ORGANIC COMPOUNDS

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Coumarin 106, $C_{18}H_{19}NO_2$

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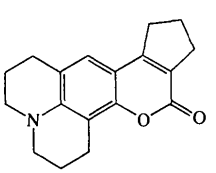
Abstract

The title compound, 2,3,6,7,10,11-hexahydro-1*H*,5*H*-cyclopenta[3,4][1]benzopyrano[6,7,8-*ij*]quinolizin-12-(9*H*)-one, as an entity is nearly planar. One piperidine ring is disordered. The piperidine rings adopt flattened conformations and the cyclopentene ring an envelope conformation. The molecules are stacked in a parallel fashion in the crystal.

Comment

The title compound, (I) (Eastman Kodak Co., Rochester, NY, USA), is one of the coumarin derivatives which are efficient laser dyes. The derivative having a structurally rigid amino group has been reported to show a high quantum yield of fluorescence in polar solvents (Reynolds & Drexhage, 1975). In order to understand the correlation between structure and laser efficiency, the present analysis was undertaken.



(I)

An *ORTEP*II (Johnson, 1976) drawing of the title compound, together with the atomic numbering and ring-labelling schemes, is shown in Fig. 1. In one piperizine ring (*A*), the C5 atom is disordered and the site occupancies were initially refined then fixed at 0.7 and 0.3 for C5*a* and C5*b*, respectively, in the final refinement. Atoms C5*a* and C5*b* are located on the opposite sides of the least-squares plane of ring *A*. The coumarin moiety is planar and the molecule as a whole is nearly planar. Ring *A* containing the C5*a* atom adopts a half-chair conformation, while the ring with the C5*b* atom has a boat conformation. The mean absolute torsion angles in rings *A* with C5*a* and C5*b*, and *B* are 30.1 (4), 11.2 (7) and 30.7 (3)°, respectively. The two piperidine rings have flattened conformations, while rings *B* and *E* adopt half-chair and envelope conformations, respectively.

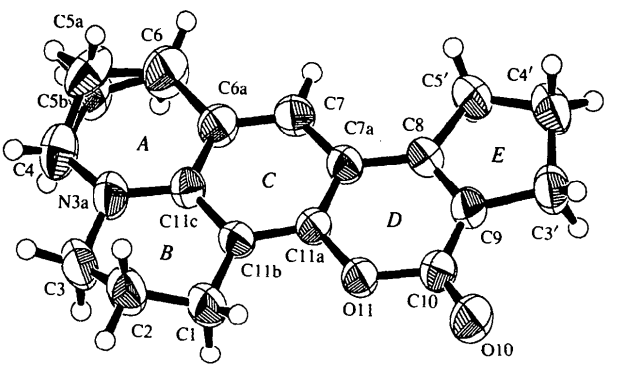


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) representing heavy atoms as 50% probability ellipsoids and H atoms as circles of arbitrary size.

The values of the bond lengths and angles in the molecule are very similar to the corresponding values in 2,3,6,7-tetrahydro-9-methyl-1*H*,5*H*-quinolizino[9,1-*gh*]-coumarin (TMQC; Chinnakali, Sivakumar & Natarajan, 1990). The carbonyl C11=O bond length and the C6a—C7 bond length are significantly shorter than the corresponding distances in TMQC. The exocyclic bond angles around the carbonyl group are highly asymmetric, as in TMQC.

The molecules of the title compound are stacked in a parallel fashion. The interplanar spacing between the quinolizine ring and the courmarin moiety is 3.7 (6) Å, which is longer than the van der Waals contact distances.

Experimental

Crystals of the title compound were grown from an ethanol solution kept in a dark room at 293 (5) K.

Crystal data

$C_{18}H_{19}NO_2$
M_r = 281.35
Monoclinic
$P2_1/a$
a = 10.322 (3) Å
b = 14.909 (1) Å
c = 9.8059 (8) Å
β = 109.48 (1)°

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 30–35°
μ = 0.679 mm^{-1}
T = 293 (2) K
Plate

$V = 1422.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.31$ Mg m^{-3}
D_m not measured

$0.3 \times 0.2 \times 0.02$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3225 measured reflections
3071 independent reflections
2054 observed reflections $[F > 3\sigma(F)]$

$R_{int} = 0.035$
$\theta_{max} = 74.9°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 0.24%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.066$
$S = 2.85$
2054 reflections
270 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}

Extinction correction: $F = |F_{calc}|/(1 + gI_{calc})$
Extinction coefficient: $g = 4.8336 \times 10^{-6}$
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)*

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

	x	y	z	B_{eq}
O10	0.7554 (2)	0.0514 (1)	1.1710 (2)	6.46 (4)
O11	0.8408 (1)	0.11383 (8)	1.0156 (1)	4.25 (3)
N3a	1.0087 (2)	0.2287 (1)	0.6537 (2)	4.78 (4)
C1	0.9437 (3)	0.0747 (2)	0.7957 (3)	5.34 (6)
C2	0.9451 (3)	0.0706 (2)	0.6437 (3)	5.63 (6)
C3	1.0435 (3)	0.1385 (2)	0.6210 (3)	5.92 (6)
C3′	0.7045 (3)	0.2339 (2)	1.2841 (2)	5.08 (5)
C4	1.0689 (3)	0.3009 (2)	0.5951 (3)	5.85 (6)
C4′	0.6842 (3)	0.3352 (2)	1.2657 (3)	5.53 (6)
C5′	0.7717 (3)	0.3678 (2)	1.1753 (3)	5.24 (5)
C5*a*†	0.9977 (5)	0.3870 (3)	0.5993 (5)	6.3 (1)
C5*b*‡	1.068 (1)	0.3907 (7)	0.658 (1)	6.2 (2)
C6	0.9950 (4)	0.4103 (2)	0.7453 (3)	7.30 (7)
C6a	0.9515 (2)	0.3316 (1)	0.8166 (2)	4.59 (5)
C7	0.8998 (2)	0.3451 (1)	0.9263 (2)	4.52 (5)
C7a	0.8593 (2)	0.2744 (1)	0.9956 (2)	3.81 (4)
C8	0.8003 (2)	0.2825 (1)	1.1081 (2)	3.88 (4)
C9	0.7649 (2)	0.2098 (1)	1.1686 (2)	3.97 (4)
C10	0.7831 (2)	0.1209 (1)	1.1248 (2)	4.35 (4)
C11c	0.9658 (2)	0.2429 (1)	0.7709 (2)	3.72 (4)
C11b	0.9292 (2)	0.1696 (1)	0.8407 (2)	3.70 (4)
C11a	0.8772 (2)	0.1879 (1)	0.9512 (2)	3.54 (4)

