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10-[2-(4-Acetylpiperzin-1-yl)ethyl]-9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-2*H*,5*H*-acridine-1,8-dione

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.079
wR factor = 0.216
Data-to-parameter ratio = 20.7

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

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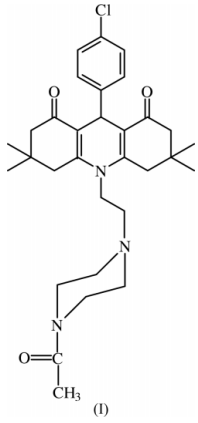
In the title compound, $C_{31}H_{40}N_3O_3Cl$, the central N-containing ring adopts a boat conformation and the two outer rings adopt conformations intermediate between half-chair and sofa. In the crystal structure, C—H···O hydrogen bonds link the symmetry-related molecules to form centrosymmetric hydrogen-bonded tetramers with $R_4^4(24)$ and $R_4^4(52)$ motifs.

Comment

Acridinediones were found to act as laser dyes, lasing around 475–495 nm (Murugan *et al.*, 1998; Selladurai *et al.*, 1990). The effectiveness of lasing can be controlled by the substitutents at C9 and N10 of the acridine chromophore. Decahydroacridine-1,8-diones act as photo-sensitizers (Timpe *et al.*, 1993) and also possess other important photophysical and electrochemical properties (Mohan *et al.*, 1996). Apart from the above applications, acridine and its derivatives exhibit a wide spectrum of biological activites, such as mutagenic, antitumour (Talacki *et al.*, 1974), antiamoebic (Prasad Krishna *et al.*, 1984), hypertensive, anti-inflammatory (Asthana *et al.*, 1991). An acridine-moiety-containing drug has been found to possess anti-protozoal activity (Karolak-Wojciechowska *et al.*, 1996) and is considered to be an efficient drug for the treatment of Alzheimer's disease (Bandoli *et al.*, 1994). The ability of acridine to intercalate between the base-pairs of DNA is also well known (Neidle, 1979; Fan *et al.*, 1997). Substituted hexahydro-acridine-1,8-diones resemble K-channel openers, which relax KCl preconcentrated urinary-bladder smooth muscle *in vitro* (Li *et al.*, 1996; Trivedi *et al.*, 1995). The present investigation was carried out to establish the three-dimensional structure of the title compound, (I).



(I)

The central ring (*B*) of the acridinedione moiety adopts a boat conformation, with puckering parameters (Cremer & Pople, 1975) $q_2 = 0.333\ (3)$, $q_3 = -0.091\ (3)$, $Q = 0.345\ (3)$ Å, φ_2

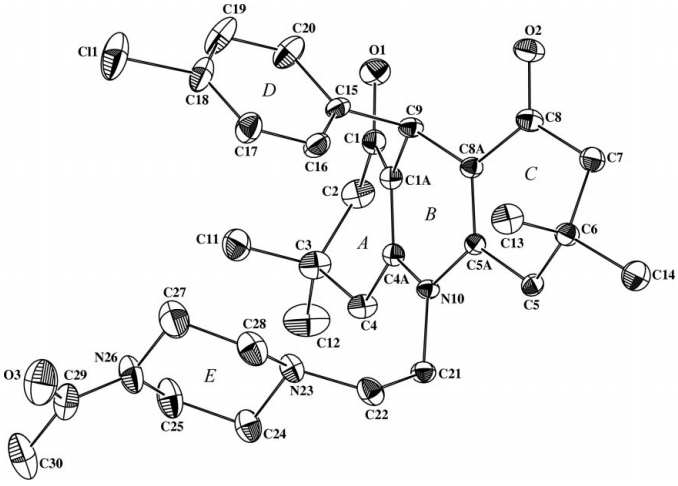


Figure 1
The molecular structure of the title compound, showing 35% probability displacement ellipsoids. H atoms have been omitted for clarity.

