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Structure of 7-Ethylamino-4,6-dimethylcoumarin

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Abstract. $C_{13}H_{15}NO_2$, $M_r = 217{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}343$ (1), $b = 7{\cdot}800$ (2), $c = 19{\cdot}589$ (4) Å, $\beta = 91{\cdot}45°$, $V = 1121{\cdot}6$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}29$ (2) (flotation), $D_x = 1{\cdot}286$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}618$ cm^{-1}, $F(000) = 464$, $T = 298$ K. Final R value is 0·051 for 1451 observed reflections. The coumarin moiety is planar and the ethylamino group is coplanar with the ring system. The crystal structure is stabilized by intermolecular N—H···O hydrogen bonds between glide-related molecules with N···O = 3·119 (3) Å and N—H···O = 173 (4)°.

Introduction. Coumarin dyes are widely used in the field of lasers owing to tunability and high gain. Some, in weakly polar solvents, give dual fluorescence (Masilamani, Chandrasekar, Sivaram, Sivashankar & Natarajan, 1986). The title compound has been found to give two bands, one around 415 nm and the other around 435 nm under nitrogen laser pumping (Masilamani, Sastikumar, Natarajan & Natarajan, 1987). This dual fluorescence is attributed to the Twisted Intramolecular Charge Transfer (TICT) effect in the excited state (Grabowski, Rotkiewicz, Siemiarczuk, Cowley & Baumann, 1979; Rettig, 1986). The crystal and molecular structure of this compound has been determined in order to study the conformation of the molecule in the ground state.

Experimental. Compound obtained from Exiton, New York; colourless rectangular crystals from a mixture of aqueous ethanol and chloroform, crystal size 0·7 × 0·5 × 0·1 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, cell parameters from the least-squares treatment of the setting angles of 25 reflections with $30 \le \theta \le 45°$; $\omega/2\theta$ scan technique, intensity variation of the two standard reflections monitored every 100 reflections is less than 3%, 2028 unique reflections measured with $2\theta \le 120°$; 1451 reflections are observed [$I \ge 3\sigma(I)$], h −8 to 8, k 0 to 9, l 0 to 23. Data were corrected for Lp but not for absorption, structure solution by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), no immediate solution was obtained. The coumarin molecule was then given as the input to calculate a spherically averaged molecular scattering factor and statistically weighted tangent refinement was used to obtain the structure. Full-matrix least-squares refinement on F using *SHELX*76 (Sheldrick, 1976): H atoms from difference Fourier map, anisotropic thermal parameters for non-H and isotropic for H atoms, $w = 1/[\sigma^2(F_o) + 0{\cdot}0013F_o^2]$, final $R = 0{\cdot}051$, $wR = 0{\cdot}056$, $S = 1{\cdot}69$, $(\Delta/\sigma)_{max} = 0{\cdot}027$, final difference map is featureless with max. and min. peak heights 0·20 and −0·30 e Å^{-3}; no correction for secondary extinction, atomic scattering factors for all atoms as in *SHELX*76 (Sheldrick, 1976), other geometrical calculations using *PARST* (Nardelli, 1983). An IBM 360/44 computer was used.

Discussion. Final atomic parameters are listed in Table 1.* Atom numbering and bond lengths and angles are

*Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51741 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

