

Declercq & Woolfson, 1980). Full-matrix least-squares refinement on F values with *SHELX76* (Sheldrick, 1976). Non-H atoms refined anisotropically, H atoms calculated geometrically (except for OH which was located from the difference map) and allowed to 'ride' on associated heavy atoms with two common isotropic temperature factors for methylene, and methine H and OH, respectively, for a total of 133 variables. $R = 0.041$, $wR = 0.046$ where $w = 2.6203/[\sigma^2(F) + 0.0010F^2]$. Final $(\Delta/\sigma)_{\max} < 0.02$, $\Delta\rho_{\max} = 0.16$ and $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$ on final difference map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).^{*} Atom parameters are listed in Table 1 and bond lengths and angles in Table 2. The molecule and numbering scheme are shown in Fig. 1.

Related literature. Structures of 39 compounds containing the 1,3-dithianyl moiety are listed in the Cambridge Crystallographic Database. Of these, seven have the ring system unsubstituted except by a group attached through C at the 2-position. The ring geometry in the functionally simplest derivative, 2-phenyl-1,3-dithiane (Kalf & Romers, 1966), is similar to the ring geometries in the present structure.

^{*} Lists of structure factors, H-atom coordinates and isotropic temperature factors, and anisotropic temperature factors for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43535 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

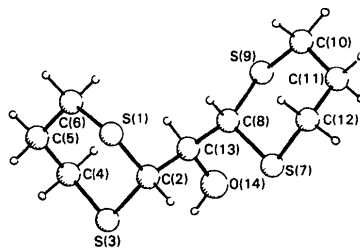


Fig. 1. A view of the molecule drawn with *PLUTO* (Motherwell & Clegg, 1978).

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References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KALFF, H. T. & ROMERS, C. (1966). *Acta Cryst.* **20**, 490–496.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of a Photochromic Benzoxazine Derivative

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Abstract. 1,3,3,5,6-Pentamethylspiro(indoline-2,3'-3H-pyrido[3,2-f][1,4]benzoxazine), $C_{23}H_{23}N_3O$, $M_r = 357.5$, monoclinic, $P2_1/c$, $a = 11.091$ (1), $b = 16.115$ (2), $c = 11.085$ (1) Å, $\beta = 92.83$ (2)°, $V = 1978.8$ Å³, $Z = 4$, $D_x = 1.200 \text{ Mg m}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.55 \text{ mm}^{-1}$, $F(000) = 760$, $T = 293 \text{ K}$, $R = 0.097$ for 1308 unique observed reflections. The monomeric molecule, with no short intermolecular contacts, consists of a substituted benzoxazine ring

linked to an indoline ring through a spiro C atom. There is a 1:1 disorder of NMe and CMe₂ in the indoline ring.

Experimental. Compound prepared by literature method (Kwak & Hurditch, 1984) as a mixture of 1,3,3,5,6- and 1,3,3,4,5-isomers. Crystallization by slow evaporation of an acetone solution at room temperature produces needle-like yellow crystals of the title compound (I) and block yellow crystals of the 1,3,3,4,5-

isomer (II) (X-ray structural data on the latter isomer confirm its formulation but are of poor quality). Crystal size $0.62 \times 0.12 \times 0.08$ mm, Siemens AED2 diffractometer, cell parameters from 2θ values of 30 reflections ($20 < 2\theta < 35^\circ$), 4111 reflection intensities measured in ω/θ scan mode, scan width $0.85^\circ + \alpha$ -doublet splitting, scan time 14–70 s, $2\theta_3 \rightarrow 115^\circ$, $h-12 \rightarrow 12$, $k 0 \rightarrow 17$, $l-11 \rightarrow 4$. No absorption correction. No significant intensity variation of three standard reflections. 2692 unique reflections ($R_{\text{int}} = 0.077$), 1308 with $F > 6\sigma(F)$. Structure solved by direct methods and difference syntheses, refined by blocked-cascade least squares to minimize $\sum w\Delta^2$; $w^{-1} = \sigma^2(F)$. Anisotropic thermal parameters for all non-H atoms, H atoms constrained to give C–H = 0.96 \AA , H–C–H = 109.5° , olefinic and aromatic C–H on external C–C–C angles, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The NMe and CMe₂ groups of the indoline ring are disordered by mutual exchange. A simple disorder model was adopted, with each group refined as CMeMe*, where Me is a normal and Me* a half-occupied site for methyl. (Free refinement of site occupation factors for all four methyl sites gave two values insignificantly different from 1.0 and two of essentially 0.5, supporting this simple model.) Thus, differences in scattering power of N and C, and differences in the expected geometry around these atoms, are not allowed for, and this imperfect disorder model accounts for the high final R indices.

