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2-Ethylthio-9-methyl-1,4-dihydroacridine-1,4-dione and 9-methyl-2-(4-tolylthio)-1,4-dihydroacridine-1,4-dione

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Abstract

The title compounds, C₁₆H₁₃NO₂S, (I), and C₂₁H₁₅NO₂S, (II), have similar molecular structures that differ only in the side groups attached to the S atom. The crystal packing is dominated by π - π stacking interactions, involving acridinedione–acridinedione overlap in (I) and both acridinedione–acridinedione and acridinedione–tolyl overlap in (II).

Comment

Compounds (I) and (II) were synthesized (Copp *et al.*, 1999), and their structures determined, as part of a study of the structure–activity relationship of the cytotoxic marine alkaloid ascididemin (Kobayashi *et al.*, 1988). Both (I) and (II) exhibited less potent cytotoxicity to the marine leukaemia cell-line P388 than ascididemin (*IC*₅₀ 0.8, 28 and 0.4 μ M, respectively). These results are in support of other data which suggest that the cytotoxicity of the pyrido[2,3,4-*k*]acridine-based alkaloid ascididemin requires structurally complete rings *A* and *E* (Lindsay *et al.*, 1995). Poor water solubility, coupled with instability in DMSO solutions, precluded further antitumour evaluation of compounds (I) and (II).

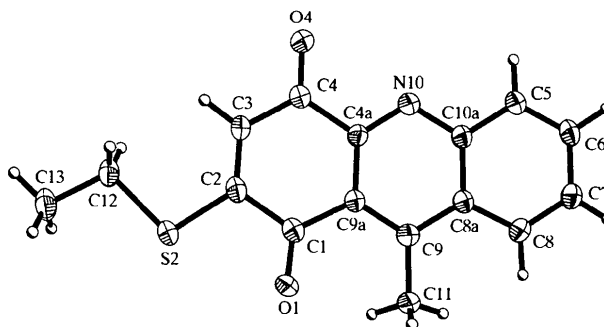
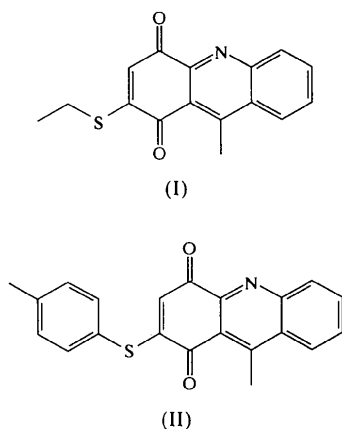


Fig. 1. Displacement ellipsoid drawing of molecule 1 of compound (I), showing the atom-numbering scheme. Molecule 2 appears identical. Ellipsoids are drawn at the 50% probability level for non-H atoms and the H atoms are shown as spheres of an arbitrary radius.

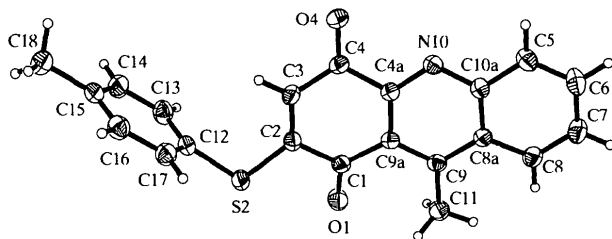


Fig. 2. Displacement ellipsoid drawing of compound (II), showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level for non-H atoms and the H atoms are shown as spheres of an arbitrary radius.

Experimental

Compounds (I) and (II) were synthesized according to the method described by Copp *et al.* (1999) and recrystallized from saturated dichloromethane solutions. The rate of evaporation was controlled to obtain suitable crystals.

Compound (I)

Crystal data

$C_{16}H_{13}NO_2S$
 $M_r = 283.3$
 Triclinic
 $P\bar{1}$
 $a = 7.736$ (6) Å
 $b = 11.690$ (4) Å
 $c = 14.704$ (5) Å
 $\alpha = 82.58$ (4)°
 $\beta = 79.28$ (4)°
 $\gamma = 88.56$ (4)°
 $V = 1295.6$ (12) Å³
 $Z = 4$
 $D_x = 1.453$ Mg m⁻³
 D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.852$, $T_{\max} = 0.972$
 6048 measured reflections
 5622 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.154$
 $S = 1.031$
 5622 reflections
 407 parameters
 H atoms treated by a mixture of independent and constrained refinement

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 11.50$ – 14.31 °
 $\mu = 0.250$ mm⁻¹
 $T = 203$ (2) K
 Prism
 $0.28 \times 0.14 \times 0.11$ mm
 Orange

3920 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 26.97$ °
 $h = 0 \rightarrow 9$
 $k = -14 \rightarrow 14$
 $l = -18 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0943P)^2 + 0.2332P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{21}H_{15}NO_2S$
 $M_r = 345.40$
 Monoclinic
 $P2_1/n$
 $a = 9.2792$ (2) Å
 $b = 8.7627$ (2) Å
 $c = 20.1726$ (5) Å
 $\beta = 98.4450$ (10)°
 $V = 1622.47$ (6) Å³
 $Z = 4$
 $D_x = 1.414$ Mg m⁻³
 D_m not measured

