

## 2,6-Dibromophenyl acridine-9-carboxylate

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## Key indicators

Single-crystal X-ray study

T = 290 K

Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$ 

R factor = 0.028

wR factor = 0.081

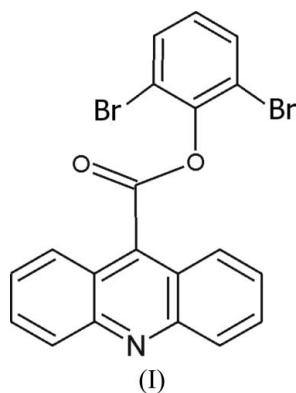
Data-to-parameter ratio = 12.8

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

Adjacent molecules of the title compound,  $\text{C}_{20}\text{H}_{11}\text{Br}_2\text{NO}_2$ , are oriented either parallel or antiparallel; in the latter case, there are four intermolecular  $\pi-\pi$  interactions between acridine rings. The acridine and benzene ring systems are inclined at an angle of  $41.2(2)^\circ$  to each other. There is also a short intermolecular  $\text{Br}\cdots\text{Br}$  contact.

## Comment

Phenyl acridine-9-carboxylates have become interesting chemiluminescent agents, since they can be oxidized by  $\text{H}_2\text{O}_2$ , persulfates, peroxides or other oxidants to electronically excited 9-acridinones (Dodeigne *et al.*, 2000; Razawi & McCapra, 2000), which are known to be efficient light emitters (Bouzyk *et al.*, 2003). For this reason, these compounds are widely applied as chemiluminescent indicators, or fragments of chemiluminescent labels, in immunological, medical, environmental and biochemical analyses (Dodeigne *et al.*, 2000). Continuing the search for new, analytically useful chemiluminogens, we synthesized dibromophenyl acridine-9-carboxylate, (I), in order to find out how the presence of the Br atoms affects the stability and chemiluminogenic properties of this group of compounds. This paper, together with our earlier publications on the crystallography of phenyl acridine-9-carboxylates (Meszko *et al.*, 2002; Sikorski *et al.*, 2005a,b), thus extends the prospects of finding further chemiluminogens with interesting practical applications.



Bond lengths and angles may be regarded as typical for acridine-based derivatives (Table 1).

The acridine and benzene ring systems are planar, with average deviations of  $0.012(3)$  and  $0.005(3) \text{ \AA}$ , respectively. The least-squares planes (defined by all non-H atoms) of the acridine and benzene moieties are inclined at an angle of  $41.2(2)^\circ$  to each other (Fig. 1).

The angle between the least-squares planes of the acridine ring system and the carboxyl group, defined by atoms C15,

Received 26 May 2005

Accepted 26 August 2005

Online 7 September 2005

O16 and O17, is 51.0 (3)°. Adjacent molecules are oriented either parallel or antiparallel. In the latter case, there are four intermolecular  $\pi$ - $\pi$  interactions involving the acridine rings (Fig. 2 and Table 2). In addition, there is a short intermolecular Br  $\cdots$  Br contact [Br24  $\cdots$  Br24(2 - x, -1 - y, 1 - z) = 3.54 (1) Å].

## Experimental

The title compound was synthesized by heating commercially available acridine-9-carboxylic acid with a fivefold excess of thionyl chloride (370 K for 3.5 h). The product of this reaction, the acid chloride, was reacted with an equimolar amount of 2,6-dibromophenol (Sato, 1996). The synthesis was carried out in dichloromethane in the presence of triethylamine (fourfold molar excess relative to the acid chloride) and catalytic amounts of 4-(*N,N*-dimethylamino)pyridine. The crude product (yield 90%) was purified chromatographically (SiO<sub>2</sub>, *n*-hexane/ethyl acetate, 3:2 *v/v*). Elemental analysis (% found/calculated): C 51.9/52.5, H 2.3/2.4, N 3.0/3.1. Yellow crystals suitable for X-ray analysis were grown from cyclohexane (m.p. 428–429 K).

### Crystal data

C<sub>20</sub>H<sub>11</sub>Br<sub>2</sub>NO<sub>2</sub>  
*M<sub>r</sub>* = 457.12  
 Triclinic, *P* $\bar{1}$   
*a* = 9.385 (2) Å  
*b* = 9.840 (2) Å  
*c* = 11.246 (2) Å  
 $\alpha$  = 66.22 (3)°  
 $\beta$  = 77.23 (3)°  
 $\gamma$  = 61.85 (3)°  
*V* = 837.4 (4) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.813 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 50 reflections  
 $\theta$  = 2.5–25.0°  
 $\mu$  = 4.85 mm<sup>-1</sup>  
*T* = 290 (2) K  
 Prism, yellow  
 0.5 × 0.4 × 0.3 mm

### Data collection

Kuma KM-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.112, *T<sub>max</sub>* = 0.233  
 3074 measured reflections  
 2909 independent reflections  
 1803 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.034  
 $\theta_{\max}$  = 25.0°  
*h* = -10 → 11  
*k* = -10 → 10  
*l* = 0 → 13  
 3 standard reflections  
 every 200 reflections  
 intensity decay: 0.4%

