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The Conformation of Non-Aromatic Ring Compounds. VII.[†] Crystal Structure of *trans*-2,5-Dichloro-1,4-dioxane at −125 °C

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trans-2,5-Dichloro-1,4-dioxane crystallizes in the triclinic system: space group $P\bar{1}$, $Z=1$,

$$a=4\cdot573,\ b=5\cdot491,\ c=6\cdot665\ \text{Å};\ \alpha=86\cdot25°,\ \beta=104\cdot10°,\ \gamma=106\cdot23°$$

at room temperature. Three independent sets of data were used to refine the atomic coordinates:

(i) Reflexion intensities of the zones [100] and [001], with Mo $K\alpha$ radiation at room temperature.
(ii) Reflexion intensities of the zones [100] and [001], with Mo $K\alpha$ radiation at −125 °C.
(iii) Three-dimensional reflexion intensities observed with Cu $K\alpha$ radiation at −125 °C.

The dioxane ring has the chair form with the chlorine atoms in axial positions. Some bond lengths show interesting deviations from the expected values:

$$\text{C(1)–Cl}=1\cdot845\pm0\cdot006,\ \text{C(1)–O}=1\cdot388\pm0\cdot007,\ \text{C(2)–O}=1\cdot428\pm0\cdot007,$$
$$\text{C(1)–C(2')}=1\cdot513\pm0\cdot008\ \text{Å at }-125\ °\text{C}.$$

1. Introduction

The present study is the first of a series of crystal structure analyses of halogeno-1,4-dioxanes initiated in this laboratory during the past few years. The properties and conformation of this class of substituted heterocyclic molecules have also been investigated in solution by infrared and Raman spectroscopy and by measurements of electric dipole moments (Altona, Romers & Havinga, 1959; Altona, 1963). This research was undertaken in order to determine the preferred conformation or conformations and to compare the results with those from earlier studies of analogous cyclohexane derivatives, both in solution (Kwestroo, Meijer & Havinga, 1954) and in the solid state (Hassel & Vihovde, 1953).

A *cis* and a *trans* form of 2,5-dichlorodioxane are theoretically possible. Only one isomer is known (Bryan, Smedley & Summerbell, 1950). The *trans* configuration has been inferred from the low value (0·60 D) of the dipole moment (Altona, Romers & Havinga, 1959) and is now confirmed by X-ray analysis.

The structure was first refined in projections from molybdenum radiation data obtained at room temperature. Because the carbon–chlorine bond appeared to be unusually long, we decided to improve on the accuracy of the determination by application of Mo $K\alpha$ radiation at low temperature. After completion of this second analysis, digital computing facilities became available and a third refinement was carried out with full three-dimensional Cu $K\alpha$ data, also collected at −125 °C. These three determinations offer interesting material for comparative purposes.

2. Experimental

trans-2,5-Dichloro-1,4-dioxane, $C_4H_6O_2Cl_2$, m.p. 122–124 °C, was prepared by chlorination of a mixture of 1,4-dioxane and carbon tetrachloride at 10 °C in the presence of a trace of dibenzoyl peroxide (Bryan, Smedley & Summerbell, 1950). The compound crystallizes from carbon tetrachloride in the form of white triclinic laths with principal zone [100] and faces {010} and {001}. Plates with main faces {010} were also found. The crystal faces are rough and the angles α, β and γ were not measured directly with an optical goniometer. The specimens chosen for X-ray diffraction were carefully sealed in dry Lindemann glass capillaries, because the crystals decompose rapidly in the presence of traces of moisture. They were also dipped into liquid air in order to minimize primary extinction effects.

Unit cell dimensions and angles at 20 °C and at −125 °C were measured from zero-level Weissenberg photographs about [100], [010] and [001], taken with unfiltered copper radiation (λ Cu $K\alpha=1\cdot5418$ Å) and superposed with aluminum powder diffraction lines ($a=4\cdot0489$ Å at 20 °C). No discontinuous structure transition was found between 20 °C and −125 °C. It is interesting to note (Table 1) that angle α^* changes from acute to obtuse on cooling and special care was exercised in indexing the films. The triclinic unit cell contains one molecule. The molecular symmetry is an inversion centre if the space group is $P\bar{1}$, an assumption confirmed by the straightforward refinement.

All intensity records were obtained on non-inte-

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Table 1. *Unit cell dimensions, angles, and densities at* 20 °C *and at* −125 °C

	20 °C	−125 °C
a	4·573 ± 0·01 Å	4·521 ± 0·007 Å
b	5·491 ± 0·01	5·432 ± 0·01
c	6·665 ± 0·01	6·616 ± 0·01
α	86·25 ± 0·1°	85·73 ± 0·1°
β	104·10 ± 0·15	103·85 ± 0·2
γ	106·23 ± 0·2	106·40 ± 0·25
d (100)	4·268 ± 0·005 Å	4·222 ± 0·003 Å
d (010)	5·272 ± 0·005	5·211 ± 0·005
d (001)	6·464 ± 0·005	6·423 ± 0·005
α^*	89·85 ± 0·05°	90·42 ± 0·05°
β^*	76·40 ± 0·1	76·80 ± 0·1
γ^*	74·20 ± 0·2	74·13 ± 0·2
U	155·8 ± 0·4 Å^3	151·3 ± 0·4 Å^3
$D_x (Z=1)$	1·676 g.cm^{-3}	1·727 g.cm^{-3}
D_m	1·65	—

grated equi-inclination Weissenberg photographs by the application of the multiple film technique. The films used for exposures with Mo $K\alpha$ radiation were interleaved with thin copper foils in order to reduce the intensities on successive films. The low temperature exposures were made according to the method described by Kreuger (1955). Since the exposure times were long (Table 2), an automatic filling system was designed in order to keep the liquid nitrogen in the cooling jacket at a constant level. A full description of the technical details will be given elsewhere (Altona, 1963).

Apart from preliminary Weissenberg photographs taken with copper radiation at room temperature, three sets of data were collected:

1. Reflexion intensities of the zones [100], [001] and [101] with Mo $K\alpha$ radiation at room temperature.
2. Reflexion intensities of the zones [100] and [001] with Mo $K\alpha$ radiation at −125 °C.
3. Reflexion intensities of the layers 0–3 about [100] and 0–4 about [001] with Cu $K\alpha$ radiation at −125 °C.

