Stoe & Cie (1987b) *EMPIR. Empirical Absorption Correction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987c) *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

An Orange Form of Coumarin 314

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Abstract

A new form of the title compound, ethyl 2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij]-quinolizine-10-carboxylate, $C_{18}H_{19}NO_4$, was recrystallized from ethanol and is orange in colour. The coumarin moiety is planar and the conformation of the ethoxycarbonyl group is different from that of the yellow form. One of the piperidine rings is disordered and the N atom is in a planar configuration. The crystal packing is governed by van der Waals interactions.

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 a high quantum yield of fluorescence in polar solvent (Reynolds & Drexhage, 1975). In order to understand the correlation between their structure and laser efficiency, crystal structure analyses of these derivatives are indispensable. The crystal structure of the yellow form of the title compound, recrystallized from a mixture of chloroform and ethanol, has been reported recently (Yip *et al.*, 1995). We have obtained a second polymorph, the orange form, from an ethanol solution and undertaken the X-ray analysis which is presented here.

(I)
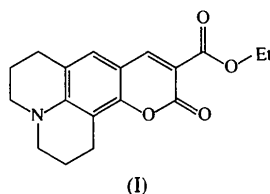
An *ORTEP*II drawing (Johnson, 1976) of the title compound together with the atomic numbering scheme is shown in Fig. 1. The coumarin moiety is almost planar, with a mean deviation from the least-squares plane of 0.010 (2) Å; atom O2 deviates significantly from the least-squares plane [0.029 (2) Å]. One of the piperazine rings (C6—C7—N18—C17—C16—C15) is disordered at the C16 atom. Two positions of the atom were located and refined with occupancies for C16A and C16B of 0.75 and 0.25, respectively. Both rings adopt sofa conformations. The ring containing atom C16B adopts a more flattened conformation. The torsion angles in the major and minor rings are in the ranges −52.1 (3) to 48.1 (3)° and −31.3 (9) to 29 (1)°, respectively. The conformation of the ring in the yellow form is between a sofa and a half chair. The second piperidine ring (C7—C8—C21—C20—C19—N18) also takes a sofa conformation, as in the yellow form. The conformation of the ethoxycarbonyl group is remarkably different from that in the yellow form, the carbonyl O atom being *cis* with respect to the C2 atom in the yellow form but *trans* in the orange form. The group is planar and makes a dihedral angle of 4.4 (2)° with the plane of the coumarin moiety, which is significantly smaller than the value of 12.29 (7)° found in the yellow form.
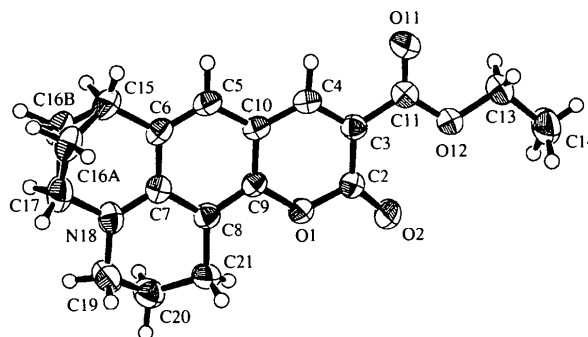

Fig. 1. *ORTEP*II drawing (Johnson, 1976) representing heavy atoms as 50% probability ellipsoids and H atoms as circles of arbitrary size.

The C2—C3 and O11—C11 bonds are significantly longer and the C20—C21 and N18—C7 bonds significantly shorter than the corresponding values in the yellow form (Yip *et al.*, 1995). The sum of the bond angles around the N18 atom is 360.0 (2)° and indicates that the N18 atom adopts a completely planar configuration, as in the yellow form. The exocyclic bond angles around the carbonyl group are highly asymmetric, just as in the yellow form. The bond angles around the C11 atom are significantly different from the corresponding values in the yellow form, the O11—C11—C3 angle being remarkably smaller. The molecules are packed together in the crystal according to van der Waals interactions.

Experimental

Crystals of the title compound were grown from ethanol solution by slow evaporation in the dark at room temperature.

