organic compounds

3,6-Bis(dimethylamino)-10-(10-iodo-decyl)acridinium iodide

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In the title compound, $C_{27}H_{39}IN_3^+ \cdot I^-$, the acridinium system shows the usual approximate mirror symmetry about the central $C \cdots N$ line, and the corresponding bond lengths and angles in the two halves agree within experimental error. The alkyl chain at the ring N atom is initially perpendicular to the ring plane and then bends sharply at the fourth C atom. Pairs of centrosymmetrically related cations overlap two of their rings and the dimethylamino groups are also partly involved in the overlap. Each I^- ion is involved in short-range interactions with two cations. These interactions give rise to a 14-membered cyclic structure, which involves pairs of cations and anions across an inversion centre.

Comment

Interest in acridine cationic dyes is connected to their ability to bind DNA, thus interfering with replication processes. As has been widely reported (Lerman, 1961; Karle *et al.*, 1980; Nandi *et al.*, 1990), the association of the dye with DNA occurs by intercalation of the planar moiety of the molecule between subsequent base pairs along the DNA chain, and it is also favoured by electrostatic interactions with phosphate groups. Moreover, the structural similarity to some antibiotics qualifies these dyes as useful models to study the interactions of drugs with receptors.

These dyes self-associate in aqueous solution through interactions of their π-electron systems, forming pairs or larger aggregates (Vitagliano, 1983; Costantino *et al.*, 1984; Markovits *et al.*, 1989). Crystallographic studies of these compounds are able to give a detailed description of the molecular arrangements in the solid state and provide valuable information on the fine geometry of self-association processes, such as the scheme and extent of overlap (Mattia *et al.*, 1984; Sivaraman *et al.*, 1996; Copp *et al.*, 2000; Puliti & Mattia, 2001). This information, in addition to spectroscopic and thermo-

dynamic data, is useful in modelling both self-aggregation in solution and intercalation phenomena with biological macromolecules. In continuing our studies of the structural characterization of the solid-state associations of acridine cationic dyes, we have carried out the crystallographic analysis of the title compound, (I), and the results are presented here.
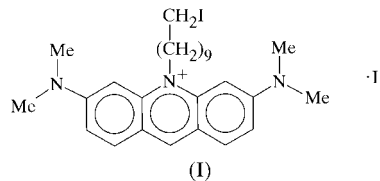

(I)

Fig. 1 shows a view of (I) approximately normal to the mean plane of the acridinium system. On average, all the geometrical parameters are in the expected ranges (Kuroda & Shinomiya, 1992; Lutz & Spek, 1998; Puliti & Mattia, 2001). In particular, the mean values of the C—C and C—N bonds in the acridinium moiety are 1.40 (2) and 1.3835 (17) Å, respectively. The C—C bond lengths of the alkyl chain are in the range 1.497–1.544 Å and the I2—C30 bond distance is 2.083 (13) Å. The acridinium system displays the usual mirror symmetry about the C9···N10 line (Jones & Neidle, 1975; Mattia *et al.*, 1984, 1995), and the corresponding bond lengths and angles in the two halves agree within experimental error (3σ).

The bonding geometry at the central N10 atom is planar and the sum of the valency angles subtended is 360.0 (9)°. Moreover, the C11—N10—C14 angle [121.7 (5)°] is larger than the adjacent intra-ring angles [N10—C11—C13 118.9 (6)° and N10—C14—C12 118.6 (6)°], as found in other pyridine structures substituted at N10 (Kuroda & Shinomiya, 1992; Lutz & Spek, 1998; Foces-Foces *et al.*, 1999; Puliti & Mattia, 2001). The tricyclic system is roughly planar, and the greatest atomic displacements pertain to atoms C6 and N10, which are
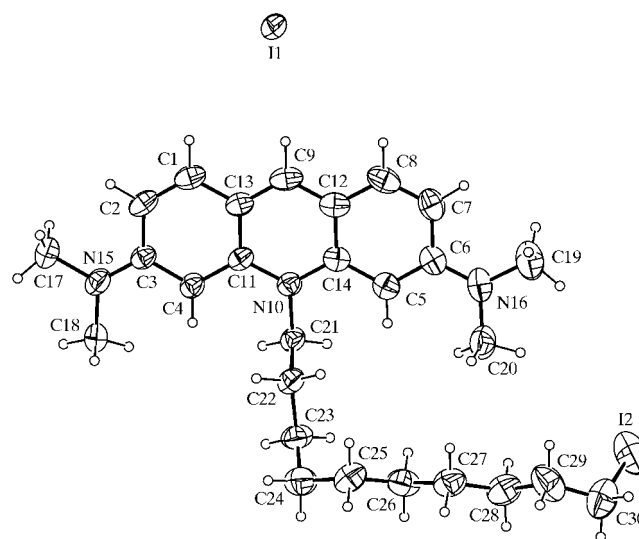

