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10-(4-Fluorophenyl)-3,3,6,6,9-pentamethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione and 10-(4-fluorophenyl)-3,3,6,6-tetramethyl-9-propyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione

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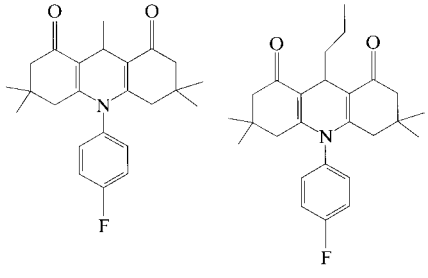
10-(4-Fluorophenyl)-3,3,6,6,9-pentamethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione, $C_{24}H_{28}FNO_2$, (I), crystallizes with two crystallographically independent molecules (which differ slightly in conformation), while 10-(4-fluorophenyl)-9-propyl-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione, $C_{26}H_{32}FNO_2$, (II), crystallizes with one molecule per asymmetric unit. In both structures, the central ring in the acridine moiety is in a sofa conformation, while the outer rings adopt intermediate half-chair/sofa conformations. The central pyridine ring is orthogonal to the substituted phenyl ring. In both structures, the packing of the crystal is stabilized by C—H···O intermolecular hydrogen bonds.

Comment

Acridine and its derivatives exhibit a wide spectrum of biological activities, such as antibacterial (Acheson, 1956), mutagenic and antitumour (Talacki *et al.*, 1974), and antiamoebic (Prasad Krishna *et al.*, 1984). The potency of acridines as antiviral and antibacterial agents is due to their ability to bind DNA by intercalation (Neidle, 1979; Nandi *et al.*, 1990). Substitutions at C9 and N10 make the central ring of acridine buckled along the C9···N10 direction, with the dihedral angle formed by the two halves ranging from 7 to 13°. These values are smaller than those found in the present work. This buckling was postulated as the cause of their biological properties by Glusker *et al.* (1972). In acridine-1,8-diones, the electron delocalization is along a stretch of nine non-H atoms (O1═C1—C13═C14—N10—C11═C12—C8═O2), which facilitates the exhibition of fluorescence and laser activity (Selladurai *et al.*, 1990). The effectiveness of this laser activity can be controlled by the substituents at the 9- and 10-positions of the acridine chromophore. The decahydroacridine-1,8-diones act as photo-sensitizers (Timpe *et al.*, 1993). Acridinediones have also been found to behave as laser dyes, acting at around 475–495 nm (Murugan *et al.*, 1998). The present study of the title compounds, (I) and (II), is part of a series of investigations on the crystal structures of acridinedione derivatives.



Compound (I) has two molecules in the asymmetric unit, designated (I*a*) and (I*b*). Fig. 1 shows the molecular structure and the atom-labelling scheme for both (I*a*) and (I*b*). Compound (II) has one molecule per asymmetric unit and Fig. 2 shows the molecular structure and atom-labelling scheme for (II).

The C═O and Csp^2—F bond lengths in both structures are comparable with the values found in the literature (Allen *et al.*, 1987). The average C═O [1.224 (3) Å in (I*a*), 1.233 (3) Å in (I*b*) and 1.228 (3) Å in (II)] and N—C [1.417 (3) Å in (I*a*),

