

4,5,6-Tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose Diethyl Dithioacetal

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Abstract. $C_{35}H_{42}O_6S_4$, monoclinic, $P2_1$, $a = 9.185$ (1), $b = 10.0160$ (8), $c = 20.448$ (2) Å, $\beta = 99.29$ (1)°, $D_x = 1.23$ g cm⁻³ for $Z = 2$, $F(000) = 728$. Direct methods were used to determine the structure from four-circle diffractometer intensity measurements. Least-squares refinements using large blocks converged with $R = 0.091$. The absolute configuration was determined from the anomalous dispersion of the S atoms and confirmed that assigned by chemical and NMR methods. The molecule has a bent-chain conformation similar to that found in solution.

Introduction. Systematic absences noted on all Weissenberg and precession photographs ($0k0$, k odd) and the compound's optical activity suggested the space group to be $P2_1$. This assignment has been confirmed by the successful refinement.

A colourless crystal of dimensions $0.05 \times 0.30 \times 0.45$ mm was used for X-ray intensity measurements. 2042 independent reflexions [maximum $\theta = 50^\circ$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å] were measured on a Hilger & Watts diffractometer employing the ω - 2θ scan technique. The intensities were corrected for Lorentz and polarization effects, with the local program *HILGOUT*, but no absorption corrections were calculated ($\mu = 25.89$ cm⁻¹ for Cu $K\alpha$). The structure was solved by application of the tangent formula with *MULTAN* (Main, Woolfson & Germain, 1971). An E map computed from a set of 367 phased and weighted normalized structure factors ($R_{\text{Karle}} = 0.35$) revealed the positions of 17 out of 45 non-hydrogen atoms. An F_o Fourier synthesis following a least-squares refinement cycle revealed a further 23 atoms. The remaining non-hydrogen positions were established from repeated Fourier syntheses following least-squares refinement cycles.

Full-matrix refinement of positional and isotropic thermal parameters for the 1343 reflexions with $F_o^2 > 3\sigma(F_o^2)$ converged at $R = 0.120$. At this stage, structure factor calculations, including the anomalous scattering of the S atoms, demonstrated correct chirality ($R = 0.120$) in comparison with a model of opposite chirality ($R = 0.125$). For the final refinements the 1519

reflexions with $F_o^2 > 2\sigma(F_o^2)$, were regarded as 'observed'. Anisotropic thermal parameters were refined for the S and terminal O atoms, the ethyl groups and the phenyl rings.

Because eight intense, low-angle reflexions showed evidence of extinction, an extinction parameter was refined, and in every case resulted in significant improvement in these discrepancies between calculated and observed structure factors. The final value of the extinction parameter (EC), $0.7(2) \times 10^{-6}$, was obtained by minimizing the function $\sum w(f_o' - f_c')^2 \{ EC \times \beta \times I_o + [1 + (EC \times \beta \times I_o)^2]^{1/2} \}^2$, where β is Zachariasen's β function. This model converged with $R = 0.091$. The conventional value for all 2042 reflexions is 0.123. In the final cycle of refinement, the largest shift was 0.62σ and the average shift was 0.07σ . The standard error in an observation of unit weight is 1.47. The scattering factors of Cromer & Mann (1968) were used, with the anomalous dispersion corrections of Cromer (1965) applied to the scattering factors for S. The highest peaks in a final difference Fourier synthesis corresponded to H atom positions with a maximum calculated electron density (0.38 e Å⁻³) of about one third the height of the last C atom located by such methods.

Final positional parameters of all non-hydrogen atoms are given in Table 1. H atoms were not included in structure factor calculations but coordinates were derived for the seven H atoms attached to the C atoms of the central chain. These positions are listed in Table 2. Interatomic distances are given in Table 3.*

Calculations were carried out at the University of Canterbury on IBM360/44 and Burroughs B6718 computers. The structure factor calculations and full-matrix least-squares refinements were carried out with the program *CUCLS* and Fourier summations with the program *FOURIER*. These are highly modified ver-

* Lists of structure factors, anisotropic thermal parameters, interatomic angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32644 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

sions of *ORFLS* (Busing, Martin & Levy, 1962) and *FORDAP* (Zalkin, 1965). Figures were prepared with the program *ORTEP* (Johnson, 1970).

