

Diethyl 2,2-Difluoro-3-phenyl-1,3,2-oxazaborino[6,5-*b*]indole-4,9-dicarboxylate

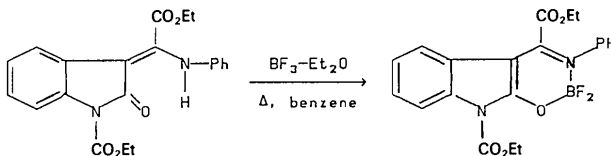
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(Received 6 October 1989; accepted 1 November 1989)

Abstract. $C_{21}H_{19}BF_2N_2O_5$, $M_r = 428.20$, monoclinic, $P2_1/n$, $a = 7.459$ (1), $b = 11.170$ (2), $c = 25.518$ (3) Å, $\beta = 97.84$ (1)°, $V = 2106$ (1) Å³, $Z = 4$, $D_x = 1.350$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.1$ mm⁻¹, $F(000) = 888$, room temperature, final $R = 0.050$ for 2734 observed reflections [$I > 2\sigma(I)$]. The crystal structure shows that the conformation of the six-membered heterocyclic ring can be described as a mesomeric form, with $N \rightarrow B-O$ and $N-B \leftarrow O$ bonds.

Introduction. Studying the synthesis of new compounds with possible biological activity, Marchesini (1989) starting from the 2-indolone derivative (I) obtained the new heterocycle (II), according to the scheme:



X-ray analysis of (II) was undertaken to confirm the structure of the new heterocycle and, moreover, because in the crystallographic literature there are very few compounds containing an O, B, N six-membered heterocycle.

Experimental. IR data (Nujol): 1763, 1738, 1625 cm⁻¹; ¹H NMR data (CHCl₃): 8.3 (1H, *m*), 7.55 (3H, *m*), 4.75 (2H, *q*), 4.33 (2H, *q*), 1.68 (3H, *t*), 1.15 (3H, *t*); melting point 427–428 K. Crystals suitable for X-ray analysis obtained by slow evaporation from dichloromethane. Crystal size 0.40 × 0.28 × 0.24 mm. Nonius CAD-4 diffractometer with graphite monochromator; lattice parameters measured with 25 reflections in the θ range 16–18°; data collection: $0 < \theta < 27.5^\circ$; hkl range: 0 → 9, 0 → 14, -33 → 33; three standard reflections, no significant variation of intensities. Of 4834 independent data collected, 2734 with $I > 2\sigma(I)$ were considered observed. Data were corrected for Lorentz and polarization coefficients, but not for absorption. The structure was solved by direct methods using

MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All 30 heavy atoms were obtained from the 'best' E map. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4I_o/[\sigma^2(I_o) + 0.0004I_o^2]$ and I_o is the intensity on absolute scale. Heavy atoms were refined with anisotropic thermal parameters, H atoms with isotropic ones. H atoms bonded to methyl groups and to C(26) were placed in calculated positions and not refined. A secondary-extinction parameter g [Larson (1967), equation (3)] was refined [final value $6.0(7) \times 10^{-6}$]. The range of the final difference Fourier map was ± 0.3 e Å⁻³; in the last cycle, $(\Delta/\sigma)_{\max} = 0.05$, $S = 1.89$, $R = 0.050$ and $wR = 0.044$ for 2734 observed reflections. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Programs used include Enraf-Nonius *SDP-Plus* (Frenz, 1983), *ORTEPII* (Johnson, 1976), *PARST* (Nardelli, 1982), and various in-house programs for refinement and geometrical analysis running on a Gould NP1 computer.

