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## The Conformation of Non-Aromatic Ring Compounds. VIII.\* The Crystal Structure of *cis*-2,3-Dichloro-1,4-dioxane at $-140^{\circ}\text{C}$

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*cis*-2,3-Dichloro-1,4-dioxane crystallizes in the orthorhombic system, space group  $P2_12_12_1$ ,  $Z = 4$ , and  $a = 4.463$ ,  $b = 10.67$ ,  $c = 13.13$  Å at  $-140^{\circ}\text{C}$ .

The structure was refined in three projections by means of data obtained at about  $-140^{\circ}\text{C}$  with molybdenum radiation.

The dioxane ring has the chair form. The two carbon-chlorine bonds are unequal in length: C(1)-Cl(1) (axial) =  $1.819 \pm 0.009$  Å, C(2)-Cl(2) (equatorial) =  $1.781 \pm 0.007$  Å.

### Introduction

It seemed worthwhile to determine the structure of *cis*-2,3-dichloro-1,4-dioxane by X-ray methods, since this compound is the only known dihalogeno-1,4-dioxane in which an equatorial carbon-halogen bond was expected to be present (Altona, Romers & Havinga, 1959).

### Experimental

*cis*-2,3-Dichloro-1,4-dioxane was prepared by chlorination of a refluxing mixture of 1,4-dioxane and carbon

tetrachloride (Summerbell & Lunk, 1957). The compound crystallizes from carbon tetrachloride as colourless needles, elongated along the  $a$  axis. The crystals are soft and tend to disintegrate when even slight pressure is applied in directions perpendicular to the needle axis. After several trials some good crystals were obtained that could be cut along [010] and [001]. Their cross sections were roughly hexagonal with faces {001} and {011} about equally developed. A central capillary hole with a radius of approximately 0.02 mm ran along the full length of all these needles.

The dimensions of the unit cell were determined from zero-layer Weissenberg photographs taken with unfiltered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) about [100],

\* Part VII: Altona, Knobler & Romers (1963); for earlier parts see van Dort & Havinga (1963).

[010], and [001] at  $-140^\circ\text{C}$ . The powder diffraction lines of aluminum ( $a=4.0189\text{ \AA}$  at  $20^\circ\text{C}$ ) were superposed on the films.

#### Crystal data

*cis*-2,3-Dichloro-1,4-dioxane,  $\text{C}_4\text{H}_6\text{O}_2\text{Cl}_2$ , m.p.  $53.5\text{--}54^\circ\text{C}$ . Orthorhombic,  $a=4.463 \pm 0.01$ ,  $b=10.72 \pm 0.02$ ,  $c=13.13\text{ \AA}$ , measured at  $-140^\circ\text{C}$ .

$D_x$  from data obtained at  $20^\circ\text{C}$  ( $Z=4$ ),  $1.63\text{ g.cm}^{-3}$ ;  $D_m$  at  $20^\circ\text{C}$ ,  $1.59\text{ g.cm}^{-3}$ . Absorption coefficient for  $\text{Mo } K\alpha$  rays ( $\lambda=0.7107\text{ \AA}$ )  $\mu=9.4\text{ cm}^{-1}$ . Space group, from absent spectra,  $P2_12_12_1$ .†

Table 1. Technical data concerning the intensity records

Zone	Exposure time (hr)	Number of observed reflexions	$(\sin\theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	Temperature ( $^\circ\text{C}$ )	Cross section (mm)
[100]	77	247	0.96	-130	$0.4 \times 0.4$
[010]	94	140	1.10	-142	$0.4 \times 0.5$
[001]	71	90	1.03	-142	$0.6 \times 0.6$

Intensity records were obtained on zero-layer Weissenberg exposures about [100], [010], and [001], taken with filtered  $\text{Mo } K\alpha$  radiation at low temperatures (Table 1). The multiple-film technique was used with thin copper foils inserted between films. The crystal specimens were sealed in Lindemann glass capillaries. The visually estimated intensities were corrected for Lorentz and polarization factors by the usual methods. Absorption effects were neglected since  $\mu R=0.38\text{--}0.56\text{ cm}^{-1}$  for  $\text{Mo } K\alpha$  radiation. Preliminary scale and temperature factors changed less than 3% in later stages of the analysis; the absolute scale was established by correlation of the observed with the calculated structure factors. Additional technical data are collected in Table 1.

#### Determination and refinement of the structure

The Patterson functions  $P(vw)$  and  $P(uw)$  were calculated from preliminary  $\text{Mo } K\alpha$  data obtained at room temperature. From the Patterson maps the positions of the chlorine atoms could be determined without difficulty once it was recognized that the two atoms almost completely overlap in the [010] projection (Fig. 1(b)). An electron density projection  $\rho(yz)$ , calculated with 65% of the structure factors whose signs were based upon the chlorine contributions, clearly showed the carbon and oxygen atoms. This method worked less well for the projection along [010], because the chlorine atoms contribute only to about half of the structure factors  $F(h0l)$ . Since the main features of the molecule were now known, the  $x$  parameters of the atoms in the dioxane ring could be taken from a model. An electron density map

† In a preliminary paper (Altona, Romers & Havinga, 1959) the space group was erroneously reported to be  $P2_1/n$ .

