C19	0.33498 (9)	1.2482 (4)	−0.0988 (4)	0.0693 (11)
C21	0.32667 (12)	1.4357 (4)	0.0085 (8)	0.0960 (15)
C23	0.31329 (9)	1.2533 (5)	0.1187 (5)	0.0820 (13)
C22	0.31507 (11)	1.3767 (6)	0.1172 (7)	0.105 (2)
C6	0.28749 (9)	0.8963 (6)	0.0775 (4)	0.0689 (12)
N3	0.38187 (6)	0.9913 (2)	0.0066 (2)	0.0374 (8)
C4	0.41785 (7)	0.9636 (3)	0.0618 (3)	0.0373 (9)
C5	0.44116 (8)	1.0624 (3)	0.0154 (3)	0.0574 (10)
C11	0.46488 (7)	0.8062 (3)	0.0913 (3)	0.0461 (9)
C18	0.41083 (9)	0.5995 (3)	−0.1039 (4)	0.0668 (11)
C9	0.42779 (6)	0.8343 (2)	0.0246 (3)	0.0328 (9)
C10	0.42589 (8)	0.8141 (3)	−0.1324 (3)	0.0476 (10)
C14	0.47280 (8)	0.6598 (3)	−0.0965 (4)	0.0636 (11)
C17	0.41327 (8)	0.6159 (3)	0.0530 (4)	0.0564 (10)
C12	0.40327 (7)	0.7450 (3)	0.0842 (3)	0.0470 (9)
C15	0.47474 (8)	0.6773 (3)	0.0599 (4)	0.0565 (10)
C13	0.43588 (9)	0.6850 (3)	−0.1634 (4)	0.0566 (10)
C16	0.45016 (8)	0.5909 (3)	0.1188 (4)	0.0632 (11)
C2	0.35655 (7)	1.0057 (2)	0.0863 (5)	0.0366 (9)

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

O1—C2	1.216 (7)	C11—C9	1.520 (4)
O2—C6	1.321 (8)	C18—C13	1.506 (6)
O2—C1	1.424 (4)	C18—C17	1.508 (9)
O3—C6	1.199 (5)	C9—C10	1.517 (9)
C1—C8	1.484 (8)	C9—C12	1.519 (5)
C1—C2	1.517 (5)	C10—C13	1.510 (7)
C7—C6	1.467 (6)	C14—C15	1.507 (9)
N3—C2	1.318 (5)	C14—C13	1.509 (5)
N3—C4	1.451 (4)	C17—C16	1.505 (5)
C4—C5	1.509 (5)	C17—C12	1.511 (7)
C4—C9	1.526 (7)	C15—C16	1.498 (6)
C11—C15	1.507 (7)		
C6—O2—C1	116.1 (3)	C12—C9—C4	109.3 (3)
O2—C1—C8	107.7 (3)	C11—C9—C4	109.8 (2)
O2—C1—C2	109.3 (3)	C13—C10—C9	110.5 (2)
C8—C1—C2	109.4 (2)	C15—C14—C13	109.3 (3)
C19—C8—C1	119.6 (4)	C16—C17—C18	109.8 (3)
C23—C8—C1	121.8 (4)	C16—C17—C12	109.7 (3)
O3—C6—O2	122.7 (4)	C18—C17—C12	108.9 (3)
O3—C6—C7	125.5 (5)	C17—C12—C9	110.4 (3)
O2—C6—C7	111.8 (5)	C16—C15—C11	109.7 (4)
C2—N3—C4	123.4 (4)	C16—C15—C14	109.7 (3)
N3—C4—C5	108.3 (3)	C11—C15—C14	109.6 (3)
N3—C4—C9	111.4 (2)	C18—C13—C14	109.5 (3)
C5—C4—C9	115.4 (3)	C18—C13—C10	108.8 (4)
C15—C11—C9	110.6 (3)	C14—C13—C10	109.7 (3)
C13—C18—C17	109.8 (3)	C15—C16—C17	109.3 (3)
C10—C9—C12	108.8 (3)	O1—C2—N3	125.0 (3)
C10—C9—C11	108.5 (3)	O1—C2—C1	121.0 (3)
C12—C9—C11	107.6 (3)	N3—C2—C1	114.0 (4)
C10—C9—C4	112.7 (2)		
C6—O2—C1—C8	173.9 (3)	C15—C11—C9—C12	59.2 (4)
C6—O2—C1—C2	−67.3 (4)	C15—C11—C9—C4	178.0 (2)
O2—C1—C8—C19	−149.6 (3)	N3—C4—C9—C10	62.2 (3)
C2—C1—C8—C19	91.7 (4)	N3—C4—C9—C12	−58.9 (4)
C1—O2—C6—O3	−1.9 (5)	N3—C4—C9—C11	−176.7 (2)
C2—N3—C4—C5	−121.8 (3)	C4—N3—C2—C1	171.2 (2)
C2—N3—C4—C9	110.3 (3)	O2—C1—C2—N3	153.7 (3)
C15—C11—C9—C10	−58.4 (3)	C8—C1—C2—N3	−88.6 (3)

