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The Conformation of Non-Aromatic Ring Compounds.* XXXIV. The Crystal Structure of *trans*-2,3-Dichloro-1,4-thioxane at -185°C

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Crystals of *trans*-2,3-dichloro-1,4-thioxane are orthorhombic. The space group is $P2_12_12_1$, $a=14\cdot808$, $b=7\cdot120$, $c=6\cdot318$ Å at -185°C and $Z=4$. The structure has been solved by the heavy-atom technique and refined by use of eye-estimated Mo data (1813 observed reflexions) collected at -185°C , the final R value being 8.5%. The molecule has a chair conformation with the chlorine atoms in axial positions. Its overall geometry is halfway between the conformations of the corresponding *trans*-2,3-dichloro derivatives of 1,4-dioxane and 1,4-dithiane. A comparison is made with the corresponding halogeno-substituted dioxane, dithiane and 5- α -cholestane compounds.

Introduction

The conformational analysis of 1,4-thioxane and its halogeno-substituted derivatives forms a continuation of earlier investigations of the molecular shape of dioxane and dithiane compounds (*cf.* Table 5 for references). To our knowledge the conformations of 1,4-thioxane and its halogeno derivatives have not yet been determined. From a study of electric dipole moments and nuclear magnetic resonance spectra of 1,4-thioxane and of *trans*-2,3-dichloro-1,4-thioxane (hereafter TDT) it is concluded (de Wolf, Henniger & Havinga, 1967) that these molecules are chair-shaped and that the chlorine atoms occupy axial positions. X-ray analysis of TDT corroborates these conclusions. The crystal structure of 1,4-thioxane will be dealt with in a separate paper.

Experimental

TDT is prepared by addition of chlorine to a solution of thioxene in carbon tetrachloride (Haubein, 1959). The crystals are brittle, colourless, irregular blocks which decompose in moist air. Two specimens, I and II, of cross-section $0\cdot028 \times 0\cdot042$ cm² and $0\cdot02 \times 0\cdot02$ cm² were sealed in Lindemann-glass capillaries and

mounted on goniometer heads about the directions [001] and [010], respectively.

Glancing angles θ corresponding to spacings $d(hk0)$ and $d(h0l)$ were measured on zero layer Weissenberg photographs taken with copper radiation ($\lambda=1\cdot5418$ Å) about [001] and [010] with crystals I and II, respectively. Aluminum powder lines ($a=4\cdot0489$ Å at 20°C) were superposed on the films for calibration purposes. The unit-cell dimensions (Table 1) derived from these measurements were refined by a least-squares procedure and the stated errors are three times the calculated standard deviations in the cell edges. Absent reflexions $h00$ for $h=\text{odd}$, $0k0$ for $k=\text{odd}$ and $00l$ for $l=\text{odd}$ determine the space group $P2_12_12_1$. The measured density (floatation method) indicates that the unit cell contains four molecules.

Intensity measurements (eye-estimation with a calibrated intensity strip) were recorded on equi-inclination Weissenberg photographs of the layers $hk0$

Table 1. *Crystal data of TDT*

trans-2,3-Dichloro-1,4-thioxane, $\text{C}_4\text{H}_6\text{OSCl}_2$.
Melting point $37\text{--}38^{\circ}\text{C}$.
Orthorhombic, $P2_12_12_1$;
 $a=14\cdot808 \pm 0\cdot012$, $b=7\cdot120 \pm 0\cdot012$, $c=6\cdot318 \pm 0\cdot015$ Å
at -185°C ;
 $d_{\text{exp}}^{20} = 1\cdot64$, $d_x^{-185} = 1\cdot73$ g.cm⁻³, $Z=4$;
 $F(000)=352$; $V=666\cdot1$ Å³;
 $\mu(\text{Cu } K\alpha) = 107$ cm⁻¹, $\mu(\text{Mo } K\alpha) = 11\cdot6$ cm⁻¹.

* Part XXXIII, C. Altona, H. R. Buys, H. J. Hageman & E. Havinga, to be published.

through $hk10$ and the layers $h0l$ through $h4l$. The camera was loaded with three films interleaved with thin copper foils and the exposures (~ 24 h) were made with zirconium-filtered molybdenum radiation ($\lambda = 0.7107 \text{ \AA}$). All diffraction photographs were made at -185°C according to a technique described earlier (Altona, 1964a).