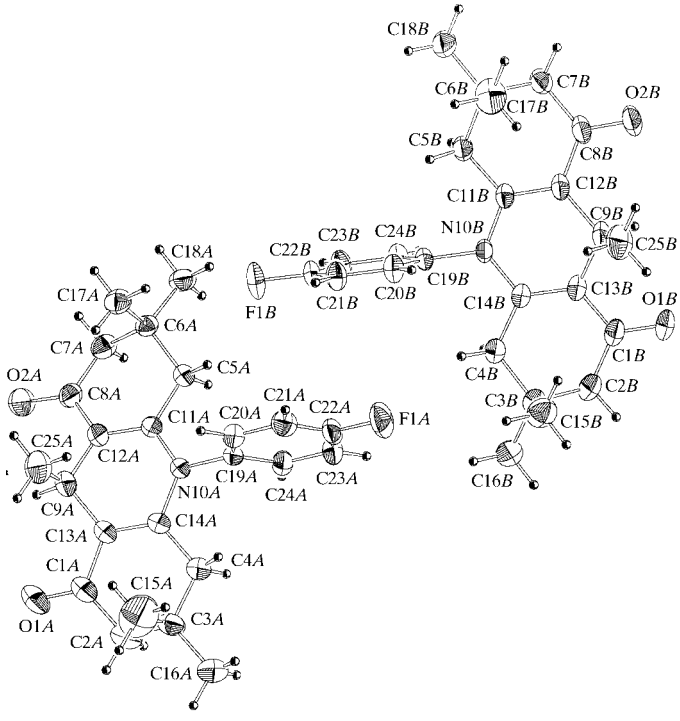


Figure 1
The molecular structure of the two independent molecules of (I) with the atom-labelling scheme and 30% probability displacement ellipsoids. H atoms are displayed as small spheres of arbitrary radii.

1.418 (2) Å in (I*b*) and 1.415 (3) Å in (II)] bond lengths agree well with the values in several related structures (Jeyakanthan *et al.*, 2000; Gunasekaran *et al.*, 1996; Britto-Arias *et al.*, 1996). Selected geometric parameters are given in Tables 1 and 3.

The acridine moiety is folded about the line passing through atoms C9 and N10, and the dihedral angle between the two halves is 27.4 (1)° in (I*a*), 18.8 (1)° in (I*b*) and 21.5 (1)° in (II). These values compare well with those reported in similar acridine derivatives (Gunasekaran *et al.*, 1996; Sivaraman *et al.*, 1994, 1996). The dihedral angle between the outer rings *A* and *C* of the acridine moiety is 18.0 (1)° in (I*a*), 9.1 (1)° in (I*b*) and 15.0 (1)° in (II), and this shows considerable buckling of the acridine nucleus.

The phenyl ring *D* is orthogonal to the central ring *B* in both structures, forming a dihedral angle of 88.3 (1)° in (I*a*), 87.1 (1)° in (I*b*) and 87.5 (1)° in (II). The valence angles around the N atom sum to 359.8 (2)° in (I*a*), 359.0 (2)° in (I*b*) and 358.9 (2)° in (II), and these values are indicative of sp^2 hybridization of the N atom.

The C25*A* and C25*B* methyl groups in (I) and the C25 propyl group in (II) are axial, as indicated by the angles formed by the C9—C25 and C9—H9 bonds with the plane through O1/C1/C13/C14/C11/C12/C8/O2 [C9*A*—C25*A* 88.1, C9*A*—H9*A* 21, C9*B*—C25*B* 77.6 and C9*B*—H9*B* 30° in (I), and C9—C25 79.7 and C9—H9 18° in (II)]. The deviation of atoms O1 and O2 from the mean planes passing through rings *A* and *C* are 0.144 (3) and 0.175 (2) Å in (I*a*), 0.022 (2) and 0.098 (2) Å in (I*b*), and 0.018 (2) and 0.101 (2) Å in (II), respectively.

The puckering amplitudes (Cremer & Pople, 1975) of the rings in the acridine moiety (Table 5) agree well with those of related structures (Gunasekaran *et al.*, 1997; Jeyakanthan *et al.*, 2000). The conformations of the rings of the acridine moiety in both structures are defined by asymmetry parameters (Nardelli, 1983*a*), also given in Table 5.

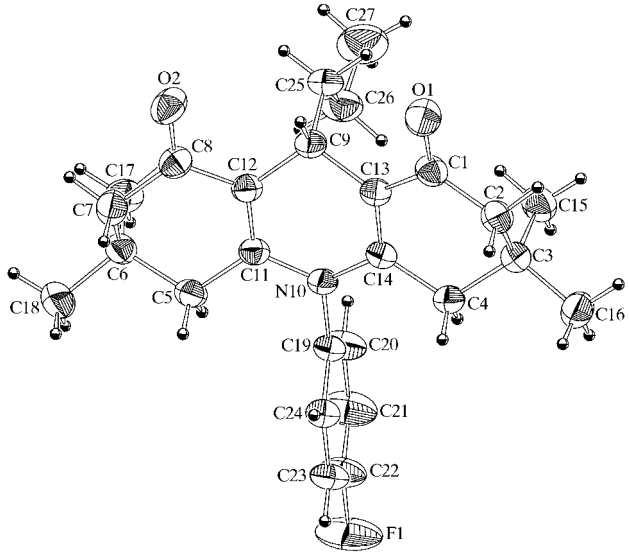


Figure 2
The molecular structure of (II) with the atom-labelling scheme and 30% probability displacement ellipsoids. H atoms are displayed as small spheres of arbitrary radii.

