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2-[5-(Diethylaminosulfonyl)-2-methoxyphenylhydrazono]-3-oxo-*N*-phenylbutyramide

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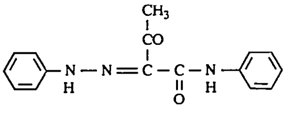
Abstract

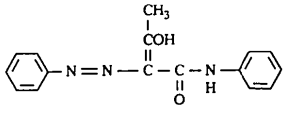
The X-ray structure determination of the title compound, $C_{21}H_{26}N_4O_5S$, shows that it crystallizes as the hydrazone tautomer and that the H atom of the hydrazone group and that of the CONH group both take part in intramolecular hydrogen bonding typical of this type of azo pigment.

Comment

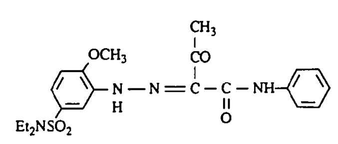
Crystal structure determinations of azo pigments derived from acetoacetanilide have highlighted the existence of several common features. Thus, in the solid, it has been found that molecules exist in the form of the hydrazone tautomer (1) rather than the azo form (2) and that the H atom in the hydrazone group and that in the CONH group both take part in hydrogen bonding (Whitaker, 1988). The availability of crystals of the title compound (3) prompted us to determine its structure to see what effects the presence of a diethylaminosulfonyl substituent and a methoxy group have on the overall structure.



(1)



(2)



(3)

Examination of the observed bond lengths confirms that the hydrazone tautomer best describes the structure of (3). The interatomic distances O(1)···N(3) [2.569 (4) Å] and O(3)···N(3) [2.629 (4) Å] suggest that the N(3) atom has a bifurcated hydrogen-bond interaction with atoms O(1) and O(3). There is also a single hydrogen bond between the H atom on N(1) and O(2) [O(2)···N(1) 2.669 (3) Å]. Bifurcated hydrogen bonds with similar bond lengths have been found in previously

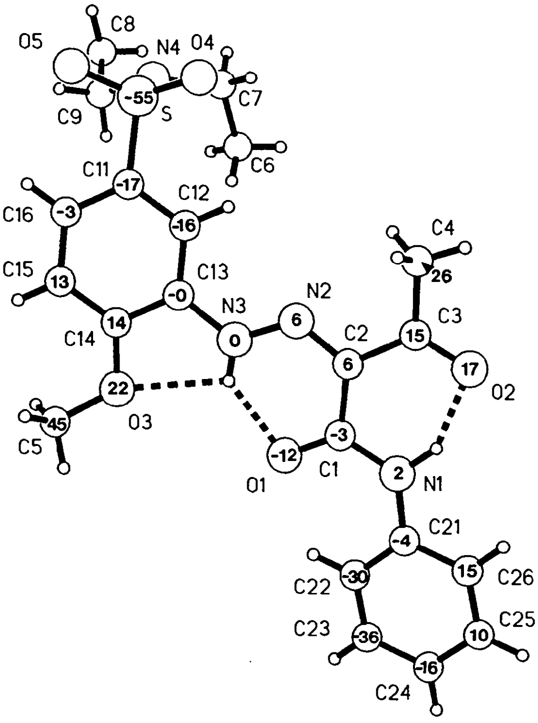


Fig. 1 Structure of the title molecule (*SHELXTL/PC*; Sheldrick, 1991) showing the deviations of the atoms (10^{-2} Å) from the plane of projection. The intramolecular bonds are indicated by broken lines.

determined structures (Whitaker, 1988). The molecule is approximately planar (Fig. 1) but less so than the examples of Whitaker (1988). In (3), the deviations from the plane are greater than previously observed and the phenyl rings are inclined at an angle of 17.2° with respect to each other.

The molecules lie in columns parallel to the *b* axis with an interplanar stacking distance of 3.58 Å, the diethylaminosulfonyl groups inducing anti-parallel stacking. The normal to the molecular plane is at an angle of 41.6° to the *b* axis. There is no evidence of $CH_3\cdots O$ intermolecular hydrogen bonds of the type observed by Whitaker & Walker (1987).

Experimental

The title compound was prepared by the addition of an aqueous solution of sodium nitrite (0.02 mol) to a solution of *N*,*N*-diethyl-2-amino-4-methoxysulfonamide (0.02 mol) in aqueous hydrochloric acid at 273–278 K. Sodium acetate (0.06 mol) was added to the resulting diazonium salt solution and the mixture was added slowly with stirring to an aqueous solution of acetoacetanilide (0.02 mol) and sodium carbonate (9.4 mmol). The product was recrystallized from trichloromethane.