Crystal data

$C_{18}H_{19}NO_4$	Cu $K\alpha$ radiation
$M_r = 313.34$	$\lambda = 1.54184$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 12.266\,(1)$ Å	$\theta = 30–38°$
$b = 11.879\,(1)$ Å	$\mu = 0.799$ mm^{-1}
$c = 10.412\,(2)$ Å	$T = 297\,(2)$ K
$\beta = 93.76\,(1)°$	Rod
$V = 1513.8\,(3)$ Å^3	$0.75 \times 0.50 \times 0.38$ mm
$Z = 4$	Orange
$D_x = 1.366$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 Turbo	$R_{int} = 0.011$
diffractometer	$\theta_{max} = 74.9°$
$\omega/2\theta$ scans	$h = -15 \rightarrow 15$
Absorption correction:	$k = 0 \rightarrow 14$
none	$l = 0 \rightarrow 13$
3465 measured reflections	3 standard reflections
3296 independent reflections	frequency: 60 min
2751 observed reflections	intensity decay: 0.964%
$[F > 3\sigma(F)]$	

Refinement

Refinement on F	Extinction correction:
$R = 0.055$	$F = |F_{calc}|/(1 + gI_{calc})$
$wR = 0.089$	Extinction coefficient:
$S = 4.29$	4.10825×10^{-6}
2751 reflections	Atomic scattering factors
291 parameters	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.01$	(1974, Vol. IV)
$\Delta\rho_{max} = 0.38$ e Å^{-3}	
$\Delta\rho_{min} = -0.20$ e Å^{-3}	

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	0.85365 (9)	0.1187 (1)	0.5300 (1)	3.46 (3)
O2	0.7962 (1)	0.2406 (1)	0.3836 (1)	4.67 (3)
O11	1.0969 (1)	0.4147 (1)	0.4318 (2)	5.84 (4)
O12	0.9397 (1)	0.4019 (1)	0.3142 (1)	4.27 (3)
N18	0.9488 (1)	-0.1564 (1)	0.8490 (1)	3.93 (3)
C2	0.8716 (1)	0.2138 (1)	0.4558 (2)	3.26 (3)
C3	0.9772 (1)	0.2674 (1)	0.4788 (2)	3.29 (3)
C4	1.0510 (1)	0.2250 (1)	0.5702 (2)	3.36 (3)
C5	1.1037 (1)	0.0832 (2)	0.7393 (2)	3.60 (4)
C6	1.0784 (1)	-0.0105 (2)	0.8071 (2)	3.59 (4)
C7	0.9747 (1)	-0.0637 (1)	0.7813 (2)	3.18 (3)
C8	0.8984 (1)	-0.0188 (1)	0.6870 (2)	3.20 (3)
C9	0.9286 (1)	0.0759 (1)	0.6212 (2)	2.98 (3)
C10	1.0298 (1)	0.1294 (1)	0.6438 (2)	3.21 (3)
C11	1.0109 (2)	0.3685 (2)	0.4075 (2)	3.79 (4)
C13	0.9726 (2)	0.5003 (2)	0.2440 (2)	4.98 (5)
C14	0.8865 (3)	0.5238 (3)	0.1417 (3)	6.61 (7)
C15	1.1554 (2)	-0.0574 (2)	0.9127 (3)	5.57 (6)
C16A*	1.1395 (2)	-0.1806 (3)	0.9292 (3)	4.55 (6)
C16B†	1.1215 (8)	-0.1299 (9)	0.9931 (9)	4.9 (2)
C17	1.0245 (2)	-0.2094 (2)	0.9451 (2)	5.01 (5)
C19	0.8422 (2)	-0.2116 (2)	0.8308 (3)	5.00 (5)
C20	0.7540 (2)	-0.1345 (2)	0.7787 (2)	4.68 (5)
C21	0.7875 (2)	-0.0721 (2)	0.6615 (2)	4.19 (4)

* Occupancy of 0.75.   † Occupancy of 0.25.

