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

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Abstract

The title compounds, $C_{16}H_{13}NO_2S$, (I), and $C_{21}H_{15}-NO_2S$, (II), have similar molecular structures that differ only in the side groups attached to the S atom. The crystal packing is dominated by $\pi-\pi$ 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 μM , respectively). These results are in support of other data which suggest that the cytotoxicity of the pyrido[2,3,4-*kl*]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).

Crystals of (I) contain two molecules in the asymmetric unit. Both molecules have three-ring chromophores that are measurably non-planar, although the deviations are small. The maximum displacement from the sulfur-substituted ring defined by C1, C2, C3, C4, C4a and C9a is 0.045(2) Å. The exocyclic atoms S2, O1 and O4 are displaced by -0.028(4), -0.052(4) and -0.096 (2), and -0.077 (4), 0.204 (4) and -0.013 (4) Å, for molecule 1 (unprimed) and molecule 2 (primed) respectively. The S-ethyl groups lie in the plane of the chromophores, with the following torsion angles for molecule 1: C1–C2–S2–C12 $(\tau_1) = -179.7(2)$ and C2—S2—C12—C13 (τ_2) = 173.3 (2)°, and the following for molecule 2: $\tau_1 = -177.3(2)$ and $\tau_2 =$ $-178.5(2)^{\circ}$. The chromophores of molecules 1 and 2 form a ...1212.. anti-parallel $\pi - \pi$ stacking interaction which extends throughout the length of the crystal in the a direction. The separation between individual chromophores is 3.5 Å for 1-2 interactions and 3.6 Å for 2-1 interactions.

In the structure of (II), the sulfur-substituted ring deviates more significantly from planarity, with an overall r.m.s. deviation of 0.045 Å. The maximum ring atom displacement is 0.068(1)Å for C1. The ring substituents show considerable deviation from the calculated plane [-0.173(2) for S2, 0.235(2) for O1 and 0.165 (2) Å for O4]. The torsion angles involving the S atom are different in (II) from those observed in (I); C1–C2–S2–C12 $(\tau_1) = -179.6(1)$ and C2– S2—C12—C13 (τ_2) = 93.3 (1)°, revealing that the tolyl group projects perpendicular to the chromophore plane. Stacking interactions in (II) are again important for stabilizing the crystal packing, but they are localized overlaps of the aromatic ring systems, instead of the extended stacking found in (I). Two types of overlap occur, namely, between two neighbouring acridinediones (separation 3.3 Å), and between an acridinedione and a tolyl group from a neighbouring molecule (separation 3.6 Å).







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.

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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 $P\overline{1}$ a = 7.736 (6) Å b = 11.690(4) Å c = 14.704(5) Å $\alpha = 82.58 (4)^{\circ}$ $\beta = 79.28 (4)^{\circ}$ $\gamma = 88.56 (4)^{\circ}$ $V = 1295.6(12) \text{ Å}^3$ Z = 4 $D_x = 1.453 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer $\omega/2\theta$ scans Absorption correction: ψ scan (North *et al.*, 1968) $T_{\rm min} = 0.852, T_{\rm max} = 0.972$ 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 = 1.0315622 reflections 407 parameters H atoms treated by a mixture of independent and constrained refinement Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ Å}$ Cell parameters from 25 reflections $\theta = 11.50 - 14.31^{\circ}$ $\mu = 0.250 \text{ mm}^-$ T = 203 (2) KPrism $0.28 \times 0.14 \times 0.11$ mm Orange

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

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

Compound (II)

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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)^{\circ}
V = 1622.47 (6) Å<sup>3</sup>
Z = 4
D_x = 1.414 \text{ Mg m}^{-3}
D_m not measured
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Data collection

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

Refinement

| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0441)]$ |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | + 0.6126 <i>P</i>] |
| $wR(F^2) = 0.094$ | where $P = (F_o^2 + 2F_c^2)$ |
| S = 1.042 | $(\Delta/\sigma)_{\rm max} = 0.075$ |
| 3593 reflections | $\Delta \rho_{\rm max} = 0.28 \ {\rm e} \ {\rm \AA}^{-3}$ |
| 228 parameters | $\Delta \rho_{\rm min} = -0.24 \ {\rm e} \ {\rm \AA}^{-3}$ |
| H atoms treated by a | Extinction correction: no |
| mixture of independent | Scattering factors from |
| and constrained refinement | International Tables fo |
| | Crystallography (Vol. |
| | |

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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Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ Å}$ Cell parameters from 6056 reflections $\theta = 2.04 - 27.47^{\circ}$ $\mu = 0.214 \text{ mm}^{-1}$ T = 203 (2) KPrism $0.32 \times 0.24 \times 0.15$ mm Orange

 $I > 2\sigma(I)$ $R_{\rm int} = 0.016$ $\theta_{\rm max} = 27.47^{\circ}$ $h = -12 \rightarrow 11$ $k = 0 \rightarrow 11$ $l = 0 \rightarrow 26$ Intensity decay: none

3078 reflections with

 $P)^2$)/3 ne C)

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

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Abstract

The title compound, $C_6H_{16}N_4O_2^{2+}\cdot 2ClO_4^-$, 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.





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 $[N1 \cdots O13 2.932(5) Å]$.



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 acidcatalyzed hydrolysis.

Crystal data

 $C_6H_{16}N_4O_2^{2+}\cdot 2ClO_4^{-1}$ Mo $K\alpha$ radiation $M_r = 375.13$ $\lambda = 0.71073 \text{ Å}$ Cell parameters from 478 Monoclinic $P2_1/n$ reflections $\theta = 6.05 - 25.00^{\circ}$ a = 8.517(2) Å $\mu = 0.516 \text{ mm}^{-1}$ b = 7.731(2) Å T = 293 (2) Kc = 10.830(2) Å Prismatic $\beta = 90.38(3)^{\circ}$ $0.25\,\times\,0.20\,\times\,0.15$ mm V = 713.1 (3) Å³ Yellow Z = 2 $D_x = 1.747 \text{ Mg m}^{-3}$ D_m not measured

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