2,6-Diiodophenyl acridine-9-carboxylate

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In the orthorhombic crystalline phase of the title compound, $C_{20}H_{11}I_2NO_2$, all the benzene rings are parallel, whereas the acridine systems are either parallel or perpendicular to each other; this generates a herring-bone pattern. The acridine systems and benzene rings are inclined at an angle of 45.5 (1)° to each other, and the acridine systems and carboxylate groups are inclined at an angle of 54.2 (1)°. Oppositely oriented consecutive molecules, with π–π interactions between their acridine systems and I$\cdots$I and I$\cdots$N contacts, are aligned in stacks along the a axis. These stacks, interacting through π–π contacts between benzene rings, are arranged in layers.

Comment

Phenyl acridine-9-carboxylates are the precursors of chemiluminescent indicators and chemiluminogenic fragments of chemiluminescent labels commonly applied in immuno-assay tests (Weeks *et al.*, 1986; Rongen *et al.*, 1994; Razawi & McCapra, 2000a,b). Such chemiluminogens are readily oxidized by H_2O_2, persulfates, peroxides and other oxidants (the phenyl fragment is removed) to electronically excited 9-acridinones (Dodeigne *et al.*, 2000; Razawi & McCapra, 2000a,b), which are efficient light emitters (Boużyk *et al.*, 2003). Since oxidation takes place in alkaline media, side reactions leading to non-excited 9-acridinones always occur (Rak *et al.*, 1999). These unwanted reactions lower the efficiency of chemiluminescence and reduce the stability of the chemiluminogens. There has been a sustained research effort to find chemiluminogens able to participate in the oxidation reaction but which are much more resistant to hydrolysis.

(I)
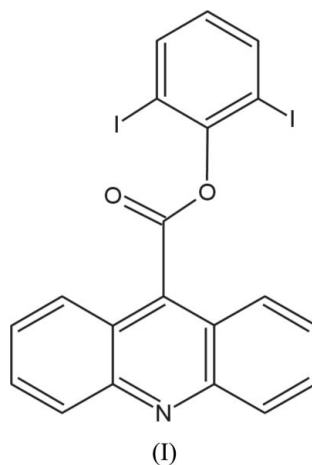
In a continuation of the search for new, analytically useful chemiluminogens, we prepared diiodophenyl acridine-9-carboxylate, (I), in order to find out how the presence of the I
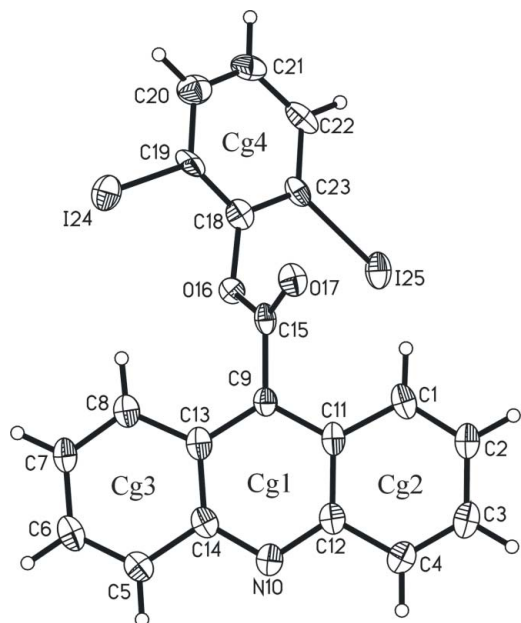
doi:10.1107/S1600536805038729

Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.
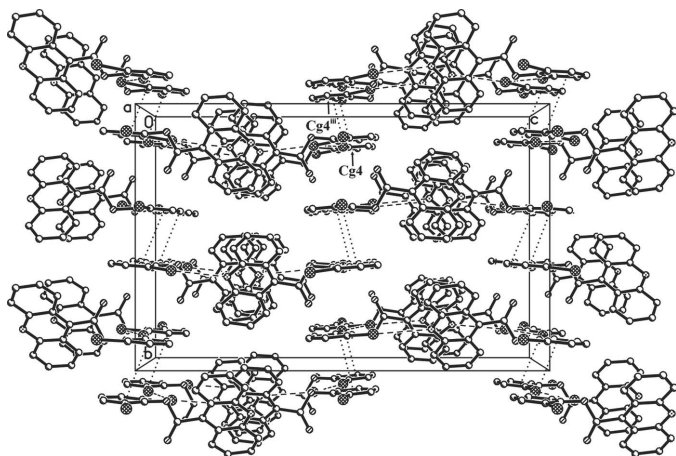

Figure 2
The arrangement of the molecules in the crystal structure, viewed along the *a* axis. The π–π ($Cg4\cdots Cg4$) interactions are represented by dotted lines [symmetry codes: (iii) $1 - x, -y, 1 - z$]. H atoms have been omitted.

atoms in phenyl substituents affects the stability and properties of this group of compounds. Together with our recent publications on the crystallography of dihalophenyl acridine-9-carboxylates (Sikorski *et al.*, 2005, 2005*a*,*b*,*c*), this paper provides data for comparison of the influence of halogens on the features of these compounds and extends the prospects for finding chemiluminogens with interesting analytical applications.

Table 1 gives selected parameters characterizing the geometries of the central acridine ring, the carboxylate fragment and the C—I bond lengths. These are typical of acridine-based derivatives.