Some technical details of these sets of exposures are given in Table 2.

Within the Cu $K\alpha$ limiting sphere about 690 reflexions are possible; 653 reflexions were recorded, 35 of which were too weak to be observed.

The visually estimated intensities were corrected in the usual way for Lorentz, polarization, and spot-shape factors. The linear absorption coefficient μ (Mo $K\alpha$) = 9·5 cm^{-1} and μ (Cu $K\alpha$) = 85 cm^{-1}. It follows that the specimens chosen for Mo $K\alpha$ exposures (Table 2) were sufficiently small to neglect absorption errors. An absorption correction (cylindrical approximation) was applied to the intensities obtained from the Cu $K\alpha$ exposures.

The (0*kl*) and (*hk*0) observed structure factors of set (3) were put on an approximately absolute scale by comparison with the corresponding calculated structure factors F_c of set (2); all higher levels of the former set were then scaled by a thorough cross-correlation procedure. About 360 structure factors F_o occurred on the a-axis as well as on the c-axis photographs. Their mean value F_m was compared with the difference $F_m - F_o$. The 'agreement factor'

$$R_m = \Sigma|F_m - F_o|/\Sigma F_m = 4{\cdot}9\%$$

gives an indication of the accuracy of the measurements.

3. Two-dimensional refinements

The simple structure (Fig. 1) became evident after solution of the Patterson projections $P(uv)$ and $P(vw)$. With $Z=1$ the asymmetric unit consists of one chlorine atom, one oxygen atom, two carbon and three hydrogen atoms. The numbering of the atoms can be seen in Fig. 3.

Refinement of the structure by means of the room temperature Mo $K\alpha$ data (set 1) proceeded by calculation of successive cycles of structure factors, Fourier syntheses and difference maps in projections along [100] and [001]. An anisotropic temperature factor

$$\exp\left[-(B_1 + B_2 \cos^2 \varphi)\,(\sin \theta/\lambda)^2\right]$$

was introduced for the chlorine atom in the $F(0kl)$ structure factor calculations, the angle between the direction of maximum vibration and the z axis being 48 °C. The hydrogen atoms were incorporated into the molecular model by accepting C–H bond distances of 1·03 Å and tetrahedral bond angles. Final agreement indices R, taken over all observed reflexions, were:

$$R(0kl) = 5{\cdot}9\% \quad \text{and} \quad R(hk0) = 8{\cdot}5\% .$$

Table 2. *Technical data concerning the three sets of photographs taken*†

Set	Radiation	T	Reflexions	Crystal cross-section	Number of observed reflexions	Exposure time	$\sin\theta/\lambda$ max
1	Mo $K\alpha$	20°	0*kl*	0·20 × 0·35 mm	100	64 hr	0·83
			*hk*0	0·17 × 0·23	74	180	0·84
2	Mo $K\alpha$	−125°	0*kl*	0·30 × 0·30	161	64	1·02
			*hk*0	0·25 × 0·30	96	92	0·96
3	Cu $K\alpha$	−125°	0*kl* − 3*kl*	0·15 × 0·15	618	4–8	0·64
			*hk*0 − *hk*4	0·15 × 0·15			

† See text.

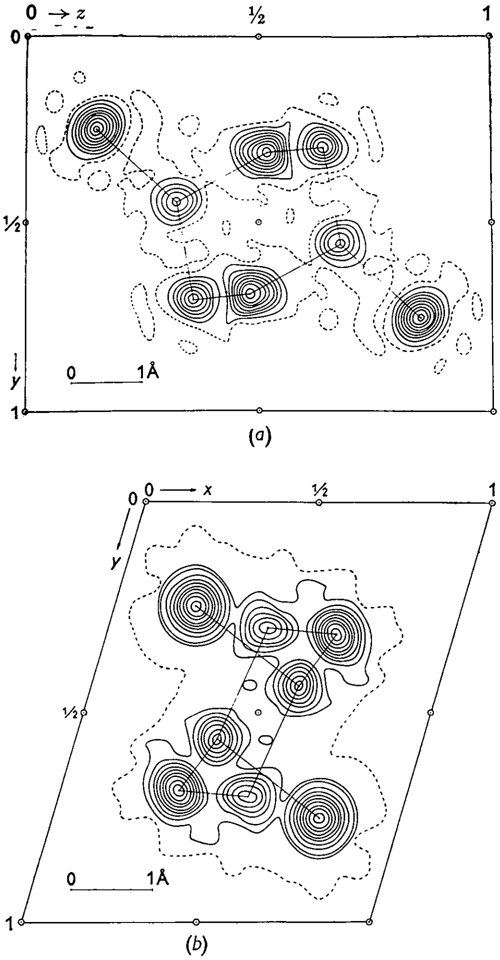


Fig. 1. Electron density projection of *trans*-2,5-dichloro-1,4-dioxane (*a*) along [100], calculated from the low temperature Mo $K\alpha$ data (set 2); (*b*) along [001]. Contours are drawn at 2, 4, 6, ... e.Å^{-2}; those about the chlorine atom are drawn at 4, 8, 12, ... e.Å^{-2}. Zero and negative contour lines are broken.

The low-temperature structure (Mo $K\alpha$ data, set 2) was refined in much the same way. Fourier maps (Fig. 1) and a number of difference syntheses were calculated at intervals of 1/120. The direction of maximum vibration of the chlorine atom in projection along [100] was the same as noted previously. All hydrogen atoms were located close to the expected positions in difference maps that included low-angle reflexions only (Jellinek, 1958). Theoretical hydrogen coordinates, however, were used in the final structure factor calculations.

The value of $R(0kl)$ was 8·6% at this stage. Because $F_o < F_c$ for many strong reflexions, a correction for primary extinction was applied (Vand, 1955). The final R indices were: $R(0kl) = 6{\cdot}3\%$ and $R(hk0) = 6{\cdot}9\%$. The results of the two analyses will be discussed in § 5 and 6. The observed and calculated structure factors of sets (1) and (2) will be given elsewhere.

