

Crystal and Molecular Structure of *p*-Tercyclohexane-1 (Isomeric Form 1 of 1,4-Dicyclohexylcyclohexane), C₁₈H₃₂

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Isomeric form 1 of *p*-tercyclohexane (PTCH-1) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions $a=4.770$, $b=6.226$, $c=14.290$ Å, $\alpha=88.92$, $\beta=95.98$ and $\gamma=112.90^\circ$. $D_m=1.06$, $D_x=1.061$ g cm⁻³, m.p. 163.5°C. The phase problem was solved by direct methods and the structure refined by the anisotropic least-squares method to a final R of 0.108 for the most reliable reflexions. The molecule, similar to the isomeric form 2 (PTCH-2), consists of three cyclohexane rings linked by single bonds. The rings maintain the chair conformation of the free cyclohexane ring. While in form 2 the molecule has an *L* shape, in form 1 the three rings form a linear molecular chain, with approximately a non-crystallographic mirror plane passing through the atoms of the bonds linking the rings.

Introduction

p-Tercyclohexane has been prepared by Heidt, Kiss, Jäger & Benke (1965) from terphenyl by catalytic hydration. The end product contained two isomeric forms (PTCH-1 and PTCH-2), in almost equal proportions, with melting points 161–162° and 51–52°C respectively. Because of their different solubility properties the two isomeric forms could be separated. Recrystallization from solution in methanol, in which PTCH-1 is almost insoluble, gave PTCH-2 as rather well developed crystals. The separated PTCH-1 was recrystallized from solution in benzene as very small crystals. Both isomeric forms have been investigated by infrared and n.m.r. spectroscopy by Heidt, Neszmélyi, Imre & Kiss (1967) who supplied the crystals for the present X-ray investigation. A short preliminary report of the structure determination of the isomeric form 2 (PTCH-2) has been given elsewhere (Sasvári, 1972). The structure determination of PTCH-1 is the subject of the present paper which also provides complementary data on the structure determination of PTCH-2.

Experimental

The title compound (PTCH-1) crystallizes in very thin colourless transparent lath-shaped needles elongated in the *a* direction. From the crystalline product it was difficult to find a sample with the right thickness for X-ray diffraction. The crystal used was 0.5 × 0.3 × 0.05 mm. The melting point was re-determined on a Mettler instrument and found to be 163.5°C.

The cell dimensions were determined from Buerger precession photographs taken around the crystallographic axes with Cu $K\alpha$ radiation and later refined from diffractometer powder data with the program of Lindqvist & Wengelin (1967).

Crystal data

$a=4.770$ (3), $b=6.226$ (5), $c=14.290$ (7) Å, $\alpha=88.92$ (4), $\beta=95.98$ (3), $\gamma=112.90$ (6)°. M.W. 248.45, $D_m=1.06$, $D_x=1.061$ g cm⁻³, $Z=1$, $F(000)=140$, $\mu(\text{Cu } K\alpha)=4.06$ cm⁻¹.

The presence of a centre of symmetry was deduced from the uneven intensity distribution and the space group was taken as $P\bar{1}$, which was later verified. Reflexions from reciprocal layers $0kl-4kl$ were collected on a semi-automatic two-circle Stoe-Güttinger single-crystal diffractometer operated in the equi-inclination Weissenberg mode. Intensities were measured around a in a 2θ range of 5° to 120° and calculated according to a procedure described elsewhere (Sasvári, Simon, Bognár & Makleit, 1974). With $\mu R \leq 0.3$ no absorption correction was made. After Lorentz-polarization corrections the absolute scale and approximate overall temperature factor ($B=5.306$ Å²) were determined by a Wilson plot from all the three-dimensional data.