Figure 1
A view of (I) approximately on the mean plane of the acridine system, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

shifted by 0.068 (6) and 0.077 (5) Å, respectively, in opposite directions out of the best ring plane. On the whole, the edgewise profile of the acridine moiety appears slightly bent around the C9···N10 line.

The alkyl chain at N10 is initially perpendicular to the ring plane [C14—N10—C21—C22 88.9 (7)°] and then bends sharply at atom C24. The best planes through atoms C21/C22/C23/C24 and C24/C25–C30 are essentially normal to each other and form an angle of 98.1 (4)°.

The I$^-$ ion lies at a distance of 3.04 Å from H(C9) and 3.16 Å from H(C2)^i [symmetry code: (i) $-x, 1 - y, 1 - z$], and is 1.6235 (5) and 0.6890 (5) Å, respectively, out of the mean planes of the corresponding acridinium systems. The I$^-$···H distances are a little shorter than the sum of the accepted van der Waals radii for I (2.15 Å) and H (1.2 Å) (Whuler *et al.*, 1980). In addition, the H atoms are properly positioned to make stabilizing interactions between the I$^-$ anion and the activated atoms C9 and C2. These interactions produce a 14-membered cyclic structure, which involves pairs of cations and anions across a symmetry centre. The geometry of the C—H···I interactions, together with the symmetry codes of the donors, are given in Table 2.

A pair of cations, related by an inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, overlap their acridinium *A* and *B* rings at an interplanar distance of 3.51 Å. The dimethylamino groups are partly involved in the vertical overlap, whose extent is shown in Fig. 2 as a shaded region. Moreover, it is to be noted that each molecule of the pair related by the inversion centre at $(1\frac{1}{2},0)$ places the terminal part of the alkyl chain (C24–C30) edgewise over the partner acridine system; the three shortest distances from the best ring plane involve atoms C25, C27 and C29, and are in the range 3.75–3.79 Å.

The main features of the molecular packing are shown in Fig. 3. The shortest interaction between dimethylamino groups is C17···C17($-x, 2 - y, 1 - z$) 3.527 (8) Å. Regarding the iododecyl chains, all the intermolecular methylene distances are normal van der Waals contacts and the shortest I···I distance is I2···I2($3 - x, -y, -z$) of 4.1715 (16) Å.
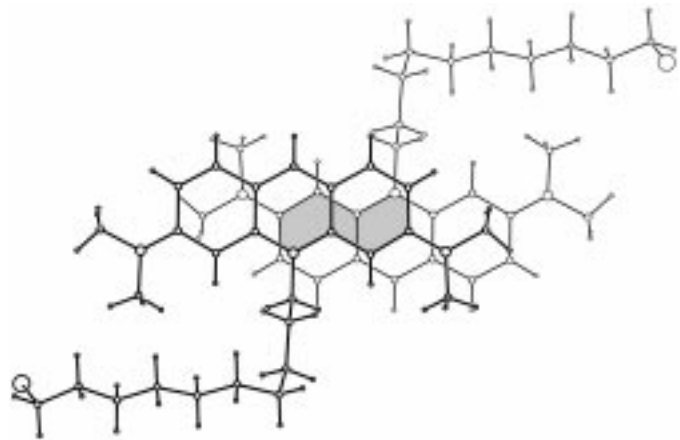

Figure 2
A pair of overlapping acridine cations in (I). The shading indicates the extent of the overlap.

The steric hindrance of the alkyl chain at the pyridine N10 atom does not prevent overlap of the aromatic rings, so that the stacking interactions play a prevailing role in stabilizing the crystalline environment, as it is found in most acridine structures. In comparison with the packing observed in the
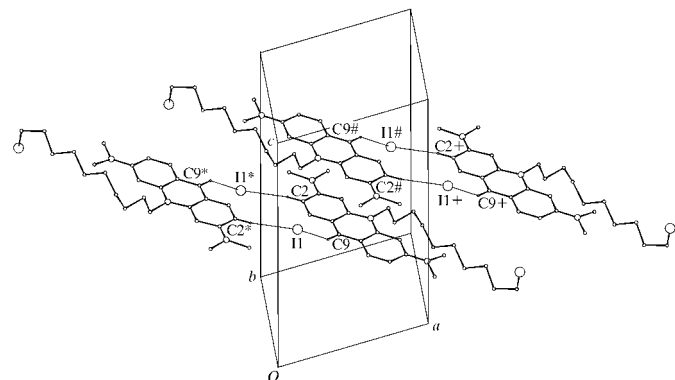

