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Structure of 3,10-Dithiabicyclo[10.2.2]hexadeca-12,14(1),15-triene

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Abstract. $C_{14}H_{20}S_2$, $M_r = 252\cdot446$, monoclinic, $P2_1/c$, $a = 16\cdot487$ (2), $b = 10\cdot213$ (2), $c = 8\cdot351$ (1) Å, $\beta = 99\cdot17$ (1)°, $V = 1388\cdot2$ (10) Å^3, $Z = 4$, $D_x = 1\cdot211$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot3469$ mm^{-1}, $F(000) = 544$, room temperature. Final $R = 0\cdot052$ for 1792 unique observed reflections. In the title compound, the molecule contains weak attractive interactions (hydrogen-bond-like) between one H of a CH_2 group and two π electrons in the aromatic ring. The distances are 2·604 and 2·646 Å respectively. The intramolecular bond lengths and angles show that the carbon framework is not strained.

Introduction. Proton NMR study (Ricci, Danieli, Phillips & Ridd, 1974) showed that the central methylene groups of the title compound are placed closely over the π-electron system of the phenyl ring. A large upfield shift (9·05 relative to Me_4Si) for the methylene group in question, which arises from the ring-current effect of the phenyl ring, was observed in deuterochloroform in comparison with the standard value. However, details of the relative conformation of the methylene groups are still unclear, because of the relatively large flexibility of the methylene system in solution. Here, we have undertaken a crystal-structure determination of this material to reveal the stereochemistry of the flexible methylene system in connection with the possible presence of a particular C—H$\cdots\pi$ interaction.

Experimental. Compound synthesized by a method of Voegtle (1970), recrystallized from hexane solution. Crystal 0·2 × 0·2 × 0·3 mm. Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined by least-squares methods on the basis of 25 2θ values ($33 < 2\theta < 38°$). Intensity measurement performed to $2\theta = 50°$. ω–2θ-scan technique, scan speed 2° min^{-1}. Three reference reflections showed no significant change in intensities, $0\cdot980 < |F_o|/|F_o|_{\rm initial} < 1\cdot020$. Space group $P2_1/c$, determined from systematic absences ($0k0$, k odd; $h0l$, l odd). 2457 reflections measured, $0 \le h \le 19$, $0 \le k \le 12$, $-9 \le l \le 9$, 191 weak reflections classified as unobserved [$|F_o| \le 3\sigma(|F_o|)$], 474 zero, 1792 non-zero unique reflections, corrected for Lorentz–polarization, not for absorption, direct methods, *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Full-matrix least-squares refinements with anisotropic thermal parameters using *UNICS*II (1967) computation programs. All H atoms found from difference syntheses and refined with isotropic thermal parameters. Unit weights on all reflections. $\sum||F_o| - |F_c||^2$ minimized. Final $R = 0\cdot052$, $wR = 0\cdot067$, $S = 1\cdot2$. $\Delta/\sigma < 0\cdot2$ for non-H atoms and $< 0\cdot3$ for H atoms. Max. and min. height in final difference synthesis $\pm 0\cdot2$ e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The fractional atomic coordinates are listed in Table 1.* The bond lengths, bond angles and torsion angles are shown in Table 2. The molecular structure and the numbering schemes are given in Fig. 1 and the packing arrangement of the molecules in Fig. 2 (Johnson, 1965).

The bond lengths and angles show that the carbon framework is under no strain at all. The molecule has no symmetry or pseudosymmetry elements. Two S atoms are located on the same side of the phenyl ring plane and three bonds of the hexamethylene group adopt *trans* (*anti*) conformation and the remaining two the *gauche* conformation (Table 2). The present stable

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43721 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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structure can be derived by a simple displacement of the atoms from a hypothetical conformation with a mirror symmetry that has the highest energy, since it contains a *cis* conformation about C6—C7. Short non-bonding interatomic distances were found between an H atom, H5*a* [$x = 0{\cdot}222\ (2)$, $y = 0{\cdot}418\ (3)$ and $z = 0{\cdot}695\ (4)$], in the hexamethylene group and two C atoms, C14 and C1, in the aromatic ring (2·604 and 2·646 Å respectively). These values are considerably smaller than the sum of the van der Waals radii for H and C (2·9 Å). The hexamethylene group, together with the two S atoms, can be librated around the longest axis C11—C12—C1—C2 without changing its conformation. If no attractive force between the phenyl ring and the methylene groups is operative, it should be possible to place atom H5*a* in a position relative to atom C14 so as to maintain the sum of the van der Waals radii (2·89 Å); however, even then the distance between atoms H5*a* and C1 remains the same. Furthermore, the crystal structure shows that atom H5*a* is almost above the *p* orbital of atom C14 (rather than atom C1); its overlap with the orbitals concerned seems to be favourable for the interaction, which has been described as a C—H···π interaction in the recent literature (Oda, Ohnuma & Ban, 1978; Fisher & Shigel, 1980; Kunieda, Endo, Hirota, Kodama & Nishio, 1983). Thus the present results suggest the possibility of the presence of this interaction between atoms H5*a* and C14. This material with a simple structure seems to be a suitable model for the detection of the presence of a weak association like the C—H···π interaction. If molecules have a complex structure or polar groups, a variety of factors may be operative in the determination of their stereochemistry, and thus participation of such weak association may be ordinarily masked by the above factors.

