ture of (V) each molecule is linked to two adjacent molecules across inversion centres. These interactions result in molecular layers extending along the [100] and [010] directions. The naphthyl rings are oriented with a significant overlap of their π-electron systems (the spacing between the rings is 3·47 Å), and form layers of hydrophobic regions sandwiched between layers of hydrophilic regions in the crystal.

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Structure of 7-Dimethylamino-4-trifluoromethylcoumarin

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Abstract. $C_{12}H_{10}F_3NO_2$, $M_r = 257{\cdot}2$, orthorhombic, $Pnma$, $a = 15{\cdot}161\ (2)$, $b = 6{\cdot}880\ (2)$, $c = 10{\cdot}719\ (1)$ Å, $V = 1118{\cdot}1\ (4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}537$, $D_x = 1{\cdot}528$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 11{\cdot}727$ cm^{-1}, $F(000) = 528$, $T = 298$ K, final R value is 0·050 for 847 observed reflections. The molecule lies on the mirror plane with two of the F atoms related by mirror symmetry. In the mirror plane the molecules are linked by hydrogen bonds of the C—H···O type with C···O = 3·319 (4) Å, C—H···O = 164 (4)°.

Introduction. Aminocoumarins, which are used as laser dyes for the blue-green spectral region (Drexhage, 1973), vary in their photophysical properties for different kinds of chemical substitutions (Jones, Jackson & Kanoktanaporn, 1980; Jones, Jackson, Choi & Bergmark, 1985; Masilamani, Sastikumar, Natarajan & Natarajan, 1987). The title compound (Fig. 1), a fluorinated aminocoumarin also called coumarin 485, is found to give low fluorescence quantum yield in polar solvents and enhanced performance in low polarity solvents, unlike its unfluorinated analogue (Schimitschek, Trias, Hammond & Atkins, 1974; Guo & Feng, 1987). The structural study of this compound may be useful in understanding the effect of the trifluoromethyl group in the excited state dynamics of the molecule.

Experimental. The compound was from Exciton (USA); greenish yellow needle shaped crystals were from a mixture of aqueous ethanol and chloroform, D_m by flotation method, crystal size 0·5 × 0·3 × 0·1 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Cell parameters were from least-squares fit of 25 reflections in the range $30 < \theta < 45°$; $\omega/2\theta$ scan technique; intensity variation of two standard reflections monitored for crystal stability and orientation at every 100 reflections was less than 3%. 1101 unique reflections were measured with $\theta \le 70°$; 847 were judged observed with $|F_o| > 4\sigma(|F_o|)$. $h = 0$ to 18, $k = 0$ to 8 and $l = 0$ to 13; intensity data were corrected for Lp but not for absorption. From the systematic

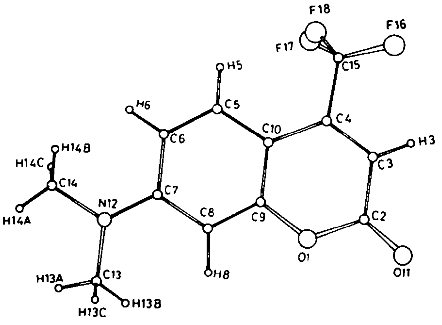

Fig. 1. Numbering scheme for the molecule.

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

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

	x	y	z	B_{eq}(Å^2)
O(1)	0·5977 (1)	0·2500	0·4951 (2)	3·51 (5)
C(2)	0·6529 (2)	0·2500	0·5967 (3)	3·61 (7)
C(3)	0·6124 (2)	0·2500	0·7179 (2)	3·43 (6)
C(4)	0·5240 (2)	0·2500	0·7308 (2)	2·85 (6)
C(5)	0·3740 (2)	0·2500	0·6250 (2)	3·20 (7)
C(6)	0·3268 (2)	0·2500	0·5170 (3)	3·62 (7)
C(7)	0·3684 (2)	0·2500	0·3988 (2)	3·11 (6)
C(8)	0·4612 (2)	0·2500	0·3969 (2)	3·16 (6)
C(9)	0·5070 (2)	0·2500	0·5072 (2)	2·70 (6)
C(10)	0·4673 (2)	0·2500	0·6244 (2)	2·74 (6)
O(11)	0·7312 (1)	0·2500	0·5767 (2)	5·39 (7)
N(12)	0·3205 (2)	0·2500	0·2914 (2)	4·25 (7)
C(13)	0·3628 (2)	0·2500	0·1707 (3)	4·65 (9)
C(14)	0·2253 (2)	0·2500	0·2936 (3)	5·89 (9)
C(15)	0·4860 (2)	0·2500	0·8598 (2)	3·58 (7)
F(16)	0·5470 (1)	0·2500	0·9485 (2)	5·09 (6)
F(17)*	0·4353 (1)	0·0944 (2)	0·8797 (1)	5·23 (4)

* Except this atom, all the atoms have occupancy 0·5.

