On the Structure of Some Pentaerythritol-Related Molecular Crystals with Pseudotetrahedral Molecular Structure. Ordered Structure of 2,2-Bis(bromomethyl)-1,3-propanediol and Orientationally Disordered Structure of 2-Chloromethyl-2-methyl-1,3-dichloropropane; ^{35}Cl NQR *

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$C(CH_2Cl)_3(CH_3)$, melting point $T_m = 291.3$ K, shows in the DTA/DSC experiment a phase transition from an orientationally disordered plastic phase I into an ordered phase II at $T_{I\to II} = 235.9$ K. From 77 K up to $T_{II\to I}$ the ^{35}Cl NQR spectrum is a triplet with (ν in MHz, $T = 77$ K) $\nu_1 = 34.213$, $\nu_2 = 34.183$, $\nu_3 = 33.786$. The ^{35}Cl NQR fade-out temperature $T_f = 247$ K coincides with $T_{II\to I}$ found from the DSC experiment. The plastic phase of 2-chloromethyl-2-methyl-1,3-propanediol is cubic bcc, Im3m, $Z = 2$ and the lattice constant increases linearly 755 pm at 235 K to 768 pm at 283 K. In the heating cycle we found (ΔH in kJ/mol): $\Delta H_{II\to I} = 12.0$, $\Delta S_m/R = 1.0$. The compound belongs to the group of plastic molecules formed by ellipsoid like distorted tetrahedra and is derived by substitution from methane.

The crystal structure of 2,2-bis(bromomethyl)-1,3-propanediol was determined. DTA-DSC show that an orientationally disordered plastic phase does not exist. At room temperature $C(CH_2Br)_2(CH_2OH)_2$ crystallizes monoclinic, space group Cc, $Z = 4$, $a = 628.2$ pm, $b = 2015.5$ pm, $c = 659.6$ pm, $\beta = 94.27°$. The molecules interact by intermolecular hydrogen bonds between the OH-groups and by van der Waals forces Br···Br.

Introduction

Tetrakis(hydroxymethyl)methane (pentaerythritol) forms a cubic orientationally disordered plastic high temperature phase I, Fm3m, $Z = 4$, $a = 896.3$ pm at 503 K. The melting point $T_m = 531$ K, $T_{I\to II} = 457$ K; extensive work has been published on the properties of this compound. For the thermodynamics, see e.g. Murrill and Breed [1]. Nitta and coworkers have studied the plastic phase I [2–8] as well as the ordered phase II. The latter one was studied by several groups of authors extensively: Llewellyn et al. [9], Eilerman and Rudman [10], Hvoslef [11], Shiono et al. [12], Lonsdale [13], and Ladd [14]. For diffuse scattering on pentaerythritol see also Terauchi [15]. Further structural studies on pentaerythritol have been published, such as ^{1}H-NMR by van der Lugt et al. [16] and by Smith [17]; for surface conductivity see Thomas and Evans [18]. A variety of thermodynamical studies on $C(CH_2OH)_4$ besides the ones already mentioned are found in literature, see Barone et al. [19], Bradley et al. [20], Sbirrazzuoli et al. [21, 22], Schwarz et al. [23], Westrum and Payne [24], Westrum [25], and Wilmet et al. [26].

For vibrational spectroscopy see Ballaus and Wagner [27], Marzocchi and Castellucci [28]. Geiseler and Ratz [29, 30] and Gatial et al. [31] report on vibrational spectroscopy on pentaerythritol derivatives. For thermodynamics of such derivatives see [24, 25], Backer and Perdok [32], Clever et al. [33], Murrill et al. [34], Nitta and Seki [35], Payne and Westrum [36], Trowbridge and Westrum [37]. Structural work on derivatives on $C(CH_2OH)_4$ is given by Hassel and Strömmel [38], Khusainov et al. [39], Klaeboe et al. [40], and Wagner and Dengel [41]. Also electron diffraction including molecular orbital calculations are known for several compounds of this group by Braathen and Stølevik [42], by Laszlo [43], Rustad and Stølevik [44], Stølevik [45], Stølevik and Bakken [46]. Studies on the dipole moments and molecular structure by Le Fèvre et al. [47], Lumbroso and Lauransan [48] and Mortimer et al. [49] are known.

Replacing the OH group by F does not change the general thermodynamic behavior of the compounds

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considered. $C(CH_2F)_4$ shows a plastic high temperature phase [24, 25, 29, 37] and Baughman and Turnbull [50]. $T_{II\to I}=249.40$ K, $T_{I\to m}=367.06$ K [37]. Also $C(CH_2OH)_3(CH_2F)$ and $C(CH_2OH)_2(CH_2F)_2$ show an orientationally disordered plastic state [34]. In contrast, no orientational disorder transition is observed in $C(CH_2Cl)_4$, $C(CH_2Br)_4$, and $C(CH_2I)_4$ [24, 25, 29, 36, 40], whereas for $C(CH_2OH)_3(CH_2Cl)$ the existence of a plastic phase is reported [34]. We found it interesting to study how the appearance of a plastic phase in pentaerythritol related molecular compounds is connected with the substitution pattern and report here some properties of 2,2-bis(bromomethyl)-1,3-propanediol, $C(CH_2Br)_2(CH_2OH)_2$, a compound $(A)_2(B)_2$ and of 2-chloromethyl-2-methyl-1,3-dichloropropane, $C(CH_2Cl)_3(CH_3)$, a compound $C(A)_3B$, that is the exchange of two OH groups of pentaerythritol by Br, respectively the exchange of one CH_2Cl group in $C(CH_2Cl)_4$ by CH_3. Martinsen et al. [51] found for 2-chloromethyl-2-methyl-1,3-dichloropropane in infrared studies $T_{m\to I}=289$ K and a plastic phase reaching down to $T_{I\to II}=253$ K. Also electron diffraction, molecular orbital calculations, and the dipole moment are known for this compound [48], Stølevik [52], Bushweller et al. [53] and Braathen et al. [54].

