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5-Acetyl-6-methyl-3-phenyl-4-thioxo-3,4-dihydro-2*H*-1,3-oxazin-2-one

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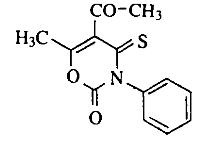
Abstract

In the title compound, $C_{13}H_{11}NO_3S$, the 1,3-oxazine ring is planar and makes an angle of 88.7 (2)° with the plane of the phenyl ring. Bond lengths involving the N atom indicate a small amount of delocalization of the N-atom lone pair into the ring.

Comment

2*H*-1,3-Oxazine-2,4(3*H*)-dione derivatives have a wide spectrum of biological activity which includes antibiotic (oxazinomycin; Suhadolnik, 1981), antibacterial (Toyama Chemical Co. Ltd, 1982), antiviral (Hasobe, Saneyoshi & Isono, 1986) and herbicidal activity (Ooms, Kunisch, Santel, Schmidt & Strang, 1988). The reaction of phosgene with acetylthioacetarylides containing an acetyl group in the α position was studied by Zankowska-Jasińska, Burgieł, Danel & Syguła (1988) who postulated, on the basis of elemental and spectral analyses, that the reaction product was 5-acetyl-6-methyl-3-phenyl-4-thioxo-3,4-dihydro-2*H*-1,3-oxazin-2-one, (I). Because of the importance of this system the X-ray analysis was undertaken to confirm unambiguously its molecular structure.



(I)

The molecular structure of the title compound together with the atom-numbering scheme and crystal packing is shown in Fig. 1. Selected torsion angles are included in Table 2. The oxazinone ring is planar with a maximum deviation of 0.016 (3) Å for atom C(4). This planarity includes the N atom and we presume therefore, that the lone pair occupies an orbital of almost pure *p* character. Involvement of this lone pair in delocalization can be inferred from the N—C(2) and N—C(4) bond lengths which are equal within error and which have values (see Table 2) less than those expected for single bonds (Allen *et al.*, 1987). The plane of the phenyl ring is almost perpendicular to that of the oxazine ring [dihedral angle = 88.7 (2)°], but the plane of the acetyl group makes a dihedral angle of 81.1 (1)° with the oxazine plane. The C(5)=C(6) distance of 1.336 (4) Å is typical of a double bond (Allen *et al.*, 1987). The length of the formal double bond C(4)=S [1.640 (3) Å] is at the short end of the range of such bonds quoted by Allen *et al.* (1987). Analysis of the intermolecular distances shows no unusual short contacts.

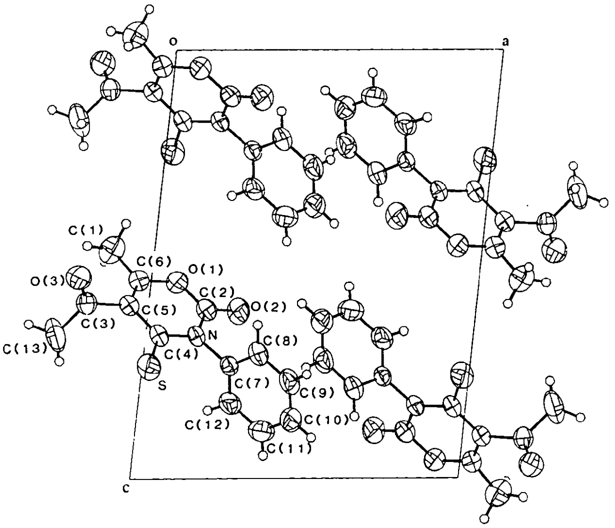


Fig. 1. The molecular structure and atom-numbering scheme of the title compound, together with packing of the molecules in an (010) projection, drawn with *SNOOPI* (Davies, 1982). Displacement ellipsoids are drawn at the 20% probability level.

Experimental

Crystal data

$C_{13}H_{11}NO_3S$
$M_r = 261.301$
Monoclinic
$P2_1/c$
$a = 10.604$ (1) Å
$b = 9.066$ (1) Å
$c = 13.904$ (1) Å
$\beta = 96.62$ (1)°

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2$–$20°$
$\mu = 0.231$ mm^{-1}
$T = 291$ K
Prisms

$V = 1327.9$ (2) Å^3
$Z = 4$
$D_x = 1.31$ Mg m^{-3}
$D_m = 1.29$ Mg m^{-3}
0.30 × 0.15 × 0.10 mm
Yellow

Data collection

Enraf–Nonius FAST diffractometer
MADNES (1991) scans
Absorption correction: none
6133 measured reflections
4054 independent reflections
1838 observed reflections [$F_o > 3\sigma(F)_o$]
$R_{\text{int}} = 0.048$
$\theta_{\text{max}} = 53.03°$
$h = -11 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 16$