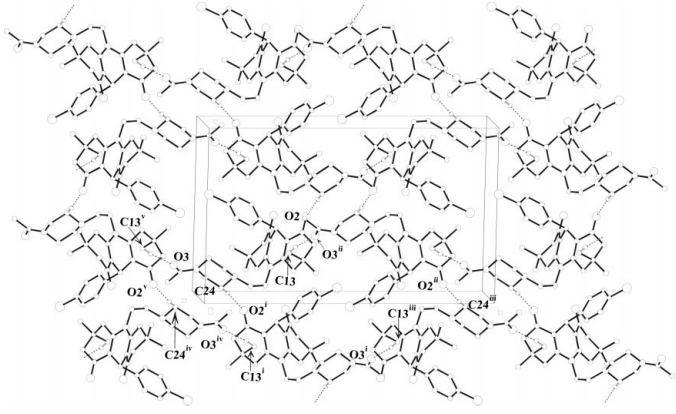


Figure 2
A view of the $R_4^4(24)$ and $R_4^4(52)$ rings [symmetry codes: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, -z$; (iii) $1-x, 1-y, -z$; (iv) $1-x, -y, -z$; (v) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. For clarity, H atoms not involved in hydrogen bonding have been omitted.

= −4.7 (5) and θ = 105.3 (5)°; atoms C9 and N10 deviate by 0.406 (3) and 0.175 (2) Å, respectively, from the weighted least-squares plane through atoms C1*A*, C4*A*, C5*A* and C8*A*. The two outer rings, *A* and *C*, adopt conformations intermediate between half-chair and sofa, with Cremer & Pople (1975) puckering parameters q_2 = 0.433 (3), q_3 = 0.238 (4), Q = 0.495 (4) Å, φ_2 = −101.2 (4) and θ = 61.2 (4)° for ring *A* and q_2 = 0.411 (3), q_3 = −0.248 (3), Q = 0.480 (4), φ_2 = 109.1 (5) and θ = 121.1 (4)° for ring *C*. The piperazine ring *E* adopts a chair conformation. As reported in related acridine derivatives (Sivaraman *et al.*, 1994, 1996; Gunasekaran *et al.*, 1996; Subbiah Pandi *et al.*, 2001; Seshadri *et al.*, 2002), the acridine moiety is folded about the line passing through C9 and N10, with a dihedral angle of 28.7 (1)° between the planes C1/C4/C4*A*/N10/C9/C1*A* and C5/C8/C8*A*/C9/N10/C5*A*. The weighted least-squares plane through atoms C1*A*, C4*A*, C5*A* and C8*A* forms a dihedral angle of 87.1 (1)° with the chlorophenyl ring. The torsion angle C5*A*—C8*A*—C9—C15 is 91.7 (4)°, showing that the chlorophenyl ring is psuedo-axial to the acridine moiety.

The C—N bond lengths in the *B* ring are in agreement with values observed for related structures (Gunasekaran *et al.*, 1996; Ganesh *et al.*, 1998; Subbiah Pandi *et al.*, 2001; Jeyakanthan *et al.*, 2000, 2002). The average N—C [1.451 (5) Å] and C—C [1.489 (6) Å] bond lengths in the piperazine ring agree well with those reported in the literature (Perales *et al.*, 1977; Yogavel *et al.*, 2002). The sum of the bond angles around N10 [359.6 (3)°] and N26 [359.9 (4)°] confirm the sp^2 hybridization of these atoms; the angles around the atom N23 sum to 333.7 (3)°, which is indicative of sp^3 hybridization.

In the cyrstal, C24—H24*B*···O2^{i} hydrogen bonds link symmetry-related molecules to form chains parallel to [101], whereas C13—H13*C*···O3^{ii} hydrogen bonds (symmetry codes as in Fig. 2) form chains parallel to [110]. The C24—H24*B*···O2^{i} and C13—H13*C*···O3^{ii} hydrogen bonds create motifs with graph sets $C(12)$ and $C(14)$, respectively. The interesting feature in the crystal structure of (I) is the formation of centrosymmetric hydrogen-bonded tetramers with $R_4^4(24)$ and $R_4^4(52)$ motifs (Bernstein *et al.*, 1995). The first tetramer is formed *via* C24—H24*B*···O2^{i}, C13^{i}—H13*C*^{i}···O3^{iv}, C24^{iv}—H24*B*^{iv}···O2^{v} and C13^{v}—H13*C*^{v}···O3 hydrogen bonds. The second tetramer is formed *via* C13—H13*C*···O3^{ii}, C24^{iii}—H24*B*^{iii}···O2^{ii}, C13^{iii}—H13*C*^{iii}···O3^{i} and C24—H24*B*···O2^{i} hydrogen bonds (Fig. 2).