Even at the data-collection stage the unusual intensity distribution was striking. A few reflexions were very strong while most of them very weak, giving rise

Table 1. Distribution statistics of the F_o structure factor value magnitudes of the collected reflexions of PTCH-1 (451 observed and all reflexions respectively)

Magnitude of F_o	Observed reflexions		All reflexions	
	Number of reflexions	Percentage	Number of reflexions	Percentage
0–1	45	9.8	599	59.4
1–2	143	31.7	146	14.5
2–4	101	22.3	101	10.0
4–10	107	23.6	107	10.6
10–20	36	7.9	36	3.6
>20	19	4.7	19	1.9
Total	451	100.0	1008	100.0

to the structure factor statistics reported in Table 1. 1008 reflexions were collected, 557 of which were designated as unobserved. The unusual structure factor statistics resulted in a very poor E statistics and average E as can be seen in Table 2.

Table 2. E value averages and distribution statistics for all reflexions of PTCH-1

	Exper.	Theoretic	
		Centric	Non-centric
$\langle E \rangle$	0.591	0.798	0.886
$\langle E^2 \rangle$	1.000	1.000	1.000
$\langle E^2 - 1 \rangle$	1.467	0.968	0.736
$E > 1$	14.58	32.00%	36.80%
$E > 2$	6.25	5.00	1.80
$E > 3$	2.78	0.30	0.01

Determination of the structure

The phase problem was solved by direct methods using E value magnitudes deduced from the observed structure factor values. In spite of the intensity distribution, 147 reflexions with $E \geq 1.0$ could be collected with a fairly even distribution in the eight parity groups. For sign determination the *LSAM* program (Main, Woolfson & Germain, 1968) was used, with four starting reflexions in addition to three origin-fixing reflexions and acceptance of signs with a probability greater than 0.80. The E map calculated with the sign set with the highest figures of merit revealed 12 peaks of almost equal height forming a partial structure compatible with the molecular formula (Fig. 1), with an indication that the complete ring is the middle ring of the molecule which, however, is displaced with respect to a centre of symmetry in the unit cell.

Following the procedure of Karle & Karle (1971) this molecular fragment was taken as a partial structure in space group $P1$, and the phases based on this partial structure and calculated for space group $P1$ were used for a Fourier synthesis. This revealed the whole molecule (Fig. 2) with the coordinates tabulated in Table 3, and gave an R of 0.37 for the 451 observed reflexions.

Comparison of F_o and $|F_c|$ values indicated that a large number of reflexions were so weak that their F_o values were of the order of the experimental error. With this in mind only those 251 reflexions that satisfied the two conditions $F_o > 3.9$ and $(F_o - |F_c|)/\max(F_o, |F_c|) \leq 0.3$ were accepted for least-squares refinement.

From the atomic coordinates derived from the Fourier synthesis (Table 3) it can be stated that the

molecule has a centre of symmetry at the centre of the middle ring with coordinates 0.36, -0.03, 0.26. Before least-squares refinement with the reduced number of reflexions, the molecule was shifted by the above vector to the correct position with respect to the origin (Table 4) in order to reduce the number of independent parameters. All further calculations were performed in space group $P\bar{1}$.

The least-squares refinement was performed by minimizing the function $\Phi = \sum_n w_n (F_{oh} - (1/G)|F_{ch}|)^2$ where G is the scale and $w_n = 1/(1 + F + 0.16F^2)$ the weighting factor. After three cycles of full-matrix least-squares refinement of non-hydrogen atoms with isotropic temperature factors ($R = 0.169$) the H atoms were geometrically generated and given the isotropic thermal par-

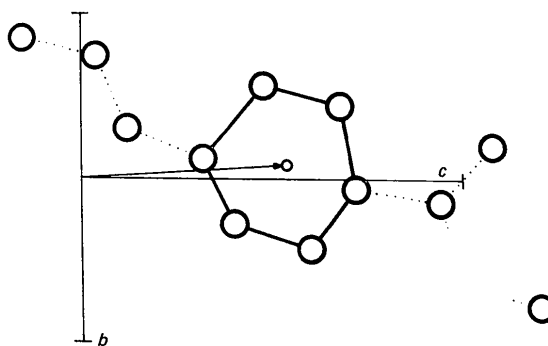


Fig. 1. The partial structure of the PTCH-1 molecule derived from the E map in space group $P1$ and displaced with respect to the centre of symmetry.

