Table 3. *Geometry of intra- and intermolecular hydro-gen bonds with e.s.d.'s in parentheses*

X—H···Y	H···Y (Å)	X···Y (Å)	X—H···Y (°)
N(8)—H(8)···O(18)	2·02 (2)	2·646 (3)	135 (2)
N(8)—H(8)···Cl	2·85 (2)	3·433 (2)	131 (2)
N(14)—H(14)···Cl	2·33 (2)	3·118 (2)	174 (2)
N(20)—H(20)···Cl^i	2·39 (2)	3·103 (2)	169 (2)

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

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2,3,6,7-Tetrahydro-9-methyl-1*H*,5*H*-quinolizino[9,1-*gh*]coumarin

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Abstract. 2,3,6,7-Tetrahydro-9-methyl-1*H*,5*H*,11*H*-pyrano[2,3-*d*]benzo[1,2,3-*ij*]quinolizin-11-one,$C_{16}H_{17}$-NO_2, $M_r = 255\cdot32$, monoclinic, $P2_1/a$, $a = 8\cdot253$ (2), $b = 15\cdot660$ (7), $c = 10\cdot112$ (4) Å, $\beta = 95\cdot82$ (3)°, $V = 1300\cdot2$ (6) Å^3, $Z = 4$, $D_m = 1\cdot315$, $D_x = 1\cdot304$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot80$ cm^{-1}, $F(000) = 544$, $T = 296$ K. The final R value is 0·065 for 1020 observed reflections. The coumarin moiety is planar and the two piperidine rings adopt flattened half-chair conformations with mean absolute torsion angles of 24·6 and 28·8° respectively.

Introduction. Coumarin derivatives having an amino group in the 7-position are very efficient laser dyes in the blue and green region of the spectrum (Drexhage, 1973). The mobility of the amino group reduces the fluorescence efficiency of these dyes in polar solvents (Tuccio, Drexhage & Reynolds, 1973; Reynolds & Drexhage, 1975) but, with a structurally rigid amino group, these derivatives show a high quantum yield of fluorescence in polar solvents. The title compound (I), which is such a derivative, is found to have excellent laser efficiency at 480 nm (Marling, Hawley, Liston & Grant, 1974; Reynolds & Drexhage, 1975). The structural study of this compound was performed to understand the ground-state conformation of the fused quinolizine ring system.
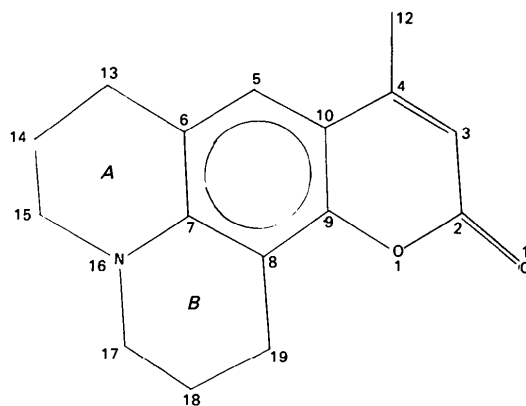
(I)

Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

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

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0·8319 (4)	0·3559 (2)	0·2517 (3)	4·3 (1)
C(2)	0·8819 (7)	0·4149 (4)	0·1619 (6)	5·5 (2)
C(3)	0·9486 (7)	0·3822 (4)	0·0478 (5)	4·8 (1)
C(4)	0·9647 (6)	0·2973 (4)	0·0271 (5)	4·3 (1)
C(5)	0·9261 (6)	0·1491 (4)	0·1115 (5)	4·6 (1)
C(6)	0·8781 (6)	0·0945 (3)	0·2073 (5)	4·2 (1)
C(7)	0·8105 (5)	0·1290 (3)	0·3193 (5)	3·7 (1)
C(8)	0·7966 (5)	0·2179 (3)	0·3322 (4)	3·4 (1)
C(9)	0·8491 (6)	0·2691 (3)	0·2327 (5)	3·4 (1)
C(10)	0·9136 (6)	0·2379 (3)	0·1212 (4)	3·5 (1)
O(11)	0·8597 (6)	0·4898 (3)	0·1884 (4)	7·4 (1)
C(12)	1·0340 (8)	0·2673 (4)	−0·0963 (5)	6·6 (2)
C(13)	0·8933 (7)	−0·0006 (4)	0·1889 (7)	6·6 (2)
C(14)	0·8740 (12)	−0·0487 (4)	0·3117 (8)	9·8 (3)
C(15)	0·7542 (8)	−0·0164 (4)	0·3947 (7)	6·9 (2)
N(16)	0·7646 (5)	0·0752 (3)	0·4163 (4)	4·6 (1)
C(17)	0·6701 (7)	0·1095 (4)	0·5174 (6)	6·3 (2)
C(18)	0·7328 (7)	0·1945 (4)	0·5639 (5)	5·7 (2)
C(19)	0·7319 (6)	0·2572 (3)	0·4521 (5)	4·0 (1)

