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3-(2-Benzothiazolyl)-7-(diethylamino)-coumarin

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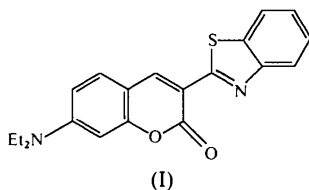
(Received 9 October 1992; accepted 5 April 1994)

Abstract

The coumarin and benzothiazolyl ring systems in the title compound, $C_{20}H_{18}N_2O_2S$, are planar. The pyrone ring in the coumarin moiety is bent slightly (2.30°) compared to the thiazolyl ring in the benzothiazolyl moiety. The crystal structure is stabilized by van der Waals forces.

Comment

The title compound, (I), also known as coumarin 6 (Eastman Kodak Chemical Co., Rochester, NY, USA) or coumarin 540 (Exiton Inc., Dayton, Ohio, USA) has been used with efficient dye lasers in the ultraviolet region (Muto, Ito & Inaba, 1982) and in the visible region (Uchino, Mizunami, Maeda & Miyazoe, 1979; Collins, Taylor & Lee, 1978; Yarborough, 1974; Marling, Hawley, Liston & Grant, 1974; Tuccio, Drexhage & Reynolds, 1973). A number of structural fea-



tures of this compound are in good agreement with those of other coumarin derivatives (Murthy, Ramamurthy & Venkatesan, 1988; Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985). The increase in the bond angle $C2-C3-C4$ by 0.3° and the decrease in $C3-C4-C10$ by the same amount from the mean value may be due to the benzothiazolyl group substituted at C3. A slight decrease in the $N12-C13$ and $N12-C14$ bond lengths in the diethylamino moiety by 0.05 and 0.008 Å, respectively, is observed (Messager & Delugeard, 1974). The $C7-N12$ bond in the aminocoumarin group [$1.355(2)$ Å] is slightly shortened in comparison with related derivatives, indicating significant double-bond character (Chinnakali, Sivakumar

& Natarajan, 1990; Chinnakali, Sivakumar, Natarajan, McGuire & Clearfield, 1991). The $C2'-S1'$ and $C8'-S1'$ distances [$1.754(2)$ and $1.730(2)$ Å, respectively] in the thiazolyl ring are normal.

Both the pyrone and benzene rings in the coumarin motif are essentially planar ($\chi^2 = 116.1$ and 31.1° , respectively). The dihedral angle between them is 1.41° ; thus the coumarin moiety is essentially planar. In the benzothiazolyl moiety the angle between the planar benzene ($\chi^2 = 6.3^\circ$) and thiazolyl ($\chi^2 = 39.8^\circ$) rings is 1.00° , establishing an essentially planar arrangement. The pyrone ring makes an angle of 2.30° with the thiazolyl ring and an angle of 3.29° with the benzene ring in the benzothiazolyl moiety.

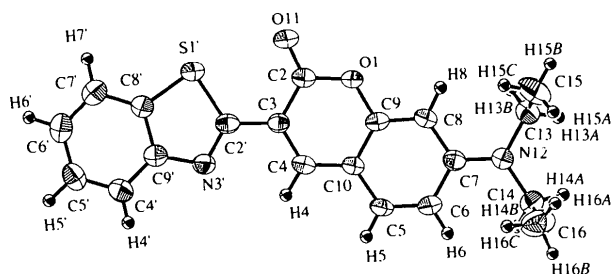


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystal data

$C_{20}H_{18}N_2O_2S$
 $M_r = 350.43$
 Triclinic
 $P\bar{1}$
 $a = 8.962(1)$ Å
 $b = 11.136(2)$ Å
 $c = 8.922(1)$ Å
 $\alpha = 95.14(1)^\circ$
 $\beta = 104.50(1)^\circ$
 $\gamma = 86.74(1)^\circ$
 $V = 858.0(2)$ Å³
 $Z = 2$
 $D_x = 1.356$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å
 Cell parameters from 25 reflections
 $\theta = 21.2-24.7^\circ$
 $\mu = 0.1945$ mm⁻¹
 $T = 296.0$ K
 Needle
 $1.00 \times 0.20 \times 0.20$ mm
 Orange
 Crystal source: Sigma Chemical Co., St. Louis, Mo., USA; grown from EtOH