The total number of observed and symmetry-independent reflexions is 1813. They were reduced in the usual way to structure factor moduli after multiplication by Lorentz, polarization and spot-shape factors. Absorption correction was neglected. Structure factors of the first eight reciprocal layers $hk0$ through $hk7$ and all recorded layers $h0l$ through $h4l$ were put on a common relative scale by the least-squares correlation procedure of Rollett & Sparks (1960). The agreement index R_m between the two sets I and II of scaled structure factors is

$$R_m = 200 \Sigma (F_I - F_{II}) / \Sigma (F_I + F_{II}) = 10\% .$$

The reciprocal layers $hk8$, $hk9$ and $hk10$ were scaled during the final stages of refinement and added to the bulk reflexions (see below).

Refinement

The positions of the heavy atoms Cl(1), Cl(2) and S (cf. Fig. 1 for the numbering of atoms) were derived from three-dimensional Patterson functions and resulted in calculated structure factors with an R value of 27.7%. The remaining atoms C(1), C(2), C(3), C(4) and O were located in a Fourier synthesis. The model obtained ($R = 17.3\%$) was refined straightforwardly by

the method of least squares as described by Geise, Romers & Rutten (1966). The scattering curves were taken from *International Tables for X-ray Crystallography* (1962).

During the first three iterations one overall scale factor, isotropic temperature factors (B 's) and positional parameters for all atoms except hydrogen were refined.

At this stage ($R = 12.2\%$) a difference Fourier synthesis clearly showed the positions of all hydrogen atoms and indicated anisotropic motions of the heavier atoms. A careful check was made for false indexing and other errors in the original list of structure factors. The hydrogen atoms were now introduced at calculated positions, their isotropic B 's being set equal to the B 's of the carbon atoms to which they are attached. Their positional and temperature parameters were not refined. After three cycles of anisotropic refinement ($R = 8.51\%$) structure factors were calculated for the levels $hk8$, $hk9$ and $hk10$ which so far had not been included in the refinement. These levels were scaled and now added to the remaining reflexion data. After two more cycles ($R = 8.47\%$)* the refinement was stopped, since the largest shift in U_{11} , U_{22} and U_{33} was one fourth and the largest shift in positional parameters was one tenth of the corresponding standard deviations. The thermal parameters U_{11} , U_{12} etc. are defined by the temperature factor

$$\exp [-2\pi^2(h^2a^*{}^2U_{11} + k^2b^*{}^2U_{22} + l^2c^*{}^2U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})] .$$

* A list of structure factors is available upon request.

Table 2. Positional parameters of cycle 8 (in fractions of cell edges), their standard deviations (\AA) and isotropic B 's of cycle 3

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Cl(1)	0.5582	0.0011	-0.1069	0.0014	0.0401	0.0017	0.74
Cl(2)	0.3045	0.0012	-0.4002	0.0013	-0.0358	0.0019	0.87
S	0.3900	0.0014	-0.1251	0.0015	-0.3305	0.0016	0.72
O	0.3898	0.0043	-0.0273	0.0039	0.1571	0.0048	0.72
C(1)	0.4405	0.0051	-0.1782	0.0053	0.0896	0.0059	0.48
C(2)	0.4072	0.0049	-0.2782	0.0055	-0.1085	0.0063	0.61
C(3)	0.3243	0.0051	0.0522	0.0055	-0.1913	0.0068	0.84
C(4)	0.3729	0.0053	0.1213	0.0053	0.0059	0.0065	0.82
H(1)	0.441		-0.280		0.219		0.70
H(2)	0.458		-0.381		-0.156		0.70
H(3)	0.259		-0.006		-0.140		0.70
H(4)	0.310		0.170		-0.293		0.70
H(5)	0.334		0.232		0.080		0.70
H(6)	0.436		0.184		-0.044		0.70

Table 3. Vibrational parameters (10^{-4} \AA^2) and their standard deviations (in brackets, 10^{-4} \AA^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl(1)	82 (3)	98 (4)	202 (5)	4 (7)	-3 (11)	-60 (8)
Cl(2)	105 (4)	77 (4)	265 (6)	-40 (7)	24 (11)	34 (9)
S	115 (4)	132 (5)	114 (5)	3 (8)	27 (10)	-7 (9)
O	114 (13)	76 (12)	152 (17)	50 (23)	-10 (29)	5 (31)
C(1)	89 (15)	83 (16)	119 (20)	29 (28)	23 (33)	-9 (30)
C(2)	79 (15)	89 (17)	146 (21)	8 (26)	25 (35)	-1 (31)
C(3)	79 (15)	112 (18)	204 (26)	56 (27)	74 (39)	-4 (36)
C(4)	141 (17)	70 (16)	209 (26)	78 (28)	66 (38)	13 (34)

The positional parameters and their standard deviations of the final cycle and the isotropic B 's of the third cycle are listed in Table 2. The anisotropic vibrational parameters are to be found in Table 3.