Discussion. Table 1 lists final coordinates and U_{eq} values for non-H atoms.* Fig. 1 shows the molecule with the numbering scheme of the heavy atoms. Table 2 reports some geometrical parameters of the O, B, N heterocycle of (II) compared with those of the same ring in diphenyl[salicylidinaminato-*O,N*]-boron [(III), Kliegel, Rettig & Trotter, 1984] and in bis[diphenyl[salicylidiniminato(2-)]boron] [(IV), Rettig & Trotter (1983)]. Table 3 lists the remaining bond distances and bond angles of (II) involving the heavy atoms. As can be seen from Table 2, the most relevant differences of (II) with respect to (III) and (IV) are the shortening of O(1)–C(13) and C(4)–C(5) bond distances, the elongation of N(3)–C(4), and the reduced torsion angles along the ring, *i.e.* a more marked planarity of the same. All these structural data are consistent with a greater

* 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 52760 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and U_{eq} (Å²)
$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	U_{eq}
F(14)	0.3820 (2)	0.3751 (1)	0.21451 (5)	0.0801 (5)
F(15)	0.1351 (2)	0.2809 (1)	0.17388 (5)	0.0777 (5)
O(1)	0.2680 (2)	0.4317 (1)	0.12979 (5)	0.0617 (5)
O(23)	0.4612 (2)	0.0265 (1)	0.06628 (6)	0.0725 (5)
O(24)	0.6984 (2)	0.1498 (1)	0.06960 (5)	0.0147 (5)
O(28)	0.1208 (2)	0.6766 (2)	0.00944 (7)	0.0919 (7)
O(29)	0.1765 (2)	0.6439 (1)	0.09659 (6)	0.0779 (6)
N(3)	0.4209 (2)	0.2343 (1)	0.14578 (6)	0.0482 (6)
N(12)	0.2387 (2)	0.4986 (2)	0.04159 (7)	0.0573 (6)
C(4)	0.4350 (2)	0.2272 (2)	0.09474 (7)	0.0446 (6)
C(5)	0.3578 (3)	0.3144 (2)	0.05995 (7)	0.0465 (6)
C(6)	0.3524 (3)	0.3346 (2)	0.00348 (8)	0.0523 (7)
C(7)	0.4039 (3)	0.2673 (2)	-0.03776 (8)	0.0638 (8)
C(8)	0.3799 (3)	0.3143 (2)	-0.08814 (9)	0.079 (1)
C(9)	0.3067 (4)	0.4276 (3)	-0.09758 (9)	0.087 (1)
C(10)	0.2542 (3)	0.4965 (2)	-0.05783 (9)	0.0745 (9)
C(11)	0.2783 (3)	0.4486 (2)	-0.00707 (8)	0.0574 (8)
C(13)	0.2857 (3)	0.4152 (2)	0.08068 (8)	0.0523 (7)
C(16)	0.5201 (3)	0.1507 (2)	0.18228 (8)	0.515 (7)
C(17)	0.7053 (3)	0.1591 (2)	0.19295 (8)	0.0625 (8)
C(18)	0.8007 (3)	0.0772 (2)	0.2265 (1)	0.083 (1)
C(19)	0.7116 (4)	-0.0106 (3)	0.2490 (1)	0.093 (1)
C(20)	0.5272 (4)	-0.0173 (3)	0.2391 (1)	0.103 (1)
C(21)	0.4294 (3)	0.0636 (2)	0.2059 (1)	0.0805 (9)
C(22)	0.5321 (3)	0.1212 (2)	0.07522 (7)	0.0481 (6)
C(25)	0.8134 (3)	0.0527 (2)	0.0543 (1)	0.085 (1)
C(26)	1.0003 (3)	0.0844 (2)	0.0699 (1)	0.092 (1)
C(27)	0.1717 (3)	0.6159 (2)	0.04674 (9)	0.0668 (8)
C(30)	0.1122 (4)	0.7636 (2)	0.1073 (1)	0.096 (1)
C(31)	0.1065 (6)	0.7718 (3)	0.1643 (1)	0.138 (2)
B(2)	0.2984 (3)	0.3310 (2)	0.1681 (1)	0.0545 (8)