Crystal data

$C_{21}H_{26}N_4O_5S$
$M_r = 446.53$
Triclinic
$P\bar{1}$
$a = 12.301$ (20) Å
$b = 9.020$ (11) Å
$c = 11.482$ (4) Å
$\alpha = 117.1$ (1)°
$\beta = 88.79$ (2)°
$\gamma = 97.88$ (1)°
$V = 1122$ (3) Å^3
$Z = 2$
$D_x = 1.32$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 244 reflections
$\theta = 7$–15°
$\mu = 0.172$ mm^{-1}
$T = 293$ K
Irregular plate
0.56 × 0.40 × 0.12 mm
Yellow

Data collection

Stoe Stadi-2 diffractometer
ω scans
Absorption correction: none
3606 measured reflections
3594 independent reflections
2621 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.011$

$\theta_{\rm max} = 25°$
$h = -14 \rightarrow 14$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 12$
1 standard reflection monitored every 50 reflections intensity variation: <4%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.058$
2621 reflections
284 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\rm max} = 0.078$

$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.41$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
S	0.47526 (7)	−0.01879 (11)	0.25533 (9)	0.0490 (4)
N(1)	−0.07830 (22)	0.3004 (3)	−0.0512 (3)	0.0465 (13)
N(2)	0.13523 (20)	0.1351 (3)	0.05283 (25)	0.0429 (12)
N(3)	0.12005 (23)	0.1888 (4)	0.18101 (28)	0.0464 (13)
N(4)	0.56709 (22)	0.1495 (3)	0.30101 (26)	0.0487 (13)
O(1)	−0.03625 (20)	0.3364 (3)	0.15717 (24)	0.0625 (13)
O(2)	0.04672 (20)	0.1219 (3)	−0.24332 (23)	0.0586 (12)
O(3)	0.06178 (19)	0.2682 (3)	0.42156 (23)	0.0588 (12)
O(4)	0.47324 (20)	−0.10719 (29)	0.11323 (22)	0.0600 (12)
O(5)	0.49968 (20)	−0.10128 (29)	0.33295 (24)	0.0600 (12)
C(1)	−0.01871 (25)	0.2772 (4)	0.0369 (3)	0.0434 (15)
C(2)	0.07136 (24)	0.1723 (4)	−0.0192 (3)	0.0400 (14)
C(3)	0.09863 (27)	0.1002 (4)	−0.1613 (3)	0.0469 (16)
C(4)	0.1899 (3)	−0.0053 (5)	−0.2063 (4)	0.0640 (20)
C(5)	0.0172 (4)	0.3040 (8)	0.5474 (4)	0.0972 (29)
C(6)	0.5177 (4)	0.3707 (6)	0.2399 (6)	0.091 (3)
C(7)	0.5833 (3)	0.2299 (5)	0.2113 (4)	0.0614 (20)
C(8)	0.6969 (4)	0.3567 (7)	0.4841 (6)	0.1060 (29)
C(9)	0.5829 (3)	0.2617 (5)	0.4450 (4)	0.0632 (19)
C(11)	0.34584 (14)	0.04940 (27)	0.30305 (19)	0.0454 (15)
C(12)	0.28301 (14)	0.08122 (27)	0.21938 (19)	0.0445 (15)
C(13)	0.18703 (14)	0.15259 (27)	0.26220 (19)	0.0420 (14)
C(14)	0.15385 (14)	0.19214 (27)	0.38872 (19)	0.0469 (15)
C(15)	0.21669 (14)	0.16030 (27)	0.47237 (19)	0.0552 (17)
C(16)	0.31268 (14)	0.08894 (27)	0.42954 (19)	0.0539 (17)
C(21)	−0.16794 (16)	0.39284 (27)	−0.02687 (21)	0.0441 (15)
C(22)	−0.20334 (16)	0.49146 (27)	0.09766 (21)	0.0546 (17)
C(23)	−0.29151 (16)	0.57958 (27)	0.11179 (21)	0.0593 (18)
C(24)	−0.34430 (16)	0.56907 (27)	0.00137 (21)	0.0649 (20)
C(25)	−0.30890 (16)	0.47047 (27)	−0.12315 (21)	0.0725 (22)
C(26)	−0.22073 (16)	0.38236 (27)	−0.13727 (21)	0.0594 (18)

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

N(4)—S	1.639 (3)	C(9)—N(4)	1.494 (4)
O(4)—S	1.452 (2)	C(1)—O(1)	1.259 (4)
O(5)—S	1.454 (2)	C(3)—O(2)	1.248 (4)
C(11)—S	1.771 (2)	C(5)—O(3)	1.443 (5)
C(1)—N(1)	1.368 (4)	C(14)—O(3)	1.362 (2)
C(21)—N(1)	1.420 (3)	C(2)—C(1)	1.497 (4)
N(3)—N(2)	1.341 (4)	C(3)—C(2)	1.506 (5)
C(2)—N(2)	1.330 (4)	C(4)—C(3)	1.501 (4)
C(13)—N(3)	1.427 (3)	C(7)—C(6)	1.504 (5)
C(7)—N(4)	1.503 (4)	C(9)—C(8)	1.500 (6)
O(4)—S—N(4)	106.7 (2)	C(1)—C(2)—N(2)	122.7 (3)
O(5)—S—N(4)	106.7 (1)	C(3)—C(2)—N(2)	113.8 (3)
O(5)—S—O(4)	120.7 (1)	C(3)—C(2)—C(1)	123.5 (3)
C(11)—S—N(4)	107.5 (1)	C(2)—C(3)—O(2)	122.5 (3)
C(11)—S—O(4)	108.3 (1)	C(4)—C(3)—O(2)	119.0 (3)
C(11)—S—O(5)	106.4 (1)	C(4)—C(3)—C(2)	118.5 (3)
C(21)—N(1)—C(1)	127.9 (3)	C(6)—C(7)—N(4)	115.5 (3)
C(2)—N(2)—N(3)	120.7 (3)	C(8)—C(9)—N(4)	112.6 (3)
C(13)—N(3)—N(2)	122.6 (2)	C(12)—C(11)—S	119.8 (1)
C(7)—N(4)—S	117.8 (2)	C(16)—C(11)—S	119.8 (1)
C(9)—N(4)—S	116.2 (2)	C(12)—C(13)—N(3)	122.3 (1)
C(9)—N(4)—C(7)	117.8 (3)	C(14)—C(13)—N(3)	117.7 (1)
C(14)—O(3)—C(5)	118.7 (3)	C(13)—C(14)—O(3)	114.7 (1)
O(1)—C(1)—N(1)	124.3 (3)	C(15)—C(14)—O(3)	125.2 (1)
C(2)—C(1)—N(1)	115.3 (3)	C(22)—C(21)—N(1)	124.2 (1)
C(2)—C(1)—O(1)	120.5 (3)	C(26)—C(21)—N(1)	115.8 (1)