Discussion of the structure

The molecule of TDT has in the solid state a chair conformation with the chlorine atoms in axial positions. A schematic drawing of the molecule is given in Fig. 1. Fig. 1(a) shows the interatomic bond distances and Fig. 1(b) the valency and torsional angles about the endocyclic bonds. The use of torsional (dihedral) angles is indispensable for the characterization of conformations and, therefore, these angles will be discussed throughout in this article.

The bond lengths l_{ij} and their standard deviations $\sigma(l_{ij})$ are also given in Table 4. They are not corrected for vibrational effects. In view of the small vibrational parameters (see Table 3) corrections of at most 0.003 Å should be added to the given numbers. The standard deviations in valency angles are about 0.7° and those in torsional angles about 1.5°. We realize that the given

Table 4. Bond lengths l_{ij} (Å) of *trans*-2,3-dichloro-1,4-thioxane at -185°C, their standard deviations $\sigma(l_{ij})$, some differences Δ and corresponding standard deviations $\sigma(\Delta)$

	l_{ij}	$\sigma(l_{ij})$	Δ	$\sigma(\Delta)$
C(1)-Cl(1)	1.842	0.0053	0.032	0.0075
C(2)-Cl(2)	1.810	0.0053		
C(2)-S	1.795	0.0063	0.025	0.0086
C(3)-S	1.820	0.0059		
C(1)-O	1.378	0.0067	0.069	0.0099
C(4)-O	1.447	0.0073		
C(1)-C(2)	1.522	0.0092		
C(3)-C(4)	1.521	0.0088		

standard deviations computed from diagonal elements in the inverse matrix of normal equations reflect underestimations of all errors and that the 'true' standard deviations are, perhaps, 30% or more higher.

In spite of these restrictions we conclude (see Table 4) that the differences between the bonds C(1)-Cl(1) and C(2)-Cl(2) and between C(1)-O and C(4)-O are significant and that the difference between C(2)-S and C(3)-S lies in the range of possible significance. The same peculiarity in bond lengths (Table 5) is shown by the corresponding derivatives of 1,4-dioxane and 1,4-dithiane and by chloromethyl methyl ether. A remarkable aspect of nearly all these compounds is the preference of the halogen atoms for axial positions. Compared with paraffinic C-Cl and C-Br bond distances (1.79 and 1.93 Å) the carbon-halogen distances are too long in all these molecules. The observed trend seems to be weaker for sulphur than for oxygen compounds. The C-X-C-Y arrangement of all these molecules has the *gauche* conformation with a dihedral angle about the central bond X-C in the range of 70-75°. A full account and possible explanation of these phenomena, also occurring in C-O-C-O, C-O-C-N and C-O-C-S systems of α - and β -D-pyranosides, nucleosides and nucleotides, will be given elsewhere (Altona & Sundaralingam, 1967).

A second feature of TDT, also present in axially 2,3-dihalogeno-substituted derivatives of 1,4-dioxane and 1,4-dithiane and 5 α -cholestane, are the small valency angles C-C-Y (Table 6) in the so-called anti-group (Altona & Romers, 1967). Moreover, this anti-group is not planar. Its dihedral angle φ about the central C-C bond has the value 165.3° implying that the vectors C(1)-Cl(1) and C(2)-Cl(2) are not anti-parallel but make an angle α of 165.9°, nearly equal to the value of φ . Consequently cyclic compounds with axially 2,3-

Table 5. Bond distances (Å) and torsional angles φ about X-C in the group C-X-C-Y

Average values are indicated by an asterisk.