In addition to the normal van der Waals interactions, the packing of the crystals in both structures is stabilized by C—H···O intermolecular hydrogen bonds. In (I), an intermolecular C—H···O hydrogen bond joins the molecules in a chain along the *b* direction. In (II), four C—H···O interactions occur with H···O distances less than the sum of the van der Waals radii (Bondi, 1964) (Table 4). In this structure, the acridine molecules are stacked in a head-to-head manner (Dauter *et al.*, 1976) and are alternately parallel with each other. This type of stacking is also found in acridinedione (Sivaraman *et al.*, 1996) and 9-aminoacridine structures (Talacki *et al.*, 1974).

Experimental

The title compounds were synthesized as follows: a mixture of 2,2′-ethylidenebis(5,5-dimethylcyclohexane-1,3-dione) (2 g, 6.5 mmol) and 4-fluoroaniline (0.63 ml, 6.5 mmol) for compound (I), and a mixture of 2,2′-butylidenebis(5,5-dimethylcyclohexane-1,3-dione) (2 g, 6.0 mmol) and 4-fluoroaniline (0.60 ml, 6.0 mmol) for compound (II), were taken as starting materials. The reaction mixtures were refluxed in acetic acid (25 ml) for 7 h, after which time they were concentrated and poured onto ice. The yellow solids obtained were filtered and dried to afford the title compounds in yields of 1.8 g (72.3%) for (I) and 1.75 g (71.3%) for (II). The compounds were then dissolved in a mixture of chloroform and methanol (2:1). Slow evaporation of the solvent at room temperature produced crystals of (I) and (II) suitable for X-ray analysis.

Compound (I)

Crystal data

$C_{24}H_{28}FNO_2$
M_r = 381.47
Monoclinic, $P2_1/c$
a = 17.1481 (2) Å
b = 17.39090 (10) Å
c = 15.8023 (3) Å
β = 112.8490 (10)°
V = 4342.79 (10) Å^3
Z = 8
D_x = 1.167 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8324 reflections
θ = 1.3–28.3°
μ = 0.08 mm^{-1}
T = 293 (2) K
Block, pale yellow
0.48 × 0.38 × 0.28 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.963, T_{max} = 0.978
29 750 measured reflections
10 547 independent reflections
4439 reflections with $I > 2\sigma(I)$
R_{int} = 0.075
θ_{max} = 28.3°
$h = -22 \rightarrow 22$
$k = -23 \rightarrow 20$
$l = -20 \rightarrow 21$

Table 1
Selected geometric parameters (Å, °) for (I).

F1*A*—C22*A*	1.359 (3)	F1*B*—C22*B*	1.353 (2)
O1*A*—C1*A*	1.216 (3)	O1*B*—C1*B*	1.227 (3)
O2*A*—C8*A*	1.232 (3)	O2*B*—C8*B*	1.239 (2)
N10*A*—C11*A*	1.401 (3)	N10*B*—C11*B*	1.399 (3)
N10*A*—C14*A*	1.401 (3)	N10*B*—C14*B*	1.402 (2)
N10*A*—C19*A*	1.449 (3)	N10*B*—C19*B*	1.453 (2)
C11*A*—N10*A*—C14*A*	118.98 (18)	C11*B*—N10*B*—C14*B*	120.13 (16)
C11*A*—N10*A*—C19*A*	120.14 (17)	C11*B*—N10*B*—C19*B*	119.04 (17)
C14*A*—N10*A*—C19*A*	120.64 (17)	C14*B*—N10*B*—C19*B*	119.81 (17)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.0465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.188$	$\Delta\rho_{max} = 0.72$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
10 547 reflections	
505 parameters	
H-atom parameters constrained	