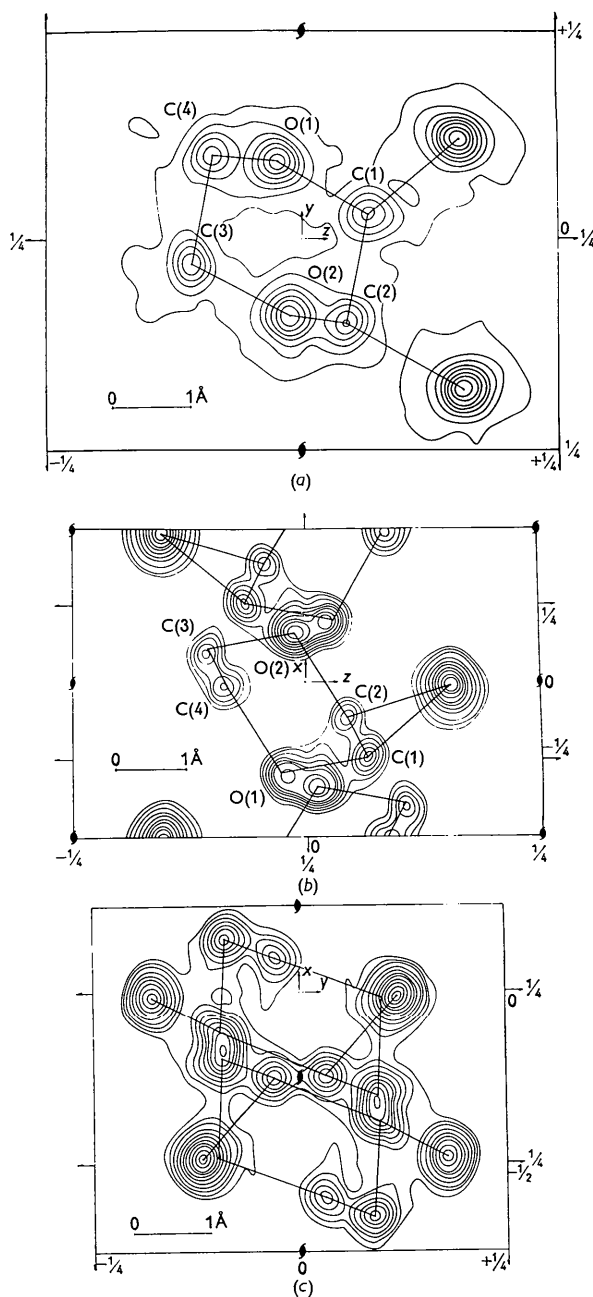


Fig. 1. Electron-density projections of *cis*-2,3-dichloro-1,4-dioxane. (a) Projection along [100]; contour lines around the carbon and oxygen atoms are drawn at 0, 2, 4, ...  $\text{e.\AA}^{-2}$ , those around the chlorine atoms at 0, 2, 5, 10, ...  $\text{e.\AA}^{-2}$ . (b) Projection along [010]; contour lines around C and O: 5, 7.5, 10, ...  $\text{e.\AA}^{-2}$ ; around Cl: 5, 10, 15, ...  $\text{e.\AA}^{-2}$ . (c) Projection along [001]; contour lines around C and O: 5, 8, 10, ...  $\text{e.\AA}^{-2}$ ; around Cl: 5, 8, 12, ...  $\text{e.\AA}^{-2}$ .

$\rho(xz)$  showed that this model was essentially correct; however, serious overlap of atomic peaks in the [010] and [001] projections soon prevented further progress.

In view of our favourable experiences with low

Table 2. Observed and calculated structure factors

In each column the running index is followed by 10  $F_o$  and 10  $F_c$ , in that order. The non-observed reflexions, indicated by x, are inserted at the minimum observable value.