Compound	Reference†	X	Y	C(4)-X	X-C(1)	C(1)-Y	φ
<i>trans</i> -2,3-Dibromodioxane	(1)	O	Br	1.47*	1.37*	2.02*	71.0*
<i>trans</i> -2,3-Dichlorodioxane	(2)	O	Cl	1.428*	1.382*	1.838*	70*
<i>cis</i> -2,3-Dichlorodioxane	(1)	O	Cl	1.466	1.394	1.819	71
<i>trans</i> -2,5-Dichlorodioxane	(2)	O	Cl	1.428	1.388	1.845	70
Chloromethyl methyl ether	(3)	O	Cl	1.414	1.368	1.813	74
<i>trans</i> -2,3-Dichlorothioxane		O	Cl	1.447	1.378	1.842	68
<i>trans</i> -2,3-Dichlorothioxane		S	Cl	1.820	1.795	1.810	72
<i>trans</i> -2,3-Dichlorodithiane	(4)	S	Cl	1.84*	1.79*	1.815*	
<i>trans</i> -2,5-Dibromodithiane	(4)	S	Br	1.81	1.81	1.99	

† (1) Altona, Knobler & Romers (1963a,b); (2) Altona & Romers (1963a,b); (3) Planje, Toneman & Dallinga (1965); (4) Kalf & Romers (1965, 1966).

Table 6. Valency angle C-C-Y (average values), torsional angle φ , vector angle α and electric dipole moment μ (Debye units) in the system Y-C-C-Y

Compound	Reference*	C-C-Y	φ	α	μ
<i>trans</i> -2,3-Dibromodioxane	(1)	106°	161.6°	162.2°	1.88
<i>trans</i> -2,3-Dichlorodioxane	(4)	106	162.3	163.0	1.62
<i>trans</i> -2,3-Dichlorothioxane		106.9	165.3	165.0	1.64
<i>trans</i> -2,3-Dichlorodithiane	(4)	107.4	166.7	167.3	1.63
<i>trans</i> -2,3-Dichlorocholestane	(5)	106	156	157	1.26

* (1), (4): see footnote to table 5. (5) Geise, Romers & Rutten (1966).

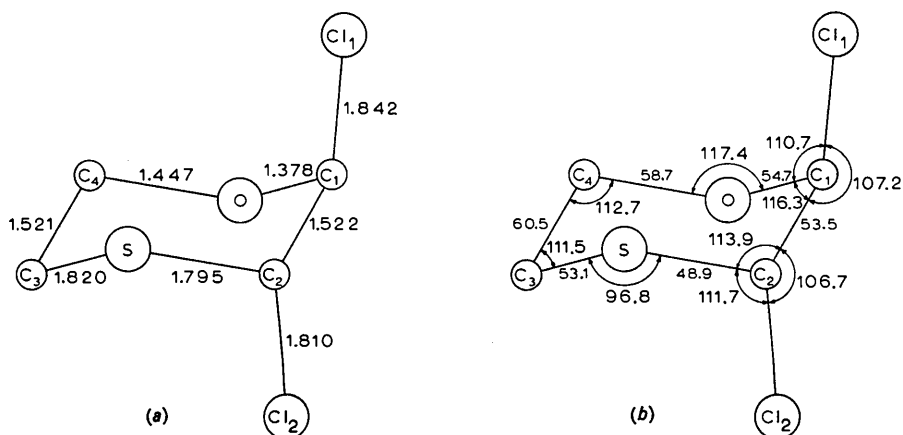


Fig. 1. Schematic drawing of the molecule of *trans*-2,3-dichloro-1,4-thioxane. (a) Interatomic distances. (b) Valency and torsional angles.

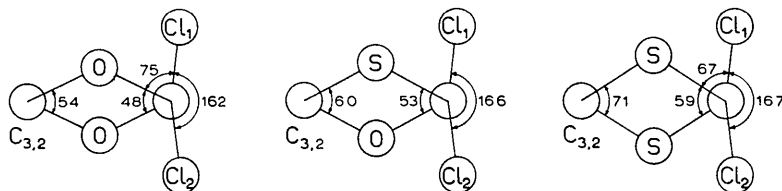


Fig. 2. Newman projections along the bonds C(2)-C(1) and C(3)-C(4) of the molecules of (left to right) *trans*-2,3-dichloro-1,4-dioxane, *trans*-2,3-dichloro-1,4 thioxane and *trans*-2,3-dichloro-1,4-dithiane.