Table 2. *Bond lengths (Å), bond angles (°) and selected torsion angles (°) involving non-H atoms with e.s.d.'s in parentheses*

O(1)—C(2)	1·387 (7)	C(7)—C(8)	1·404 (6)
O(1)—C(9)	1·382 (6)	C(7)—N(16)	1·375 (6)
C(2)—C(3)	1·423 (8)	C(8)—C(9)	1·389 (6)
C(2)—O(11)	1·221 (7)	C(8)—C(19)	1·505 (6)
C(3)—C(4)	1·354 (8)	C(9)—C(10)	1·384 (7)
C(4)—C(12)	1·500 (8)	C(13)—C(14)	1·475 (10)
C(4)—C(10)	1·425 (7)	C(14)—C(15)	1·451 (11)
C(5)—C(6)	1·380 (7)	C(15)—N(16)	1·452 (7)
C(5)—C(10)	1·399 (7)	N(16)—C(17)	1·450 (7)
C(6)—C(7)	1·419 (7)	C(17)—C(18)	1·487 (8)
C(6)—C(13)	1·508 (7)	C(18)—C(19)	1·497 (7)

C(2)—O(1)—C(9)	121·5 (4)	C(7)—C(8)—C(9)	118·1 (4)
O(1)—C(2)—O(11)	115·8 (5)	C(9)—C(8)—C(19)	120·6 (4)
O(1)—C(2)—C(3)	117·1 (5)	O(1)—C(9)—C(8)	115·0 (4)
C(3)—C(2)—O(11)	127·0 (5)	C(8)—C(9)—C(10)	124·1 (4)
C(2)—C(3)—C(4)	122·0 (5)	O(1)—C(9)—C(10)	120·9 (4)
C(3)—C(4)—C(12)	119·2 (5)	C(5)—C(10)—C(9)	116·4 (4)
C(3)—C(4)—C(10)	119·8 (5)	C(4)—C(10)—C(9)	118·5 (4)
C(10)—C(4)—C(12)	120·9 (5)	C(4)—C(10)—C(5)	124·9 (4)
C(6)—C(5)—C(10)	122·6 (4)	C(6)—C(13)—C(14)	112·5 (5)
C(5)—C(6)—C(13)	119·5 (5)	C(13)—C(14)—C(15)	116·5 (5)
C(5)—C(6)—C(7)	119·2 (4)	C(14)—C(15)—N(16)	113·4 (5)
C(7)—C(6)—C(13)	121·3 (4)	C(7)—N(16)—C(15)	120·9 (4)
C(6)—C(7)—N(16)	119·7 (4)	C(15)—N(16)—C(17)	116·4 (4)
C(6)—C(7)—C(8)	119·6 (4)	C(7)—N(16)—C(17)	118·9 (4)
C(8)—C(7)—N(16)	120·7 (4)	N(16)—C(17)—C(18)	111·1 (5)
C(7)—C(8)—C(19)	121·3 (4)	C(17)—C(18)—C(19)	111·9 (5)
		C(8)—C(19)—C(18)	111·4 (4)

C(6)—C(13)—C(14)—C(15)	37·3 (8)	N(16)—C(17)—C(18)—C(19)	57·7 (6)
C(13)—C(14)—C(15)—N(16)	−46·4 (8)	C(17)—C(18)—C(19)—C(8)	−44·4 (6)
C(14)—C(15)—N(16)—C(7)	33·4 (8)	C(18)—C(19)—C(8)—C(7)	16·2 (6)
C(15)—N(16)—C(7)—C(6)	−12·1 (7)	C(19)—C(8)—C(7)—N(16)	0·2 (7)
N(16)—C(7)—C(6)—C(13)	3·0 (7)	C(8)—C(7)—N(16)—C(17)	13·0 (7)
C(7)—C(6)—C(13)—C(14)	−15·4 (8)	C(6)—C(7)—N(16)—C(17)	−169·2 (5)
C(7)—N(16)—C(17)—C(18)	−41·8 (6)	C(8)—C(7)—N(16)—C(15)	170·2 (5)

