Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Chloro-2-(4-chlorophenyl)-1-formyl-1,2-dihydroquinoline

S. Thinagar,[a] D. Velmurugan,[a]* V. Rajakannan,[a] Il-Hwan Suh[b] and S. Akila[c]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India, [b]Department of Physics, Chungnam National University, Republic of Korea, and [c]Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

Correspondence e-mail: d_velu@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.049
wR factor = 0.113
Data-to-parameter ratio = 14.0

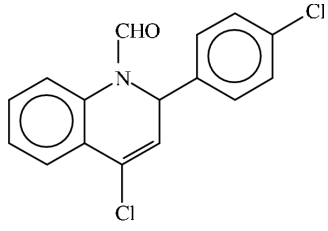
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 May 2002
Accepted 15 July 2002
Online 19 July 2002

The dihydropyridine ring of the title molecule, $C_{16}H_{11}Cl_2NO$, adopts a half-chair conformation. The chlorophenyl ring is perpendicular to the mean plane through the dihydroquinoline moiety. The CHO group is involved in C—H···O intermolecular hydrogen bonds.

Comment

Quinoline-containing compounds are present in a large number of natural products and they are found in numerous commercial products including pharmaceuticals, fragrances and dyes (Padwa *et al.*, 1999). Aminoquinoline-based ligands possess a strong fluorescent property which could be used as a probe for DNA binding (Fahrni & O'Halloran, 1999; Nasir *et al.*, 1999). Synthetic tetrahydroquinoline derivatives possess high antibacterial, anti-arrhythmic and antihypertensive activities (Jones, 1977; Yates, 1984). They also act as potent virucides and analgesics. Tetrahydroquinoline derivatives exhibit antitumour activities (Jaton *et al.*, 1997) and also act as potent antipsychotic agents (Norman *et al.*, 1996) and a compound containing the tetrahydroquinoline moiety acts as an antischistosomal drug (Billings & Heidelberger, 1982). They also possess anti-inflammatory (Ohnishi *et al.*, 1981), anti-amoebic (Bailey *et al.*, 1979), anti-ulcer (Uchida *et al.*, 1989) and analgesic (Shaaban *et al.*, 1977) activities. Norfloxacin is a broad (spectrum of 4) fluoroquinolone antibiotic used in the treatment of urinary tract infections. Alkynylquinolines comprise an important class of biologically active compounds which have been considered as bactericides, fungicides and analgesics (Smith, 1950; Blumenthal, 1959; Burckhardt & Zimmermann, 1972).



(I)

Fig. 1 shows a displacement ellipsoid plot of the title molecule. The dihydropyridine ring adopts a half-chair conformation, with asymmetry parameter ΔC_2(N1—C1) = 0.005 (1) (Nardelli, 1983); atoms N1 and C1 deviate from the plane containing the other four atoms constituting the ring by −0.272 (3) and 0.317 (3) Å, respectively. The mean plane through the dihydropyridine ring makes a dihedral angle of 12.1 (1)° with that through the fused benzene ring. The mean

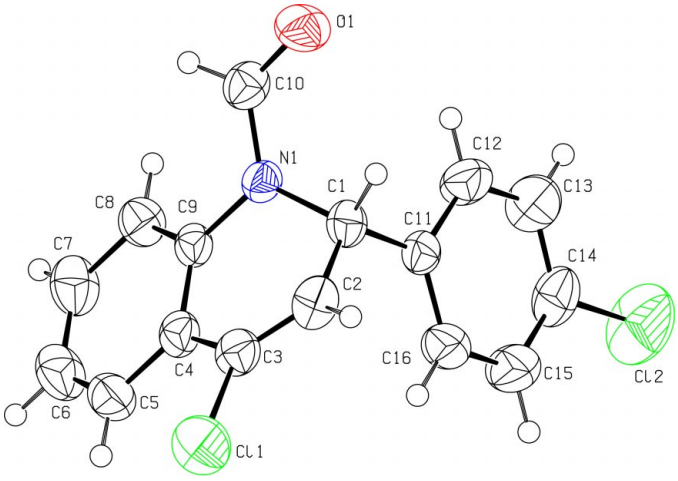


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

plane through the dihydroquinoline moiety is perpendicular to the plane of the chlorophenyl ring [89.32 (8)°]. The sum of the bond angles around N1 is 359.7 (3)°, an indication of the sp^2 hybridization. The orientation of the substituents at C1 and N1 is better described by the torsion angles C2—C1—C11—C16 [10.4 (4)°] and C9—N1—C10—O1 [−179.2 (3)°], respectively. The bond angles C8—C9—N1 [121.8 (3)°] and C5—C4—C3 [125.1 (3)°] are larger than the normal value of 120°. This is due to the steric interactions imposed by the substituents. The C—N and C—C bond lengths show normal values (Allen *et al.*, 1987). The C10—O1 [1.208 (3) Å] and N1—C10 [1.359 (4) Å] bond distances compare well with the literature values (Simonsen *et al.*, 1996). The bond angles C9—N1—C1 [117.5 (2)°] and N1—C10—O1 [124.9 (3)°] agree well with the values observed for similar quinoline derivatives (Simonsen *et al.*, 1996; Henao-Martínez *et al.*, 1999). The molecular packing in the crystal is stabilized by weak intermolecular C—H···O hydrogen bonds, involving the CHO groups (Table 2), and van der Waals interactions.

