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# 2-Methylphenyl acridine-9-carboxylate

**Artur Sikorski,[a] Karol Krzymiński,[a] Agata Białońska,[b] Tadeusz Lis[b] and Jerzy Błażejowski[a]***

[a]University of Gdańsk, Faculty of Chemistry, J. Sobieskiego 18, 80-952 Gdańsk, Poland, and [b]University of Wrocław, Faculty of Chemistry, F. Joliot-Curie 14, 50-383 Wrocław, Poland

Correspondence e-mail: bla@chem.univ.gda.pl

**Key indicators**

Single-crystal X-ray study
$T$ = 100 K
Mean $\sigma$(C–C) = 0.007 Å
$R$ factor = 0.067
$wR$ factor = 0.192
Data-to-parameter ratio = 11.7

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

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In the monoclinic crystalline phase, the molecules of the title compound, $C_{21}H_{15}NO_2$, form columns extending along the [001] direction. The crystals are stabilized by $\pi$–$\pi$ stacking interactions, formed between acridine systems, and C—H$\cdots\pi$ hydrogen-bond contacts, in which benzene rings are involved. The layers, resulting in the C—H$\cdots\pi$ hydrogen-bond contacts, formed between acridine H atoms and benzene rings of neighboring columns, are parallel to the (100) plane. C—H$\cdots$N hydrogen bonds between layers stabilize the crystal structure. All the acridine rings are parallel in the crystal structure, while the benzene rings are either parallel or inclined at 52.8 (2)°. The acridine systems and benzene rings in the molecules are inclined at 30.0 (2)° to each other, and the acridine systems and carboxylate groups at 58.0 (3)°.

## Comment

Phenyl esters of acridine-9-carboxylic acids are precursors of practically important chemiluminescent indicators and the chemiluminogenic fragments of chemiluminescent labels (Dodeigne *et al.*, 2000; Zomer & Jacquemijns, 2001). This is because 9-carboxy-10-methylacridinium phenyl esters react efficiently with hydrogen peroxide in alkaline media, producing electronically excited light-emitting 10-methyl-9-acridinones (Rak *et al.*, 1999). The intensity of the emitted light is related directly to the concentration of the entity assayed; this is the foundation for the analytical application of chemiluminescence. This phenomenon is utilized in quantitative assays of macromolecules present in living matter, *e.g.* in immunological, medical, environmental and biochemical analyses (Kaltenbach & Arnold, 1992; Pringle, 1999; Dodeigne *et al.*, 2000; Smith *et al.*, 2000; Zomer & Jacquemijns, 2001; Kricka, 2003; Roda *et al.*, 2003). However, the use of acridinium esters as chemiluminescent indicators or labels entails certain disadvantages. These compounds are not very stable since, in parallel with oxidation, they fairly readily undergo hydrolysis, which leads to non-emitting entities (Rak *et al.*, 1999; Razawi & McCapra, 2000*a*,*b*). There has been a long search for 9-carboxy-10-methylacridinium phenyl esters susceptible to oxidation but resistant to hydrolysis. Since the phenyl fragment is removed during the oxidation of these compounds, it has been hypothesized that the phenyl ring substituents exert the greatest influence on the stability of 9-carboxy-10-methylacridinium phenyl esters and their ability to chemiluminescence (Sato, 1996; Rak *et al.*, 1999). Despite the long interest shown in this group of compounds, there are only two publications (by our own research team) on the crystallography of alkylphenyl-9-carboxylates (Meszko *et al.*, 2002; Sikorski *et al.*, 2005). It is thus important to extend investigations to further representatives of this group, especially in

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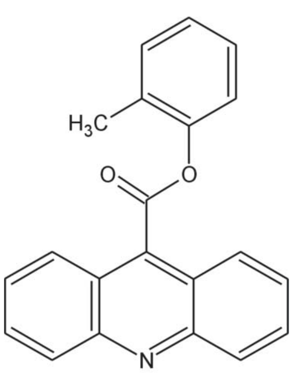
view of the fact that information on the structure, crystal packing and other features may help in the design of hydrolysis-resistant compounds able to react efficiently with oxidizing agents to produce light. This paper presents the crystal structure of phenyl acridine-9-carboxylate methyl-substituted in the phenyl group.



(I)

Table 1 gives parameters characterizing the geometries of the central acridine ring and the ester group. These are typical of acridine-based derivatives (Hempel *et al.*, 1979; Meszko *et al.*, 2002; Mrozek *et al.*, 2002; Sikorski *et al.*, 2005).

