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C—Halogen···π interactions in 4-chloro-2-(9-ethylcarbazol-3-yl)-1,2-dihydroquinoline-1-carbaldehyde

P. G. Aravindan,[a]

S. Selvanayagam,[a]

D. Velmurugan,[a]*

K. Ravikumar,[b]

R. Nagarajan[c] and

P. T. Perumal[c]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, [b]Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and [c]Organic Chemistry Division, Central Leather Research Institute, Adyar 600 020, India

Correspondence e-mail: d_velu@yahoo.com

The title compound, $C_{24}H_{19}ClN_2O$, consists of a carbazole skeleton with ethyl and 4-chloroquinoline-N-aldehyde substituents. The dihydropyridine ring adopts a half-chair conformation. The molecular packing is stabilized by C—Cl···π interactions.

Comment

Carbazole derivatives exhibit a wide range of pharmaceutical properties, such as antitumor (Moinet-Hedin *et al.*, 2000; Itoigawa *et al.*, 2000), antimycobacterial, antifungal (Sunthitikawinsakul *et al.*, 2003), antiosteoporotic (Wang *et al.*, 2003), antiestrogenic (Golob *et al.*, 2000) and antioxidant (Tachibana *et al.*, 2001) activities. Carbazole behaves as a fluorescence carrier for the preparation of a doxycycline sensor, which can be used for the analysis of urine samples (Chen *et al.*, 2003). *N*-ethyl carbazole derivatives have been used for potential optical applications (Timofeeva *et al.*, 2000). Quinoline-containing carbazole derivatives are also used as antidepressant drugs (Oshiro *et al.*, 2000). The X-ray crystal structure analysis of the title compound, (I), was carried out as part of our studies on indole and carbazole derivatives containing the quinoline moiety.

(I)
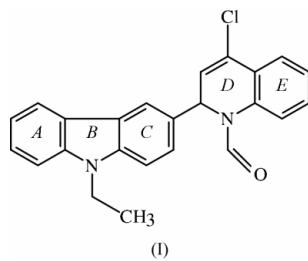
Observed bond lengths and angles in the carbazole moiety agree with those in related structures (Hökelek *et al.*, 2001*a*,*b*; Aravindan *et al.*, 2003). The sum of the bond angles around N20 [359.9°] is an indication of sp^2 hybridization. The ethyl group is disordered over two positions, with an occupancy ratio of 0.516 (8):0.484 (8). The dihydropyridine ring adopts a half-chair conformation, with asymmetry parameter ΔC_2(C11—N20) = 0.013 (1) (Nardelli, 1983); atoms C11 and N20 deviate from the plane through the other four ring atoms by −0.204 (2) and 0.235 (1) Å, respectively.

In the crystal structure, short intramolecular C—H···O, C—H···N and C—H···Cl interactions are observed (Table 2). The crystal packing is stabilized by C—Cl···π interactions [Cl1···CgB^i = 3.355 (2) Å, C13—Cl1···CgB^i = 146°; symmetry code: (i) x, 1 + y, z; CgB denotes the centroid of ring B], as shown in Fig. 2.
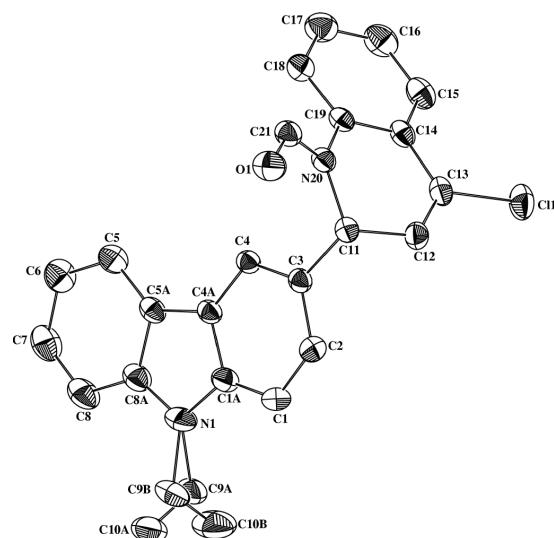
Figure 1
The molecular structure of the title compound, showing 35% probability displacement ellipsoids and both disorder components. H atoms are omitted.
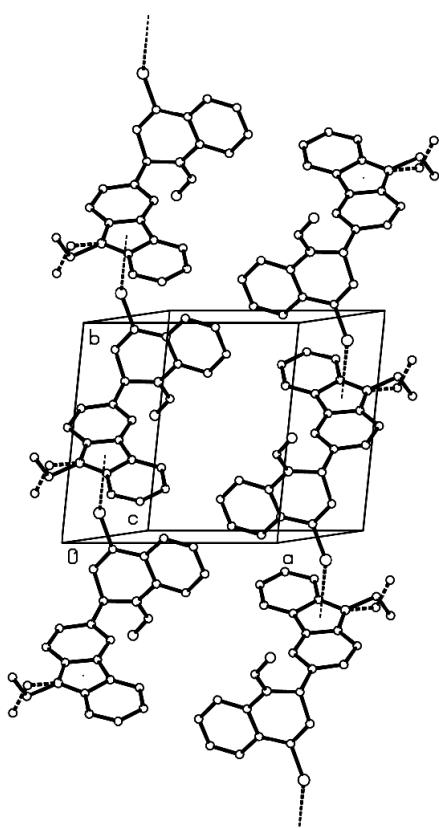