The H atoms bonded to N atoms were located from difference Fourier maps and refined as normal atoms. All other H atoms were included in calculated positions (C—H = 0.95 Å). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refinement was by full-matrix least-squares techniques using *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, bond distances and angles involving H atoms and non-bonded contact distances have been deposited with the IUCr (Reference: HA1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Photochromic Pyrido-Annulated 2,2-Diphenylchromene

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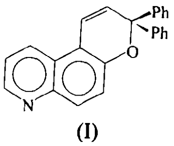
Abstract

A photochromic pyrido-annulated chromene, 3,3-diphenylpyrano[5,6-*f*]quinoline, $C_{24}H_{17}NO$, has been studied. The photoreactive C_{sp^3}—O bond length is longer than the standard values observed for oxygen-containing heterocycles as a result of steric interactions between the two phenyl groups.

Comment

Previous X-ray studies of spiropyrans containing nitrogen, oxygen and sulfur as additional heteroatoms (Hoffman *et al.*, 1972; Shustov, Zolotoy & Kostyanovskii, 1982; Aldoshin, Kholmanskij & Atovmian, 1986; Aldoshin *et al.*, 1987) have showed that specific *n*–*s** orbital interactions influence the length of the C—O bond which is broken upon photoexcitation. The efficiency of this interaction is influenced considerably by the conformation of the heterocycle, the nature of the substituents and their arrangement in the molecule. In this work we have carried out an X-ray study of the chromene (I), which contains a single pyran heterocycle, and in which an *n*–*s** interaction cannot affect the C—O bond length. Despite this, the compound is photochromic. The specific structural features of the chromene responsible for its photochromic properties are discussed.



(I)

The pyran ring in (I) is nonplanar. The ring is bent along the C2—O and C3—O vectors by 23.2 (2) and 12.0 (2)°, respectively. The valence angles at the sp^3 hybridized C atom show substantial distortion away from the ideal value for tetrahedral geometry. The C1—O bond [1.458 (4) Å] is longer than a typical C—O bond in a six-membered heterocycle (1.41–1.43 Å; Birukov & Unkovskij, 1976), such as those in the photochromic spiropyrans studied earlier (Hoffman *et al.*, 1972; Shustov, Zolotoy & Kostyanovskii, 1982; Aldoshin, Kholmanskij & Atovmian, 1986; Aldoshin *et al.*, 1987).

The phenyl rings in the molecule are almost perpendicular to each other, the angle between the planes of the rings being 91.0 (2)°. The orientation of the rings with respect to the pyran ring is characterized by the angle between the plane formed by O, C1 and C2 and the plane of the phenyl ring C13–C18 [74.1 (2)°] and the angle between the plane formed by O, C1 and C2 and the plane of the phenyl ring C19–C24 [51.9 (2)°]. Analysis of the intramolecular contacts [O···H20 = 2.46 (3), O···C20 = 2.793 (3) Å, O···H20—C20 = 102 (2)°; C1—O···H20 = 79 (2)°; C5—O···H20 = 115 (1)°; O···H18 = 2.36 (2), O···C18 = 2.687 (3) Å, O···H18—C18 = 100 (2)°; C1—O···H18 = 83 (2)°; C5—O···H18 = 128 (1)°] allows us to assume the presence of weak C18—H18···O and C20—H20···O hydrogen bonds (Desideraju, 1989) which are apparently responsible for the orientation of the phenyl rings in the molecule. It should also be noted that the conditions for a secondary interaction between the C24—H24 bond and the p_z orbital of the C2=C3 bond are favorable [C24···C2 = 2.851 (3), H24···C2 = 2.48 (3) Å, C3—C2···H24 = 115 (2), C24—H24···C2 = 104 (2)°]. Geometrical modeling shows that a planar conformation of the pyran ring leads to a parallel orientation of the phenyl rings,