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The Crystal and Molecular Structure of 1,2-Dichloroethane at −140° C.

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Below the broad, very marked transition, the monoclinic unit cell of the low-temperature modification of 1,2-dichloroethane has the parameters $a = 4{\cdot}66$, $b = 5{\cdot}42$, $c = 7{\cdot}88$ Å, and $\beta = 103{\cdot}5°$. The molecule is in the extended, *trans* configuration with dimensions C–Cl = $1{\cdot}80 \pm 0{\cdot}02$ Å, C–C = $1{\cdot}49 \pm 0{\cdot}04$ Å and $\angle$ C–C–Cl = $105{\cdot}5 \pm 0{\cdot}5°$. While the high-temperature modification shows disorder about, approximately, the Cl · · · Cl axis, the low-temperature modification is completely ordered. The transition occurs without the simultaneous appearance of two phases.

Introduction

In a previous investigation (Milberg & Lipscomb, 1951) 1,2-dichloroethane at −50° C. was shown to have almost complete rotational or orientational disorder about, approximately, the Cl · · · Cl axis of the extended, *trans* form of the molecule. This structure undergoes a remarkably broad phase transition with a maximum at −96° C. and a width at half height of about 25° C. (Pitzer, 1940). The calorimetric study (Pitzer, 1940), the spectroscopic studies (Mizushima, Morino & Noziri, 1936; Mizushima, Morino, Watanabe, Simanouti & Yamaguchi, 1949) and the nuclear magnetic resonance study (Gutowsky & Pake, 1950) suggest that this is a gradual disorder–order type of transition, a conclusion which is confirmed as a certainty by the present investigation. In addition the molecular dimensions of the molecule have been measured and are compared with those of the most recent electron-diffraction study (Ainsworth & Karle, 1952).

Experimental techniques

Low-temperature techniques for X-ray diffraction studies of single crystals have been described many times (Ruhemann, 1932; Vonnegut & Warren, 1936; Kaufman & Fankuchen, 1949; Abrahams, Collin, Lipscomb & Reed, 1950; Post, Schwartz & Fankuchen, 1951). Because of increased interest in this field, we would like to add some experimental details to those already described.

The type of cooling apparatus that we have used for the last few years is shown in Fig. 1. A large dewar, one gallon or larger in volume, is fitted with a cork stopper in which there are holes for (1) a large tube for filling, (2) a smaller tube containing a cork bob, with a long, thin glass rod or tube, to indicate the level of the coolant, (3) the vacuum jacketed nozzle through which the cold gases are blown on the crystal, and (4) a pair of wires carrying a heating element dipping to the bottom of the liquid nitrogen. This heating element is used to boil the liquid nitrogen at a rate controlled by a Variac. In addition a second opening in the nozzle allows the introduction of dry, warm nitrogen through a sensitive needle valve. Mixture of the warm and cold gases gives any desired temperature down to −180° C. A thermocouple, mounted in the tip of the nozzle, records the temperature of the crystal. The apparatus has been placed in an air-conditioned, dehumidified laboratory in order to avoid condensation of frost on the crystal. The use of a sheath of dry gas around the cold stream has been described (Post, Schwartz & Fankuchen, 1951), and is equally effective and less expensive than air conditioning, which, however, has other advantages. Temperature fluctuations are sufficiently small to allow the slow growth of single crystals over a period of several hours if necessary. This apparatus requires one gallon of liquid nitrogen per hour at −180° C. or per six hours at −50° C., and will permit a crystal to be preserved indefinitely.

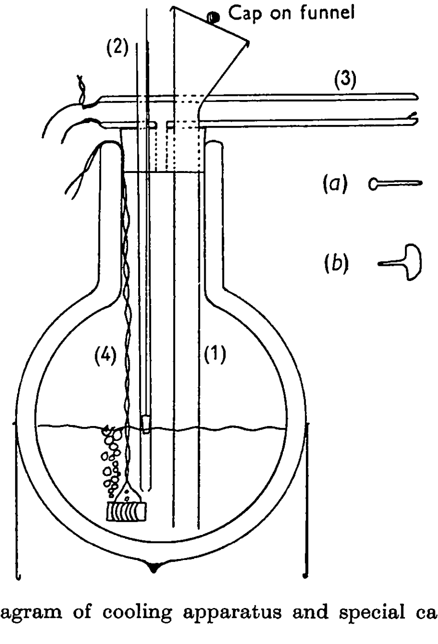

Fig. 1. Diagram of cooling apparatus and special capillaries.