Experimental

Commercial (Aldrich) 2,2-bis(bromomethyl)-1,3-propanediol, $C_5H_{10}Br_2O_2$, was purified by recrystallization from n-hexane. The thermodynamic data were measured with homemade DTA equipment and Setaram DSC 121. On selected small crystals the structure was determined by single crystal diffractometry. From the collected diffraction intensities, after correction for absorption and Lorentz-polarisation factor, the structure was determined by direct methods (Shelix programs [55, 56]. No phase transition solid ↔ solid was observed by DTA/DSC.

Commercial (Aldrich) 1,1,1-tris(chloromethyl)ethane, $C_5H_9Cl_3$, was fractionated by distilling it twice in vacuo. X-ray powder diffraction was applied for the structure determination of phase I. The lattice constant at 235 K was found from least squares refinement of the reflections (110), (200), and (211). At higher temperatures only the reflections (110) and (200) have been of sufficient intensity to determine the cubic lattice constant a.

The ^{35}Cl NQR powder spectrum was taken from 77 K up to the fade out temperature T_f of the signals in the usual way. The rather strong NQR signals (S/N = 20–50 at 77 K, decreasing with increasing temperature) show a line width of 15 kHz. Temperature measurements have been accurate to ±0.5 K [57]; the frequency measurements are reliable to ±5 kHz, the accuracy limited by the line width (15–20 kHz).

Results and Discussion

$C(CH_2OH)_2(CH_2Br)_2$

First we shall report the crystal structure of 2,2-bis(bromomethyl)-1,3-propanediol. In Table 1 we have collected the experimental conditions of the crystal structure work and crystallographic data found for $C_5H_{10}Br_2O_2$. Figure 1 shows the numbering of the atoms in the molecule $C_5H_{10}Br_2O_2$, including the 50% contour of the electron density (thermal ellipsoids). In Fig. 2 the unit cell of 2,2-bis(bromomethyl)-1,3-propanediol is projected along the axis [100] onto the bc plane. The projection along [001] is

Table 1. Crystal structure data and experimental conditions for the structure determination of 2,2-bis(bromomethyl)-1,3-propanediol, $C(CH_2Br)_2(CH_2OH)_2$, $C_5H_{10}Br_2O_2$, $M=261.97$. Diffractometer: Stoe-Stadi 4; wave length: 710.69 pm (MoKα); Monochromator: Graphite (002); Scan: $2\theta/\Omega$.

Crystal size (mm^3)	$1.3\times0.48\times0.17$	
Temperature/K	293(2)	
Absorpt. Coeff. μ/m^{-1}	946.9	
θ-range for data coll.	$2.02\leq\theta/^\circ\leq29.95$	
Index range	$-8\leq h\leq7$; $0\leq k\leq15$; $-9\leq l\leq9$	
Lattice constants/pm	$a=628.2(3)$	$\alpha=90.00^\circ$
	$b=2015.5(8)$	$\beta=94.27(2)^\circ$
	$c=659.6(3)$	$\gamma=90.00^\circ$
$V\cdot10^{-6}/(pm^3)$	832.8(6)	
Space group	C_s^4–Cc	
Formula units Z	4	
$\varrho_{calc}/(Mg\cdot m^{-3})$	2.089(3)	
$F(000)$	504	
Reflections coll.	2954	
Symmetry independ.	2358	
$[R_{int}]$	[0.0204]	
Data/	2355	
Restraints/parameters	4/89	
Goodness of fit on F^2	1.085	
Final $R(I>2\sigma(I))$	$R_1=0.0694$; $wR_2=0.2022$	
Final R(all data)	$R_1=0.0850$; $wR_2=0.2308$	
Absolute struct. param.	0.40(4)	
Largest diff. (peak/hole)/ $(10^{-6}\,e(pm^3))$	1.203/−1.394	
Max., Min. Transm.		
Extinct. coeff.	0.007(2)	
Point positions	all atoms in 4a: (0, 0, 0; ½, ½, 0) +(x, y, z; x, −y, ½+z)	

