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Two benzoylaminoacridinedione derivatives

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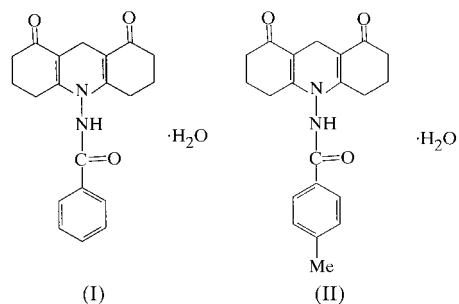Correspondence e-mail: crystal@giasmd01.vsnl.net.in

The title compounds, 10-benzoylamino-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione monohydrate, $C_{20}H_{20}N_2O_3 \cdot H_2O$, and 10-*p*-toluoylamino-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione monohydrate, $C_{21}H_{22}N_2O_3 \cdot H_2O$, consist of partially hydrogenated acridine moieties with one benzoylamino substituent on the central ring. The acridine moiety suffers considerable deviations from planarity. The central ring in the acridine moiety is a boat, while the outer rings adopt sofa conformations.

Comment

Aminoacridinyl derivatives have general uses in medicine, especially as antitumor agents, and have also been used as antibacterial agents for wound therapy (Acheson, 1956).

Acridines bind to DNA by intercalation (Lerman, 1961; Karle *et al.*, 1980; Nandi *et al.*, 1990; Reddy *et al.*, 1979; Sakore *et al.*, 1979; Peacocke & Skerrett, 1956). In addition to this, these compounds are said to possess antiamoebic (Prasad Krishna *et al.*, 1984), hypertensive, anti-inflammatory and anti-implantation (Asthana *et al.*, 1991) activities. The use of decahydroacridine-1,8-diones as photo-sensitizers is also well known (Timpe *et al.*, 1993). Acridinediones also act as laser dyes whose laser activity has been studied extensively (Murugan *et al.*, 1998). The present study of the title
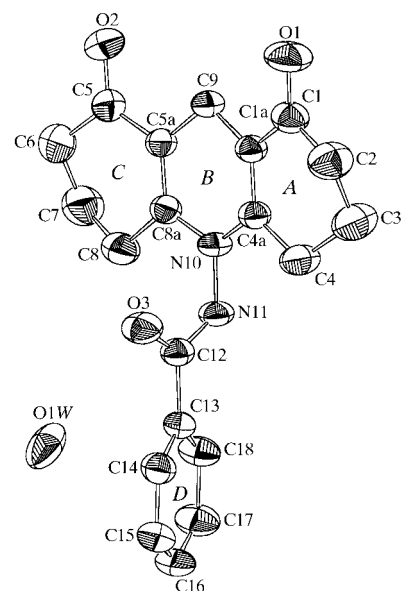

Figure 1
ORTEP (Zsolnai, 1997) diagram of (I) with ellipsoids at the 50% probability level.

compounds, (I) and (II), is part of a series of investigations on the crystal structures of acridine derivatives.

Perspective views of the title compounds, together with the atomic numbering schemes, are shown in Figs. 1 and 2. Owing to the π conjugation along C1a—C4a—N10—C8a—C5a, the puckering of the central *B* rings is quite small. The variations in the multiple bond characters in the central-ring bond lengths are in agreement with those of related acridine derivatives (Ganesh, Banumathi *et al.*, 1998; Sankaranarayanan *et al.*, 1998; Brito-Arias *et al.*, 1996; Selladurai *et al.*, 1989, 1990, 1998; Sivaraman *et al.*, 1994). The angles around atom N10 sum to 359.1 (1)° in (I) and 359.9 (2)° in (II), which are indi-
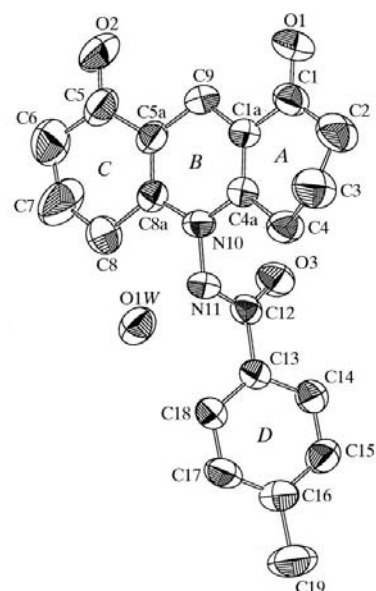

Figure 2
ORTEP (Zsolnai, 1997) diagram of (II) with ellipsoids at the 50% probability level.

