by copper. This arrangement of Cu and Zn ions in the structure is in agreement with the results of chemical analysis (Cu:Zn atomic ratio of 1·9) and serpierite can be regarded as a mineral of calcium, copper and zinc having the formula:

$$Ca_2Cu_5Zn(Zn_{0 \cdot 88}Cu_{0 \cdot 12})_2(OH)_{12}(SO_4)_4 . 6H_2O$$

The chief difference between devillite and serpierite is in the reciprocal stacking of copper–oxygen layers; in devillite two adjacent layers are shifted by $\frac{1}{4}b$ with respect to the array they have in serpierite: this fact causes a rearrangement of the calcium–oxygen polyhedra and SO_4^{2-} groups, which form the layers interposed between the copper–oxygen sheets. In Fig. 4 S and Ca layers in the two minerals are schematically shown. It is interesting to note that, notwithstanding the rearrangement of the atoms, the configuration of each Ca ion in devillite, and the role played in the structure, are the same as in serpierite.

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The Crystal and Molecular Structure of *cis*-4-t-Butylcyclohexane-1-carboxylic Acid

By H. van Koningsveld

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, *Delft, The Netherlands*

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The structure of *cis*-4-t-butylcyclohexane-1-carboxylic acid, $C_{11}O_2H_{20}$, has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$. The unit cell, of dimensions $a = 17·132$, $b = 6·271$, $c = 10·380$ Å and $\beta = 92·17°$, contains four molecules. The structure has been solved using a symbolic phasing procedure and Fourier synthesis. Refinement by the least-squares (block-diagonal approximation) method converged to a final R index of 5·7% for 1542 independent non-zero reflexions. The structure consists of infinite zigzag chains of molecules along the a axis. In each chain the antipodes form centric dimers through approximately linear hydrogen bonds of 2·640 Å. The axial carboxyl group is nearly coplanar with an α,β-bond in the ring (torsion angle $= 6·4°$), the carbonyl oxygen being eclipsed with the C^{β} atom. The equatorial t-butyl group is twisted away by about 8° from the prefectly staggered form and a puckering of the t-butyl side of the ring is observed; the mean C–C–C bond angle, mean C–C bond distance and mean torsion angle in the ring are 111·5°, 1·529 Å and 54·8° respectively.

Introduction

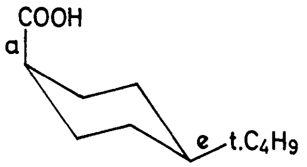
X-ray studies on carboxylic acids (Groth & Hassel, 1965; Dunitz & Strickler, 1966; Kanters, Kroon, Peerdeman & Schoone, 1967), pK_a-measurements on cyclohexanecarboxylic acids (Sicher, Tichý & Šipoš, 1966; van Bekkum, Verkade & Wepster, 1971), empirical valence force-field calculations (Altona & Sundaralingam, 1970) and nuclear magnetic resonance spectroscopic studies on t-butylcyclohexane (Remijnse, van Bekkum & Wepster, 1971) show some interesting features:

1. The carbonyl oxygen atom (in an axial carboxyl group if cyclohexanecarboxylic acids are considered) is always in an (almost) eclipsed position with the α-substituent or β-carbon atom; however, a few exceptions have been found (Bootsma & Schoone, 1967; Kadoya, Hanazaki & Iitaka, 1965);

2. The generally accepted perfectly staggered conformation of t-butylcyclohexane is not confirmed by valence force calculations: the t-butyl group should be twisted away by ±17°;

3. The calculated bond angles, bond distances and torsion angles in the cyclohexane ring have anomalous values at the t-butyl side of the ring.

The aim of this investigation was to verify these aspects by determining the molecular structure of *cis*-4-t-butylcyclohexane-1-carboxylic acid (CIS):



Experimental

A sample of the compound, $C_{11}O_2H_{20}$, was kindly provided by Professor H. van Bekkum of this laboratory.