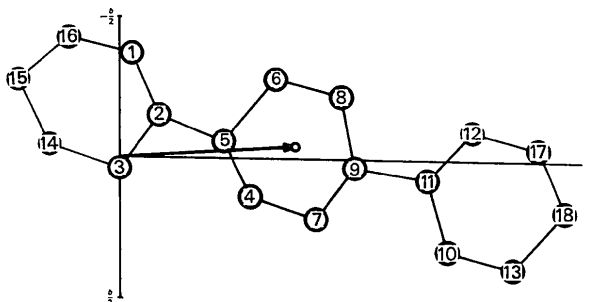


Fig. 2. The molecule of PTCH-1 derived by Fourier synthesis using phases based on the partial structure in space group $P1$. The molecule has a centre of symmetry at the centre of the middle ring marked by its vector, which indicates the displacement of the molecule relative to the origin.

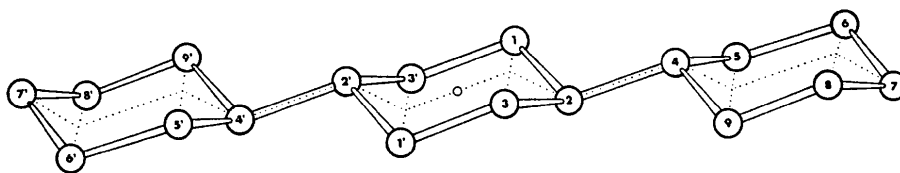


Fig. 3. Perspective view of the PTCH-1 molecule with numbering of the carbon atoms. Unprimed numbers refer to atoms of the asymmetric unit of the molecule.

ameters of the C atoms to which they belong. After three further cycles of refinement of non-hydrogen atoms with anisotropic thermal parameters, H parameters being kept constant, the parameter shifts became less than $\sigma/2$ and the refinement was terminated. All but two H atom positions were obtained by a difference Fourier synthesis.

The final parameters are in Tables 4 and 5; the R values are 0.108 and 0.193 for the 251 most reliable and the 451 observed reflexions respectively. For all the reflexions $R=0.298$.

Tables of the anisotropic thermal parameters of the non-hydrogen atoms and fractional coordinates of the H atoms with isotropic thermal parameters for PTCH-2, and structure factors for PTCH-1 and PTCH-2 have been deposited.* The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

* These tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31504 (10 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

The geometry of the molecule

The atomic numbering is given in Fig. 3. The molecule consists of three cyclohexane rings, all in the chair

Table 5. *Generated fractional coordinates and isotropic thermal parameters (\AA^2) of the hydrogen atoms of the asymmetric part of the PTCH-1 molecule*

The thermal parameters are those of the carbon atoms (after final isotropic refinement) to which the hydrogen atoms belong.

	x	y	z	B
H(1)	0.257	0.398	0.052	5.3
H(1')	-0.112	0.251	0.042	5.3
H(2)	0.335	0.051	0.097	3.9
H(3)	-0.317	-0.230	0.079	4.4
H(3')	0.058	-0.209	0.107	4.4
H(4)	-0.094	0.108	0.215	4.4
H(5)	0.556	0.368	0.227	5.3
H(5')	0.301	0.475	0.196	5.3
H(6)	0.494	0.569	0.361	5.8
H(6')	0.130	0.417	0.350	5.8
H(7)	0.360	0.261	0.473	7.5
H(7')	0.592	0.230	0.402	7.5
H(8)	0.171	-0.139	0.415	6.3
H(8')	-0.071	-0.023	0.381	6.3
H(9)	0.358	-0.080	0.267	5.5
H(9')	-0.008	-0.226	0.253	5.5

Table 3. *Atomic coordinates of the carbon atoms of the PTCH-1 molecule in the $P1$ cell derived from the Fourier synthesis and in the $P\bar{1}$ cell after the origin is shifted by the vector (0.36, -0.03, 0.26) to the centre of the molecule (note: in the two cells the atoms are numbered differently)*