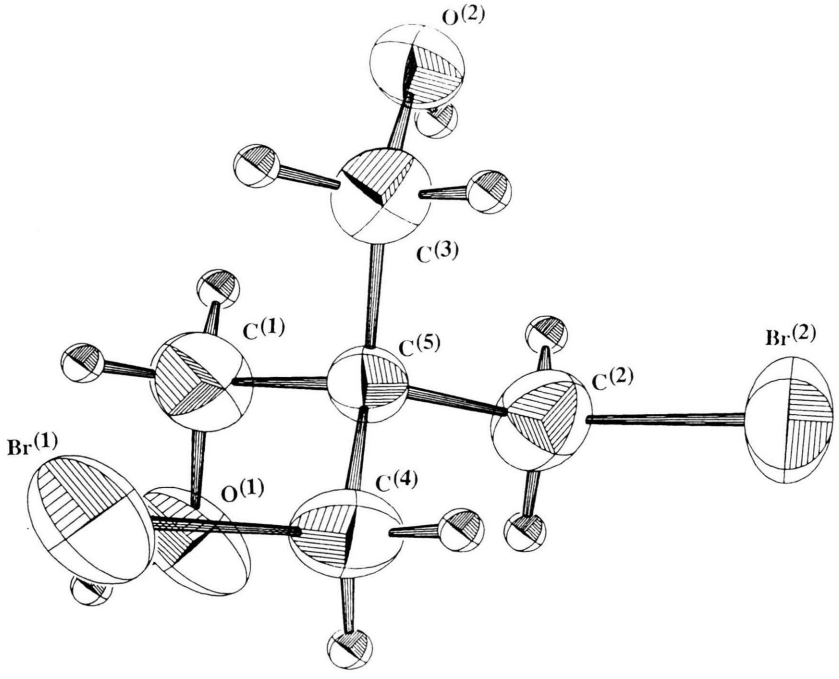

Fig. 1. Molecule $C_5H_{10}Br_2O_2$: Numbering of the atoms and thermal ellipsoids (50% electron density contour).

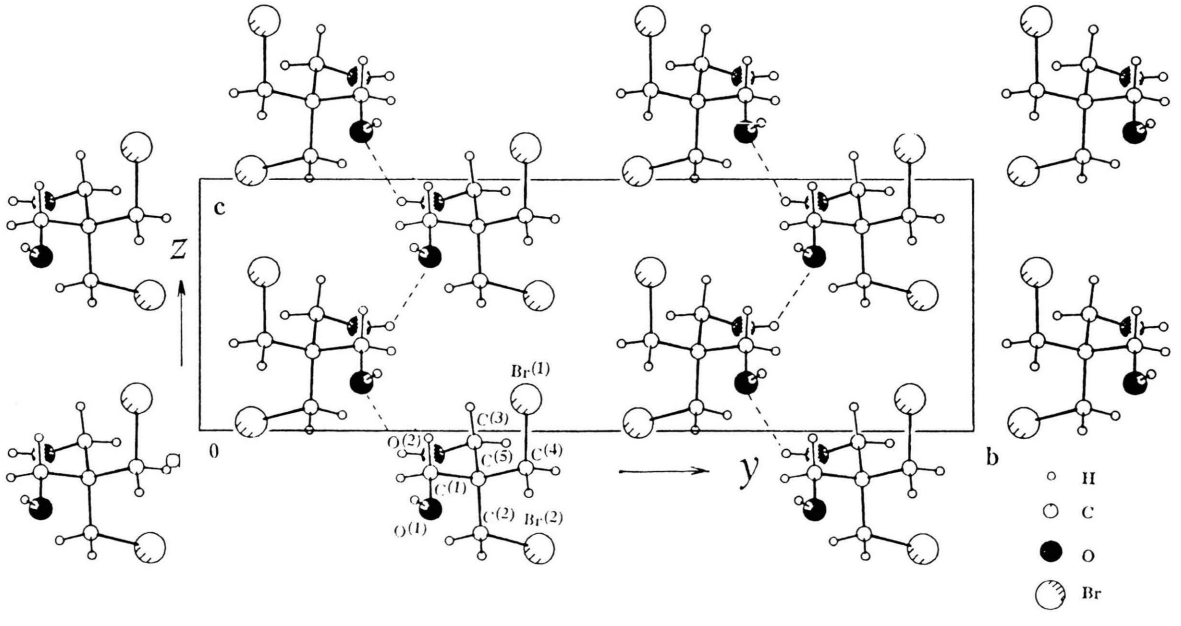

Fig. 2. Projection of the unit cell of $C_5H_{10}Br_2O_2$ along the axis [100] ($a = 660$ pm) onto the bc plane. The molecule for which the coordinates are given in Table 2 is marked.

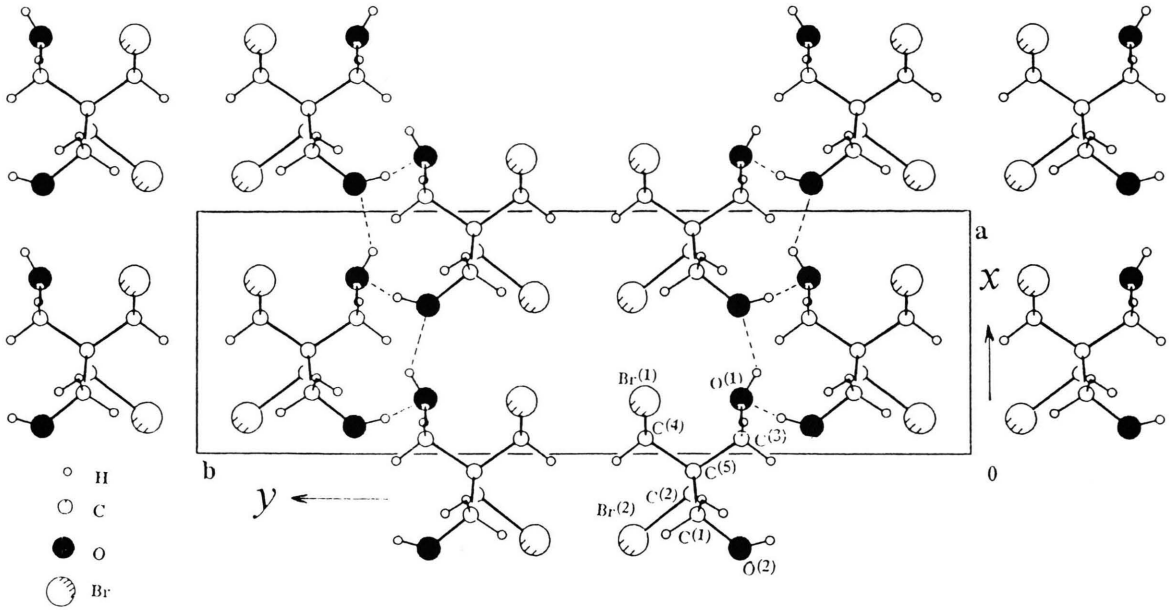

Fig. 3. Projection of the unit cell of $C(CH_2Br)_2(CH_2OH)_2$ along the axis [001]. The hydrogen bonds O–H···O are marked by dashed lines. The numbered atoms correspond to the ones given in Table 2.