### Refinement

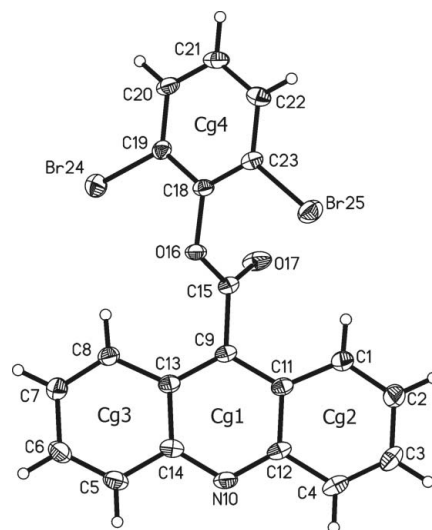
Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.028  
*wR*(*F*<sup>2</sup>) = 0.081  
*S* = 0.85  
 2909 reflections  
 227 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0039 (11)

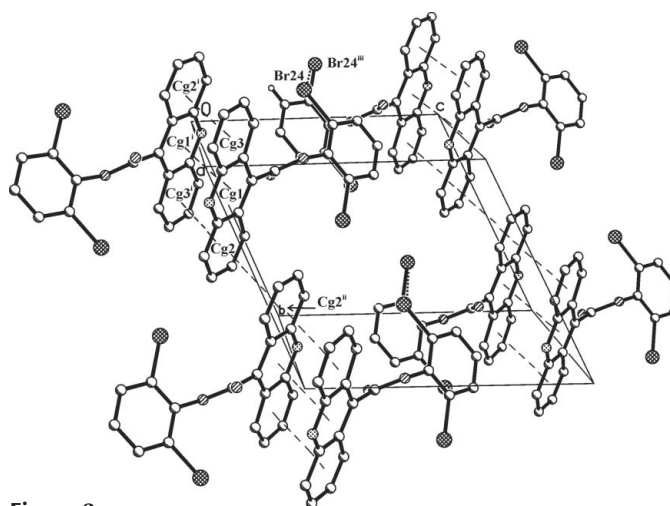
**Table 1**

Selected geometric parameters (Å, °).

C9–C11	1.401 (5)	C15–O17	1.182 (4)
C9–C15	1.493 (4)	O16–C18	1.393 (3)
N10–C12	1.339 (5)	C18–C19	1.382 (5)
C15–O16	1.369 (4)	C19–Br24	1.881 (3)
C9–C15–O16	111.0 (3)	C15–O16–C18	116.1 (2)
C9–C15–O17	126.6 (3)	O16–C15–O17	122.4 (3)
C9–C15–O16–C18	169.8 (3)	C15–O16–C18–C19	95.5 (3)
C11–C9–C15–O17	48.4 (5)	O16–C18–C19–Br24	-3.6 (4)



**Figure 1**  
 The molecular structure of the title compound, showing the atom-labelling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.



**Figure 2**

The arrangement of the molecules of the title compound in the unit cell, viewed approximately along the *a* axis. The  $\pi$ - $\pi$  interactions are represented by dashed lines [symmetry codes: (i) 2 - *x*, 1 - *y*, -*z*; (ii) 2 - *x*, -*y*, -*z*] and Br  $\cdots$  Br contacts by dotted lines [symmetry code: (iii) 2 - *x*, -1 - *y*, 1 - *z*]. H atoms have been omitted.

**Table 2**

$\pi$ - $\pi$  interactions (Å, °) in the title compound.

<i>CgI</i>	<i>CgJ</i>	<i>Cg</i> $\cdots$ <i>Cg</i>	Dihedral angle	Interplanar dist.	Offset
1	1 <sup>i</sup>	3.880 (2)	0.0	3.590 (3)	1.472 (2)
2	2 <sup>ii</sup>	3.766 (2)	0.0	3.491 (3)	1.413 (2)
2	3 <sup>i</sup>	3.890 (2)	2.0	3.479 (3)	1.740 (2)
3	2 <sup>i</sup>	3.890 (2)	2.0	3.530 (3)	1.634 (2)

Symmetry codes: (i) 2 - *x*, 1 - *y*, -*z*; (ii) 2 - *x*, -*y*, -*z*. Notes: *Cg* represents the centre of gravity of the rings, as follows: *Cg*1, ring C9/C11/C12/N10/C14/C13; *Cg*2, ring C1/C2/C3/C4/C12/C11; *Cg*3, ring C5/C6/C7/C8/C13/C14. *Cg*  $\cdots$  *Cg* is the distance between ring centroids. The dihedral angle is that between the planes of *CgI* and *CgJ*. The interplanar distance is the perpendicular distance of *CgI* from ring *J*. Offset is the perpendicular distance of ring *I* from ring *J*.

All H atoms were positioned geometrically and refined using a riding model, with C–H distances of 0.93 Å and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

Data collection: *KM-4 Software* (Kuma, 1989); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; 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).

In 2002–2005 this study was financed from State Funds for Scientific Research [grant No. 4 T09A 123 23, contract No. 0674/T09/2002/23 of the Polish State Committee for Scientific Research (KBN)].

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