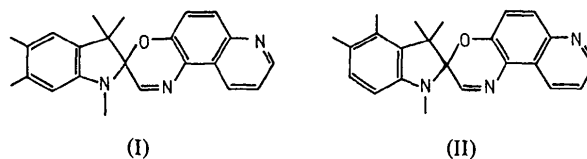
Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

	x	y	z	U_{eq}
O(1)	3001 (5)	3593 (3)	1995 (3)	74 (2)
C(2)	2750 (7)	4398 (4)	2196 (5)	58 (3)
C(3)	2622 (7)	4621 (4)	3431 (5)	69 (3)
C(4)	2401 (7)	5438 (4)	3693 (6)	74 (3)
C(5)	2288 (6)	6040 (4)	2820 (6)	58 (3)
N(6)	2042 (6)	6835 (3)	3172 (5)	80 (3)
C(7)	2007 (8)	7400 (5)	2316 (7)	85 (4)
C(8)	2157 (7)	7264 (4)	1113 (6)	77 (3)
C(9)	2407 (7)	6465 (4)	745 (6)	73 (3)
C(10)	2478 (7)	5832 (4)	1625 (6)	58 (3)
C(11)	2718 (7)	4987 (4)	1321 (6)	65 (3)
N(12)	2981 (7)	4777 (4)	134 (5)	90 (3)
C(13)	3077 (9)	3991 (5)	-102 (7)	96 (4)
C(14)	2945 (7)	3301 (4)	747 (6)	66 (3)
N(15)	3841 (7)	2663 (4)	633 (6)	57 (3)
C(16)	3317 (7)	1912 (4)	1024 (5)	73 (3)
C(17)	3822 (10)	1164 (4)	1394 (6)	101 (4)
C(18)	3146 (10)	523 (5)	1699 (8)	87 (4)
C(19)	1921 (11)	604 (5)	1624 (7)	104 (5)
C(20)	1321 (11)	1328 (5)	1266 (7)	123 (5)
C(21)	2073 (7)	2000 (4)	945 (6)	74 (3)
C(22)	1784 (8)	2839 (4)	509 (6)	69 (3)
C(23)	3664 (11)	-321 (5)	2091 (9)	167 (7)
C(24)	1045 (12)	-130 (7)	2034 (10)	174 (7)
C(25)	5019 (12)	2865 (7)	1104 (11)	177 (7)
C(26)	648 (8)	3214 (6)	1003 (9)	146 (6)
C(27)*	1301 (16)	2756 (9)	-772 (11)	86 (7)
C(27x)*	4239 (20)	2511 (14)	-655 (15)	160 (13)

* Site occupation factor = 0.5.

$R = 0.097$, $wR = 0.090$, slope of normal probability plot = 2.30, $(\Delta/\sigma)_{\text{max}} = 0.004$, $(\Delta/\sigma)_{\text{mean}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.53$, $(\Delta\rho)_{\text{min}} = -0.38 \text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *SHELXTL* (Sheldrick, 1985). Table 1 gives atom parameters and Table 2 bond lengths and angles.* Fig. 1 shows a view of the molecule.