Data collection

AFC-6S diffractometer
 $\omega/2\theta$ scans (speed 8.0° min⁻¹ in ω)
 Absorption correction: empirical (ψ scans)
 $T_{\min} = 0.981$, $T_{\max} = 1.000$
 3226 measured reflections
 3010 independent reflections
 2123 observed reflections
 $[I > 3.0\sigma(I)]$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -11 \rightarrow 11$
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.60%

† Current address: Pfizer Inc., Central Research Division, Eastern Point Road, Groton, CT 06340, USA.

Refinement

Refinement on *F**R* = 0.0359*wR* = 0.0413*S* = 1.528

2123 reflections

299 parameters

All H-atom parameters
refined*w* = 4*F*_o²/*σ*²(*F*_o²)(Δ*σ*)_{max} = 0.4404

Δ*ρ*_{max} = 0.16 e Å⁻³

Δ*ρ*_{min} = -0.22 e Å⁻³

Extinction correction:
type 2, Gaussian, isotropic
(Zachariasen, 1963)

Extinction coefficient:

1.2790 (1) × 10⁻⁶

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

C2—C3—C4	119.7 (2)	N3'—C9'—C8'	115.1 (2)
C2'—C3—C4	120.5 (2)	C4'—C9'—C8'	119.7 (2)
C3—C4—C10	122.0 (2)	C4—C10—C5	125.5 (2)
C5'—C4'—C9'	119.0 (2)	C4—C10—C9	118.5 (2)
C6—C5—C10	122.1 (2)	C5—C10—C9	116.0 (2)
C4'—C5'—C6'	121.1 (2)	N12—C13—C15	114.6 (2)
C5—C6—C7	121.5 (2)	N12—C14—C16	114.2 (2)

Weak reflections [*I* < 10.0*σ*(*I*)] were rescanned (maximum of two rescans) and the counts accumulated to assure good counting statistics. No correction for decay was applied. H atoms were located from difference Fourier maps and refined isotropically. The weighting scheme used was based on counting statistics and included a factor to down-weight the intense reflections. Plots of Σ*w*(|*F*_o| - |*F*_c|)² versus |*F*_o|, reflection order in data collection, sinθ/λ, and various classes of indices showed no unusual trends. The enantiomorphs are indistinguishable from the X-ray data.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and a packing diagram have been deposited with the IUCr (Reference: CD1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S1'	0.53462 (6)	0.44911 (5)	0.30382 (6)	0.0440
O1	0.1364 (1)	0.69047 (10)	0.0719 (1)	0.0406
O11	0.3324 (2)	0.6513 (1)	0.2674 (2)	0.0548
N3'	0.4428 (2)	0.3225 (1)	0.0409 (2)	0.0402
N12	-0.2867 (2)	0.8045 (1)	-0.3372 (2)	0.0433
C2	0.2597 (2)	0.6171 (2)	0.1396 (2)	0.0395
C2'	0.4139 (2)	0.4225 (2)	0.1172 (2)	0.0369
C3	0.2872 (2)	0.5054 (2)	0.0509 (2)	0.0339
C4	0.1928 (2)	0.4778 (2)	-0.0911 (2)	0.0369
C4'	0.6247 (2)	0.1473 (2)	0.0813 (2)	0.0483
C5	-0.0316 (2)	0.5341 (2)	-0.3049 (2)	0.0396
C5'	0.7455 (2)	0.0930 (2)	0.1816 (3)	0.0539
C6	-0.1461 (2)	0.6146 (2)	-0.3637 (2)	0.0416
C6'	0.8087 (2)	0.1470 (2)	0.3288 (3)	0.0542
C7	-0.1714 (2)	0.7251 (2)	-0.2778 (2)	0.0371
C7'	0.7525 (2)	0.2567 (2)	0.3787 (2)	0.0507
C8	-0.0716 (2)	0.7457 (2)	-0.1296 (2)	0.0383
C8'	0.6303 (2)	0.3127 (2)	0.2767 (2)	0.0401
C9	0.0432 (2)	0.6633 (2)	-0.0743 (2)	0.0352
C9'	0.5657 (2)	0.2585 (2)	0.1285 (2)	0.0391
C10	0.0694 (2)	0.5552 (2)	-0.1583 (2)	0.0339
C13	-0.3096 (2)	0.9190 (2)	-0.2511 (2)	0.0478
C14	-0.3823 (3)	0.7855 (2)	-0.4955 (2)	0.0540
C15	-0.2044 (3)	0.1016 (2)	-0.2631 (3)	0.0725
C16	-0.3058 (4)	0.8155 (3)	-0.6189 (3)	0.0830

