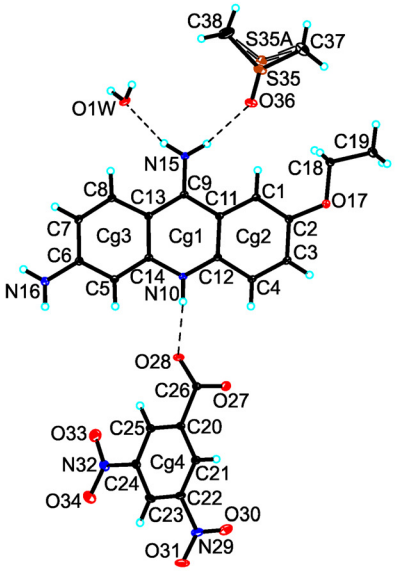
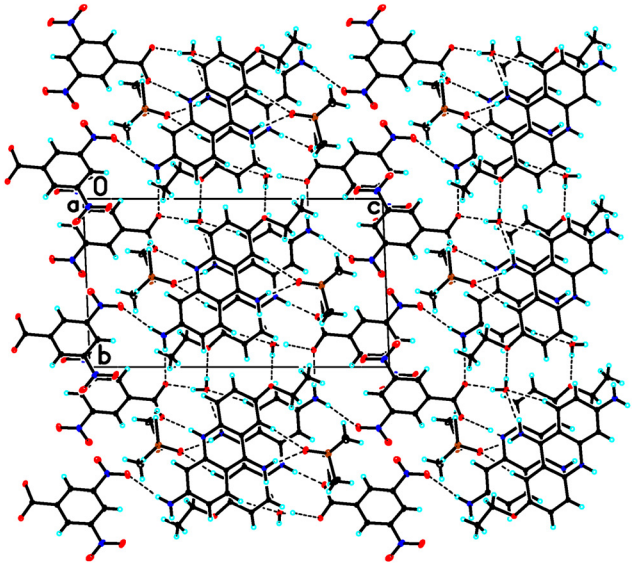
Artur Mirocki*

Crystal structure of 6,9-diamino-2-ethoxyacridinium 3,5-dinitrobenozate — dimethylsulfoxide — water (1/1/1), $C_{24}H_{27}N_5O_9S$





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***Corresponding author: Artur Mirocki**, Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland, E-mail: artur.mirocki@phdstud.ug.edu.pl. https://orcid.org/0000-0002-3189-0902

Abstract

$C_{24}H_{27}N_5O_9S$, triclinic, $P\bar{1}$ (no. 2), a = 7.5749(4) Å, b = 10.0368(5) Å, c = 17.9111(10) Å, α = 87.224(4)°, β = 83.678(4)°, γ = 85.414(4)°, V = 1348.04(12) Å^3, Z = 2, $R_{gt}(F)$ = 0.0562, w$R_{ref}(F^2)$ = 0.1477, T = 295(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All compounds were purchased from Sigma-Aldrich and used without purification. 6,9-Diamino-2-ethoxyacridine-DL-lactate monohydrate (0.03 g, 0.083 mmol) and 3,5-dinitrobenzoic acid (0.035 g, 0.165 mmol) were dissolved in 12 mL of an ethanol/water mixture (5:1 v/v) and heated in order to dissolve the sample. The solution was allowed to evaporate for a few days. Next recrystallization was performed. The sample was dissolved in 10 mL of methanol and added a few drops of CH_2Cl_2 and 3 mL dimethylsulfoxide (DMSO). The solution was allowed to evaporate for a few days to give yellow crystals (m.p. = 260.2 °C).

Experimental details

The solvent molecule is disordered. The site-occupancy factors are 0.635(3) and 0.365(3). All H atoms bound to

Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	0.42 × 0.25 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.18 mm^{-1}
Diffractometer, scan mode:	Oxford diffraction ruby, ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,840, 4726, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3319
$N(param)_{refined}$:	386
Programs:	CrysAlis [1], SHELX [2, 3], ORTEP-II [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1W	0.7318 (4)	0.1341 (2)	0.38546 (13)	0.0731 (6)
H1W	0.793 (4)	0.071 (4)	0.3891 (18)	0.080 (12)*
H2W	0.687 (5)	0.135 (4)	0.343 (2)	0.105 (13)*
C1	0.8596 (3)	0.6705 (2)	0.44288 (12)	0.0406 (5)
H1A	0.899496	0.631291	0.397487	0.049*
C2	0.8831 (3)	0.8019 (2)	0.45149 (13)	0.0423 (5)
C3	0.8260 (3)	0.8619 (2)	0.52019 (14)	0.0488 (6)
H3A	0.843426	0.951428	0.525687	0.059*
C4	0.7454 (3)	0.7899 (2)	0.57858 (14)	0.0471 (6)
H4A	0.707587	0.830287	0.623806	0.056*
C5	0.5242 (3)	0.3870 (2)	0.68933 (13)	0.0450 (6)
H5A	0.492404	0.432940	0.733239	0.054*
C6	0.4900 (3)	0.2546 (2)	0.68768 (14)	0.0460 (6)
C7	0.5369 (3)	0.1868 (2)	0.61980 (14)	0.0479 (6)
H7A	0.512541	0.097744	0.617645	0.057*
C8	0.6165 (3)	0.2498 (2)	0.55824 (13)	0.0435 (6)
H8A	0.645714	0.202972	0.514493	0.052*
C9	0.7419 (3)	0.4554 (2)	0.49519 (12)	0.0369 (5)
N10	0.6365 (2)	0.5839 (2)	0.62940 (12)	0.0427 (5)
H10A	0.600 (3)	0.621 (3)	0.6684 (15)	0.046 (7)*
C11	0.7753 (3)	0.5937 (2)	0.50233 (12)	0.0368 (5)
C12	0.7191 (3)	0.6539 (2)	0.57073 (12)	0.0384 (5)
C13	0.6568 (3)	0.3857 (2)	0.55845 (12)	0.0376 (5)
C14	0.6055 (3)	0.4530 (2)	0.62626 (12)	0.0390 (5)
N15	0.7899 (3)	0.3967 (2)	0.43089 (12)	0.0461 (5)
H15A	0.765 (3)	0.314 (3)	0.4262 (15)	0.065 (9)*
H15B	0.840 (3)	0.441 (3)	0.3920 (16)	0.051 (8)*
N16	0.4102 (3)	0.1874 (3)	0.74878 (15)	0.0650 (7)
H16A	0.390 (4)	0.228 (3)	0.7893 (18)	0.078*
H16B	0.402 (4)	0.102 (3)	0.7495 (17)	0.078*
O17	0.9597 (2)	0.88627 (16)	0.39651 (9)	0.0519 (4)
C18	1.0196 (3)	0.8305 (3)	0.32493 (14)	0.0523 (6)
H18A	0.921682	0.792703	0.304783	0.063*
H18B	1.111008	0.759103	0.332091	0.063*
C19	1.0909 (4)	0.9401 (3)	0.27360 (17)	0.0769 (9)
H19A	1.135541	0.904707	0.225752	0.115*
H19B	1.185597	0.977456	0.295143	0.115*
H19C	0.997388	1.008646	0.266940	0.115*
C20	0.4250 (3)	0.8183 (2)	0.87314 (13)	0.0489 (6)
C21	0.3201 (3)	0.9241 (3)	0.90505 (15)	0.0550 (7)
H21A	0.264189	0.988947	0.875000	0.066*
C22	0.2998 (3)	0.9320 (3)	0.98266 (16)	0.0617 (8)
C23	0.3796 (4)	0.8388 (3)	1.02930 (16)	0.0678 (8)
H23A	0.363562	0.845236	1.081267	0.081*
C24	0.4833 (4)	0.7364 (3)	0.99612 (15)	0.0630 (7)
C25	0.5067 (4)	0.7241 (3)	0.91954 (14)	0.0567 (7)
H25A	0.577624	0.652328	0.898883	0.068*
C26	0.4524 (4)	0.8048 (3)	0.78883 (14)	0.0559 (7)
O27	0.3892 (3)	0.8980 (2)	0.74987 (11)	0.0800 (6)
O28	0.5351 (3)	0.7005 (2)	0.76663 (10)	0.0846 (7)
N29	0.1918 (4)	1.0471 (3)	1.0164 (2)	0.0857 (9)
O30	0.1335 (4)	1.1341 (3)	0.97468 (18)	0.1085 (9)
O31	0.1675 (4)	1.0493 (3)	1.08421 (16)	0.1292 (11)
N32	0.5765 (5)	0.6351 (3)	1.04375 (16)	0.0856 (8)
O33	0.6839 (4)	0.5532 (3)	1.01343 (16)	0.1097 (9)
O34	0.5397 (5)	0.6401 (3)	1.11118 (15)	0.1347 (11)
S35[a]	0.91775 (19)	0.48519 (17)	0.21541 (8)	0.0899 (7)
S35A[b]	1.0676 (3)	0.4653 (2)	0.21896 (14)	0.0777 (10)*
O36	0.9633 (4)	0.5044 (3)	0.29074 (13)	0.1162 (9)
C37	1.0633 (11)	0.5732 (7)	0.1553 (3)	0.215 (4)
H37A	1.038831	0.667222	0.162712	0.323*
H37B	1.049005	0.554808	0.104265	0.323*
H37C	1.183293	0.546662	0.165257	0.323*
C38	0.9980 (8)	0.3198 (5)	0.1953 (4)	0.182 (3)
H38A	1.006934	0.308948	0.142027	0.274*
H38B	0.917494	0.258810	0.220362	0.274*
H38C	1.113454	0.301585	0.212543	0.274*

[a]Occupancy: 0.635 (3).[b]Occupancy: 0.365 (3).