shown in Fig. 3, in which also the hydrogen bonds are marked. Positional parameters of the atoms, including the thermal parameters are given in Table 2.

In Table 3 we have listed the intramolecular bond distances and bond angles. Relevant intermolecular distances and the data of the hydrogen bond scheme can also been found there.

The C–C bond distances are found in the range 151–153 pm, equal within the limits of error and within the limits for aliphatic distances d(C–C) reported in literature. There may be a very small stretching of d(C–C) by the substitution of one hydrogen atom in the CH_3 groups by OH compared to the substitution H→Br. As for the angles in the tetrahedron $C^{(1,3)}$–$C^{(5)}$–$C^{(2,4)}$, they are between 107.3° and 111.6°, quite a regular, only little distorted arrangement. The distances C–Br are 196.4 and 195.6 pm, equal within the limits of error.

The hydrogen bonds introduce some differences in the two non-equivalent C–O bond lengths, which are 146.0 and 141.9 pm. The distances O···O are 269 and 273 pm, showing that rather strong hydrogen bonds are connecting the molecules in the lattice to planes which are located at (x, 1/4, z) and (x, 3/4, z), see Figs. 2 and 3. In the planes (x, 0, z) and (x, ½, z) there are van der Waals interactions, mainly interactions Br↔Br (d_{vdw}(Br···Br) = 368 pm and d_{vdw}(Br···C) = 377 pm are the shortest ones observed within the title compound).

By DSC analysis we found for the thermodynamic data of 2,2-bis(bromomethyl)-1,3-propanediol the following data: Heating curve: 293 K→1 K/min→403 K, T_m = 387.3 K; ΔH_m = 30.1 kJ/mol; $\Delta S_m/R$ = 9.4. Cooling curve: 403 K→1 K/min→293 K; T_{cryst} = 363.4 K; ΔH = 28.3 kJ/mol; $\Delta S_{cryst}/$ = 9.3. A plastic phase does not exist.

$C(CH_2Cl)_3(CH_3)$

2-chloromethyl-2-methyl-1,3-dichloropropane melts at 291.3 K. DTA/DSC measurements have shown, see Fig. 4, that there are two phase transitions in the solid state. An orientationally disordered plastic phase I exists. Form DTA/DSC we found the thermodynamic data given in Table 4.

The DSC/DTA results show that there is no undercooling of the melt in the crystallization process. The temperature-range of the orientationally disordered phase is broad (247–291 K) in the heating cycle with a hysteresis and a depressed transition I→II in the cooling cycle, where the plastic phase extends from 291 K down to 236 K. The reduced melting entropy

Table 2. Atomic coordinates ($\times 10^4$) and displacement parameters, U_{eq} and U_{ij} of 2,2-bis(bromomethyl)-1,3-propanediol. U_{eq} is defined as one third of the trace of the orthogonalized tensor U_{ij}. The anisotropic displacement factor is of the form

$$T = \exp\{-2\pi^2 (h^2 a^{*2} U_{ii} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})\}.$$

The U_{ij} are given in $(pm)^2$.

Atom	x	y	z	U_{eq}
$Br^{(1,C4)}$	2156(3)	4189(1)	1271(4)	718(4)
$Br^{(2,C2)}$	−3535(3)	4353(1)	−4669(4)	808(5)
$O^{(1,C1)}$	2255(9)	2942(4)	−3104(10)	629(20)
$O^{(2,C3)}$	−3864(11)	2976(4)	−0949(15)	615(18)
$H^{(O1)}$	3348(125)	2739(64)	−2739(247)	755
$H^{(O2)}$	−3543(248)	2578(19)	−0888(239)	758
$C^{(1)}$	0617(16)	2944(5)	−1644(18)	561(21)
$H^{(1,C1)}$	1289(16)	2920(5)	−0274(17)	673
$H^{(2,C2)}$	−0295(16)	2559(5)	−1866(18)	673
$C^{(2)}$	−1648(19)	3595(6)	−4068(15)	589(23)
$H^{(1,C2)}$	−2441(19)	3190(6)	−4368(15)	707
$H^{(2,C2)}$	−0488(19)	3612(6)	−4958(15)	707
$C^{(3)}$	−2496(16)	3519(6)	−0419(14)	551(20)
$H^{(1,C3)}$	−1873(16)	3462(6)	0960(14)	661
$H^{(2,C3)}$	−3318(16)	3927(6)	−0471(14)	661
$C^{(4)}$	0629(18)	4181(6)	−1438(18)	568(22)
$H^{(1,C4)}$	−0290(18)	4568(6)	−1567(18)	681
$H^{(2,C4)}$	1663(18)	4218(6)	−2454(18)	681
$C^{(5)}$	−0711(13)	3569(3)	−1880(14)	352(11)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Br^{(1,C4)}$	592(6)	754(7)	780(7)	−100(6)	−137(4)	−263(6)
$Br^{(2,C2)}$	719(8)	727(8)	931(10)	86(6)	−244(6)	259(7)
$O^{(1,C1)}$	413(30)	602(40)	871(55)	99(32)	46(34)	−270(36)
$O^{(2,C3)}$	402(31)	589(38)	839(49)	−101(30)	−48(28)	258(38)
$C^{(1)}$	540(48)	398(41)	740(58)	43(35)	7(40)	−39(39)
$C^{(2)}$	705(62)	580(55)	469(41)	−56(46)	−46(39)	25(37)
$C^{(3)}$	532(47)	606(54)	514(44)	14(40)	38(35)	75(38)
$C^{(4)}$	548(51)	480(47)	669(55)	−182(40)	5(42)	43(42)
$C^{(5)}$	342(26)	307(30)	401(28)	−27(28)	−17(21)	−1(31)

