Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: local program. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1617–1619

8-Methylspiro(*syn*-10,11-benzo-8-azatricyclo[5.2.2.0^{1,5}]undec-10-ene)-9,3′-[3*H*]naphth[1,2-*b*][1,4]oxazine

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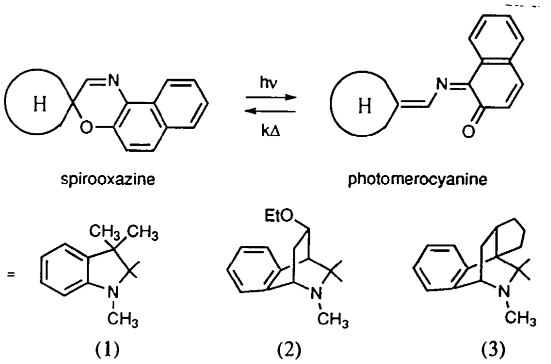
Abstract

The title compound, $C_{26}H_{24}N_2O$, is of interest in the study of the effects of steric hindrance on photochromic properties.

Comment

In the field of organic photochromic compounds, spiro[indoline–naphthoxazines], (1) (Chu, 1990), have been studied extensively for several years because of their good photochromic properties (Tardieu *et al.*, 1992; Rickwood *et al.*, 1994). In order to study the effect of the heterocyclic part, *H*, on the photochromic characteristics, we recently synthesized (Laréginie, Samat & Guglielmetti, 1995) and studied the three-dimensional structure (Reboul *et al.*, 1995) of a spiro[azabicyclonaphthoxazine], (2). To extend this preliminary work and to develop the correlation between the



substitution and the expected properties, the molecular geometry of the title compound, (3), has been established.

It is interesting to note the C16—O21 distance, the length of which increases from 1.467 (7) Å in compound (2) to 1.501 (3) Å in compound (3). Another geometry modification around the spiro C atom is observed: the length of the bond C16—N14 is 1.437 (3) compared with 1.1475 (7) Å for compound (2). As described in the previous paper (Reboul *et al.*, 1995), we tried to correlate the photochromic properties to the oxazinic ring planarity. The distance sum of the atoms to the mean plane of the ring is 0.93 Å, with a χ^2 value of 5870. Effectively, compound (3) presents better photochromic colourability than the reference compound of the series (spiro[indoline–naphthoxazine]), for which the χ^2 test value is greater (7761). The photochromic properties of (3) are similar to those of the previously analysed compound (Reboul *et al.*, 1995), which has a corresponding χ^2 value of 6241.

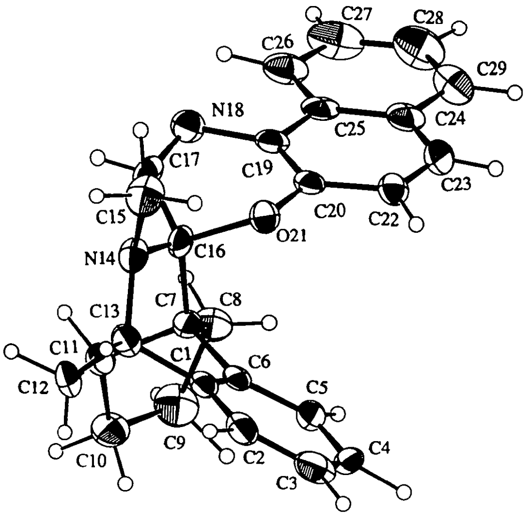


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the molecule of the title compound with displacement ellipsoids of 50% probability.

Experimental

The synthesis of the title compound will be described elswhere (Laréginie, Samat & Guglielmetti, 1995). Crystals suitable for X-ray analysis were obtained by recrystallization from heptane solution. The density D_m was measured by flotation.