Data collection was performed on synchrotron beamline X31 at EMBL – Hamburg, HASYLAB, DESY. The crystals did not diffract in a standard sealed-tube generator, but diffracted reasonably well in the synchrotron beam. The rotation method, standard for macromolecular crystallography, was employed since it provides accurate data in a fraction of the time necessary for conventional diffractometry (Grochowski, Serda, Wilson & Dauter, 1994). Data were collected with an image plate area detector, with 5° rotation per image and a total of 120°, which was enough to give 92% complete data. Space-group determination, intensity integration for diffraction spots from the images and reduction of data to the asymmetric unit were carried out using *DENZO* software (Otwinowski, 1993), widely used in macromolecular crystallography. The data quality was high as judged by $R_{\rm merge}$ [$R_{\rm merge} = \Sigma(|I-\langle I\rangle|)/(\Sigma I)$], which showed that the internal agreement for all symmetry-related and multiply recorded reflections was 5.3%. The total amount of time used was a slot of 2 h of machine-studies beam time.

Cell refinement: *DENZO SCALEPACK* (Otwinowski, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Zbigniew Dauter is thanked for help in the data collection and indexing of the rotation images.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1211). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Coumarin 343, $C_{16}H_{15}NO_4$

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Abstract

In the title compound, 2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid, the coumarin moiety is planar. The two piperidine rings take flattened sofa conformations. There

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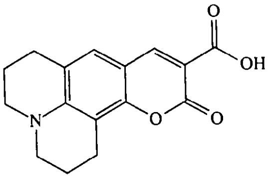
is an intramolecular hydrogen bond between the carbonyl group and the carboxylic acid group; the hydrogen bond influences the bond lengths in the pyrone ring. The crystal packing is governed by van der Waals forces.

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 present analysis has been undertaken to elucidate the correlation between the structure and the laser efficiency.



(I)

An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme is shown in Fig. 1. The coumarin moiety is planar with a mean deviation from the least-squares plane of 0.004 (2) Å. The two piperidine rings take flattened sofa conformations. In the C1—C2—C3—N3a—C11c—C11b ring, the C2 atom deviates significantly [0.670 (2) Å] from the least-squares plane defined by C1, C3, N3a, C11c and C11b. The mean deviation of the constituent atoms is 0.038 (2) Å. In the C4—C5—C6—C6a—C11c—N3a ring, the C5 atom is also deviates significantly [0.681 (2) Å] from the least-squares plane defined by the remaining five atoms. The mean deviation of the constituent atoms is 0.031 (2) Å. The carboxylic acid group is coplanar with the coumarin moiety.

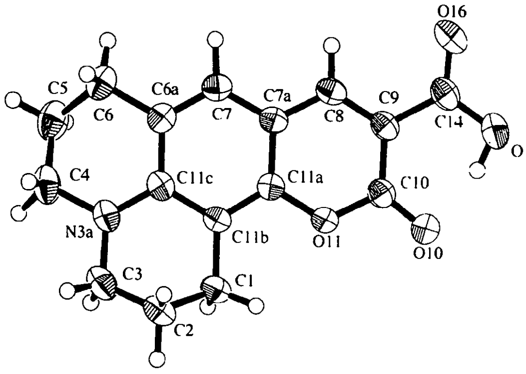


Fig. 1. *ORTEP*II (Johnson, 1976) drawing representing heavy atoms as 50% probability ellipsoids and H atoms as circles of arbitrary size.

