Fuchs, P. L. (1974). *J. Am. Chem. Soc.* **96**, 1607–1609.
Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.
Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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7-Dimethylaminocyclopenta[*c*]coumarin, in Two Polymorphic Forms

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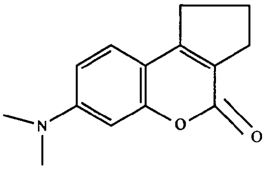
Abstract

Polymorphism in aminocoumarins has been observed in only one other instance [Jasinski & Paight (1994). *Acta Cryst.* C**50**, 1928–1930]. This structure, $C_{14}H_{15}NO_2$, represents the first reported observation of a non-centrosymmetric moiety in an aminocoumarin laser-dye compound. These differences, as well as those observed in luminescence changes, may result from the crystallization of C13 in an out-of-plane position in the cyclopenta[*c*] ring of polymorph (II). The crystal structures of both polymorphs [(I) and (II)] are stabilized by van der Waals forces.

Comment

The title compound is also known as Coumarin 138 (Kodak, USA). Aminocoumarin laser dyes, such as the title compound, are used in bicyclic dye laser-stability studies (Fletcher, 1977; Fletcher & Bliss, 1978), as fluorescent brightners and photographic sensitizers (Baczynski, Targowski, Sietek & Radomska, 1990), and as analytical fluorescent probes in micelles (Abdel-Mottalaeb, Antonious, Ali, Ismail, El-Sayed & Sherief, 1992). Both polymorphs were obtained from the same crystal crop in a fashion similar to that for (±)-β-promedol alcohol (De Camp & Ahmed, 1972). Under a black light, the centrosymmetric polymorph crystals, (I), produce a green luminescence and the non-centrosymmetric polymorph crystals, (II), give a purple luminescence.



Bond lengths and angles in the coumarin moiety are normal (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985; Murthy, Ramamurthy & Venkatesan, 1988). The dihedral angles between the least-squares planes of the planar pyrone [χ^2 = 19.4 (I), 24.4 (II)] and benzene [χ^2 = 15.1 (I), 5.6 (II)] moieties are 1.21 (3)° in (I), and 1.53 (2)° in (II). The dihedral angles between the least-squares planes of the cyclopenta[*c*] ring [χ^2 = 15.6 (I), 346.9 (II)] are tilted slightly more with respect to the benzene-ring plane, 3.72 (3) and 2.47 (2)° in (I) and (II), respectively. The torsion angles C2—C3—C4—C10 [−0.48 (4) (I), −0.9 (5)° (II)], C2—C3—C4—C14 [178.6 (3) (I), 179.6 (3)° (II)] and C10—C4—C3—C12 [−177.5 (2) (I), −179.5 (3)° (II)] indicate planar relationships that are almost identical for both polymorphs. However, the torsion angles C3—C12—C13—C14 [−0.66 (45) (I), 9.6 (5)° (II)] and C4—C14—C13—C12 [1.5 (5) (I), −9.4 (5)° (II)] indicate a deviation from planarity in polymorph (II) resulting from the displacement of C13 from the least-squares plane of the cyclopenta[*c*] ring. Therefore, the difference in luminescence behavior, along with the observed polymorphism of the two structures, may be associated with the crystallization of C13 in an out-of-plane position in (II).

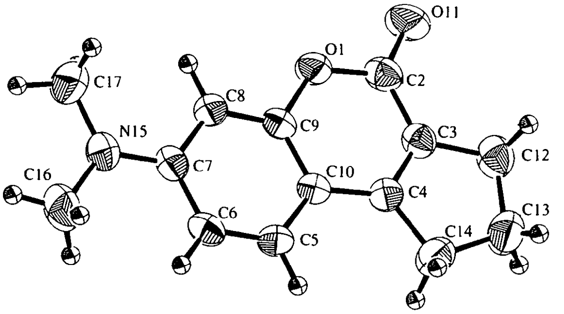


Fig. 1. *ORTEP* (Johnson, 1965) drawing and atom-numbering scheme for 7-dimethylaminocyclopenta[*c*]coumarin in two polymorphic modifications. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals of both modifications of the title compound (Sigma, USA) were grown from acetonitrile in the same beaker by slow evaporation.

Compound (I)

Crystal data

$C_{14}H_{15}NO_2$
M_r = 229.28
Orthorhombic
Pbca
a = 21.937 (8) Å
b = 15.327 (3) Å
c = 6.924 (1) Å

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 10.6–16.9°
μ = 0.082 mm^{-1}
T = 296 K

$V = 2328$ (2) Å^3
$Z = 8$
$D_x = 1.308$ Mg m^{-3}

Prism
0.80 × 0.70 × 0.40 mm
Clear yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction: empirical
$T_{\min} = 0.94$, $T_{\max} = 1.00$
2383 measured reflections
2383 independent reflections
1209 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 25°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 150 reflections intensity variation: −0.7%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.054$
$S = 2.02$
1209 reflections
215 parameters
All H-atom parameters refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.05$