Table 2. Selected geometric parameters (Å, °)

S1'—C2'	1.754 (2)	C4'—C5'	1.369 (3)
S1'—C8'	1.730 (2)	C4'—C9'	1.391 (3)
O1—C2	1.380 (2)	C5—C6	1.357 (2)
O1—C9	1.379 (2)	C5—C10	1.401 (2)
O11—C2	1.204 (2)	C5'—C6'	1.390 (3)
N3'—C2'	1.300 (2)	C6—C7	1.428 (2)
N3'—C9'	1.382 (2)	C6'—C7'	1.375 (3)
N12—C7	1.355 (2)	C7—C8	1.406 (2)
N12—C13	1.460 (2)	C7'—C8'	1.393 (3)
N12—C14	1.461 (2)	C8—C9	1.365 (2)
C2—C3	1.456 (2)	C8'—C9'	1.400 (2)
C2'—C3	1.461 (2)	C9—C10	1.400 (2)
C3—C4	1.356 (2)	C13—C15	1.505 (3)
C4—C10	1.406 (2)	C14—C16	1.504 (4)
C2'—S1'—C8'	88.81 (9)	C5'—C6'—C7'	121.2 (2)
C2—O1—C9	122.9 (1)	N12—C7—C8	121.1 (2)
C2'—N3'—C9'	110.8 (1)	N12—C7—C6	122.5 (2)
C7—N12—C13	121.0 (1)	C6—C7—C8	116.4 (2)
C7—N12—C14	121.6 (2)	C6'—C7'—C8'	117.9 (2)
C13—N12—C14	117.1 (2)	C7—C8—C9	120.6 (2)
O1—C2—O11	116.4 (2)	S1'—C8'—C7'	129.2 (2)
O1—C2—C3	117.0 (1)	S1'—C8'—C9'	109.7 (1)
O11—C2—C3	126.6 (2)	C7'—C8'—C9'	121.1 (2)
S1'—C2'—N3'	115.6 (1)	O1—C9—C8	117.0 (2)
S1'—C2'—C3	122.9 (1)	O1—C9—C10	119.7 (2)
N3'—C2'—C3	121.5 (2)	C8—C9—C10	123.3 (2)
C2—C3—C2'	119.7 (1)	N3'—C9'—C4'	125.2 (2)

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3-{2-[4-(4-Fluorobenzoyl)piperidino]-ethyl}-2-methyl-4H-pyrido[1,2-a]-pyrimidin-4-one (Pirenperone)†

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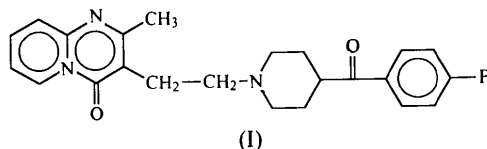
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Abstract

Pirenperone, $C_{23}H_{24}FN_3O_2$, a serotonin-2 antagonist, has a nearly planar pyrido-pyrimidine moiety connected by an ethylpiperidyl bridge to an almost planar fluoro-benzoyl moiety. The planar parts are perpendicular to each other [$98.7(2)^\circ$]. The packing of the molecules is governed only by van der Waals contacts.

