

2-Ethylphenyl acridine-9-carboxylate
and 2,5-dimethylphenyl acridine-9-
carboxylateArtur Sikorski,^a Karol Krzyński,^a Antoni Konitz^{b,a} and
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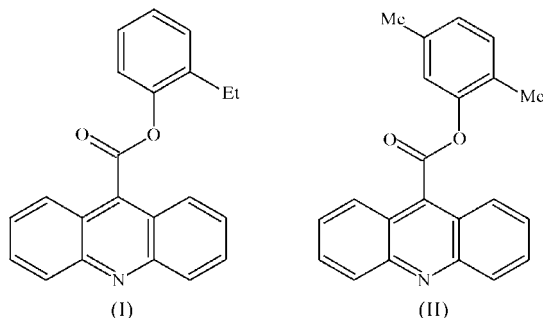
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The title compounds, 2-ethylphenyl acridine-9-carboxylate, $C_{22}H_{17}NO_2$, (I), and 2,5-dimethylphenyl acridine-9-carboxylate, $C_{22}H_{17}NO_2$, (II), form triclinic and monoclinic crystals, respectively. Related by a centre of symmetry, adjacent molecules of (I) are linked in the lattice *via* a network of C—H... π and non-specific dispersive interactions. As a result, acridine moieties and independent phenyl moieties of (I) are parallel in the lattice. The molecules of (II), arranged in a 'head-to-tail' manner and related by a centre of symmetry, form pairs stabilized *via* C—H... π interactions. These are linked in the crystal *via* dispersive interactions. Acridine and independent phenyl moieties lie parallel within the pairs, while adjacent pairs are perpendicular, forming a herring-bone pattern.

Comment

Phenyl esters of acridine-9-carboxylic acids are precursors of practically important chemiluminescent indicators and 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, which leads to electronically excited 10-methyl-9-acridinones emit-

ting radiation (Rak *et al.*, 1999). Among other things, this effect is utilized in quantitative assays of macromolecules present in living matter, that is, in immunological, medical, environmental and biochemical analyses (Adamczyk *et al.*, 1999; Dodeigne *et al.*, 2000; Razawi & McCapra, 2000; Smith *et al.*, 2000; Zomer & Jacquemijns, 2001). Despite the long-standing interest shown in this group of compounds, there is only one publication to date (our own) on the crystallography of 2-methylphenyl 2-methoxyacridine-9-carboxylate (Meszko *et al.*, 2002). It is thus important to extend investigations to further representatives of this group, especially

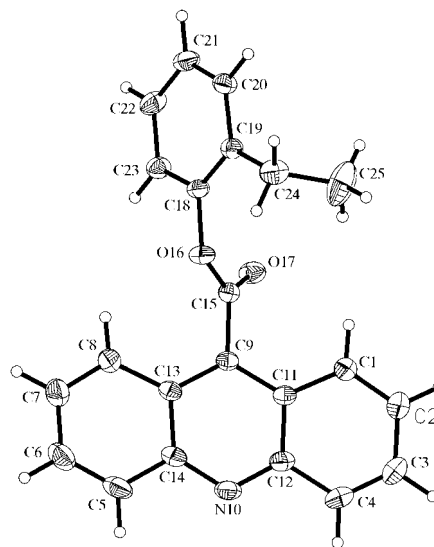


Figure 1

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.

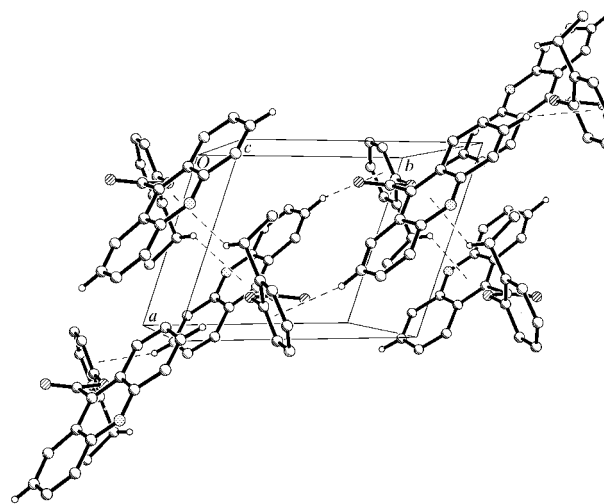


Figure 2

The arrangement of the molecules of (I) in the unit cell, viewed along the *c* axis. H atoms not involved in C—H... π interactions have been omitted. C—H... π interactions are represented by dashed lines.

since information on the structure, crystal packing and other features may help in the design of very stable compounds that are nevertheless highly reactive towards oxidizing agents (hydrogen peroxide). This paper presents the crystal structure of two isomers, (I) and (II), alkyl-substituted in the phenyl ester group, of phenyl acridine-9-carboxylate.