With average deviations from planarity of 0.011 and 0.008 Å, the acridine and benzene ring systems in (I) are oriented at 30.0 (2)° to each other (Fig. 1). The carboxylate group is twisted at an angle of 58.0 (3)° relative to the acridine skeleton. All the acridine rings are parallel in the crystal structure and the benzene rings are either parallel or inclined to each other at 52.8 (2)° (Fig. 2). $\pi$–$\pi$ stacking interactions are formed between acridine rings, and C—H$\cdots\pi$ hydrogen-bond

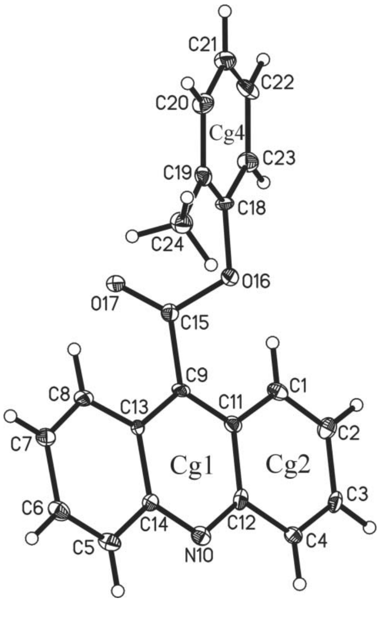


**Figure 1**
The molecular structure of (I), showing the atom-labeling scheme and 25% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

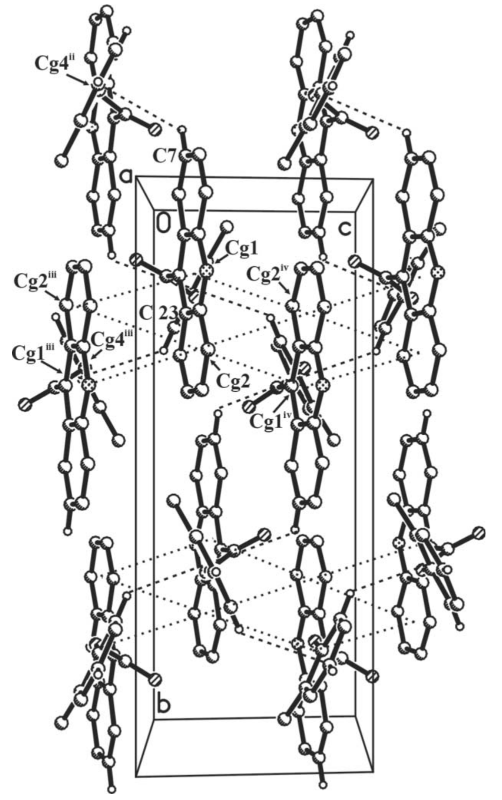


**Figure 2**
The arrangement of the molecules of (I) in the crystal phase, viewed along the [100] direction. The C–H$\cdots\pi$ contacts are represented by dashed lines [symmetry codes: (ii) $1 - x, -y, -z$; (iii) $x, -\frac{1}{2} - y, z - \frac{3}{2}$] and the $\pi$–$\pi$ interactions by dotted lines [symmetry codes: (iii) $x, -\frac{1}{2} - y, z - \frac{3}{2}$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. H atoms not involved in C–H$\cdots\pi$ contacts have been omitted.

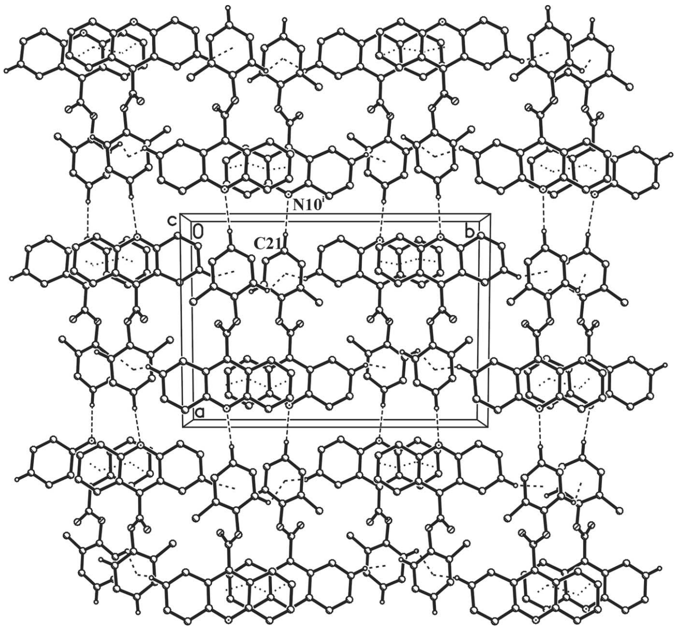


**Figure 3**
Layered crystal structure of (I) viewed along the [001] direction. The C–H$\cdots$N [symmetry codes: (i) $x - 1, y, z$] and C–H$\cdots\pi$ contacts are represented by dashed lines and the $\pi$–$\pi$ interactions by dotted lines. H atoms not involved in the hydrogen-bonding interactions have been omitted.

contacts exist between the benzene H atoms and benzene rings, forming columns extending along the [001] direction (Tables 2 and 3). The neighboring columns, linked by the C—H$\cdots\pi$ hydrogen-bond contacts, formed between the acridine H atoms and benzene rings, are arranged in layers, which are parallel to the (100) plane (Fig. 3). The crystal structure is stabilized by C—H$\cdots$N hydrogen bonds between layers.