The two-dimensional calculations were done with a desk calculator and Beevers–Lipson strips; for both sets a final cycle of structure factors and difference syntheses was carried out on the electronic X1 computer of the University of Leiden, using programs devised by Keulemans (1961). Tables of scattering factors of chlorine (Dawson, 1960), carbon and oxygen (Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal, 1955) and hydrogen (McWeeny, 1951) were used throughout this investigation.

4. Three-dimensional refinement

The data of set (3) were used to refine positions, scale-factor, and individual anisotropic temperature parameters by means of least-squares calculations. A block-diagonal approximation to the matrix of the normal equations was applied (Rollett, 1961). The calculations were carried out on the Mercury computer of the University of Manchester, England.

In the first cycle the final atomic positions and the isotropic temperature factors of the two-dimensional refinement with the data of set (2) were inserted. The few non-observed reflexions were given the value $\frac{1}{2}F_{\min}$ where $F_{\min}$ is the locally observable minimum of F_o. The $(F_o - F_c)^2$ values were weighted with a factor:

$$w = 1/[1 + \{(|F_o| - 10)/5\}^2]\,.$$

The previously assumed hydrogen parameters were included in the calculations, but were not refined.

After four cycles of calculations the shifts in the atomic positions were less than 0·001 Å. Relatively large discrepancies still remained between F_o and F_c of most strong low-order reflexions. Attempts at applying extinction corrections according to the method proposed by Vand (1955) were not successful, presumably because different extinction and residual absorption errors in the data of the two crystals used have been mixed in the three-dimensional analysis.

The observed and calculated structure factors are listed in Table 3. The final agreement index is 8·6%. Exclusion of the non-observed terms and of the nine reflexions most suffering from extinction yields an R value of 7·7%.

Since no positional standard deviations were provided by the least-squares program, several three-dimensional Fourier sections through each atom were calculated at intervals of 1/360. From these maps the central curvatures $\partial^2\varrho/\partial x^2$ *etc.* were obtained. The hydrogen maxima were found to lie close to the expected positions with peak densities 1·0–1·5 Å^{-3}, but no new hydrogen parameters were derived.

5. Atomic parameters and accuracy

Table 4 presents the following information, obtained from the three independent sets of data: the final atomic coordinates, the root mean square (r.m.s.) of the nearly isotropic coordinate standard deviations

Table 3. *Observed and calculated structure factors* (set 3)

Each group of reflexions is preceded by a ● and by the values of h and k common to that group. The remaining lines show l, F_o and F_c (× 50). Non-observed reflexions, inserted as $\frac{1}{2}F_{\min}$, are indicated by X