	x	y	z	B_{eq}(Å^2)
O(1)	0·8485 (2)	0·2142 (2)	0·6113 (1)	3·27 (4)
C(2)	0·9307 (3)	0·2710 (3)	0·6705 (1)	3·43 (6)
C(3)	1·1063 (3)	0·3524 (3)	0·6651 (1)	3·38 (5)
C(4)	1·1907 (3)	0·3694 (3)	0·6053 (1)	2·84 (5)
C(5)	1·1720 (3)	0·3161 (3)	0·4782 (1)	2·78 (5)
C(6)	1·0806 (3)	0·2566 (3)	0·4209 (1)	2·76 (5)
C(7)	0·9044 (3)	0·1821 (3)	0·4284 (1)	2·60 (5)
C(8)	0·8324 (3)	0·1700 (3)	0·4931 (1)	2·70 (5)
C(9)	0·9307 (3)	0·2311 (3)	0·5491 (1)	2·60 (5)
C(10)	1·1020 (3)	0·3057 (2)	0·5440 (1)	2·64 (5)
O(11)	0·8487 (2)	0·2469 (3)	0·7223 (1)	5·20 (5)
N(12)	0·8123 (2)	0·1223 (2)	0·3718 (1)	3·21 (5)
C(13)	0·6303 (3)	0·0498 (3)	0·3745 (1)	3·11 (5)
C(14)	0·5628 (3)	0·0006 (4)	0·3039 (1)	4·19 (6)
C(15)	1·1633 (3)	0·2664 (3)	0·3516 (1)	3·67 (6)
C(16)	1·3759 (3)	0·4501 (3)	0·6026 (1)	3·90 (6)

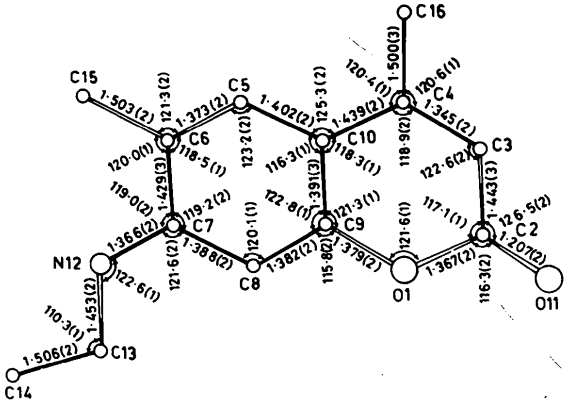

Fig. 1. Atom numbering, bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

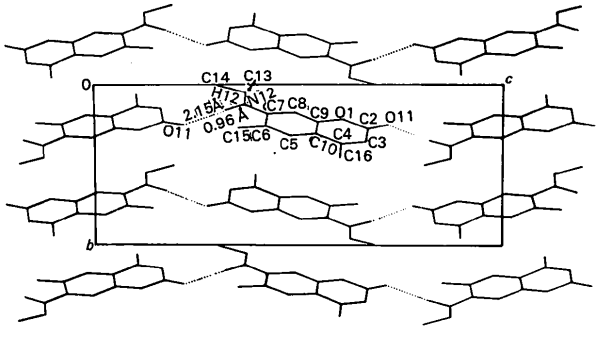

Fig. 2. Molecular packing of the title compound in the unit cell viewed down **a**.

shown in Fig. 1. Bond lengths and angles in this structure agree, within experimental error, with those observed in other coumarin derivatives (see *e.g.* Messager & Delugeard, 1974; Sivakumar, 1987; Murthy, Ramamurthy & Venkatesan, 1988). The pyrone ring is nearly planar, with a maximum deviation of 0·011 (2) Å for C(2) ($\chi^2 = 63·4$), and the benzene ring is perfectly planar ($\chi^2 = 7·6$). The dihedral angle between the pyrone and benzene rings is only 1·05 (6)°, confirming the planarity of the coumarin moiety. The ethylamino group is coplanar with the coumarin ring system and C(7)—N(12) is a single bond [1·366 (2) Å], as in the case of 7-diethylamino-4-methylcoumarin [1·364 (6) Å: Messager & Delugeard (1974)]. The donor (ethylamino) and acceptor (coumarin) groups are expected to twist about C(7)—N(12) in the excited state. The C(3)—C(4) distance, 1·345 (2) Å, confirms that this is a localized double bond.

The molecular packing in the unit cell, viewed down **a**, is shown in Fig. 2. The structure is stabilized by intermolecular N—O···O hydrogen bonds between glide-related molecules [N(12)—H(12), 0·96 (5); N(12)···O(11)′, 3·119 (3); H(12)···O(11)′, 2·15 (5) Å; N(12)—H(12)···O(11)′, 173 (4)°].

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