Discussion. When 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene- α -D-glucufuranose (II) is treated with ethanethiol in the presence of an acid catalyst a tetrathio product (I) is obtained which, initially (Brigl & Schinle, 1932), was described as 3,5,6-tri-*O*-benzoyl-2,4-di-*S*-ethyl-2,4-dithio-D-glucose diethyl dithioacetal. A reinvestigation, however, (Bethell & Ferrier, 1972*a,b*, 1973) led to the conclusion that the compound carried the ethylthio groups at C(1), C(1), C(2) and C(3)

Table 1. *Positional parameters* ($\times 10^4$) *for the non-hydrogen atoms with standard deviations in parentheses*

	x	y	z
S(1a)	991 (5)	299 (7)	6781 (2)
S(1b)	2456 (6)	2714	7448 (3)
S(2)	3373 (5)	-123 (6)	8170 (2)
S(3)	5912 (5)	1540 (6)	6690 (2)
O(4)	7846 (9)	1060 (10)	8212 (4)
O(41)	6845 (10)	993 (12)	9141 (4)
O(5)	6487 (10)	-1558 (10)	7079 (5)
O(51)	8021 (13)	-1780 (15)	6359 (6)
O(6)	7971 (11)	-2345 (13)	8399 (5)
O(61)	7616 (16)	-4136 (13)	7752 (6)
C(1)	2735 (17)	1212 (19)	6955 (8)
C(1a1)	1299 (50)	-429 (59)	5864 (29)
C(1a2)	775 (76)	580 (98)	5585 (39)
C(1b1)	1497 (35)	3633 (25)	6819 (14)
C(1b2)	1045 (36)	4978 (36)	7127 (15)
C(2)	3928 (15)	313 (16)	7372 (6)
C(21)	3214 (27)	-1966 (21)	8068 (10)
C(22)	2718 (20)	-2515 (24)	8698 (8)
C(3)	5433 (14)	1017 (15)	7492 (6)
C(31)	7044 (27)	2983 (20)	6912 (11)
C(32)	7344 (27)	3614 (22)	6250 (12)
C(4)	6669 (15)	138 (16)	7897 (7)
C(41)	7760 (14)	1415 (14)	8852 (6)
C(42)	8903 (15)	2390 (13)	9095 (6)
C(43)	8826 (20)	3057 (19)	9714 (7)
C(44)	9949 (24)	3968 (19)	9931 (10)
C(45)	11018 (20)	4329 (18)	9597 (9)
C(46)	11120 (21)	3731 (23)	8989 (8)
C(47)	10001 (16)	2749 (17)	8717 (7)
C(5)	7597 (14)	-730 (16)	7486 (6)
C(51)	6893 (17)	-1962 (17)	6493 (7)
C(52)	5736 (21)	-2788 (17)	6092 (7)
C(53)	5990 (29)	-3154 (22)	5473 (9)
C(54)	5021 (47)	-3897 (33)	5059 (12)
C(55)	3691 (38)	-4217 (29)	5234 (15)
C(56)	3313 (35)	-3814 (39)	5838 (16)
C(57)	4425 (29)	-3000 (31)	6275 (12)
C(6)	8668 (17)	-1653 (18)	7914 (8)
C(61)	7400 (16)	-3596 (18)	8259 (7)
C(62)	6695 (16)	-4137 (18)	8793 (8)
C(63)	5866 (20)	-5314 (19)	8621 (9)
C(64)	5160 (21)	-5816 (20)	9085 (12)
C(65)	5240 (25)	-5252 (27)	9721 (11)
C(66)	6060 (23)	-4126 (28)	9904 (9)
C(67)	6767 (19)	-3555 (17)	9413 (7)

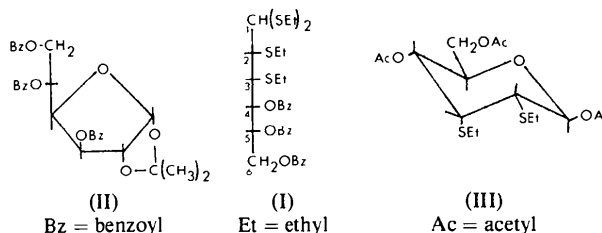
Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms*

	x	y	z
H(1)	305	146	655
H(2)	402	-49	713
H(3)	534	180	775
H(4)	625	-39	820
H(5)	812	-17	722
H(6a)	903	-229	764
H(6b)	946	-114	814