Figure 2
The molecular packing of (I), viewed down the *c* axis.

Experimental

To a stirred ice-cold solution of 1-(2-aminophenyl)-3-(9-ethyl-carbazol-3-yl)-prop-2-en-1-one (2.5 mmol) in DMF (10 ml), $POCl_3$ (0.7 ml, 7.5 mmol) was added in drops and the solution heated over a water bath for 3 h. After completion of the reaction, as evidenced by

TLC, the reaction mixture was poured over crushed ice and neutralized with 10% NaOH solution, extracted with ethyl acetate (3 × 10 ml) and the combined organic layer washed with water and brine, then dried over Na_2SO_4, filtered and the solvent evaporated. The residue was purified by column chromatography, eluting with ethyl acetate: petroleum ether (1:1) to afford the title compound.

Crystal data

$C_{24}H_{19}ClN_2O$	$Z = 2$
$M_r = 386.86$	$D_x = 1.356$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.4147$ (8) Å	Cell parameters from 2301
$b = 9.6714$ (8) Å	reflections
$c = 11.1245$ (9) Å	$\theta = 2.3$–27.3°
$\alpha = 85.336$ (1)°	$\mu = 0.22$ mm^{-1}
$\beta = 70.235$ (1)°	$T = 293$ (2) K
$\gamma = 84.351$ (2)°	Block, colourless
$V = 947.37$ (14) Å^3	$0.24 \times 0.18 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3187 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: none	$\theta_{max} = 28.0°$
5918 measured reflections	$h = -11 \rightarrow 11$
4119 independent reflections	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.0963P]$
$wR(F^2) = 0.141$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
4119 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
274 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cl1—C13	1.751 (2)	N1—C9B	1.500 (7)
O1—C21	1.212 (2)	C11—N20	1.471 (2)
N1—C8A	1.384 (3)	C19—N20	1.425 (2)
N1—C1A	1.390 (2)	N20—C21	1.365 (2)
N1—C9A	1.487 (7)		
C8A—N1—C1A	108.9 (2)	C21—N20—C19	121.1 (2)
C8A—N1—C9A	123.9 (3)	C21—N20—C11	117.9 (2)
C1A—N1—C9A	124.8 (3)	C19—N20—C11	120.9 (2)
C8A—N1—C9B	125.4 (3)		
C4—C3—C11—N20	12.0 (2)	C11—N20—C21—O1	−7.4 (3)
C19—N20—C21—O1	177.1 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$N20	0.93	2.55	2.882 (2)	102
C11—H11$\cdots$O1	0.98	2.37	2.751 (2)	102
C15—H15$\cdots$Cl1	0.93	2.69	3.085 (2)	106

H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms, with C—H distances in the range 0.93–098 Å and with U_{iso}(H) = $1.2U_{eq}$ (parent C). The ethyl group bonded to N1 was statistically disordered. The occupation factors of the two orientations were refined, with with their sum constrained to unity [C9A, C10A = 0.516 (8); C9B, C10B = 0.484 (8)].

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