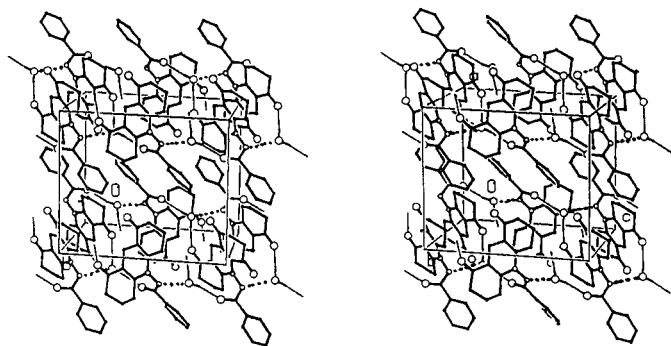**1109**

organic compounds

Figure 3
Packing stereodiagram of (I).

cative of sp^2 hybridization (Hempel *et al.*, 1979; Gunasekaran *et al.*, 1996). The acridine moiety is folded about the line passing through atoms C9 and N10, and the dihedral angle between the two halves is 6.4 (1)° in (I) and 12.4 (1)° in (II), and compares well with those values reported in related acridine derivatives (Ganesh, Velmurugan *et al.*, 1998; Ganesh, Banumathi *et al.*, 1998; Sankaranarayanan *et al.*, 1998; Clark *et al.*, 1986; Gunasekaran *et al.*, 1996). The dihedral angle between rings *A* and *C* is 4.6 (1)° in (I) and 14.9 (1)° in (II). The dihedral angle between rings *B* and *D* is 67.9 (1)° in (I) and 48.4 (1)° in (II).

The average C=O [1.233 (2) Å in (I) and 1.218 (3) Å in (II)] and N—N bond lengths [1.408 (2) Å in (I) and 1.395 (2) Å in (II)] agree well with several related structures (Allen *et al.*, 1987; Ganesh, Banumathi *et al.*, 1998; Ganesh, Velmurugan *et al.*, 1998; Gunasekaran *et al.*, 1996; Brito-Arias *et al.*, 1996).

The sofa (for rings *A* and *C*) and boat conformations (for ring *B*) are confirmed by the puckering amplitudes (Cremer & Pople, 1975): $Q = 0.409$ (3), 0.398 (3), 0.120 (2) Å, $\theta = 125.3$ (2), 53.8 (3), 81.1 (9)°, and $\varphi = -73.3$ (4), 105.1 (2), −58.0 (1)° for rings *A*, *C* and *B*, respectively, in (I), and $Q = 0.425$ (4), 0.234 (5), 0.132 (3) Å, $\theta = 55.1$ (3), 58.9 (7), 76.5 (1)°, and $\varphi = 113.1$ (1), 113.4 (1) and −67.9 (1)° for rings *A*, *C* and *B*, respectively, in (II).

Hydrogen bonds involving the water molecule for both (I) and (II) are shown in Figs. 3 and 4. Intermolecular O—H···O

hydrogen bonds are present in order to stabilize the crystal structures. The water molecules take part in O—H···O hydrogen-bond formation with acridinedione and benzoyl-amino, where the water molecule acts as a donor and the O1 and O2 atoms of acridinedione and O3 of the benzoylamino group act as acceptors. For compound (I), the hydrogen bonds formed are O*W*1···O2, O*W*1···O3 and O*W*1···N11; the same amide N11 atom forms an intermolecular hydrogen bond with the O atom of the water molecule. For compound (II), the hydrogen bonds formed are O1*W*···O1, O1*W*···O2 and an intermolecular N11—H11···O1*W* hydrogen bond.

Experimental

To a solution of 2,2′-methylenebis(cyclohexane-1,3-dione) (1.0 g, 4.2 mmol) and benzoic hydrazide (0.58 g, 4.2 mmol) in ethanol (40 ml), a catalytic amount of P_2O_5 was added and the resulting solution refluxed on a steam bath for 5 h. The reaction mixture was concentrated and poured onto ice; the yellow solid obtained was filtered, dried and recrystallized from a mixture of chloroform and ethanol (1:1) to afford compound (I); yield 1.25 g, 88.5% (m.p. 411–413 K). Compound (II) was prepared in a similar way to compound (I), replacing benzoic hydrazide with 4-methylbenzoic hydrazide (0.635 g, 4.2 mmol); yield 1.2 g, 81% (m.p. 501–503 K).

Compound (I)

Crystal data

$C_{20}H_{20}N_2O_3 \cdot H_2O$	$D_x = 1.279$ Mg m^{-3}
$M_r = 354.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 6167
$a = 11.4056$ (2) Å	reflections
$b = 12.25010$ (10) Å	$\theta = 1.79–28.31°$
$c = 13.1746$ (3) Å	$\mu = 0.090$ mm^{-1}
$\beta = 91.4970$ (10)°	$T = 293$ (2) K
$V = 1840.12$ (5) Å^3	Slab, yellow
$Z = 4$	$0.48 \times 0.40 \times 0.08$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	$R_{int} = 0.032$
	$\theta_{max} = 28.44°$
ω scans	$h = -15 \rightarrow 13$
12 199 measured reflections	$k = -15 \rightarrow 16$
4512 independent reflections	$l = -15 \rightarrow 17$
3066 reflections with $I > 2\sigma(I)$	Intensity decay: 1%