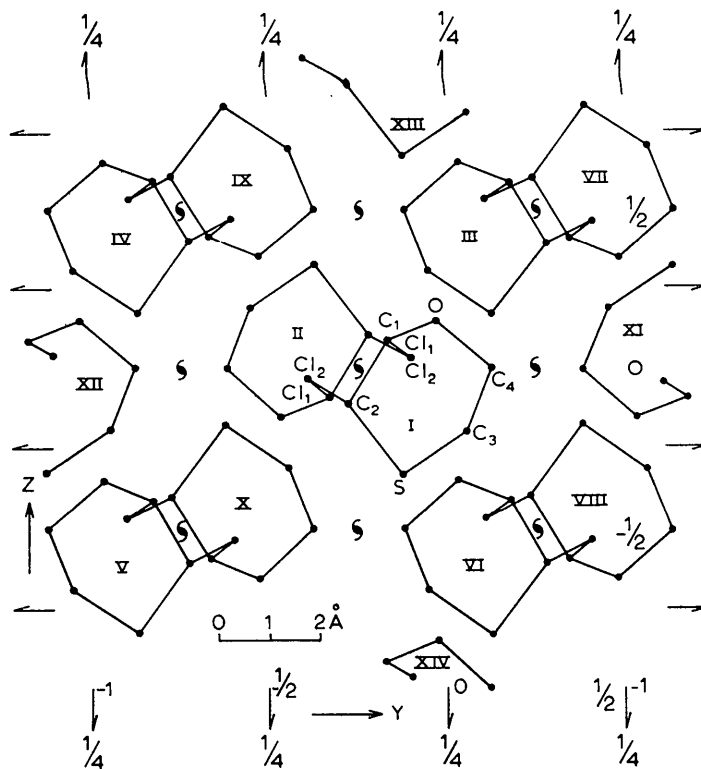


Fig. 3. Projection of the structure along [100]. The Roman numerals are explained in the text.

disubstituted halogen atoms (Table 6) have an appreciable electric dipole moment. The disagreement between the calculated (~ 0.8 D) and the observed (1.2–1.9 D) moment appears to be due to large inductive moments in the ring (Wessels, 1961; Altona, 1964*b*; Geise, Tieleman & Havinga, 1966).

In Fig. 2 are reproduced the Newman projections of *trans*-2,3-dichloro-1,4-dioxane, *trans*-2,3-dichloro-1,4-thioxane and *trans*-2,3-dichloro-1,4-dithiane. The picture shows clearly that the conformation of TDT is intermediate between those of the corresponding dioxane and dithiane compounds and that the puckering of all three molecules is least at the carbon atoms with exocyclic chlorine atoms.

It is interesting to note that the valency angle C(2)–S–C(3) of TDT (97.0°) is smaller than the corresponding C–S–C angles of *trans*-2,3-dichloro-1,4-dithiane (mean value 100.6°). On the other hand, the valency angle C(1)–O–C(4) (117.6°) is significantly larger than the corresponding angles in *trans*-2,3-dichloro-1,4-dioxane (mean value 112.5°). This effect can be understood when the normal intramolecular C(1)···C(4) and C(2)···C(3) distances in the respective C–O–C (2.35 Å) and C–S–C (2.80 Å) moieties of the molecule are compared with the actually observed values. We note that C(2)···C(3) (2.71 Å) is smaller and that C(1)···C(4) (2.43 Å) is larger. Evidently the misfit of the two halves of the molecule is neutralized by an adaptation of the valency angles.

Fig. 3 is a projection of the crystal structure along [100]. Within an upper limit of 4.3 Å the reference molecule I at x, y, z is surrounded by 14 neighbours at

$$\begin{aligned} & \pm \frac{1}{2} + x, -\frac{1}{2} - y, -z \text{ (II);} \\ & \frac{1}{2} - x, -y, \pm \frac{1}{2} + z \text{ (III, VI);} \\ & \frac{1}{2} - x, -1 - y, \pm \frac{1}{2} + z \text{ (IV, V);} \\ & 1 - x, \frac{1}{2} + y, \pm \frac{1}{2} - z \text{ (VII, VIII);} \\ & 1 - x, -\frac{1}{2} + y, \pm \frac{1}{2} - z \text{ (IX, X);} \\ & x, \pm 1 + y, z \text{ (XI, XII);} \\ & \text{and } x, y, \pm 1 + z \text{ (XIII, XIV).} \end{aligned}$$

The shortest contacts (I···XIII and I···XIV, distance 3.31 Å) are between sulphur and oxygen atoms. Fig. 3 shows that the chlorine atoms nearly coincide in this projection. They provide for the sole contacts (3.65 Å) in the direction parallel to [100].

Notwithstanding the absence of very short intermolecular distances the molecules are tightly packed. The dense packing explains why the crystals are brittle and why it was very difficult to cut a crystal suitable for *b*-axis exposures.

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