Table 2. *Bond lengths* (Å) *and bond angles* (°), *involving non-*H *atoms*

O(1)—C(2)	1·373 (4)	C(6)—C(7)	1·415 (4)
O(1)—C(9)	1·381 (3)	C(7)—C(8)	1·407 (4)
C(2)—C(3)	1·437 (4)	C(7)—N(12)	1·361 (3)
C(2)—O(11)	1·206 (3)	C(8)—C(9)	1·371 (3)
C(3)—C(4)	1·347 (4)	C(9)—C(10)	1·393 (3)
C(4)—C(10)	1·428 (3)	N(12)—C(13)	1·444 (4)
C(4)—C(15)	1·498 (3)	N(12)—C(14)	1·443 (4)
C(5)—C(6)	1·361 (4)	C(15)—F(16)	1·326 (3)
C(5)—C(10)	1·414 (4)	C(15)—F(17)	1·335 (2)

C(2)—O(1)—C(9)	122·1 (2)	C(7)—C(8)—C(9)	119·6 (2)
O(1)—C(2)—O(11)	117·3 (3)	O(1)—C(9)—C(8)	115·0 (2)
O(1)—C(2)—C(3)	117·1 (3)	C(8)—C(9)—C(10)	124·0 (3)
C(3)—C(2)—O(11)	125·5 (3)	O(1)—C(9)—C(10)	121·0 (2)
C(2)—C(3)—C(4)	121·2 (2)	C(5)—C(10)—C(9)	115·9 (2)
C(3)—C(4)—C(15)	118·5 (2)	C(4)—C(10)—C(9)	117·4 (3)
C(3)—C(4)—C(10)	121·1 (2)	C(4)—C(10)—C(5)	126·7 (2)
C(10)—C(4)—C(15)	120·4 (2)	C(7)—N(12)—C(14)	121·3 (2)
C(6)—C(5)—C(10)	121·5 (2)	C(7)—N(12)—C(13)	122·4 (3)
C(5)—C(6)—C(7)	121·8 (3)	C(13)—N(12)—C(14)	117·3 (2)
C(6)—C(7)—N(12)	121·3 (3)	C(4)—C(15)—F(17)	111·6 (1)
C(6)—C(7)—C(8)	117·3 (2)	C(4)—C(15)—F(16)	113·2 (2)
C(8)—C(7)—N(12)	121·4 (4)	F(16)—C(15)—F(17)	106·7 (1)

absences, also as the density measurements showed four molecules in the unit cell, the space group was assigned as *Pna*2$_1$ and the structure solution was obtained by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on *F* using *SHELX76* (Sheldrick, 1976) showed poor precision in *z* coordinates, large deviations in C—F bond lengths and also high (Δ/σ) values. Hence, the space group was reassigned as *Pnma* with four molecules in the unit cell; structure solution was obtained by direct methods using *SHELXS86* (Sheldrick, 1986). Except F(17) all the atoms in the molecule lie on the mirror plane and the position of F(18) can be obtained from that of F(17) by mirror symmetry. Full-matrix least-squares refinement on *F* using *SHELX76* (Sheldrick, 1976); H atoms were from difference Fourier map, anisotropic thermal parameters for non-H and isotropic for H atoms. H atoms were refined isotropically, final $R = 0{\cdot}050$, $wR = 0{\cdot}045$, $w = 1{\cdot}0/[\sigma^2(F_o) + 0{\cdot}0046F_o^2]$, goodness of fit $= 1{\cdot}85$, $(\Delta/\sigma)_{\max} = 0{\cdot}002$, final difference Fourier map was featureless with max. and min. peak heights 0·24 and $-0{\cdot}35$ e Å^{-3}; no correction for secondary extinction, atomic scattering factors for all atoms were as in *SHELX76* (Sheldrick, 1976), geometrical calculations performed using *PARST* (Nardelli, 1983).

Discussion. The final positional parameters for the non-H atoms are given in Table 1. Bond lengths and valence angles involving the non-H atoms are listed in Table 2.* Bond lengths and angles in the coumarin moiety are in good agreement, within experimental error, with those observed in other coumarin derivatives (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985; Chinnakali, Sivakumar & Natarajan, 1989). The double-bond nature of C(3)=C(4) is clear from the bond length 1·347 (4) Å.