Monoclinic crystals of CIS were obtained by recrystallization from petroleum spirit (80–100°) at 5 °C. The unit-cell dimensions, deduced from measurements on a Nonius automatic single-crystal diffractometer (Cu $K\alpha_1 = 1{\cdot}54051$ Å), are $a = 17{\cdot}132$ (4), $b = 6{\cdot}271$ (2), $c = 10{\cdot}380$ (3) Å and $\beta = 92{\cdot}17$ (2)°. The axes have been chosen in such a way that the systematic extinctions (0*k*0 for *k* odd and *h*0*l* for *h*+*l* odd)

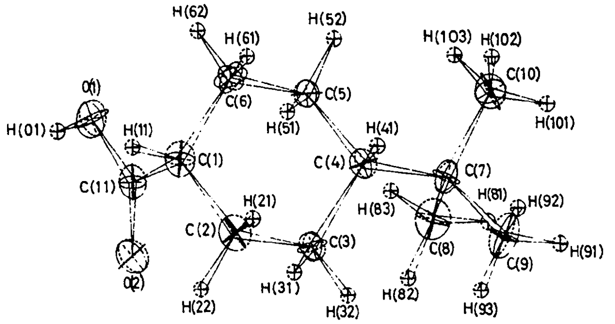


Fig. 1. Molecular conformation observed in the crystal structure of CIS, showing atomic numbering and thermal ellipsoids.

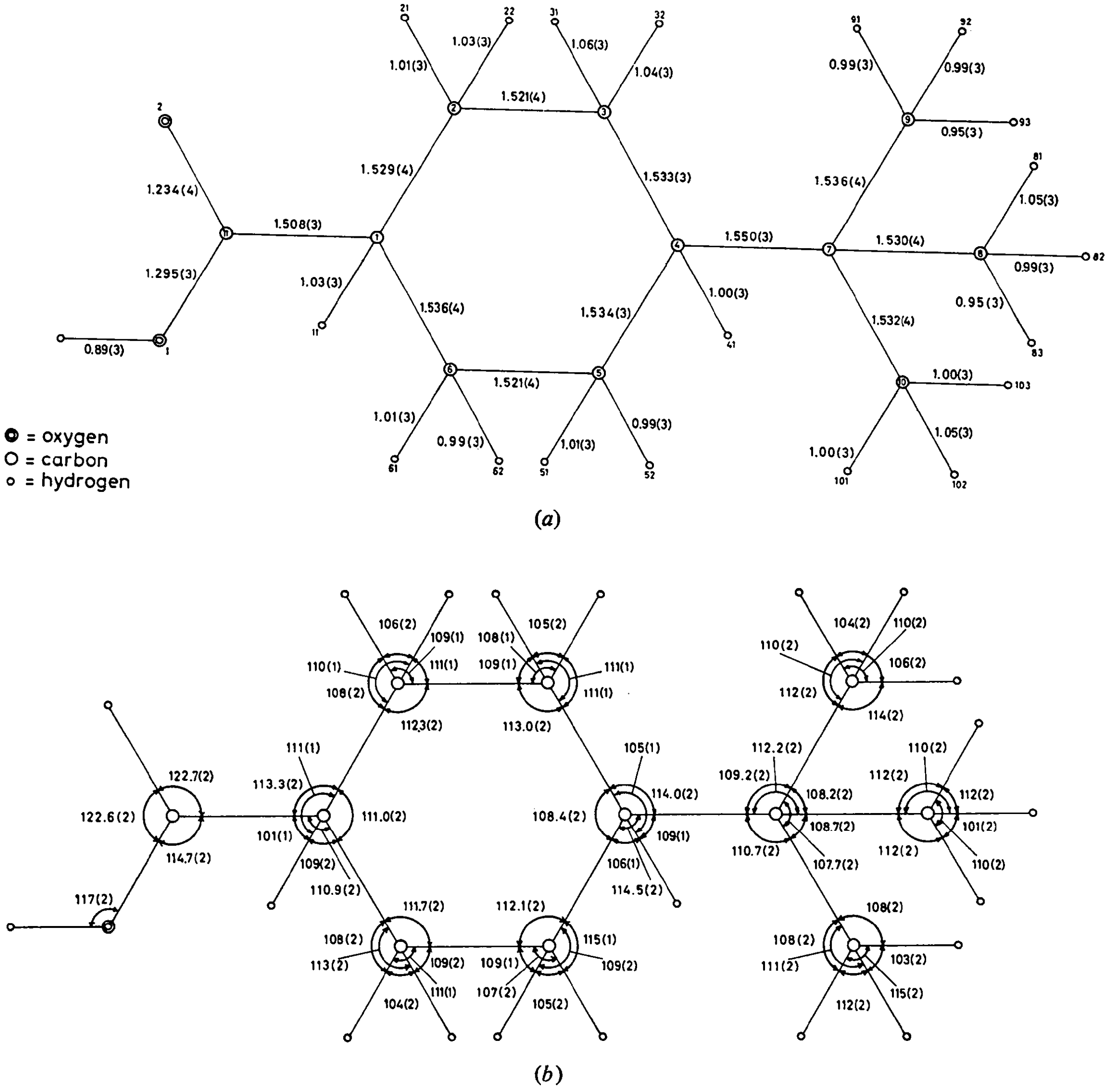


Fig. 2. (*a*) Bond lengths and (*b*) bond angles in CIS with e.s.d.'s in brackets.

are consistent with the space group $P2_1/c$. With four molecules per unit cell, $D_c = 1{\cdot}091$ g.cm^{-3} compared with the density determined by flotation, $D_m = 1{\cdot}08$ g.cm^{-3}. The crystals are elongated along the shorter crystallographic axis and could be easily cleaved along (100).