o k l	o 4 l	o 9 l	o 14 l	1 0 l	5 0 l	1 x 0
17 70 65	6 45 48	4 94 -110	2 328 -331	1 207 -209	10 397 -424	
18 29 43	7 173 -167	5 78 77	3 12x	2 101 -99	11 25 33	
19 62 -53	8 29x -24	6 99 98	4 113 127	3 66 59	12 112 118	
2 628 613	20 45 -52	9 181 195	7 58 -59	5 690 706	4 94 -92	13 37 -55
4 575 -551	21 99 -86	10 49 -39	6 29 -24	6 16x -9	5 238 241	14 165 183
6 727 740		11 99 88	9 62 -58	7 507 527	6 47 66	15 58 -52
8 103 98		12 74 78	10 86 -91	8 18x 28	7 74 80	20 66 -74
10 370 -395	0 5 l	13 164 -157	11 62 57	9 452 423	8 47 65	
12 226 237		14 58 65	12 78 67	10 47 51	9 156 -144	
14 90 105	1 21 25	15 41 -24	13 40x 4	11 519 -476	10 74 64	2 x 0
16 230 -240	2 99 -97	16 40x -2	14 40x 9	12 70 -81	11 90 -85	
18 29 33	3 41 -57	17 40x 38	15 40x -31	13 66 70	12 105 -110	0 637 -626
20 8x 78	4 14x -140	18 40x 32	16 66 -56	14 23 36	13 30x -40	1 16x 20
22 90 -80	5 78 -71	19 49 -42		15 167 214	14 30x 11	2 318 312
	6 156 -169			16 25x -27	15 113 95	3 103 -104
	7 103 101			17 191 194	16 30x -25	4 409 396
	8 53 -51	0 10 l	0 15 l	18 25x -14	17 31 44	5 66 -82
	9 119 129			19 97 -95	18 32x 27	6 236 -230
1 x 55	10 21 26	0 254 -281	1 37x -19	20 86 72	19 32x 10	7 37 12
2 350 -397	11 53 -47	1 374 372	2 37x 15	21 125 -102	20 39 29	8 66 -52
3 58 -50	12 90 -99	2 103 -115	3 37x 17	22 31 -55	21 57 60	9 91 -89
4 395 415	13 31 -37	3 160 166	4 37x 9	23 47 -48	25 31 54	10 95 -94
5 197 203	14 123 -138	4 28x 19	5 62 -44	24 20x 18		11 50 -18
6 107 130	15 37 23	5 333 -321	6 62x -23	25 58 53		12 62 86
7 103 111	16 66 -65	6 111 -118	7 38x -21	26 30x -22	6 0 l	13 35x 26
8 279 -296	17 37 -33	7 131 132	8 38x -26	27 47 34		14 157 156
9 74 -71	18 62 -57	8 31x -26	9 62 60		0 125 129	15 38x -20
10 218 237	19 40x -4	9 156 153	16 49 38		1 31 26	16 165 -179
11 37 38	20 40x -35	10 53 52			2 35 53	17 40x 53
12 345 371	21 46 37	11 205 -216			3 117 134	18 83 -77
13 29x 12		12 37 -37	0 16 l	0 593 613	4 47 -34	19 41x -3
14 29x -17		13 36x -5		1 144 -150	5 31x -40	20 83 77
15 62 -63	0 6 l	14 36x -1	0 37x 22	2 511 514	6 164 -179	
16 35x 15		15 86 96	1 37 -38	3 265 268	7 35 -51	
17 53 52	0 62 58	16 74 74	2 119 -114	4 788 -772	8 55 51	3 k 0
18 99 105	1 242 -245	17 82 -80	3 39x -27	5 78 -101	9 33x -10	
19 62 54	2 411 400	18 41x -17	4 119 -109	6 370 -366	10 58 57	1 54 56
	3 107 123	19 41x 13	5 39x 9	7 78 96	11 39 -47	2 360 351
	4 374 383	20 41x -17	6 99 99	8 43 44	12 82 92	3 227 231
	5 501 500	21 70 55	7 40x -17	9 257 -253	13 86 91	4 467 436
	6 53 -60		8 40x 20	10 331 335	14 55 -52	5 66 71
0 488 -445	7 144 -157	0 11 l	9 40x -2	11 94 100	16 66 -78	6 385 -396
1 12x -9	8 70 65		10 103 -88	12 273 241		7 28x -13
2 518 -533	9 234 -233	1 127 127	11 42x 10	13 51 61	7 0 l	8 277 -288
3 140 -143	10 136 137	2 149 148	12 42x 31	14 86 -110		9 29x -32
4 140 -147	11 197 220	3 156 -167	13 42x -16	15 22x 22		10 252 -262
5 292 -300	12 74 -85	4 149 146	14 49 46	16 285 -266	1 86 -67	11 62 -59
6 259 261	13 31x 17	4 111 -126	15 43x -3	17 25x -38	2 30x 23	12 37 34
7 144 -137	14 31x 38	5 31x 28	16 49 -35	18 39 -44	3 30x 13	17 83 -78
8 25 -28	15 160 -168	6 45 -43		19 31 -45	4 121 -114	
9 78 83	16 35x 16	7 94 97		20 148 152	5 125 126	
10 144 -149	17 58 48	8 53 55	0 17 l	21 55 61	6 39 47	4 k 0
11 27x -24	18 74 -69	9 131 -142		22 55 31	7 31x -8	
12 78 86	19 62 51	10 86 -74	1 40x 0	23 47 -50	8 39 53	0 335 347
