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3,6-Bis(dimethylamino)-10-propylacridinium iodide

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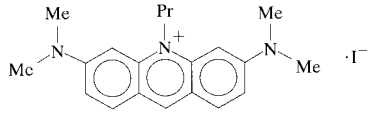
In the title compound, $C_{20}H_{26}N_3^+\cdot I^-$, the acridinium moiety shows mirror symmetry about the central C—N vector. The fused tricyclic system is only approximately planar and the geometry is affected by the presence of both dimethylamino groups and the propyl substitution at the central N atom. The propyl chain adopts an extended *trans* conformation and the plane through the chain C atoms is perpendicular to the mean plane through the rings. The I^- ion is involved in short-range hydrogen-bonding interactions with two centrosymmetrically related cations *via* three activated acridinium C atoms. Stacks of acridinium cations propagate through the crystal along the *c* direction. The ring overlap is partial, but the dimethylamino groups also participate in the stacking.

Comment

Cationic dyes such as acridine derivatives are of biological interest because of their ability to interact with genetic material, causing mutagenic effects. In particular, these planar chromophores bind to DNA by intercalation between subsequent base pairs (Lerman, 1961; Karle *et al.*, 1980; Nandi *et al.*, 1990), thereby interfering with the replication process. The DNA–dye association is also favoured by interactions between the cations and phosphate groups. It is well known that these dyes self-associate, both in aqueous solution and in the solid state, through interaction between the π electrons of their aromatic systems, showing different stacking modes and overlap extensions (Mattia *et al.*, 1984; Costantino *et al.*, 1984; Sivaraman *et al.*, 1994, 1996). Crystal structure determinations of acridine derivatives can therefore usefully increase our knowledge of the association modes, and also give information about the aggregation and intercalation mechanisms in solution. While the association phenomena in solution can be observed by many spectrophotometric techniques (absorption and fluorescence spectra, NMR *etc.*) or thermodynamic determinations, these methods permit only a qualitative interpretation of the phenomena, without differentiating between the alternative association models. Furthermore, in the biomedical field, their structural similarity with some antibiotics makes these dyes useful models for the study of the binding mechanisms and effectiveness of therapeutic agents. For these reasons, the structural analysis of the title compound, (I), was undertaken.



(I)

Fig. 1 shows a view of (I) approximately normal to the ring plane. All molecular geometry parameters lie within expected ranges (Kuroda & Shinomiya, 1992; Lutz & Spek, 1998). The acridinium system shows 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 to within 2σ for distances and to within 3σ for angles.

The bonding geometry at N10 is planar and the sum of the subtended angles is 360.0 (5)°. The larger value for C11—N10—C14 [122.3 (3)°] compared with N10—C11—C13 [118.4 (4)°] and N10—C14—C12 [118.3 (3)°] is typical of other pyridine systems with substituted nitrogen (Kuroda & Shinomiya, 1992; Lutz & Spek, 1998; Foces-Foces *et al.*, 1999, and references therein). By comparison with related compounds lacking substituents at C3 and C6 (Baker *et al.*, 1999), it is clear that the presence of the dimethylamino groups causes variations in the distances within the rings: single-bond character is slightly but significantly increased for C2—C3 and C3—C4, and in the equivalent pair C6—C7 and C5—C6 (Table 1), while there is a shortening of C1—C2 and C4—C11, and of the corresponding C7—C8 and C5—C14 bonds, indicative of increased double-bond character.

Overall, the fused tricyclic system is somewhat puckered, but the two outer rings are each individually planar within experimental error and their best planes form a dihedral angle of 4.1 (8)°. The central ring is, by contrast, only approximately planar, with atoms N10 and C14 showing the greatest deviations from the ring plane, at distances of 0.029 (3) and −0.025 (4) Å, respectively. The N10-propyl chain adopts an extended *trans* conformation and the plane through the chain C atoms is perpendicular to that of the ring system [dihedral angle 92.4 (3)°]. The I^- ion is approximately coplanar with the acridinium system (displaced by only 0.132 Å) and lies within 3.1 Å of the H atoms bonded to the acridinium C7, $C8^i$ and $C9^i$ atoms [symmetry code: (i) $-x, -y, -z$]. Such distances are within the sum of the accepted van der Waals radii for H (1.2 Å) and I (2.15 Å) (Whuler *et al.*, 1980). Moreover, these H atoms are well positioned to make C—H···I interactions between the I^- anion and these activated C atoms. The pertinent geometry, and the symmetry codes of the donors, are given in Table 2.

Acridinium cations related by glide operations partially overlap to form stacks extending along the *c* direction. Within each stack, the superposition involves different outer rings of subsequent acridinium units, with a perpendicular separation

of 3.63 Å. Furthermore, the central rings partially overlap with the dimethylamino groups which thereby also contribute to the stacked structure (Fig. 2). The crystal packing is characterized, along the *b* direction, by an alternation of stacks of acridinium cations having $b \sim \frac{1}{4}$, and regions near $b = 0$ containing both I^- anions and propyl chains, the latter facing each other across inversion centres at distances of 4.188 (8) Å. The shortest I···I distance is 5.8189 (4) Å.