Table 2. Bond distances (Å), bond angles and torsion angles (°) in O, B, N heterocycle of (II), compared with equivalent parameters found in (III) and (IV); data from (III) refer to the two molecules in the asymmetric unit, and those from (IV) to two equivalent parts of the molecule

	(II)	(III)	(IV)
O(1)—B(2)	1.487 (3)	1.513, 1.512	1.467, 1.486
O(1)—C(13)	1.291 (3)	1.350, 1.353	1.347, 1.345
N(3)—B(2)	1.571 (3)	1.600, 1.603	1.599, 1.572
N(3)—C(4)	1.323 (2)	1.279, 1.279	1.275, 1.277
C(4)—C(5)	1.389 (3)	1.434, 1.438	1.441, 1.442
C(5)—C(13)	1.384 (3)	1.407, 1.403	1.403, 1.409
C(13)—O(1)—B(2)	120.2 (2)	121.9, 121.4	119.5, 119.4
O(1)—B(2)—N(3)	109.0 (2)	103.8, 103.9	104.6, 104.8
C(4)—N(3)—B(2)	121.8 (2)	124.6, 124.8	123.1, 124.2
N(3)—C(4)—C(5)	120.4 (2)	120.2, 119.8	118.5, 118.3
C(4)—C(5)—C(13)	118.4 (2)	119.1, 119.3	118.3, 118.6
O(1)—C(13)—C(5)	125.7 (2)	120.0, 120.4	121.3, 120.8
C(13)—O(1)—B(2)—N(3)	22.3 (2)	37.0, 37.0	41.4, 41.2
O(1)—B(2)—N(3)—C(4)	-21.6 (2)	-27.6, -27.5	-35.9, -34.2
B(2)—N(3)—C(4)—C(5)	7.5 (3)	6.7, 6.7	9.6, 8.8
N(3)—C(4)—C(5)—C(13)	7.7 (3)	9.8, 9.1	14.6, 13.2
C(4)—C(5)—C(13)—O(1)	-6.8 (3)	-0.1, 0.9	-8.3, -5.2
C(5)—C(13)—O(1)—B(2)	-10.2 (3)	-26.8, -27.4	-23.6, -25.5

Table 3. Bond lengths (Å) and bond angles (°) for (II), not included in Table 2

F(14)—B(2)	1.354 (3)	F(15)—B(2)	1.367 (3)
O(23)—C(22)	1.191 (3)	O(24)—C(22)	1.308 (3)
O(24)—C(25)	1.468 (3)	O(28)—C(27)	1.188 (3)
O(29)—C(27)	1.306 (3)	O(29)—C(30)	1.459 (3)
N(3)—C(16)	1.449 (3)	N(12)—C(11)	1.429 (3)
N(12)—C(13)	1.375 (3)	N(12)—C(27)	1.415 (3)
C(4)—C(22)	1.508 (3)	C(5)—C(6)	1.454 (3)
C(6)—C(7)	1.389 (3)	C(6)—C(11)	1.400 (3)
C(7)—C(8)	1.378 (3)	C(8)—C(9)	1.386 (4)
C(9)—C(10)	1.372 (4)	C(10)—C(11)	1.390 (3)
C(25)—C(26)	1.441 (3)	C(30)—C(31)	1.464 (4)
C(22)—O(24)—C(25)	116.5 (2)	C(7)—O(29)—C(30)	115.9 (2)
C(16)—N(3)—B(2)	118.8 (2)	C(4)—N(3)—C(16)	119.5 (2)
C(13)—N(12)—C(27)	128.2 (2)	C(11)—N(12)—C(27)	124.1 (2)
C(11)—N(12)—C(13)	107.7 (2)	N(3)—C(4)—C(22)	118.6 (2)
C(5)—C(4)—C(22)	121.0 (2)	C(4)—C(5)—C(6)	134.1 (2)
C(6)—C(5)—C(13)	107.0 (2)	C(5)—C(6)—C(11)	106.8 (2)
C(5)—C(6)—C(7)	133.9 (2)	C(7)—C(6)—C(11)	119.3 (2)
C(6)—C(7)—C(8)	119.1 (2)	C(7)—C(8)—C(9)	120.5 (2)
C(8)—C(9)—C(10)	121.9 (2)	C(9)—C(10)—C(11)	117.3 (2)
C(6)—C(11)—C(10)	121.8 (2)	N(12)—C(11)—C(10)	130.1 (2)
N(12)—C(11)—C(6)	108.2 (2)	N(12)—C(13)—C(5)	110.4 (2)
O(1)—C(13)—N(12)	123.9 (2)	N(3)—C(16)—C(21)	120.1 (2)
N(3)—C(16)—C(17)	119.7 (2)	O(24)—C(22)—C(4)	110.5 (2)
O(23)—C(22)—C(4)	122.7 (2)	O(23)—C(22)—O(24)	126.8 (2)
O(24)—C(25)—C(26)	108.9 (2)	O(29)—C(27)—N(12)	110.4 (2)
O(28)—C(27)—N(12)	122.2 (2)	O(28)—C(27)—O(29)	127.4 (2)
O(29)—C(30)—C(31)	107.4 (2)	F(15)—B(2)—N(3)	109.2 (2)
F(15)—B(2)—O(1)	108.8 (2)	F(14)—B(2)—N(3)	110.3 (2)
F(14)—B(2)—O(1)	108.1 (2)	F(14)—B(2)—F(15)	111.4 (2)