Table 3. Intramolecular bond distances (in pm) and angles (in degree) for 2,2-bis(bromomethyl)-1,3-propanediol. The relevant intermolecular data to describe the hydrogen bond network and the van der Waals interactions are included. Only distances ≤400 pm are considered.

Connection	d/pm	Connection	Angle/°
$Br^{(1,C4)}-C^{(4)}$	196.4(12)	$Br^{(1,C4)}-C^{(4)}-H^{(1,C4)}$	108.7(4)
$Br^{(2,C2)}-C^{(2)}$	195.6(12)	$Br^{(1,C4)}-C^{(4)}-H^{(2,C4)}$	108.7(3)
$O^{(1,C1)}-C^{(1)}$	146.0(13)	$Br^{(2,C2)}-C^{(2)}-H^{(1,C2)}$	108.8(3)
$O^{(1)}-H^{(O1)}$	82.0(4)	$Br^{(2,C2)}-C^{(2)}-H^{(2,C2)}$	108.8(3)
$O^{(2,C3)}-C^{(3)}$	141.9(13)	$C^{(1)}-O^{(1,C1)}-H^{(O1)}$	109.5(5)
$O^{(2,C3)}-H^{(O2)}$	83	$C^{(3)}-O^{(2,C3)}-H^{(O2)}$	109.6(5)
$C^{(5)}-C^{(1)}$	151.2(12)	$C^{(5)}-C^{(1)}-O^{(1)}$	110.2(8)
$C^{(5)}-C^{(2)}$	151.8(13)	$C^{(5)}-C^{(1)}-H^{(1,C1)}$	109.6(5)
$C^{(5)}-C^{(3)}$	153.5(12)	$C^{(5)}-C^{(1)}-H^{(2,C1)}$	109.6(5)
$C^{(5)}-C^{(4)}$	151.0(12)	$H^{(1,C1)}-C^{(1)}-H^{(2,C1)}$	108.1
$C^{(1)}-H^{(1,C1)}$	97	$O^{(1)}-C^{(1)}-H^{(1,C1)}$	109.6(5)
$C^{(1)}-H^{(2,C1)}$	97	$O^{(1)}-C^{(1)}-H^{(2,C1)}$	109.6(5)
$C^{(2)}-H^{(1,C2)}$	97	$C^{(5)}-C^{(3)}-O^{(2)}$	110.8(8)
$C^{(2)}-H^{(2,C2)}$	97	$C^{(5)}-C^{(3)}-H^{(1,C3)}$	109.5(5)
$C^{(3)}-H^{(1,C3)}$	97	$C^{(5)}-C^{(3)}-H^{(2,C3)}$	109.5(5)
		$H^{(1,C3)}-C^{(3)}-H^{(2,C3)}$	108.1(7)
$C^{(3)}-H^{(2,C3)}$	97	$O^{(2)}-C^{(3)}-H^{(1,C3)}$	109.5(5)
$C^{(4)}-H^{(1,C4)}$	97	$O^{(2)}-C^{(3)}-H^{(2,C3)}$	109.5(5)
$C^{(4)}-H^{(2,C4)}$	97	$C^{(1)}-C^{(5)}-C^{(4)}$	111.6(8)
Connection	angle/°		
$C^{(1)}-C^{(5)}-C^{(2)}$	107.3(8)	$C^{(4)}-C^{(5)}-C^{(2)}$	109.0(7)
$C^{(1)}-C^{(5)}-C^{(3)}$	107.7(7)	$C^{(4)}-C^{(5)}-C^{(3)}$	110.7(7)
$C^{(2)}-C^{(5)}-C^{(3)}$	110.5(8)	$C^{(5)}-C^{(4)}-Br^{(1)}$	114.0(7)
$C^{(5)}-C^{(4)}-H^{(1,C4)}$	108.7(6)	$C^{(5)}-C^{(4)}-H^{(2,C4)}$	108.8(8)
$H^{(1,C4)}-C^{(4)}-H^{(2,C4)}$	107.6(8)	$C^{(5)}-C^{(2)}-Br^{(2)}$	113.9(7)
$C^{(5)}-C^{(2)}-H^{(1,C2)}$	108.5(5)	$C^{(5)}-C^{(2)}-H^{(2,C2)}$	108.8(5)
$H^{(1,C3)}-C^{(3)}-H^{(2,C3)}$	108.8(5)		
Hydrogen bond scheme:			
$O^{(1,C1)}\cdots O^{(2,C3)a}$	273.0(11)	$O^{(1)}-H^{(O1)}\cdots O^{(2)a}$	134.4(94)
$H^{(O1)}\cdots O^{(2,C3)a}$	209(10)		
$O^{(2,C3)}\cdots O^{(1,C1)b}$	269.1(10)	$O^{(2)}-H^{(O2)}\cdots O^{(1)b}$	123.9(97)
$H^{(O2)}\cdots O^{(1,C1)b}$	214(14)		
Intermolecular distances within the sum of van der Waals radii:			
Connection	d/pm	Connection	d/pm
$Br^{(1)}\cdots Br^{(2)c}$	367.8(4)	$Br^{(1)}\cdots Br^{(2)d}$	407.4(3)
$Br^{(2)}\cdots Br^{(2)e}$	420.5(4)	$Br^{(1)}\cdots C^{(4)f}$	376.9(4)
$Br^{(1)}\cdots H^{(1,C4)}$	331.5	$Br^{(1)}\cdots H^{(2,C4)}$	333.9