Three-dimensional intensity data were collected with the Nonius diffractometer using Cu $K\alpha$ radiation and the $\theta/2\theta$ scan mode with a maximum θ value of 66°. High intensities were reduced by nickel filters. The background intensity was measured at each side of a reflexion for half the scan time. From the 2155 measured reflexions 1548 were significantly different from the background intensity. The crystal had approximate dimensions of $0{\cdot}2 \times 0{\cdot}5 \times 0{\cdot}5$ mm and was mounted about the unique axis. In the reduction of intensities to structure factors no correction for absorption was made [μ(Cu $K\alpha$) = $5{\cdot}86$ cm^{-1}].

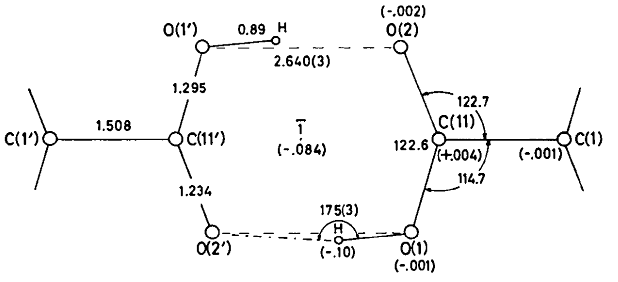


Fig. 3. The carboxylic dimer. Numbers in parentheses denote distances to the least-squares plane through C(1), C(11), O(1) and O(2).

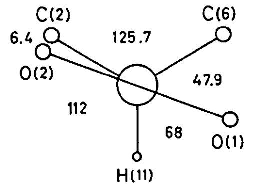


Fig. 4. Newman projection along the C(1)–C(11) bond showing the orientation of the carboxyl group.

Structure determination

The structure of CIS has been solved by means of a direct method for which Dr Spek suggests the name 'Symbolic Phasing Procedure' (SPP).*

A list is made of triple products with a high probability of being positive. A phase symbol is assigned to each of 25 reflexions with a large E value. Together with the phases of three origin determining reflexions (which were chosen zero) the phases of 316 other reflexions were expressed in these phase symbols. Afterwards 21 symbols were eliminated. A Fourier summation, calculated for the phase combination which might give the 'best' solution out of the 2^4 possibilities, revealed all the heavy atoms in the asymmetric unit.

Refinement

The form factors used for all structure factor calculations were taken from Doyle & Turner (1968) for oxygen, from Allmann (1967) for carbon and from Stewart, Davidson & Simpson (1965) for hydrogen. The calculations were carried out, attributing equal weights to all reflexions.

A block-diagonal least-squares refinement of the coordinates and isotropic temperature factors of the heavy atoms, using the 1548 non-zero reflexions, converged to $R(=\sum||F_o|-|F_c||/\sum|F_o| \times 100) = 16\%$. Three cycles of refinement of anisotropic thermal parameters lowered R to 12%.

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* The way in which the SPP was applied in our case is described in this paper. Full details of this procedure will be published soon by Dr A. T. Spek, Laboratory of Crystal Chemistry, University of Utrecht, who developed and wrote this program.

Table 1. *Final fractional atomic coordinates and thermal parameters*

The fractional atomic coordinates are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms. The B_{ij} coefficients (Å$^2 \times 10^2$) are given by the expression:

$$\exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2a^*b^*hkB_{12}+2b^*c^*klB_{23}+2c^*a^*lhB_{31})\right].$$