Experimental

A mixture of 2,2′-(4-chlorobenzylidine)bis(5,5-dimethylcyclohexane-1,3-dione) (1.0 g, 2.49 mmol) and *N*-aminoethylpiperazine (0.32 g, 2.49 mmol) was refluxed in acetic acid (15 ml) for 14 h. The reaction mixture was cooled and poured on to crushed ice. The resulting solid was filtered and purified by column chromatography over silica gel and eluted with $CHCl_3$–MeOH (9:1), to isolate the title compound.

Crystal data

$C_{31}H_{40}ClN_3O_3$
M_r = 538.11
Monoclinic, $P2_1/n$
a = 10.3624 (6) Å
b = 21.4915 (12) Å
c = 13.5314 (8) Å
β = 101.492 (1)°
V = 2953.1 (3) Å^3
Z = 4
D_x = 1.210 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4320 reflections
θ = 1.8–28.3°
μ = 0.17 mm^{-1}
T = 293 (2) K
Plate, light yellow
0.50 × 0.24 × 0.14 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
19702 measured reflections
7195 independent reflections
2446 reflections with $I > 2\sigma(I)$
R_{int} = 0.118
θ_{max} = 28.3°
$h = -13 \rightarrow 13$
$k = -25 \rightarrow 28$
$l = -13 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.216
S = 0.90
7195 reflections
348 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C18	1.749 (4)	C22—N23	1.458 (4)
O1—C1	1.232 (4)	N23—C28	1.449 (4)
O2—C8	1.230 (4)	N23—C24	1.452 (4)
C4*A*—N10	1.396 (4)	C25—N26	1.459 (5)
C5*A*—N10	1.399 (4)	N26—C29	1.310 (5)
N10—C21	1.471 (4)		
C4*A*—N10—C5*A*	117.9 (3)	C24—N23—C22	112.5 (3)
C4*A*—N10—C21	121.8 (3)	C29—N26—C27	121.1 (4)
C5*A*—N10—C21	119.9 (3)	C29—N26—C25	125.7 (4)
C28—N23—C24	109.0 (3)	C27—N26—C25	113.1 (3)
C28—N23—C22	112.2 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O1	0.98	2.47	2.842 (4)	102
C9—H9···O2	0.98	2.44	2.810 (4)	102
C27—H27*A*···O3	0.97	2.27	2.693 (6)	105
C24—H24*B*···O2^{i}	0.97	2.50	3.461 (4)	171
C13—H13*C*···O3^{ii}	0.96	2.40	3.354 (5)	171

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

All the H atoms were positioned geometically and were allowed to ride on their parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and displacement parameters. At this stage, the maximum difference density of 0.62 e Å^{-3} indicated the presence of a possible atom site. A check for the solvent-accessible volume using *PLATON* (Spek, 1990) showed a void of 28 Å^3. This peak was found near C25, at a distance of 3.21 (2) Å. Attempts to refine this peak as a water oxygen with full occupancy resulted in a high U_{iso} value and hence it was refined with partial occupancy. The refinement resulted in an occupancy of 0.15, maximum density of 0.19 e Å^{-3} and *R* value of 0.074. However, we prefer to report the structure without the solvent water oxygen, as the solvent-accessible volume of 28 Å^3 is less than the expected volume of 40 Å^3 for a hydrogen-bonded water molecule (Spek, 1990). Owing to the poor diffraction quality of the crystal, the ratio of observed to unique relections is low (0.34) and R_{int} (0.12) value is high.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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