● 0	0	
1	-405	-499
2	-229	-269
3	-728	-893
4	-490	-494
5	-211	-161
6	737	770
7	148	158
8	108	71
● 0	1	
-8	387	388
-7	261	259
-6	-418	-417
-5	-414	-409
-4	-423	-390
-3	-211	-193
-2	1093	1467
-1	1120	1352
0	-841	-925
1	-342	-327
2	-1210	-1391
3	-198	-162
4	441	386
5	800	789
6	67	90
7	-99	-114
8	-587	-388
● 0	2	
-7	-198	-207
-6	-396	-406
-5	-45X	-35
-4	292	268
-3	1043	1086
-2	-112	-57
-1	-265	-231
0	-1488	-1569
1	-157	-147
2	-49	-10
3	904	915
4	571	561
5	-94	-127
6	-535	-515
7	-252	-225
● 0	3	
-7	-202	-172
-6	283	241
-5	265	245
-4	499	545
-3	-297	-261
-2	-585	-588
-1	-719	-678
0	351	324
1	-54	-23
2	1259	1278
3	-49	-50
4	-445	-432
5	-477	-480
6	-112	-125
● 0	4	
-6	288	277
-5	139	155
-4	-427	-411
-3	-459	-467
-2	45X	0
-1	36X	40
0	728	692
1	612	567
2	-522	-500
3	-418	-412
4	-333	-318
5	-58	-51
6	391	370
● 0	5	
-5	-202	-237
-4	-162	-184
-3	99	105
-2	184	184
-1	648	625
0	-216	-194
1	-279	-277
2	-490	-465
3	-67	-73
4	198	186
5	481	446
● 0	6	
-3	198	227
-2	157	163
-1	-238	-221
0	-306	-288
1	-292	-279
2	270	232
3	171	189
● 1	-6	
-4	247	261
-3	36X	14
-2	-423	-414
-1	-301	-322
0	63X	31
1	184	203
2	351	336
3	22	41
● 1	-5	
-6	360	404
-5	-31X	-21
-4	-157	-176
-3	-531	-583
-2	-121	-129
-1	121	155
0	576	630
1	121	59
2	99	80
3	-405	-405
4	-297	-297
5	54	65
● 1	-4	
-7	135	174
-6	-216	-215
-5	-252	-266
-4	-643	-672
-3	265	233
-2	616	603
-1	531	505
0	-130	-109
1	-54	-41
2	-859	-965
3	121	96
4	220	236
5	252	278
6	94	126
● 1	-3	
-7	-85	-100
-6	-553	-589
-5	-166	-189
-4	580	606
-3	657	652
-2	67	46
-1	202	157
0	-1120	-1123
1	-580	-603
2	472	441
3	418	401
4	391	411
5	40X	32
6	-256	-304
7	-207	-288
● 1	-2	
-8	-193	-213
-7	-495	-509
-6	445	428
-5	441	444
-4	684	641
-3	-292	-264
-2	-508	-485
-1	-1506	-1741
0	666	613
1	328	343
2	1084	1186
3	-175	-120
4	-126	-128
5	-486	-565
6	-193	-207
7	67	118
● 1	-1	
-7	423	383
-6	477	472
-5	265	210
-4	-670	-659
-3	-598	-640
-2	-791	-881
-1	540	675
0	1264	1533
1	769	861
2	-697	-715
3	-144	-127
4	-913	-973
5	121	126
6	391	445
7	279	288
● 1	0	
-8	283	307
-7	427	420
-6	-486	-490
-5	-288	-277
-4	-675	-720
-3	-103	-65
-2	1129	1338
-1	1313	1639
0	-940	-1072
1	85	58
2	-1097	-1258
3	-535	-524
4	558	643
5	450	552
6	130	111
● 1	1	
-8	-45	-54
-7	-409	-396
-6	-121	-112
-5	-598	-588
-4	737	761
-3	697	750
-2	436	437
-1	-719	-748
0	-333	-317
1	-1502	-1775
2	737	762
3	621	582
4	675	639
5	-121	-138
6	-180	-246
7	-414	-470
● 1	2	
-7	-292	-272
-6	81	91
-5	603	573
-4	364	387
-3	-85	-86
-2	-630	-654
-1	-746	-778
0	-274	-237
1	796	807
2	724	668
3	337	330
4	-513	-516
5	-324	-339
6	-346	-349
7	126	134
● 1	3	
-7	270	275
-6	162	205
-5	265	290
-4	-504	-523
-3	-342	-337
-2	-436	-410
-1	369	326
0	571	534
1	814	808
2	-549	-534
3	-351	-345
4	-418	-412
5	-94	-132
6	360	394
● 1	4	
-6	-54	-74
-5	-450	-437
-4	-40X	-51
-3	-166	-158
-2	468	449
-1	567	530
0	99	67
1	-594	-605
2	-139	-135
3	-414	-462
4	333	333
5	387	435
● 1	5	
-5	-72	-86
-4	67	95
-3	382	384
-2	198	205
-1	-319	-286
0	-274	-264
1	-315	-315
2	40X	16
3	391	437
4	243	265
● 1	6	
-2	-247	-274
-1	-139	-181
0	-148	-113
1	261	279
2	166	213
● 2	-7	
-1	-166	-278
● 2	-6	
-4	-319	-349
-3	-328	-320
-2	-189	-205
-1	157	195
0	225	225
1	445	391
2	-211	-177
3	-135	-158
● 2	-5	
-6	-85	-120
-5	-378	-360
-4	-382	-380
-3	49X	24
-2	414	415
-1	432	410
0	126	122
1	-252	-264
2	-445	-461
3	-135	-141
4	256	245
● 2	-4	
-7	-283	-288
-6	-337	-324
-5	-405	-401
-4	639	651
-3	328	298
-2	400	424
-1	-211	-208
0	-571	-534
1	-661	-653
2	508	466
3	103	115
4	360	379
5	85	97
● 2	-3	
-7	-468	-403
-6	193	194
-5	648	650
-4	139	102
-3	490	443
-2	-854	-796
-1	-895	-784
0	-90	-79
1	666	643
2	243	223
3	616	585
4	-445	-400
5	-364	-347
6	-202	-204
● 2	-2	
-8	-103	-120
-7	607	542
-6	211	200
-5	432	390
-4	-436	-407
-3	-908	-836
-2	-585	-489
-1	639	580
0	634	567
1	755	702
2	-126	-101
3	-535	-535
4	-477	-484
5	-58X	-34
6	355	328
● 2	-1	
-8	378	388
-7	126	140
-6	54X	72
-5	-859	-760
-4	-288	-249
-3	-612	-525
-2	1282	1334
-1	553	529
0	558	506
1	-827	-772
2	-549	-525
3	-737	-691
4	693	654
5	306	299
6	283	226
● 2	0	
-7	-324	-292
-6	-378	-324
-5	-450	-391
-4	418	374
-3	1133	1150
-2	-162	-97
-1	63	34
0	-881	-882
1	-944	-874
2	112	99
3	949	901
4	126	105
5	274	284
6	-378	-329
7	-279	-377
● 2	1	
-8	-171	-205
-7	-225	-214
-6	-162	-162
-5	890	883
-4	157	127
-3	193	156
-2	-607	-539
-1	-908	-821
0	-558	-514
1	1093	1024
2	427	372
3	373	353
4	-225	-185
5	-504	-525
6	-297	-282
● 2	2	
-7	256	243
-6	468	448
-5	-85	-68
-4	-49X	-13
-3	-773	-773
-2	-347	-309
-1	103	65
0	935	884
1	243	215
2	243	162
3	-639	-648
4	-342	-305
5	-238	-211
6	400	410
● 2	3	
-5	-409	-358
-4	-265	-268
-3	-58	-74
-2	396	363
-1	666	640
0	67	39
1	-400	-371
2	-427	-407
3	-315	-311
4	148	155
5	535	543
● 2	4	
-5	-22X	-4
-4	-58	-53
-3	549	580
-2	108	121
-1	-198	-172
0	-333	-345
1	-265	-266
2	-180	-168
3	571	569
4	211	228
● 2	5	
-4	220	302
-3	-171	-149
-2	-94	-118
-1	-279	-309
0	-153	-128
1	216	206
2	400	412
● 3	-6	
-4	-85	-91
-3	-144	-132
-2	297	279
-1	333	330
0	184	160
1	-319	-296
2	-157	-168
● 3	-5	
-6	-328	-373
-5	-49	-69
-4	58	68
-3	576	560
-2	153	144
-1	45X	42
0	-603	-556
1	-180	-206
2	-40X	-27
3	310	298
4	94	155
● 3	-4	
-7	-216	-246
-6	36X	43
-5	504	484
-4	220	216
-3	256	234
-2	-450	-421
-1	-657	-657
0	49X	15
1	238	235
2	288	310
3	351	346
4	-139	-152
5	-225	-367
● 3	-3	
-7	247	260
-6	391	366
-5	103	110
-4	175	149
-3	-1079	-1112
-2	-49X	-29
-1	40X	60
0	585	541
1	360	392
2	234	212
3	-621	-666
4	-162	-172
5	-94	-87
● 3	-2	
-8	198	213
-7	261	217
-6	67	106
-5	-499	-519
-4	-639	-649
-3	283	254
-2	229	183
-1	850	826
0	180	152
1	-252	-250
2	-706	-739
3	-94	-91
4	40X	45
5	436	416
● 3	-1	
-7	-139	-128
-6	-567	-587
-5	-103	-87
-4	135	102
-3	845	856
-2	252	209
-1	36X	13
0	-693	-724
1	-558	-563
2	49X	43
3	477	515
4	274	267
5	184	174
6	-153	-193
● 3	0	
-8	-117	-140
-7	-436	-382
-6	99	104
-5	450	415
-4	549	546
-3	-301	-254
-2	108	79
-1	-1097	-1132
0	-67	-34
1	382	367
2	594	570
3	162	137
4	153	120
5	-670	-622
● 3	1	
-7	306	285
-6	423	377
-5	45X	13
-4	-72	-6
-3	-553	-521
-2	-702	-664
-1	544	468
0	463	428
1	418	399
2	162	103
3	-396	-390
4	-558	-539
5	85	71
● 3	2	
-7	126	152
-6	-76	-73
-5	-94	-107
-4	-544	-614
-3	162	133
-2	283	255
-1	535	531
0	157	121
1	-162	-161
2	-594	-581
3	-157	-191
4	94	112
5	283	371
● 3	3	
-6	-148	-197
-5	-184	-202
-4	211	201
-3	265	292
-2	364	380
-1	-297	-277
0	-193	-191
1	-472	-468
2	36X	23
3	310	323
4	297	334
● 3	4	
-4	256	311
-3	-94	-92
-2	-130	-142
-1	-220	-248
0	-283	-267
1	265	268
2	342	346
● 4	-6	
-3	310	354
-2	283	270
-1	-126	-154
0	-180	-181
● 4	-5	
-4	418	483
-3	-63	-73
-2	-135	-127
-1	-450	-484
0	-27	-21
1	54	67
2	324	331
● 4	-4	
-4	-153	-159
-3	-409	-428
-2	-382	-380
-1	256	268
0	99	89
1	477	542
2	-40X	-29
3	-270	-272
● 4	-3	
-4	-472	-552
-3	202	196
-2	81	84
-1	495	496
0	382	353
1	-369	-356
2	-396	-390
3	-112	-108
4	-22X	-8
● 4	-2	
-4	243	297
-3	157	134
-2	764	745
-1	-324	-297
0	-382	-345
1	-441	-478
2	54	66
3	171	153
4	445	424
● 4	-1	
-4	302	381
-3	189	194
-2	-454	-415
-1	-468	-437
0	-369	-332
1	387	396
2	274	261
3	369	348
4	-103	-96
● 4	0	
-4	-121	-136
-3	-270	-322
-2	-607	-623
-1	378	344
0	319	288
1	346	348
2	193	175
3	-261	-334
4	-445	-416
● 4	1	
-4	-328	-412
-3	-112	-124
-2	486	514
-1	40X	73
0	445	461
1	-274	-270
2	-441	-414
3	-256	-231
● 4	2	
-4	153	214
-3	135	214
-2	229	266
-1	36X	56
0	-391	-413
1	-265	-288
2	-27X	-46
3	180	256
● 4	3	
-4	76	151
-3	103	137
-2	-225	-248
-1	-157	-200
0	-243	-264
1	193	233
● 5	-5	
-3	-139	-205
-2	-243	-254
-1	13X	3
● 5	-4	
-4	-108	-199
-3	-162	-158
-2	229	238
-1	189	206
0	346	364
1	-279	-296
● 5	-3	
-4	-45X	-11
-3	265	280
-2	369	371
-1	31X	29
0	-477	-478
1	-49	-59
2	-216	-201
● 5	-2	
-4	288	340
-3	274	263
-2	-427	-425
-1	-225	-250
0	-211	-207
1	76	69
2	342	333
● 5	-1	
-4	-45X	-3
-3	-409	-451
-2	-157	-139
-1	-108	-124
0	405	395
1	171	191
2	220	207
● 5	0	
-4	-310	-380
-3	-31X	-40
-2	189	197
-1	225	259
0	229	232
1	-45	-41
● 5	1	
-4	81	99
-3	171	210
-2	148	172
-1	171	192
0	-423	-428
1	-117	-197