Two special types of capillaries have been useful for certain problems. The capillary shown at (*a*) in Fig. 1 was used in the present study of 1,2-dichloroethane, which normally grows with the *b* axis along the direction of the capillary. The small bulb allowed us to grow seed crystals with the *b* axis at right angles to the capillary, and hence made possible Weissenberg photography about the *a* axis. The capillary shown at (*b*) in Fig. 1 was used in our studies of N_2O_2 and N_2O_3, and should prove useful for low-temperature studies of other compounds which are gaseous at ordinary temperatures.

Procedure and results for 1,2-dichloroethane

The unit cell is monoclinic with parameters

$$a = 4{\cdot}66\pm0{\cdot}03,\ b = 5{\cdot}42\pm0{\cdot}02,\ c = 7{\cdot}88\pm0{\cdot}02\ \text{Å},\quad \beta = 103{\cdot}5\pm0{\cdot}5^\circ$$

and $V = 194$ Å^3. These values may be compared with $a = 5{\cdot}04$, $b = 5{\cdot}56$, $c = 8{\cdot}00$ Å and $\beta = 109{\cdot}5^\circ$ for the unit cell at -50° C., which is larger by 18 Å^3.

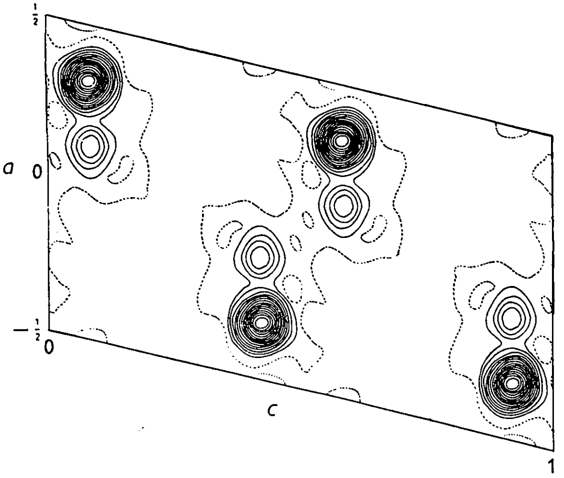

Fig. 2. Projection of the electron density along the *b* axis. Contours are at 2 e.Å^{-2}. The two-electron contour is broken.

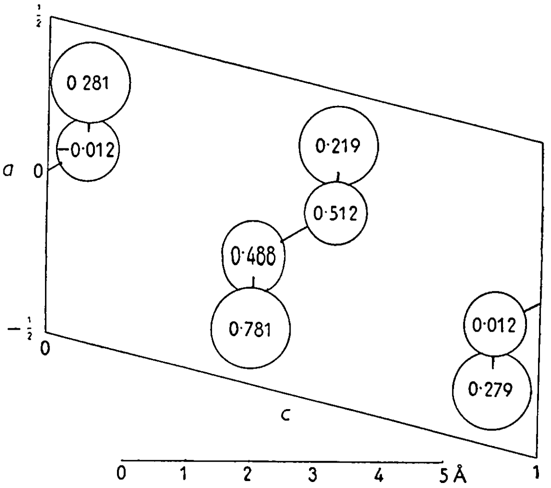

Fig. 3. Line diagram of Fig. 2, showing out-of-plane coordinates of atoms. The large circles represent chlorine; the small circles represent carbon.

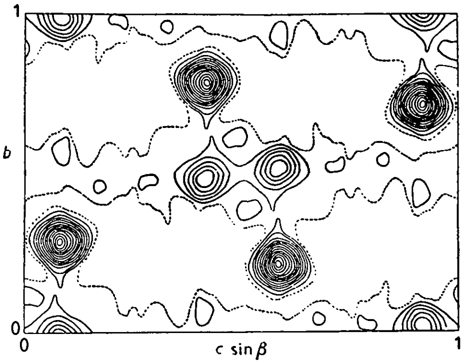

Fig. 4. Projection of the electron density along the *a* axis. Contours are in intervals of 2 e.Å^{-2}. The two-electron contour is broken.

