

THE MOLECULAR STRUCTURE, CONFORMATIONS AND VIBRATIONAL SPECTRA OF 2,2-DI(CHLOROMETHYL)-1,3-DICHLOROPROPANE AND 2,2-DI(BROMOMETHYL)-1,3-DIBROMOPROPANE

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ABSTRACT

The IR and Raman spectra of 2,2-di(chloromethyl)-1,3-dichloropropane ($C(CH_2Cl)_4$) and 2,2-di(bromomethyl)-1,3-dibromopropane ($C(CH_2Br)_4$) were recorded as melts and as solutes in various solvents. Spectra of the solids were observed at various temperatures between the melting points and 90 K. High pressure IR spectra (0–20 kbar) of the compounds were recorded between 300 and 450 K. The crystal structures of both compounds were determined by X-ray crystallographic measurements of single crystals at ca. 130 K.

In the crystalline state both compounds exist in the D_{2d} conformer, whereas in the melt and in solution an additional conformer, probably of symmetry S_4 was assigned supported by force constant calculations. Unlike neopentane and various chlorinated neopentanes with one, two or three chlorine substituents, no plastic crystalline phase was detected for the title compounds. The structure of both molecules were disordered with two molecules in the monoclinic unit cell ($P2_1/n$).

INTRODUCTION

Often in these pages authors can state that they are studying for the first time newly synthesized compounds, hitherto unavailable. We make no such claim. The two title compounds were first reported in 1907 and 1893, respectively [1, 2]. Nor can we claim that ours is the first investigation with structural implications; such studies began in the 1930's.

In 1932 Wagner and Denge [3] performed a crystallographic study supported by X-ray measurements and concluded that the molecules possessed C_{2h} symmetry. A model molecule having all carbon atoms in one plane and the four halogen atoms and the central carbon atom in another plane was found to be in accordance with their experimental findings. A vapour phase electron diffraction study of the bromo (and iodo) compound was carried out in 1934; a structure having the halogen atoms and the central carbon coplanar and with the four other carbon atoms tetrahedrally arranged about

the central carbon was suggested [4]. Hassel and Strömme [5] showed in 1937 that the unit cell determined by Wagner and Denger was too small, that the symmetry requirement of the molecule accordingly was in error, and that the crystal structure must be quite complicated. They also carried out electron diffraction on the chloro, bromo and iodo compounds [5]. No simple rigid atomic arrangement of atoms agreed with their data and they suggested that an internal movability must be taken into account.

The title compounds were first examined by spectroscopic methods in 1940. Crystalline powder data were recorded and from the Raman spectrum of the molten chloro compound Ballaus and Wagner [6] postulated two molecular forms in the liquid, a surprisingly modern interpretation. More recently dipole and measurements infrared data over a very short range were reported [7] for the chloro compound. Geiseler and Ratz [8] published extensive infrared (above 400 cm^{-1}) and Raman spectra for both compounds. Their data were interpreted on the basis of an assumed D_{2d} molecular symmetry in the solid. The conformers having parallel 1:3 interactions as well as that possessing S_4 symmetry were not seriously considered.

Finally, Stölevik [9] and Rustad and Stölevik [10] studied both compounds in the vapour phase by electron diffraction. In both cases they found substantial amounts of the only two conformers in which parallel 1:3 interactions are absent. The chloro compound at 378 K contains approximately equal amounts of conformers with D_{2d} and S_4 symmetry, while the bromo compound at 413 K contains about 58% D_{2d} and 42% S_4 . This is the first study in which unequivocal direct evidence on the conformations present has appeared.

To this time, in spite of half a century of intermittent study, the conformer present in the solid phases has still been in doubt. In the present communication we report a full spectroscopic investigation supplemented by results from X-ray diffraction.

EXPERIMENTAL

Chemicals

The compounds $C(CH_2Cl)_4$ (tetrachloroneopentane, TCN) and $C(CH_2Br)_4$ (tetrabromoneopentane, TBN) were purchased from Fluka. They were purified by recrystallization and sublimation and the purity was checked by gas chromatography.

Spectroscopy

IR spectra were obtained with a Perkin-Elmer model 225 spectrometer ($4000\text{--}200\text{ cm}^{-1}$), a Bruker model 114 C Fourier transform spectrometer ($4000\text{--}50\text{ cm}^{-1}$) and a Perkin-Elmer Hitachi FIS-1 spectrometer ($400\text{--}100\text{ cm}^{-1}$). Raman spectra were recorded on a Cary 81 spectrometer, modified

for perpendicular excitation and on a DILOR RT30 triple monochromator spectrometer, interfaced with the ASPECT 2000 of the Bruker FTIR. The spectra were excited by a CRL model 52 G argon ion laser, using the 5145 and 4880 Å lines.

IR spectra of TCN and TBN were recorded as KBr (4000—400), and polyethylene (600—50 cm^{-1}) pellets, as Nujol mulls and as solid films between CsI plates at various temperatures between the melting points and 90 K. Amorphous and crystalline samples were studied by shock-freezing the vapours on a CsI or polyethylene window, and subsequent annealing to 250 K. Infrared spectra of both compounds were obtained as capillary melts between KBr plates with the aid of a Perkin-Elmer heated sample holder. In the mid IR, spectra were recorded of saturated solutions of TCN and TBN in CS_2 and CCl_4 in sealed cells with KBr and CsI windows. Far IR spectra in C_6H_6 and C_6H_{12} solutions were obtained in vacuum tight cells with polyethylene windows. A vapour spectrum of TCN in a 9 cm cell was observed at ca. 430 K.

High pressure IR spectra were recorded in a diamond anvil cell (DAC) which was equipped with electric heating, using gaskets of brass and stainless steel. The neat samples were run at pressures up to 25 kbar, while carbon disulfide solutions were investigated up to ca. 10 kbar pressure. A Perkin-Elmer 4x beam condenser was employed and the spectra recorded in the Perkin-Elmer 225 as well as in the Bruker 114c spectrometers.

Raman spectra of the crystalline solids were recorded at various temperatures between melting and 90 K. Additional spectra of saturated solutions of TCN and TBN in CCl_4 and C_6H_6 and a molten sample of TCN were obtained and polarization measurements were carried out. When TBN was heated above melting (435 K) a brownish colour of free bromine prevented the Raman spectrum from being recorded.

X-ray work

Single crystals suitable for diffraction measurements were grown by slow evaporation of the solvent from saturated CCl_4 -solutions. The X-ray data were measured on a Syntex P1 diffractometer equipped with a modified Enraf Nonius gas-flow cooling device. The chloro and the bromo compounds were found to be isomorphous. When different, values specific for the latter are listed in parentheses.