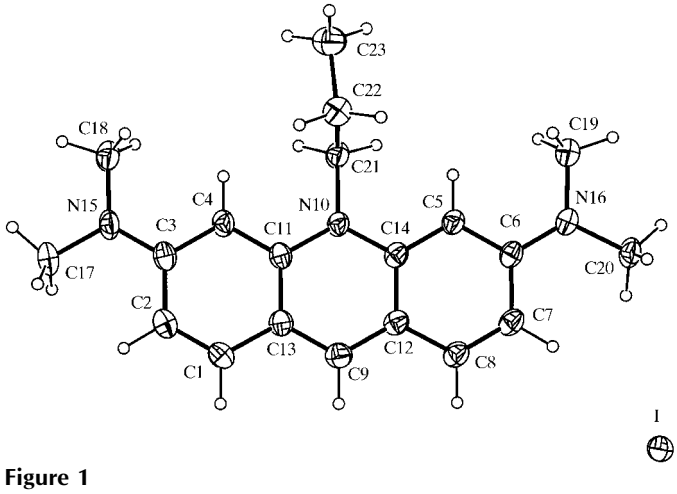


Figure 1
A perspective view of the asymmetric unit of (I) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

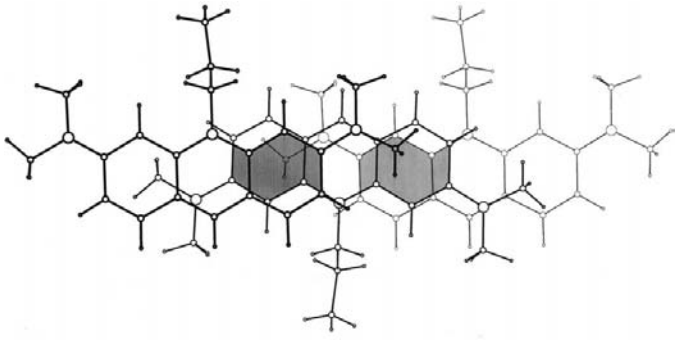


Figure 2
The stacking of three subsequent acridinium bases. The shading indicates the extent of the overlap.

As in the structures of many acridine compounds, the stacking interactions in (I) have a prevailing role in stabilizing the crystalline environment, the size and geometry of overlaps being affected by the substituent and counter-ion in each structure. In this case, the overlap is less extensive than in other structures, where the stacking involves only dimers (Mattia *et al.*, 1984; Kuroda & Shinomiya, 1992). Furthermore, the stacking distance here is appreciably longer, by about 0.15 Å, than the average value in related unsubstituted structures. Both these features can be attributed to the bulkiness of the dimethylamino groups involved in the stacking, the presence of the N10-propyl chain and, finally, the lack of specific interactions between the iodide and N10 atoms.

Experimental

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

Crystal data

$C_{20}H_{26}N_3^+\cdot I^-$
$M_r = 435.35$
Monoclinic, $P2_1/c$
$a = 11.002$ (6) Å
$b = 17.208$ (3) Å
$c = 11.157$ (7) Å
$\beta = 114.86$ (2)°
$V = 1916.5$ (17) Å^3
$Z = 4$
$D_x = 1.509$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20$–25°
$\mu = 13.16$ mm^{-1}
$T = 293$ K
Rectangular prism, red
0.33 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans, as suggested by peak-shape analysis
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.594$, $T_{max} = 0.999$
3933 measured reflections
3933 independent reflections
3493 reflections with $I > 2.5\sigma(I)$
$\theta_{max} = 74.9°$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 13$
4 standard reflections
frequency: 300 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.043$
$S = 0.96$
3493 reflections
221 parameters
H-atom treatment: see below
$w = 1/[\sigma^2(F_o) + (0.012F_o)^2 + 1.3]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.351 (6)	C7—C8	1.345 (5)
C1—C13	1.421 (5)	C8—C12	1.423 (5)
C2—C3	1.421 (7)	C9—C12	1.382 (5)
C3—C4	1.406 (5)	C9—C13	1.388 (5)
C4—C11	1.391 (5)	N10—C11	1.391 (4)
C5—C6	1.403 (5)	N10—C14	1.386 (5)
C5—C14	1.389 (5)	C11—C13	1.419 (6)
C6—C7	1.425 (6)	C12—C14	1.427 (6)
C11—N10—C14	122.3 (3)	C17—N15—C18	117.4 (4)
C11—N10—C21	118.7 (3)	C6—N16—C19	121.0 (4)
C14—N10—C21	119.1 (3)	C6—N16—C20	122.9 (3)
N10—C11—C13	118.4 (4)	C19—N16—C20	115.8 (4)
N10—C14—C12	118.3 (3)	N10—C21—C22	111.9 (4)
C3—N15—C17	121.5 (3)	C21—C22—C23	111.7 (4)
C3—N15—C18	121.1 (4)		
C2—C3—N15—C18	176.3 (4)	C11—N10—C21—C22	89.9 (5)
C5—C6—N16—C20	177.7 (4)	N10—C21—C22—C23	−174.0 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···I	1.00	3.10	4.077 (4)	167
C8—H8···I^{i}	1.00	3.08	3.977 (4)	150
C9—H9···I^{i}	1.00	3.10	3.991 (4)	149

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

All H atoms were clearly observed in difference Fourier maps and included in the final refinements with expected geometry and with U_{iso}(H) = U_{eq}(parent atom). Aromatic and alkyl H atoms were constrained to lie 1.00 and 1.02 Å, respectively, from their parent atoms. The H atoms of the methyl groups attached to Nsp^2 atoms were refined as parts of rigid groups allowed to rotate about the local N—C bond.

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: *SDP*; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1459). Services for accessing these data are described at the back of the journal.

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