Cl—C5	1.790 (2)	C2—C3	1.507 (3)
O2—C3	1.457 (2)	C4—C5	1.504 (2)
N1—C4	1.453 (2)	C6—C7	1.523 (3)
O1—P—O2	110.66 (7)	C1—N2—C7	115.90 (14)
O1—P—N1	117.89 (7)	C1—N2—P	115.47 (11)
O2—P—N1	106.17 (7)	C7—N2—P	107.74 (11)
O1—P—N2	117.98 (7)	N2—C1—C2	113.29 (14)
O2—P—N2	105.17 (7)	C3—C2—C1	111.01 (15)
N1—P—N2	97.36 (7)	O2—C3—C2	110.68 (14)
C3—O2—P	115.08 (10)	N1—C4—C5	113.29 (13)
C4—N1—C6	117.64 (13)	C4—C5—C1	111.38 (12)
C4—N1—P	121.13 (11)	N1—C6—C7	106.32 (13)
C6—N1—P	111.59 (11)	N2—C7—C6	106.29 (13)

The crystals of compound (1), although large, were mostly of poor quality and invariably shattered on attempts to cut them. We therefore used a crystal that may have been larger than the homogeneous beam area.

For compound (2), the crystal was also large. Furthermore, a referee has drawn our attention to the fact that absorption corrections might have been desirable (calculated systematic errors are *ca* 10%). In priniciple he is correct, although for compound (1) the wide and irregular reflection profiles would have militated against successful ψ scans. It is possible that the U values may be systematically affected to some extent by the factors mentioned here. However, we have campaigned for, rather than against, the use of large crystals (Jones, 1995).

Data collection: *XSCANS* (Siemens, 1994*a*) for (1); *DIF*4 (Stoe & Cie, 1991*a*) for (2). Cell refinement: *XSCANS* for (1); *DIF*4 for (2). Data reduction: *XSCANS* for (1); *REDU*4 (Stoe & Cie, 1991*b*) for (2). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Coumarin 338

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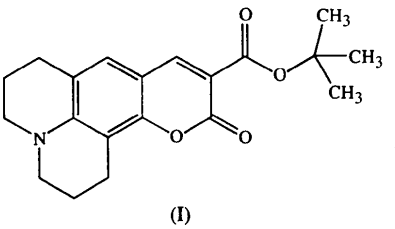
Abstract

In the title compound, 1,1-dimethylethyl 2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]-quinolizine-10-carboxylate, $C_{20}H_{23}NO_4$, the coumarin moiety is approximately planar. The two piperidine rings have sofa conformations and one is disordered. The N atom adopts a planar configuration and the carboxyl group is out of the coumarin plane.

Comment

The title compound, (I), (Eastman Kodak Co., Rochester, NY, USA) is used as an efficient laser dye. Derivatives with a structurally rigid amino group such as the title compound have been reported to show high quantum yields of fluorescence in polar solvents (Reynolds & Drexhage, 1975). The crystal structure



(I)

analysis of such derivatives is indispensable in understanding the correlations between the structure and the laser efficiency. In order to determine the effect of the 1,1-dimethylethyl group on the molecular structure, we have undertaken the X-ray structure analysis.

An *ORTEP*II (Johnson, 1976) drawing of the title compound together with the atomic numbering scheme is shown in Fig. 1. The coumarin moiety is approximately planar. The O2, C3, C5, C8, C10 and C7 atoms deviate significantly [by −0.119 (2), 0.111 (2) −0.068 (2), 0.050 (2), −0.037 (2) and 0.030 (2) Å, respectively] from the least-squares plane through the coumarin moiety. The dihedral angle between the pyrone and benzene rings is 3.36 (6)°. The piperidine ring *B* is disordered at the C20 atom. Two positions of the atom were located and refined with site occupancies of 0.50 for C20*a* and C20*b*. Both rings adopt sofa conformations. The torsion angles in the rings are between −40.3 (5) and 47.2 (5)° and between −30.3 (7) and 34.7 (6)° for the C7—C8— C21—C20*a*—C19—N18 and C7—C8—C21—C20*b*—C19—N18 rings, respectively. This indicates that the C7—C8—C21—C20*b*—C19—N18 ring is more flattened. The piperidine ring *A* also adopts a sofa conformation with the ring torsion angles in the range −53.8 (4)–52.7 (3)°. The carboxylate group is significantly out of the coumarin plane with C4—C3—C11—O11 and C2—C3—C11—O12 torsion angles of 25.5 (3) and 30.3 (2)°, respectively. The sum of the bond angles around N18 is 359.3 (4)°, indicating that N18 has a completely planar configuration. The molecules are packed in the crystal by van der Waals interactions.