Table 3. *Interatomic distances* (Å) *with standard deviations in parentheses*

S(1a)-C(1)	1.83 (2)	C(1)-C(2)	1.56 (2)
S(1a)-C(1a1)	2.07 (5)	C(2)-C(3)	1.54 (2)
S(1b)-C(1)	1.85 (2)	C(3)-C(4)	1.56 (2)
S(1b)-C(1b1)	1.71 (3)	C(4)-C(5)	1.56 (2)
S(2)-C(2)	1.84 (1)	C(5)-C(6)	1.52 (2)
S(2)-C(21)	1.86 (2)	C(1a1)-C(1a2)	1.22 (9)
S(3)-C(3)	1.84 (1)	C(1b1)-C(1b2)	1.57 (4)
S(3)-C(31)	1.80 (2)	C(21)-C(22)	1.54 (2)
C(41)-O(41)	1.18 (1)	C(31)-C(32)	1.56 (3)
C(51)-O(51)	1.13 (2)	C(41)-C(42)	1.46 (1)
C(61)-O(61)	1.21 (2)	C(51)-C(52)	1.49 (2)
C(41)-O(4)	1.37 (1)	C(61)-C(62)	1.46 (2)
C(51)-O(5)	1.37 (2)	C(4)-O(4)	1.49 (2)
C(61)-O(6)	1.37 (2)	C(5)-O(5)	1.46 (2)
C-C(Ph4)	1.33 (3)-1.47 (2)	C(6)-O(6)	1.44 (2)
C-C(Ph5)	1.34 (2)-1.49 (3)		
C-C(Ph6)	1.33 (2)-1.42 (2)		

(direct NMR evidence), and that it had the *D-allo* configuration. This latter conclusion was based upon the conversion of the compound, by a four-step process, into 1,4,6-tri-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio- β -D-allopyranose (III), the relative configuration of which was readily determined by ring proton coupling analysis. In the deduction that (I) has the same configuration at C(2)-C(5) as (III) it was assumed that, in the intermediate steps of their interconversion, no stereochemical alterations occurred. The structure analysis reported here confirms the validity of this assumption and the assigned structure (I), including the absolute configuration. The numbering of the atoms in the central carbon chain is indicated on (I).



The favoured conformation for acyclic aldoose derivatives is the extended planar zigzag arrangement except for those configurations where this conformation would give rise to eclipsing interactions between substituents on alternate C atoms (Jeffrey & Kim, 1970; Angyal, Le Fur & Gagnaire, 1972). In such cases including acyclic aldoose derivatives, rotations about C—C bonds to give bent chains are expected [*e.g.* allitol (Azarnia, Jeffrey & Shen, 1972)].

The single-molecule diagram (Fig. 1) and the conformational angles (Fig. 2) show that in (I) there is a rotation about C(3)—C(4) [C(2)—C(3)⋯C(4)—C(5) is 93° rather than 180°] away from a planar zigzag. Thus, S(1*a*), C(1), C(2), C(3) and C(4) lie within 0.042 Å of one plane and C(3), C(4), C(5) and C(6) lie within 0.037 Å of a second plane at 88° from the first. The observation of S(1*a*) in the plane of the C chain atoms C(1) to C(4) is not surprising since this is the only staggered conformation about C(1)—C(2) that does not result in parallel interactions between S(3) and S(1*a*) or S(1*b*). However, the spatial arrangement of the S atoms about C(1) and C(2) does result in short non-bonded interatomic distances S(1*a*)—S(2) (3.32 Å) and S(1*b*)—S(2) (3.25 Å) (the van der Waals radius of S is 1.85 Å). This feature has been reported in the crystal structure of 2-*S*-ethyl-2-thio-*D*-mannose diethyl dithioacetal (Ducruix & Pascard-Billy, 1974).

NMR analysis (Bethell & Ferrier, 1972*a*) suggests that the molecule in chloroform solution adopts a somewhat similar mean conformation ($J_{2,3}$, 8.5 Hz; $J_{3,4}$, 4.8 Hz; $J_{4,5}$, 4.8 Hz), but that there is more flexibility at the C(4)—C(6) end than at the other end. This follows from the presence at C(1) of the two large thio substituents which act as a conformational constraint since they avoid eclipsing interactions with S(3).

The bond distances and angles of (I) are similar to those reported elsewhere, especially those determined for the mannose derivative mentioned above, ethyl 2-*S*-ethyl-1,2-dithio- α -*D*-mannofuranoside (Ducruix & Pascard-Billy, 1972) and tri-*O*-benzoyl- β -*D*-xylopyranosyl bromide (Luger, Durette & Paulsen, 1974).

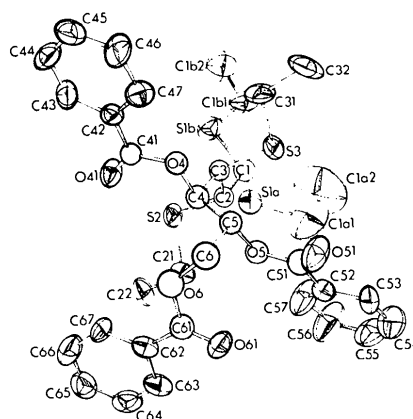


Fig. 1. A perspective view of one molecule.

