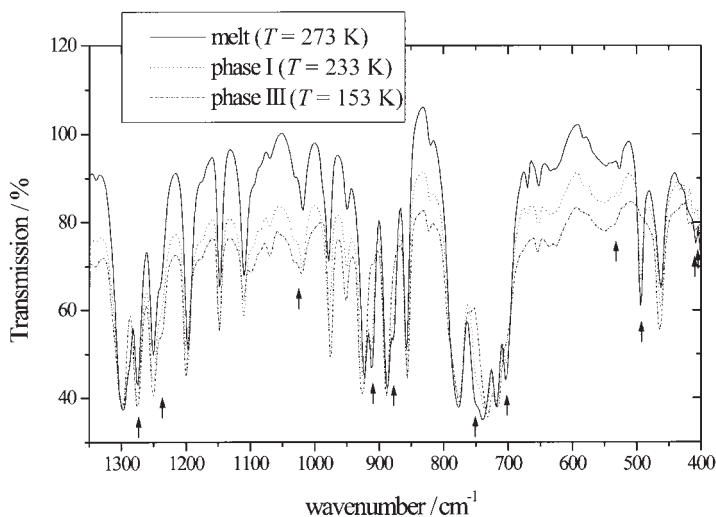


Figure 7. Infrared spectra of 1,3-dichloro-2,2-dimethylpropane (**2**) at three different temperatures. The arrows indicate a strong change of absorbance.

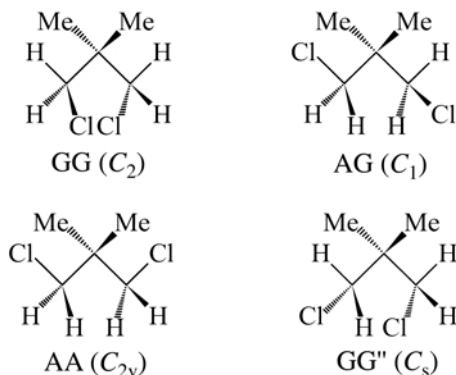


Figure 8. Four distinguishable conformers out of nine possible of 1,3 dichloro-2,2-dimethylpropane (**2**). A = anti, G = gauche, the symmetry is given, as well.

In the region from 1470 cm^{-1} downwards, several bands are sensitive to the given conformer.

The IR-spectra reveal a considerable difference in the intensities between 233 K and 213 K in the bands attributed to AG, which is related with a lower presence of this conformer in the crystalline phase III where steric considerations do not favour that conformer in the crystalline state. The DSC-experiments gave a transition temperature of $T_{\text{I} \rightarrow \text{II,III}} = 194.3\text{ K}$. The difference between the IR and the thermal analysis may be due to experimental conditions. Another explanation is a steric hindrance of the vibrations of the AG conformer already above the actual transition temperature.

In agreement with the literature data, the AG-conformer was detected in the liquid and in the plastic phase identified by eight bands. At 213 K, only three bands out of these eight were observed. Crowder only detected the GG conformer at 80 K.¹⁰

The results presented above together with literature values indicate the presence of a limited amount of AG conformer in phase III. Both conformers differ only in the relative position of chlorine atoms in the molecule, which can be transformed by rotation of the chloromethyl groups. It is therefore supposed that phase III is still disordered and a further transition to a completely ordered phase should exist between 100 K (lower limit of own experiment) and 80 K.

CONCLUSION

Two derivatives of propane were examined in order to study the influence of different substituents on the formation of plastic phases. No plastic

phase was detected in 3-chloro-2,2-bis(chloromethyl)propionic acid-1. The crystalline structure is stabilized by the three chlorine atoms and does not show any further phase transition. The dimerization *via* hydrogen bridges does not prevent the formation of plastic phases, as found in the mono- and disubstituted compounds. The molecule of 1,3-dichloro-2,2-dimethylpropane does not only show a plastic phase but a sequence of phase transitions due to the existence of at least two conformers.

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SAŽETAK

Kristalne strukture i fazni prijelazi 3-kloro-2,2-bis(klorometil)propionske kiseline-1 i 1,3-dikloro-2,2-dimetilpropana

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Kristalna struktura 3-kloro-2,2-bis(klorometil)propionske kiseline-1 određena je difrakcijom rentgenskih zraka na jediničnom kristalu. Spoj kristalizira s necentrosimetričnom prostornom skupinom $P2_1$. Konstante jedinične ćelije pri $T = 304$ K iznose: $a = 6,961(1)$ Å, $b = 9,979(2)$ Å, $c = 12,0569(3)$ Å i $\beta = 94,01(2)^\circ$. Struktura je utočnjena na temelju 1736 neovisnih refleksa pri čemu je postignut faktor nepouzdanosti $R = 0.041$. U kristalnom stanju dolazi do dimerizacije molekula vodikovim vezama. Termičkom analizom te rentgenografskim i IR mjerenjima obavljenim pri različitim temperaturama nije ustanovljeno da dolazi do faznih prijelaza u području $150 \text{ K} < T < 384 \text{ K}$. Fazni prijelaz red/nered otkriven je za 1,3-dikloro-2,2-dimetil-

propan pri $T_{I \rightarrow II} = 194,3$ K uz postojanje plastične kubične faze u području $194,3$ K < $T < 259,1$ K. Konstanta jedinične ćelije u prostornoj skupini $Fm\bar{3}m$ je $a = 9,24$ Å pri 220 K s termičkim ekspanzijskim koeficijentom koji iznosi $\alpha_{(200\text{ K})} = 2,6769 \times 10^{-4}$ K⁻¹. Pri temperaturama tališta $T_m = 259,1$ K i fazne pretvorbe kruto/kruto $T_{I \rightarrow II} = 194,3$ K promjena entropije je neznatna i daje prilično čvrste dokaze za postojanje plastične faze. Rentgenogram praha uređene faze pri $T = 160$ K ukazuje na postojanje monoklinske simetrije s konstantama jedinične ćelije: $a = 12,27$ Å, $b = 10,86$ Å, $c = 10,68$ Å i $\beta = 111,8^\circ$. Konformacija molekule utvrđena je infracrvenim mjerenjima napravljenim pri različitim temperaturama.