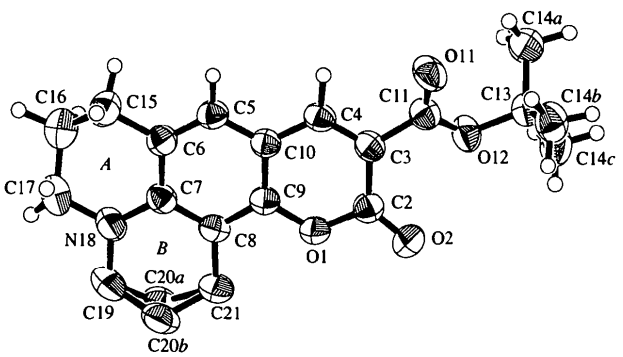


Fig. 1. *ORTEP*II (Johnson, 1976) drawing with heavy atoms as 50% probability ellipsoids and H atoms as circles of arbitrary radius.

Bond lengths and angles in the coumarin ring system of the title compound, (I), display normal values and are in agreement with those observed in coumarin 314 (Yip, Fun, Sivakumar, Zhou, Shawkataly & Teoh, 1995), 2,3,6,7-tetrahydro-9-methyl-1*H*,5*H*-quinolizino-[9,1-*gh*]coumarin (Chinnakali, Sivakumar & Natarajan, 1990), and 10-cyano-1,2,5,6-tetrahydro-3*H*,7*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one (Chinnakali, Selladurai, Sivakumar, Subramanian & Natarajan, 1990) in which an amino group at the 7-position is made rigid by the fused quinolizine ring.

Experimental

The crystals were grown from ethanol solution by slow evaporation at 293 (5) K in the dark room.

Crystal data

$C_{20}H_{23}NO_4$
M_r = 341.41
Monoclinic
$P2_1/a$
a = 9.1259 (8) Å
b = 21.802 (1) Å
c = 9.0555 (9) Å
β = 102.850 (8)°
V = 1756.6 (2) Å^3
Z = 4
D_x = 1.29 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 30–35°
μ = 0.731 mm^{-1}
T = 293 (2) K
Rod
0.80 × 0.40 × 0.10 mm
Yellow

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3978 measured reflections
3752 independent reflections
3102 observed reflections [$F > 3\sigma(F)$]
R_{int} = 0.012
θ_{max} = 74.9°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 27$
$l = -11 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: −0.412%

Refinement

Refinement on F
R = 0.052
wR = 0.087
S = 2.30
3102 reflections
305 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: $|F_{calc}|/(1+gI_{calc})$
Extinction coefficient: 2.26760 × 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}
O1	0.2771 (1)	−0.02182 (5)	0.5835 (1)	4.31 (3)
O2	0.3566 (2)	−0.10928 (6)	0.6919 (2)	5.59 (3)
O11	0.1580 (2)	−0.07793 (7)	1.0509 (2)	5.78 (3)
O12	0.3803 (1)	−0.10610 (6)	1.0047 (1)	4.76 (3)
N18	0.1022 (2)	0.15947 (7)	0.3098 (2)	5.18 (3)
C2	0.2920 (2)	−0.06201 (8)	0.7036 (2)	4.09 (3)
C3	0.2247 (2)	−0.04305 (7)	0.8276 (2)	3.90 (3)
C4	0.1343 (2)	0.00720 (8)	0.8114 (2)	3.98 (3)
C5	0.0289 (2)	0.09955 (8)	0.6636 (2)	4.14 (3)
C6	0.0220 (2)	0.13695 (8)	0.5419 (2)	4.14 (3)
C7	0.1049 (2)	0.12143 (7)	0.4299 (2)	3.94 (3)
C8	0.1913 (2)	0.06729 (7)	0.4460 (2)	4.00 (3)

C9	0.1931 (2)	0.03067 (7)	0.5709 (2)	3.64 (3)
C10	0.1150 (2)	0.04569 (7)	0.6830 (2)	3.68 (3)
C11	0.2480 (2)	−0.07805 (8)	0.9718 (2)	4.22 (3)
C13	0.4259 (2)	−0.14583 (8)	1.1393 (2)	4.31 (3)
C14*c*	0.5818 (3)	−0.1660 (1)	1.1269 (3)	6.21 (5)
C14*b*	0.3185 (3)	−0.1996 (1)	1.1253 (3)	5.91 (5)
C14*a*	0.4315 (3)	−0.1098 (1)	1.2832 (2)	5.99 (5)
C15	−0.0731 (3)	0.1948 (1)	0.5227 (3)	5.59 (5)
C16	−0.0109 (4)	0.2416 (1)	0.4353 (3)	7.56 (7)
C17	0.0118 (4)	0.2151 (1)	0.2875 (3)	7.50 (7)
C19	0.1708 (4)	0.1419 (1)	0.1859 (3)	7.12 (7)
C20*a*	0.2955 (5)	0.1027 (2)	0.2321 (5)	4.77 (8)
C20*b*	0.2249 (7)	0.0797 (2)	0.1841 (5)	5.9 (1)
C21	0.2784 (3)	0.0490 (1)	0.3303 (2)	5.66 (5)