[a] $O^{(2)}$: $1+x, y, z$; [b] $O^{(1)}$: $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; [c] $Br^{(2)}$: $1+x, y, 1+z$; [d] $Br^{(2)}$: $1+x, 1-y, \frac{1}{2}+z$; [e] $Br^{(2)}$: $x, 1-y, \frac{1}{2}+z$; [f] $C^{(4)}$: $x, 1-y, \frac{1}{2}+z$

$\Delta S_m/R = 1.0$ is in the range of $\Delta S_m/R$ one finds for plastic phases.

The structure of the disordered phase I is bcc, Im3m, $Z = 2$. The lattice constant is shown in Fig. 5 as a function of temperature. It should be mentioned that also the space group with the lowered bcc symmetry $I\bar{4}3m$ should be discussed. However there is no decision on the basis of the presently available X-ray diffraction data. At 235 K we observe $a_{(235\,K)} = 755.2(1)$ pm. The linear thermic expansion coefficient is $\alpha_{(235\,K)} = 1/a_{(235\,K)}\,(da/dT)_p = 3.434 \cdot 10^{-4}\,K^{-1}$.

As one expects in first approximation, the ^{35}Cl NQR spectrum is a fairly narrow triplet which was studied from 77 K up to the fade out temperature T_f. It covers the frequency range form 34.2 MHz (ν_1, 77 K) to 33.1 MHz (ν_3, 246 K). In Table 5 the results of the ^{35}Cl NQR study are collected: resonance frequencies at selected temperatures and the coefficients a_1 of the power series development $\nu_i = \sum a_i T^i$, $-1 \le i \le 2$. The three Cl atoms in the molecule are chemically equivalent and the splitting is due to the crystal field. This field leads also to a molecular symmetry in the solid phase II, which does not show any symmetry element. Furthermore we learn from NQR

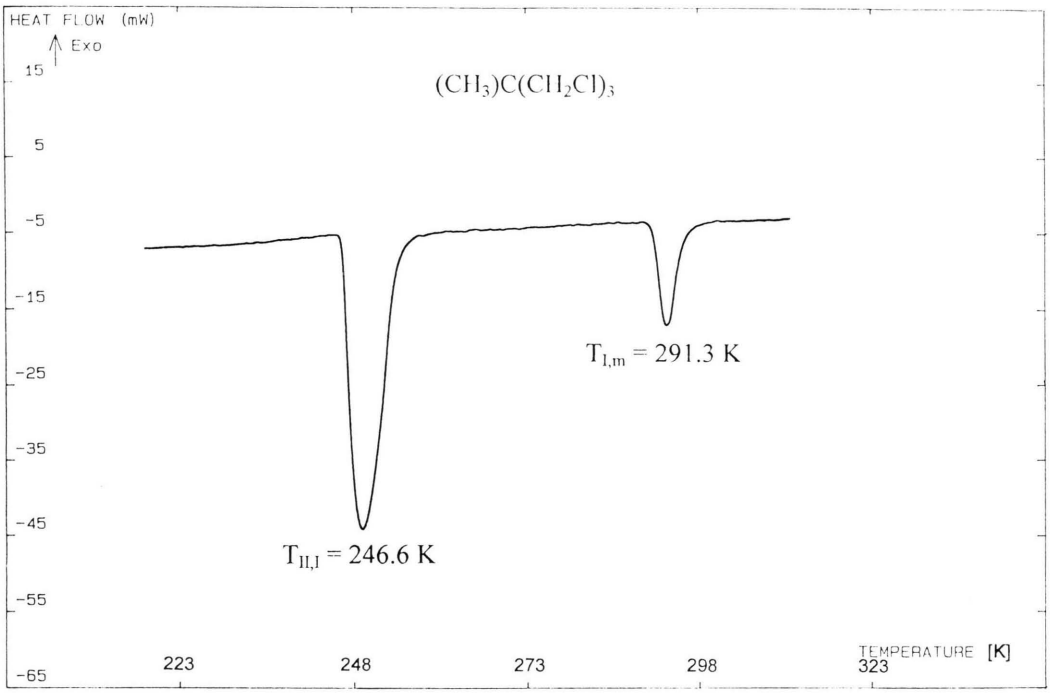

Fig. 4. DSC diagram of 2-chloromethyl-2-methyl-1,3-dichloropropane.