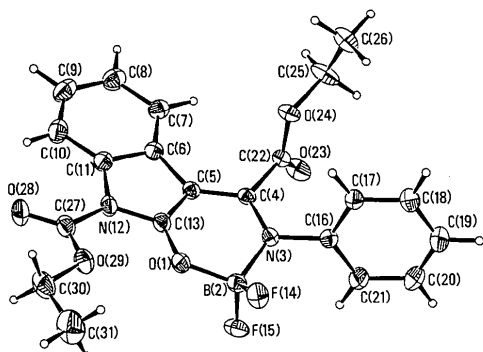
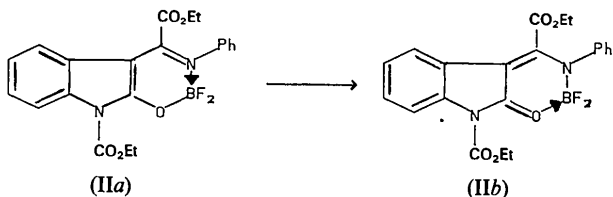


Fig. 1. ORTEP plot of (II) with numbering scheme; thermal ellipsoids are at 20% probability; H atoms are not to scale.

contribution of the structure (IIb) to the overall mesomeric structure (IIa) ↔ (IIb) in (II) with respect to the analogous ones in (III) and (IV).



The conformation of the ring B(2), N(3), C(4), C(5), C(13), O(1) is between envelope (¹E) and boat

(^{1,4}B) with puckering ring coordinates (Cremer & Pople, 1975) $Q_1 = 0.219 (2) \text{ \AA}^2$, $\varphi = -3.1 (5)$ and $\theta = 68.5 (5)^\circ$, while in (III) and (IV) the same ring is between boat and half-chair. The fused benzene ring is strictly planar, while the pyrrole and the phenyl rings are slightly distorted [$Q_1 = 0.012 (2)$ and $Q_2 = 0.017 (2) \text{ \AA}^2$ respectively].