The acridine and phenyl moieties in (I), with average deviations from planarity of 0.0123 and 0.0033 Å, respectively, are oriented at an angle of 62.1 (2)° (defined as γ , the angle between the mean planes delineated by all the non-H atoms of the acridine and phenyl moieties; Fig. 1 and Table 1). The carboxyl group is twisted relative to the acridine skeleton, at an angle of 67.3 (2)° (defined as δ , the angle between the mean planes delineated by all the non-H atoms of the acridine moiety and atoms C15, O16 and O17).

In the crystalline phase, adjacent molecules of (I), related by a centre of symmetry, are linked *via* a network of C—H... π

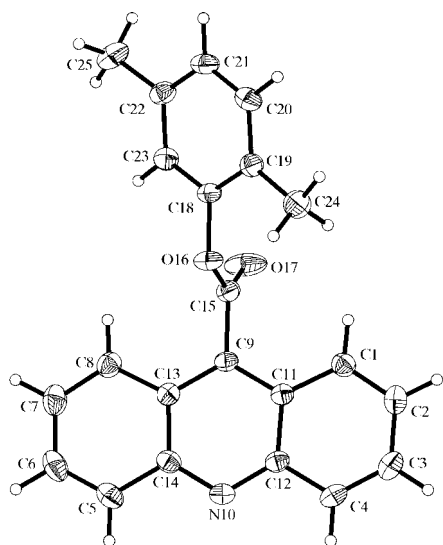


Figure 3
The molecular structure of (II), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

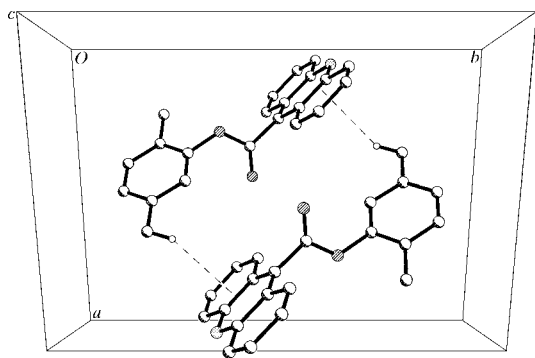


Figure 4
Part of the crystal structure of (II) in the unit cell, viewed along the *c* axis, showing the centrosymmetric linking of the molecules by pairs of C—H... π interactions (dashed lines). H atoms not involved in C—H... π interactions have been omitted.

interactions and non-specific dispersive interactions (Fig. 2 and Table 2). As a result, the acridine moieties and independent phenyl moieties are parallel in the lattice.

The planes of the acridine and phenyl moieties in (II), with average deviations from planarity of 0.0013 and 0.0056 Å, respectively, have a γ angle of 35.7 (2)° (Fig. 3 and Table 3). The carboxyl group is twisted relative to the acridine skeleton, with a δ angle of 68.1 (2)°.

Arranged in a 'head-to-tail' manner, the molecules of (II) form pairs stabilized through C—H... π interactions (Table 4). These pairs of molecules, related by a centre of symmetry, are linked in the crystal *via* dispersive interactions. The acridine moieties and independent phenyl moieties within the pairs are parallel, while adjacent pairs, which form a herring-bone pattern in the crystal, lie perpendicular to one another (Fig. 4).

Experimental

Compounds (I) and (II) were synthesized by conversion of commercially available acridine-9-carboxylic acid to acid chloride, and by reaction of the latter with 2-ethylphenol for (I) or 2,5-dimethylphenol for (II) (Sato, 1996). The crude products were purified chromatographically (SiO₂, cyclohexane/ethyl acetate, 3:2 *v/v*). Elemental analyses (% found/calculated) for (I): C 81.07/80.71, H 5.07/5.23, N 4.34/4.28; for (II): C 80.49/80.71, H 5.09/5.23, N 4.22/4.28. In both cases, pale-yellow crystals suitable for X-ray investigations were grown from cyclohexane [m.p. 387–389 K for (I) and 452–454 K for (II)].