Experimental. Compound from Exciton (USA), hexagonal rod-shaped crystals from a mixture of aqueous ethanol and chloroform, D_m by flotation method. Rigaku *AFC5R* diffractometer, graphite-monochromated Mo $K\alpha$ radiation, crystal dimensions $0\cdot3 \times 0\cdot2 \times 0\cdot2$ mm, cell dimensions from 20 angles in the range $15 < 2\theta < 20°$, $2\theta_{max} = 45°$. Intensities measured in the range $h = 0$ to 8, $k = 0$ to 16 and $l = -10$ to 10, ω–2θ scan; three standard reflections (13$\bar{1}$, $\bar{1}$2$\bar{1}$, $\bar{2}$0$\bar{2}$) monitored every 150 measurements showed no significant change. 1387 unique reflections measured, 1020 observed with $|F_o| > 2\sigma(|F_o|)$, Lp corrected, no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), 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, H-atom positions not refined, final $R = 0\cdot065$, $wR = 0\cdot071$, $w = 1\cdot9088/[\sigma^2(|F_o|) + 0\cdot0013F_o^2]$, $S = 1\cdot59$, $(\Delta/\sigma)_{max} = 0\cdot005$, final difference map featureless with max. and min. peak heights $0\cdot25$ and $-0\cdot28$ e Å^{-3}, no correction for secondary extinction, atomic scattering factors for all atoms are as in *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.* Bond lengths and valence angles are listed in Table 2. Bond lengths and angles in the coumarin moiety are normal (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985; Murthy, Ramamurthy &
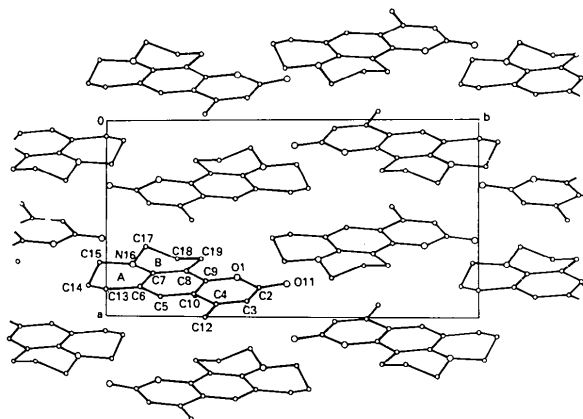
Fig. 1. Molecular packing of the title compound in the unit cell viewed down the *c* axis.

Venkatesan, 1988). $C(sp^3)$—$C(sp^3)$ distances in the two piperidine rings are shorter than the $C(sp^2)$—$C(sp^3)$ distances. This feature is found to be common in the fused piperidine ring systems (Chinnakali, Sivakumar & Natarajan, 1990). The benzene and pyrone rings are planar ($\chi^2 = 5\cdot2$ and $4\cdot6$) and the dihedral angle between them is $0\cdot8$ (1)°, thus mak ·· the coumarin moiety exactly planar.

Endoc, ic torsion angles characterizing the piperidine-ring conformations are given in Table 2. The two piperidine rings A and B adopt significantly flattened half-chair conformations [$\Delta C_2(6-7) = 3\cdot6$ and $\Delta C_2(7-8) = 2\cdot9°$] (Duax, Weeks & Rohrer, 1976). This flattening results from the fusion of the piperidine rings with the benzene ring of the coumarin moiety. The average values of the absolute magnitudes of the torsion angles are $24\cdot6$ and $28\cdot8°$ respectively.

The packing of the molecules viewed down the c axis is shown in Fig. 1. The crystal structure is stabilized by van der Waals interactions.

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Conformation of 1,3,5-Tri-*p*-tolylmethyl-1,3,5-triazacyclohexane

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Abstract. $C_{27}H_{33}N_3$, $M_r = 399\cdot62$, triclinic, $P\bar{1}$, $a = 6\cdot020$ (2), $b = 15\cdot326$ (2), $c = 13\cdot009$ (1) Å, $\alpha = 97\cdot00$ (1), $\beta = 98\cdot05$ (2), $\gamma = 90\cdot55$ (2)°, $V = 1179$ (1) Å^3, $Z = 2$, $D_x = 1\cdot13$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 0\cdot07$ mm^{-1}, $F(000) = 432$, $T = 293$ K, $R = 0\cdot047$ for 2713 independent observed reflections. The triazacyclohexane ring adopts a chair conformation with equatorial–diaxial orientation of the *p*-tolylmethyl groups. The torsion angles around the N—C bonds in the triazacyclohexane ring are $50\cdot6$ (2)–$61\cdot1$ (2)°, the CH$_2$—N—CH$_2$ angles in the ring are $108\cdot0$ (2)–$109\cdot4$(2)°, the N—CH$_2$—N angles are $111\cdot5$ (2)–$116\cdot8$ (2)°, and the N—C ring bonds are $1\cdot446$ (3)–$1\cdot477$ (3) Å. The axial N—CH$_2$ exocyclic bonds are bent outwards from ideal tetrahedral positions by *ca* 9° to reduce 1,3-diaxial repulsion.

Introduction. Conformational effects of non-bonding electrons are a feature of heterocyclic chemistry (Riddell, 1980). The heterocyclic nucleus in the 1,3,5-trialkyl-1,3,5-triazacyclohexanes (1) (hexahydro-*s*-triazines) is expected to adopt a chair conformation and four distinct types of substituent orientation can be postulated, *eee*, *eea*, *eaa* and *aaa*, where *e* = equatorial and *a* = axial; all four conformers have axial repulsions involving substituents and/or lone pairs of electrons on the N atoms. Several 1,3,5-trialkyl derivatives have been investigated in solution by NMR spectroscopy and dipole-moment measurements and the results interpreted in terms of the *eee* conformer (Farmer & Hamer, 1968; Gutowsky & Temussi, 1967; Lehn, Riddell, Price & Sutherland, 1967), the *eea* conformer (Bushweller, Lourandos & Brunelle, 1974; Baker, Ferguson,