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1,2,3,3,8-Pentamethyl-5-trifluoromethyl-2,3-dihydro-1*H*-pyrrolo[2,3-*g*]quinolin-7(8*H*)-one

By K. CHINNAKALI, K. SIVAKUMAR AND S. NATARAJAN

Department of Physics, Anna University, Madras 600 025, India

AND NANCY K. MCGUIRE AND A. CLEARFIELD

Department of Chemistry, Texas A&M University, College Station, Texas, TX 77843, USA

Abstract. $C_{17}H_{19}F_3N_2O$, $M_r = 324.34$, monoclinic, $P2_1/a$, $a = 10.694$ (3), $b = 12.216$ (3), $c = 12.356$ (4) Å, $\beta = 94.24$ (3)°, $V = 1609.8$ (8) Å^3, $Z = 4$, $D_x = 1.338$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.02$ cm^{-1}, $F(000) = 680$, $T = 296$ K, $R = 0.044$ for 1781 observed reflections. The quinolone ring is planar and the dihydropyrrole ring adopts an envelope conformation with a mean absolute torsion angle of 25°.

Introduction. The title compound (I), a laser dye (Schimitschek, Trias, Hammond, Henry & Atkins, 1976), has been found to give simultaneous dual super-radiant emission in benzene- and toluene-like solvents under nitrogen laser excitation: one emission around 438 nm and another around 469 nm (Sastikumar & Masilamani, 1990). This interesting photophysical property has also been observed in alkylaminocoumarin derivatives and it is attributed to both normal and twisted intramolecular charge transfer (TICT) states of the molecule in the excited state (Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986; Masilamani, Sastikumar, Natarajan & Natarajan, 1987; Ramalingam, Palanisamy, Masilamani & Sivaram,

1989). In the TICT state the plane of the alkylamino (donor) group is said to be perpendicular to the plane of the acceptor moiety. The concept that the twisting of the donor group produces the anomalous band has been supported by the observation that the inhibition of twisting through the use of a rigid amino group results in only one band (Masilamani, 1987). But the dual emission by the title compound contradicts this hypothesis as the donor group here is part of the five-membered ring which cannot allow a 90° twist in the N—C(sp^2) bond of the alkylamino group. The structural study of this compound suggests another possible model for the dual emission.

Experimental. Compound from Exciton (USA), yellow cubic crystals from methanol; Rigaku AFC5R diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions $0.2 \times 0.2 \times 0.2$ mm; cell dimensions from 20 angles in the range $15 \le 2\theta \le 20°$, $2\theta_{max} = 50°$. Intensities measured in the range $h = 0$ to 13, $k = 0$ to 15 and $l = -15$ to 15, ω–2θ scan; three standard reflections ($\bar{2}0\bar{2}$, $\bar{1}\bar{1}3$, $\bar{2}0\bar{1}$) monitored every 150 measurements showed no significant change. 2417 unique reflections ($R_{int} = 0.023$) of

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

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

	x	y	z	$B_{eq}(Å^2)$
N(1)	0·1590 (2)	0·0823 (2)	0·9332 (2)	3·43 (6)
C(2)	0·1805 (3)	0·1934 (2)	0·9471 (2)	3·92 (8)
C(3)	0·1012 (3)	0·2648 (2)	0·8798 (2)	4·04 (8)
C(4)	0·0146 (3)	0·2266 (2)	0·8044 (2)	3·39 (7)
C(5)	-0·0929 (3)	0·0659 (2)	0·7103 (2)	3·33 (7)
C(6)	-0·1071 (2)	-0·0440 (2)	0·7012 (2)	3·43 (7)
C(7)	-0·0335 (3)	-0·1149 (2)	0·7702 (2)	3·36 (7)
C(8)	0·0547 (3)	-0·0743 (2)	0·8471 (2)	3·47 (7)
C(9)	0·0698 (2)	0·0396 (2)	0·8563 (2)	3·03 (7)
C(10)	-0·0048 (2)	0·1115 (2)	0·7891 (2)	3·04 (7)
O(11)	0·2627 (2)	0·2276 (2)	1·0137 (2)	5·63 (6)
N(12)	-0·0628 (2)	-0·2221 (2)	0·7463 (2)	3·88 (6)
C(13)	-0·1866 (3)	-0·2230 (2)	0·6832 (3)	4·48 (9)
C(14)	-0·1904 (3)	-0·1117 (2)	0·6229 (2)	3·90 (7)
C(15)	0·2367 (4)	0·0093 (3)	1·0028 (3)	4·64 (9)
C(16)	-0·0313 (4)	-0·3085 (3)	0·8230 (3)	4·71 (10)
C(17)	-0·2070 (5)	-0·3254 (3)	0·6150 (5)	6·71 (14)
C(18)	-0·1311 (4)	-0·1165 (4)	0·5138 (3)	5·54 (11)
C(19)	-0·3235 (3)	-0·0685 (4)	0·6069 (4)	5·43 (11)
C(20)	-0·0593 (3)	0·3086 (2)	0·7360 (2)	4·17 (8)
F(21)	-0·1830 (2)	0·2946 (1)	0·7355 (2)	5·70 (5)
F(22)	-0·0334 (2)	0·3025 (2)	0·6321 (1)	6·60 (7)
F(23)	-0·0378 (2)	0·4111 (1)	0·7667 (2)	7·17 (?)