Table 1. *Final fractional coordinates and* $B_{\rm eq}$ *thermal factors for non-*H *atoms*

E.s.d.'s in parentheses are in the units of the least-significant digit.

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j b_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{\rm eq}$(Å^2)
C1	0·1737 (3)	0·5932 (5)	0·8936 (6)	3·8 (1)
C2	0·0839 (3)	0·5574 (6)	0·8914 (7)	5·2 (2)
S3	0·0559 (1)	0·4026 (2)	0·7801 (2)	5·0 (4)
C4	0·0941 (3)	0·4341 (6)	0·5870 (6)	4·6 (2)
C5	0·1794 (3)	0·3774 (5)	0·5880 (5)	3·7 (1)
C6	0·2124 (3)	0·4197 (5)	0·4322 (5)	4·1 (1)
C7	0·2949 (3)	0·3522 (5)	0·4197 (6)	4·4 (2)
C8	0·3632 (3)	0·3735 (5)	0·5597 (6)	4·2 (1)
C9	0·3931 (3)	0·5147 (5)	0·5767 (5)	4·1 (1)
S10	0·4697 (1)	0·5358 (2)	0·7582 (2)	5·8 (5)
C11	0·4258 (3)	0·6712 (6)	0·8640 (6)	5·0 (2)
C12	0·3390 (3)	0·6432 (5)	0·8827 (5)	3·7 (1)
C13	0·3171 (3)	0·5418 (5)	0·9798 (5)	3·6 (1)
C14	0·2346 (3)	0·5169 (5)	0·9853 (5)	3·6 (1)
C15	0·1955 (3)	0·6969 (5)	0·8003 (6)	4·4 (2)
C16	0·2781 (3)	0·7202 (5)	0·7954 (6)	4·5 (2)

Table 2. *Intramolecular bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

C1—C2	1·523 (7)	C8—C9	1·524 (7)
C1—C14	1·398 (6)	C9—S10	1·824 (4)
C1—C15	1·395 (7)	S10—C11	1·849 (6)
C2—S3	1·855 (6)	C11—C12	1·492 (7)
S3—C4	1·850 (5)	C12—C13	1·398 (7)
C4—C5	1·520 (7)	C12—C16	1·387 (7)
C5—C6	1·549 (7)	C13—C14	1·393 (7)
C6—C7	1·542 (7)	C15—C16	1·391 (8)
C7—C8	1·505 (6)		

C14—C1—C15	120·2 (4)	C8—C9—S10	111·1 (3)
C14—C1—C2	119·0 (4)	C9—S10—C11	102·3 (2)
C15—C1—C2	120·7 (4)	S10—C11—C12	111·2 (4)
C1—C2—S3	112·0 (4)	C11—C12—C13	122·9 (4)
C2—S3—C4	101·3 (3)	C11—C12—C16	117·5 (5)
S3—C4—C5	111·8 (3)	C13—C12—C16	119·6 (4)
C4—C5—C6	109·7 (4)	C12—C13—C14	119·9 (4)
C5—C6—C7	111·3 (4)	C13—C14—C1	120·0 (4)
C6—C7—C8	116·3 (4)	C1—C15—C16	119·1 (4)
C7—C8—C9	113·6 (4)	C15—C16—C12	121·2 (5)

S3—C4—C5—C6	−173·7 (3)	C6—C7—C8—C9	−66·3 (5)
C4—C5—C6—C7	−173·9 (3)	C7—C8—C9—S10	175·2 (3)
C5—C6—C7—C8	−57·2 (5)		

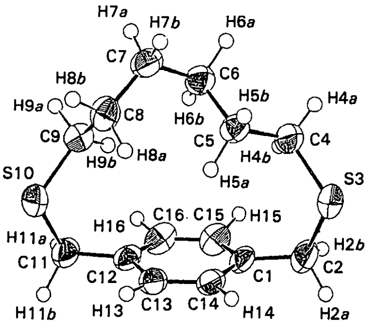

Fig. 1. Molecular structure with the atom-numbering scheme.