$P1$ cell				$P\bar{1}$ cell			
C(1)	0.010	-0.370	0.018	C(5')	-0.350	-0.340	-0.242
C(2)	0.245	-0.150	0.060	C(4')	-0.115	-0.120	-0.200
C(3)	0.220	0.040	0.000	C(9')	-0.140	0.070	-0.260
C(4)	0.450	0.135	0.200	C(3')	0.090	0.165	-0.060
C(5)	0.210	-0.060	0.160	C(2')	-0.150	-0.030	-0.100
C(6)	0.270	-0.280	0.240	C(1')	-0.090	-0.250	-0.020
C(7)	0.430	0.210	0.300	C(1)	0.070	0.240	0.040
C(8)	0.260	-0.220	0.340	C(3)	-0.100	-0.190	0.080
C(9)	0.510	0.030	0.360	C(2)	0.150	0.060	0.100
C(10)	0.720	0.320	0.500	C(5)	0.360	0.350	0.240
C(11)	0.480	0.070	0.470	C(4)	0.120	0.100	0.210
C(12)	0.510	-0.100	0.540	C(9)	0.150	-0.070	0.280
C(13)	0.690	0.380	0.600	C(6)	0.330	0.410	0.340
C(14)	0.230	-0.040	-0.110	C(8')	-0.130	-0.010	-0.370
C(15)	-0.030	-0.270	-0.160	C(7')	-0.390	-0.240	-0.420
C(16)	0.020	-0.440	-0.080	C(6')	-0.340	-0.410	-0.340
C(17)	0.500	-0.040	0.640	C(8)	0.140	-0.010	0.380
C(18)	0.760	0.180	0.680	C(7)	0.400	0.210	0.420

Table 4. *The final fractional coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) for the non-hydrogen atoms of the asymmetric part of the PTCH-1 molecule*

The estimated standard deviations referred to the last figures are in parentheses. The b_{ij} are defined by:

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	930 (25)	2451 (18)	333 (9)	915 (63)	407 (34)	74 (7)	458 (72)	-107 (33)	-188 (25)
C(2)	1315 (19)	605 (15)	1013 (7)	650 (53)	316 (30)	77 (7)	-17 (62)	101 (31)	-221 (22)
C(3)	-976 (23)	-1747 (17)	671 (8)	746 (52)	420 (35)	70 (7)	289 (65)	-20 (33)	-169 (27)
C(4)	1184 (21)	1182 (17)	2065 (8)	833 (52)	442 (31)	51 (7)	648 (60)	-23 (31)	-119 (22)
C(5)	3430 (24)	3594 (16)	2369 (8)	910 (69)	323 (35)	50 (7)	212 (85)	-54 (37)	-79 (26)
C(6)	3367 (28)	4089 (20)	3429 (9)	1183 (76)	534 (36)	60 (8)	370 (82)	115 (36)	-189 (26)
C(7)	3778 (27)	2212 (24)	4075 (10)	984 (77)	765 (50)	86 (9)	611 (102)	-179 (40)	-235 (33)
C(8)	1383 (28)	-141 (20)	3728 (10)	1061 (72)	484 (39)	78 (9)	450 (85)	-20 (40)	-187 (29)
C(9)	1537 (24)	-715 (18)	2744 (10)	807 (61)	428 (35)	97 (9)	393 (74)	-22 (39)	-178 (27)

form, which are linked by C-C single bonds to form a linear molecular chain. The molecule has a centre of symmetry at the centre of the middle ring, which

locates the molecule with respect to the origin of the unit cell.

The carbon atoms C(1), C(3), C(1'), C(3') and C(5),

Table 6(a). Atomic least-squares planes of the PTCH-1 molecule with normals to planes for atoms forming the planes and also for some other atoms of the molecule

The plane constants ($Ax + By + Cz = D$) are referred to crystal axes and coordinates are in Å.