13 90 -97	20 40x -21	11 35x -10	2 123 -129	24 28x 22	9 31x -10	1 29x 10
14 33 -38	21 49 -50	12 58 -48	3 40x -4	25 43 36	10 31x 5	2 79 -92
15 62 56		13 127 134	4 90 88	26 58 -65	11 78 -66	3 116 121
16 74 -74	0 7 l	14 40x 1	5 40x -13		12 32x -22	4 174 -172
17 78 72		15 40x -13	6 66 57		13 35 30	5 30 25
18 38x 6	1 283 -284	16 86 -82	7 41x -11	3 0 l	14 35 -41	6 141 145
19 38x 11	2 197 173	17 49 -48	8 111 -104			7 103 -111
20 38x 27	3 596 609	18 49 -48	14 82 -66	2 187 -174	8 0 l	8 50 37
21 66 50	4 25 -35			3 16 5		9 62 65
	5 25x 24	0 12 l	0 18 l	4 43 -46	0 58 51	10 34x 34
	6 25x -9			5 519 528	1 31x 22	11 66 -80
	7 349 -367	0 31x -4	0 41x -9	6 20x 26	2 31x 4	12 70 -78
1 283 278	8 144 148	1 49 54	1 41x 3	7 179 186	3 58 64	13 124 -109
2 756 -723	9 185 180	2 62 62	2 42 37	8 187 189	4 35 -31	14 45 31
3 510 -507	10 30x 16	3 32x 23		9 269 -245	5 32x -42	15 50 -57
4 629 613	11 30x 16	4 119 124		10 101 -121	6 32x -5	
5 111 -110	12 41x -34	5 29 -26	0 19 l	11 289 -280	7 32x 8	
6 353 366	13 205 -201	6 25 33		12 43 41	8 32 -31	5 k 0
7 131 135	14 74 85	7 53 63	1 42x 15	13 25x -18	9 32x -3	
8 407 -423	15 148 143	8 30x -23	2 42 -44	14 58 -48	10 78 50	1 149 156
9 201 -224	16 58 64	9 58 41		15 214 200		2 66 -59
10 37 52	17 115 113	10 58 54		16 47 -50		3 79 -81
11 53 -51	18 39x -3	11 37x -35		17 78 74	9 0 l	4 116 -136
12 152 173	19 86 -79	12 37x 23		18 70 65		5 37 -37
13 181 203	20 41x 10	13 37x 14	0 49 -52	19 30x 17	8 39 50	6 141 133
14 164 -169	21 41x 13	14 74 -58	1 42x -25	20 35 22	9 35 -28	7 35 26
15 33 -34	22 41x 16		2 43 37	21 136 -142		8 35 19
16 53 -36	23 49 39		3 42x 0	22 33x -74		9 152 -188
17 123 -118		0 13 l	4 49 60	27 35 40		10 182 -188
18 152 141			5 42x 34	28 33x 25		11 41 39
19 38x 15	0 8 l	1 111 109	6 42 -39			12 45 -44
20 62 -50		2 177 167				13 45 -50
21 38x -4	0 62 75	3 156 -161				14 45 -54
22 38x -26	1 37 29	4 74 -92				15 45 -54
23 38x -36	2 25x 30	5 53 48				16 45 -54
24 49 38	3 193 -197	6 35x -36	0 14 l	0 324 331	2 488 451	0 132 -130
	4 62 -63	7 152 159		1 226 227	4 906 -909	1 79 75
	5 152 -159	8 164 168		2 179 162	6 62 -74	2 79 75
	6 295 -261	9 90 -76		3 21x -20	8 70 76	3 30 -38
	7 94 99	10 38x -28		4 308 -297	10 271 316	4 145 136
0 908 -901	8 29 47	11 45 -43	2 600 -616	5 109 132	12 31x -16	7 74 73
1 501 -472	9 58 67	12 103 -105	4 546 -558	6 214 -206	14 294 -316	
2 140 -160	10 30x -23	13 45 50	6 753 -764	7 121 -137	16 40x 31	
3 86 -93	11 107 -104	14 66 69	8 121 -103	8 23 -47	18 40x 5	7 k 0
4 70 48	12 33 -42	15 41x -31	10 448 435	9 82 -76	20 66 -82	
5 452 444	13 53 47	16 41x 33	12 265 259	10 246 240		1 38 -28
6 509 -500	14 58 39	17 41x -10	14 136 -116	11 24x 1		2 41 25
7 131 -132	15 78 71	18 49 -35	16 277 -305	12 168 186		3 62 55
8 82 -86		19 49 44	18 52 -54	13 86 96		4 45 38
9 90 -100			20 125 130	14 125 -137	1 310 305	5 62 -48
10 232 238	0 9 l	0 14 l	22 136 121	15 43 48	2 87 75	6 62 -61
11 201 222			24 35 -41	16 133 -138	3 103 -104	
12 107 -120	1 185 -180		26 58 -43	17 78 -86	4 232 -236	
13 58 -43	2 28x 16	0 242 261		18 30x 13	5 95 -97	8 k 0
14 70 -75	3 164 165	1 86 -86		19 30x 6	6 496 529	
15 90 -94	4 27 26	2 34x -3	1 0 l	20 47 39	7 24x 7	0 66 53
16 164 174	5 74 -86	3 34x -29	1 717 -711	21 33x -4	8 136 136	1 66 54
				22 47 59	9 66 50	7 83 -70