Figure 3
Part of the crystal structure of (I), showing the C—H···I interactions (drawn as thin lines), as well as the π–π overlap. Atoms marked with an asterisk (*), hash (#) or plus sign (+) are at the symmetry positions ($-x, 1 - y, 1 - z$), ($1 - x, 1 - y, 1 - z$) and ($1 + x, y, z$), respectively.

10-propylacridinium iodide crystal (Puliti & Mattia, 2001), the base overlap in the present structure is organized in pairs instead of infinite stacks. Moreover, the extent of the area of superposition is wider and the stacking interplanar distance (3.51 Å) is 0.12 Å shorter. This distance compares well with the average values observed in correlated structures without a substituent at the pyridine N atom (Mattia *et al.*, 1984, 1995; Sharma & Clearfield, 2000).

Experimental

Compound (I) was obtained as a secondary product during the synthetic process for obtaining bifunctional dyes ('dimer' molecules) formed by two acridinium moieties joined through a decyl chain. The method used was that described by Vitagliano *et al.* (1978). Single crystals of (I) were obtained by slow evaporation from ethanol.

Crystal data

$C_{27}H_{39}IN_3^+\cdot I^-$	$Z = 2$
$M_r = 659.41$	$D_x = 1.579$ Mg m^{-3}
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 10.1338$ (9) Å	Cell parameters from 24
$b = 11.996$ (3) Å	reflections
$c = 13.421$ (2) Å	$\theta = 20.5$–$24.5°$
$\alpha = 67.496$ (17)°	$\mu = 17.93$ mm^{-1}
$\beta = 76.903$ (11)°	$T = 298$ (2) K
$\gamma = 67.574$ (11)°	Needle, red
$V = 1387.0$ (5) Å^3	$0.18 \times 0.07 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4	3602 reflections with $I > 2\sigma(I)$
diffractometer	$\theta_{max} = 68°$
ω/θ scans, as suggested by	$h = 0 \rightarrow 12$
peak-shape analysis	$k = -13 \rightarrow 14$
Absorption correction: ψ scan	$l = -15 \rightarrow 16$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.281$, $T_{max} = 0.341$	every 300 reflections
5035 measured reflections	intensity decay: 2%
5035 independent reflections	

organic compounds

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.160$
$S = 1.09$
5035 reflections
293 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 2.5829P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Table 1
Selected bond and torsion angles (°).

C11—N10—C14	121.7 (5)	C18—N15—C17	115.9 (6)
C11—N10—C21	120.5 (5)	C6—N16—C19	124.8 (8)
C14—N10—C21	117.8 (5)	C6—N16—C20	120.3 (7)
C3—N15—C18	122.4 (5)	C19—N16—C20	114.2 (8)
C3—N15—C17	121.5 (6)		
C2—C3—N15—C18	177.5 (6)	C23—C24—C25—C26	−63.0 (11)
C7—C6—N16—C20	175.6 (7)	C24—C25—C26—C27	−176.1 (7)
C14—N10—C21—C22	88.9 (7)	C25—C26—C27—C28	177.6 (8)
N10—C21—C22—C23	−177.6 (6)	C26—C27—C28—C29	173.5 (8)
C21—C22—C23—C24	174.9 (7)	C27—C28—C29—C30	169.9 (9)
C22—C23—C24—C25	−63.9 (11)	C28—C29—C30—I2	64.0 (12)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H2$\cdots$I1^i	0.96	3.160	4.005 (5)	148
C9—H9$\cdots$I1	0.96	3.036	3.896 (7)	150

Symmetry code: (i) $-x, 1 - y, 1 - z$.

All H atoms were observed in difference Fourier maps and included in the final refinements as riding atoms, with $U_{iso}(H) = U_{eq}$(parent atom). Aromatic and alkyl H atoms were constrained to lie 0.96 and 1.00 Å, respectively, from their parent atoms. The H atoms of the methyl groups attached to the Nsp^2 atoms were refined as part of rigid groups, allowing rotation about the respective N—C bonds.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Enraf–Nonius, 1985); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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