A crystal of dimensions $0.38 \times 0.28 \times 0.14$ mm ($0.32 \times 0.16 \times 0.11$) was mounted in general orientation. The temperature in the N_2 stream was 130 K. From 15 centered reflections (registered by polaroid film) a monoclinic cell was deduced; the symmetry and the space group were confirmed by the symmetry of and the systematic absences in the intensity data. Accurate cell dimensions were later determined by least squares refinement on 45 (30) 2θ -values of centered reflections. Intensity data for one quadrant

were registered by the $\theta-2\theta$ scan mode, scan speed (in 2θ) 3° min^{-1} , scan range from 1.2° (1.0) below the $K\alpha_1$ - to 1.4° (1.2) above the $K\alpha_2$ -value, $2\theta_{\text{max}}$ equal to 60° , background to scanning time ratio 0.7, and using graphite-monochromated $\text{MoK}\alpha$ radiation. Three reference reflections measured every 60 reflection showed no decrease (15% decrease) during the data collection.

The reference reflections were used for scaling the data, absorption correction based upon the gaussian grid method was performed, the transmission factor varying from 0.704 (0.068) to 0.802 (0.166). The X-ray cross section values were taken from ref. 11. Estimated standard deviations in the intensities were calculated from counting statistics including a 2% uncertainty to account for long term fluctuations. The 1104 (895) intensities greater than 2σ were considered observed, those less were only used in the structure determination by direct methods [12a]. Our unit cell measurements show that one of the axes as determined earlier [3] (the c axis) has to be doubled. We have now also chosen a face diagonal for the c -axis. The new cell dimensions (see crystal data) are related to the old by the transformations: a (new) = $-a$, c (new) = $a + 2c$. No attempts were made to observe intensity data for the weak layer lines reported [5] at the diffractometer. However, they were too weak to be registered neither on Guinier diagrams of both compounds recorded at room temperature nor on a Guinier-Simon diagram of TBN down to 115 K.

RESULTS

Infrared and Raman spectroscopy

Our results from vibrational spectroscopy and from X-ray diffraction are discussed separately below. Happily, these two lines of investigation, pursued independently, have led to the same conclusion for the molecular conformation in the solid state. While X-ray diffraction is, of course, a much more direct method for obtaining the structure, the structures of these compounds have been in doubt for so long that it seems of interest to present all the evidence bearing on this case.

The IR spectra of TCN as a capillary melt at 370 K between KBr plates and the same crystallized sample at ambient temperature in the region $1500-400 \text{ cm}^{-1}$ are given in Fig. 1. Far IR spectra of TCN as a solute in C_6H_6 and as a polyethylene pellet are given in Figs. 2 and 3, while the melt and crystal spectra in the Raman are shown in Figs. 4 and 5, respectively. The maxima of the observed IR and Raman bands are listed in Table 1. The IR spectrum of TBN as a KBr pellet is given in Fig. 6, while far IR spectra of a C_6H_6 solution and a polyethylene pellet are shown in Figs. 7 and 8. Finally, a Raman spectrum of solid TBN is given in Fig. 9 and the spectral results for this compound are listed in Table 2.

The present spectral data are much more complete than those reported by earlier workers [8]. Moreover, a significant number of IR and Raman bands,

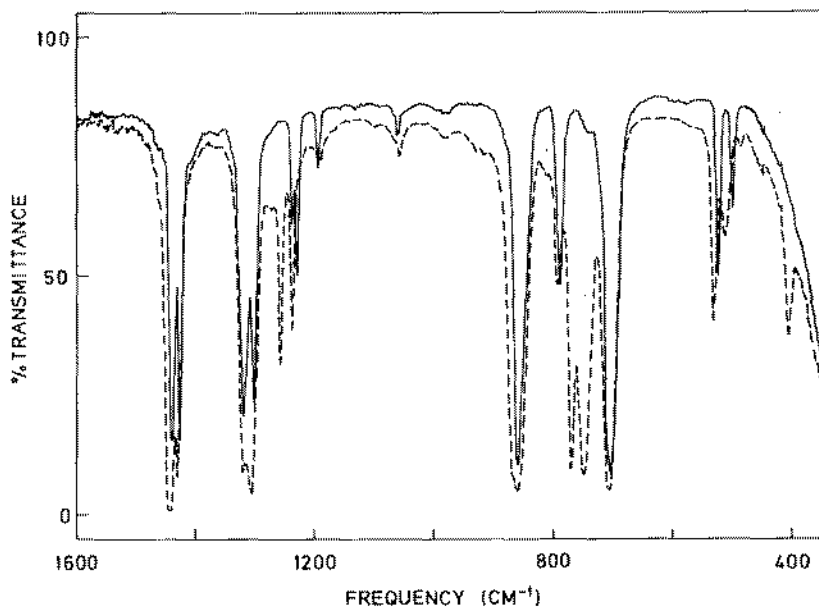


Fig. 1. Mid IR spectra of 2,2-di(chloromethyl)1,3-dichloropropane (TCN) as a melt (dotted curve) and polycrystalline solid (solid curve).

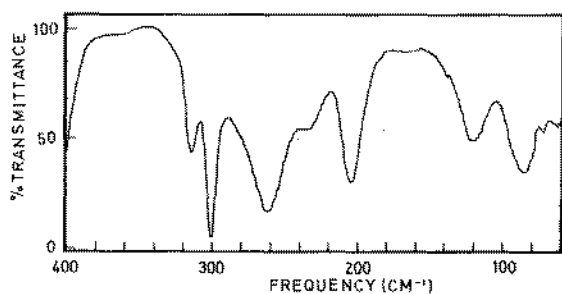


Fig. 2. Far IR spectrum of TCN dissolved in C₆H₁₂.

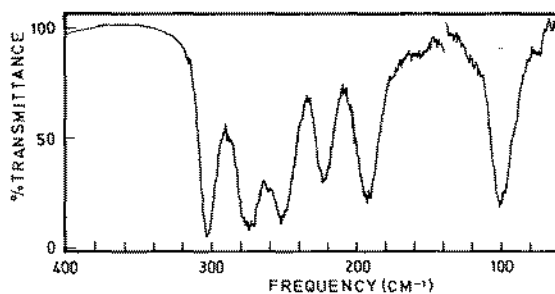


Fig. 3. Far IR spectrum of TCN as a polyethylene pellet.

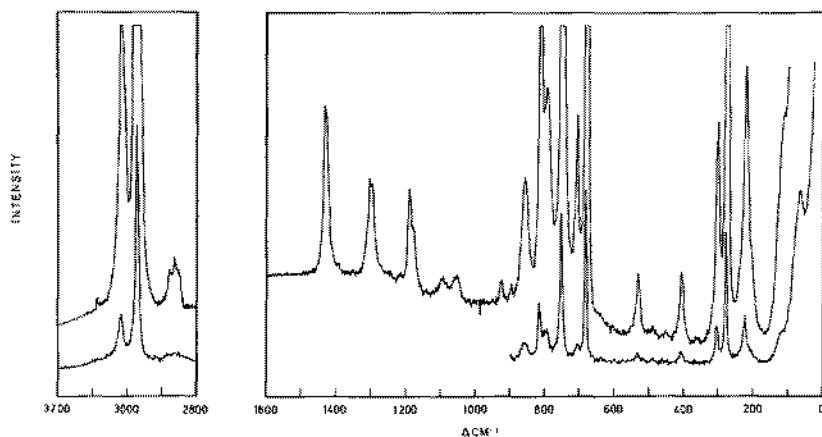


Fig. 4. Raman spectrum of TCN as a melt.

