

## Structure of 3-(2-Benzimidazolyl)-7-(diethylamino)coumarin

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**Abstract.**  $C_{20}H_{19}N_3O_2$ ,  $M_r = 333.39$ , triclinic,  $P\bar{1}$ ,  $a = 10.350$  (7),  $b = 12.990$  (5),  $c = 6.753$  (3) Å,  $\alpha = 100.89$  (4),  $\beta = 106.23$  (4),  $\gamma = 98.84$  (5)°,  $V = 835.2$  (8) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.345$ ,  $D_x = 1.325$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.817$  cm<sup>-1</sup>,  $F(000) = 352$ ,  $T = 296$  K. Final  $R$  value is 0.071 for 1626 observed reflections. The coumarin and benzimidazole ring systems are planar. Intramolecular hydrogen bonds of N—H...O type exist. The crystal structure is stabilized by van der Waals forces.

**Introduction.** Some aminocoumarin derivatives, in weakly polar solvents and under laser excitation, give an anomalous band due to the TICT (twisted intramolecular charge transfer) state. Solute–solvent interactions aid the stability of this state (Masilamani, Sastikumar, Natarajan & Natarajan, 1987). The title compound (also called coumarin 7) is found to give laser action at 525 nm in the vapour phase (Logunov, Startsev & Stoilov, 1981), and in a mixture of water and *N,N*-dipropylacetamide (Tuccio, Drexhage & Reynolds, 1973). The possibility of occurrence and stability of the TICT state for the title compound is discussed on a structural basis.

**Experimental.** Compound from Exciton, Ohio; rod shaped yellowish crystals from a mixture of EtOH(aq)/CHCl<sub>3</sub>, density measured by flotation. Crystal dimensions 0.4 × 0.4 × 0.2 mm. Rigaku AFC5R diffractometer, graphite-monochromated Mo  $K\alpha$  radiation, cell dimensions determined from 25  $2\theta$  angles in the range  $15 < 2\theta < 20^\circ$ . Intensities measured up to  $2\theta = 50^\circ$  for  $h = 0$  to 12,  $k = -15$  to 15 and  $l = -8$  to 8,  $\omega$ - $2\theta$  scans, three standard reflections ( $\bar{1}0\bar{1}$ ,  $03\bar{1}$ ,  $\bar{2}40$ ) monitored every 150 measurements showed no significant change. 2282 unique reflections measured, 1626 observed with  $|F_o| \geq 2\sigma(|F_o|)$ ,  $L_p$  corrected but no absorption correction. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986), no correct solution in the space group  $P\bar{1}$ , attempts with  $P1$  gave the correct solution with two centrosymmetrically related molecules. Origin shifted to that centre of symmetry, full-matrix least-squares refinement on  $F$ , using *SHELX76* (Sheldrick, 1976), for space group  $P\bar{1}$ . H atoms located on a difference density map,

anisotropic thermal parameters for non-H and isotropic for H atoms, final  $R = 0.071$ ,  $wR = 0.067$ ,  $S = 1.65$ ,  $w = 1.9825/[\sigma^2(|F_o|) + 0.00004F_o^2]$ . The  $R$  value is high due to poor crystal quality,  $(\Delta/\sigma)_{\text{max}} = 0.014$ , final difference map featureless with max. and min. peak heights 0.35 and  $-0.27$  e Å<sup>-3</sup>; no correction for secondary extinction, atomic scattering factors for all atoms as in *SHELX76* (Sheldrick, 1976), geometrical calculations using *PARST* (Nardelli, 1983).

**Discussion.** The final positional parameters for the non-H atoms are given in Table 1.\* Bond lengths and angles are listed in Table 2. Bond lengths within the coumarin moiety are in good agreement, within experimental error, with those observed in other coumarin derivatives (Murthy, Ramamurthy & Venkatesan, 1988; Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985). The increase in bond angle C(2)—C(3)—C(4) by 2° and decrease in C(3)—C(4)—C(5) by the same amount from the mean value may be due to the benzimidazole group substituted at C(3). Bond lengths and angles in the diethylamino group are normal (Messenger & Delugeard, 1974). The C(12)=N(20) bond in the benzimidazolyl group [1.323 (7) Å] is elongated by comparison with a normal  $C_{sp^2}$ =N distance (1.28 Å).