Table 4. Thermodynamic data for 2-chloromethyl-2-methyl-1,3-dichloropropane (T in K; ΔH in kJ · mol^{-1}; ΔS in J/(K · mol); R = gas constant):

A) Heating cycle (170 K → 2 K/min → 305 K)			
$T_{I\to melt}$	$\Delta H_{I\to m}$	$\Delta S_{I\to m}$	$\Delta S_{I\to m}/R$
291.3	2.5	8.4	1.0
$T_{II\to I}$	$\Delta H_{II\to I}$	$\Delta S_{II\to I}$	$\Delta S_{II\to I}/R$
246.6	12.0	48.2	5.8
B) Cooling cycle (295 K → 3 K/min → 170 K)			
$T_{melt\to I}$	$\Delta H_{m\to I}$	$\Delta S_{m\to I}$	$\Delta S_{m\to I}/R$
291.1	2.5	8.5	1.0
$T_{I\to II}$	$\Delta H_{I\to II}$	$\Delta S_{I\to II}$	$\Delta S_{I\to II}/R$
235.9	11.4	49.0	5.9

Table 5. ^{35}Cl NQR frequencies of $(ClH_2C)_3C(CH_3)$ at selected temperatures and coefficients a_i of the power series development $\nu_i = \sum (a_i T^i)$, $-1 \le i \le 2$. z is the number of experimental measurements, σ is the mean squares deviation (in kHz). The power series approximation is valid for the range $77 \le T/K \le 240$.

ν_1(77 K)/MHz	ν_1(201 K)/MHz	ν_1(246 K)/MHz
34.213	33.793	33.611
ν_2(77 K)/MHz	ν_2(201 K)/MHz	ν_2(246 K)/MHz
34.183	33.671	33.430
ν_3(77 K)/MHz	ν_3(201 K)/MHz	ν_3(246 K)/MHz
33.786	33.346	33.129

ν_i	z	σ / kHz	a_0 / MHz	a_{-1} / MHz · K	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^{-6}$ / MHz · K^{-2}
ν_1	17	5	34.72003	−14.84240	−3.98304	−1.36518
ν_2	17	5	34.88717	−22.92559	−5.13440	−1.81816
ν_3	17	3	34.23512	−13.33043	−3.25498	−4.25429

that there is no intramolecular disorder (in the arrangement of the CH_2Cl groups). The electric field gradient, EFG, is defined at each of the three Cl sites. The frequencies of the ^{35}Cl NQR decrease with increasing temperature, as one expects according to the Bayer model [58] for a molecular crystal temperature dependence of NQR frequencies. It is interesting to note that $T_f = 246$ K for the NQR lines coincides with the thermodynamically determined $T_{II\to I}$, showing that the dynamics of the CH_2Cl groups in phase II is rather weak, up to $T_{II\to I}$, and the ordered phase II has no "predisorder" below $T_{II\to I}$. In Fig. 6 the temperature dependence of the ^{35}Cl NQR triplet is shown graphically.

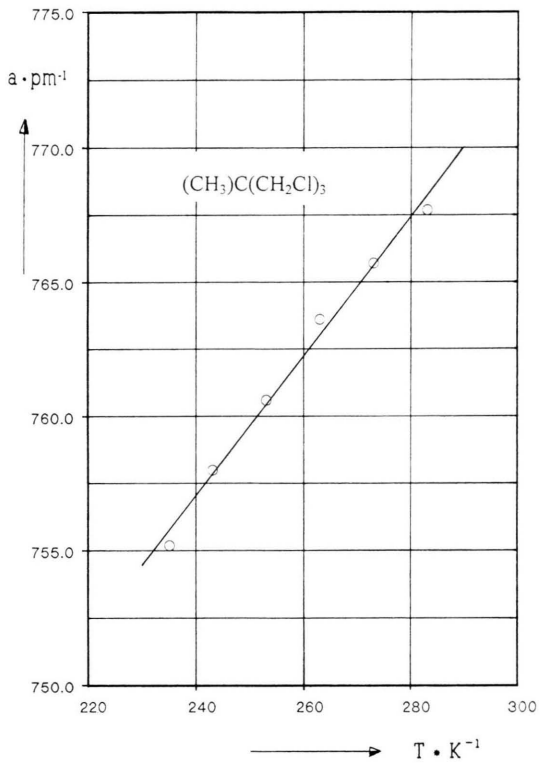

Fig. 5. Lattice constant a of the orientationally disordered cubic phase (bcc) of $(CH_3)C(CH_2Cl)_3$ as function of temperature.

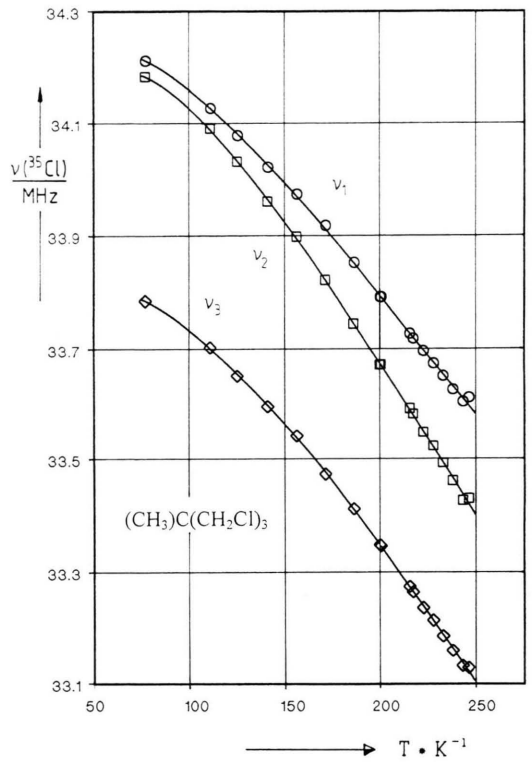

Fig. 6. ^{35}Cl NQR spectrum of 2-chloromethyl-2-methyl-1,3-dichloropropane, phase II, as function of temperature.