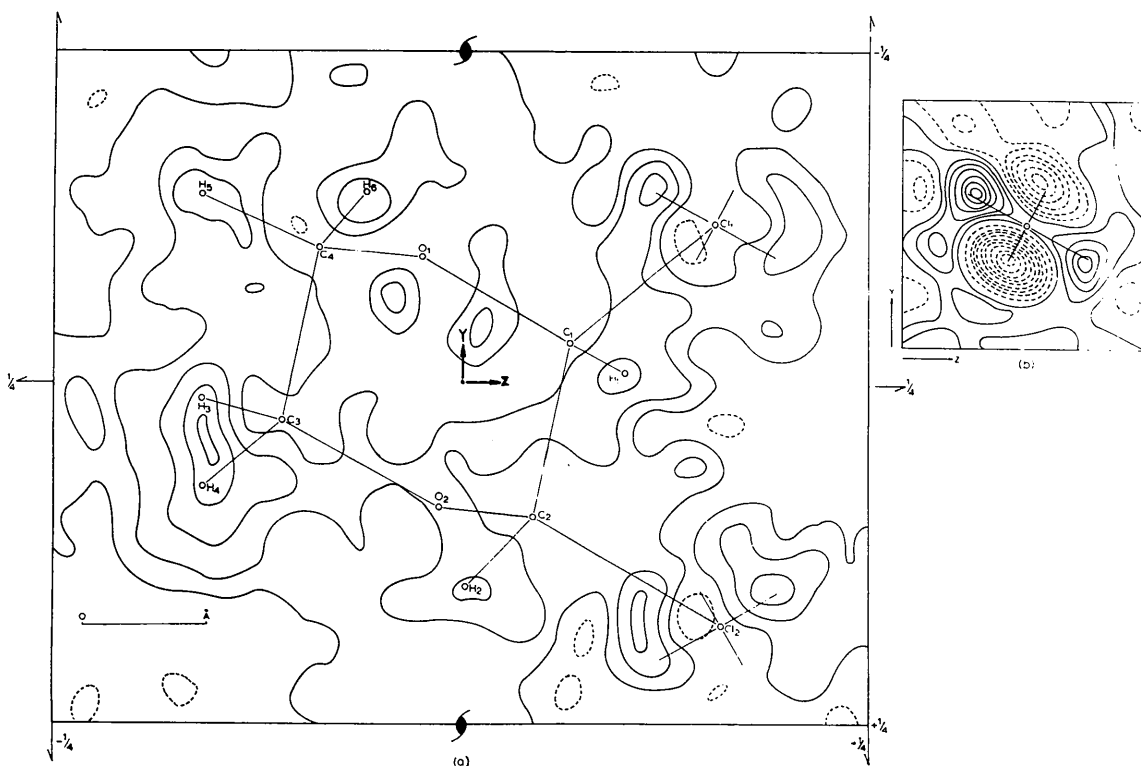


Fig. 2. Difference Fourier syntheses. (a) The final  $F_o - F_c$  projection along [100], showing the principal axes of the thermal vibration ellipses of the chlorine atoms. Contour lines are drawn at 0, 0.4, 0.8, ...  $e \cdot \text{\AA}^{-2}$ , negative contours are broken. (b) Region around chlorine atom Cl(1) before a correction was applied (see text) for the thermal anisotropy. Contours are drawn at approximately 0, 0.3, 0.6, ...  $e \cdot \text{\AA}^{-2}$ ; negative contours are broken.

temperature data in the analysis of the structure of the *trans*-2,5-isomer (Altona, Knobler & Romers, 1963), we decided to continue the refinement by using a new set of Mo  $K\alpha$  reflexions collected at  $-140^\circ\text{C}$ . Calculation of two cycles of structure factors and Fourier syntheses (Fig. 1) yielded the following reliability factors  $R$  and temperature constants  $B$ :

$$\begin{aligned} F(0kl), \quad R &= 14.9\%, \quad B = 2.32 \text{ \AA}^2; \\ F(h0l), \quad R &= 14.7\%, \quad B = 1.77 \text{ \AA}^2; \\ F(hk0), \quad R &= 13.2\%, \quad B = 1.98 \text{ \AA}^2. \end{aligned}$$

The structure was further refined in four successive cycles of structure factors and difference syntheses with contributions of the heavy atoms subtracted. Atomic positions and individual isotropic temperature factors were adjusted. Except in cases of severe overlap, each projection was treated independently; this was done partly in order to obtain a check upon the accuracy of the positional parameters and partly because systematic discrepancies were noted between the observed high-angle  $F(00l)$  values derived from the  $(0kl)$  and from the  $(h0l)$  films respectively (Table 2). These discrepancies may be due to photographic errors or to a fairly large temperature difference between the two crystals. Such a difference could

occur if the  $a$ -axis crystal had not been placed in the centre of the cold gas stream during the exposure.

The thermal vibrations of the chlorine atom were markedly anisotropic (Fig. 2(b)). A correction for this effect was applied by substituting for each chlorine atom two half-atoms placed 0.08–0.12  $\text{\AA}$  apart in the direction of maximum vibration (Kantha & Ahmed, 1960; Vos & Smits, 1961). The final separations were about 15% larger than those calculated initially from the formulae proposed by Kantha & Ahmed (1960). Although this method is approximative, satisfactory results were obtained; in the final difference maps no significant electron density details remained in the vicinity of the chlorine atoms (Fig. 2(a)).

In an attempt to find reliable hydrogen atom positions, difference maps were calculated in which only low-angle reflexions were used ( $\sin \theta / \lambda < 0.55 \text{ \AA}^{-1}$ ). The hydrogen maxima showed up clearly with peak heights of 0.6–0.8  $e \cdot \text{\AA}^{-2}$ . Because of overlap, however, some hydrogen parameters could not be determined. We therefore preferred to insert these atoms into the molecular model by accepting a C–H distance of 1.03  $\text{\AA}$  and tetrahedral angles.