The pyrone ring is essentially planar ( $\chi^2 = 59.3$ ) and the benzene ring in the coumarin moiety is also planar ( $\chi^2 = 34$ ). The dihedral angle between these two planes is 2.3 (1)°. The benzimidazolyl group is planar ( $\chi^2 = 26$ ) and makes an angle of 9.5 (1)° with the plane through the complete coumarin ring system. Torsion angles related to the diethylamino group are given in Table 2.

The packing of the molecules in the unit cell viewed down the 'c' axis is shown in Fig. 1. An intramolecular hydrogen bond N(13)—H...O(11) is observed [N(13)—H(N13) 0.93 (5), N(13)—O(11)

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, torsion angles and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52274 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

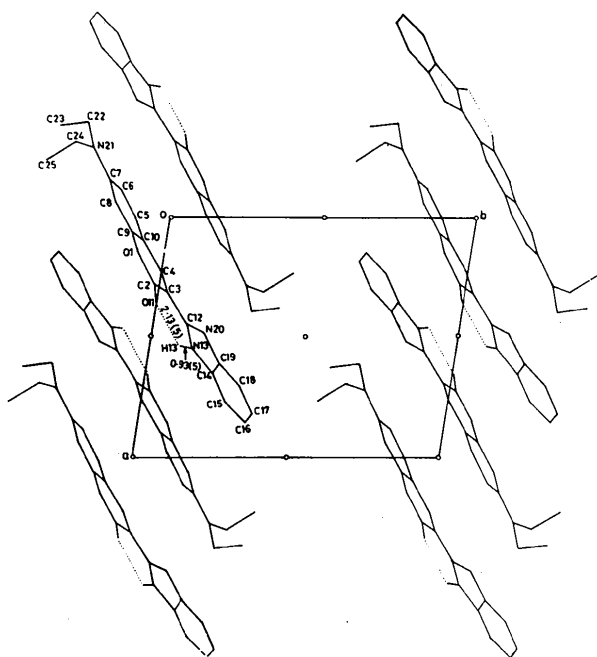
Table 1. Positional parameters and equivalent isotropic thermal parameters

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

	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	0-1513 (3)	-0-0873 (3)	0-6418 (5)	3-54 (1)
C(2)	0-2789 (5)	-0-0188 (4)	0-7015 (7)	3-54 (2)
C(3)	0-3163 (5)	0-0281 (4)	0-5453 (7)	2-94 (2)
C(4)	0-2326 (5)	-0-0037 (4)	0-3407 (7)	3-11 (2)
C(5)	0-0102 (5)	-0-1124 (4)	0-0711 (7)	3-45 (2)
C(6)	-0-1170 (5)	-0-1778 (4)	0-0288 (7)	3-49 (2)
C(7)	-0-1545 (5)	-0-2169 (4)	0-1925 (7)	3-17 (2)
C(8)	-0-0594 (5)	-0-1840 (4)	0-3973 (7)	3-26 (2)
C(9)	0-0643 (5)	-0-1166 (4)	0-4338 (7)	2-89 (2)
C(10)	0-1040 (5)	-0-0756 (4)	0-2785 (7)	2-92 (2)
O(11)	0-3462 (4)	-0-0031 (3)	0-8898 (5)	4-65 (1)
C(12)	0-4462 (5)	0-1069 (4)	0-6063 (7)	2-98 (2)
N(13)	0-5413 (4)	0-1349 (3)	0-8056 (6)	3-77 (1)
C(14)	0-6484 (5)	0-2144 (4)	0-8119 (8)	3-62 (2)
C(15)	0-7677 (6)	0-2710 (4)	0-9658 (9)	4-76 (2)
C(16)	0-8533 (6)	0-3457 (4)	0-9148 (11)	5-57 (2)
C(17)	0-8183 (6)	0-3646 (4)	0-7094 (11)	5-59 (3)
C(18)	0-6979 (6)	0-3076 (4)	0-5543 (9)	4-89 (2)
C(19)	0-6087 (5)	0-2309 (4)	0-6026 (8)	3-46 (2)
N(20)	0-4820 (4)	0-1650 (3)	0-4811 (6)	3-80 (2)
N(21)	-0-2829 (5)	-0-2828 (3)	0-1499 (6)	4-08 (1)
C(22)	-0-3892 (6)	-0-3104 (4)	-0-0598 (8)	4-85 (2)
C(23)	-0-3739 (7)	-0-4051 (5)	-0-2130 (9)	6-63 (3)
C(24)	-0-3084 (6)	-0-3418 (4)	0-3056 (8)	4-38 (2)
C(25)	-0-2311 (8)	-0-4303 (5)	0-3254 (10)	6-66 (3)