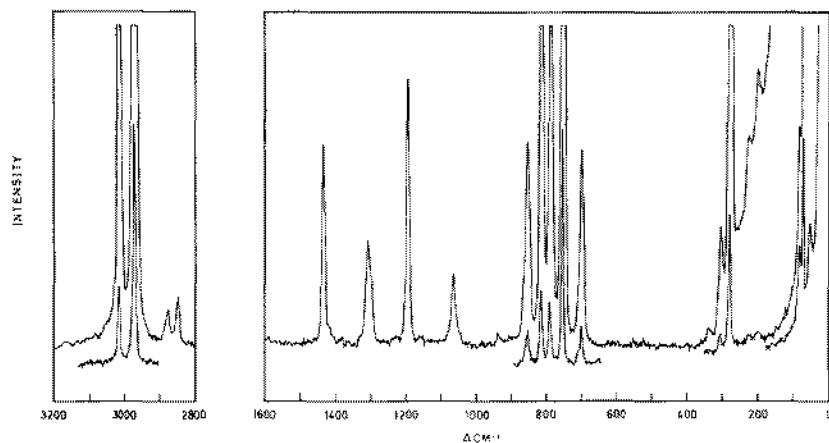


Fig. 5. Raman spectrum of TCN as a polycrystalline solid.

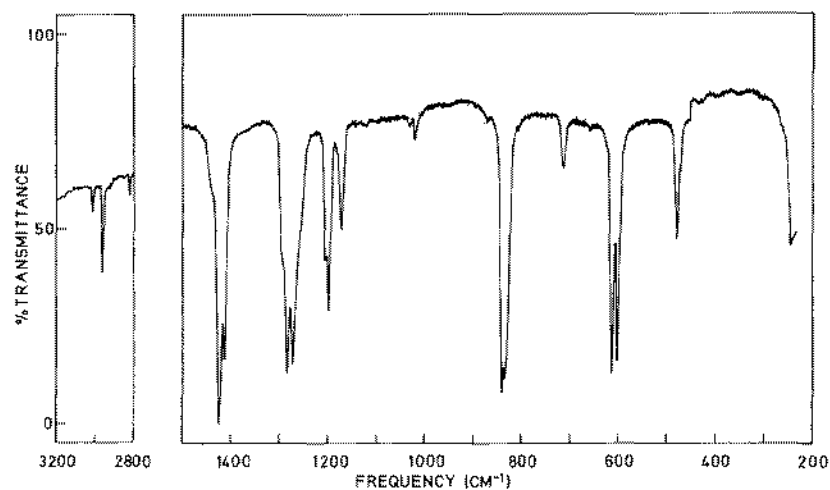


Fig. 6. Mid IR spectrum of 2,2-di(bromomethyl)-1,3-dibromo-propane (TBN) as a KBr pellet.

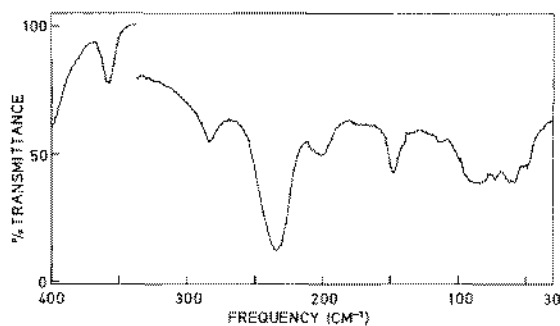


Fig. 7. Far IR spectrum of TBN dissolved in C_6H_6 .

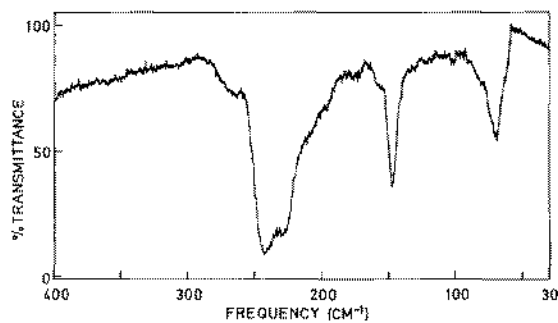


Fig. 8. Far IR spectrum of TBN as a polyethylene pellet.

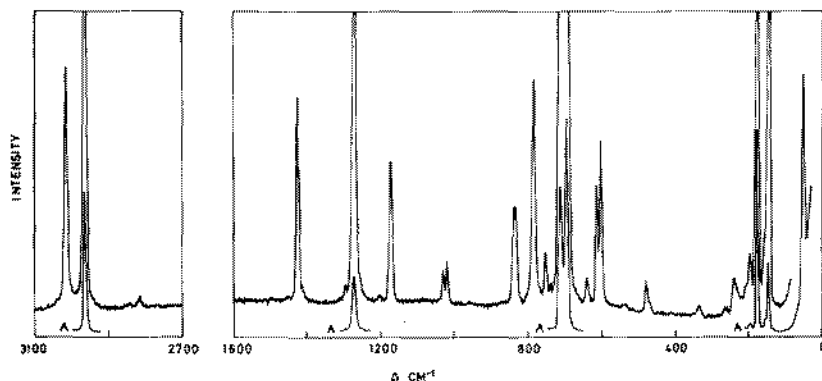


Fig. 9. Raman spectrum of TBN as a polycrystalline solid.

some of these with high intensities, which were present in the melt, solution and vapour vanished in the crystal spectra. Apparently, two or more conformers exist in these phases while only one conformer is present in the crystals of both TCN and TBN.

X-ray work: calculations

The unit cell contains two molecules rather than four, so each is located in a special position on the inversion centre. Since the molecule cannot possess a centre of symmetry, the structure must be disordered. Data for TBN were mainly recorded in case isomorphous replacement methods had to be considered for the structure determination. However, direct methods were first applied.

The intensity data for TCN were used in the MULTAN program system [12a]. Half atoms of carbon and chlorine were introduced. The resulting electron density map contained two large peaks within an asymmetric unit located at distances of 2.7 Å away from a peak at a centre of symmetry, corresponding to the expected distance between the central carbon atom and the chlorine atoms in TCN. The four halogen atoms of one molecule must accordingly be (nearly) coplanar. Furthermore, the halogen positions of one molecule and of a centrosymmetrically related molecule cannot be resolved in the Fourier map. Four smaller peaks were identified as half carbon atoms. The halogen atoms of a molecule of S_4 symmetry are far from coplanar, and this conformer could accordingly be ruled out.