The final  $R$  indices, excluding non-observed reflexions, were:

$$R(0kl) = 6.3\%, R(h0l) = 7.3\%, R(hk0) = 7.1\% .$$

The atomic scattering factors for carbon and oxygen were those calculated by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), for chlorine those by Tomiie & Stam (1958), and for hydrogen those by McWeeny (1951). The difference Fourier syntheses (at intervals of 1/128 of the cell edges) and the corresponding structure factors were calculated on a ZEBRA computer with programs devised by Smits (1961). A list of the observed and calculated structure factors is given in Table 2. In order to retain a centre of symmetry in each projection, the three-dimensional origin was shifted according to the following scheme: [100], (0, -1/4, 0); [010], (0, 0, 1/4); [001], (1/4, 0, 0).

The agreement between the positional parameters derived from each projection was satisfactory. Eleven of the fourteen parameters that were determined twice showed differences less than the sum of the respective standard errors. None of the remaining differences was possibly significant. Since the projection along [001] suffered from overlap effects (Fig. 1(c)), the  $x$  parameters were taken from the [010] projection and the  $y$  values from the [100] projection. The  $z$  parameters of O(2), O(1), C(1), C(2) and C(4) are weighted means. The final atomic positions are shown in Table 3. Their standard errors were estimated by Cruickshank's (1949) method. Since only two-dimensional methods were employed, these standard errors might be too low and should perhaps be increased by about 50%.

Table 3. *Final atomic coordinates (in fractions of the cell edges) and standard deviations*

Atom	(Å, × 10 <sup>-3</sup> )		
	$x$	$y$	$z$
Cl(1)	-0.0129 (3)	0.1206 (2)	0.1515 (2)
Cl(2)	-0.0161 (3)	-0.1785 (2)	0.1580 (2)
O(1)	-0.3000 (9)	0.0945 (6)	-0.0252 (5)
O(2)	0.1555 (9)	-0.0916 (5)	-0.0140 (5)
C(1)	-0.2470 (11)	0.0302 (8)	0.0653 (7)
C(2)	-0.1140 (10)	-0.0985 (7)	0.0439 (6)
C(3)	0.0900 (11)	-0.0279 (7)	-0.1109 (7)
C(4)	-0.0300 (13)	0.1012 (8)	-0.0886 (7)
H(1)	-0.441	0.005	0.100
H(2)	-0.267	-0.150	0.001
H(3)	0.264	-0.012	-0.159
H(4)	-0.038	-0.078	-0.159
H(5)	-0.096	0.141	-0.160
H(6)	0.105	0.160	-0.050

The central curvatures and the peak electron densities are shown in Table 4. These values are of the same order of magnitude as those found in the low temperature projections of *trans*-2,5-dichlorodioxane. The individual isotropic temperature factors, as well as the values of  $B_{\min}$  and  $B_{\max}$  for each chlorine atom, are also given in Table 4. The directions of the vibrational axes, projected along [100],

Table 4. *Isotropic temperature factors  $B$  (Å<sup>2</sup>), peak electron densities  $\rho_0$  (e.Å<sup>-2</sup>) and average central curvatures (e.Å<sup>-4</sup>)*

Two values are shown for each chlorine atom, the one between brackets pertains to the component in the direction of maximum vibration

	[100]			[010]			[001]
	$B$	$\rho_0$	$\delta^2\rho/\delta r^2$	$B$	$\rho_0$	$\delta^2\rho/\delta r^2$	$B$
Cl(1)	1.65 (2.50)	38.7	675 (560)	1.65 (3.05)	*	*	1.18 (2.08)
Cl(2)	1.68 (2.44)	38.9	625 (485)	1.65 (3.05)	*	*	1.48 (2.48)
O(1)	2.29	15.5	200	1.17	20.8	305	1.38
O(2)	2.01	15.7	215	1.00	22.6	320	1.50
C(1)	1.88	10.6	140	1.31	15.6	255	1.22
C(2)	1.92	12.1	185	0.90	17.0	300	1.54
C(3)	1.95	11.2	160	1.12	15.3	250	1.54
C(4)	2.17	11.0	145	1.25	14.3	210	1.62
H	2.00			1.00			1.30

\* The chlorine atoms suffer from overlap in the projection along [010].

are shown in Fig. 2. In the [010] and [001] projections the maximum vibration vector almost coincided with the  $x$  axis.