Crystal data

$C_{26}H_{24}N_2O$
$M_r = 380.5$
Monoclinic
$P2_1/a$
$a = 14.078(3)$ Å
$b = 9.473(2)$ Å
$c = 14.899(3)$ Å
$\beta = 79.51(3)°$
$V = 1953.7(4)$ Å^3
$Z = 4$
$D_x = 1.29$ Mg m^{-3}
$D_m = 1.30(2)$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 15$–$45°$
$\mu = 0.579$ mm^{-1}
$T = 293$ K
Square platelet
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
θ scans
Absorption correction: none
4324 measured reflections
4324 independent reflections
3918 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 45°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 15$
4 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.0442$
$wR = 0.0442$
$S = 0.71$
3918 reflections
334 parameters
H atoms refined with $U_{\rm iso} = 0.05$ Å^2
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.15$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C1	0.6343 (1)	−0.1429 (2)	0.1002 (1)	2.14 (6)
C2	0.6365 (1)	−0.2520 (2)	0.0389 (1)	2.89 (7)
C3	0.5826 (1)	−0.3727 (2)	0.0643 (1)	3.70 (8)
C4	0.5256 (1)	−0.3827 (2)	0.1503 (2)	3.56 (9)
C5	0.5218 (1)	−0.2726 (2)	0.2125 (1)	2.68 (7)
C6	0.5777 (1)	−0.1534 (2)	0.1879 (1)	2.08 (5)
C7	0.5832 (1)	−0.0204 (2)	0.2443 (1)	2.12 (5)
C8	0.5360 (1)	−0.0312 (2)	0.3454 (1)	2.83 (7)
C9	0.6117 (2)	−0.1144 (2)	0.3894 (1)	3.88 (9)
C10	0.7090 (1)	−0.0982 (2)	0.3243 (1)	3.47 (8)
C11	0.6920 (1)	0.0077 (2)	0.2504 (1)	2.66 (7)
C12	0.7573 (1)	−0.0032 (2)	0.1566 (1)	2.79 (7)
C13	0.6900 (1)	−0.0082 (2)	0.0847 (1)	2.35 (6)
N14	0.6257 (1)	0.1154 (1)	0.1053 (1)	2.31 (5)
C15	0.5946 (2)	0.1838 (2)	0.0263 (1)	3.49 (8)
C16	0.5521 (1)	0.1024 (2)	0.1855 (1)	2.38 (6)
C17	0.5320 (1)	0.2411 (2)	0.2356 (1)	2.64 (7)
N18	0.4526 (1)	0.2769 (1)	0.2857 (1)	2.68 (5)
C19	0.3766 (1)	0.1793 (2)	0.2892 (1)	2.08 (5)
C20	0.3790 (1)	0.0785 (2)	0.2232 (1)	1.96 (5)
O21	0.4592 (1)	0.0594 (1)	0.1573 (1)	2.29 (4)
C22	0.2993 (1)	−0.0083 (2)	0.2171 (1)	2.39 (6)
C23	0.2183 (1)	0.0049 (2)	0.2836 (1)	2.91 (7)
C24	0.2134 (1)	0.1016 (2)	0.3570 (1)	2.72 (6)
C25	0.2941 (1)	0.1916 (2)	0.3594 (1)	2.39 (6)
C26	0.2886 (1)	0.2894 (2)	0.4325 (1)	3.22 (7)
C27	0.2071 (2)	0.2949 (3)	0.4985 (1)	4.47 (9)
C28	0.1279 (2)	0.2072 (3)	0.4962 (1)	4.55 (9)
C29	0.1299 (1)	0.1128 (2)	0.4276 (1)	3.78 (9)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.376 (3)	C16—N14	1.437 (3)
C1—C6	1.405 (3)	C16—C17	1.512 (3)
C1—C13	1.493 (3)	C16—O21	1.501 (3)
C2—C3	1.386 (3)	C17—N18	1.272 (3)
C3—C4	1.386 (3)	C19—N18	1.408 (3)
C4—C5	1.390 (3)	C19—C20	1.367 (3)