A molecule of approximate D_{2d} symmetry located at a centre of symmetry having halogen positions coinciding with its centrosymmetrical equivalent was introduced in the full-matrix least-squares refinement of $M = \Sigma [\Delta F / \sigma(F_0)]^2$. Isotropic refinement converged for $R = 18\%$, introduction of anisotropic thermal parameters lowered the R -value to 7%. Hydrogen atoms at fixed positions ($C-H = 1.0$ Å) and with a common temperature factor ($B = 2.75$ Å²) and an isotropic extinction factor (0.4×10^{-4}) were included in the final refinement resulting in the following agreement indices for the 1045 observed reflections: $R = 0.062$, $R_w = 0.068$, "goodness of fit" $S = 4.2$.

TABLE 1

Infrared and Raman spectral data^a for 2,2-di(chloromethyl)-1,3-dichloropropane

Melt		Solid		Interpretation	
IR	Raman	IR	Raman	D_{2d}	S_4
3011 w ^b	3014 s, D	3008 w	3011 s	$\nu_{12}\nu_{24} b_1, e$	$\nu_1\nu_{12}\nu_{24} a, b, e$
2965 ms	2968 vs, P 2894 w	2965 ms	2967 vs	$\nu_1\nu_{17}\nu_{25} a_1, b_2, e$	$\nu_2\nu_{13}\nu_{25} a, b, e$
~2880 vw, sh					
	2874 w	2872 vw	2872 vw		
~2860 w, sh	2859 w	~2860 vw			
2852 w	2847 w	2850 w			
		2842 w	2842 w		
1460 vw, sh		1460 vw			
1440 vs	1443 vs, D 1437 s, sh, P	1440 s	1442 s	$\nu_{18} b_2$	$\nu_{14} b$
1428 s	~1425 w, sh	1427 s	1425 vw	$\nu_2 a_1$	$\nu_3 a$
~1395 vw, sh		~1400 vw, sh		$\nu_{26} e$	$\nu_{26} e$
1365 vw		1368 vw			
1318 s	1314 s, P	{ ~1325 w, sh 1318 ms 1310 w, sh	1316 m	$\nu_3\nu_{27} a_1, e$	$\nu_4\nu_{15}\nu_{27} a, b, e$
1304 s	1304 m, sh, D	1302 m	1307 m	$\nu_{19} b_2$	
~1270 vw		~1280 vw			
1255 m	~1255 vw	*			$\nu_{16} b$
1235 s	~1225 vw ?	{ 1238 mw 1229 m	~1235 vw	$\nu_{28} e$	$\nu_{28} e$
1205 vw					
1190 w	1198 s, D	1194 w	1200 s	$\nu_{13} b_1$	
	1186 m, P		*		$\nu_5 a$
1162 vw		1158 vw	1163 vw	$\nu_{20} b_2$	
1140 vw		1134 vw			
		1119 vw	1120 vw		
1098 vw	1099 m, D		*		$\nu_{29} e$
1065 vw, sh					$\nu_{17} b$
1055 w	1061 m, D	1060 w	{ 1068 w 1061 w	$\nu_{29} e$	
1047 vw, sh		~1045 vw, sh			
1018 vw					
1005 vw		1005 vw			
982 vw, bd					
929 vw	929 m, P		*		$\nu_6 a$
915 vw					
~890 vw, sh		~890 vw, sh			
868 s, sh		*			$\nu_{18}\nu_{30} b, e$
860 s	861 ms, bd, D	{ 860 s 855 s, sh	860 m, sh 854 m	$\nu_{30} e$	
	818 vs, P	818 vw	816 ms	$\nu_4 a_1$	
812 vw	812 m, sh, P		*		$\nu_7 a$
794 m	795 ms, D	790 m	790 ms	$\nu_{21} b_2$	
770 s	770 vw	*	*		$\nu_{19} b$
	755 vs, P		755 vs	$\nu_5 a_1$	
748 s	~745 m, sh	742 w	*		$\nu_{31} e$
		~720 w, sh			
706 s	707 w, bd, D?	{ 709 s 700 s	709 w 700 m	$\nu_{31} e$	
	683 vs, P		*		$\nu_8 a$
		~600 vw			
~570 vw		~575 vw	567 vw?		
531 m	532 s, D	*	*		$\nu_{20} b$
512 m		{ 523 m 500 w	494 w	$\nu_{32} e$	

TABLE 1 (continued)

Melt		Solid		Interpretation	
IR	Raman	IR	Raman	D_{2d}	S_4
486 w ?	487 w, P?				
406 m	407 s, D	*	*		$\nu_{32} e$
	363 vw, P?		~350 vw	$\nu_{15} b_1$	
315 mw ^c	~315 vw, sh	*			$\nu_{21} b$
301 m	303 ms, P	303 m	302 mw	$\nu_{22} b_2$	$\nu_9 a$
	275 s, P		278 s	$\nu_6 a_1$	
262 m, bd		{ 274 m	255 vw, sh	$\nu_{33} e$	
		254 m			
236 w	235 w, sh	*	*		$\nu_{33} e$
	221 vs, P		*		$\nu_{10} a$
204 m	205 m, sh, D	{ 221 mw	222 mw	$\nu_{23} b_2$	
		194 mw	195 mw		
123 w	120 s, D?		125 vw ?	$\nu_7 a_1$	$\nu_{22}\nu_{34} b, e$
88 w		99 m	~100 w	$\nu_{34} e$	
	65 s, bd, D		77 vs	$\nu_{16} b_1$	$\nu_{11}\nu_{23} a, b$
			48 s	l.m.	
			28 s	l.m.	

^aWeak bands in the regions (5000–3100 cm^{-1}) and (2800–1500 cm^{-1}) have been omitted.

^bAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; P, Polarized; D, Depolarized; *, denotes bands disappearing in the anisotropic solid state; l.m., lattice mode. ^cThe Far IR spectra have been recorded of CCl_4 and C_6H_6 solutions.

The positional parameters were used as starting parameters in an isotropic refinement of the TBN-data, resulting in unreasonable thermal parameters for some of the (half) carbon atoms ($R = 17\%$). Anisotropic thermal parameters for the bromine atoms and a common isotropic thermal parameter for the carbon atoms were introduced in the final refinement (hydrogen parameters included as above) of 855 reflections, excluding those 40 with the largest F -values. The agreement indices were $R = 0.085$, $R(\text{all}) = 0.101$, $R_w = 0.094$, $S = 3.9$. The final atomic parameters for the non hydrogen atoms of both compounds are listed in Table 3, bond distances, bond angles and some dihedral angles are given in Table 4, and an ORTEP drawing [12b] of the TCN molecule is shown in Fig. 10. Atomic scattering factors [11] were applied in the calculations, using programs [12, 13] adapted for an ND100/500 computer. Lists of observed and calculated structure factors and thermal parameters are available from one of the authors (B.K.) upon request.