The isotropic factors are in Å^2.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	$2B_{12}$	$2B_{23}$	$2B_{13}$
C(1)	1085 (1)	3876 (5)	2372 (2)	446 (12)	665 (16)	452 (13)	−39 (22)	−278 (23)	71 (21)
C(2)	1590 (2)	5712 (5)	1910 (2)	551 (12)	582 (14)	443 (13)	99 (22)	16 (21)	71 (21)
C(3)	2314 (1)	6057 (4)	2777 (2)	481 (12)	395 (13)	473 (13)	−26 (22)	8 (18)	156 (21)
C(4)	2807 (1)	4032 (4)	2962 (2)	457 (12)	417 (11)	396 (9)	−9 (17)	−78 (17)	242 (14)
C(5)	2285 (1)	2269 (4)	3484 (3)	504 (12)	356 (11)	607 (13)	−17 (22)	−3 (21)	249 (21)
C(6)	1574 (2)	1849 (4)	2598 (3)	563 (12)	469 (14)	633 (13)	−232 (22)	−349 (23)	355 (21)
C(7)	3583 (1)	4381 (4)	3753 (2)	446 (12)	529 (14)	439 (13)	−56 (22)	−13 (21)	142 (21)
C(8)	3452 (2)	5421 (5)	5061 (3)	645 (12)	763 (19)	448 (13)	−86 (30)	−167 (26)	64 (21)
C(9)	4119 (2)	5842 (6)	2993 (3)	539 (12)	911 (22)	628 (17)	−438 (30)	130 (31)	135 (21)
C(10)	4010 (2)	2260 (6)	3976 (3)	574 (12)	752 (20)	861 (22)	266 (30)	−39 (34)	−71 (28)
C(11)	636 (1)	4423 (5)	3549 (2)	363 (12)	643 (16)	504 (13)	9 (22)	−159 (23)	7 (21)
O(1)	259 (1)	2842 (4)	4034 (2)	668 (12)	692 (13)	788 (13)	−150 (22)	−260 (21)	639 (21)
O(2)	620 (1)	6239 (3)	4005 (2)	633 (12)	617 (11)	693 (9)	−17 (17)	−317 (18)	426 (14)

Table 1 (*cont.*)

	x/*a*	*y*/*b*	*z*/*c*	*B*
H(11)	64 (2)	356 (5)	171 (3)	4·9
H(21)	176 (2)	536 (5)	101 (3)	4·8
H(22)	126 (2)	708 (5)	183 (3)	4·8
H(31)	214 (1)	667 (4)	368 (2)	4·3
H(32)	264 (1)	727 (4)	238 (2)	4·3
H(41)	294 (1)	359 (4)	207 (2)	3·9
H(51)	210 (2)	271 (5)	436 (2)	4·6
H(52)	255 (2)	89 (5)	364 (2)	4·6
H(61)	173 (2)	131 (5)	172 (3)	5·1
H(62)	127 (2)	66 (5)	296 (3)	5·1
H(81)	397 (2)	549 (5)	563 (3)	5·8
H(82)	321 (2)	685 (5)	494 (3)	5·8
H(83)	306 (2)	471 (5)	552 (3)	5·8
H(91)	464 (2)	604 (5)	344 (3)	6·3
H(92)	425 (2)	517 (5)	216 (3)	6·3
H(93)	389 (2)	718 (5)	278 (3)	6·3
H(101)	454 (2)	258 (5)	435 (3)	6·8
H(102)	403 (2)	139 (5)	312 (3)	6·8
H(103)	368 (2)	133 (5)	452 (3)	6·8
H(O1)	−6 (2)	314 (5)	466 (3)	6·6

At this stage all hydrogen atoms, except the hydroxyl hydrogen atom, were clearly located on a difference map with peak heights between 0·5 and 0·9 e.Å^{-3}. Only low-order reflexions were used in this difference synthesis. The hydroxyl hydrogen atom was placed on the expected position in the eight-membered ring around the centre of symmetry. At this position only a very small peak (0·25 e.Å^{-3}) was observed in the difference map.

During further refinement the hydrogen temperature factors were kept fixed on the *B* value of the associated heavy atom. In the later cycles positional parameters for all atoms and anisotropic thermal parameter for the heavy atoms were refined. The *R* index reduced to 7%. Inspection of the structure factors revealed that six very strong low-order reflexions were apparently subject to extinction. Continued refinement with omission of these six reflexions reduced *R* to 5·7%. The refinement was terminated at this point as the ratio's of the shifts to the estimated standard deviations were in general less than 0·5. A final difference synthesis, which showed a residual density between −0·3 and +0·3 e.Å^{-3} also justified termination of the refinement.

The positional and thermal parameters of the atoms are listed in Table 1 together with their standard deviations as calculated from the block-diagonal least-squares refinement. Fig. 1 shows the atomic numbering used and the anisotropic thermal ellipsoids of the heavy atoms. The bond lengths and bond angles are given in Fig. 2 together with their e.s.d.'s. A list of structure factors is available from the laboratory.