$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: Zachariasen type-2 Gaussian isotropic
Extinction coefficient: 1.6798×10^{-4}
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) *for* (I)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.08244 (8)	0.0582 (1)	0.1897 (3)	3.9 (1)
O11	0.1810 (1)	0.0276 (2)	0.1876 (3)	5.8 (1)
N15	−0.1296 (1)	0.1185 (2)	0.2422 (4)	4.7 (1)
C2	0.1393 (1)	0.0603 (2)	0.1008 (4)	3.9 (3)
C3	0.1420 (1)	0.1024 (2)	−0.0832 (4)	3.5 (1)
C4	0.0922 (1)	0.1375 (2)	−0.1654 (4)	3.2 (1)
C5	−0.0200 (1)	0.1692 (2)	−0.1443 (5)	3.7 (2)
C6	−0.0737 (1)	0.1645 (2)	−0.0420 (5)	3.9 (2)
C7	−0.0763 (1)	0.1235 (2)	0.1393 (4)	3.5 (1)
C8	−0.0217 (1)	0.0886 (2)	0.2136 (5)	3.5 (1)
C9	0.0309 (1)	0.0939 (2)	0.1071 (4)	3.1 (1)
C10	0.0338 (1)	0.1340 (2)	−0.0738 (4)	3.1 (1)
C12	0.1988 (2)	0.1166 (3)	−0.1989 (5)	4.7 (2)
C13	0.1757 (2)	0.1675 (4)	−0.3748 (7)	6.0 (2)
C14	0.1074 (2)	0.1794 (3)	−0.3546 (6)	5.1 (2)
C16	−0.1857 (2)	0.1514 (4)	0.1609 (8)	6.0 (2)
C17	−0.1308 (2)	0.0832 (3)	0.4343 (6)	5.4 (2)

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

O1—C2	1.391 (3)	C4—C14	1.497 (5)
O1—C9	1.380 (3)	C5—C6	1.376 (4)
O11—C2	1.204 (3)	C5—C10	1.387 (4)
N15—C7	1.371 (4)	C6—C7	1.405 (4)
N15—C16	1.445 (5)	C7—C8	1.410 (4)
N15—C17	1.436 (5)	C8—C9	1.372 (4)
C2—C3	1.432 (4)	C9—C10	1.396 (3)
C3—C4	1.343 (4)	C12—C13	1.533 (5)
C3—C12	1.496 (4)	C13—C14	1.516 (5)
C4—C10	1.431 (4)		
C2—O1—C9	122.8 (2)	C5—C6—C7	121.2 (3)
C7—N15—C16	120.3 (3)	N15—C7—C6	121.5 (3)
C7—N15—C17	121.2 (3)	N15—C7—C8	121.0 (3)
C16—N15—C17	118.5 (3)	C6—C7—C8	117.5 (3)
O1—C2—O11	116.8 (3)	C7—C8—C9	119.8 (3)
O1—C2—C3	116.3 (3)	O1—C9—C8	116.3 (3)
O11—C2—C3	126.9 (3)	O1—C9—C10	120.6 (3)
C2—C3—C4	121.5 (3)	C8—C9—C10	123.1 (3)
C2—C3—C12	125.2 (3)	C4—C10—C5	126.3 (3)
C4—C3—C12	113.3 (3)	C4—C10—C9	117.0 (3)
C3—C4—C10	121.8 (3)	C5—C10—C9	116.7 (3)
C3—C4—C14	111.1 (3)	C3—C12—C13	102.9 (3)
C10—C4—C14	127.2 (3)	C12—C13—C14	108.3 (3)
C6—C5—C10	121.8 (3)	C4—C14—C13	104.5 (3)

Compound (II)

Crystal data

$C_{14}H_{15}NO_2$
$M_r = 229.28$
Orthorhombic
$Pna2_1$
$a = 8.779$ (2) Å
$b = 22.042$ (5) Å
$c = 6.043$ (2) Å
$V = 1169.3$ (8) Å^3
$Z = 4$
$D_x = 1.302$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 21.3$–$24.8°$
$\mu = 0.0814$ mm^{-1}
$T = 296$ K
Prism
1.00 × 1.00 × 0.40 mm
Clear

Data collection

AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction: empirical
$T_{\min} = 0.909$, $T_{\max} = 1.000$
1601 measured reflections
1601 independent reflections
1042 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 150 reflections intensity variation: −0.4%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.043$
$S = 1.81$
1042 reflections
210 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.1459$

$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: Zachariasen type 2 Gaussian isotropic
Extinction coefficient: $5.683 (1) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.2319 (2)	−0.10595 (8)	0.5582	0.0534
O11	0.2680 (3)	−0.19865 (10)	0.6869 (6)	0.0725
N15	0.1145 (3)	0.0931 (1)	0.3119 (6)	0.0514
C2	0.3029 (4)	−0.1626 (1)	0.5444 (8)	0.0511
C3	0.4068 (3)	−0.1708 (1)	0.3678 (7)	0.0500
C4	0.4356 (3)	−0.1264 (1)	0.2194 (7)	0.0442
C5	0.3771 (4)	−0.0203 (1)	0.0852 (7)	0.0487
C6	0.2976 (4)	0.0321 (1)	0.1102 (7)	0.0514