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ )

O(1)—C(2)	1-379 (5)	C(2)—O(1)—C(9)	121-8 (4)
O(1)—C(9)	1-383 (5)	O(1)—C(2)—O(11)	114-4 (5)
C(2)—C(3)	1-425 (7)	O(1)—C(2)—C(3)	118-1 (4)
C(2)—O(11)	1-227 (5)	C(3)—C(2)—O(11)	127-4 (6)
C(3)—C(4)	1-354 (6)	C(2)—C(3)—C(12)	119-6 (4)
C(3)—C(12)	1-460 (6)	C(2)—C(3)—C(4)	119-4 (5)
C(4)—C(10)	1-406 (6)	C(4)—C(3)—C(12)	120-9 (4)
C(5)—C(6)	1-375 (6)	C(3)—C(4)—C(10)	122-3 (4)
C(5)—C(10)	1-406 (6)	C(6)—C(5)—C(10)	121-7 (5)
C(6)—C(7)	1-422 (7)	C(5)—C(6)—C(7)	120-7 (4)
C(7)—C(8)	1-397 (6)	C(6)—C(7)—N(21)	120-7 (4)
C(7)—N(21)	1-387 (6)	C(6)—C(7)—C(8)	117-6 (5)
C(8)—C(9)	1-365 (7)	C(8)—C(7)—N(21)	121-6 (4)
C(9)—C(10)	1-391 (8)	C(7)—C(8)—C(9)	119-8 (4)
C(12)—N(13)	1-370 (5)	O(1)—C(9)—C(8)	115-7 (4)
C(12)—N(20)	1-323 (7)	C(8)—C(9)—C(10)	124-2 (5)
N(13)—C(14)	1-379 (6)	O(1)—C(9)—C(10)	119-9 (5)
C(14)—C(15)	1-364 (6)	C(5)—C(10)—C(9)	115-7 (5)
C(14)—C(19)	1-424 (7)	C(4)—C(10)—C(9)	118-1 (5)
C(15)—C(16)	1-370 (9)	C(4)—C(10)—C(5)	126-3 (5)
C(16)—C(17)	1-411 (9)	C(3)—C(12)—N(20)	124-2 (5)
C(17)—C(18)	1-375 (7)	C(3)—C(12)—N(13)	123-8 (5)
C(18)—C(19)	1-400 (8)	N(13)—C(12)—N(20)	111-8 (5)
C(19)—N(20)	1-383 (5)	C(12)—N(13)—C(14)	108-9 (4)
N(21)—C(22)	1-470 (6)	N(13)—C(14)—C(19)	103-2 (5)
N(21)—C(24)	1-470 (7)	N(13)—C(14)—C(15)	133-9 (5)
C(22)—C(23)	1-510 (8)	C(15)—C(14)—C(19)	122-8 (5)
C(24)—C(25)	1-503 (9)	C(14)—C(15)—C(16)	118-2 (5)
		C(15)—C(16)—C(17)	120-9 (6)
		C(16)—C(17)—C(18)	120-8 (6)
		C(17)—C(18)—C(19)	119-3 (5)
		C(14)—C(19)—C(18)	117-9 (5)
		C(18)—C(19)—N(20)	131-4 (5)
		C(14)—C(19)—N(20)	110-7 (5)
		C(12)—N(20)—C(19)	105-3 (4)
		C(7)—N(21)—C(24)	119-7 (4)
		C(7)—N(21)—C(22)	122-5 (4)
		C(22)—N(21)—C(24)	117-1 (5)
		N(21)—C(22)—C(23)	113-3 (5)
		N(21)—C(24)—C(25)	113-5 (5)
O(1)—C(2)—C(3)—C(12)	175-6 (5)	C(6)—C(7)—N(21)—C(24)	166-2 (5)
O(11)—C(2)—C(3)—C(12)	-2-0 (9)	C(8)—C(7)—N(21)—C(22)	174-3 (5)
C(2)—C(3)—C(12)—N(13)	4-3 (7)	C(8)—C(7)—N(21)—C(24)	-15-8 (8)
C(2)—C(3)—C(12)—N(20)	-170-9 (5)	C(3)—C(12)—N(20)—C(19)	177-9 (5)
C(4)—C(3)—C(12)—N(13)	-173-6 (5)	C(3)—C(12)—N(13)—C(14)	-177-3 (5)
C(4)—C(3)—C(12)—N(20)	11-2 (9)	C(7)—N(21)—C(24)—C(25)	-69-3 (7)
C(12)—C(3)—C(4)—C(10)	-176-9 (5)	C(22)—N(21)—C(24)—C(25)	101-1 (6)
C(5)—C(6)—C(7)—N(21)	179-9 (5)	C(24)—N(21)—C(22)—C(23)	-85-2 (6)
C(6)—C(7)—N(21)—C(22)	-3-7 (8)		