The N3a—C11c, O11—C10 and C9—C10 bonds are remarkably shorter than the corresponding distances in coumarin 314 (Yip *et al.*, 1995). In particular, N3a—C11c is very short. The C7a—C8 and C11a—C11b bonds are also significantly shorter than the corresponding bonds in coumarin 314. On the other hand, the O10—C10 and C11b—C11c bonds are significantly longer than the corresponding distances in coumarin 314. The sum of bond angles around N3a is 360.0 (2)° and N3a takes a completely planar configuration. The exocyclic bond angles around the carbonyl group are highly asymmetric, as in coumarin 314.

There is an intramolecular hydrogen bond between the carbonyl and carboxylic acid groups [O10···O15 = 2.591 (1), O10···H15 = 1.70 (3) Å, O10···H15—O15 = 162 (1)°]. It may be due to this hydrogen bond that the bond lengths around C2 differ significantly from the corresponding bonds of coumarin 314, in which O10 is not involved in any hydrogen bonds.

The molecules are packed by van der Waals contacts and there is no intermolecular hydrogen bond in the crystal.

Experimental

Crystals were grown from chloroform solution by slow evaporation at 293 (5) K in a dark room.

Crystal data

$C_{16}H_{15}NO_4$
$M_r = 285.30$
Orthorhombic
Pbca
$a = 13.9887\ (9)$ Å
$b = 23.444\ (1)$ Å
$c = 7.8082\ (6)$ Å
$V = 2560.7\ (2)$ Å^3
$Z = 8$
$D_x = 1.48$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 30$–$35°$
$\mu = 0.889$ mm^{-1}
$T = 293\ (2)$ K
Rod
0.5 × 0.3 × 0.2 mm
Orange

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3024 measured reflections
3024 independent reflections
2201 observed reflections [$F > 3\sigma(F)$]

$\theta_{\max} = 74.9°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 29$
$l = -9 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 0.58%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.058$
$S = 2.56$
2201 reflections
251 parameters

$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: $|F_{\rm calc}|/(1 + gI_{\rm calc})$
Extinction coefficient: 1.6874×10^{-6}

H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$

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

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

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

	x	y	z	B_{eq}
O10	0.18481 (9)	−0.04613 (5)	0.9297 (2)	4.02 (3)
O11	0.11514 (7)	0.02299 (5)	0.7871 (1)	3.04 (2)
O15	0.0918 (1)	−0.13784 (6)	1.0106 (2)	1.35 (3)
O16	−0.0589 (1)	−0.14516 (5)	0.9295 (2)	4.39 (3)
N3a	−0.0162 (1)	0.17968 (6)	0.4842 (2)	3.50 (3)
C1	0.1473 (1)	0.13100 (8)	0.6446 (3)	3.63 (4)
C2	0.1591 (2)	0.16806 (8)	0.4864 (3)	4.00 (4)
C3	0.0765 (2)	0.20831 (8)	0.4694 (3)	4.19 (4)
C4	−0.0965 (2)	0.21220 (8)	0.4136 (3)	4.40 (5)
C5	−0.1914 (2)	0.19139 (9)	0.4799 (3)	4.71 (5)
C6a	−0.1167 (1)	0.09841 (7)	0.5440 (2)	3.01 (3)
C6	−0.1989 (1)	0.12762 (9)	0.4556 (3)	3.78 (4)
C7a	−0.0498 (1)	0.01832 (6)	0.7001 (2)	2.77 (3)
C7	−0.1265 (1)	0.04585 (7)	0.6166 (2)	3.10 (3)
C8	−0.0554 (1)	−0.03539 (7)	0.7769 (2)	2.96 (3)
C9	0.0215 (1)	−0.05973 (6)	0.8569 (2)	2.93 (3)
C10	0.1105 (1)	−0.02935 (7)	0.8623 (2)	2.99 (3)
C11a	0.0384 (1)	0.04772 (6)	0.7054 (2)	2.66 (3)
C11b	0.0527 (1)	0.10053 (7)	0.6354 (2)	2.81 (3)
C11c	−0.0264 (1)	0.12731 (7)	0.5532 (2)	2.84 (3)
C14	0.0135 (1)	−0.11722 (7)	0.9343 (2)	3.36 (3)

