Kornelia Fennig and Artur Sikorski*

The crystal structure of acridin-10-ium 2-carboxybenzoate, $C_{21}H_{15}NO_4$

<https://doi.org/10.1515/ncrs-2018-0003>

Received January 3, 2018; accepted April 25, 2018; available online May 16, 2018

Abstract

$C_{21}H_{15}NO_4$, monoclinic, $P2_1/n$ (no. 14), $a = 7.2223(3)$ Å, $b = 9.1850(4)$ Å, $c = 25.2304(10)$ Å, $\beta = 92.604(3)^\circ$, $V = 1671.97(11)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0498$, $wR_{ref}(F^2) = 0.1205$, $T = 295(2)$ K.

CCDC no.: 1839520

Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

All the chemicals were purchased from Sigma-Aldrich and used without further purification. Acridine (0.050 g, 0.279 mmol) and 2-carboxybenzoic acid (0.046 g, 0.279 mmol) were dissolved in 50 mL of an ethanol/water mixture (10:1, v/v) and boiled for *ca.* 30 min. The clear solution was allowed to evaporate for a few days to give dark yellow crystals of title compound (m.p. = 160–161 °C).

Table 1: Data collection and handling.

Crystal:	Dark yellow block
Size:	$0.55 \times 0.45 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.10 mm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Ruby, ω -scans
$\theta_{\max}$, completeness:	25° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	21089, 2934, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2711
$N(\text{param})_{\text{refined}}$:	241
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], ORTEPII [4]

Experimental details

Coordinates of hydrogen atoms bonded to O and N-atoms were refined without constraints or restraints with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. All other H atoms were positioned geometrically and refined using a riding model, with C–H distances of 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

This contribution is part of our continuing interest in synthesis and structural characterization of the molecular complexes formed from acridine and aromatic carboxylic acids [5, 6].

Single-crystal X-ray diffraction measurements show that there is one acridinium and one 2-carboxybenzoate ions in the asymmetric unit (*cf.* left part of the figure). Analysis of the intermolecular interactions in the structure of title compound shows that the 2-carboxybenzoate

*Corresponding author: Artur Sikorski, Faculty of Chemistry, University of Gdańsk, W. Stwosza 63, 80-308 Gdańsk, Poland, e-mail: artur.sikorski@ug.edu.pl

Kornelia Fennig: Faculty of Chemistry, University of Gdańsk, W. Stwosza 63, 80-308 Gdańsk, Poland

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.3618(3)	1.3052(3)	0.01850(14)	0.0691(8)
H1	0.355225	1.377522	−0.007321	0.083*
C2	0.4236(4)	1.3382(3)	0.06740(16)	0.0843(10)
H2	0.458973	1.433278	0.075550	0.101*
C3	0.4358(3)	1.2316(4)	0.10646(13)	0.0771(9)
H3	0.479108	1.257179	0.140464	0.093*
C4	0.3862(3)	1.0906(3)	0.09651(9)	0.0563(6)
H4	0.397051	1.020772	0.123151	0.068*
C5	0.1423(3)	0.7290(3)	−0.02398(10)	0.0560(6)
H5	0.150590	0.659983	0.002984	0.067*
C6	0.0751(3)	0.6923(4)	−0.07398(14)	0.0818(10)
H6	0.036131	0.597300	−0.080735	0.098*
C7	0.0641(4)	0.7956(5)	−0.11524(13)	0.0916(12)
H7	0.019406	0.767607	−0.148854	0.110*
C8	0.1164(4)	0.9324(4)	−0.10680(10)	0.0764(9)
H8	0.108554	0.998903	−0.134609	0.092*
C9	0.2396(3)	1.1192(3)	−0.04492(9)	0.0521(6)
H9	0.232505	1.188315	−0.071868	0.063*
N10	0.26669(19)	0.91444(17)	0.03376(6)	0.0335(3)
H10	0.287(3)	0.837(2)	0.0606(8)	0.040*
C11	0.3049(3)	1.1600(2)	0.00486(9)	0.0436(5)
C12	0.3182(2)	1.0527(2)	0.04498(7)	0.0356(4)
C13	0.1843(3)	0.9784(3)	−0.05596(7)	0.0452(5)
C14	0.1983(2)	0.8737(2)	−0.01456(7)	0.0358(4)
C15	0.2970(2)	0.57659(18)	0.17757(7)	0.0307(4)
C16	0.4838(2)	0.56902(19)	0.19459(7)	0.0321(4)
C17	0.5365(3)	0.4805(2)	0.23725(8)	0.0470(5)
H17	0.661013	0.473780	0.248055	0.056*
C18	0.4068(3)	0.4026(3)	0.26377(9)	0.0569(6)
H18	0.443922	0.343195	0.292147	0.068*
C19	0.2220(3)	0.4127(3)	0.24825(9)	0.0553(6)
H19	0.133693	0.362022	0.266611	0.066*
C20	0.1686(3)	0.4983(2)	0.20536(8)	0.0413(5)
H20	0.043702	0.503796	0.194800	0.050*
C21	0.2346(2)	0.66395(19)	0.12976(7)	0.0316(4)
O22	0.06701(17)	0.67816(17)	0.11785(5)	0.0487(4)
O23	0.35990(18)	0.71759(18)	0.10307(6)	0.0568(4)
C24	0.6363(2)	0.6558(2)	0.17166(7)	0.0350(4)
O25	0.6692(2)	0.78037(17)	0.18288(7)	0.0620(5)
O26	0.74193(19)	0.57607(16)	0.14191(6)	0.0480(4)
H26	0.850(4)	0.623(3)	0.1351(10)	0.072*