Crystal data

$\text{C}_5\text{H}_8\text{Cl}_4$, monoclinic, $P2_1/n$, $T = 130$ K.

$a = 6.799(1)$, $b = 6.157(1)$, $c = 10.245(1)$ Å, $\beta = 104.02(1)^\circ$, $V = 416.1$ Å³.
 $M = 209.91$, $Z = 2$, $F(000) = 212$, $D_x = 1.675$ g cm^{-3} , $\sigma = 0.71069$ Å, $\mu = 13.4$ cm^{-1} .

$\text{C}_5\text{H}_8\text{Br}_4$, monoclinic, $P2_1/n$, $T = 130$ K.

$a = 7.085(1)$, $b = 6.227(1)$, $c = 10.757(2)$ Å, $\beta = 104.01(2)^\circ$, $V = 460.4$ Å³.
 $M = 387.73$, $Z = 2$, $F(000) = 356$, $D_x = 2.796$ g cm^{-3} , $\lambda = 0.71069$ Å, $\mu = 172.4$ cm^{-1} .

TABLE 2

Infrared and Raman spectral data^a for 2,2-di(bromomethyl)-1,3-dibromopropane

Solution ^b		Solid		Interpretation	
IR	Raman	IR	Raman	D_{2d}	S_4
3009 w	3007 m	3015 w	3015 s	$\nu_{12}\nu_{24} b_1, e$	$\nu_1\nu_{12}\nu_{24} a, b, e$
2955 m	2956 s	2961 m	2964 vs	$\nu_1\nu_{17}\nu_{25} a_1, b_2, e$	$\nu_2\nu_{13}\nu_{25} a, b, e$
2914 w					
2843 vw			2843 vw		
2828 vw					
2820 vw		2820 w			
1440 w		~1440 w, bd, sh			
1428 w, sh?		1432 m, sh			
1422 vs	1423 m	1425 vs	1427 m	$\nu_{18} b_2$	$\nu_{14} b$
	~1415 m, sh		1422 m	$\nu_2 a_1$	$\nu_3 a$
1411 m		1414 s	~1415 w, sh	$\nu_{26} e$	$\nu_{26} e$
1307 vw		1310 w, bd			
1297 vw		~1295 w	1295 vw		
1283 s	1285 vw	1282 s		$\nu_{27} e$	$\nu_{13}\nu_{27} b, e$
1269 s	1265 m, P	1270 s	1273 s	$\nu_3\nu_{19} a_1, b_2$	$\nu_4 a$
~1255 w, sh		~1260 m, sh	~1260 vw, sh		
~1245 vw	~1245 vw				
1227 w, sh					
1220 m		*			$\nu_{16} b$
1200 ms		{ 1205 m	1205 vvw	$\nu_{28} e$	$\nu_{28} e$
		{ 1199 s			
1183 w					
1170 w	1166 m, D	1173 m	1173 m	$\nu_{13}\nu_{20} b_1, b_2$	$\nu_5 a$
	~1150 vw				
~1125 vw, bd					
1063 w, bd		*			$\nu_{29} e$
~1020 vw	1020 vw	{ 1030 vw	1030 w	$\nu_{29} e$	$\nu_{17} b$
	~880 w	{ 1020 vw	1020 w		$\nu_6 a$
			*		$\nu_{18} b$
845 m, sh		*			$\nu_{30} e$
835 s	835 m	{ 840 vs	839 m	$\nu_{30} e$	$\nu_{30} e$
		{ 834 s	833 m		
		{ 804 vw			
794 vw					
787 vw					
	780 m, P		785 m	$\nu_4 a_1$	$\nu_7 a$
716 w	715 s, D	713 m	713 vs	$\nu_{21} b_2$	
700 mw	700 vs, P		696 vs	$\nu_5 a_1$	
672 m	672 m, D	*	*		$\nu_{19} b$
668 m, sh		*			$\nu_{31} e$
611 s	616 vs, P	{ 614 s	614 m	$\nu_{31} e$	$\nu_8 a$
		{ 602 s	603 m		$\nu_{20} b$
482 w	482 w, bd	*	*		
476 w		{ 478 m	479 vw	$\nu_{32} e$	
		{ 471 w, sh	472 vw		
358 w	359 vw	*	*		$\nu_{32} e$
			~335 vw, bd	$\nu_{15} b_1$	
283 w	280 vw	*	*		$\nu_9\nu_{21} a, b$
235 m	234 vw	{ 242 m	~240 vw, bd	$\nu_{22} b_2$	
		{ 229 m			
202 vw		~200 w, bd, sh	196 vw	$\nu_{35} e$	$\nu_{33} e$
	180 m, P		179 vs	$\nu_6 a_1$	
	152 m, P		*		$\nu_{10} a$
148 w	147 mw, sh, D	148 m	148 m	$\nu_{23} b_2$	
90 vw	~95 w	*	*		$\nu_{34} e$
73 vw		70 w	~70 vw	$\nu_{34} e$	
60 vw		*			$\nu_{22} b$
50 vw		*			$\nu_{23} b$
			53 s	l.m.	
			38 s	l.m.	
			22 s	l.m.	

^aWeak bands in the regions 5000–3100 cm^{-1} and 2800–1500 cm^{-1} have been omitted. For abbreviations see Table 1. ^bSolvents used: IR, CCl_4 and CS_2 ; Raman, CCl_4 , C_6H_6 and CS_2 .

TABLE 3

Fractional positional parameters ($\times 10^4$) and eigenvalues of the B -tensors (\AA^2) for the heavy atoms in TCN and TBN
(The numbers in parentheses denote estimated standard deviations.)

Atom	x	y	z	B
Cl 1	-1092(1)	2629(1)	1880(1)	4.22, 3.51, 1.16
Cl 2	3363(1)	2659(1)	388(1)	3.74, 3.41, 1.37
C 1	178(8)	219(9)	1490(5)	2.70, 2.25, 1.49
C 2	0	0	0	1.81, 1.40, 1.34
C 3	850(8)	2076(9)	-584(5)	2.53, 1.94, 1.45
C 4	1306(7)	-2011(9)	-139(5)	2.97, 1.76, 1.37
C 5	-2160(7)	-164(8)	-830(5)	2.27, 2.11, 1.80
Br 1	-1034(2)	2634(2)	1971(1)	4.27, 2.71, 0.64
Br 2	3466(2)	2689(2)	456(2)	3.70, 2.46, 1.24
C 1	219(30)	72(35)	1418(22)	1.10
C 2	0	0	0	1.10
C 3	894(32)	2069(36)	-450(21)	1.10
C 4	1284(30)	-1970(37)	-96(22)	1.10
C 5	-2060(30)	-8(35)	-725(22)	1.10

DISCUSSION

Conformations

The two conformers of Fig. 11, the D_{2d} (having the appearance of a cross) and the S_4 (a swastika) were both observed in nearly equal amounts in the vapour phase at 378 K (TCN) [9] and 413 K (TBN) [10]. One form is converted to the other by rotation of two of the CH_2X groups by 120° . These conformers are the only two in which 1:3 parallel C-X interactions are absent.