## Experimental

Commercially available acridine-9-carboxylic acid was heated with a fivefold molar excess of thionyl chloride (350 K, 3.5 h) to obtain the acid chloride (yield 92%). The title compound was synthesized by the reaction of the acid chloride with an equimolar amount of 2-methylphenol (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*-dimethylamino)-pyridine (room temperature, 25 h). The crude product (yield 90%), was purified chromatographically (SiO$_2$, cyclohexane/ethyl acetate, 3:2 *v*/*v*). Elemental analysis found: C 80.68, H 4.81, N 4.45%; calculated: C 80.49, H 4.82, N 4.47%. Pale-yellow crystals suitable for X-ray investigations were grown from cyclohexane (m.p. 411–412 K). It was hard to obtain good quality crystals. X-ray data for one selected crystal among several available appeared to be the most reliable.

### *Crystal data*

$C_{21}H_{15}NO_2$
$M_r = 313.34$
Monoclinic, $P2_1/c$
$a = 12.376$ (5) Å
$b = 17.725$ (6) Å
$c = 7.100$ (3) Å
$\beta = 97.42$ (3)°
$V = 1544.4$ (10) Å$^3$
$Z = 4$

$D_x = 1.348$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 5392 reflections
$\theta = 3.1$–25.0°
$\mu = 0.09$ mm$^{-1}$
$T = 100$ (2) K
Needle, pale yellow
0.3 × 0.1 × 0.1 mm

### *Data collection*

Kuma KM-4 CCD *κ*-geometry diffractometer
*ω* scans
Absorption correction: none
5572 measured reflections
2551 independent reflections

1064 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.073$
$\theta_{\rm max} = 25.0°$
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 21$
$l = -8 \rightarrow 6$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.192$
$S = 1.00$
2551 reflections
218 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.26$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C9—C11 | 1.400 (6) | C15—O16 | 1.366 (5) |
| C9—C15 | 1.494 (6) | C15—O17 | 1.203 (5) |
| N10—C12 | 1.347 (6) | O16—C18 | 1.409 (5) |
| C9—C15—O16 | 110.8 (4) | C9—C15—O17 | 126.7 (5) |
| C11—C9—C15—O17 | 124.2 (6) | C15—O16—C18—C19 | 84.7 (5) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H$\cdots$*A* | *D*—H | H$\cdots$*A* | *D*$\cdots$*A* | *D*—H$\cdots$*A* |
|---|---|---|---|---|
| C21—H21$\cdots$N10$^{\rm i}$ | 0.95 | 2.55 | 3.446 (6) | 156 |
| C7—H7$\cdots$*Cg*4$^{\rm ii}$ | 0.95 | 2.91 | 3.435 (6) | 116 |
| C23—H23$\cdots$*Cg*4$^{\rm iii}$ | 0.95 | 2.90 | 3.421 (6) | 116 |

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

**Table 3**
$\pi$–$\pi$ interactions (Å, °) in (I).

| *CgI* | *CgJ* | *Cg*$\cdots$*Cg* | Dihedral angle | Interplanar distance | Offset |
|---|---|---|---|---|---|
| 1 | 2$^{\rm iii}$ | 3.656 (3) | 2.0 | 3.431 (3) | 1.262 (2) |
| 1 | 2$^{\rm iv}$ | 3.739 (3) | 2.0 | 3.519 (3) | 1.264 (2) |
| 2 | 1$^{\rm iii}$ | 3.739 (3) | 2.0 | 3.490 (3) | 1.342 (2) |
| 2 | 1$^{\rm iv}$ | 3.656 (3) | 2.0 | 3.470 (3) | 1.151 (2) |
| 2 | 2$^{\rm iii}$ | 3.809 (3) | 1.1 | 3.489 (3) | 1.528 (2) |
| 2 | 2$^{\rm iv}$ | 3.809 (3) | 1.1 | 3.461 (3) | 1.591 (2) |

*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 perpendicular distance of ring *I* from ring *J*. Symmetry codes: (iii) $x, -\frac{1}{2}-y, z-\frac{3}{2}$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$. *Cg* represents the centroids of the rings, as follows: *Cg*1 ring C9/C11/C12/N10/C14/C13 and *Cg*2 ring C1/C2/C3/C4/C12/C11.

All H atoms were positioned geometrically and refined using a riding model, with C–H distances of 0.95 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) [C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for the methyl group]. A few small-angle reflections, which show large differences between $F_o^2$ and $F_c^2$, were omitted in the last cycles of refinement.

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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