* 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 43618 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O(1)–C(2)	1.347 (8)	O(1)–C(14)	1.460 (7)
C(2)–C(3)	1.429 (9)	C(2)–C(11)	1.356 (9)
C(3)–C(4)	1.374 (10)	C(4)–C(5)	1.371 (9)
C(5)–N(6)	1.372 (8)	C(5)–C(10)	1.392 (9)
N(6)–C(7)	1.314 (10)	C(7)–C(8)	1.369 (11)
C(8)–C(9)	1.384 (10)	C(9)–C(10)	1.410 (9)
C(10)–C(11)	1.431 (9)	C(11)–N(12)	1.403 (8)
N(12)–C(13)	1.299 (10)	C(13)–C(14)	1.468 (10)
C(14)–N(15)	1.439 (10)	C(14)–C(22)	1.500 (11)
N(15)–C(16)	1.420 (10)	N(15)–C(25)	1.420 (15)
N(15)–C(27x)	1.535 (19)	C(16)–C(17)	1.383 (10)
C(16)–C(21)	1.385 (12)	C(17)–C(18)	1.329 (13)
C(18)–C(19)	1.363 (17)	C(18)–C(23)	1.532 (12)
C(19)–C(20)	1.391 (13)	C(19)–C(24)	1.611 (16)
C(20)–C(21)	1.424 (13)	C(21)–C(22)	1.466 (10)
C(22)–C(26)	1.524 (13)	C(22)–C(27)	1.499 (14)
C(2)–O(1)–C(14)	117.8 (5)	O(1)–C(2)–C(3)	115.5 (5)
O(1)–C(2)–C(11)	123.7 (6)	C(3)–C(2)–C(11)	120.6 (6)
C(2)–C(3)–C(4)	118.1 (6)	C(3)–C(4)–C(5)	122.7 (6)
C(4)–C(5)–N(6)	118.2 (6)	C(4)–C(5)–C(10)	119.3 (6)
N(6)–C(5)–C(10)	122.5 (6)	C(5)–N(6)–C(7)	116.1 (6)
N(6)–C(7)–C(8)	126.4 (7)	C(7)–C(8)–C(9)	118.1 (6)
C(8)–C(9)–C(10)	118.3 (6)	C(5)–C(10)–C(9)	118.6 (6)
C(5)–N(10)–C(11)	119.4 (6)	C(9)–C(10)–C(11)	122.0 (6)
C(2)–C(11)–C(10)	119.8 (6)	C(2)–C(11)–N(12)	120.2 (6)
C(10)–C(11)–N(12)	120.0 (6)	C(11)–N(12)–C(13)	116.5 (6)
N(12)–C(13)–C(14)	126.7 (7)	O(1)–C(14)–C(13)	111.3 (5)
O(1)–C(14)–N(15)	108.4 (6)	C(13)–C(14)–N(15)	113.2 (7)
O(1)–C(14)–C(22)	108.8 (6)	C(13)–C(14)–C(22)	112.0 (6)
N(15)–C(14)–C(22)	102.7 (6)	C(14)–N(15)–C(16)	106.8 (6)
C(14)–N(15)–C(25)	115.5 (7)	C(16)–N(15)–C(25)	117.8 (7)
C(14)–N(15)–C(27x)	115.3 (9)	C(16)–N(15)–C(27x)	106.7 (10)
C(25)–N(15)–C(27x)	94.4 (10)	N(15)–C(16)–C(17)	131.9 (8)
N(15)–C(16)–C(21)	108.3 (6)	C(17)–C(16)–C(21)	119.7 (7)
C(16)–C(17)–C(18)	121.8 (10)	C(17)–C(18)–C(19)	118.9 (8)
C(17)–C(18)–C(23)	123.6 (10)	C(19)–C(18)–C(23)	117.4 (8)
C(18)–C(19)–C(20)	124.0 (9)	C(18)–C(19)–C(24)	121.7 (8)
C(20)–C(19)–C(24)	114.2 (10)	C(19)–C(20)–C(21)	115.5 (10)
C(16)–C(21)–C(20)	120.0 (7)	C(16)–C(21)–C(22)	108.5 (7)
C(20)–C(21)–C(22)	131.5 (8)	C(14)–C(22)–C(21)	103.1 (6)
C(14)–C(22)–C(26)	117.3 (6)	C(21)–C(22)–C(26)	114.8 (7)
C(14)–C(22)–C(27)	118.3 (8)	C(21)–C(22)–C(27)	107.0 (7)
C(26)–C(22)–C(27)	96.5 (9)		

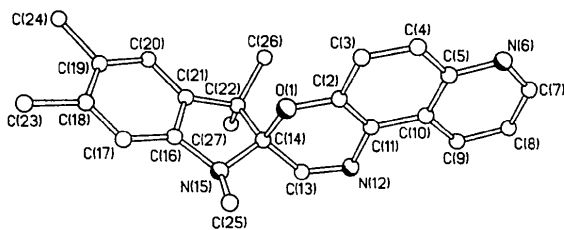


Fig. 1. A view of the molecule showing the atom-numbering scheme adopted. Only one component of the disorder is shown; the other exchanges the role of N(15) and C(22), replacing C(27) by C(27 x) attached to N(15). H atoms omitted.