which 1781 observed with $|F_o| \geq 4\sigma(|F_o|)$, Lp corrected, no absorption correction. Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986), full-matrix least-squares refinement on *F*, using *SHELX*76 (Sheldrick, 1976). H-atom positions from difference Fourier map, anisotropic thermal parameters for non-H and isotropic for H atoms, H-atom positions refined, final $R = 0.044$, $wR = 0.05$, $w = 2.0204/[\sigma^2(|F_o|) + 0.00074F_o^2]$, $S = 1.76$, $(\Delta/\sigma)_{max} = 0.003$, final difference map featureless with max. and min. peak heights 0·15 and $-0.21\,e\,Å^{-3}$, no correction for secondary extinction, atomic scattering factors for all atoms from *SHELX*76 (Sheldrick, 1976), geometrical calculations using *PARST* (Nardelli, 1983).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* The title compound is shown in Fig. 1. Bond lengths and valence angles (Table 2) in the quinolone ring are normal (Kido & Nakagawa, 1982) with C(3)—C(4), 1·348 (4) Å, indicative of a localized double bond; the C(7)—N(12) distance of 1·374 (3) Å shows some double-bond character (Ammon, Mazzocchi, Regan & Colicelli, 1979). The angles C(4)—C(10)—C(5) and C(3)—C(2)—O(11) are greater than 120°. Whilst N(1)—C(2)—C(3) is smaller than 120°, as commonly

* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53212 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

N(1)—C(2)	1·385 (3)	C(7)—N(12)	1·374 (3)
N(1)—C(9)	1·397 (3)	C(8)—C(9)	1·404 (3)
N(1)—C(15)	1·456 (4)	C(9)—C(10)	1·414 (3)
C(2)—C(3)	1·438 (4)	N(12)—C(13)	1·486 (4)
C(2)—O(11)	1·232 (3)	N(12)—C(16)	1·442 (4)
C(3)—C(4)	1·348 (4)	C(13)—C(14)	1·549 (4)
C(4)—C(10)	1·432 (3)	C(13)—C(17)	1·515 (5)
C(4)—C(20)	1·498 (4)	C(14)—C(18)	1·532 (5)
C(5)—C(6)	1·355 (3)	C(14)—C(19)	1·517 (5)
C(5)—C(10)	1·418 (3)	C(20)—F(21)	1·333 (4)
C(6)—C(7)	1·414 (3)	C(20)—F(22)	1·335 (3)
C(6)—C(14)	1·512 (3)	C(20)—F(23)	1·324 (3)
C(7)—C(8)	1·381 (4)		

C(9)—N(1)—C(15)	120·3 (2)	C(4)—C(10)—C(9)	117·5 (2)
C(2)—N(1)—C(9)	123·3 (2)	C(4)—C(10)—C(5)	124·0 (2)
N(1)—C(2)—O(11)	121·2 (2)	C(7)—N(12)—C(16)	121·2 (2)
N(1)—C(2)—C(3)	115·9 (2)	C(7)—N(12)—C(13)	107·5 (2)
C(3)—C(2)—O(11)	122·8 (2)	C(13)—N(12)—C(16)	119·7 (2)
C(2)—C(3)—C(4)	122·4 (2)	N(12)—C(13)—C(17)	112·6 (3)
C(3)—C(4)—C(20)	117·7 (2)	N(12)—C(13)—C(14)	103·7 (2)
C(3)—C(4)—C(10)	121·1 (2)	C(14)—C(13)—C(17)	117·3 (3)
C(10)—C(4)—C(20)	121·1 (2)	C(6)—C(14)—C(13)	100·3 (2)
C(6)—C(5)—C(10)	120·7 (2)	C(13)—C(14)—C(19)	111·1 (2)
C(5)—C(6)—C(14)	130·7 (2)	C(13)—C(14)—C(18)	113·1 (3)
C(5)—C(6)—C(7)	120·2 (2)	C(6)—C(14)—C(19)	113·3 (2)
C(7)—C(6)—C(14)	109·1 (2)	C(6)—C(14)—C(18)	108·7 (2)
C(6)—C(7)—N(12)	110·3 (2)	C(18)—C(14)—C(19)	110·1 (3)
C(6)—C(7)—C(8)	121·1 (2)	C(4)—C(20)—F(23)	113·4 (2)
C(8)—C(7)—N(12)	128·6 (2)	C(4)—C(20)—F(22)	111·5 (2)
C(7)—C(8)—C(9)	118·7 (2)	C(4)—C(20)—F(21)	113·5 (2)
N(1)—C(9)—C(8)	119·6 (2)	F(22)—C(20)—F(23)	106·5 (2)
C(8)—C(9)—C(10)	120·7 (2)	F(21)—C(20)—F(23)	105·9 (2)
N(1)—C(9)—C(10)	119·7 (2)	F(21)—C(20)—F(22)	105·3 (2)
C(5)—C(10)—C(9)	118·5 (2)	C(2)—N(1)—C(15)	116·4 (2)