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

O1—C2	1.379 (2)	C3—C11	1.487 (2)
O1—C9	1.368 (2)	C6—C15	1.519 (2)
O2—C2	1.203 (2)	C8—C21	1.503 (2)
O11—C11	1.204 (2)	C15—C16	1.479 (4)
O12—C11	1.327 (2)	C16—C17	1.513 (4)
O12—C13	1.478 (2)	C19—C20*a*	1.411 (5)
N18—C7	1.363 (2)	C19—C20*b*	1.446 (6)
N18—C17	1.456 (3)	C20*a*—C21	1.499 (4)
N18—C19	1.453 (3)	C20*b*—C21	1.466 (5)
C2—O1—C9	123.5 (1)	C15—C16—C17	110.8 (2)
C11—O12—C13	122.1 (1)	N18—C17—C16	112.3 (2)
C7—N18—C17	121.8 (2)	N18—C19—C20*a*	112.9 (2)
C7—N18—C19	121.4 (2)	N18—C19—C20*b*	117.6 (2)
C17—N18—C19	116.1 (2)	C19—C20*a*—C21	117.8 (3)
O11—C11—O12	125.1 (2)	C19—C20*b*—C21	117.6 (3)
O11—C11—C3	122.6 (2)	C8—C21—C20*a*	110.3 (2)
O12—C11—C3	112.3 (1)	C8—C21—C20*b*	112.8 (3)
O11—C11—C3—C4	25.5 (3)	N18—C7—C6—C15	2.1 (3)
O11—C11—O12—C13	5.8 (3)	C8—C7—N18—C19	8.2 (3)
C17—N18—C19—C20*a*	158.6 (3)	C7—N18—C19—C20*a*	−30.4 (4)
C17—N18—C19—C20*b*	−163.1 (4)	C7—N18—C19—C20*b*	7.9 (5)
C7—C6—C15—C16	−28.1 (3)	N18—C19—C20*a*—C21	47.2 (5)
C6—C15—C16—C17	52.7 (3)	N18—C19—C20*b*—C21	−30.3 (7)
N18—C17—C16—C15	−53.8 (4)	C8—C21—C20*a*—C19	−40.3 (5)
C7—N18—C17—C16	28.4 (4)	C8—C21—C20*b*—C19	34.7 (6)
C16—C17—N18—C19	−160.7 (3)	C7—C8—C21—C20*a*	16.7 (3)
C6—C7—N18—C17	−2.5 (3)	C7—C8—C21—C20*b*	−19.3 (4)
N18—C7—C8—C21	−1.8 (3)		

Most non-H atoms were located by direct methods using the program *SAPI*91 (Fan, 1991). The other non-H atoms and most H atoms were found from difference Fourier maps. The positions of the remaining H atoms, except those attached to atoms C19, C20 and C21, were calculated geometrically. All non-H atoms were refined anisotropically and some 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 solve structure: *SAPI*91 (Fan, 1991). 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: KH1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Studies of Mitomycins. VIII. Mitomycin D Hydrate, $C_{15}H_{18}N_4O_5.1.5H_2O$

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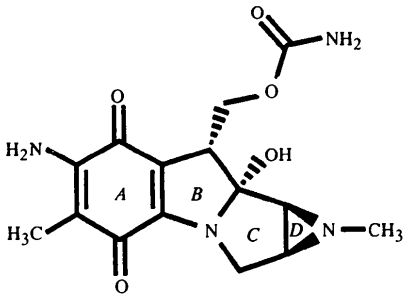
(*Received 30 October 1995; accepted 29 March 1996*)

Abstract

The title compound, [1a*S*]-6-amino-1,1a,2,4,7,8,8a,8b-octahydro-8a-hydroxy-1,5-dimethyl-4,7-dioxoazirino[2′,-3′:3,4]pyrrolo[1,2-*a*]indol-7-ylmethyl, is a mitomycin derivative, mitomycins being antitumor antibiotics. The O atoms of the quinone ring deviate significantly from the least-squares plane through the quinone ring.

Comment

Mitomycins are very effective antitumor antibiotics. An understanding of the relationships between the three-dimensional structures and their biological activities is very important when designing better antitumor agents.



(I)