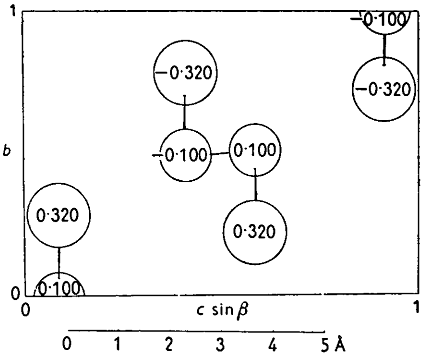

Fig. 5. Line diagram of Fig. 4 showing out-of-plane coordinates.

Extinctions of *h*0*l* for *l* odd and 0*k*0 for *k* odd indicate the same space group, $P2_1/c$, as that at -50° C. Assumption of two molecules in this unit cell gives the very reasonable calculated density of 1·70 g.cm.$^{-3}$, and requires a centrosymmetric molecule. Thus the crystallography of the two modifications is very similar, and diffraction photographs taken at 20° C. intervals during cooling indicate a gradual, continuous change in the unit-cell parameters.

The molecular structure was determined from Weissenberg photographs about *a* (zero level) and about *b* (zero, first and second levels), with the use of the multiple-film technique with interleaving brass sheets; Mo $K\alpha$ radiation was used. Fourier projections and structure factors were calculated with the use of International Business Machines. The refinement, which followed the usual procedure, led to the final Fourier projections shown in Figs. 2 and 4, and to the final parameters, corrected for back-shift,

$$x^{\text{Cl}} = 0{\cdot}320\pm0{\cdot}001,\ y_{\text{Cl}} = 0{\cdot}281\pm0{\cdot}001,\ z_{\text{Cl}} = 0{\cdot}084\pm0{\cdot}001\ ,$$

$$x_{\text{C}} = 0{\cdot}100\pm0{\cdot}004,\ y_{\text{C}} = -0{\cdot}012\pm0{\cdot}004 \text{ and } z_{\text{C}} = 0{\cdot}084\pm0{\cdot}004\ .$$

These parameters refer to the positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$ (*Internationale Tabellen*, 1935). They lead to the molecular parameters C–C=1·49±0·04 Å, C–Cl=1·80±0·02 Å, Cl · · · Cl=4·24±0·02 Å and ∠ C–C–Cl=105·5±0·5°. Our values are thus in reasonable agreement with those determined by the electron-diffraction method (Ainsworth & Karle, 1952), namely, C–C=1·49±0·03 Å, C–Cl=1·78±0·03 Å and Cl · · · Cl=4·31±0·02 Å. The shorter Cl · · · Cl distance found in the present investigation is identical with that, 4·24±0·04 Å, found in the −50° C. modification. The intermolecular Cl · · · Cl distances of 3·99 Å and 4·06 Å at −140° C. compare favorably with the corresponding distances 3·79 and 4·01 Å at −50° C.

The probable errors listed above were estimated by comparison with other compounds on which complete least-squares calculations had been made, as well as by trial-and-error adjustments of the parameters of the present study. Average back-shift corrections were 0·005 Å for Cl and 0·03 Å for C. In the calculation of structure factors the value of $B = 1{\cdot}94$ Å^2 was determined in the usual way for the temperature factors $\exp\left[-B \sin^2 \theta/\lambda^2\right]$, which have been multiplied into the F_c of Table 1. Agreement with the observed structure factors F_o, also shown in Table 1, is satisfactory; additional comparison is afforded by the reliability factor, $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$, which is 12% when all observed reflections are included.

Our results indicate that the phase transition in 1,2-dichloroethane is thus associated with a gradual disappearance of the rotational or orientational disorder about the Cl · · · Cl axis of the extended molecule, as the temperature is lowered. Accompanying this molecular orientation, which leads to a completely configurationally ordered structure at −140° C., there is a volume contraction of 9 Å^3 per molecule, and there is no evidence of the appearance of a second phase if the cooling is carried out slowly. On the other hand, if the crystals are cooled rapidly a powder results, but no attempt has been made to investigate the structure of the powdered sample. The possibility of a different type of transition under certain, perhaps exceptional, conditions is suggested by a sharp transition at −66° C. observed once in many attempts by Morino (1939). We have not observed this sharp transition in our relatively few observations by use of X-ray patterns and the polarizing microscope. Although the β-modification of 1,2-dibromoethane (Meerman, 1943) has the same structure as the −140° C. modification of 1,2-dichloroethane, its transition, on the other hand, extends over only a