† Site occupancy = 0.7. ‡ Site occupancy = 0.3.

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

O10—C10	1.204 (2)	O11—C10	1.391 (2)
O11—C11a	1.385 (2)	N3a—C3	1.456 (3)
N3a—C4	1.454 (3)	N3a—C11c	1.379 (2)
C1—C2	1.497 (3)	C1—C11b	1.504 (3)
C2—C3	1.502 (4)	C4—C5*a*	1.486 (6)
C4—C5*b*	1.47 (1)	C5*a*—C6	1.483 (5)
C5*b*—C6	1.35 (1)	C6—C6a	1.508 (3)
C6a—C7	1.365 (3)	C6a—C11c	1.420 (3)
C7—C7a	1.392 (3)	C7a—C8	1.432 (3)
C7a—C11a	1.393 (2)	C8—C9	1.344 (3)
C9—C10	1.425 (3)	C11b—C11a	1.388 (3)
C11c—C11b	1.407 (3)	C3′—C9	1.507 (3)
C3′—C4′	1.528 (4)	C4′—C5′	1.540 (3)
C5′—C8	1.506 (3)		
O11—C10—C9	115.8 (2)	O10—C10—O11	116.2 (2)
O10—C10—C9	128.0 (2)	C8—C9—C10	122.3 (2)
C9—C8—C7a	121.3 (2)	C7—C7a—C8	125.9 (2)
C11a—C7a—C8	117.0 (2)	C7—C7a—C11a	117.1 (2)
C6a—C7—C7a	122.2 (2)	C11a—C11b—C11c	117.6 (2)
C11b—C11a—C7a	123.6 (2)	O11—C11a—C11b	115.7 (2)
C11a—O11—C10	122.8 (1)	C2—C1—C11b	111.4 (2)
C1—C2—C3	110.6 (2)	N3a—C3—C2	111.2 (2)
C4—N3a—C3	115.3 (2)	C11c—N3a—C3	119.9 (2)
C11c—N3a—C4	120.9 (2)	N3a—C4—C5*a*	110.4 (3)
N3a—C4—C5*b*	116.4 (4)	C6—C5*a*—C4	113.5 (3)
C6—C5*b*—C4	122.9 (7)	C5*a*—C6—C6a	111.7 (3)
C5*b*—C6—C6a	116.3 (5)	C11c—C11b—C1	121.3 (2)
C11a—C11b—C1	121.1 (2)	C9—C8—C5′	111.5 (2)
C9—C3′—C4′	102.8 (2)	C7a—C8—C5′	127.2 (2)
C8—C9—C3′	112.4 (2)	C10—C9—C3′	125.3 (2)
C3′—C4′—C5′	107.2 (2)	C8—C5′—C4′	103.0 (2)
C1—C11b—C11a—C7a	−178.9 (2)	C2—C1—C11b—C11a	156.6 (2)
C2—C3—N3a—C11c	39.9 (3)	C2—C3—N3a—C4	−162.1 (2)
C3—C2—C1—C11b	48.2 (3)	C3—N3a—C4—C5*a*	164.4 (3)
C3—N3a—C4—C5*b*	−163.8 (5)	C3—N3a—C11c—C6a	170.5 (2)
N3a—C3—C2—C1	−57.4 (3)	N3a—C4—C5*a*—C6	54.8 (4)
N3a—C4—C5*b*—C6	−12 (1)	N3a—C11c—C6a—C6	−5.3 (3)
N3a—C11c—C6a—C7	175.4 (2)	N3a—C11c—C11b—C1	3.6 (3)
N3a—C11c—C11b—C11a	−175.4 (2)	C4—N3a—C11c—C11b	−169.5 (2)
C4—C5*a*—C6—C6a	−47.2 (4)	C4—C5*b*—C6—C6a	19 (1)
C5*a*—C4—N3a—C11c	−37.9 (3)	C5*b*—C4—N3a—C11c	−6.0 (6)
C5*a*—C6—C6a—C7	−158.6 (3)	C5*b*—C6—C6a—C7	168.1 (6)
C3′—C4′—C5′—C8	17.3 (2)	C4′—C3′—C9—C10	−169.5 (2)
C4′—C5′—C8—C7a	169.4 (2)	C5′—C4′—C3′—C9	−16.7 (2)
C2—C1—C11b—C11c	−22.3 (3)	C4—N3a—C11c—C6a	13.8 (3)
C5*a*—C6—C6a—C11c	22.1 (4)	C5*b*—C6—C6a—C11c	−11.2 (7)

Most of the non-H atoms were located by direct methods using *SAPI*91 (Fan, 1991). The positions of atom C5*b* and most of the H atoms, except those attached to the C5*a* and C5*b* atoms, were found from difference Fourier maps. All non-H atoms were refined anisotropically and most of the H atoms isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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