Conclusion

The substitution of the four hydrogen atoms of a methane molecule by two hydroxymethyl-, $HOCH_2$-, and two bromomethyl-groups, $BrCH_2$-, results in the title compound investigated here, which shows no plastic high temperature phase. When substituting all hydrogen atoms by four $BrCH_2$-groups, one obtains the also non plastic tetrakis(bromomethyl)methane, $C(CH_2Br)_4$ [33]. If the replacement is done by two $BrCH_2$-groups and two methyl-groups, the compound 1,3-dibromo-2,2-dimethylpropane, $(CH_3)_2C(CH_2Br)_2$, is formed, which also shows no plastic high temperature phase, as shown via vibrational spectroscopy by Gatial et al. [31]. Looking at the shape of this molecules, we can conclude that mainly size effects suppress the existence of a plastic phase. The plastic phase in tetrakis(hydroxymethyl)methane, $C(CH_2OH)_4$, disappears by substituting two OH-groups by two Br-atoms. Following Bondi [59], the van der Waals radius r_{vdW} for a $HOCH_2$-group is approximately 310 pm. That one of a $BrCH_2$-group is remarkably larger ($r_{vdW}(BrCH_2\text{-}) = 350$ pm). Therefore the van der Waals surface in $C(CH_2OH)_2(CH_2Br)_2$ deviates considerably from globular shape. This leads, within the structure of the crystalline phase II, to a severe molecular interlocking and finally to a suppression of molecular rotation in the lattice.

From the crystallographic point of view there is another basis for interpretation. The distances O···O in the crystal structure of $C(CH_2OH)_2(CH_2Br)_2$ are 269 and 273 pm, showing that the molecules in the lattice are connected together to layers by rather strong hydrogen bonds. Parallel to these layers, other planes are running in which the molecules are only connected by van der Waals interactions, mainly Br↔Br. One can imagine now that by supplying thermal energy the weaker bonded layers are widened more easily by lattice vibrations than the polar ones, thus leading to destruction of the crystal lattice and

melting before molecular rotation sets in. However, in pentaerythritol, $C(CH_2OH)_4$, the hydrogen bonds are directed in three dimensions, so the lattice is expanding symetrically until the thermal energy is sufficient to break the hydrogen bonds and transform to the plastic phase. This shows us the important influence of hydrogen bonding on the appearance or non-appearance of a rotator phase.

1,1,1-tris(chloromethyl)ethane, $(CH_3)C(CH_2Cl)_3$, shows an even more complicated behaviour. Substituting step by step the methyl-groups in neopentane, $C(CH_3)_4$, which forms as plastic phase [60, 61], by chloromethyl-groups leads to the compounds $C(CH_3)_{4-n}(CH_2Cl)_n$ ($n=1-4$). With the exception of tetrakis(chloromethyl)methane, $C(CH_2Cl)_4$, they all show an orientationally disordered plastic phase [33, 51, 62, 63]. That the latter exhibits no plastic behaviour seems to be surprising, because one would expect that the molecule with highest symmetry should be most easily excited to rotation. But if we look upon the series of four times substituted derivatives of neopentane, $C(CH_2X)_4$ (X = F, OH, Cl, Br, I), we can see that the compounds X = F, OH form plastic phases [1, 2, 37], those with X = Cl, Br, I do not [33]. We suppose that here also the size of the halomethyl-groups, XCH_2-, is a determining factor for the existence of a high temperature phase. In tetrakis(fluoromethyl)methane, $C(CH_2F)_4$ ($r_{vdW}(CH_2F)=290$ pm), and in pentaerythritol, $C(CH_2OH)_4$ ($r_{vdW}(CH_2OH)=310$ pm), the molecules show an approximately spherical van der Waals surface. In the compounds $C(CH_2X)_4$ (X = Cl, Br, I) the halomethyl-groups are already so voluminous ($r_{vdW}(CH_2Cl)=350$ pm, $r_{vdW}(CH_2Br)=375$ pm, $r_{vdW}(CH_2I)=410$ pm) that the van Waals surfaces of the molecules show increasing depressions. This leads to a considerable molecular interlocking of the molecules and thus suppresses the transition to a plastic phase. In the compounds $C(CH_3)_{4-n}(CH_2Cl)_n$ ($n=1,2,3$) the molecules show a severe deviation from the ideal spherical shape. Due to the lower symmetry of the molecules, however, one can assume a molecular arrangement that will result in a less dense packing, thus effectively reducing the interlocking between the molecules. That is why rotation of molecules is facilitated in those compounds. But all these assumptions we can not prove because for the compounds with $n=1,2,3$ the crystal structures of the crystalline low temperature phases are not known.

Possibly also a mass effect plays a part. So, the thermodynamics region of existence of the plastic phase decreases remarkably from $n=1$ to $n=3$, while the melting temperatures are increasing. This shows that more and more thermal energy must be supplied for a transition to a plastic phase.

In conclusion one can state that mainly three influences are responsible for the appearance of an order-disorder transition in the pentaerythritol derivatives discussed here and in literature. One is the size effect of the substituents (van der Waals radii) on the shape of the molecules, another the existence of hydrogen bonds, and last but not least the symmetry of the molecules. But the interplay and interaction of these effects is complex, and so it is hard to decide which is the determining factor for the appearance or non-appearance of a plastic phase.

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