Description of the structure

The carboxyl group

The axial C(1)C(11)O(1)O(2) group is planar within experimental error. Two carboxyl groups form the well-known eight-membered ring around a centre of symmetry (Fig. 3). The O(1)···O(2′) distance is 2·640 (3) Å and the O(1)–H···O(2′) angle is 175 (3)°, which are normal values for an approximately linear hydrogen bond.

The C(1)–C(11) distance is short, 1·508 (3) Å. The same value was observed in *trans*-1,4-cyclohexanedicarboxylic acid (Dunitz & Strickler, 1966), in propionic acid (Strieter, Templeton, Scheuerman & Sass, 1962; Derissen, 1971*b*) and in gaseous acetic acid dimer (Derissen, 1971*a*).

The conformation of the carboxyl group is in agreement with the situation usually found in aliphatic carboxylic acids (Kanters, Kroon, Peerdeman & Schoone, 1967) and with the proposed conformation for an axial carboxyl group in cyclohexanecarboxylic acids (van Bekkum, Verkade & Wepster, 1971). The carbonyl oxygen atom is twisted away from the C(2)-eclipsed position by 6·4° (Fig. 4). Besides packing effects this may be due to intramolecular non-bonded oxygen–hydrogen contacts which are drawn in Fig. 5.

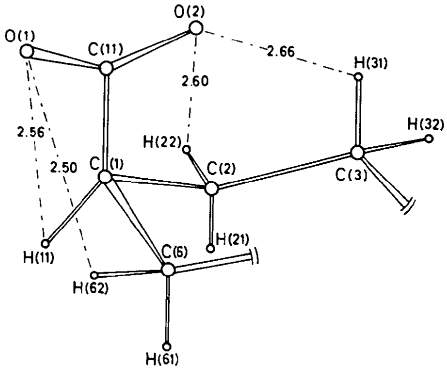


Fig. 5. Short non-bonded intramolecular oxygen–hydrogen distances (e.s.d.'s, 0·03 Å).

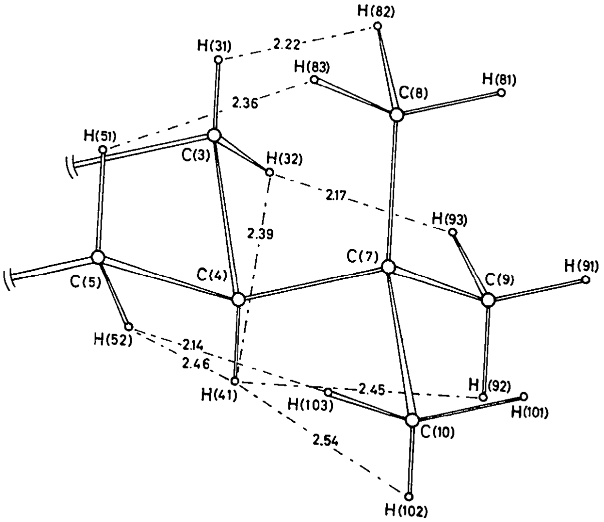
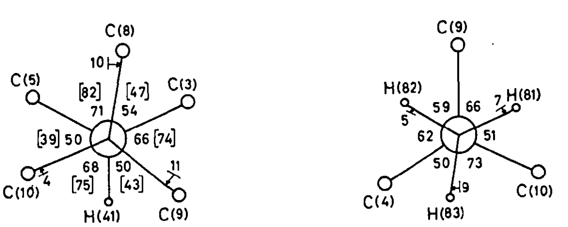
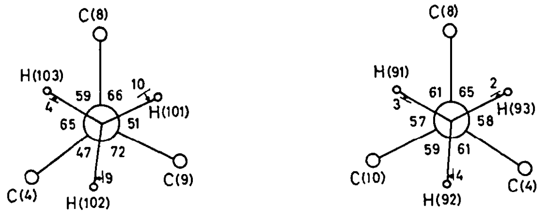


Fig. 6. Short non-bonded intramolecular distances (e.s.d.'s, 0·04 Å) between hydrogen atoms on C(3), C(4), C(5) and on C(8), C(9), C(10).



a along C(7)-C(4); average twist angle 8° [17°]

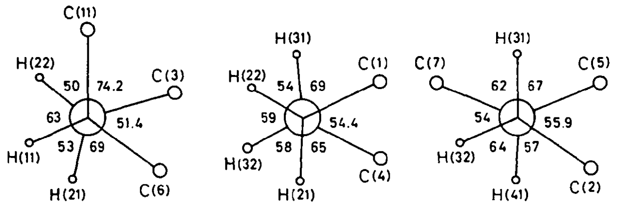
b along C(8)-C(7); average twist angle 7° [7°]



c along C(10)-C(7); average twist angle 8° [8°]

d along C(9)-C(7); average twist angle 3° [0°]

