

triclinic unit cells. However, because of the fourfold axes, the two anions in the unit cell have different orientations, unlike the triclinic case. This is shown in Fig. 3, which is a projection of the unit cell down a . Note the similarity to body-centring of the contents of the unit cell. This diagram can be compared with Fig. 1 of Drew, Mitchell & Pygall (1977), which shows the $K_5[Mo(CN)_7] \cdot H_2O$ structure.

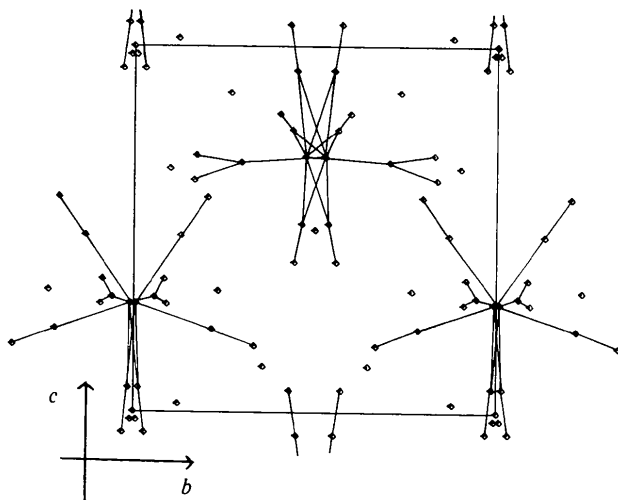


Fig. 3. The unit cell in the a projection.

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The Crystal Structure of the Low-Temperature Phase of Poly[1,2-bis(*p*-tolylsulphonyloxymethylene)-1-buten-3-ynylene]

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The title compound ($C_{20}H_{18}O_6S_2$)_n undergoes a phase change below 170 K. The space group of the low-temperature phase is $P2_1/c$, $a = 14.93$ (1), $b = 4.910$ (5), $c = 25.56$ (2) Å, $\beta = 92$ (1)°, $Z = 4$. The crystal structure has been determined and refined by full matrix least-squares analysis of intensities obtained from equi-inclination Weissenberg photographs taken at 120 K. Intensities were estimated visually. The final R index was 0.10. The phase transition is characterized by the torsions of the side groups attached to the polymer backbone. The phenyl rings in adjacent rows of polymer chains turn in opposite directions. This movement creates two different species of polymer chains in the unit cell. The splitting of levels observed in the optical spectra taken at low temperatures can be attributed to this phase change.

Introduction

Many substituted diacetylenes undergo solid-state polymerization by 1:4 addition of adjacent molecules

(Wegner, 1972). Polymerization takes place by annealing or exposure to UV, X-ray or γ -ray radiation and leads to polymers containing fully conjugated polymer chains. In this way large, nearly defect-free polymer

single crystals can be obtained. The title compound, in the following abbreviated to PT, is of particular interest because it is a good model substance for a quasi-one-dimensional solid showing a large degree of anisotropy in its physical behaviour, especially in electronic properties (Wilson, 1975). We have recently reported the observation of a phase change occurring in PT below 170 K (Enkelmann & Wegner, 1977). This phase change is approximately of second order and is connected with the splitting of the electronic bands in the spectra (Batchelder & Bloor, 1976; Reimer, Bässler, Hesse & Weiser, 1976). The aim of this study was to elucidate the nature of this phase transition and to give a basis for the correlation of the electronic properties with molecular movements which occur during the phase change.

Experimental

The monomer crystallizes from acetone in the form of diamond-shaped crystals elongated along **a**. Polymerization was carried out by annealing the crystals at 60°C for 2 d. During the polymerization the colourless

crystals develop a dark purple colour. Fully polymerized PT crystals show a bronze metallic lustre. The specimen used for intensity-data collection was cut before the polymerization to the dimensions 0.6 × 0.2 × 0.2 mm. The space group $P2_1/c$ was determined from the systematic absences $0k0$ for k odd and $h0l$ for l odd. The intensities were collected by multiple-film equi-inclination Weissenberg photographs with Ni-filtered $\text{Cu } K\alpha$ radiation, for layer lines 0 to 4 about **b** and 0 to 7 about **a**. During the intensity-data collection the temperature was maintained at 120 ± 3 K by means of a low-temperature attachment. Unit-cell dimensions were determined from Straumanis-type double-radius Weissenberg photographs ($R = 57.3$ mm) taken at 120 K. 1367 independent reflexions with $\sin \theta/\lambda < 0.6$ were observed, of which 341 were considered to have intensities less than the threshold value. These were given the threshold value of observable intensity and were given zero weight during the refinement. Intensities were estimated visually by comparison with a series of timed exposures of a selected reflexion and were corrected for Lorentz and polarization effects. No absorption correction was applied ($\mu = 32.3 \text{ cm}^{-1}$).