Experimental

To a stirred solution of 2′-amino-4-chlorochalcone (1.29 g, 5 mmol) in 10 ml DMF at 273 K, $POCl_3$ (3 ml) was added dropwise. The reaction mixture was warmed to room temperature and heated at 363 K over a water bath for 4 h. The reaction mixture was poured over 250 g of crushed ice and neutralized with 10% NaOH, followed by extraction with ethyl acetate. Distillation of the solvent, followed by column chromotography, afforded the pure compound in 80% yield, with m.p. = 383 K. Single crystals were grown by slow evaporation from a methanol solution.

Crystal data

$C_{16}H_{11}Cl_2NO$
M_r = 304.16
Monoclinic, $C2/c$
a = 13.5899 (14) Å
b = 14.344 (4) Å
c = 15.667 (3) Å
β = 110.174 (13)°
V = 2866.6 (10) Å^3
Z = 8
D_x = 1.410 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 2.1–25.0°
μ = 0.45 mm^{-1}
T = 293 (2) K
Slab, colourless
0.19 × 0.13 × 0.11 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2630 measured reflections
2528 independent reflections
1512 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.114
S = 1.03
2528 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.9418P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C10	1.359 (4)	O1—C10	1.208 (3)
C9—N1—C1	117.5 (2)	C8—C9—N1	121.8 (3)
C5—C4—C3	125.1 (3)	O1—C10—N1	124.9 (3)
C9—N1—C10—O1	−179.2 (3)	C2—C1—C11—C16	10.4 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1	0.98	2.38	2.806 (4)	105
C5—H5···Cl1	0.93	2.75	3.118 (3)	104
C7—H7···O1^{i}	0.93	2.52	3.192 (4)	129
C10—H10···O1^{ii}	0.93	2.52	3.278 (4)	139

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, y, \frac{1}{2}-z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

ST and DV thank the UGC (India) for providing funding under a major project.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bailey, D. M., Mount, E. M., Siggins, J., Carlson, J. A., Yarinsky, A. & Slighter, R. G. (1979). *J. Med. Chem.* **22**, 599–601.
Billings, P. C. & Heidelberger, C. (1982). *Cancer Res.* **42**, 2692–2696.
Blumenthal, J. H. (1959). US Patent 2 874 162; *Chem. Abstr.* (1959), **53**, 12311b.
Burckhardt, U. & Zimmermann, M. (1972). German Patent 2 209 470; *Chem. Abstr.* (1972). **77**, 164744m.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Fahrni, C. J. & O'Halloran, T. V. (1999). *J. Am. Chem. Soc.* **121**, 11448–11458.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Henao-Martínez, J. A., Palma, A. R., Kouznetsov, V. V., Aguirre-Hernández, G., Fernando-Ortega, C. & Soriano-Gracia, M. (1999). *Acta Cryst.* C**55**, 1181–1183.
Jaton, J. C., Roulin, K., Rose, K., Sirotnak, F. M., Lewenstein, A., Brunner, G., Fankhauser, C. P. & Burger, U. (1997). *J. Nat. Prod*. **60**, 356–360.
Jones, G. (1977). *Chemistry of Heterocyclic Compounds*, Vol. 32, edited by G. Jones, Part I, *Quinolines*, pp. 93–318. Chichester: Wiley.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Nasir, M. S., Fahrni, C. J., Suhy, D. A., Kolodsick, K. J., Singer, C. P. & O'Halloran, T. V. (1999). *J. Biol. Inorg. Chem.* **4**, 775–783.
Norman, M. H., Navas, F., Thompson, J. B. & Rigdon, G. C. (1996). *J. Med. Chem.* **39**, 4692–4703.
Ohnishi, H., Kosuzume, H., Yamaguchi, K., Ohkura, M., Satoh, M., Uohama, M., Toyonaka, Y. & Suzuki, Y. (1981). *Jpn. J. Pharmacol.* **31**, 747–756.
Padwa, A., Brodney, M. A., Liu, B., Satake, K. & Wu, T. (1999). *J. Org. Chem.* **64**, 3595–3607.
Shaaban, M. A., Ghoneim, K. M. & Khalifa, M. (1977). *Pharmazie*, **32**, 90–92.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Simonsen, O., Singh, S. K., Wengel, J. & Parmar, V. S. (1996). *Acta Cryst.* C**52**, 3195–3196.
Smith, J. M. (1950). US Patent 2 512 180; *Chem. Abstr.* (1950), **44**, 9487*c*.
Uchida, M., Chihiro, M., Morita, S., Kanbe, T., Yamashita, H., Yamasaki, K., Yabuuchi, Y. & Nakagawa, K. (1989). *Chem. Pharm. Bull.* (Tokyo), **37**, 2109–2116.
Yates, F. S. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 2, edited by A. R. Katrizky and C. W. Rees, p. 511. New York: Pergamon Press.
Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.