Refinement

Refinement on F
$R = 0.037$
$wR = 0.039$
1838 reflections
189 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\text{max}} = 1.7$
$\Delta\rho_{\text{max}} = 0.299$ e Å^{-3}
$\Delta\rho_{\text{min}} = 0.239$ e Å^{-3}
Atomic scattering factors from *SHELX*80 (Sheldrick, 1980)

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

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N	0.1552 (2)	−0.1516 (2)	0.6677 (1)	0.0390 (7)
O(1)	0.0782 (2)	−0.3096 (2)	0.5418 (1)	0.0503 (7)
O(2)	0.2742 (2)	−0.3347 (2)	0.6110 (1)	0.0655 (8)
O(3)	−0.2213 (2)	0.0268 (3)	0.5295 (2)	0.0699 (9)
S	0.0215 (1)	0.0609 (1)	0.7383 (1)	0.0679 (3)
C(1)	−0.1302 (3)	−0.3155 (4)	0.4640 (3)	0.0696 (13)
C(2)	0.1778 (3)	−0.2689 (3)	0.6075 (2)	0.0449 (10)
C(3)	−0.1890 (3)	−0.0624 (3)	0.5906 (2)	0.0484 (10)
C(4)	0.0416 (2)	−0.0776 (3)	0.6657 (2)	0.0404 (10)
C(5)	−0.0590 (2)	−0.1327 (3)	0.5962 (2)	0.0379 (9)
C(6)	−0.0378 (3)	−0.2439 (3)	0.5371 (2)	0.0438 (9)
C(7)	0.2643 (2)	−0.1099 (3)	0.7368 (2)	0.0413 (10)
C(8)	0.3489 (3)	−0.0083 (3)	0.7095 (2)	0.0512 (12)
C(9)	0.4522 (3)	0.0294 (5)	0.7754 (2)	0.0634 (14)
C(10)	0.4690 (3)	−0.0373 (5)	0.8646 (3)	0.0703 (14)
C(11)	0.3833 (3)	−0.1376 (5)	0.8900 (2)	0.0729 (15)
C(12)	0.2790 (3)	−0.1742 (4)	0.8256 (2)	0.0595 (12)
C(13)	−0.2734 (3)	−0.1152 (5)	0.6626 (3)	0.0931 (19)

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

C(2)—N	1.391 (4)	C(4)—N	1.377 (4)
C(7)—N	1.466 (4)	C(2)—O(1)	1.365 (4)
C(6)—O(1)	1.362 (4)	C(2)—O(2)	1.180 (4)
C(3)—O(3)	1.194 (4)	C(4)—S	1.640 (3)
C(6)—C(1)	1.479 (4)	C(5)—C(3)	1.512 (4)
C(13)—C(3)	1.497 (6)	C(5)—C(4)	1.444 (4)
C(6)—C(5)	1.336 (4)	C(8)—C(7)	1.369 (5)
C(12)—C(7)	1.359 (4)	C(9)—C(8)	1.388 (5)
C(10)—C(9)	1.373 (5)	C(11)—C(10)	1.360 (6)
C(12)—C(1)	1.381 (5)		
C(4)—N—C(2)	124.8 (3)	C(7)—N—C(2)	114.5 (3)
C(7)—N—C(4)	120.7 (3)	C(6)—O(1)—C(2)	122.6 (3)
O(1)—C(2)—N	115.9 (3)	O(2)—C(2)—N	124.7 (3)
O(2)—C(2)—O(1)	119.4 (3)	C(5)—C(3)—O(3)	120.5 (3)
C(13)—C(3)—O(3)	123.2 (4)	C(13)—C(3)—C(5)	116.3 (3)
S—C(4)—N	122.4 (3)	C(5)—C(4)—N	115.0 (3)
C(5)—C(4)—S	122.6 (3)	C(4)—C(5)—C(3)	119.2 (3)
C(6)—C(5)—C(3)	120.2 (3)	C(6)—C(5)—C(4)	120.6 (3)
C(1)—C(6)—O(1)	111.4 (3)	C(5)—C(6)—O(1)	121.1 (3)
C(5)—C(6)—C(1)	127.5 (4)	C(8)—C(7)—N	119.0 (3)
C(12)—C(7)—N	119.0 (4)	C(12)—C(7)—C(8)	122.0 (4)
C(9)—C(8)—C(7)	118.4 (4)	C(10)—C(9)—C(8)	119.9 (5)
C(11)—C(10)—C(9)	120.5 (4)	C(12)—C(11)—C(10)	120.1 (4)
C(11)—C(12)—C(7)	119.0 (4)		
C(2)—N—C(4)—C(5)	1.5 (4)	N—C(4)—C(5)—C(6)	−2.4 (4)
C(4)—C(5)—C(6)—O(1)	1.0 (4)	C(2)—O(1)—C(6)—C(5)	1.4 (4)
C(6)—O(1)—C(2)—N	−2.2 (4)	C(4)—N—C(2)—O(1)	0.7 (4)
C(4)—N—C(7)—C(8)	−91.5 (3)	C(2)—N—C(7)—C(12)	−90.6 (3)
C(2)—N—C(4)—S	−179.5 (2)	C(3)—C(5)—C(6)—O(1)	−179.3 (2)
C(1)—C(6)—O(1)—C(2)	−176.3 (3)	O(2)—C(2)—O(1)—C(6)	176.4 (3)