Planes	A	B	C	D	
P1	0.97463	-0.31965	-0.11061	0.0	
P2	0.97543	-0.31979	0.10678	1.25852	
P3	0.03255	0.88993	-0.22321	0.0	
P4	0.82761	-0.40598	-0.63415	-0.55178	
P5	0.82596	-0.40513	-0.63647	-1.70983	
P6	0.79915	-0.39605	-0.67108	-3.01311	
P1	C(1), C(3), C(1'), C(3')	0.0	0.0	0.0	0.0
-	C(2), C(4), C(5), C(9)	0.651	0.642	1.254	1.291
P2	C(5), C(6), C(8), C(9)	-0.017	0.017	-0.018	0.018
-	C(2), C(4), C(7), C(1)	-0.613	-0.628	0.681	-1.260
-	C(3)	-1.262			
P3	C(7), C(4), C(2), C(2')	-0.016	0.015	0.033	-0.033
-	C(4), C(7)	-0.015	0.016		
-	C(1), C(3), C(5), C(9)	1.266	-1.197	1.289	-1.248
-	C(6), C(8)	1.224	-1.246		
P4	C(1), C(2), C(3)	0.0	0.0	0.0	
P5	C(4), C(5), C(9)	0.0	0.0	0.0	
P6	C(6), C(7), C(8)	0.0	0.0	0.0	

Dihedral angles in the rings

P1, P4 47.2°

P2, P5 47.0

P2, P6 49.6

Inclination angles of planes in the molecule

P1, P2 0.3° P1, P3 93.0°

P4, P5 0.1 P5, P3 92.7

P4, P6 2.7 P6, P3 93.0

Table 6(b). Atomic least-squares planes of the PTCH-2 molecule with normals to planes for atoms forming the planes and also for some other atoms of the molecule

The atomic numbering is as previously reported (Sasvári, 1972).

The plane constants ($Ax + By + Cz = D$) are referred to crystal axes and coordinates are in Å.

Planes	A	B	C	D	
P1	0.23829	0.61068	-0.75641	0.03874	
P2	0.23468	0.69236	0.68108	8.84799	
P3	0.34523	0.65982	0.66560	10.24086	
P4	0.95171	-0.30697	-0.00731	1.76478	
P1	C(2), C(3), C(5), C(6)	0.0002	-0.0002	0.0002	-0.0002
-	C(1), C(4), C(7)	0.6740	-0.6418	-0.5255	
P2	C(8), C(9), C(11), C(12)	0.0011	-0.0011	0.0011	-0.0011
-	C(4), C(7), C(10), C(13)	-2.2290	-0.6921	0.6639	0.6654
P3	C(14), C(15), C(17), C(18)	-0.0086	0.0085	-0.0085	0.0085
-	C(13), C(16)	-0.6601	0.6604		
P4	C(1), C(4), C(7), C(10)	0.0045	-0.0044	0.0191	-0.0076
-	C(13), C(16)	-0.0400	0.0283		
-	C(2), C(3), C(5), C(6)	-1.2568	-1.2319	1.2618	1.2267
-	C(8), C(9), C(11), C(12)	-1.2276	-1.2551	1.2354	1.2454
-	C(14), C(15), C(17), C(18)	-1.2117	-1.2840	1.1900	1.2472

Dihedral angles referred to the three four-atomic planes P1, P2 and P3 of the rings in sequence from left to right.

P1 50.5° 47.0°

P2 49.3 48.6

P3 48.6 49.7

Inclination angles of planes in the molecule

P1, P2 87.9° P4, P1 92.4°

P1, P3 88.9 P4, P2 90.5

P2, P3 6.7 P4, P3 97.2

C(6), C(8), C(9) of two neighbouring rings, not involved in linking, are coplanar, forming the planes P1 and P2 (Table 6), with a maximum deviation of 0.02 Å. The planes are parallel to each other with a deviation angle of 0.2°. The normal between these planes is 1.27 Å. The outside rings of the molecule are parallel because of crystallographic symmetry. C(7), C(4), C(2), C(2'), C(4') and C(7') are coplanar too, with a maximum deviation of 0.03 Å. This plane (P3 in Table 6) is almost perpendicular to P1 and P2 and to the planes formed by C(1), C(2), C(3); C(4), C(5), C(9); and C(6), C(7), C(8), with an average angle of 93.0° (maximum deviation of 0.3°). Atomic least-squares planes of the molecule and deviations of atoms from these planes are given in Table 6.

The C(2)–C(4) bond linking neighbouring rings and involved in the plane P3 is parallel to P1 and P2 with an average normal distance of 0.63 Å and maximum deviation of 0.02 Å. The dihedral angles of the cyclohexane rings are given in Table 6.