(s.d.'s), and orthogonal coordinates, calculated by means of the transformations given by Cruickshank (1961). The s.d.'s were estimated by use of the expressions appropriate to the triclinic system (Cruickshank, 1949).

The coordinates of sets (2) and (3) can be compared directly. The agreement is satisfactory and their r.m.s. difference equals 0·008 Å for the lighter atoms. The individual differences are not significant, except for the chlorine atom in the x direction, where the difference is in the 1–5% probability range (Cruickshank & Robertson, 1953).

The final temperature factors of the three sets are shown in Table 5. For comparative purposes the

Table 4. *Final atomic coordinates in fractions of the cell edges*

The root mean square standard deviations (Å), and orthogonal atomic coordinates (Å) from the three sets of data; the hydrogen positions are theoretical (see text)

Atom	Set	y/a	x/b	z/c	σ	X	Y	Z
Cl	1	0·2290	0·2495	0·1545	0·0030 Å	0·7638 Å	1·1447 Å	0·9987 Å
	2	0·22950	0·24900	0·15400	0·0018	0·7634	1·1355	0·9892
	3	0·23085	0·24881	0·15462	0·0013	0·7684	1·1330	0·9932
O	1	0·6630	0·3155	0·5155	0·0070	2·105	1·110	3·332
	2	0·6640	0·3135	0·5140	0·0045	2·106	1·109	3·302
	3	0·6648	0·3133	0·5129	0·0037	2·103	1·109	3·295
C(1)	1	0·5940	0·4440	0·3260	0·0110	2·098	1·821	2·107
	2	0·5940	0·4450	0·3250	0·0064	2·087	1·819	2·088
	3	0·5936	0·4428	0·3267	0·0056	2·082	1·808	2·098
C(2)	1	0·4540	0·3000	0·6400	0·0100	0·992	1·346	4·137
	2	0·4490	0·2970	0·6435	0·0056	0·978	1·357	4·133
	3	0·4467	0·2969	0·6411	0·0055	0·972	1·358	4·118
H(1)	calc.	0·770	0·470	0·254	—	2·96	1·70	1·63
H(2)	calc.	0·238	0·178	0·578	—	0·16	0·95	3·71
H(3)	calc.	0·548	0·227	0·786	—	1·19	0·92	5·05

