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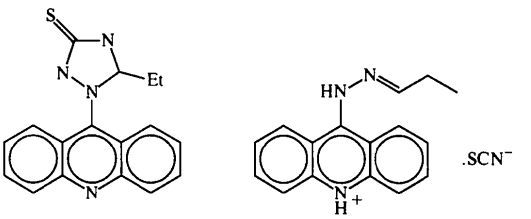

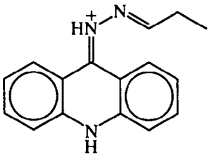

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9-Propylidenehydrazino-10-acridinium Thiocyanate at 173 K

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Abstract

The acridinium ring in the title compound, $C_{16}H_{16}N_3^+.SCN^-$, deviates slightly from planarity; the angle between the planes of the outer rings is 6.20 (14)°. There are significant distortions of the hydrazine side chain caused by steric interactions with the acridinium ring. The cations stack into columns with short interplanar spacings and hydrogen bonds cross-link the stacks *via* the anions.

Comment

Bifunctional isothiocyanates react with hydrazines to give thiosemicarbazides, which can be cyclized to the corresponding substituted triazolidines (Kutschy, Kristian, Dzurilla & Kováč, 1980; Richter, Klatt, Feuerer & Schulze, 1992). Similar products were also obtained from the reaction of 1-ethoxy-1-isothiocyanatopropane with phenylhydrazines (Bernát, Kristian, Guspanová, Imrich & Bušová, 1997). This reaction has been used to synthesize a triazolidine derivative, (I), with a biologically active acridine skeleton (Abu-Shady, Ragab & Ali, 1990), however, the spectral data of the product were inconsistent with the expected structure. An X-ray structural analysis revealed the product to be the title compound, (II). The synthesis and spectral results have been reported elsewhere (Kristian *et al.*, 1996).

The acridinium ring system of (II) has a similar geometry to most other examples of this moiety. The bond lengths within the outer rings follow the usual pattern of long and short bonds observed in acridines, acridinium cations (Jones & Neidle, 1975) and anthracene (Brock & Dunitz, 1990). This is the pattern expected by merging the four possible Kekulé structures of acridine (Clark, Robinson, Denny & Lee, 1993). The acridinium ring is not completely planar, but forms a shallow and slightly twisted butterfly conformation folded about the C9···N10 axis, with the angle between the planes of the outer rings being 6.20 (14)°. Although acridine (Phillips, 1956; Phillips, Ahmed & Barnes, 1960) and the 9-aminoacridinium cation (Talacki, Carrell & Glusker, 1974) are almost planar, deviations from planarity are often observed and the magnitude of the deviation appears to be related to the degree of substitution (Jones & Neidle, 1975).

The short N1—C9 bond displays considerable double-bond character due to the contribution of the resonance structure (III), consistent with the 9-aminoacridinium cation (Talacki, Carrell & Glusker, 1974), 9-aminoacridine (Chaudhuri, 1983) and most derivatives thereof. An examination of the structures of 17 9-aminoacridine and 11 9-aminoacridinium compounds extracted from the Cambridge Structural Database (October 1996 release; Allen & Kennard, 1993) shows that when the amino N atom of neutral 9-aminoacridine compounds is bonded to another π system, the N1—C9 bond becomes significantly longer [1.40 (1) Å for four compounds *cf.* 1.35 (1) Å for all other neutral 9-aminoacridines]. Similar substituents on 9-aminoacridinium cations, however, have no significant influence on the length of the N1—C9 bond [1.35 (2) Å for four such examples, including the title compound, *cf.* 1.33 (1) Å for all structures with 9-aminoacridinium cations].

The hydrazine side chain is planar from N1 to C13, with a maximum deviation of 0.024 (3) Å. This plane makes an angle of 9.64 (10)° with the mean plane of the acridinium moiety and is tilted towards the convex side of the acridinium ring distortion.

The relative coplanarity of the entire cation results in a short intramolecular contact between the ring H atom at C1 and the N2 atom of the hydrazine side chain [H1···N2 2.25 (3) Å]. This steric strain causes a significant enlargement of the N1—C9—C9a and N2—N1—C9 bond angles and is probably necessitated by the requirement for planarity introduced by the double-bond character of the N1—C9 bond.

The cations stack into columns within which adjacent cations are related by a centre of inversion. The interplanar spacings between one acridinium moiety and its two neighbours are 3.35 (10) and 3.56 (10) Å. This indicates a significant interaction between the π systems of adjacent rings since the van der Waals radius of carbon π systems in graphite is 1.8 Å (Kitajgorodski, 1973). The acridinium rings are tilted with respect to the stacking direction so that they do not overlap exactly, but are slightly offset with one acridinium moiety being approximately 50% eclipsed by the rings of the adjacent cation. A similar stacking has been observed for 9-aminoacridinium chloride monohydrate (Talacki, Carrell & Glusker, 1974) and related 9-aminoacridine derivatives (Carrell, 1972; Karle, Cysyk & Karle, 1980). Clark, Robinson, Denny & Lee (1993) have noted the trend that 9-aminoacridines which exhibit acridine stacking in the solid state do not possess antitumour activity. It would be interesting to see if compound (II) also fits this hypothesis.

Hydrogen bonds cross-link the cationic stacks *via* the anions; the acridinium N10—H group interacts with the N atom of the thiocyanate ion, while the S atom accepts a weak hydrogen bond from the side chain N1—H group of a different cation (Fig. 1 and Table 2). These interactions link the ions into infinite one-dimensional chains which run parallel to the *y* axis; graph set: $\mathbf{N}_2 = \mathbf{C}_2^2(10)$ (Bernstein, Davis, Shimoni & Chang, 1995).