Table 7. Bond lengths (Å) and angles (°) of the PTCH-1 molecule with their estimated standard deviations in parentheses

C(1)–C(3')	1.512 (16)	C(3')–C(1)–C(2)	110.0 (9)
C(1)–C(2)	1.545 (15)	C(1)–C(2)–C(3)	108.3 (9)
C(2)–C(3)	1.499 (15)	C(1')–C(3')–C(2)	116.9 (9)
C(2)–C(4)	1.565 (14)	C(3)–C(2)–C(4)	113.9 (8)
C(4)–C(5)	1.505 (15)	C(1)–C(2)–C(4)	112.8 (8)
C(4)–C(9)	1.564 (16)	C(2)–C(4)–C(5)	112.2 (9)
C(5)–C(6)	1.557 (17)	C(2)–C(4)–C(9)	112.2 (9)
C(6)–C(7)	1.536 (19)	C(4)–C(5)–C(6)	111.4 (9)
C(7)–C(8)	1.518 (19)	C(5)–C(6)–C(7)	113.2 (10)
C(8)–C(9)	1.473 (18)	C(6)–C(7)–C(8)	108.2 (11)
		C(7)–C(8)–C(9)	113.7 (11)
		C(8)–C(9)–C(4)	111.2 (10)
Mean: C–C = 1.527 Å		Mean: C–C–C = 112.0°	

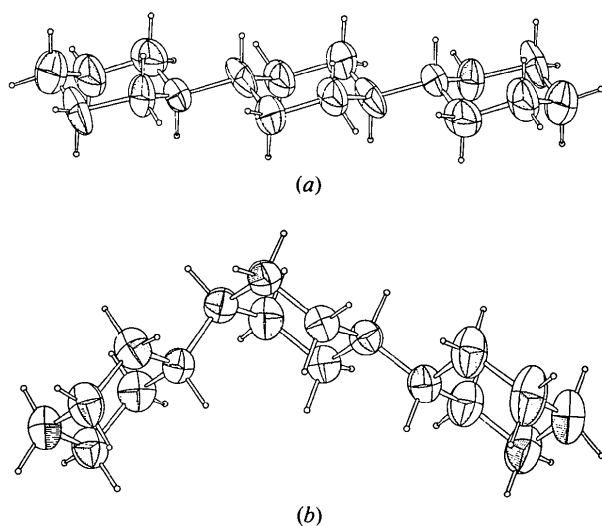


Fig. 4. (a) Perspective view of the PTCH-1 molecule. (b) Perspective view of the PTCH-2 molecule. The atoms are represented by their 50% probability thermal vibration ellipsoids.

The orientation of the molecule in the unit cell can unambiguously be given by the inclination angles of plane P3 with the (010) and (001) axial planes (167.1 and 78.6° respectively) and of plane P1 with the (100) axial plane (160.1°).

The bond lengths and bond angles of the molecule are given in Table 7.

Thermal motion analysis

Perspective views (*ORTEP*; Johnson, 1965) of the molecules of the two isomeric forms PTCH-1 and PTCH-2 can be seen in Fig. 4(a) and (b) respectively, where the non-hydrogen atoms are represented by their thermal vibration ellipsoids.

The thermal motion of the molecules of both isomeric forms was also analysed by the rigid-body assumption with the program of Schomaker & Trueblood (1968). The observed and calculated U tensors of the individual atoms show rather large deviations when either the whole molecules or the individual rings are assumed to behave as rigid bodies. Thus, neither of the molecules of the two isomeric forms can be treated as a rigid body.

Discussion of the structure

In the PTCH-1 molecule, as in PTCH-2 (Sasvári, 1972), the cyclohexane rings maintain the chair conformation of the free cyclohexane ring (Davis & Hassel, 1963), but while in PTCH-2 the molecule has an L shape, in PTCH-1 the rings form a linear molecular chain. The plane P3 [Table 6(a)] approximates to a non-crystallographic mirror plane of the molecule. The atomic deviations from this plane for all quasi-symmetric atomic pairs not involved in forming the plane, have an average value of 0.044 Å; *i.e.*, they are within 3σ of the C–C bond lengths. With respect to this plane, however, the planes C(1), C(3), C(1'), C(3') and C(5), C(6), C(8), C(9) of the asymmetric part of the molecule are inclined in the same direction at angles of 93.03 and 93.09°, respectively, destroying somewhat the right mirror symmetry.