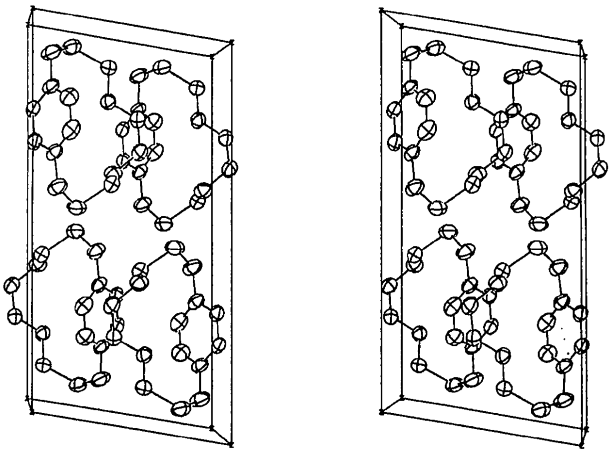

Fig. 2. Packing scheme of the molecules viewed along the *b* axis.

Calculations were carried out on a FACOM-M382 computer at the Data Processing Center, Kyoto University. The values for the molecular geometry were calculated using a part of the *KPPXRAY* (Taga, Higashi & Iizuka, 1985) program package.

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Structure of a Galacto-Benzofuranone Oxime

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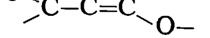
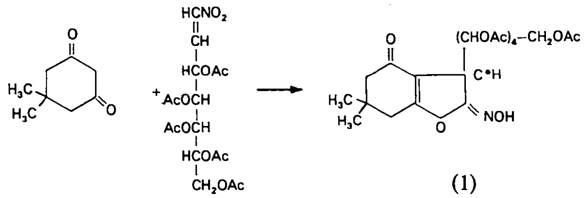
Abstract. (3*R*)-3,5,6,7-Tetrahydro-2-hydroxyimino-6,6-dimethyl-3-(1,2,3,4,5-penta-*O*-acetyl-D-*galacto*-pentitol-1-yl)benzofuran-4(2*H*)-one, $C_{25}H_{33}NO_{13}$, $M_r = 555{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}105\ (1)$, $b = 30{\cdot}316\ (2)$, $c = 8{\cdot}436\ (1)$ Å, $V = 2840{\cdot}0\ (4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}29$, $D_x = 1{\cdot}30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}0989$ mm^{-1}, $F(000) = 1176$, $T = 300$ K, final $R = 0{\cdot}092$, $wR = 0{\cdot}062$ for 1934 observed $[I > 2\sigma(I)]$ independent reflections. The form of the oxime is *E*. The cyclohexene ring conformation is 'half-chair' and the dihedral angle between the plane part of the cyclohexane ring and the furan plane is 7·1 (5)°. There is some electron delocalization along the resonance system  $\mathrm{O{=}C{-}C{=}C(C{-})(O{-})}$ of the benzofuranone group. The configuration around the chiral centres of the sugar chain is *R*, *S*, *R* and *S* respectively, that is D-*galacto*. The new chiral centre C(3′) is *R*. Packing is governed by an intermolecular hydrogen bond between the oxime oxygen and the oxygen of the cyclohexenone group which stabilizes the crystal structure. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

Introduction. This compound is one of a series of benzofuran-4(5*H*)-one 'derivatives' that we are investigating in order to determine their stereochemistry in the solid state. We have previously reported the crystal structure of an analogue, the (3*R*)-3-(D-*galacto*-pentaacetoxypentyl-6,7-dihydro-2-hydroxyimino-4(5*H*)-benzofuranone (Diánez, López-Castro & Márquez, 1986). The title compound was obtained by an abnormal Michael reaction of 5,5-dimethylcyclohexane-1,3-dione with pentaacetoxy-1,2-dideoxy-1-nitrohept-1-enitol (Gómez-Sánchez, Galán, Rico & Bellanato, 1985).



(1)

These compounds are substances of considerable interest as precursors of *C*-glycosyl benzofuranones. A new chiral centre is produced (marked with an asterisk) and only an X-ray crystallographic study can help us to establish the crystal and molecular structure and the stereochemistry of this compound.

Experimental. Crystals are colourless prisms with well shaped faces (0·48 × 0·25 × 0·40 mm). D_m measured

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