With respective average deviations from planarity of 0.02 (2) and 0.02 (4) Å, the acridine and benzene ring systems
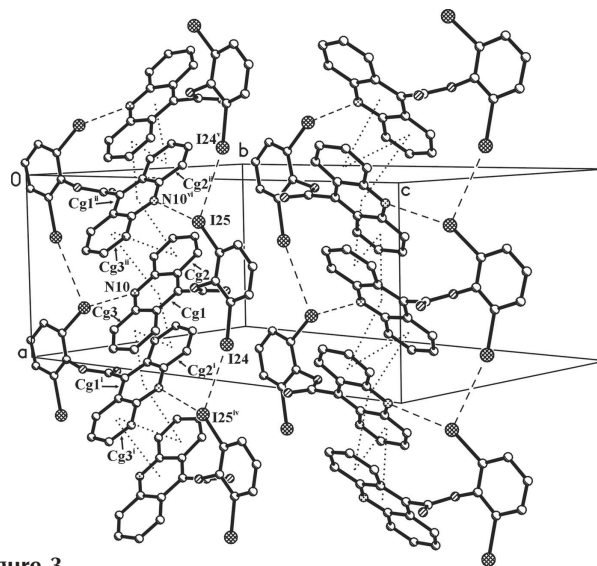

Figure 3
The arrangement of the molecules in the crystal structure, viewed in an oblique direction. The π–π stacking interactions are represented by dotted lines [symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$], and I$\cdots$I and N$\cdots$I contacts by dashed lines [symmetry codes: (iv) $1 + x, y, z$; (v) $-1 + x, y, z$]. H atoms have been omitted.

in (I) are oriented at 45.5 (1)° to each other (Fig. 1). The carboxylate group is twisted at an angle of 54.2 (1)° relative to the acridine skeleton.

Oppositely oriented consecutive molecules of (I) are aligned in stacks along the *a* axis (Fig. 2), in which the 6-membered rings of the acridine systems are engaged in π–π interactions (Fig. 3 and Table 2), all the iodine atoms in I$\cdots$I contacts, and half of the I atoms in N$\cdots$I contacts (Fig. 3 and Table 3). Alternately oriented stacks, interacting *via* π–π contacts between the benzene rings, are arranged in folded layers (a saw-like pattern) (Fig. 2). Dispersive interactions between the interlocking and folded layers stabilize the crystal structure (Fig. 2). Acridine systems in adjacent stacks within a given layer are oriented parallel, whereas in neighbouring stacks of adjacent layers they are perpendicular, giving a herring-bone pattern.

Experimental

Commercially available acridine-9-carboxylic acid was heated with a fivefold excess of thionyl chloride (370 K for 3.5 h) to obtain the acid chloride. 2,6-Diiodophenol was prepared from 2,6-diiodo-4-nitro-phenol by reduction with $Na_2S_2O_3$ in an alkaline medium and then by the reaction of the product (2,6-diiodo-4-aminophenol) with $NaNO_2$ in acidic solution (Woollett *et al.*, 1937). Crude 2,6-diiodophenol was purified chromatographically [SiO$_2$, cyclohexane/ethyl acetate (1/1 *v/v*); yield 45%; m.p. = 340–341 K]. The title compound was synthesized by the reaction of the acid chloride with an equimolar amount of 2,6-diiodophenol (Sato, 1996). The synthesis was carried out in dichloromethane in the presence of a fourfold molar excess of triethylamine and catalytic amounts of 4-(*N*,*N*-dimethyl-amino)pyridine (room temperature, 36 h). The crude product (yield 60%) was purified chromatographically [SiO$_2$, cyclohexane/ethyl acetate (3/2 *v/v*)]. Yellow crystals suitable for X-ray investigation were grown from cyclohexane (m.p. = 448–449 K).

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

C9—C11	1.404 (6)	C15—O17	1.200 (5)
C9—C15	1.488 (6)	O16—C18	1.399 (6)
N10—C12	1.353 (6)	C19—I24	2.095 (5)
C15—O16	1.375 (5)	C23—I25	2.107 (5)
C9—C15—O17	126.3 (4)	C9—C15—O16	111.0 (4)
C11—C9—C15—O17	−49.6 (6)	C15—O16—C18—C19	−89.1 (5)

Table 2
π–π interactions (Å, °) in (I). Cg represents the centroids of the rings, as follows: Cg1 ring C9/C11/C12/N10/C14/C13, Cg2 ring C1/C2/C3/C4/C12/C11, Cg3 ring C5/C6/C7/C8/C13/C14 and Cg4 ring C18/C19/C20/C21/C22/C23 (Fig. 1).

CgI	CgJ	$Cg\cdots Cg$	Dihedral angle	Interplanar dist.	Offset
1	2^i	3.522 (3)	3.5	3.243 (3)	1.374 (3)
1	3^{ii}	3.725 (3)	2.3	3.312 (3)	1.705 (3)
2	1^{ii}	3.522 (3)	3.5	3.319 (3)	1.178 (3)
2	3^{ii}	3.796 (3)	2.6	3.322 (3)	1.837 (3)
3	1^i	3.725 (2)	2.3	3.290 (3)	1.747 (3)
3	2^i	3.797 (3)	2.6	3.279 (3)	1.915 (3)
4	4^{iii}	3.748 (3)	0.0	3.531 (3)	1.257 (3)

Notes: $Cg\cdots Cg$ is the distance between ring centroids. The dihedral angle is that between the planes of the rings CgI and CgJ. The interplanar distance is the perpendicular distance of CgI from ring J. The offset is the lateral displacement of ring I relative to ring J. Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$; (iii) $1 - x, -y, 1 - z$.

Table 3
$I\cdots I$ and $N\cdots I$ contacts (Å, °) in (I).

X	I	J	$I\cdots J$	$X-I\cdots J$
C19	I24	I25^{iv}	4.029 (5)	162.8 (2)
C23	I25	I24^v	4.029 (5)	103.3 (2)
C23	I25	N10^{ii}	3.593 (4)	153.7 (2)

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

All H atoms in (I) were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The largest residual electron-density peak lies 1.09 Å from atom I24.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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