Similarly, in PTCH-2 the C atoms linking the cyclohexane rings form a plane, with a maximum deviation of 0.04 Å, which can be regarded as a non-crystallographic mirror plane of the molecule. This has the same inclination to the three- and four-atom planes of the rings, differing slightly from 90°, as was found in PTCH-1 [Table 6(b)].

The four-atom planes of the three cyclohexane rings are parallel to each other and shifted slightly with a normal of 1.27 Å. This is similar to the corresponding shift (1.31 Å) in PTCH-2.

In the chair-form rings of the molecule the three dihedral angles (in the asymmetric part of the molecule) associated with planes P1 and P2 are 47.2, 47.0 and 49.6°, respectively. Thus the chairs are flattened to the same extent, relative to the ideal 60°, as was found in

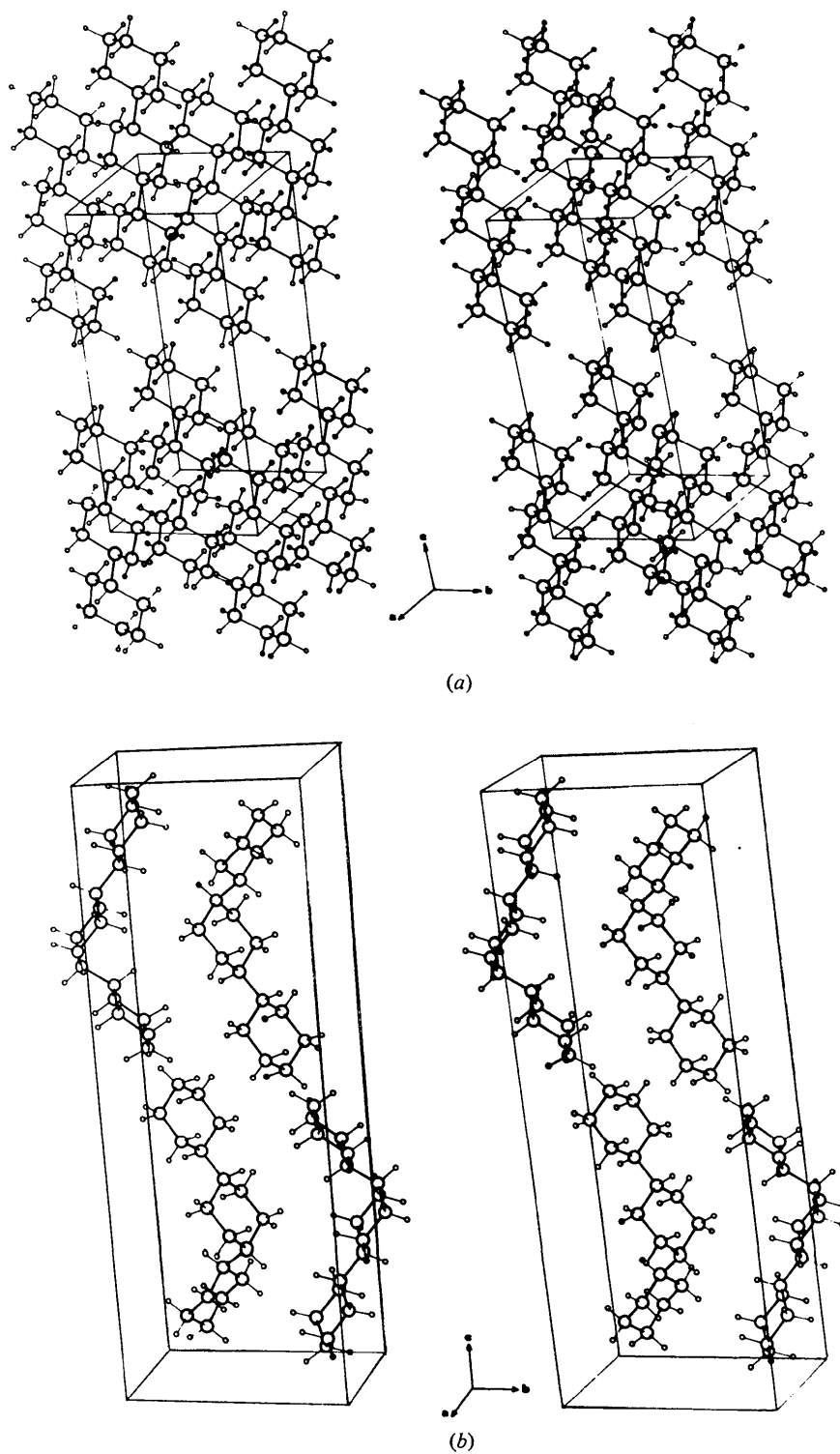


Fig. 5. (a) Stereoscopic projection of the unit-cell contents of PTCH-1 down a direction deviating from the *a* axis by a rotation of the crystal about its *b* and *c* axes through angles of 30° and -20° respectively. (b) Stereoscopic projection of the unit-cell contents of PTCH-2 down a direction deviating from the *a* axis by a rotation of the crystal about its *b* and *c* axes through angles of 20° and -20° respectively.

PTCH-2, where the dihedral angles ranged from 47.0 to 50.5° [Table 6(b)]. The same phenomenon has also been found for bicyclohexylidene (Sasvári & Löw, 1965) with almost the same dihedral angles (49.4 and 51.1°) and also for the free cyclohexane molecule (Wohl, 1964). In the present case the largest dihedral angle belongs to the very end of the molecule. Thus the flattening is more apparent within the linear molecular chain.

All C–C bonds of the molecule are single bonds of sp^3 -hybridized C atoms and their lengths vary from 1.473 to 1.565 Å with a mean value of 1.527 Å (Table 7). Although the maximum deviation of 0.054 Å from the mean value is rather significant, it is within 3σ of the C–C bond lengths and can be attributed to the fact that only a restricted number of intensities were used for the accurate refinement. The average value of the bond lengths (1.527 Å) is in good agreement with the values of 1.524 and 1.523 Å found in PTCH-2 and bicyclohexylidene (Sasvári & Löw, 1965) respectively.