Table 1. *Transformed fractional coordinates ($\times 10^4$) x', y', z' of the room-temperature structure (Kobelt & Paulus, 1974) compared with the atomic parameters x, y, z of the low-temperature structure*

The coordinates reported for the room-temperature structure can be transformed into coordinates of the low-temperature unit cell by the equations $x' = \frac{1}{2}(x - \frac{1}{2}) - z$; $y' = y$; $z' = \frac{1}{2}(x - \frac{1}{2}) + \frac{1}{2}$. The coordinates of the second independent fragment of the low-temperature structure [S(2) to C(20)] can be derived by application of the transformation equations to the coordinates of atoms related to the asymmetric unit of the room-temperature structure by the symmetry operation $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

	x'	x	y'	y	z'	z	B (Å ²)
S(1)	6876	6847 (4)	2370	2491 (11)	6066	6122 (2)	1.05 (12)
O(1)	6137	6122 (10)	4320	4408 (32)	5807	5849 (6)	1.42 (33)
O(2)	6429	6396 (11)	1105	1403 (33)	6475	6558 (7)	1.84 (33)
O(3)	7254	7198 (13)	786	638 (25)	5667	5732 (6)	2.17 (36)
C(1)	5300	5302 (19)	5994	5995 (34)	5065	5065 (5)	0.65 (40)
C(2)	5077	5079 (17)	8813	8811 (32)	5017	5018 (9)	0.95 (41)
C(3)	6234	6265 (16)	5270	5354 (45)	5274	5299 (10)	2.10 (53)
C(4)	7700	7725 (12)	4582	4714 (33)	6330	6332 (7)	1.38 (49)
C(5)	7577	7610 (17)	5855	6229 (50)	6797	6792 (9)	2.42 (60)
C(6)	8242	8305 (18)	7565	7892 (48)	7002	6976 (9)	1.05 (39)
C(7)	9010	9145 (17)	8010	7973 (45)	6750	6721 (8)	1.38 (43)
C(8)	9115	9231 (18)	6723	6250 (50)	6282	6290 (10)	1.53 (47)
C(9)	8469	8525 (17)	4995	4719 (41)	6073	6080 (9)	1.15 (45)
C(10)	9703	9944 (20)	9941	9709 (54)	6969	6932 (12)	3.00 (61)
S(2)	1876	1956 (4)	2630	2777 (13)	6066	6029 (2)	1.11 (12)
O(4)	1137	1160 (12)	2680	789 (35)	5807	5793 (7)	1.69 (35)
O(5)	1429	1500 (11)	3895	4347 (31)	6475	6418 (7)	1.84 (34)
O(6)	2254	2387 (12)	4214	4142 (30)	5667	5612 (7)	2.01 (36)
C(11)	300	301 (14)	9006	9004 (34)	5065	5067 (8)	0.83 (41)
C(12)	77	78 (16)	6187	6189 (35)	5017	5016 (8)	1.38 (39)
C(13)	1234	1259 (18)	9730	9766 (42)	5274	5242 (10)	0.95 (41)
C(14)	2700	2763 (17)	418	515 (45)	6330	6347 (9)	1.21 (47)
C(15)	2577	2580 (18)	9145	9587 (49)	6797	6846 (9)	1.29 (45)
C(16)	3342	3218 (19)	7435	7736 (52)	7002	7073 (10)	2.80 (54)
C(17)	4010	3948 (16)	6990	6836 (46)	6750	6808 (8)	2.54 (55)
C(18)	4115	4100 (17)	8277	7841 (50)	6282	6308 (9)	1.30 (40)
C(19)	3469	3509 (18)	10005	9665 (49)	6073	6071 (10)	2.11 (54)
C(20)	4703	4582 (18)	5059	4733 (52)	6969	7056 (10)	1.96 (49)

Finally, the F^2 values from the various sets of photographs were correlated by an averaging process. The scale factors were allowed to vary during the refinement.

Structure determination

The crystal structure was solved by direct methods with the program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). 20 of the 28 non-hydrogen atoms could be located in the resulting E maps. All other atoms showed up in one additional electron-density-map calculation. The H atoms were assigned physically reasonable parameters, and their contributions were included in structure factor calculations. Refinement was by full-matrix least-squares analysis. Unit weights were used throughout the refinement. On termination, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.10. When anisotropic thermal parameters were introduced, the R index showed no significant improvement considering the added number of degrees of freedom. The final atomic parameters of the low-temperature phase in comparison

with the parameters for the room-temperature phase (Kobelt & Paulus, 1974) are given in Table 1.* The computer programs used were, unless otherwise stated, those of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1968) for the non-hydrogen atoms and for H from Stewart, Davidson & Simpson (1965).