Table 1. *Comparison of observed and calculated structure factors*

hkl	F_o	F_c
002	34·6	+34·9
004	27·2	−22·8
006	28·0	−29·6
008	10·9	−10·0
0,0,10	9·3	+ 7·7
0,0,12	8·6	+10·0
100	6·4	− 9·9
102	48·0	−45·0
104	26·7	−24·6
106	6·1	+ 7·5
108	13·0	+15·7
1,0,10	8·0	+ 7·6
$10\bar{2}$	43·1	+43·2
$10\bar{4}$	31·2	+32·3
$10\bar{6}$	8·2	+ 4·5
$10\bar{8}$	14·9	−11·0
$1,0,\overline{10}$	9·1	−12·5
200	20·8	−21·6
202	5·8	+ 6·2
204	17·9	+19·5
206	10·1	+10·0
208	< 6·5	− 2·7
$20\bar{2}$	25·0	−28·1
$20\bar{4}$	6·6	− 5·7
$20\bar{6}$	14·0	+14·2
$20\bar{8}$	12·4	+13·3
$2,0,\overline{10}$	< 6·6	+ 3·6
300	24·8	+25·5
302	11·7	+11·3
304	8·3	− 8·1
306	11·1	−12·3
308	< 6·9	− 4·2
$30\bar{2}$	12·0	+ 9·3
$30\bar{4}$	12·2	−12·5
$30\bar{6}$	16·5	−19·3
$30\bar{8}$	8·2	− 6·4
$3,0,\overline{10}$	7·5	+ 5·9
400	6·7	− 7·9
402	19·7	−20·6
404	10·7	−10·5
406	< 6·5	+ 4·3
408	< 6·6	+ 8·7
$40\bar{2}$	15·6	+17·1
$40\bar{4}$	20·7	+23·0
$40\bar{6}$	7·9	+ 5·9
$40\bar{8}$	10·6	−11·8
$4,0,\overline{10}$	10·3	−11·8
500	13·7	−15·8
502	< 6·6	− 0·1
504	9·8	+10·7
506	9·6	+ 7·4
508	< 7·5	− 0·2
$50\bar{2}$	14·4	−15·6
$50\bar{4}$	< 6·5	+ 0·3
$50\bar{6}$	12·3	+14·3
$50\bar{8}$	8·5	+11·1
$5,0,\overline{10}$	< 6·8	− 0·4
600	7·8	+ 7·0
602	8·2	+ 7·3
604	< 7·0	+ 1·5
606	< 7·2	− 3·9
$60\bar{2}$	< 6·7	− 1·7
$60\bar{4}$	9·2	− 9·9
$60\bar{6}$	7·8	− 6·6
$60\bar{8}$	< 6·9	+ 1·5
011	11·0	+ 5·2
012	28·3	−32·8
013	< 4·4	0·0
014	28·0	−27·8
015	< 4·7	− 0·7
016	< 4·9	+ 0·6
017	< 5·1	− 0·4
018	11·9	+14·6
019	< 5·5	0·0
0,11,0	8·1	+ 9·4
110	44·6	−48·2
111	13·2	+13·9
112	< 4·1	− 2·4
113	< 4·3	+ 1·1
114	23·8	+25·6
115	7·5	− 5·2
116	18·6	+19·4
117	< 5·3	− 4·5
118	< 5·5	+ 0·5
119	< 5·6	− 0·3
$11\bar{1}$	17·8	+15·8
$11\bar{2}$	31·7	−39·9
$11\bar{3}$	< 4·2	− 0·9
$11\bar{4}$	6·0	+ 2·8
$11\bar{5}$	8·2	− 7·8
$11\bar{6}$	18·9	+20·5
$11\bar{7}$	< 5·0	− 3·9
$11\bar{8}$	12·5	+14·9
$11\bar{9}$	< 5·5	+ 0·8
$1,1,\overline{10}$	< 5·6	− 1·3
210	29·1	+28·8
211	< 4·4	− 0·8
212	25·9	+29·7
213	10·8	−10·5