Fig. 1. Molecular packing of the title compound in the unit cell viewed down the 'c' axis. (Distances given in  $\text{\AA}$ .)

2-744 (6), H(13)···O(11) 2-13 (5)  $\text{\AA}$  and N(13)—H(N13)···O(11) 121 (4) $^\circ$ ].

Like all other aminocoumarin derivatives the title compound gives laser action by reaching the ground state ( $S_0$ ) from the first excited singlet state  $S_1$ . In the excited state the molecule, which is polarized due to

charge transfer from the donor (amino) to acceptor (carbonyl oxygen), may have the donor group in the twisted form (Masilamani, 1987). The possibility of the benzimidazolyl group twisting away from the nearly planar conformation decreases, since in the excited state the carbonyl oxygen acquires more negative charge and attracts H(N13), thereby strengthening the N—H···O hydrogen bond. As the carbonyl oxygen is involved in the intramolecular hydrogen bond the solvent molecule is required to complex only with the donor site and hence enhances the stability of the TICT state. So we conclude that there is a possibility of observing an anomalous band in the title compound, as in 7-(diethylamino)-4-methylcoumarin which gives two bands at 425 and 450 nm (Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986).

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## Structure of $\alpha$ -D-N-Acetyl-1-O-methylneuraminic Acid Methyl Ester

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**Abstract.**  $C_{13}H_{23}NO_9$ ,  $M_r = 337.33$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.8479$  (9),  $b = 9.691$  (2),  $c = 18.121$  (4) Å,  $V = 1553.8$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.442$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 0.11$  mm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 100$  K, final  $R = 0.034$  for 3398 observed diffractometer data. The conformation of the glycerol side chain is the same as in the structures of the two  $\beta$  forms of *N*-acetylneuraminic acid. The crystal consists of a two-dimensional network of hydrogen-bonded molecules and in the third direction there are only hydrophobic contacts.

**Introduction.** Sialic acids frequently occur as  $\alpha$ -glycosidically linked terminal groups of carbohydrate chains in glycoproteins and glycolipids (Corfield & Schauer, 1982). The large range of their biological activity includes, for example, (anti)recognition of low- and high-molecular-weight compounds, influ-

ence on transport processes, hormone action, cellular adhesiveness and the life span of glycoproteins (Reuther, Köttgen, Bauer & Gerok, 1982). For these biological functions the charge and the conformation of the molecules are essential features.

*N*-Acetylneuraminic acid is one of the most frequently occurring sialic acids. So far only the crystal structures of two  $\beta$ -glycosidical forms,  $\beta$ -D-*N*-acetylneuraminic acid dihydrate ( $\beta$ Neu5Ac; Flippen, 1973) and  $\beta$ -D-*N*-acetylneuraminic acid methyl ester monohydrate (1Me $\beta$ Neu5Ac; O'Connell, 1973) have been determined. It is of interest to study the  $\alpha$ -glycosidic form of neuraminic acid because it is this form that occurs in nature, and effects on the conformation with respect to the  $\beta$  forms can be expected by the axial position of the carboxyl group. Therefore, we here report the crystal and molecular structure of  $\alpha$ -D-*N*-acetyl-1-*O*-methylneuraminic acid methyl ester (1,2diMe $\alpha$ Neu5Ac). Because the intra-