Discussion

Some aspects of the phase transition occurring in PT are illustrated in Fig. 1. The transition is caused by the torsion of the side groups attached to the polymer backbone in a manner resembling the formation of periodic stacking faults. All side groups belonging to a

* A list of structure factors, together with the parameters of the hydrogen atoms, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32584 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

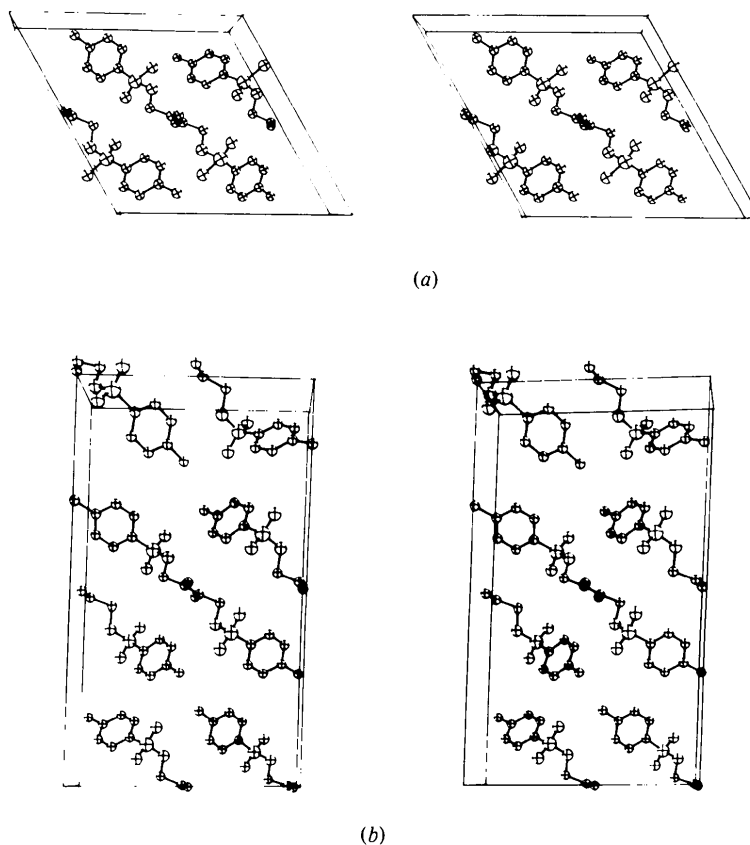


Fig. 1. Stereoscopic drawings (Johnson, 1965) of the crystal structures of the room-temperature and low-temperature phases of PT. (a) Room-temperature structure viewed along *b*. (b) Low-temperature structure viewed along *b*.

Table 2. *Crystal data for the room-temperature and low-temperature phases of PT*

The values in the last column have been calculated on the assumption that no lattice distortion occurs during the phase change. The corresponding lattice vectors are related by the equations $a' = -c$, $b' = b$, and $c' = 2a + c$.

	Room-temperature cell (Kobelt & Paulus, 1974)	Low-temperature cell found at 120 K	Calculated
a (Å)	14.493 (8)	14.93 (1)	14.936
b (Å)	4.910 (3)	4.910 (5)	4.910
c (Å)	14.936 (10)	25.56 (2)	25.591
β (°)	118.14 (4)	92 (1)	92.83
D_x (g cm ⁻³)	1.483	1.48	1.483
V_z (Å ³)	937.2	1872.6	1874.4
Z	2	4	4
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

row of polymer chains situated in the (102) cleavage plane of the high-temperature unit cell will move in one direction. In the neighbouring rows the side-group movement is in the opposite direction. This gives rise to a doubling of the unit cell. The molecular arrangement of the high-temperature structure is still visible as an 'almost symmetry' in the photographs. It should be noted that within the limit of experimental accuracy the phase change is not accompanied by a change of density or a lattice distortion. The unit-cell dimensions found in this study agree fairly well with the values found by Batchelder (1976) and Reimer, Bässler &

Debaerdemaeker (1977), who failed to observe the phase transition. The pertinent crystallographic data for the low-temperature and room-temperature phases of PT are listed in Table 2. The results of least-squares planes calculations are given in Table 3. Within the experimental error the phenyl rings are planar. During

Table 3. *Least-squares planes*

The values given are the distances in Å from the calculated plane which can be expressed as $P(xa) + Q(yb) + R(zc) = S$.