Compound (I)

Crystal data

C ₂₂ H ₁₇ NO ₂	<i>Z</i> = 2
<i>M_r</i> = 327.37	<i>D_x</i> = 1.278 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.995 (2) Å	Cell parameters from 50 reflections
<i>b</i> = 9.465 (2) Å	θ = 2.3–26.0°
<i>c</i> = 11.899 (2) Å	μ = 0.08 mm ⁻¹
α = 92.12 (3)°	<i>T</i> = 293 (2) K
β = 98.96 (3)°	Prism, yellow
γ = 106.28 (3)°	0.5 × 0.4 × 0.3 mm
<i>V</i> = 850.7 (4) Å ³	

Data collection

Kuma KM-4 diffractometer	<i>h</i> = -9 → 9
$\theta/2\theta$ scans	<i>k</i> = -11 → 11
3507 measured reflections	<i>l</i> = -14 → 0
3337 independent reflections	3 standard reflections
1788 reflections with <i>I</i> > 2 σ (<i>I</i>)	every 200 reflections
<i>R</i> _{int} = 0.017	intensity decay: 1.3%
θ _{max} = 26.0°	

Table 1

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

C9—C11	1.400 (3)	C15—O16	1.351 (2)
C9—C15	1.491 (2)	C15—O17	1.195 (2)
N10—C12	1.339 (3)	O16—C18	1.414 (2)
C9—C15—O16	111.19 (16)	C15—O16—C18	117.60 (14)
C9—C15—O17	125.0 (2)	O16—C15—O17	123.74 (17)
C9—C15—O16—C18	-177.82 (16)	C15—O16—C18—C19	-116.7 (2)
C11—C9—C15—O17	50.8 (3)		

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.125$
 $S = 1.02$
 3337 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.1515P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.027 (4)

Table 2

Geometry of C—H... π interactions (Å, °) for (I).

C_gA is the centroid of the six-membered ring *A* (atoms C18–C23) and C_gB is the centroid of the six-membered ring *B* (atoms C9/N10/C11–C14) (Fig. 1).

	D—H	H...A	D...A	D—H...A
C2—H2A... C_gA^i	0.96	2.81	3.608 (3)	142
C6—H6A... C_gA^{ii}	0.96	2.81	3.540 (3)	133
C24—H24A... C_gB^{iii}	0.96	2.70	3.576 (3)	151

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x, -y + 2, -z + 2$; (iii) $-x + 1, -y + 2, -z + 2$.

Compound (II)

Crystal data

$C_{22}H_{17}NO_2$
 $M_r = 327.37$
 Monoclinic, $P2_1/c$
 $a = 11.769 (2) \text{ Å}$
 $b = 15.404 (3) \text{ Å}$
 $c = 10.125 (2) \text{ Å}$
 $\beta = 115.18 (3)^\circ$
 $V = 1661.1 (7) \text{ Å}^3$
 $Z = 4$

$D_x = 1.309 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 50 reflections
 $\theta = 2.3\text{--}26^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism, yellow
 $0.5 \times 0.4 \times 0.3 \text{ mm}$

Data collection

Kuma KM-4 diffractometer
 $\theta/2\theta$ scans
 3424 measured reflections
 3267 independent reflections
 1619 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 26.0^\circ$

$h = 0 \rightarrow 14$
 $k = -19 \rightarrow 0$
 $l = -12 \rightarrow 11$
 3 standard reflections every 200 reflections
 intensity decay: 0.6%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.103$
 $S = 0.92$
 3267 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0155 (17)

All H atoms were placed geometrically and refined using a riding model, with C—H distances of 0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

For both compounds, data collection: *KM-4 Software* (Kuma, 1989); cell refinement: *KM-4 Software*; data reduction: *KM-4 Soft-*

Table 3

Selected geometric parameters (Å, °) for (II).

C9—C11	1.395 (2)	C15—O16	1.330 (2)
C9—C15	1.487 (2)	C15—O17	1.182 (2)
N10—C12	1.335 (2)	O16—C18	1.413 (2)
C9—C15—O16	110.12 (13)	C15—O16—C18	119.69 (12)
C9—C15—O17	126.07 (15)	O16—C15—O17	123.80 (15)
C9—C15—O16—C18	176.78 (13)	C15—O16—C18—C23	71.6 (2)
C11—C9—C15—O17	79.4 (2)		

Table 4

Geometry of C—H... π interactions (Å, °) for (II).

C_gC is the centroid of the six-membered ring *C* (atoms C5–C8/C13/C14) (Fig. 3).

	D—H	H...A	D...A	D—H...A
C25—H25C... C_gC^i	0.96	2.87	3.622 (2)	136

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

ware; 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1086). Services for accessing these data are described at the back of the journal.

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