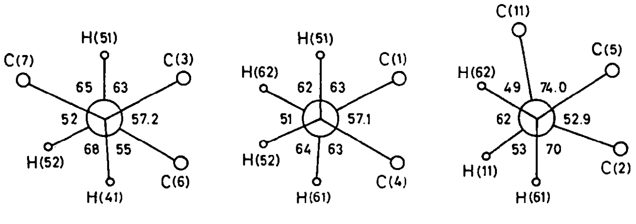
Fig. 7. Newman projections along C–C bonds of the t-butyl group showing the twist of the t-butyl group (*a*) and the methyl groups (*b*, *c*, *d*).



along C(1) – C(2)

along C(2)-C(3)

along C(3)-C(4)



along C(4)-C(5)

along C(5)-C(6)

along C(6)-C(1)

Fig. 8. Newman projections along the bonds of the cyclohexane ring.

The t-butyl group

The bond angles and bond distances are given in Fig. 2. No anomalous values are found.

Intramolecular non-bonded contacts between hydrogen atoms bonded to C(3), C(4), C(5) and those belonging to the t-butyl group are represented in Fig. 6. Some of these distances are appreciably shorter than the accepted van der Waals distance (2·40 Å) and cause steric interactions. The t-butyl group as well as the three methyl groups are twisted away from their perfectly staggered position (Fig. 7). This twisting phenomenon reveals itself in high anisotropic thermal parameters for the atoms concerned (Table 1; Fig. 1). A quantitative analysis of the thermal motion of the molecule has not been made.

The results are in excellent agreement with the empirical valence force field calculations of Altona & Sundaralingam (1970). Their parameters, calculated for an isolated t-butylcyclohexane molecule, are inserted in Fig. 7 between brackets.

The cyclohexane ring

The bond distances, bond angles and torsion angles are given in Table 2 together with the corresponding values taken from the 'Altona model' (Altona & Sundaralingam, 1970).

The observed C–C bond distances differ considerably from the corresponding calculated values but the mean distances agree fairly well: 1·529 Å (observed) and 1·533 Å (Altona & Sundaralingam, 1970).* The value of 1·529 Å was also found by Groth (1968) in *trans*-1,4-aminomethylcyclohexanecarboxylic acid.

The mean C–O–C bond angle and torsion angle are 111·4 and 54·8° respectively. The corresponding calculated values are 111·2 and 55·4°. The ring in CIS shows slightly more flattening than the ring in t-butylcyclohexane. The geometry of the ring is determined by the torsion angles; starting with the C(1)–C(2) bond the observed torsion angles along the successive

Table 2. *Comparison between observed bond angles, bond distances and torsion angles in CIS and the corresponding calculated values in t-butylcyclohexane* (*Altona & Sundaralingam*, 1970).

	CIS	t-Butylcyclohexane
Bond distance		
1–2	1·529 Å	1·518 Å
1–6	1·536	1·520
2–3	1·521	1·539
5–6	1·521	1·534
3–4	1·533	1·546
4–5	1·534	1·542
mean	1·529	1·533
Bond angle		
6–1–2	111·1°	111·3°
1–2–3	112·3	111·4
1–6–5	111·7	110·2
2–3–4	113·0	113·0
6–5–4	112·1	112·8
3–4–5	108·4	108·8
mean	111·4	111·2
Torsion angle		
6–1–2–3	51·4°	55·6°
2–1–6–5	52·9	57·0
1–2–3–4	54·4	54·3
1–6–5–4	57·1	57·7
2–3–4–5	55·9	52·7
3–4–5–6	57·2	54·8
mean	54·8	55·4

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* The force field in its present form yields C–C bond distances that are systematically too high by 0·005 to 0·006 Å.