### Conformation of the molecule

The dioxane ring has the chair form with one chlorine atom (Cl1) in the axial and the other (Cl2) in the equatorial position (Fig. 3). This conformation was predicted earlier from dipole moment data (Altona, Romers & Havinga, 1959). The bond distances and angles are shown in Table 5 (see also Fig. 3). The important features can be summarized as follows:

Table 5. *Intramolecular distances, angles and estimated standard deviations*

Bond	Distance	$\sigma$
C(1)-Cl(1)	1.819 Å	9 × 10 <sup>-3</sup> Å
C(2)-Cl(2)	1.781	7
C(1)-C(2)	1.528	11
C(3)-C(4)	1.513	11
C(1)-O(1)	1.394	9
C(2)-O(2)	1.425	12
C(3)-O(2)	1.466	9
C(4)-O(1)	1.473	12
Non-bonded		
Cl(1)···O(1)	2.664	7
Cl(1)···Cl(2)	3.207	4
Bonds		
O(1)-C(1)-C(2)	110.8°	0.7°
C(1)-C(2)-O(2)	112.3	0.7
O(2)-C(3)-C(4)	109.1	0.7
C(3)-C(4)-O(1)	110.8	0.7
C(1)-O(1)-C(4)	111.6	0.6
C(2)-O(2)-C(3)	108.5	0.6
Cl(1)-C(1)-O(1)	111.3	0.5
Cl(1)-C(1)-C(2)	111.8	0.6
Cl(2)-C(2)-C(1)	112.0	0.6
Cl(2)-C(2)-O(2)	105.5	0.6

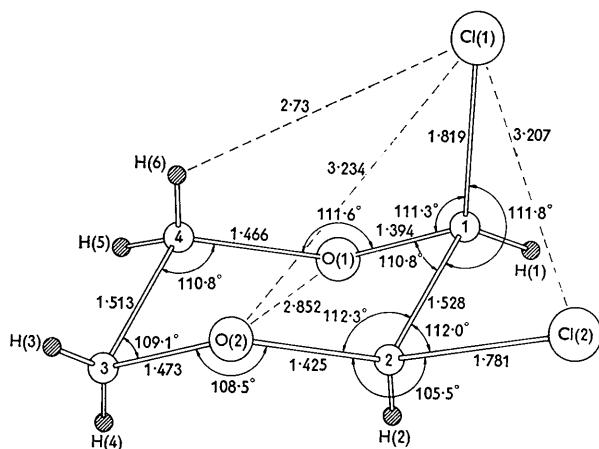


Fig. 3. Atomic distances and bond angles in *cis*-2,3-dichloro-1,4-dioxane.

(1) The axial carbon-chlorine bond distance ( $1.819 \pm 0.009$  Å) is significantly larger ( $p=0.2\%$ ; Cruickshank & Robertson, 1953) than the equatorial one ( $1.781 \pm 0.007$  Å).

(2) The bond C(1)–O(1) ( $1.394 \pm 0.009$  Å), adjacent to the axial C(1)–Cl(1) bond, is perhaps ( $p=1.5\%$ ) shorter than the carbon-oxygen bond in dimethyl ether ( $1.416 \pm 0.003$  Å, Kimura & Kubo, 1959). The bond distance of C(2)–O(2), adjacent to the equatorial C(2)–Cl(2) bond, appears to be normal ( $1.425 \pm 0.012$  Å).

(3) The bond distances of C(4)–O(1) ( $1.466 \pm 0.013$  Å) and C(3)–O(2) ( $1.473 \pm 0.010$  Å) are relatively large and deviate significantly ( $p=0.1\%$ ) from the C–O bond distance in dimethyl ether quoted above.

(4) The 'equatorial half' of the molecule, consisting of the atoms Cl(2), C(2), O(2) and C(3), does not deviate significantly from planarity. The equation of the plane, obtained by a least-squares procedure, is:

$$0.2758X + 1.1035Y + 0.5421Z + 1 = 0.$$

All four atoms are at distances less than  $0.007$  Å from this plane. The angles between the bonds lying in the plane, Cl(2)–C(2)–O(2) ( $105.5 \pm 0.6^\circ$ ) and C(2)–O(2)–C(3) ( $108.5 \pm 0.6^\circ$ ) are smaller than the corresponding angles in the 'axial half'.

Not too much stress should be laid on relatively small differences in bond lengths in view of the uncertainties in the estimation of two-dimensional standard errors (see preceding section).

One might expect some steric strain to be present in this molecule, owing to the close approach of the two chlorine atoms ( $3.207$  Å). However, it is remarkable that, compared with the conventional chair model (tetrahedral angles), the vectorial angle between the C–Cl bonds is narrowed from  $70.5$  to  $66^\circ$ , and the dihedral angle is only  $50.5$  instead of  $60^\circ$ .

The bond distances and angles in the 'axial half' of the molecule resemble those occurring in the *trans*-2,5-

isomer, in which compound a long axial C–Cl bond ( $1.845$  Å) is present adjacent to a short C–O bond ( $1.388$  Å; Altona, Knobler & Romers, 1963). Similar effects occur in *trans*-2,3-dichloro-1,4-dioxane (Altona & Romers, 1963).

### Molecular environment

All intermolecular atomic distances  $< 4.4$  Å have been calculated on the X<sub>1</sub> computer, University of Leiden, using a program (A 200) written in ALGOL 60 by Mr H. L. Jonkers. A selection of these distances is listed in Table 6 (see also Fig. 4).