Table 2. *Geometric parameters (Å, °)*

O11—C10	1.362 (2)	O10—C10	1.230 (2)
C9—C10	1.436 (2)	C8—C9	1.368 (2)
C9—C14	1.481 (2)	C7a—C8	1.397 (2)
C7a—C7	1.411 (2)	C7a—C11a	1.414 (2)
C6a—C7	1.363 (2)	C6a—C6	1.505 (2)
C6a—C11c	1.435 (2)	N3a—C11c	1.348 (2)
C11b—C11c	1.425 (2)	C11a—C11b	1.368 (2)
C1—C11b	1.505 (2)	O11—C11a	1.377 (2)
C1—C2	1.519 (3)	C2—C3	1.497 (3)
N3a—C3	1.465 (2)	N3a—C4	1.466 (2)
C4—C5	1.505 (3)	C5—C6	1.511 (3)
O15—C14	1.337 (2)	O15—H15	0.92 (3)
O16—C14	1.207 (2)		
C10—O11—C11a	122.8 (1)	O10—C10—O11	115.7 (1)
O10—C10—C9	126.0 (1)	O11—C10—C9	118.4 (1)
C8—C9—C10	119.2 (1)	C8—C9—C14	120.4 (1)
C10—C9—C14	120.3 (1)	C7a—C8—C9	121.9 (1)
C7—C7a—C8	124.7 (1)	C7—C7a—C11a	117.0 (1)
C8—C7a—C11a	118.4 (1)	C6—C6a—C7	121.7 (2)
C6—C6a—C11c	118.7 (2)	C7—C6a—C11c	119.6 (1)
N3a—C11c—C6a	120.2 (1)	N3a—C11c—C11b	119.9 (1)
C6a—C11c—C11b	119.9 (1)	C1—C11b—C11a	122.6 (1)
C1—C11b—C11c	119.7 (1)	C11a—C11b—C11c	117.7 (1)
O11—C11a—C7a	119.2 (1)	O11—C11a—C11b	116.9 (1)
C7a—C11a—C11b	123.8 (1)	C2—C1—C11b	109.2 (2)
C1—C2—C3	110.4 (2)	N3a—C3—C2	112.8 (1)
C3—N3a—C4	114.3 (2)	C3—N3a—C11c	122.8 (1)
C4—N3a—C11c	122.9 (2)	N3a—C4—C5	112.2 (2)
C4—C5—C6	109.8 (2)	C5—C6—C6a	109.9 (2)
C6a—C7—C7a	122.0 (1)	O15—C14—O16	120.3 (2)
O15—C14—C9	116.7 (2)	O16—C14—C9	123.0 (2)
O15—C14—C9—C10	1.4 (2)	C5—C4—N3a—C11c	19.9 (3)
N3a—C4—C5—C6	−51.5 (2)	C2—C3—N3a—C11c	17.8 (3)
C3—C2—C1—C11b	55.8 (2)	N3a—C3—C2—C1	−49.8 (2)
C3—N3a—C11c—C11b	8.1 (2)	C2—C1—C11b—C11a	148.9 (2)
C5—C6—C6a—C7	146.9 (2)	C4—N3a—C11c—C6a	6.6 (2)
C4—C5—C6—C6a	57.0 (2)		

Most non-H atoms were located by direct methods using the program *SAPI*91 (Fun, 1991). Some H atoms were found from difference Fourier maps. The positions of the remaining H atoms were calculated geometrically. All non-H atoms were refined anisotropically and all 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. 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: AS1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cyclic Hexa-Pseudopeptide Constructed from *N*,*N*′-Ethylene-Bridged (*S*)-Phenylalanyl-(*S*)-Phenylalanine and Glycine

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Abstract

(6*S*,9*S*,15*S*,18*S*)-6,9,15,18-Tetrabenzyl-1,4,7,10,13,16-hexaazatricyclo[14.2.2.2^{7,10}]docosane-2,5,8,11,14,17-hexaone crystallizes with two water molecules ($C_{44}H_{46}N_6O_6$.-$2H_2O$). The two piperazin-2-one rings are perpendicular to the 18-membered ring, thus producing a molecular cavity. A water molecule is located in this cavity and interacts with the macrocyclic ring.

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