Intensity data were recorded following the procedure described by Hursthouse, Karaulov, Ciechanowicz-Rutkowska, Kolasa & Zankowska-Jasińska (1992) with the settings DIST = 40 mm, $\theta_D = -18°$ and width = 0.15 mm. Comparison of equivalent reflections from data recorded at the beginning and end of data collection showed no significant change in intensity levels throughout the experiment. The chosen weighting scheme gave acceptable agreement analyses. The highest $(\Delta/\sigma)_{\text{max}}$ was for the x coordinate of the C(13) atom. This atom had high thermal motion and the coordinate oscillated during the refinement. Aromatic H atoms were freely refined isotropically and methyl H atoms were refined as components of idealized rigid groups with one common U_{iso} for each. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Geometrical calculations were carried out using *PARST* (Nardelli, 1983).

We are grateful to the British Council for a short-term grant enabling us to carry out this research and to the Polish State Committee for partial financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: AB1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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9-(1,3-Dithian-2-yl)-10-oxa-1-azatricyclo-[7.4.0.0^{3,8}]trideca-3,5,7-trien-2-one

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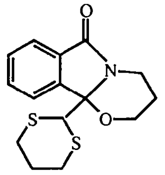
Abstract

The title compound, $C_{15}H_{17}NO_2S_2$, was produced during attempts to synthesize new serotonergic agents based upon the NAN-190 compounds [Dawson, Lawrence, Wilson, Olverman & Kelly (1991). *Br. J. Pharmacol.* **102**, 244P]. While the geometry around the N atom shows some distortion from ideal tetrahedral geometry, the remaining bond lengths and angles are well within the expected limits.

Comment

The title compound (I) was prepared by reacting *N*-(3-bromopropyl)phthalimide with one equivalent of lithiated 1,3-dithiane. The synthesis of *N*-(3-dithianylpropyl)phthalimide was attempted in order to use it as a synthon in the Fischer indole synthesis of a novel serotonergic agent similar to the NAN-190 compounds (Glennon, Naiman, Lyon & Titeler, 1988; Glennon, Naiman, Poerson, Titeler, Lyon & Weisberg, 1988) but with an S atom in the ring system rather than an N atom. Addition of the dithiane anion to the carboxyl group of the phthalimide group occurred preferentially under the conditions used (refluxing in THF), with concomitant intramolecular O-alkylation by the bromopropyl group to give the title compound.



(I)

In the crystal, the geometry of the group of atoms C(7), C(8) and C(11)–C(14) conforms to that of a near perfect benzene ring. The angles at the N atom are somewhat distorted from true tetrahedral values, which is probably due to the strain caused by cyclizing atoms C(2), C(3), C(4) and O(5). The molecules form stacks parallel to the *b* axis with a herringbone pattern typical of aromatic systems.

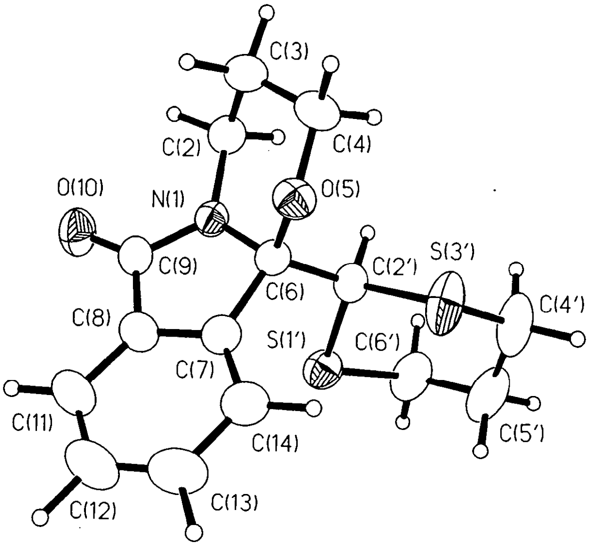


Fig. 1. A general view of the molecule showing the numbering scheme with the H atoms numbered according to the atoms to which they are attached. Displacement ellipsoids of the non-H atoms are drawn at the 50% probability level and H-atom radii are 0.15 Å.

Experimental

Crystal data

$C_{15}H_{17}NO_2S_2$
$M_r = 306.42$
Monoclinic
$P2_1/c$
$a = 12.2411\ (15)$ Å
$b = 8.0563\ (9)$ Å
$c = 15.3544\ (20)$ Å
$\beta = 98.997\ (13)°$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 15–16°$
$\mu = 0.341\ \text{mm}^{-1}$
$T = 293$ K
Prism