Table 6. Some intermolecular distances\* and angles

Atoms	Distance
O(2) $\cdots$ O(1) [0] <sub>x</sub>	3.14 Å
O(2) $\cdots$ C(1) [0] <sub>x</sub>	3.14
O(2) $\cdots$ H(1) [0] <sub>x</sub>	2.55
O(2) $\cdots$ H(2) [0] <sub>x</sub>	2.65
C(3) $\cdots$ O(1) [0] <sub>x</sub>	3.22
Cl(2) $\cdots$ H(1) [0] <sub>x</sub>	2.92
Cl(2) $\cdots$ H(3) [1] <sub>x</sub>	2.96
H(5) $\cdots$ Cl(2) [1] <sub>x</sub>	2.98
Cl(1) $\cdots$ O(1) [2] <sub>x</sub>	3.60
Cl(2) $\cdots$ O(2) [2] <sub>y</sub>	3.43
Cl(2) $\cdots$ Cl(2) [3]	3.30
	Angle
$\angle$ C(1)–Cl(1) $\cdots$ Cl(2) [3]	147.3°
$\angle$ C(2)–Cl(2) $\cdots$ Cl(1) [3] <sub>-y</sub>	161.9

\* The four molecules are numbered [0], [1], [2] and [3], with:

[0] at	$x$ ,	$y$ ,	$z$ ;
[1] at	$\frac{1}{2}-x$ ,	$-y$ ,	$\frac{1}{2}+z$ ;
[2] at	$\frac{1}{2}+x$ ,	$\frac{1}{2}-y$ ,	$-z$ ;
[3] at	$-x$ ,	$\frac{1}{2}+y$ ,	$\frac{1}{2}-z$ .

Translation of the unit cell along one of the crystallographic axes is indicated by a subscript.

The main short approach distances occur between molecules related by the unit translation along [100], indicating a close stacking in this direction. Of particular interest are the separations of C(3)  $\cdots$  O(2) ( $3.22$  Å) and of O(2)  $\cdots$  C(1) ( $3.14$  Å). Similar or shorter non-hydrogen bonded C  $\cdots$  O distances have been reported in recent years (Sime & Abrahams, 1960; Chu, Jeffrey & Sakurai, 1962; Romers, 1963); however, all of these were found to occur between molecules in which at least one of the atoms involved takes part in a  $\pi$ -bonded system.

The packing is less dense in all other directions, in accord with the easy cleavage of the crystals along planes in the [100] zone. Noteworthy is the short distance ( $3.303 \pm 0.007$  Å) that occurs between axial and equatorial chlorine atoms approximately in the directions [011], [01 $\bar{1}$ ] *etc.* The approach is even closer than that found in *trans*-2,5-dichloro-1,4-dioxane ( $3.38$  Å) and in  $\beta$ -2-chloro-*p*-benzoquinone-4-oxime acetate ( $3.33$  Å, Fischman, MacGillavry & Romers, 1961). A short Cl  $\cdots$  Cl distance ( $3.34 \pm 0.04$  Å) also occurs in solid chlorine (Collin, 1952).



### Proton magnetic resonance

It is of interest to note that a single crystal of *cis*-2,3-dichloro-1,4-dioxane contains either right-handed or left-handed molecules. Here we have an example of an asymmetric conformational transformation induced by crystallization (*cf.* Havinga, 1954). The solution is optically inactive, because at room temperature in the liquid phase the equilibrium between the two enantiomeric conformations (*ea* and *ae*) is readily established; *i.e.* an axial atom becomes an equatorial one and *vice versa* by chair-chair interconversion.

Proton magnetic resonance (p.m.r.) spectra were taken at various temperatures in order to verify these conclusions (Smidt & Altona, 1962). At temperatures between +20 and -100 °C only one sharp resonance peak is observed for the two non-equivalent protons at C(1) and C(2); hence the ring inversion is rapid to the extent that the chemical shifts of equatorial H and axial H are averaged to a single value. This 'collapsed' signal is found at higher field ( $\tau=4.37$ ) than that of the (*ee*) protons in the *trans*-2,3-isomer ( $\tau=4.10$ ) in accordance with a well known rule (Lemieux, Kullnig & Moir, 1958). At -118 °C the inversion rate is reduced sufficiently to effect an appreciable broadening of the resonance signal and at -128 °C two lines are observed. This temperature is surprisingly low. Recent p.m.r. studies have shown that splitting of the appropriate resonance peaks of cyclohexane (Jensen, Noyce, Sederholm & Berlin, 1960; Moniz & Dixon, 1961) and of several halogeno-cyclohexanes (Berlin & Jensen, 1960; Reeves & Strømme, 1960, 1961; van Dort & Sekuur, 1963) takes place at temperatures between -60 and -80 °C.

After completion of this work a publication appeared (Caspi, Wittstruck & Piatak, 1962) in which a conformation of *cis*-2,3-dichloro-1,4-dioxane in solution was derived from p.m.r. data. The spectrum is in excellent agreement with that taken at 20 °C by Smidt & Altona (1962). However, the conclusion that the molecule probably exists in solution as a rigid boat conformation is unjustified as it was not based upon measurements performed at a sufficiently low temperature. Furthermore, the infrared spectra of the *cis* compound in the solid state (KBr disc) and in solution (CS<sub>2</sub>) are practically identical (Altona, 1963). This fact also indicates that the (*ea*) chair form occurring in the crystal is also the preferred one in solution.

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