A Schiff base formed from sulfanilic acid and dimethylformamide

ANDREW HEMPEL,[a] NORMAN CAMERMAN,[a] DONALD MASTROPAOLO[b] AND ARTHUR CAMERMAN[b]

[a]*Department of Biochemistry, University of Toronto, Medical Sciences Building, Toronto, Canada M5S 1A8, and* [b]*Ardono Research, 659 NE Northlake Way, Seattle, WA 98105, USA. E-mail: andrew.hempel@utoronto.ca*

Abstract

The crystal structure the Schiff base contains one 4-dimethylaminomethyleneaminobenzenesulfonic acid molecule in zwitterionic form [4-(dimethylaminomethyleneammonio)benzenesulfonate], and one water molecule in the asymmetric unit ($C_9H_{12}N_2O_3S \cdot H_2O$). Protonation occurs at nitrogen atom N1, but the charge is delocalized.

Comment

In a program of syntheses of new therapeutics, an acid chloride was needed to produce an amide of sulfanilic acid. A standard method in the preparation of an acid chloride from a carboxylic acid is to use thionyl chloride, with dimethyl formamide (DMF) as a catalyst. Thionyl chloride and DMF react to form a chloroiminium ion, which attacks the carboxylic acid, forming the acid chloride and regenerating DMF. However, some of the chloroiminium ions were unknowingly carried along with the acid chloride to the amide step and reacted with the amino group of sulfanilic acid forming a 4-dimethylaminomethyleneaminobenzenesulfonic acid derivative, (I). We now report the structure of this unexpected product.

(I)
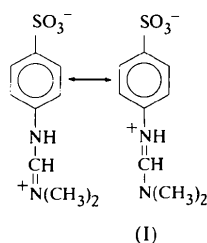
The molecule of (I) (Fig. 1) is made up of two planes: the phenyl ring and the Schiff-base chain, with an angle of 15.3 (3)° between their normals. The molecule is a zwitterion, as was also observed in the crystal structure of sulfanilic acid monohydrate (Rae & Maslen, 1962). The SO_3 group has a negative charge and although

protonation occurs at N1, the positive charge is divided between the N1 and N2 atoms, as evidenced from the C7—N1 and C7—N2 bond distances [1.307 (3) and 1.305 (3) Å, respectively], forming a delocalized double-bond system. This is further evidenced by the planarity of atoms C4, N1, C7, N2, C8 and C9 (maximum deviation is 0.05 Å). The C4—N1 distance is 1.420 (3) Å, closer to the 1.387 (2) Å value in sodium sulfanilate dihydrate (Bats & Coppens, 1975) where the N atom is not ionized, than to 1.49 (3) Å in sulfanilic acid monohydrate where the positive charge is localized on N1. The S—O2 bond length is 0.01 Å shorter than the other two S—O lengths, reflecting the non-involvement of O2 in hydrogen bonds, similar to the sodium sulfanilate dihydrate results. Other molecular parameters have normal values. The range of C—H distances and H-atom U_{iso} values and their associated s.u.'s are 0.87 (5)–1.04 (3) Å and 0.044 (6)–0.21 (3) $Å^2$, respectively. In the crystal structure the molecules lie in sheets roughly parallel to the (001) plane, and pairs of sheets are held together in infinite networks by hydrogen bonds from the protonated N atom to the water of crystallization, and from the water to the sulfate O3 and O4 in two different molecules. There are only van der Waals contacts between each set of two sheets.
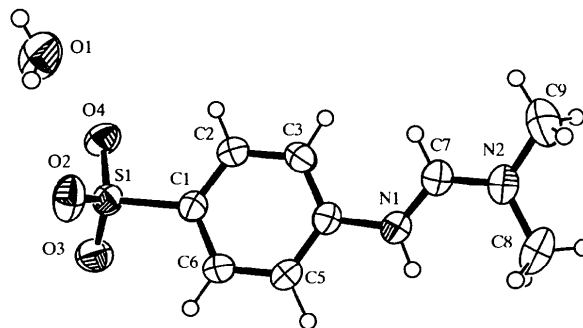
Fig. 1. *ORTEP*III (Burnett & Johnson, 1996) view of the title compound showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of an arbitrary radius.

Experimental

The title compound was synthesized and crystallized in our laboratories.