The IR and Raman activities derived for D_{2d} and S_4 symmetry are listed in Table 5. These predictions are of great importance to us here. With gas phase mixtures which are approximately 1:1 [9] and 3:2 [10] the decision as to which conformer persists in the crystal cannot be made by observing whether a stronger or weaker set of bands remains in the crystal. We must also regard this as two decisions, not one, as there is no compelling reason to expect that the same form necessarily exists in the crystalline phase of both compounds.

Our spectroscopic results and normal coordinate calculations indicate that both compounds crystallize in a D_{2d} conformation. In TCN we were able to make this decision with a great deal of confidence. The most compelling

TABLE 4

Bond distances (Å) and bond angles (°) in TCN and TBN

	TCN ^a			TBN		
	Calc. value	Mean value	ED ^a value	Calc. value	Mean value	ED ^b value
C2—C1	1.508			1.496		
C2—C3	1.579	1.537	1.539	1.563	1.521	1.552
C2—C4	1.550			1.546		
C2—C5	1.512			1.479		
X1—C1	1.809			1.986		
X1'—C4	1.795	1.811	1.792	2.024	1.974	1.949
X2—C3	1.793			1.886		
X2'—C5	1.848			2.001		
C1—C2—C4	104.9	104.3	106.1	100.1	102.6	
C3—C2—C5	103.6			105.2		
C1—C2—C3	111.3			109.9		109.5
C1—C2—C5	113.9	112.1	111.2	112.5	112.9	
C3—C2—C4	110.0			110.1		
C4—C2—C5	113.2			119.0		
X1—C1—C2	111.8			112.7		
X1'—C4—C2	110.5	110.6	113.5	108.5	112.3	114.2
X2—C3—C2	109.8			115.0		
X2'—C5—C2	110.2			112.9		
X1—C1—C2—C4	175.4			174.1		
X1'—C4—C2—C1	175.4	175.3		174.3	173.9	
X2—C3—C2—C5	175.2			173.8		
X2'—C5—C2—C3	175.3			173.3		

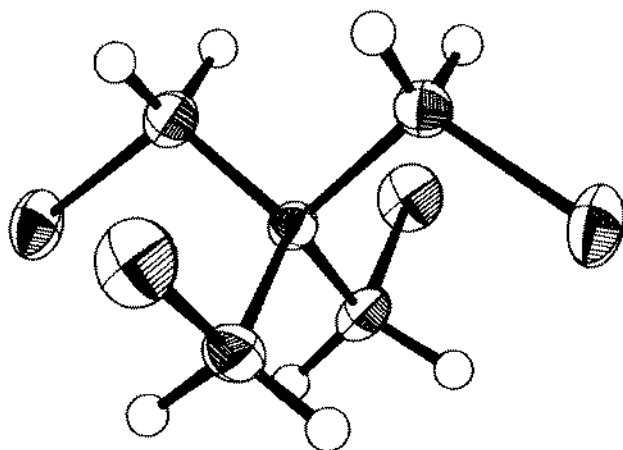
^aData from ref. 9. ^bData from ref. 10.

Fig. 10. An ORTEP drawing of TCN (thermal ellipsoids are drawn at 50% probability level).

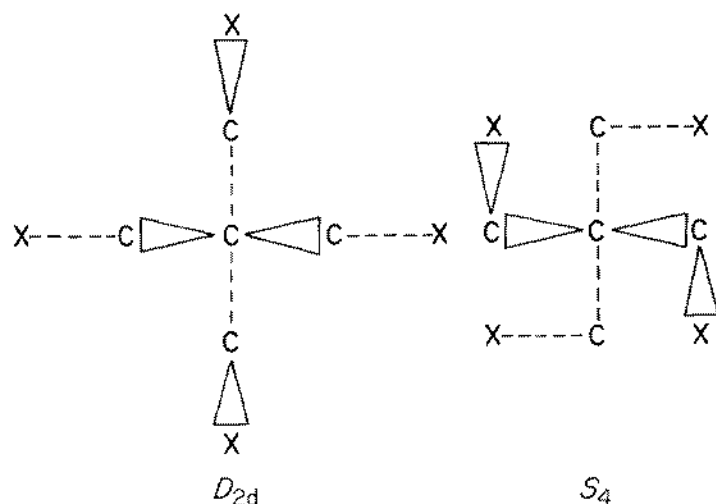


Fig. 11. The stable conformers D_{2d} (left, cross) and S_4 (right, swastika).

feature proved to lie in the polarized Raman bands. For the D_{2d} conformer, if we exclude the three modes associated with CH stretching, CH_2 scissoring, and torsion, four polarized bands (ν_3 – ν_6) are expected between 150 cm^{-1} and 1350 cm^{-1} . For the S_4 conformer we expect 7 polarized bands (ν_4 – ν_{10}) in this region.

Several of the polarized bands in our spectra are observed to have infrared counterparts. However, for both conformers, the species which have polarized bands are active only in the Raman. In each such case, then, there must be at least two coinciding bands, either from the same or different conformers. On the other hand, any infrared active fundamental, and indeed any band which is infrared active, can have associated with it a Raman band which is allowed. The assignment, with the help of the normal coordinate calculations, is made with remarkably little difficulty. Central to this, of course, was our good fortune in obtaining reliable polarization data from the melt rather than being forced to depend upon polarization data patched together from solution studies.

For the bromo compound, the results were slightly less convincing because of the absence of polarization data from the pure melt. Various experiments were performed in which the compounds were sublimed onto cold windows or onto a cold copper block. The amorphous film which resulted gave spectra which contained bands belonging to the less stable conformer; these disappeared upon annealing.

Spectra of the compounds dissolved in a variety of solvents of differing polarity showed no consistent variation with the polarity of the solvent. This is not surprising as the dipole moments of both conformers should be quite small [14].

Spectra were recorded of both compounds in a diamond anvil cell up to pressures of ca. 30 kbar. Aside from the usual tendency for the spectral bands to shift to slightly higher frequency and the weakening of two minor peaks

in the spectrum of the bromo compound, there were essentially no changes. In particular, there was no evidence whatsoever of any conversion from one conformational form to another.