Comment

Pirenperone, (I), which is chemically related to Ketanserin (Peeters, Blaton & De Ranter, 1982), has been reported to be a selective serotonin-2 ($5-HT_2$) antagonist and a specific D-LSD antagonist (Colpaert, Niemegeers & Janssen, 1982). The X-ray structural study of the title compound has been carried out as part of our studies on serotonin antagonists in an attempt to correlate structural features with the antagonistic activities (Blaton, Peeters & De Ranter, 1985).



The atoms in the phenyl ring are nearly coplanar: the largest deviation is $0.016(7)$ Å for C7. The endocyclic angles reflect the *para*-disubstitution (Domenicano &

† Internal code of the Janssen Research Foundation: R47465.

Murray-Rust, 1979). The carbonyl group is slightly inclined with respect to the phenyl group, the torsion angle C4—C5—C8—O9 being $175.1(7)^\circ$.

The piperidine ring has rotational disorder around the C10—N13 axis, as can be deduced from the large U_{33} values for atoms C11, C12, C13 and C15, and their displacement ellipsoids in Fig. 1. The appreciable shortening of the N—C bond lengths [$1.43(1)$ and $1.41(1)$ Å compared to the value of 1.473 Å given by Allen *et al.* (1987)] is caused by the displacement of the atomic positions towards the rotation axis. This shift is a consequence of the approximation of a real kidney-like displacement of an ellipsoid. Because the motion is not known exactly, the effect has not been treated; this explains the relatively high R value of 0.0748.

The ethyl bridge between the piperidine ring and the pyrido-pyrimidine moiety has an antiperiplanar conformation. The geometry of the latter is in good agreement with those of similar structures (Hermecs, Vasvari-Debrezcy & Simon, 1988). The pyrido-pyrimidine ring system deviates significantly from planarity with maximum deviations for C18 and C27 [$0.058(7)$ and $0.046(7)$ Å, respectively]. The dihedral angles between the least-squares planes of the three-ring system [phenyl (A), piperidine (atoms C11, C12, C14 and C15) (B) and pyrido-pyrimidine (C)] are: $A^{\wedge}B$ $59.2(3)$, $A^{\wedge}C$ $98.7(2)$ and $B^{\wedge}C$ $40.3(2)^\circ$.

The packing of the molecules is governed only by van der Waals contacts.

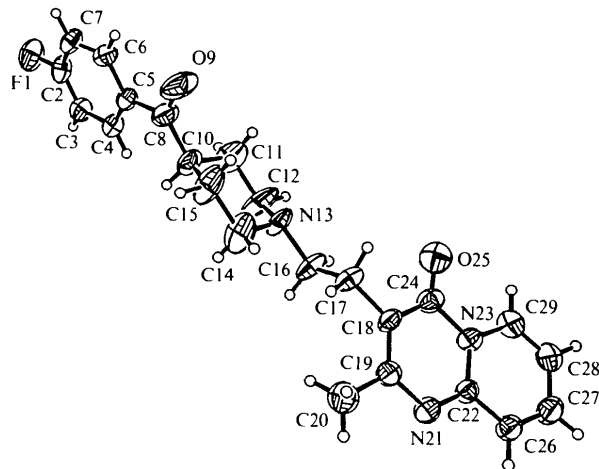


Fig. 1. ORTEX (McArdle, 1993) diagram of the molecule showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 40% probability level.

Experimental

Crystal data

$C_{23}H_{24}FN_3O_2$
 $M_r = 393.45$

Cu $K\alpha$ radiation
 $\lambda = 1.54184$ Å