N/O-atoms were located on a difference Fourier map and refined freely. All H atoms bound to aromatic C atoms were placed geometrically (C–H = 0.93 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C). All H atoms from the methyl group were positioned geometrically (C–H = 0.98 Å) and refined using a riding model, with U_{iso}(H) = 1.5U_{eq}(C).

Comment

An acridine derivative – 6,9-diamino-2-ethoxyacridine – has antiviral and antibacterial properties, and it is also helpful in curing various infections [5–7]. As a continuation of my recent study on the acridine derivatives [8–10], in this paper, the crystal structure of 6,9-diamino-2-ethoxyacridinium 3,5-dinitrobenozate dimethylsulfoxide monosolvate monohydrate is described.

The title compound crystallizes in the triclinic $P\bar{1}$ space group with one 6,9-diamino-2-ethoxyacridinium cation, one 3,5-dinitrobenzoate anion, a dimethylsulfoxide (DMSO) molecule and water molecule in the asymmetric unit (Figure). The C–O bond lengths in the carboxylic group (1.236–1.237 Å) indicating a proton transfer occurring between the carboxylic group of 3,5-dinitrobenzoic acid and the endocyclic N-atom of 6,9-diamino-2-ethoxyacridine. The 6,9-diamino-2-ethoxyacridinium cation interacts with the 3,5-dinitrobenzoate anion through the $N_{(acridine)}$–H···$O_{(carboxylate)}$ hydrogen bond between the endocyclic N-atom and the carboxylate group [*d*(H10A···O28) = 1.96(3) Å, and angle (N10–H10A···O28) = 174(3)°] to form a heterodimer. The adjacent heterodimers are linked *via* the $O_{(water)}$–H···$O_{(carboxylate)}$ hydrogen bond between water molecule and carboxylate group [*d*(H2W···O27) = 1.87(4) Å, and angle (O1W–H2W···O27) = 169(4)°] and the $N_{(amino)}$–H···$O_{(water)}$ hydrogen bond between C9-amino group and

water molecule [*d*(H15A···O1W) = 2.02(3) Å, and angle (N15–H15A···O1W) = 164(2)°] to form a heterohexamer. The same or similar heterohexamers have appeared in earlier works about on acridines [8–11]. The adjacent 6,9-diamino-2-ethoxyacridinium cations involved in hetetrohexameric synthon interact with each other *via* π–π interactions (with the distance between centroids (Cg···Cg) ranging from 3.915(1) Å to 3.979(1) Å and separation 3.450 Å between the mean planes of the 6,9-diamino-2-ethoxyacridine skeleton) to form π-stacked columns. The neighbouring columns are lined *via* the $O_{(water)}$–H···$O_{(ethoxy)}$ hydrogen bond [*d*(H1W···O17) = 2.17(4) Å, and angle (O1W–H1W···O17) = 177(4)°] between the water molecule and the ethoxy group from the acridinium cation, the $N_{(amino)}$–H···$O_{(carboxylate)}$ hydrogen bond between the C6-amino group and the carboxylate group [*d*(H16B···O27) = 2.06(3) Å, and angle (N16–H16B···O27) = 179(4)°], and the $N_{(amino)}$–H···$O_{(nitro)}$ hydrogen bond between the C6-amino group and the O-atom of one of the nitro groups [*d*(H16A···O34) = 2.40(3) Å, and angle (N16–-H16A···O34) = 156(3)°] to form blocks. Moreover, the neighbouring anions are linked *via* $N_{(nitro)}$–O···$N_{(nitro)}$ interactions [*d*(O30···N29) = 3.163(4) Å, and angle (N29–O30···N29) = 83(1)°], [*d*(O33···N32) = 3.121(5) Å, and angle (N32–O33···N32) = 99(6)°], which have appeared in earlier works about intermolecular interactions involving nitroarene fragments in the crystal structures of molecular complexes of acridines with dinitrobenzoic acids [12, 13]. Furthermore, the dimethylsulfoxide (DMSO) molecule interacts only with the 6,9-diamino-2-ethoxyacridinium cation *via* the $N_{(amino)}$–H···$O_{(DMSO)}$ hydrogen bond [*d*(H15B···O36) = 2.04(3) Å, and angle (N15–H15B···O36) = 167(3)°] between the C9--amino group and the O-atom of DMSO to form a 3D framework structure (Figure).

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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