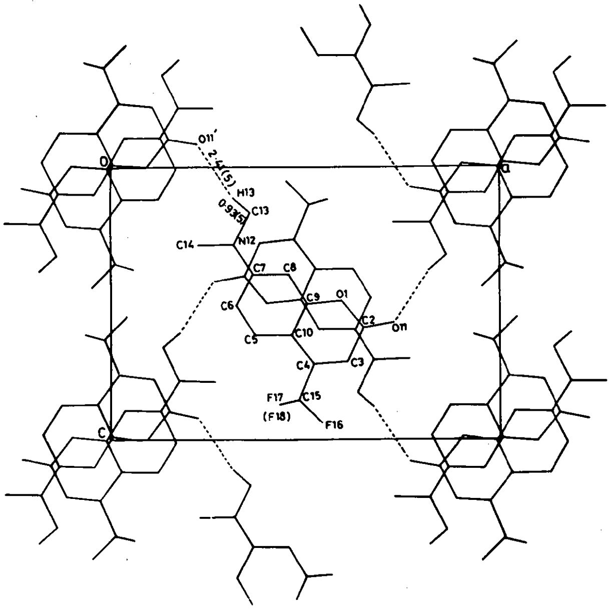

Fig. 2. Molecular packing of the title compound in the unit cell viewed down the *b* axis (hydrogen-bond distances are given in Å).

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms and intermolecular distances less than 3·5 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52506 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The independent C—F bond lengths of 1·326 (3) and 1·335 (2) Å in this structure are normal (Krishnamurthy & Vijayan, 1979). All the atoms in the molecule except F(17) lie in one plane, the torsion angle C(3)—C(4)—C(15)—F(17) is −120·4 (2)°.

In the excited state, charge transfer occurs from the amino (donor) to carboxyl (acceptor) group (Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986). The trifluoromethyl group, being a second electron-accepting moiety, is able to facilitate charge transfer from the donor site (Guo & Feng, 1987). As a consequence, twisted intramolecular charge transfer is probably enhanced in the excited state.

The packing of the molecules in the unit cell viewed down the *b* axis is shown in Fig. 2. Since the molecule as a whole lies on the mirror plane all the molecules in the unit cell are stacked along the *b* axis with a repeat distance of 3·44 Å. In the mirror plane, the molecules are linked by hydrogen bonds of the C—H···O type [C(13)···O(11)′ 3·319 (4); C(13)—H(C13) 0·93 (5); H(C13)···O(11)′ 2·41 (5) Å; C(13)—H(C13)···O(11)′ = 164 (4)°; symmetry code $x - \frac{1}{2}$, y, $\frac{1}{2} - z$] (Taylor & Kennard, 1982).

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2,3,6,7-1*H*,5*H*-Tetrahydro-10-methylquinolizino[1,9a,9-*gh*][1,4]benzoxazin[2]one

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Abstract. $C_{15}H_{16}N_2O_2$, $M_r = 256·3$, triclinic, $P\bar{1}$, $a = 8·238\,(1)$, $b = 8·358\,(1)$, $c = 10·890\,(2)$ Å, $\alpha = 77·26\,(1)$, $\beta = 74·09\,(2)$, $\gamma = 59·66\,(2)°$, $V = 619·2\,(2)$ Å^3, $Z = 2$, $D_m = 1·380$, $D_x = 1·374$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 7·07$ cm^{-1}, $F(000) = 272$, $T = 297$ K. The final R value is 0·047 for 1931 observed $[F_o \geq 2\sigma(F_o)]$ reflections. The benzoxazine moiety is planar and the two piperidine rings adopt distorted sofa conformations. The crystal structure is stabilized by van der Waals interactions.

Introduction. Benzoxazine derivatives are found to give laser action in the 500–678 nm spectral range (Le Bris, Mugnier, Bourson & Valeur, 1984; Dupuy, Rulliere, Le Bris & Valeur, 1984). Some of these derivatives exhibit a wide tuning range compared to classical coumarin dyes. The title compound, a rigified laser dye, alone is found to give laser action in the range 480–630 nm in different solvents (Chandrasekar, Sastikumar, Nagarajan, Masilamani, Sivaram & Natarajan, 1986; Sastikumar, Chandrasekar, Bhaskaran, Masilamani, Natarajan & Sivaram, 1986). The structural study of this compound (Fig. 1) was performed to examine the conformational features of the fused piperidine ring system.

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