C5—C6	1.387 (3)	C19—C25	1.419 (3)
C6—C7	1.524 (3)	C20—O21	1.367 (3)
C7—C8	1.535 (3)	C20—C22	1.407 (3)
C8—C9	1.562 (3)	C22—C23	1.373 (3)
C10—C9	1.535 (3)	C23—C24	1.419 (3)
C10—C11	1.540 (3)	C24—C25	1.426 (3)
C11—C7	1.573 (3)	C24—C29	1.432 (3)
C11—C12	1.530 (3)	C25—C26	1.421 (3)
C12—C13	1.555 (3)	C26—C27	1.369 (4)
C13—N14	1.478 (3)	C27—C28	1.396 (4)
C15—N14	1.478 (3)	C28—C29	1.354 (4)
C16—C7	1.566 (3)		
C2—C1—C6	120.3 (5)	C7—C16—N14	107.2 (4)
C13—C1—C6	113.4 (4)	C7—C16—O21	107.6 (4)
C1—C2—C3	119.6 (5)	C17—C16—C7	114.6 (4)
C2—C3—C4	120.3 (5)	C17—C16—N14	112.2 (4)
C3—C4—C5	120.7 (6)	C17—C16—O21	106.2 (4)
C4—C5—C6	118.9 (5)	N14—C16—O21	108.9 (4)
C5—C6—C7	127.6 (5)	C16—C17—N18	125.9 (5)
C1—C6—C5	120.1 (5)	C17—N18—C19	115.3 (4)
C1—C6—C7	112.2 (4)	C20—C19—N18	120.9 (5)
C6—C7—C8	115.4 (4)	C20—C19—C25	119.8 (5)
C11—C7—C6	108.6 (4)	C25—C19—N18	119.2 (4)
C11—C7—C8	101.9 (4)	C19—C20—O21	121.2 (5)
C11—C7—C16	106.3 (4)	C19—C20—C22	122.6 (5)
C16—C7—C6	105.0 (4)	C22—C20—O21	116.1 (4)
C16—C7—C8	118.9 (4)	C16—O21—C20	114.3 (4)
C7—C8—C9	103.8 (4)	C20—C22—C23	117.9 (5)
C10—C9—C8	106.4 (5)	C22—C23—C24	122.2 (5)
C11—C10—C9	106.3 (4)	C23—C24—C25	118.6 (5)
C10—C11—C7	102.2 (4)	C23—C24—C29	122.2 (5)
C10—C11—C12	117.6 (4)	C25—C24—C29	119.3 (5)
C12—C11—C7	111.4 (4)	C19—C25—C24	118.8 (5)
C11—C12—C13	106.9 (4)	C19—C25—C26	122.8 (5)
C12—C13—N14	105.1 (4)	C24—C25—C26	118.5 (5)
C1—C13—C12	106.7 (4)	C25—C26—C27	119.8 (5)
C1—C13—N14	111.1 (4)	C26—C27—C28	121.9 (7)
C13—N14—C15	116.2 (4)	C27—C28—C29	120.3 (7)
C13—N14—C16	115.2 (4)	C24—C29—C28	120.3 (5)
C15—N14—C16	115.2 (4)		

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: local program. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: PA1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Thiodicarb

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Abstract

Dimethyl *N*,*N*′-[thiobis(methyliminocarbonyloxy)]bis(ethanimidothiolate), $C_{10}H_{18}N_4O_4S_3$, is an example of a sulfenylated biscarbamate insecticide. The molecule has an approximate twofold axis through the central S atom which joins the two methyliminocarbonyloxyethanimidothiolate units. One of the two arms is planar in the crystal. Semi-empirical geometry optimization for an isolated molecule favors a model with both arms planar and, thus, crystal packing may be responsible for the observed non-planarity in one arm. Bond lengths and angles have similar values to those of the 'monomeric' carbamate insecticide methomyl.

Comment

The title compound, (I), is an example of a sulfenylated biscarbamate insecticide (D'Silva, 1985). Thiodicarb acts as a toxocant by cholinesterase inhibition and is used on many crops to control lepidopterous and other pests. It is related to the carbamate insecticide methomyl, (II), with an S atom linking two methomyl units *via* the carbamate N atoms. Both geometric isomers [(*E*) and (*Z*)] of (II) are known. Methomyl consists of the (*Z*) isomer shown (D'Silva, 1971; Waite & Sim, 1971; Takusagawa & Jacobson, 1977), but the technical grade may contain traces of the (*E*) isomer

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