Crystal data

$C_9H_{12}N_2O_3S \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 246.28$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from all
$P2_12_12_1$	reflections
$a = 5.8512 (2)$ Å	$\theta = 21$–$26°$
$b = 13.0410 (6)$ Å	$\mu = 0.287$ mm^{-1}
$c = 14.8412 (7)$ Å	$T = 293 (2)$ K
$V = 1132.47 (8)$ Å^3	Prism
$Z = 4$	$0.4 \times 0.2 \times 0.2$ mm
$D_x = 1.444$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Nonius Kappa CCD diffrac-	1912 reflections with
tometer	$I > 2\sigma(I)$
ω rotation scans	$\theta_{max} = 26.38°$
Absorption correction: none	$h = -7 \rightarrow 7$
2296 measured reflections	$k = -16 \rightarrow 16$
1355 independent reflections	$l = -18 \rightarrow 18$
(plus 941 Friedel-related	
reflections)	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
$wR(F^2) = 0.082$	Extinction correction:
$S = 1.13$	*SHELXL*97 (Sheldrick,
2296 reflections	1997)
202 parameters	Extinction coefficient:
All H-atom parameters	0.034 (4)
refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2$	*International Tables for*
$+ 0.0709P]$	*Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute structure: Flack
$(\Delta/\sigma)_{max} = 0.001$	(1983)
	Flack parameter = 0.08 (9)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^i	0.89 (2)	2.05 (2)	2.900 (3)	159 (2)
O1—H11$\cdots$O4^{ii}	0.80 (4)	2.01 (4)	2.789 (3)	166 (4)
O1—H12$\cdots$O3^{iii}	0.71 (6)	2.09 (6)	2.799 (3)	173 (5)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$; (ii) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{5}{2} - x, 1 - y, z - \frac{1}{2}$.

All H atoms were found from a difference map; during the refinement H atoms were treated isotropically. No restraints were applied to H atoms during refinement; only one bond (O1—H12) has a value outside the expected range. Nonetheless, the hydrogen-bond geometry involving this atom is almost ideal.

Data collection: Nonius Kappa CCD server software. Cell refinement: *DENZO–SMN Software* (Otwinowski & Minor, 1997). Data reduction: *DENZO–SMN Software*. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

This work was supported by the National Cancer Institute of Canada with funds from the Canadian Cancer Society (NC) and by grant AI40392 from the National Institutes of Health (AC).

References

Bats, J. W. & Coppens, P. (1975). *Acta Cryst.* B31, 1467–1472.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. *Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations.* Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* 276, 307–326.
Rae, A. I. M. & Maslen, E. N. (1962). *Acta Cryst.* 15, 1285–1291.
Sheldrick, G. M. (1997). *SHELX*97. *Program for the Solution and Refinement of Crystal Structures.* University of Göttingen, Germany.

Tri-*p*-tolyl-1,3,5-triazine

VENKAT R. THALLADI,[a] MEIYAPPAN MUTHURAMAN,[b] ASHWINI NANGIA[a] AND GAUTAM R. DESIRAJU[a]

[a]*School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, and* [b]*Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, BP 166, 38042 Grenoble CEDEX 09, France. E-mail: grdch@uohyd.ernet.in*

Abstract

The crystal structure of the title compound, $C_{24}H_{21}N_3$, is stabilized by C—H$\cdots$N and C—H$\cdots\pi$ interactions. Its crystallization in a lower symmetry space group highlights an important problem in crystal engineering, that is the failure of symmetry carry-over from the molecule to the crystal.

Comment

The crystal structure of the title compound, (I), was determined while screening trigonal molecules for octupolar non-linear optical (NLO) behaviour. The design of an octupolar NLO crystal consists of identifying a chromophore with threefold symmetry and then being able to extend the high symmetry of the molecule into the crystal (Zyss, 1991; Zyss & Ledoux, 1994). However, the carry-over of molecular symmetry into the crystal is not trivial and the inversion centre is the only symmetry element which is routinely extended into the crystal (Kitaigorodskii, 1973; Brock & Dunitz, 1994). We have recently shown that tribenzyl isocyanurate (Thalladi *et al.*, 1997) and triaryloxytriazines (Thalladi *et al.*, 1998) have non-centrosymmetric network structures that lead to octupolar NLO behaviour including, in some cases, second harmonic generation (SHG) in the solid state. However, these molecules have low molecular hyperpolarizabilities (β) due to the lack of effective conjugation between the aromatic rings and the central heterocycle. Compound (I) was thus chosen because the three tolyl rings and the central triazine ring are conjugated and