Table 2
Hydrogen-bonding and short-contact geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C9A—H9A···O1A	0.98	2.51	2.850 (4)	100
C9A—H9A···O2A	0.98	2.52	2.856 (5)	100
C9B—H9B···O1B	0.98	2.51	2.828 (4)	98
C9B—H9B···O2B	0.98	2.53	2.819 (3)	97
C24A—H24A···O2A^{i}	0.93	2.50	3.247 (3)	138

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

Compound (II)

Crystal data

$C_{26}H_{32}FNO_2$	$D_x = 1.184$ Mg m^{-3}
$M_r = 409.53$	Cu $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
$a = 27.4540$ (10) Å	$\theta = 12.5$–$18.0°$
$b = 12.2738$ (10) Å	$\mu = 0.63$ mm^{-1}
$c = 16.2792$ (10) Å	$T = 293$ (2) K
$\beta = 123.118$ (10)°	Block, pale yellow
$V = 4594.4$ (5) Å^3	0.20 × 0.18 × 0.16 mm
$Z = 8$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 34$
$\omega/2\theta$ scans	$k = 0 \rightarrow 15$
4454 measured reflections	$l = -20 \rightarrow 16$
4374 independent reflections	3 standard reflections every 200 reflections
3087 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.053$	intensity decay: <1%
$\theta_{max} = 72.7°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.0465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.196$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$S = 1.10$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
4374 reflections	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
272 parameters	Extinction coefficient: 0.00046 (13)
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (II).

F1—C22	1.355 (2)	N10—C14	1.398 (2)
O1—C1	1.227 (2)	N10—C11	1.402 (2)
O2—C8	1.230 (2)	N10—C19	1.446 (2)
C14—N10—C11	119.65 (14)	C11—N10—C19	119.14 (14)
C14—N10—C19	120.07 (14)		

Table 4
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O1	0.98	2.46	2.802 (2)	100
C9—H9···O2	0.98	2.47	2.798 (4)	99
C5—H5A···O2^{ii}	0.97	2.53	3.494 (2)	171
C24—H24···O1^{iii}	0.93	2.56	3.423 (3)	155

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

Table 5
Puckering (Å) and asymmetry parameters (°) of the ring systems in (I) and (II).

Ring and molecule	Total puckering amplitude	Asymmetry parameters	Conformation
A, (I*a*)	0.395 (4)	ΔC_s(C3A) = 0.072 (2) ΔC_2(C3A—C2A) = 0.039 (1)	Half-chair/sofa
A, (I*b*)	0.482 (3)	ΔC_s(C3B) = 0.022 (1) ΔC_2(C3B—C2B) = 0.099 (1)	Half-chair/Sofa
A, (II)	0.485 (2)	ΔC_s(C3) = 0.039 (1) ΔC_2(C3—C2) = 0.089 (1)	Half-chair/Sofa
B, (I*a*)	0.370 (3)	ΔC_s(N10A) = 0.005 (1)	Sofa
B, (I*b*)	0.255 (3)	ΔC_s(N10B) = 0.007 (1)	Sofa
B, (II)	0.281 (2)	ΔC_s(N10) = 0.005 (1)	Sofa
C, (I*a*)	0.488 (2)	ΔC_s(C6A) = 0.049 (1) ΔC_2(C7A—C6A) = 0.076 (1)	Half-chair/Sofa
C, (I*b*)	0.469 (3)	ΔC_s(C6B) = 0.042 (2) ΔC_2(C7B—C6B) = 0.077 (1)	Half-chair/Sofa
C, (II)	0.477 (2)	ΔC_s(C6) = 0.062 (1) ΔC_2(C7—C6) = 0.067 (1)	Half-chair/Sofa

In both compounds, all H atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms, with C—H = 0.93–0.98 Å, and $U_{iso} = 1.5U_{eq}$ of the attached C atoms for methyl-H atoms and $1.2U_{eq}$ for other H atoms.

For compound (I), data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*. For compound (II), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1985). For both compounds, 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, 1983*b*, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1517). Services for accessing these data are described at the back of the journal.

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