anion interacts with the acridine cation *via* O—H...N hydrogen bonds (O23...N10 = 2.583(2) Å) to form

heterodimers. The C—O bond lengths (1.241(2)–1.253(2) Å) in the COOH group indicate that proton transfer between the carboxylic acid group and the acridine N atom has occurred. The neighbouring inversion-related heterodimers are linked by weak C—H...O hydrogen bonds (C9...O22ⁱⁱ = 3.374(3) Å; (ii) = −*x*, −*y* + 2, −*z*), forming heterotetramers (*cf.* right part of the figure). The acridine moieties in these tetramers interact *via* π–π interactions (with centroid...centroid distances in the 3.621(1)–3.672(1) Å range and separations 3.565(1) Å). The adjacent tetramers in the crystal packing interact *via* O—H...O hydrogen bonds between protonated and deprotonated carboxy groups of the neighbouring 2-carboxybenzoate ions (O26...O22ⁱ = 2.625(2) Å; (i) = *x* + 1, *y*, *z*), supported by very weak C—H...O hydrogen bonds (C20...O26^{iv} = 3.482(3) Å; (iv) = *x* − 1, *y*, *z*) and *via* π–π interactions between the acridine skeletons (with centroid...centroid distances in the 3.605(1)–3.704(1) Å range and separations 3.354(1) Å) to produce columns along the *a*-axis. The neighbouring columns interact *via* weak C—H...O hydrogen bonds (C19...O25ⁱⁱⁱ = 3.595(3) Å; (iii) = −*x* + 1/2, *y* − 1/2, −*z* + 1/2) between 2-carboxybenzoate ions, forming a 3D structure (*cf.* right part of the figure).

Acknowledgements: This study was financed by the State Funds for Scientific Research (grant DS/530-8225-D493-18).

References

1. Oxford Diffraction Ltd., CrysAlis^{PRO}, Abingdon, Oxfordshire, England (2006).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Johnson, C. K.: ORTEP. Report ORNL-5138. Oak Ridge National Laboratory, TN, USA (1976).
5. Kowalska, K.; Trzybiński, D.; Sikorski, A.: Influence of the halogen substituent on the formation of halogen and hydrogen bonding in co-crystals formed from acridine and benzoic acids. *CrystEngComm* **17** (2015) 7199–7212.
6. Sikorski, A.; Trzybiński, D.: Co-crystals and salts formed from 4-fluorobenzoic acid and heteroaromatic nitrogenous bases. *Tetrahedron Lett.* **54** (2013) 1463–1466.