Spectra were also recorded of dilute (ca. 10%) solutions in CS₂ over a pressure range extending from essentially zero to 10 kbar. For each compound special attention was paid to three different pairs of bands, one member of each pair belonging to one conformer and the second to the other. Changes in the conformational equilibria which we observed were so slight that we can only quote upper limits on these changes. For the chloro compound we feel confident that the change in the equilibrium constant is less than 5% over that range, and for the bromo compound that it is less than 10%. Using the relationship [15]

$$\Delta \bar{V} = -RT \, d \ln K / dP$$

this implies that in the chloro compound ΔV between the two forms is less than 0.1 cm³ mol⁻¹ and in the bromo compound less than 0.2 cm³ mol⁻¹.

These upper limits are of about the right size. The *gauche* interaction terms identified [16] as important in differences in the molar volumes between conformers are all the same here as all the halogen atoms are *gauche* to carbon atoms. Since these terms for the Cl/C and Br/C *gauche* interactions are -0.92 and -1.53 cm³ mol⁻¹, respectively [16], it would be expected that the differences in molar volume would be perhaps in order of magnitude smaller.

Solid phase

When solid TCN or TBN were heated from ambient temperature to close to the melting point, no significant changes occurred in the IR or Raman spectra. Particularly, the IR and Raman bands assigned to the S₄ conformer which are present in the melt and solution spectra did not appear in the high-temperature crystal spectra. Therefore, it can be concluded that neither TCN nor TBN has a phase transition to a plastic phase. A phase transition between an anisotropic phase and a plastic phase is characterized not only by shifts in band positions, band intensities, band widths and lattice modes, but by the accommodation of both conformers in the plastic crystal. The absence of the S₄ bands (having asterisks in Tables 1 and 2) in the high-temperature crystal spectra is therefore a strong proof that no plastic phases are present in these compounds.

The parent compound of TCN and TBN, neopentane, has long been known to possess a plastic phase [17]. It has been demonstrated that the three intermediate compounds, C(CH₃)₃CH₂Cl [18], C(CH₃)₂(CH₂Cl)₂ [19], and C(CH₃)(CH₂Cl)₃ [20], also have plastic phases. In addition, it has been shown that C(CH₃)₂(CH₂Cl)₂ crystallizes in two different conformations, one conformer having C₂ symmetry at low temperature and one C_s symmetry at high pressure [19]. However, at ambient pressure TCN and TBN do not have

plastic phases [21] whereas the corresponding fluoro compound $C(CH_2F)_4$ has a plastic phase [22]. This is surprising in that TCN and TBN certainly have conformers of higher symmetry than do the other chlorinated neopentanes. We have suspected that this apparent lack occurs simply because the tetrachloro compound "melts too soon" and that placing it under pressure would enable us to preserve a solid phase into a region where we think a plastic phase may occur. Success here would also have given us a chance to see if we could then form a crystal containing the conformer not stable in the room temperature crystal. However, in a variety of trials at temperatures up to about 410 K, no changes in the form of the crystal have been observed.

Spectral assignments

As apparent from Table 5, we expect 18 IR and 30 Raman active modes for D_{2d} whereas the S_4 conformer should have 23 IR and 34 Raman active fundamentals. Moreover, the a_1 and b_1 modes of D_{2d} and the a modes of S_4 are only Raman active, whereas all the IR active bands are also active in Raman. S_4 is a subgroup of D_{2d} , and the species will correlate in a very straightforward manner: the a_1 , a_2 , b_1 and b_2 of D_{2d} will correlate with a and b , respectively, of S_4 and the doubly degenerate species e will correlate in both point groups.

The interpretations are listed in Table 1 (TCN) and Table 2 (TBN) and the assigned fundamentals are given in Table 6 together with the calculated frequencies. As expected, numerous coincidences must be expected in the C—H stretching and bending regions. In addition, many of the vibrational bands of one conformer will nearly coincide with the bands of the other conformer as demonstrated by the results of the force constant calculations. However, fourteen of the vibrational bands for TCN and eleven for TBN should belong to the S_4 conformer alone and have been interpreted accordingly. As apparent

TABLE 5

Spectral activities for point groups D_{2d} and S_4

Point group	Species	IR	Activity R	Number
D_{2d}	a_1	ia	pol	7
	a_2	ia	ia	4
	b_1	ia	dep	5
	b_2	a	dep	7
	e	a	dep	11
S_4	a	ia	pol	11
	b	a	dep	12
	e	a	dep	11

a, active; ia, inactive; pol, polarized; dep, depolarized.

TABLE 6

Observed and calculated fundamental frequencies of vibration for 2,2-di(chloromethyl)-1,3-dichloropropane (TCN) and 2,2-di(bromomethyl)-1,3-dibromopropane (TBN)

TCN					TBN						
D_{2d}		S_4			D_{2d}		S_4				
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.		
a_1	2968	2968	a	3014	3009	a_1	2956	2968	a	3007	3008
	1434	1445		2968	2967		1415	1426		2956	2966
	1314	1293		1434	1432		1265	1262		1415	1409
	818	811		1314	1295		780	778		1265	1266
	755	747		1186	1183		700	696		1150	1142
	275	258		929	924		180	170		880	895
	123	104		812	798			66		780	778
a_2		3005	683	690	a_2		3005	616	613		
		1180	303	310			1138	283	289		
		853	221	213			824	152	145		
		214	65	65			200		40		
b_1	3014	3010	b	3011	3010	b_1	3007	3009	b	3009	3010
	1198	1180		2965	2967		1166	1142		2955	2967
		924		1440	1442			892		1422	1419
	361	347		1318	1327		336	346		1283	1315
	65	62		1255	1240			38		1220	1209
b_2	2965	2967	1065	1067	b_2	2955	2967	1020	1027		
	1440	1445	868	858		1422	1425	845	842		
	1304	1308	770	750		1269	1283	672	672		
	1162	1156	531	512		1166	1141	482	487		
	794	802	315	327		716	730	283	288		
	301	308	123	116		235	247		75		
	204	176	65	78		148	123	50	50		
e	3011	3009	e	3011	3007	e	3009	3009	e	3009	3007
	2965	2966		2965	2967		2955	2966		2955	2967
	1428	1431		1428	1436		1411	1408		1411	1413
	1318	1325		1318	1287		1283	1310		1283	1263
	1235	1239		1235	1231		1200	1212		1200	1206
	1055	1066		1099	1099		1020	1021		1064	1068
	860	872		868	870		835	859		835	844
	706	694		748	744		611	602		668	669
	512	524		406	418		476	491		358	372
	262	265		236	232		235	235		202	198
	88	78		123	118		73	50		90	81

from Tables 1 and 2 the e modes are often split in the spectra of the crystal. Further, the disordered crystal structure leads to a break-down of the vibrational selection rules and the Raman active a_1 and b_1 modes may then have weak IR counterparts.

