

2-Methylphenyl 2-methoxyacridine-9-carboxylate

Joanna Mieszko,^a Karol Krzyński,^a Antoni Konitz^b and Jerzy Błażejowski^{a*}^aFaculty of Chemistry, University of Gdańsk, J. Sobieskiego 18, 80-952 Gdańsk, Poland, and ^bDepartment of Inorganic Chemistry, Technical University of Gdańsk, G. Narutowicza 11/12, 80-952 Gdańsk, Poland

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

Received 17 August 2001

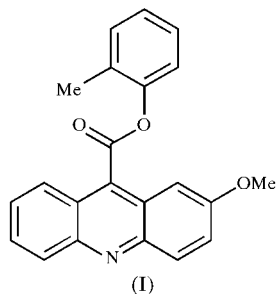
Accepted 9 January 2002

Online 20 February 2002

The title compound, $C_{22}H_{17}NO_3$, crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The molecules are arranged in centrosymmetric pairs, joined *via* the C and attached H atoms in the *meta* position relative to the methoxy group. These pairs are bonded in the crystalline phase as a result of non-specific dispersive interactions, and through a network of C—H...O interactions involving the non-bonded O atom of the carboxy group and, to some extent, the O atom of the methoxy group. The methoxy substituent lies in the plane of the almost planar acridine moiety and is directed towards the phenyl ester group. The phenyl ester group itself is twisted by $35.9(5)^\circ$ relative to the mean plane of the acridine moiety.

Comment

9-Carboxy-10-methylacridinium phenyl esters constitute the chemiluminescent fragments of chemiluminescent labels (Rak *et al.*, 1999), which have found numerous applications in



immunoassays (Zomer *et al.*, 1991; Dodeigne *et al.*, 2000), and which can potentially be used in environmental, biochemical and medical analyses (Dodeigne *et al.*, 2000). Upon preparation of one such label, we synthesized, as an intermediate product, the title compound, (I), and obtained it in a crystalline form. This prompted us to carry out X-ray measurements in order to determine its structure. Examination of the Cambridge Structural Database (Version of April 2001; Allen & Kennard, 1993) shows that this is the first structure

containing an acridine-9-carboxylic acid phenyl ester fragment.

The structure of (I) is shown in Fig. 1, and selected geometric parameters are given in Table 1. The O and C atoms of the methoxy group lie almost in the plane of the acridine moiety, which is itself almost planar, while the carboxy group is twisted relative to the acridine skeleton at an angle of $56.8(5)^\circ$. The 2-methylphenyl ester group is twisted from the mean plane of the acridine moiety by $35.9(5)^\circ$. The 2-methylphenyl fragment is almost perpendicular to the plane

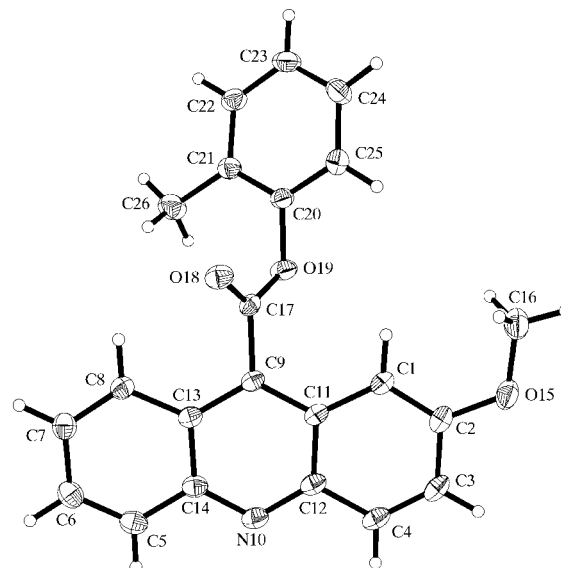


Figure 1

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

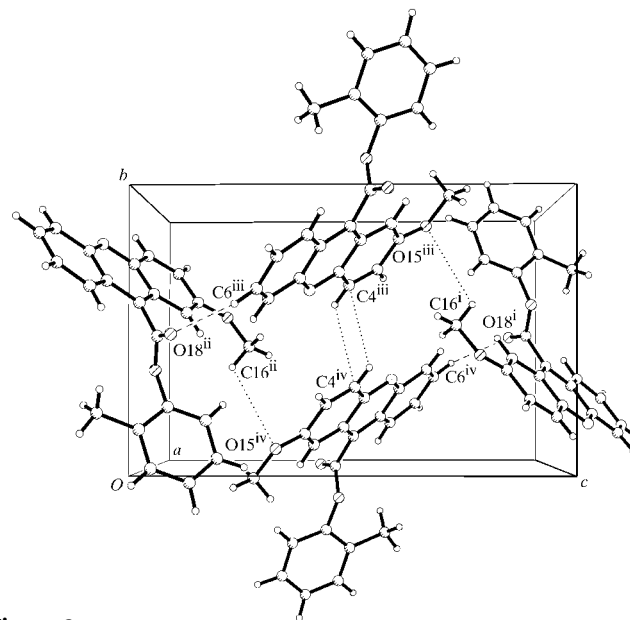
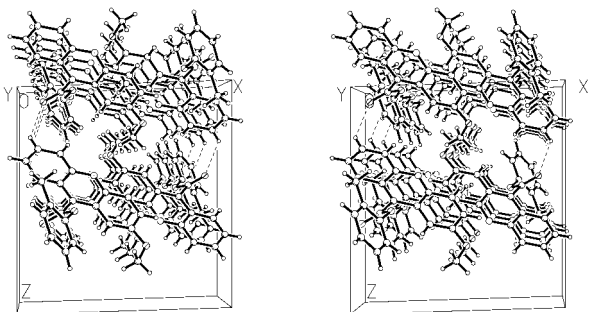


Figure 2

The arrangement of the molecules of (I) in the unit cell, viewed along the [100] axis. Short C—H...O interactions are represented by dashed lines and long C—H...O interactions or C—H...C contacts by dotted lines (Table 2). [Symmetry codes: (i) x, y, z ; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, y-\frac{1}{2}, z-\frac{1}{2}$.]