Related literature. The compound is a member of a class of spiroindolinopyridobenzoxazines which exhibit photochromic properties (Kwak & Hurditch, 1984). Additional classes of compounds, namely the spiroindolinobenzopyrans and spiroindolinonaphthoxazines (Chu, 1983) also show similar photochromic properties. This is the first report of structural data for the spiroindolinopyridobenzoxazines although structures have been reported on spiroindolinobenzopyrans

Acta Cryst. (1987). C **43**, 806–808

The Tetrasaccharide Stachyose

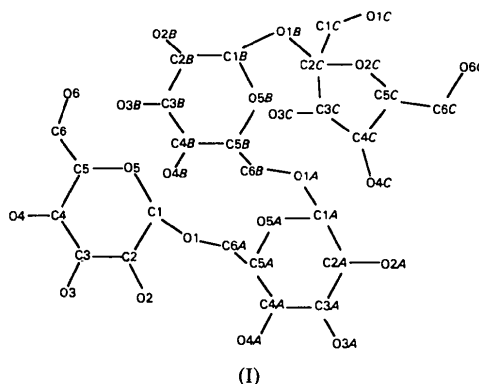
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Abstract. *O*- α -D-Galactopyranosyl-(1 \rightarrow 6)-*O*- α -D-galactopyranosyl-(1 \rightarrow 6)-*O*- α -D-glucopyranosyl (1 \rightarrow 2)- α -D-fructofuranoside pentahydrate, C₂₄H₄₂O₂₁·5H₂O, M_r = 756.7, orthorhombic, $P2_12_12_1$, a = 12.801 (6), b = 24.026 (5), c = 10.856 (6) Å, V = 3338.8 (2) Å³, Z = 4, D_x = 1.505 Mg m⁻³, λ (Cu K α) = 1.54178 Å, μ = 1.159 mm⁻¹, $F(000)$ = 1616, T = 568 K, final R = 0.060 for 3120 unique observed reflections. The three pyranose rings are normal chair forms and the fructofuranosyl ring is puckered with conformation $_3T^4$ according to the nomenclature of Jeffrey & Park [*Acta Cryst.* (1972), B **28**, 257–267]. Several distinct H₂O molecules were found in difference maps. All of the waters refined to partial occupancies; however, none could be omitted without a significant increase in the overall R factor. No single hydrogen-bonding network can involve the full set of solvent molecules which contains several pairs which cannot coexist because they are too close to one another. Several distinct hydrogen-bonding schemes are possible, each involving different sets of three or four solvent molecules.

Experimental. Crystals of the title compound (I) from a commercial sample (Sigma Chemical Co.), 0.15 \times 0.10 \times 0.30 mm, Picker FACS-I diffractometer, $\theta/2\theta$



data collection, scan width 2°, 2 θ scan rate 2° min⁻¹, 10 s background count, 2 θ < 127.3°, lattice parameters from 12 reflections with 35 < 2 θ < 50°, corrections for Lorentz and polarization but not

(Simkin, Makarov, Furmanova, Karaev & Minkin, 1984). A general discussion of these and other photochromic compounds is available (Bertelson, 1971).

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References

- BERTELSON, R. C. (1971). In *Photochromism*, edited by G. H. BROWN, ch. 3, pp. 45–431. New York: Wiley-Interscience.
- CHU, N. Y. C. (1983). *Can. J. Chem.* **61**, 300–305.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KWAK, W. S. & HURDITCH, R. J. (1984). European Patent Application No. 84113167.5.
- SHELDRIK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, revision 5. Univ. of Göttingen.
- SIMKIN, B. YA., MAKAROV, S. P., FURMANOVA, N. G., KARAIEV, K. SH. & MINKIN, V. I. (1984). *J. Gen. Chem. USSR*, **54**, 602–607, and references therein.