The spatial packing of the molecules conforms to molecular close packing in both isomeric forms and the molecules, in both cases, are held together by van der Waals forces. The shortest intermolecular H–H distances (six in PTCH-1 and 15 in PTCH-2) range from 2.42 to 2.71 Å (average 2.60 Å) and from 2.44 to 2.69 Å (average 2.59 Å) in PTCH-1 and PTCH-2 respectively, and the averages compare with the van

der Waals distances (2.54 Å). Stereographic projections of both isomeric forms are given in Fig. 5(a) and (b) (ORTEP; Johnson, 1965).

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The Crystal and Molecular Structure of 2,6-Diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde

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Crystals of 2,6-diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10.871$, $b = 10.956$, $c = 18.904$ Å, $\beta = 118.39^\circ$. The structure has been refined with a full-matrix least-squares technique to a final R index of 0.053 for 1623 observed reflexions. The thiopyran ring is non-planar. One of the C–C bonds of 1.455 (6) Å in the thiopyran ring is a shortened single bond. One of the S–C distances of 1.712 (5) Å indicates a partial double bond.

Introduction

An X-ray examination of the crystal structure of 2,6-diphenyl-3-benzyl-2*H*-thiopyran-5-carboxaldehyde, $C_{25}H_{20}OS$, was undertaken to study the nature of the heterocyclic ring. Since the exact conformation of the

thiopyran ring is the most interesting feature of the compound, its atomic parameters have been determined very precisely and the details of its geometry have been investigated. After the structure was determined and refined it was discovered that it had already been investigated (Haque & Caughlan, 1967). Since the present analysis is based on full three-dimensional diffractometer data and the results differ significantly from those obtained by Haque & Caughlan, a brief account of the new analysis seems desirable.

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