Plane 1		
S(1)	0.06	$P = 4.718$
C(4)	-0.05	$Q = 3.688$
C(5)	0.01	$R = 14.523$
C(6)	-0.01	$S = 11.151$
C(7)	-0.02	
C(8)	0.03	
C(9)	-0.04	
C(10)	0.03	

Plane 2		
S(2)	-0.05	$P = 7.716$
C(14)	0.01	$Q = 3.740$
C(15)	0.01	$R = 9.519$
C(16)	0.03	$S = 12.079$
C(17)	0.01	
C(18)	0.02	
C(19)	0.02	
C(20)	-0.06	

Angle between plane 1 and plane 2: 79.5°

Angle between plane 1 and plane of polymer backbone: 64.2°

Angle between plane 2 and plane of polymer backbone: 79.3°

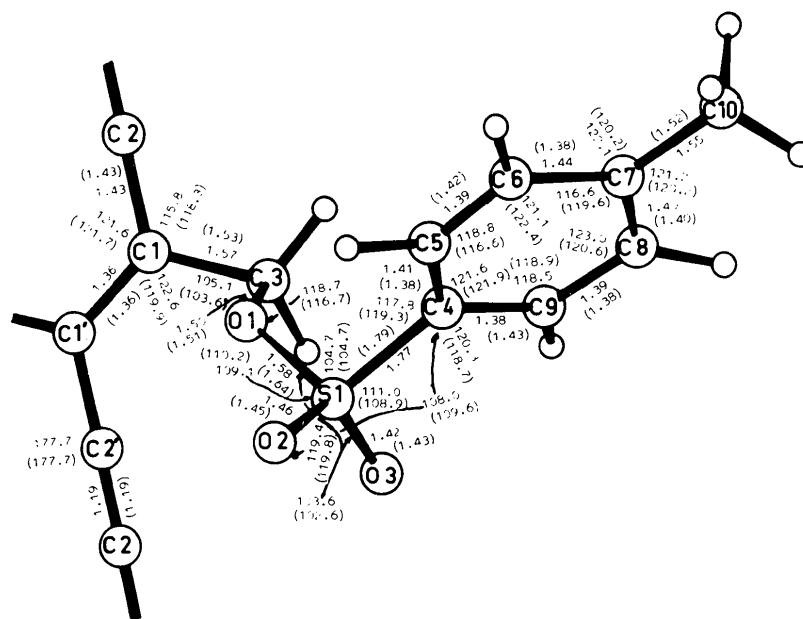


Fig. 2. Observed bond lengths and angles. The values in parentheses are the bond lengths and angles observed in the second independent fragment [S(2) to C(20)]. E.s.d.'s: S—O, 0.01; S—C, 0.02; C—C, 0.03 Å; O—S—O, 1.0; O—S—C, 1.6; C—C—C, 2.5°.

the phase transition the two rings rotate 8.0 and 7.1° in opposite directions away from the position they assume at room temperature. Here the angle between the plane of the polymer backbone and the rings is 72.2°.

Bond lengths and angles are given in Fig. 2. It should be noted that no change in bond lengths and angles can be detected during the course of the phase transition. Obviously, the change in side-chain packing accounts for the different electronic states of the polymer chain, as evidenced by spectroscopic methods. Further investigation of the temperature dependence and the kinetics of the phase change is necessary.

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The Crystal and Molecular Structure of Mascaroside, a New Bitter Glycoside from Coffee Beans

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The crystal and molecular structure of mascaroside (C₂₆H₃₆O₁₁) has been determined by direct methods and X-ray analysis. It crystallizes with two molecules of methanol in the monoclinic system, space group *P*2₁, with cell dimensions: *a* = 11.752 (6), *b* = 7.704 (4), *c* = 16.605 (8) Å, β = 106.68 (5)°, and *Z* = 2. The intensities were measured by an automatic diffractometer and refinement led to a conventional *R* value of 6%. The molecule is composed of a diterpene and a β-glucose unit attached to C(17).

Introduction

We report the structure determination of mascaroside. The compound is a bitter principle from beans of Malagasy *Coffea vianneyi* Leroy (Hammonniere, 1974). The very small amount of compound available and

chemical difficulties led us to study the structure by X-ray analysis.

A preliminary report of the preparation and structure of the title compound has already been published (Ducruix, Pascard, Hammonniere & Poisson, 1975). Here we give a detailed description of the molecular geometry.

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