Table 5. *Temperature factors* (Å^2) *from the three sets of data*

	Set (1)		Set (2)		Set (3)					
Atom	B[100]	B[001]	B[100]	B[001]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	2·11*	3·85	1·06*	1·33	1·99	2·11	1·75	0·57	0·15	−0·50
O	2·93	3·55	1·13	1·06	1·73	2·27	2·26	0·92	0·65	−0·13
C(1)	2·68	3·81	1·15	1·08	1·76	2·49	1·48	0·68	0·21	−0·29
C(2)	2·75	3·52	1·13	1·26	2·16	2·15	2·10	0·65	0·77	−0·20
H(1), (2), (3)	3·00	3·80	1·10	1·10			isotropic $B=1·10$			

* See § 3 for the thermal-anisotropy correction.

anisotropic temperature factors b_{ij}, defined by $\exp-[b_{11}h^2+2b_{12}hk+b_{22}k^2+2b_{13}hl+2b_{23}kl+b_{33}l^2]$ were converted into Å^2 units by means of the relation:

$$B_{ij}=4b_{ij}/(a_i^*a_j^*)\ .$$

Although the photographs of sets (2) and (3) have been taken at approximately the same temperature, the temperature factors obtained from the copper radiation data are larger. Probably a number of strong reflexions near the upper edge of the Cu $K\alpha$ films have been underestimated, whereas on the Mo $K\alpha$ films the weak high-order spots may have been assigned too large a value. Whatever the cause, temperature factors obtained from visually estimated intensities clearly have only qualitative significance. In order to check the directions of the thermal motion, the principal axis parameters of the vibration ellipsoid of the chlorine atom were calculated from the b_{ij} values of set (3) (Busing & Levy, 1958). The directions and magnitudes are:

$$\begin{aligned} U_s &= -0·6208\mathbf{a}+1·2814\mathbf{b}+\mathbf{c}, & B_s &= 0·55\ \text{Å}^2\\ U_m &= 4·9383\mathbf{a}+0·4421\mathbf{b}+\mathbf{c}, & B_m &= 1·88\ \text{Å}^2\\ U_l &= -1·3270\mathbf{a}-1·6741\mathbf{b}+\mathbf{c}, & B_l &= 2·98\ \text{Å}^2 \end{aligned}$$

where **a**, **b** and **c** are basic unit cell vectors defined in Table 1.

The angle between the maximum displacement vector and the carbon–chlorine bond is 108·9°. In the projection along [100] the angle between the direction of maximum vibration and **c** is 46·5°; this figure agrees with that found (48°) in both two-dimensional analyses.

The observed peak electron densities ϱ_0 and the central curvatures A are given in Table 6. These

Table 6. *Observed electron densities and central curvatures from the three sets of measurements*

The sets are indicated by subscripts 1, 2, and 3

	e.Å^{-2}		e.Å^{-3}	e.Å^{-4}		e.Å^{-5}		
Atom	ϱ_1	ϱ_2	ϱ_3	$-A_1$	$-A_2$	$-A_{3hh}$	$-A_{3kk}$	$-A_{3ll}$
Cl	28·0±0·2	46·0±0·3	44·0±0·1	520	930	432	460	446
O	12·2±0·2	19·9±0·3	16·4±0·1	180	367	161	154	152
C(1)	8·8±0·2	14·6±0·3	11·2±0·1	116	252	109	99	104
C(2)	10·2±0·2	15·4±0·3	11·4±0·1	138	307	113	103	102
H	0·6±0·2	1·1±0·3	1·4±0·1					

values generally agree with those expected on theoretical grounds (Atoji, 1957). It is well known that, because of series termination effects, lowering of the temperature has a smaller influence on the central curvatures obtained from Cu *Kα* data than on the curvatures from Mo *Kα* data. Our work illustrates that, in some favourable cases at least, the standard errors of a two-dimensional analysis with molybdenum radiation at low temperature are comparable to those of a three-dimensional refinement with Cu *Kα* data at the same temperature.

6. Results and discussion

(*a*) *Geometry of the molecule*

The ring in *trans*-2,5-dichloro-1,4-dioxane has the normal chair form and the chlorine atoms occupy axial positions (*aa*). From infrared and Raman spectroscopic data the conclusion was drawn that the same conformation predominates in solution, regardless of the solvent (Altona, Romers & Havinga, 1959; Altona, 1963). In fact, no indications were found for the existence of other conformations, such as the diequatorial one (*ee*). This behaviour is in contrast to that of *trans*-1,4-dichlorocyclohexane, a compound which occurs in solution as an equilibrium mixture containing both the (*ee*) and the (*aa*) chair forms (Kozima, Sakashita & Maeda, 1954), while in the solid state only the (*ee*) conformation has been found (Hassel & Vihovde, 1953). As a rule, the halogen atoms in dihalogeno-dioxanes occupy axial positions; the (*aa*) forms were also found in *trans*-2,3-dichlorodioxane and in *trans*-2,3-dibromodioxane, for which X-ray structure determinations have recently been accomplished (Altona & Romers, 1963; Altona, Knobler & Romers, 1963).

Table 7. *Bond distances and bond angles in trans-2,5-dichlorodioxane as determined from three independent sets of measurements*

Atoms	Set (1)	Set (2)	Set (3)
		Distances (Å)	
C(1)–Cl	1·862 ± 0·011	1·852 ± 0·007	1·845 ± 0·006
C(1)–O	1·417 ± 0·013	1·407 ± 0·008	1·388 ± 0·007
C(2)–O	1·393 ± 0·013	1·423 ± 0·008	1·428 ± 0·007
C(1)–C(2′)	1·521 ± 0·015	1·504 ± 0·009	1·513 ± 0·008
		Angles (°)	
C(2′)–C(1)–Cl	108·4 ± 0·8	109·2 ± 0·5	109·6 ± 0·4
O–C(1)–Cl	109·5 ± 0·8	109·6 ± 0·5	110·2 ± 0·4
C(1)–O–C(2)	114·2 ± 0·8	113·9 ± 0·6	113·1 ± 0·5
O–C(1)–C(2′)	111·4 ± 0·9	112·4 ± 0·6	112·4 ± 0·5
O–C(2)–C(1′)	112·8 ± 0·9	111·9 ± 0·6	111·7 ± 0·5

The bond distances and angles, calculated from the parameters in Table 4, are given in Table 7, together with the estimated standard deviations (Cruickshank & Robertson, 1953; Darlow, 1960) in which allowance has been made for the errors in the unit-cell dimensions. No corrections for the effect of molecular librations were applied, mainly because of the uncertainty in the magnitudes of the vibration parameters.