C7	0.1944 (3)	0.0404 (1)	0.2869 (7)	0.0436
C8	0.1772 (4)	−0.0078 (1)	0.4373 (7)	0.0458
C9	0.2584 (3)	−0.0607 (1)	0.4061 (6)	0.0421
C10	0.3600 (3)	−0.0690 (1)	0.2328 (7)	0.0422
C12	0.4988 (5)	−0.2273 (2)	0.3239 (9)	0.0680
C13	0.5771 (7)	−0.2129 (2)	0.104 (1)	0.1145
C14	0.5500 (5)	−0.1469 (2)	0.0525 (9)	0.0615
C16	0.1338 (6)	0.1432 (2)	0.1601 (9)	0.0643
C17	0.0074 (5)	0.1003 (2)	0.4893 (9)	0.0623

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

O1—C2	1.397 (3)	C4—C14	1.493 (5)
O1—C9	1.377 (3)	C5—C6	1.357 (4)
O11—C2	1.212 (4)	C5—C10	1.403 (4)
N15—C7	1.365 (4)	C6—C7	1.412 (4)
N15—C16	1.446 (4)	C7—C8	1.407 (4)
N15—C17	1.434 (5)	C8—C9	1.379 (4)
C2—C3	1.416 (5)	C9—C10	1.388 (4)
C3—C4	1.351 (4)	C12—C13	1.530 (7)
C3—C12	1.507 (4)	C13—C14	1.507 (6)
C4—C10	1.432 (4)		
C2—O1—C9	122.2 (3)	C5—C6—C7	121.7 (3)
C7—N15—C16	121.3 (3)	N15—C7—C6	121.6 (3)
C7—N15—C17	120.9 (3)	N15—C7—C8	121.1 (3)
C16—N15—C17	117.8 (3)	C6—C7—C8	117.3 (3)
O1—C2—O11	115.5 (3)	C7—C8—C9	119.7 (3)
O1—C2—C3	116.6 (3)	O1—C9—C8	115.7 (3)
O11—C2—C3	127.9 (3)	O1—C9—C10	121.1 (2)
C2—C3—C4	121.8 (3)	C8—C9—C10	123.2 (3)
C2—C3—C12	125.8 (3)	C4—C10—C5	126.2 (3)
C4—C3—C12	112.4 (3)	C4—C10—C9	117.2 (3)
C3—C4—C10	121.1 (3)	C5—C10—C9	116.5 (3)
C3—C4—C14	110.8 (3)	C3—C12—C13	102.8 (3)
C10—C4—C14	128.1 (3)	C12—C13—C14	108.0 (4)
C6—C5—C10	121.7 (3)		

For both modifications, weak reflections $[(I) < 10.0\sigma(I)]$ were rescanned (maximum of two rescans) and the counts accumulated to assure good counting statistics. Lp and absorption corrections based on ψ scans were applied; no decay correction. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to down weight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, 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*. All calculations were performed on a VAXStation 3520 minicomputer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CD1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abdel-Mottalaeb, M. S. A., Antonious, M. S., Ali, M. M. A., Ismail, L. F. M., El-Sayed, B. A. & Sherief, A. M. K. (1992). *Proc. Indian Acad. Sci. Chem. Sci*, **104**, 185–196.

Baczynski, A., Targowski, P., Sietek, B. & Radomska, D. (1990). *Z. Naturforsch Teil A*, **45**, 618–622.

De Camp, W. H. & Ahmed, F. R. (1972). *Acta Cryst.* **B28**, 1796–1800, 3484–3489.

Fletcher, A. (1977). *Appl. Phys.* **14**, 295–302.

Fletcher, A. N. & Bliss, D. E. (1978). *Appl. Phys.* **16**, 289–295.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Gnanaguru, K., Ramasubbu, N., Venkatesan, K. & Ramamurthy, V. (1985). *J. Org. Chem.* **50**, 2337–2346.

Jasinski, J. P. & Paight, E. S. (1994). *Acta Cryst.* **C50**, 1928–1930.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Murthy, G. S., Ramamurthy, V. & Venkatesan, K. (1988). *Acta Cryst.* **C44**, 307–311.

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2-[(3,4-Dimethoxybenzyl)(*p*-toluenesulfonyl)amino]-2-phenylethanol

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Abstract

The crystal structure of the title compound, $C_{24}H_{27}NO_5S$, was determined. The sum of the bond angles around the N atom is 356.6°, showing sp^2 character. The torsion angle N—C(10)—C(17)—O(3) [−179.0 (2)°] characterizes the antiperiplanar conformation for the N and O atoms. The crystal structure is stabilized by hydrogen bonds [C(9)—H(9)···O(4) and C(20)—H(20)···O(1)] and van der Waals forces.

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