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

O1—C2	1.394 (2)	C5—C10	1.412 (2)
O1—C9	1.375 (2)	C6—C7	1.429 (2)
O2—C2	1.196 (2)	C6—C15	1.509 (3)
O11—C11	1.201 (2)	C7—C8	1.415 (2)
O12—C11	1.324 (2)	C8—C9	1.380 (2)
O12—C13	1.450 (2)	C8—C21	1.508 (2)
N18—C7	1.356 (2)	C9—C10	1.401 (2)
N18—C17	1.463 (2)	C13—C14	1.477 (4)
N18—C19	1.465 (3)	C15—C16A	1.487 (4)
C2—C3	1.450 (2)	C15—C16B	1.29 (1)
C3—C4	1.366 (2)	C16A—C17	1.471 (4)
C3—C11	1.485 (2)	C16B—C17	1.58 (1)
C4—C10	1.403 (2)	C19—C20	1.492 (3)
C5—C6	1.366 (3)	C20—C21	1.508 (3)
C2—O1—C9	124.0 (1)	C9—C8—C21	121.5 (2)
C11—O12—C13	114.8 (2)	O1—C9—C8	117.1 (1)
C7—N18—C17	123.1 (2)	O1—C9—C10	119.5 (1)
C7—N18—C19	122.3 (2)	C8—C9—C10	123.4 (2)
C17—N18—C19	114.6 (2)	C4—C10—C5	124.4 (2)
O1—C2—O2	114.9 (1)	C4—C10—C9	118.0 (2)
O1—C2—C3	115.8 (1)	C5—C10—C9	117.6 (2)
O2—C2—C3	129.3 (2)	O11—C11—O12	123.0 (2)
C2—C3—C4	119.8 (2)	O11—C11—C3	122.3 (2)
C2—C3—C11	123.2 (1)	O12—C11—C3	114.7 (1)
C4—C3—C11	116.9 (2)	O12—C13—C14	107.8 (2)
C3—C4—C10	122.7 (2)	C6—C15—C16A	111.5 (2)
C6—C5—C10	121.6 (2)	C6—C15—C16B	120.5 (4)
C5—C6—C7	119.5 (2)	C15—C16A—C17	112.1 (2)
C5—C6—C15	121.7 (2)	C15—C16B—C17	117.6 (6)
C7—C6—C15	118.8 (2)	N18—C17—C16A	113.2 (2)
N18—C7—C6	119.8 (2)	N18—C17—C16B	113.0 (4)
N18—C7—C8	120.0 (2)	N18—C19—C20	113.1 (2)
C6—C7—C8	120.3 (2)	C19—C20—C21	111.5 (2)
C7—C8—C9	117.7 (2)	C8—C21—C20	110.8 (2)
C7—C8—C21	120.8 (2)		
O11—C11—C3—C4	-3.1 (3)	C6—C15—C16B—C17	29 (1)
O12—C11—C3—C2	-4.5 (3)	C7—N18—C17—C16A	-20.7 (3)
N18—C7—C6—C15	-1.8 (3)	C7—N18—C17—C16B	18.1 (5)
N18—C7—C8—C21	0.7 (2)	C7—N18—C19—C20	-24.5 (3)
N18—C17—C16A—C15	48.1 (3)	C7—C6—C15—C16A	29.4 (3)
N18—C17—C16B—C15	-31.3 (9)	C7—C6—C15—C16B	-12.6 (7)
N18—C19—C20—C21	50.2 (3)	C7—C8—C21—C20	25.5 (3)
C3—C11—O12—C13	-179.7 (2)	C8—C7—N18—C19	-1.6 (3)
C6—C7—N18—C17	-3.0 (3)	C8—C21—C20—C19	-49.9 (3)
C6—C15—C16A—C17	-52.1 (3)	C11—O12—C13—C14	178.2 (2)

Most non-H atoms were located by direct methods. The positions of the C16B atom and most of the H atoms, except those attached to the C16B atom, were found from difference Fourier maps. The positions of the remaining H atoms were calculated geometrically. All non-H atoms were refined anisotropically and most H atoms were refined 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).

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1,1'-Diphenyl-1,1'-bicyclopropyl and 1,1'-Diphenyl-1,1'-bicyclobutyl

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Abstract

The molecules of 1,1'-diphenyl-1,1'-bicyclopropyl, $C_{18}H_{18}$, and 1,1'-diphenyl-1,1'-bicyclobutyl, $C_{20}H_{22}$, each possess a crystallographic centre of symmetry. Both molecules adopt the *trans* conformation. The cyclopropyl rings are approximately symmetric while the cyclobutyl rings are slightly folded.