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

O1—C1	1.231 (2)	C5—C5a	1.449 (3)
O2—C5	1.242 (2)	C5a—C8a	1.369 (2)
O3—C12	1.226 (2)	C5a—C9	1.499 (3)
C1—C1a	1.465 (3)	C8—C8a	1.503 (3)
C1a—C4a	1.362 (2)	C8a—N10	1.392 (2)
C1a—C9	1.504 (3)	N10—N11	1.4075 (18)
C4a—N10	1.403 (2)	N11—C12	1.353 (2)
O1—C1—C1a	120.64 (19)	C8a—N10—C4a	121.74 (14)
O1—C1—C2	121.50 (19)	C8a—N10—N11	118.25 (14)
C1a—C4a—N10	119.89 (16)	C4a—N10—N11	119.15 (15)
N10—C4a—C4	116.30 (15)	C12—N11—N10	119.32 (14)
O2—C5—C5a	121.22 (19)	O3—C12—N11	121.73 (16)
O2—C5—C6	120.83 (19)	O3—C12—C13	123.07 (16)
C5a—C8a—N10	119.63 (16)	N11—C12—C13	115.20 (15)
N10—C8a—C8	116.45 (15)		

Figure 4
Packing stereodiagram of (II).

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N11—H11$\cdots$O1W^i	0.86	1.937	2.750 (2)	157
C16—H16$\cdots$O1^{ii}	0.93	2.593	3.180 (3)	122
C17—H17$\cdots$O1^{ii}	0.93	2.644	3.203 (3)	120
C18—H18$\cdots$O1W^i	0.93	2.705	3.407 (3)	133
O1W—H$WA\cdots$O2^{iii}	0.87	1.937	2.802 (3)	174
O1W—H$WB\cdots$O3^{iv}	0.88	2.012	2.864 (2)	164

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$+ 0.5302P]$
$wR(F^2) = 0.167$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.025$	$(\Delta/\sigma)_{max} < 0.001$
4512 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
243 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

$C_{21}H_{22}N_2O_3\cdot H_2O$	$D_x = 1.258$ Mg m^{-3}
$M_r = 368.42$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6666
$a = 23.2343$ (10) Å	reflections
$b = 13.8327$ (6) Å	$\theta = 1.89–28.34°$
$c = 16.3286$ (7) Å	$\mu = 0.088$ mm^{-1}
$\beta = 132.1400$ (10)°	$T = 293$ (2) K
$V = 3891.4$ (3) Å^3	Block, yellow
$Z = 8$	$0.48 \times 0.44 \times 0.36$ mm

Data collection

Siemens SMART CCD area-	$R_{int} = 0.031$
detector diffractometer	$\theta_{max} = 25.00°$
ω scans	$h = -27 \rightarrow 20$
10 281 measured reflections	$k = -14 \rightarrow 16$
3424 independent reflections	$l = -19 \rightarrow 19$
2634 reflections with $I > 2\sigma(I)$	Intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1225P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 2.3517P]$
$wR(F^2) = 0.190$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.945$	$(\Delta/\sigma)_{max} = 0.003$
3424 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H atoms: see text	

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

O1—C1	1.234 (3)	C5—C5a	1.450 (3)
O2—C5	1.231 (3)	C5a—C8a	1.347 (3)
O3—C12	1.219 (2)	C5a—C9	1.491 (3)
C1—C1a	1.453 (3)	C8—C8a	1.495 (3)
C1a—C4a	1.350 (3)	C8a—N10	1.390 (3)
C1a—C9	1.499 (3)	N10—N11	1.395 (2)
C4—C4a	1.503 (3)	N11—C12	1.364 (3)
C4a—N10	1.398 (3)		
O1—C1—C1a	119.2 (2)	C8a—N10—N11	119.41 (17)
O1—C1—C2	122.3 (2)	C8a—N10—C4a	122.43 (16)
C1a—C4a—N10	119.36 (19)	N11—N10—C4a	118.12 (16)
N10—C4a—C4	117.18 (17)	C12—N11—N10	118.22 (17)
O2—C5—C5a	120.3 (3)	O3—C12—N11	121.54 (19)
O2—C5—C6	120.8 (2)	O3—C12—C13	123.35 (19)
C5a—C8a—N10	119.38 (19)	N11—C12—C13	115.09 (16)
N10—C8a—C8	116.99 (19)		

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N11—H11$\cdots$O1W	0.86	2.001	2.789 (2)	152
C8—H8$A\cdots$O3^i	0.97	2.522	3.234 (1)	130
O1W—H$WB\cdots$O1^{ii}	0.93	1.828	2.730 (5)	162
O1W—H$WA\cdots$O2^{iii}	0.88	1.897	2.763 (3)	166

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

All H atoms, except the water H atoms, were included at calculated positions and refined using a riding model. The U_{iso} value for H atoms of the CH, NH and CH$_2$ or the CH$_3$ groups were taken as 1.2U_{eq} or 1.5U_{eq} of the carrier atoms, respectively. The water H atoms were found from difference Fourier syntheses and were refined isotropically.

For both compounds, 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); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1336). Services for accessing these data are described at the back of the journal.

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organic compounds

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