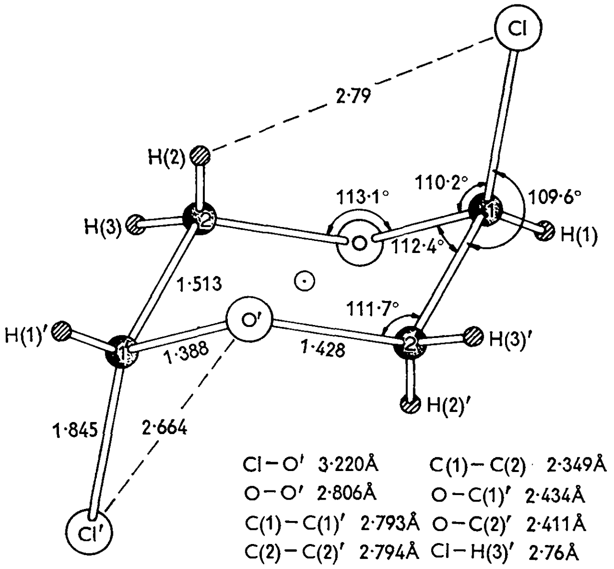


Fig. 2. Schematic drawing of the molecule of *trans*-2,5-dichloro-1,4-dioxane showing some intramolecular distances and angles.

Agreement among the three independent analyses is again gratifying; none of the differences in bond distances between each set is found to be significant. In the following discussion the distances and angles from set (3), also shown in Fig. 2, will be used, as these are considered to be the most reliable values.

The valency angles are normal: those in the ring are 2–3° larger than the tetrahedral values, in accordance with many data on aliphatic ring and open chain compounds; those about the C–Cl bond do not differ significantly from 109·5°. Interesting bond distances are found in this molecule. The C–O bonds are not equivalent: C(1)–O (1·388 Å) is 0·040 Å shorter than C(2)–O (1·428 Å). The latter bond distance does not deviate significantly from the C–O distance found in dimethyl ether (1·416 Å, Kimura & Kubo, 1959; 1·417 Å, Kasai & Myers, 1959), but C(1)–O is appreciably shorter. The C–C bond distance is comparable to that reported for ethyl chloride (1·520 ± 0·003 Å; Schwendeman & Jacobs, 1962); both are perhaps shorter than the C–C distance in normal paraffins (1·533 Å; Bartell, 1959).

The C–Cl bond length is surprisingly large (1·845 ± 0·006 Å). An average C–Cl bond distance of 1·767 Å is given by Sutton (1958). However, this figure includes distances in many compounds that contain two or three chlorine atoms attached to the same carbon atom. Few accurate C–Cl bond distances have been reported for saturated aliphatic compounds of the types –CHCl– and –CH_2Cl. The available results

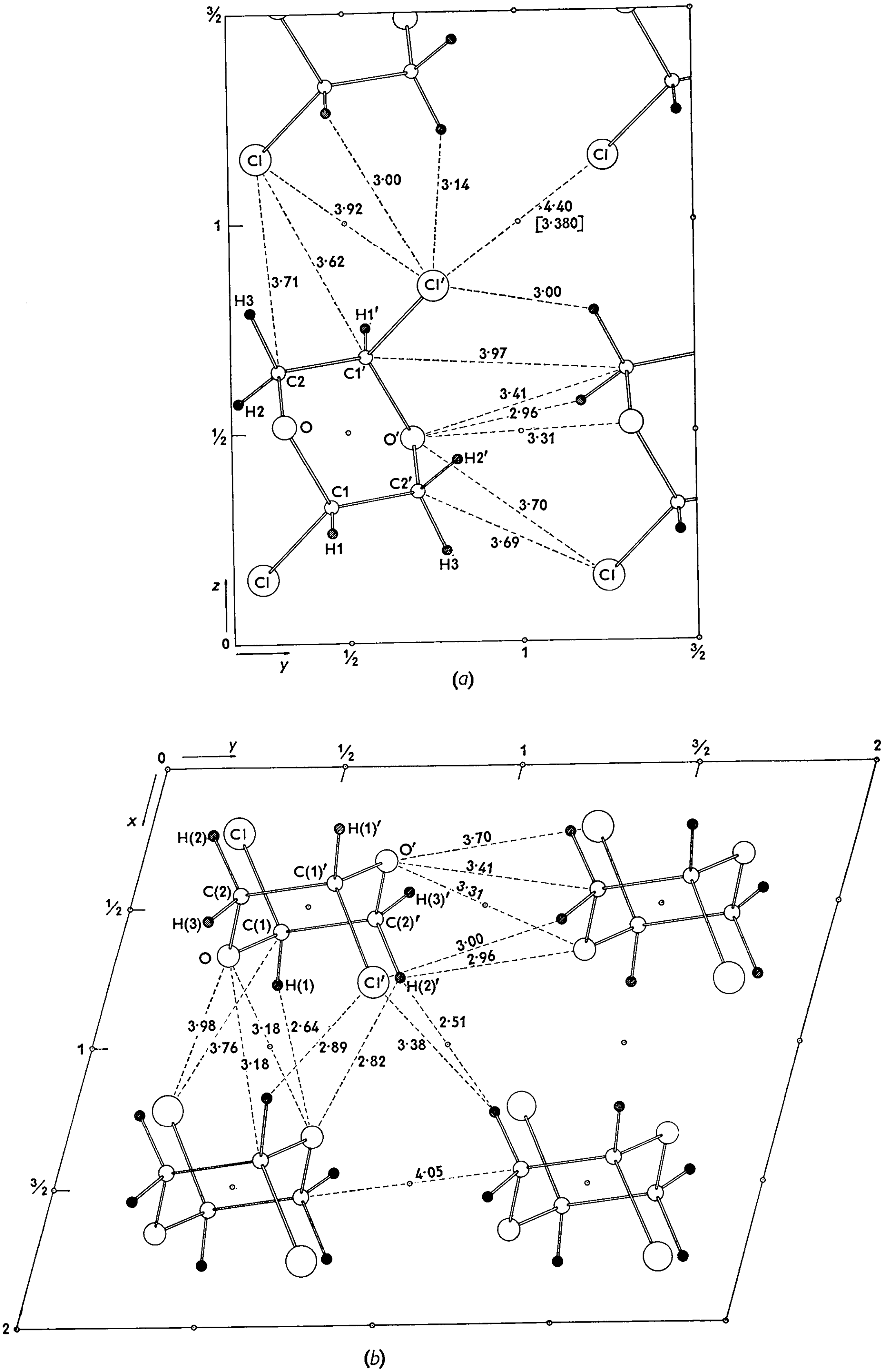
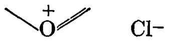