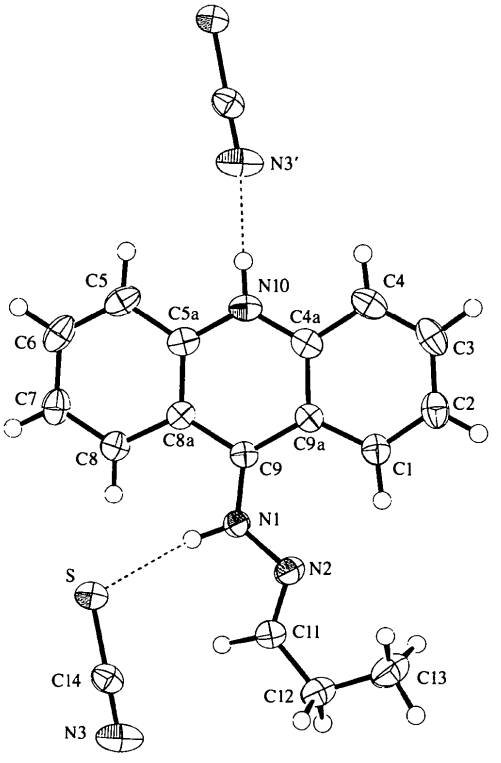

Fig. 1. View of compound (II) showing the atom-labelling scheme and the hydrogen bonding between the ions. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

Experimental

The title compound was prepared according to the method of Kristian *et al.* (1996). Suitable crystals were obtained by slow diffusion of diethyl ether into a solution of compound (II) in methanol.

Crystal data

$C_{16}H_{16}N_3^+.SCN^-$
M_r = 308.40
Triclinic
$P\bar{1}$
a = 9.054 (5) Å
b = 11.467 (4) Å
c = 8.512 (3) Å
α = 110.66 (3)°
β = 109.01 (4)°
γ = 76.51 (4)°
V = 774.7 (7) Å^3
Z = 2
D_x = 1.322 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 19.0–20.0°
μ = 0.211 mm^{-1}
T = 173 (1) K
Plate
0.50 × 0.38 × 0.06 mm
Gold

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
3793 measured reflections
3566 independent reflections
2473 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

θ_{max} = 27.5°
h = 0 → 11
k = −14 → 14
l = −11 → 10
3 standard reflections every 150 reflections
intensity decay: insignificant

Refinement

Refinement on F
R = 0.0524
wR = 0.0526
S = 2.145
2473 reflections
263 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o) + (0.008F_o)^2]$

$(\Delta/\sigma)_{max}$ = 0.0002
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—N2	1.389 (3)	C4a—C9a	1.422 (3)
N1—C9	1.341 (3)	C5—C5a	1.411 (4)
N2—C11	1.282 (3)	C5—C6	1.367 (4)
N10—C4a	1.363 (3)	C5a—C8a	1.407 (3)

N10—C5a	1.369 (3)	C6—C7	1.403 (4)
C1—C2	1.373 (4)	C7—C8	1.364 (4)
C1—C9a	1.424 (3)	C8—C8a	1.424 (4)
C2—C3	1.400 (4)	C8a—C9	1.449 (3)
C3—C4	1.359 (4)	C9—C9a	1.448 (3)
C4—C4a	1.421 (4)		
N2—N1—C9	125.5 (2)	N1—C9—C8a	116.2 (2)
N1—N2—C11	113.5 (2)	N1—C9—C9a	124.9 (2)
C4a—N10—C5a	122.6 (2)	C8a—C9—C9a	118.9 (2)
N1—C9—C8a—C8	−7.3 (4)	C4—C4a—N10—C5a	176.4 (2)
N1—C9—C9a—C1	7.2 (4)	C4a—N10—C5a—C5	−178.1 (2)
N2—N1—C9—C8a	−176.7 (2)	C8—C8a—C9—C9a	172.8 (2)
N2—N1—C9—C9a	3.1 (4)	C9—N1—N2—C11	−174.2 (3)
C1—C9a—C9—C8a	−173.0 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10···N3^{i}	0.91 (3)	1.97 (3)	2.863 (3)	167 (3)
N1—H12···S	0.91 (3)	2.62 (3)	3.425 (3)	148 (3)

Symmetry code: (i) $x, 1+y, z$.

Although the crystal was a very thin plate, ψ scans of three reflections indicated that an absorption correction was unnecessary. *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structure was solved using direct methods *SHELXS*86 (Sheldrick, 1990) and molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry, together with a view of the packing of the title compound in the unit cell, have been deposited with the IUCr (Reference: AB1449). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Dihydro-5-hydroxy-6,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (Onysilin)

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Abstract

The title compound, $C_{17}H_{16}O_5$, contains a heterocyclic ring which adopts a sofa conformation. The dihedral angle between the weighted phenyl and benzopyranone mean planes is 79.01 (5)°.

Comment

There has never been any serious doubt that the isomeric flavanones 2,3-dihydro-5-hydroxy-6,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (onysilin) and 5-hydroxy-7,8-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one are correctly represented by the structures (1) and (2), respectively (Wu, Kuoh, Ho, Yang & Lee, 1981; Wollenweber, 1982). Work in our laboratories has been directed towards the use of X-ray crystallographic data to formulate correctly the structures of isomeric flavanones. The title compound was isolated from *Uvaria dulcis Dunal* (*Annonaceae*) as yellow crystals

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