Figure 3

A stereoview of the packing of (I) viewed along the z axis. Short C—H...O interactions (Table 2) are represented by dashed lines.

formed by the atoms of the carboxy group; the angle between the respective mean planes is $87.3(5)^\circ$.

In the crystalline phase, the molecules of (I) are arranged in centrosymmetric pairs, joined through the C4 atoms and the attached H atoms, *via* a pair of C—H...C contacts, with C...C 3.58 \AA , H...C 3.01 \AA and C—H...C 119.7° (Fig. 2). These pairs are bonded as a result of non-specific dispersive interactions, and through a network of C—H...O interactions involving the O18 non-bonded atoms of the carboxy group and the H atoms attached to C6 [H...O 2.475 \AA , which is a short C—H...O interaction (Table 2)] and, to some extent, the O15 atoms of the methoxy group and the H atoms attached to C16 from neighbouring molecules [the shortest H...O distance is 3.42 \AA , which is a long C—H...O interaction (Table 2)].

The packing in the crystalline phase reveals that the molecules of (I) are in a regular arrangement and the acridine moieties are situated either parallel or perpendicular to each other; the angles between the respective mean planes are $0.0(5)$ or $84.0(5)^\circ$ (Fig. 3).

Experimental

2-Methoxyacridine-9-carboxylic acid, and subsequently (I), were synthesized following the procedures outlined by Zomer *et al.* (1991) and Batmanghelich *et al.* (1991). Light-yellow crystals of (I) suitable for X-ray investigations were grown from cyclohexane.

Crystal data

$C_{22}H_{17}NO_3$
 $M_r = 343.38$
 Monoclinic, $P2_1/c$
 $a = 13.393(3) \text{ \AA}$
 $b = 9.233(2) \text{ \AA}$
 $c = 14.162(3) \text{ \AA}$
 $\beta = 91.81(3)^\circ$
 $V = 1750.4(7) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.303 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 50 reflections
 $\theta = 3.0\text{--}60.1^\circ$
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, yellow
 $0.6 \times 0.5 \times 0.3 \text{ mm}$

Data collection

Kuma KM-4 diffractometer
 $\theta/2\theta$ scans
 7169 measured reflections
 5108 independent reflections
 2994 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 30.1^\circ$

$h = -18 \rightarrow 18$
 $k = -13 \rightarrow 0$
 $l = 0 \rightarrow 19$
 3 standard reflections every 200 reflections
 intensity decay: 1.2%

Table 1

Selected geometric parameters (\AA , $^\circ$).

C2—O15	1.361 (2)	O15—C16	1.426 (2)
C9—C11	1.406 (2)	C17—O18	1.1955 (17)
C9—C17	1.494 (2)	C17—O19	1.3474 (19)
N10—C12	1.342 (2)	O19—C20	1.4121 (18)
C1—C2—O15	125.33 (17)	C17—O19—C20	118.74 (11)
C2—O15—C16	117.23 (14)	O18—C17—O19	123.33 (14)
C9—C17—O18	126.57 (14)	O19—C20—C21	117.90 (14)
C9—C17—O19	110.07 (12)	C20—C21—C26	122.10 (16)
C11—C9—C17	120.82 (14)		
C1—C2—O15—C16	0.8 (3)	C11—C9—C17—O19	56.37 (18)
C9—C17—O19—C20	174.73 (13)	C17—O19—C20—C21	−87.90 (18)
C11—C9—C17—O18	−125.80 (17)	O19—C20—C21—C26	8.6 (2)

Table 2

Geometry of short contacts (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C6—H6A...O18 ⁱ	0.96	2.47	3.199 (3)	132
C4—H4A...C4 ⁱⁱ	0.96	3.01	3.584 (2)	120
C16—H16B...O15 ⁱⁱⁱ	0.96	3.41	3.916 (2)	115

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.3081P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
5108 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
236 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.020 (2)

All H atoms were placed in idealized positions and treated as riding, with C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *KM-4 Software* (Kuma Diffraction, 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).

The authors wish to express their gratitude to the Polish State Committee for Scientific Research for financial support through grant No. 3 T09A 083 16 (contract No. 1177/T09/99/16).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1177). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
 Batmanghelich, S., Woodhead, J. S., Smith, K. & Weeks, I. (1991). *J. Photochem. Photobiol. A Chem.* **56**, 249–254.
 Dodeigne, C., Thunus, L. & Lejeune, R. (2000). *Talanta*, **51**, 415–439.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kuma (1989). *KM-4 Software User's Guide*. Version 3.1. Kuma Diffraction, Wrocław, Poland.
 Rak, J., Skurski, P. & Blazejowski, J. (1999). *J. Org. Chem.* **64**, 3002–3008.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Zomer, G., Stavenuiter, J. F. C., Van Den Berg, R. H. & Jansen, E. H. J. M. (1991). *Pract. Spectrosc.* **12**, 505–521.