Comment

The study of steric influences is of increasing importance not only in organic chemistry. Studies of the relationships between structure and activity of drugs attest to intermolecular effects as one of the reasons for the high selectivity of biochemical and recognition processes, which have been described, *inter alia*, as docking processes between an active substance and its receptor (Yalkowsky, Sinkuk & Valvani, 1980). During a study of the relationship between thermal stability, strain and structure in a series of 1,1'-diphenyl-1,1'-bicycloalkyls (C_4–C_8), Bernlöhr, Beckhaus, Lindner & Rüchardt (1984) determined the crystal structure of 1,1'-diphenyl-1,1'-bicyclooctyl and found it to have a *trans* conformation. Using MM2 calculations, they concluded that the bicycloheptyl and -hexyl compounds would have the *trans* conformation but that the -pentyl and

-butyl compounds would adopt the *gauche* form. We have recently investigated the structures and conformational equilibrium of 1,1'-diphenyl-1,1'-bicycloheptyl, -hexyl and -pentyl (Zhang, Xu, Koh, Lam & Huang, 1993). In view of our interest in diphenylethane derivatives, we decided to investigate the structures of other members of the 1,1'-diphenyl-1,1'-bicycloalkyl family of compounds to provide the experimental structural data which had hitherto been lacking. In this paper, we report the crystal structures of 1,1'-diphenyl-1,1'-bicyclopropyl, (1), and 1,1'-diphenyl-1,1'-bicyclobutyl, (2).

(1)   (2)
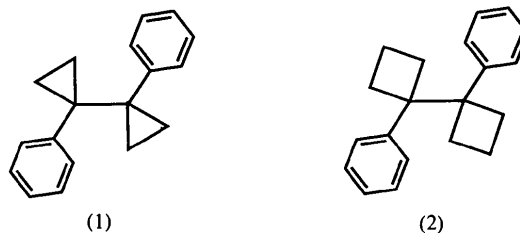
Molecule (1) is centrosymmetric and takes the *trans* conformation in the crystal, as in 1,1'-bicyclopropyl (Eraker & Rømming, 1967). This contrasts with 1-nitro-1'-nitroso-1,1'-bicyclopropyl, 1,1'-dinitro-1,1'-bicyclopropyl (Kai *et al.*, 1982) and 1,1'-dicyano-1,1'-bicyclopropyl (Schrumpf & Jones, 1987), which each exist as the *gauche* rotamer. The C(12)—C(11)—C(1) plane makes an angle of 86.9 (2)° with the plane through the central C atoms C(11), C(1) and C(1a). The central C(1)—C(1a) bond is longer than the corresponding bonds in 1,1'-bicyclopropyl (Eraker & Rømming, 1967) and the other substituted bicyclopropyls (Schrumpf & Jones, 1987; Kai *et al.*, 1982). The length of the central C—C bond appears not to be correlated with a single parameter, but to be influenced by several factors, *e.g.* conjugation between the two cyclopropane moieties, steric factors and electronic effects of the substituents at C(1) and C(1a).

The bond angles around the two central C atoms reveal evidence of intramolecular stress, the angle C(12)—C(11)—C(16) showing the largest deviation from 120° of any of the internal phenyl ring angles.

Molecule (2) is situated at a centre of symmetry with approximate C_{2h} symmetry and adopts the *trans* conformation. The C(12)—C(11)—C(1) plane is orientated at an angle of 90.8 (2)° to the C(11)—C(1)—C(1a) plane. The cyclobutyl rings are slightly folded forming a 'butterfly'-type square with C(3) bending away from the phenyl ring attached to C(1). The dihedral angle between the C(2)—C(1)—C(4) and C(2)—C(3)—C(4) planes is 17.5 (2)°. This contrasts with 1,1'-dinitro-1,1'-bicyclobutyl which exists as a *gauche* conformer in the crystalline state and has approximately planar cyclobutane rings (Kai *et al.*, 1982). The central C(1)—C(1a) bond is much longer than in (1). This is consistent with