The assignments relied heavily upon the results of the force constant calculations, although in a few cases the discrepancies between the observed

and calculated values were significant. Preliminary force constants were adopted from Snyder and Schachtschneider [23], a 42 parameter force field was adopted, and the force constants were adjusted by a least squares program to fit the observed frequencies of D_{2d} and S_4 conformers of TCN and TBN as well as those of $\text{CH}_2\text{ClC}(\text{CH}_3)_3$ [21], $(\text{CH}_2\text{Cl})_2\text{C}(\text{CH}_2)_2$ [17] and $(\text{CH}_2\text{Cl})_3\text{C}(\text{CH}_3)$ [22]. A similar procedure has previously been applied to halogenated cyclohexanes [24, 25]; the procedure and the force constants will be given elsewhere [22].

X-ray structure

The present study offers no precise bonding parameters for the molecules owing to the disorder in the solid state. However, the structure analysis shows unambiguously that the molecules possess nearly D_{2d} symmetry. The halogen atoms of an ideal D_{2d} conformer are not necessarily coplanar. The deviation from coplanarity may be different for the chloro and the bromo compound as the carbon halogen bond is lengthened with increasing size of the halogen atom. Non-planarity is not allowed for in the present model. Differences in positional parameters of overlapping atoms are usually reflected in abnormal thermal parameters. The values given in Table 3 are rather normal, indicating that the model introduced is reasonable. This conclusion is supported by the agreement indices of the refinement and by the correspondence between the mean values of different bonding parameters and the values determined by electron diffraction methods, cf. Table 4.

The deviation from D_{2d} symmetry can be seen from the values of the torsional angles between the *anti* periplanar halogen carbon and carbon carbon bonds, all being roughly 175° . Accordingly, the halogen atoms form corners of a rectangle rather than a square, the difference between the sides being 0.37 and 0.40 Å for the chloro and the bromo compound, respectively. These differences are too large to be accounted for by mixing ideal D_{2d} . However, the molecules are in an environment of lower symmetry and the differences can be caused by crystal forces. Molecular mechanics calculations [26] reveal energies of 2.7 (TCN) and 3.3 kJ mol^{-1} (TBN) for a 5° twist from the D_{2d} conformation.

A D_{2d} molecule can be transformed to a centrosymmetrical unit by superimposing on it another molecule rotated by 90° about its S_4 axis. Energy profiles corresponding to rotational displacements of a molecule from its observed position in the crystal were estimated (program PACKRB [12c]) for the chloro compound. The sum of interatomic potentials between the atoms of one molecule and all atoms of surrounding molecules (cut-off distance 7.0 Å) are calculated for different orientations of the molecule. The neighbours are static and uncorrelated motion is accordingly simulated. The energy barrier for rotation about the three axes of inertia was calculated. Minima were found for $\pm 90^\circ$ rotation about the I_C axis (largest moment of inertia), the energy difference between $\pm 90^\circ$ and 0° being less than 3 kJ mol^{-1} .

The calculation indicates that the energy needed to distort the D_{2d} conformer to the conformation observed in the crystal is less than 1.5 kJ mol^{-1} , which is of the order of the mean free kinetic energy. Although the energy barrier for rotation about I_C is far less than for the other rotations, the values being 290, 650, and 790 kJ mol^{-1} , respectively, a reorientation must be coupled.

The D_{2d} conformer is an oblate symmetrical top. When chlorine is substituted by bromine its size will increase; the radius will be lengthened while the thickness (along the S_4 axis) will remain roughly unaltered. The normal of the plane through the four halogen atoms of a molecule in the crystal forms an angle of approximately 30° with the b axis. Going from $\text{C}(\text{CH}_2\text{Cl})_4$ to $\text{C}(\text{CH}_2\text{Br})_4$ the a and c axes are lengthened by 5% where b increases by only 1%.

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REFERENCES

- 1 H. Fecht, Chem. Ber., 40 (1907) 3883.
- 2 P. Rave and B. Tollens, Ann. Chem., 276 (1883) 61.
- 3 G. Wagner and G. Dengel, Z. Phys. Chem. B, 16 (1932) 382.
- 4 H. de Laszlo, Compt. rend., 198 (1934) 2235.
- 5 O. Hassel and L. C. Strömme, Z. Phys. Chem. B, 38 (1937) 349.
- 6 O. Ballaus and J. Wagner, Z. Phys. Chem. B, 45 (1939) 165.
- 7 H. Lumbroso and D. Lauranson, Bull. Soc. Chim. Fr., (1959) 513.
- 8 G. Geiseler and L. Ratz, Z. Naturforsch., Teil A, 21 (1966) 1889.
- 9 R. Stölevik, Acta Chem. Scand. Ser. A, 28 (1974) 327.
- 10 S. Rustad and R. Stölevik, Acta Chem. Scand., Ser. A, 30 (1976) 209.
- 11 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. IV.
- 12 (a) MULTAN78, P. Main, Dept. of Physics, Univ. of York, York, U.K.
(b) ORTEP, C. K. Johnson, Report ORNL-3795, Oak Ridge National Laboratory, Oak Ridge, 1965 TN, U.S.A.
(c) PACKRB, I. Goldberg and V. Shmueli, Dept. of Chemistry, Tel-Aviv University, Tel-Aviv, Israel.
- 13 P. Groth, Acta Chem. Scand., 27 (1973) 3131.
- 14 H. B. Thompson and C. C. Sweeney, J. Phys. Chem., 64 (1960) 221.
- 15 S. D. Christian, J. Grundnes and P. Klaeboe, J. Am. Chem. Soc., 97 (1975) 3864.
- 16 F. Shahidi, P. G. Farrell and J. T. Edward, J. Phys. Chem., 83 (1979) 419.
- 17 J. G. Aston and G. H. Messerley, J. Am. Chem. Soc., 58 (1936) 2354.
- 18 P. Klaeboe, C. J. Nielsen and D. L. Powell, Spectrochim. Acta, Part A, in press.
- 19 D. L. Powell, P. Klaeboe, K. Saebö and G. A. Crowder, J. Mol. Struct., 98 (1983) 55.
- 20 K. Martinsen, D. L. Powell, C. J. Nielsen and P. Klaeboe, J. Raman Spectrosc., in press.
- 21 L. H. Clewer, W. K. Wong and E. F. Westrum, Jr. J. Phys. Chem., 69 (1965) 1209.
- 22 J. C. Towbridge and E. F. Westrum, Jr., J. Phys. Chem., 68 (1964) 255.
- 23 R. G. Snyder and J. H. Schachtschneider, J. Mol. Spectrosc., 30 (1969) 290.
- 24 T. Woldbaek, C. J. Nielsen and P. Klaeboe, J. Mol. Struct., 66 (1980) 31.
- 25 T. Woldbaek, C. J. Nielsen and P. Klaeboe, Spectrochim. Acta, Part A, 41 (1985) 43.
- 26 R. Stölevik, personal communications.