Table 1 (*cont.*)

hkl	F_o	F_c
214	< 4·9	+ 3·6
215	8·2	− 7·1
216	12·5	−14·1
217	< 5·3	+ 0·4
218	10·8	−13·9
219	< 5·8	+ 4·3
$21\bar{1}$	15·3	+14·0
$21\bar{2}$	5·1	− 6·3
$21\bar{3}$	12·1	+13·8
$21\bar{4}$	23·4	−30·0
$21\bar{5}$	< 4·7	+ 0·1
$21\bar{6}$	19·3	−20·2
$21\bar{7}$	7·6	− 7·3
$21\bar{8}$	< 5·2	+ 3·6
$21\bar{9}$	< 5·5	− 5·7
$2,1,\overline{10}$	9·5	+12·4
310	7·1	+ 7·2
311	8·5	− 8·7
312	16·8	−17·4
313	8·5	− 5·2
314	18·5	−19·0
315	< 5·4	+ 1·7
316	< 5·5	− 3·6
317	< 5·6	+ 4·8
318	9·4	+ 7·2
319	< 6·0	+ 2·6
$31\bar{1}$	< 4·7	− 2·5
$31\bar{2}$	21·5	+26·6
$31\bar{3}$	8·2	+ 6·7
$31\bar{4}$	13·1	+17·6
$31\bar{5}$	7·6	+ 8·0
$31\bar{6}$	6·6	− 6·2
$31\bar{7}$	< 5·2	+ 1·7
$31\bar{8}$	11·7	−18·5
$31\bar{9}$	< 5·6	− 4·3
410	19·6	−20·2
411	< 5·2	− 1·9
412	8·2	− 5·9
413	< 5·4	+ 0·8
414	11·2	+ 9·4
415	< 5·6	+ 2·2
416	11·6	+10·6
417	< 6·0	+ 1·2
$41\bar{1}$	< 5·1	+ 3·2
$41\bar{2}$	13·6	−13·7
$41\bar{3}$	< 5·1	− 1·5
$41\bar{4}$	7·6	+ 7·1
$41\bar{5}$	< 5·1	− 1·8
$41\bar{6}$	13·6	+17·2
$41\bar{7}$	< 5·4	+ 2·5
$41\bar{8}$	8·5	+ 8·8
$41\bar{9}$	< 5·6	+ 0·5
510	9·8	+ 9·0
511	< 5·5	− 1·9
512	11·9	+13·1
513	< 5·6	− 1·4
514	< 5·7	+ 3·9
515	< 5·8	+ 0·3
$51\bar{1}$	< 5·4	0·0
$51\bar{2}$	9·4	− 6·5
$51\bar{3}$	< 5·4	+ 6·5
$51\bar{4}$	10·7	−15·0
515	< 5·5	− 1·8
$51\bar{6}$	9·4	− 7·8
$51\bar{7}$	< 5·6	+ 0·1
610	7·1	+ 5·0
611	< 5·8	− 3·0
$61\bar{1}$	< 5·8	− 1·7
$61\bar{2}$	10·4	+11·5
$61\bar{3}$	< 5·8	− 0·7
$61\bar{4}$	8·2	+ 5·9
$61\bar{5}$	< 5·8	+ 3·4
020	22·4	−29·9
021	7·9	+ 9·5
022	14·7	−12·6
023	10·1	+14·5
024	10·1	+11·0
025	< 5·9	+ 5·0
026	13·7	+16·0
027	6·2	− 4·0
028	6·4	+ 4·9
031	20·0	+21·7
032	20·7	+24·0
033	< 5·7	− 0·3
034	17·6	+19·0
035	13·1	−14·4
036	< 6·2	− 0·4
037	11·6	−11·0
038	11·5	−11·0
040	22·5	+23·2
041	10·4	− 8·1
042	11·3	+11·0
043	14·7	−14·9
044	12·9	+ 9·9
045	< 6·3	− 5·6
046	14·0	−15·5
047	< 6·6	+ 4·7
051	11·6	−10·2
052	12·3	− 7·6
053	< 6·3	+ 0·2
054	10·8	− 6·2
055	< 6·5	+ 7·8
060	< 6·1	− 2·0
061	11·0	+ 7·4
062	< 6·3	− 1·0
063	11·8	+12·1
064	< 6·5	+ 0·8
071	12·3	+ 9·6
072	< 7·0	+ 3·0

very narrow temperature range (Pitzer, 1940). Thus there is a possibility of a relation between this sharp transition and this rarely-observed sharp transition in 1,2-dichloroethane.

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