Table 3. *Shortest intermolecular distances*

C–C, C–O, O–O below 4 Å (e.s.d., 0·004 Å), C–H, O–H below 3·0 Å (e.s.d., 0·04 Å), H–H below 3·0 Å (e.s.d., 0·05 Å). Code for symmetry-related molecules:

Superscript	Molecule at		
None	x	y	z
i	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$-x$	$1-y$	$1-z$
iii	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	x	$\frac{3}{2}-y$	$z-\frac{1}{2}$
v	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
vi	x	$y+1$	z

H(82)–H(103^{vi})	2·96 Å	C(8)—C(9^{vi})	3·974 Å
H(93)–H(102^{vi})	2·67	C(9)—C(10^{v})	3·968
H(31)–H(52^{vi})	2·74	C(2)—O(1^{i})	3·541
H(32)–H(52^{vi})	2·63	C(2)—O(2^{iv})	3·889
H(22)–H(61^{vi})	2·77	O(2)—C(1^{i})	3·604
H(22)–H(62^{vi})	2·53	O(1)—C(1^{iii})	3·847
		C(1)—O(1^{i})	3·655
C(3)—H(52^{vi})	3·18	O(2)—C(11^{i})	3·900
H(22)–C(6^{vi})	3·14	C(11)–O(1^{i})	3·717
H(32)–C(8^{iv})	3·17	O(1)—C(11^{ii})	3·446
O(2)—H(62^{vi})	3·19	O(2)—C(11^{ii})	3·414
H(11)–O(1^{i})	3·18	O(1)—O(1^{ii})	3·502
		O(1)—O(2^{ii})	2·640*
C(2)—C(6^{vi})	3·914	O(2)—O(1^{i})	3·587
C(3)—C(5^{vi})	3·965	O(2)—O(2^{ii})	3·394
C(3)—C(6^{vi})	3·850		

* Hydrogen bond.

bonds are −51·4, +54·4, −55·9, +57·2, −57·1 and +52·9° (Fig. 8). Atoms C(1) and C(2) are bent outward the centre of the ring. The deviation from the mean C–C–C bond angle is large at the substituted C(4) atom [angle C(3)–C(4)–C(5) is 108·4°] and at this side of the ring puckering occurs. This puckering of the ring at C(4) is not in agreement with the results of Altona & Sundaralingam (1970). Their calculations predict a flattening at the t-butyl side of the ring: the angle C(3)–C(4)–C(5) is 108·6° and the relevant torsion angles are −52·7 and +54·8° (Table 2). The observed puckering is in agreement with n.m.r. spectroscopic studies of Remijnse *et al.* (1971).

The crystal packing

The crystal consists of zigzag chains of molecules along the *a* axis. In each chain the molecules form centric dimers through approximately linear hydrogen bonds of 2·640 Å. The dimers in the chain are held together by non-bonding contacts between hydrogen atoms from t-butyl groups related by a centre of symmetry (Fig. 9). These contacts are not as short as many contacts between the chains (Table 3) and explain why the crystals could be easily cleaved along (100).