Fig. 3. (*a*) Orthographic projection along [100] of a layer of unit cells. Some intermolecular distances are shown. Distance between brackets refers to molecule at $x+1$, $y+1$, $z+1$. (*b*) The same along [001].

seem to indicate that the 'normal' aliphatic C–Cl bond has a length of about 1·78–1·79 Å. Examples are: methyl chloride (1·784 Å; Bartell & Brockway, 1955; 1·7815 Å, Miller, Aamodt, Dousmanis, Townes & Kraitchman, 1952) and ethyl chloride (1·788 Å; Schwendeman & Jacobs, 1962). Some examples of longer C–Cl bonds are also known, *e.g.* in 1-chloro-2-butyne (1·798 Å; Laurie & Lide, 1959) in allyl chloride (1·82 Å; Bowen, Gilchrist & Sutton, 1955), and in acetyl chloride (1·82 Å; Allen & Sutton, 1951). A C–Cl bond distance of 1·87 Å has been reported for chloromethyl methyl ether (Akishin, Vilkov & Sokolova, 1960), but a recent redetermination (Planje, Toneman & Dallinga, 1963) gave the value of 1·81 Å. We also found long C–Cl bonds in *trans*-2,3-dichlorodioxane (mean value of two chemically equivalent bonds 1·835 Å) and in *cis*-2,3-dichlorodioxane where the axial C–Cl bond has a length of 1·819 ± 0·008 Å.

Allen & Sutton (1951) observe in their discussion of the structure of the acetyl halides that all long bonds involving halogen atoms are unusually reactive in hydrolysis and dissociate easily. The halogen atoms in monochlorodioxane and in dichloro- and dibromodioxane, like those in open chain α-halo-ethers, are indeed highly reactive in hydrolysis reactions. Furthermore, the above authors conclude from dipole moment data that the increase in bond length is not correlated with a change in ionic character in the bonds. This conclusion is supported by the value of the dipole moment of monochlorodioxane, which indicates that a description in terms of contributions of mesomeric structures such as



does not seem adequate to account quantitatively for the considerable changes in the bond distances.

A satisfactory explanation for the phenomena cannot be given in the present state of our knowledge, but some points are worth noting. First, there are indications that the presence of lone electron pairs on an atom C in a compound A–B–C lengthens the bond A–B, particularly if the ion A^- is a weak base (*cf.* Bent, 1962). Secondly, the equatorial C–Cl bond in *cis*-2,3-dichlorodioxane is 'normal' in length (1·782 ± 0·008 Å). Therefore, the spatial arrangement of atoms and lone pairs may well be important. It is not known with certainty which orbitals are used by the lone pair electrons of an ether oxygen atom, but according to the available evidence (Dickens & Linnett, 1957; Gillespie & Nyholm, 1957) two lone pairs are probably equivalent. Each oxygen atom of the dioxane ring then carries one equatorial and one axial lone pair; the axial lone pair and the oxygen, carbon and the axial, but not the equatorial chlorine atoms will have a planar configuration. It is known that planar configurations of atoms play an important role in the stereochemistry of elimination reactions. It now appears that coplanarity involving a lone pair at the one end of the system and a chlorine atom at the other end may produce changes in the bond distances between the atoms in the plane. A more extensive discussion of these problems will be given elsewhere (Altona, 1963).

(*b*) *Molecular environment*

All intermolecular distances up to 4·4 Å have been calculated. Some of these are shown in Fig. 3. A fairly short Cl ··· Cl distance of 3·38 Å is found between two chlorine atoms in approximately 'head-on' positions: Cl(X, Y, Z) and Cl′($X-1, Y-1, Z-1$). The angle C(1)–Cl ··· Cl′ is 157·1°. Examples of comparable Cl ··· Cl separations are given by Fischmann, MacGillavry & Romers (1961) and by Hermodsson (1960). The chlorine atoms are coordinated by six hydrogen atoms, two belonging to the 'original' molecule (H2 and H3, Fig. 3) and four others at distances varying between 2·89 Å and 3·14 Å. The shortest distances among the remaining atoms are: H ··· H = 2·51 Å; O ··· O = 3·18 Å; H ··· O = 2·64 Å; C ··· O = 3·18 Å; Cl ··· C = 3·62 Å. The packing is seen to be relatively dense.

The intra- and intermolecular atomic distances and angles were calculated on the X1 computer by means of an exhaustive program, written in ALGOL 60 by Mr H. L. Jonkers with the collaboration of Dr A. Ollongren and one of us (C. A.) (Program A 200, Centraal Reken-Instituut, The University, Leiden).

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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 °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

$a=4\cdot463,\ b=10\cdot67,\ c=13\cdot13$ Å at −140 °C.

The structure was refined in three projections by means of data obtained at about −140 °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) $=1\cdot819\pm0\cdot009$ Å, C(2)–Cl(2) (equatorial) $=1\cdot781\pm0\cdot007$ 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 ($\lambda=1\cdot5418$ Å) about [100],

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