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.935$, $T_{\max} = 0.969$
 3593 measured reflections
 3593 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.094$
 $S = 1.042$
 3593 reflections
 228 parameters
 H atoms treated by a mixture of independent and constrained refinement

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 6056 reflections
 $\theta = 2.04$ – 27.47 °
 $\mu = 0.214$ mm⁻¹
 $T = 203$ (2) K
 Prism
 $0.32 \times 0.24 \times 0.15$ mm
 Orange

3078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 27.47$ °
 $h = -12 \rightarrow 11$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 26$
 Intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.6126P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.075$
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

All non-methyl H atoms were located in difference Fourier electron-density maps and were refined with their isotropic displacement factors fixed at 1.2 times those of the bonded C atom. Methyl H atoms were refined as riding models, with a C—H distance of 0.98 Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (I); *SMART* (Siemens, 1994a) for (II). Cell refinement: *CAD-4 Software* for (I); *SMART* for (II). Data reduction: Local program for (I); *SHELXTL* (Siemens, 1994b) for (II). For both compounds, program(s) used to solve structures: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1151). Services for accessing these data are described at the back of the journal.

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N,N'-Bis(2-ammonioethyl)oxamide diperchlorate

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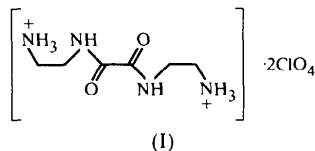
(Received 26 May 1998; accepted 9 November 1998)

Abstract

The title compound, C₆H₁₆N₄O₂²⁺·2ClO₄⁻, was obtained by an acid-catalyzed hydrolysis of the *N,N'*-bis[2-(salicylideneamino)ethyl]oxamide Schiff base. The oxamides are in a *trans*-conformation with all six non-H atoms essentially coplanar. Both primary N atoms are protonated to form the diperchlorate salt.

Comment

N,N'-disubstituted oxamides are used in the synthesis of polymetallic species with peculiar magneto-optical properties and in the design of a synthetic strategy for the development of molecular-based devices (Ojima & Nonoyama, 1988; Aguiari *et al.*, 1997). One of the advantages of these ligands is their easy *cis-trans* conformational interconversion affording symmetric and asymmetric oxamidato bridges (Benelli *et al.*, 1993). Since much research interest is focused on their conformation and bridging behaviour, it was considered useful to report the structure of the ligand itself.



(I)

The structure of the title compound, (I), consists of a doubly protonated *N,N'*-bis(2-ammonioethyl)oxamide cation and two perchlorate anions, which are joined together by hydrogen bonding. There is a crystallographically imposed centre of symmetry lying in the middle of the C1—C1(3 - *x*, 1 - *y*, 1 - *z*) bond. A drawing of the doubly protonated *N,N'*-bis(2-ammonioethyl)oxamide cation with the numbering scheme is shown in Fig. 1 and relevant distances and angles are given in Table 1. The oxamide groups take a *trans*-conformation and the six atoms are planar to ±0.002 Å. The C1—O1 and C1—N1 bonds display some double-bond character while the C—C bonds are typical for single bonds (Orpen *et al.*, 1989), suggesting electronic delocalization on the OCN group. The terminal primary N atom is protonated to form hydrogen bonds with the perchlorate anions [N1...O13 2.932 (5) Å].

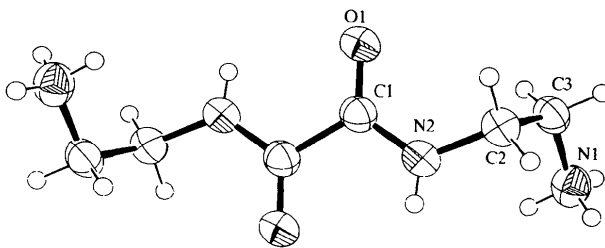


Fig. 1. Molecular structure of the *N,N'*-bis(2-ammonioethyl)oxamide cation with displacement ellipsoids at the 30% probability level.

Experimental

The compound was obtained as a by-product of the reaction of the *N,N'*-bis[2-(salicylideneamino)ethyl]oxamide Schiff base with hydrated lanthanide perchlorates in a methanol–acetonitrile medium. It was evident that the trace amount of free perchloric acid in the lanthanide salt resulted in this acid-catalyzed hydrolysis.

Crystal data

C₆H₁₆N₄O₂²⁺·2ClO₄⁻

M_r = 375.13

Monoclinic

*P*2₁/*n*

a = 8.517 (2) Å

b = 7.731 (2) Å

c = 10.830 (2) Å

β = 90.38 (3)°

V = 713.1 (3) Å³

Z = 2

D_x = 1.747 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 478 reflections

θ = 6.05–25.00°

μ = 0.516 mm⁻¹

T = 293 (2) K

Prismatic

0.25 × 0.20 × 0.15 mm

Yellow