C(7)—C(6)—C(14)—C(13)	18·9 (3)	N(12)—C(13)—C(14)—C(6)	-28·2 (3)
C(14)—C(6)—C(7)—N(12)	-1·4 (3)	C(8)—C(7)—N(12)—C(13)	163·1 (3)
C(6)—C(7)—N(12)—C(13)	-18·0 (3)	C(8)—C(7)—N(12)—C(16)	20·2 (5)
C(7)—N(12)—C(13)—C(14)	29·5 (3)		

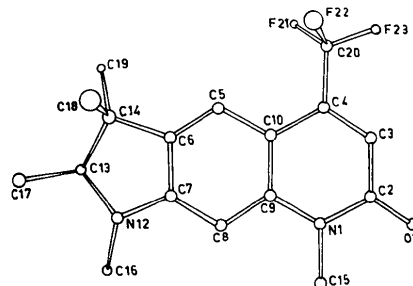
Fig. 1. View of the molecule with atom numbering.

found in quinolone derivatives (Kido & Nakagawa, 1982; Kido, Nakagawa, Fujiwara & Tomita, 1981.

The benzene and pyridine rings are planar $(\chi^2 = 30.0$ and $60.1)$. The dihedral angle between them is 0·9 (1)°, which makes the quinolone moiety essentially planar. The dihydropyrrole ring adopts the envelope conformation $[\Delta C_s(C13) = 1.1°]$, with the mean absolute value of the torsion angles being 25° (Duax, Weeks & Rohrer, 1976). N(12) lies in the benzene plane with the attached C(13) and C(16) atoms deviating from that plane by -0·421 (3) and -0·407 (4) Å, respectively. The sum of bond angles
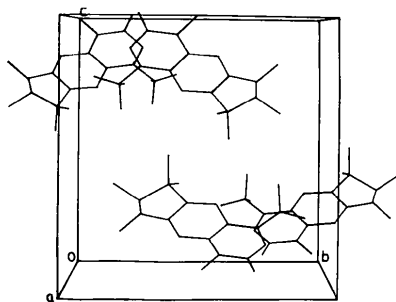
Fig. 2. Molecular packing of the title compound in the unit cell viewed down the a axis.

around N(12) is 348·4 (6)°, a 'pyramidal' value intermediate between those for sp^2(360°) and sp^3(328·4°) hybridization (Ammon, Mazzocchi, Regan & Colicelli, 1979). The plane through C(13), N(12) and C(16) makes an angle of 145·6 (2)° with the plane of the benzene ring.

The molecular packing viewed along a is shown in Fig. 2. There is a close intramolecular C—H···O contact involving the carbonyl oxygen with C(15)···O(11) 2·684 (4), H(C15)···O(11) 2·25 (4) Å and C(15)—H(C15)···O(11) 109 (2)° (Taylor & Kennard, 1982). The crystal structure is stabilized by van der Waals interactions.

The concept that two molecular conformations exist in the excited state, one fully planar and the other with the donor group perpendicular to the acceptor [due to a twist around the N̈—C(sp^2) bond], is said to be responsible for the dual band laser emission. This is not applicable for the title compound since: (i) the plane of the donor group [the alkylamino group constituting N(12), C(13) and C(16)] is not coplanar with that of the acceptor group and (ii) the donor group can *never* become perpendicular to the acceptor as the twist around N̈—C(sp^2) is restricted by cyclization. The structural investigation indicates that the geometry around

N(12) is nearly pyramidal. In the excited state, this pyramidal geometry may be in equilibrium with a trigonal planar form and these two forms may be responsible for the dual emission by the title compound. If such conformational changes are responsible for the dual emission here, then the concept is applicable for the alkylaminocoumarins, where a transition from planar to pyramidal geometry around N is also possible.

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Structure of an Unusually Non-Polar Hydroxy Ether

By M. M. Olmstead,† M. E. Price, J. Strutzel and N. E. Schore†

Department of Chemistry, University of California, Davis, California 95616, USA

Abstract. (1R*,3R*,7S*,9S*)-1,4,4-Trimethyl-9-(*tert*-butyldimethylsilyloxy)-*exo*-11-oxatricyclo[5.3.1.0^{2,6}]-undecan-3-ol, $C_{19}H_{36}O_3Si$, $M_r = 340·90$, orthorhombic, *Pbca*, $a = 10·411$ (3), $b = 13·275$ (3), $c = 29·085$ (10) Å, $V = 4019$ (2) Å^3, $Z = 8$, D_x(130 K) = 1·13 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·24$ cm^{-1},

† Address correspondence to these authors.