The thirteen-membered heterocycle is not planar, but the maximum deviation from the least-squares plane A through the perimeter atoms is only

0.245 (2) Å [for B(2)], all other distances being less than 0.08 Å. To minimize steric repulsion, the planes through the phenyl ring and the C(4)—CO₂ group are rotated by 76.99 (6) and 79.35 (5)° with respect to the plane *A*. In contrast, the N(12)—CO₂ group is tilted by only 9.90 (6)° with respect to the same plane, giving the strong intramolecular interaction O(28)⋯H(10) [2.30 (2) Å] and a good overlap between the π systems of indole and C(27)=O(28) groups. The crystal structure is mainly based on van der Waals interactions, and only a few weak H bonds are present, among which the strongest are: C(19)—H(19)⋯F(14) with C⋯F 3.304 (3) and H⋯F 2.59 (2) Å, and C(20)—H(20)⋯F(15) [C⋯F 3.494 (3), H⋯F 2.66 (2) Å].

We thank Professor Alessandro Marchesini for providing the crystals, and the Servizio Italiano di Diffusione Dati Cristallografici del CNR (Parma) for help in handling the Cambridge Data Files.

Acta Cryst. (1990). **C46**, 1503–1507

Structure of α-Hydroximinopentyl 1-Thio-β-D-glucopyranoside

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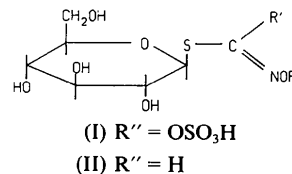
(Received 7 August 1989; accepted 4 December 1989)

Abstract. 1-(β-D-Glucopyranosylthio)pentanone oxime, C₁₁H₂₁NO₆S, *M_r* = 295.3, orthorhombic, *P*2₁2₁2₁, *a* = 9.032 (2), *b* = 11.081 (3), *c* = 14.453 (2) Å, *V* = 1446.5 (6) Å³, *Z* = 4, *D_x* = 1.356 Mg m⁻³, *F*(000) = 632, λ(Mo *K*α) = 0.71073 Å, μ = 0.233 mm⁻¹. The final *R* was 0.038, *wR* 0.041 for 1849 observed reflections (*|F|* > 2σ_{*F*}). The pyranose ring is in the usual ⁴C₁ chair conformation, the O—C—S—C glycosidic torsion angle is -73.9 (3)°, and the C(1)—S—C(=NO)—C entity is planar. The C(1)—S bond length is 1.809 (3) Å and the S—C(*sp*²) bond length is 1.764 (3) Å while the ring C(1)—O is 1.415 (3) and C(5)—O is 1.439 (3) Å. The molecules are held in three dimensions by hydrogen bonding in which all five O—H H atoms take part. Two of these H atoms form bifurcated hydrogen bonds, the weaker component being intramolecular; one of these is from the primary alcohol to the pyranose oxygen.

Introduction. Glucosinolates, (I), are found in brassica plants and render the residues poisonous

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- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 FRENZ, B. A. (1983). *Enraf-Nonius Structure Determination Package; SDP User's Guide*. Version of 6 January 1983. Enraf-Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KLIEGEL, W., RETTIG, S. J. & TROTTER, J. (1983). *Can. J. Chem.* **62**, 1363–1368.
 LARSON, R. C. (1967). *Acta Cryst.* **23**, 664–665.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MARCHESINI, A. A. (1989). Unpublished.
 NARDELLI, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. Univ. of Parma, Italy.
 RETTIG, S. J. & TROTTER, J. (1983). *Can. J. Chem.* **61**, 206–210.

after the oil has been extracted from oil seed rape, (Heaney & Fenwick, 1987). They may be detected and analyzed (Palmer, Yeung & Sang, 1987) by treatment with arylsulfatase followed by high performance liquid chromatography of the desulfo-glucosinolate, (II).



The title compound, (II), R' = C₄H₉, was synthesized (Parsons, 1986) from D-glucose and shown to be identical with one of the naturally occurring derivatives. It was of particular interest to determine whether the desulfo derivative had the same configuration about the S—C=N entity as the compound, extracted from the seeds of black mustard, known as Sinigrin, the hydrated potassium salt of myronic acid, (I), R' = allyl. The crystal structure of Sinigrin was determined by Marsh & Waser (1970) who were able to establish the absolute configuration despite

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