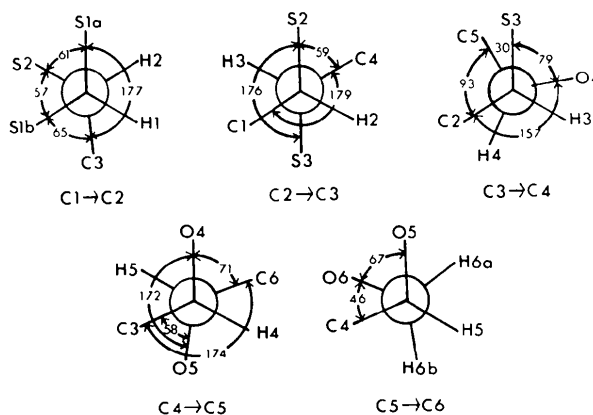


Fig. 2. Conformational angles (°) about C—C bonds.

From Fig. 1 it is apparent that the terminal ethyl group atoms C(1*a*1) and C(1*a*2) have high thermal motion. Such effects in ethyl groups attached to S atoms are not uncommon (*e.g.* Ducruix & Pascard-Billy, 1974).

This analysis provides unambiguous information for the above conformational discussion. However, the

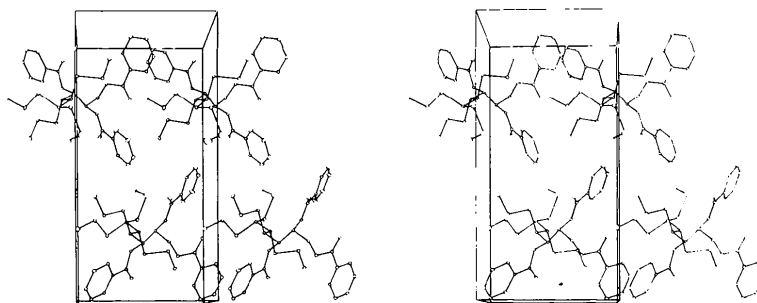


Fig. 3. Packing of molecules. View is down the *x* axis with the *y* axis horizontal.

limited extent of the data precludes useful further discussion of the bond lengths and bond angles.

The molecular packing is illustrated in Fig. 3. The molecules are well separated, the only intermolecular contacts not involving H and less than 3.5 Å being O(61)—C(31) (3.36 Å) and S(1a)—O(51) (3.43 Å).

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The Charge-Transfer Complex Phenanthrene–Pyromellitic Acid Dianhydride (PMDA)

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Abstract. C₂₄H₁₂O₆, $M_r = 396.36$. Monoclinic $P2_1/c$, $a = 7.046$ (3), $b = 13.494$ (2), $c = 19.396$ (7) Å, $\beta = 97.4$ (3)° (refined diffractometer data), $Z = 4$, D_m (flotation) = 1.40 (5), $D_c = 1.44$ g cm⁻³. Least-squares refinements using 2105 reflexion intensities have converged with $R = 0.066$. The crystal structure consists of stacks of alternating phenanthrene and PMDA molecules 3.36 Å apart with an angle of 4.11° between the normals to their planes. These normals make angles of 15.52 and 14.35° with the x axis respectively.

Introduction. π - π organic charge-transfer compounds are a class of compounds currently subject to intensive study. Such physical properties as exciton motion (Möhwald & Sackmann, 1974), photoconductivity (Haarer & Möhwald, 1975), electron mobility (Bergman & Jortner, 1974; Möhwald, Haarer & Castro, 1975) and fluorescence (Kepler, Caris,

Avakian & Abramson, 1963) are being investigated. Techniques in use include electron spin resonance (Dalal, Haarer, Bargon & Möhwald, 1975), emission and absorption spectroscopy (Haarer & Karl, 1973) and conductivity measurements (Batt, Braun & Hornig, 1968). A review of crystallographic work has been made by Herbstein (1971). The commonly occurring features he discusses are (1) the donor–acceptor separation distance of ~3.5 Å, (2) stacking of the donor and acceptor molecules in semi-infinite columns, (3) disorder, (4) centrosymmetric molecules, (5) the dihedral angle between adjacent molecules and (6) the non-perpendicularity of the planes of the component molecules with respect to the stack axis.

In the complex phenanthrene–PMDA, phenanthrene acts as an electron donor and PMDA as an electron acceptor. The physical properties of this complex have been measured by Haarer & Möhwald (1975). In their studies they have encountered a new phenomenon