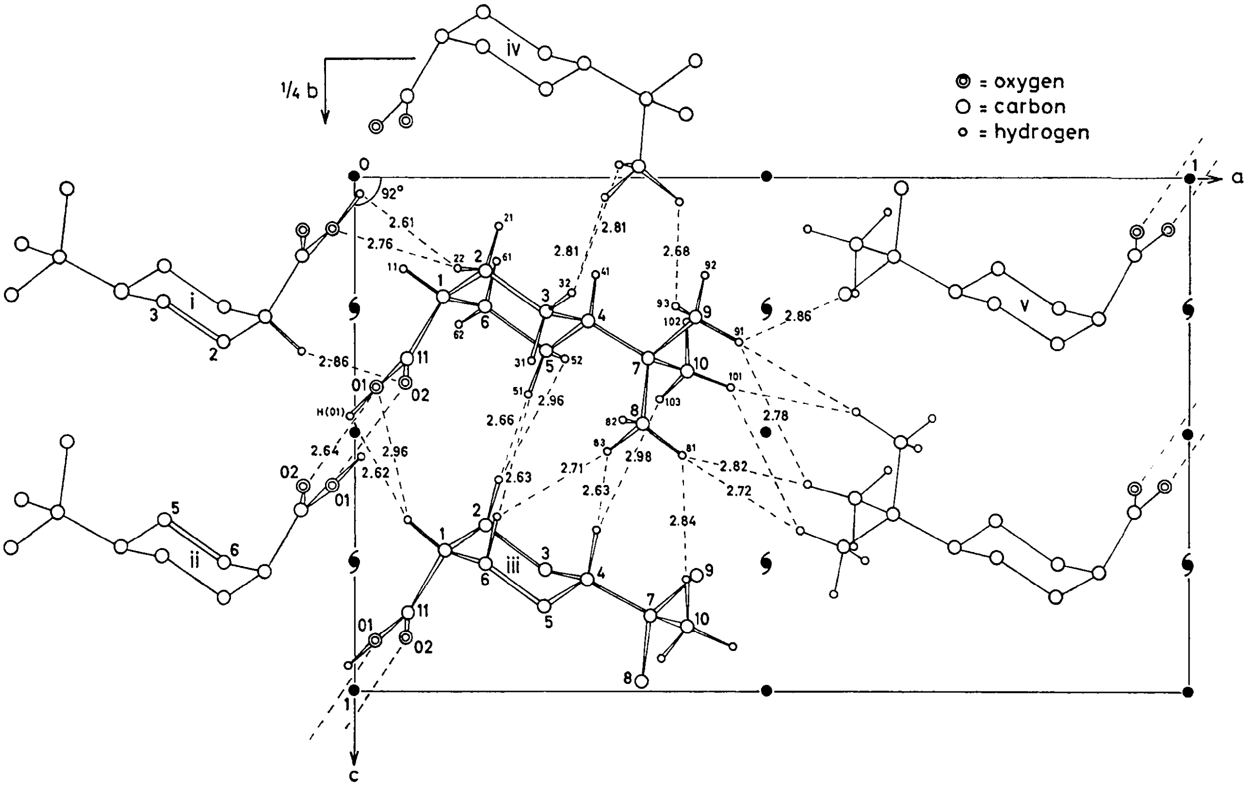

Fig. 9. Projection of the crystal structure along **b** showing the packing of the molecules. Some short hydrogen–hydrogen distances (< 3·0 Å) are indicated. Only those hydrogen atoms are drawn which serve clarity. The code for symmetry relation is given in Table 3.

The author is greatly indebted to the Utrecht University's X-rays group for computation facilities and to Professors H. van Bekkum and B. M. Wepster for suggesting the investigation.

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Structure Cristalline et Moléculaire de l'Éthyl *S*-Éthyl-2 Dithio-1,2 α-D-Mannofuranoside

PAR ARNAUD DUCRUIX ET CLAUDINE PASCARD-BILLY

Laboratoire de Cristallochimie, Institut de Chimie des Substances Naturelles, 91 Gif-sur-Yvette, France

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Ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside ($C_{10}H_{20}O_4S_2$) crystallizes in space group $P2_12_12_1$ with $a=5{\cdot}07$, $b=8{\cdot}11$, $c=32{\cdot}18$ Å and $Z=4$. The structure was solved by use of a known partial structure (the two S atoms were located on a sharpened Patterson map) in conjunction with the tangent formula. Full-matrix least-squares methods were used for refinement and the final *R* value was 11% for the 552 observed reflexions. The two *S*-alkyl groups are in *trans* positions with the *manno* configuration for the *S*-ethyl substituent in C(2). The conformation of the furanose ring is different from that observed in other compounds. Atom C(4) of the ring is 0·6 Å out of the best four-atom plane.

Introduction

Dans des travaux récents, il a été montré que la désamination nitreuse de l'amino-2 désoxy-2 D-glucose diéthyl-dithioacétal permettait d'obtenir selon les conditions ioniques de la désamination, soit le *S*-éthyl-2 thio-2 D-glucose (Horton, Magbanua & Tronchet, 1966), soit un composé pour lequel la structure d'un éthyl *S*-éthyl-2 dithio-1,2 α-D-mannofuranoside a été proposée (Defaye, Horton, Nakamura & Philips, 1970).

Si la confirmation du structure de premier composé a pu être en partie déduite de l'étude du spectre de r.m.n. (Ashmawy, Horton, Magbanua & Tronchet, 1968), les travaux correspondants sur le second composé ont nécessité en outre des corrélations faisant intervenir une série de dérivés. Connaissant la grande aptitude migratrice des radicaux soufrés qui aurait pu conduire à des modifications structurales imprévisibles lors de l'obtention de ces dérivés, il était nécessaire d'obtenir confirmation directe de cette structure par l'utilisation de la diffraction des rayons X.

Partie expérimentale

Les cristaux étudiés nous ont été fournis par le laboratoire de M. Defaye et ont été recristallisés dans un mélange chloroforme–éther de pétrole. La cristallisation a conduit à de fines aiguilles mal formées (0,02 × 0,10 mm de section). La maille cristalline a été déterminée par les méthodes de Weissenberg et de précession, sur des clichés de cristal tournant avec la radiation *Kα* du cuivre. Les principales données cristallographiques sont résumées dans le tableau suivant.

Formule brute	$C_{10}H_{20}O_0S_2$
Masse moléculaire	268
Système cristallin	orthorhombique
Groupe spatial	$P2_12_12_1$
a	$5{,}070 \pm 0{,}008$ Å
b	$8{,}113 \pm 0{,}006$
c	$32{,}18 \pm 0{,}05$
V	1323 Å^3
Z	4