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Anthranilic Acid–Picric Acid (2/1) Complex

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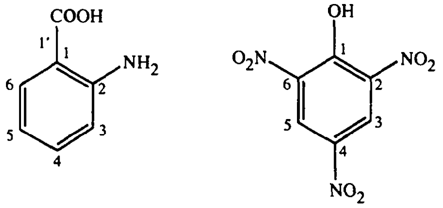
Abstract

The X-ray crystal structure of the 2:1 anthranilic acid–picric acid complex, $2C_7H_7NO_2.C_6H_3N_3O_7$, shows extensive stacking interactions, where picric acid is sandwiched between two crystallographically independent anthranilic acid molecules, with spacings of 3.29 and 3.33 Å. The carboxyl and amino groups of anthranilic acid are neutral and the former group is hydrogen bonded to the polar nitro and phenol O atoms of neighbouring picric acid molecules. The present results indicate the superior π-donating ability of anthranilic acid, as well as a superior hydrogen-bonding ability, in its interaction with an acceptor molecule such as picric acid.

Comment

It is known that picric acid functions not only as an acceptor to form π-stacking complexes with aromatic biomolecules, but also as an acidic ligand to form salts with polar biomolecules through specific electrostatic or hydrogen-bonding interactions. As part of a study estimating the π-stacking and hydrogen-bonding abilities of biomolecules (Nagata, In, Doi, Ishida & Wakahara, 1995; Nagata, In, Tomoo, Doi, Ishida & Wakahara, 1995), this paper deals with the X-ray crystal structure of a 2:1 anthranilic acid–picric acid complex. Because of the polar and aromatic characters of anthranilic acid, it is of interest to know whether the π-stacking or hydrogen-bonding ability function predominates in complex formation with picric acid.



2:1

Picric acid is found to be sandwiched by two crystallographically independent anthranilic acid molecules (Fig. 1), where the respective dihedral angles and mean interplanar spacings are 2.8 (5)° and 3.29 Å for the upper pair, and 1.4 (5)° and 3.33 Å for the lower one. No notable stacking interaction was observed between neighbouring anthranilic acid molecules. The carboxyl groups of the anthranilic acid molecules are hydrogen bonded to the polar atoms of neighbouring anthranilic acid and picric acid molecules (Fig. 2); two independent anthranilic acid molecules are linked to one another through O—H···O hydrogen bonds around the diad screw axis along the *b* axis (Table 2). Although the complex molecules are linked by O—H···O hydrogen bonds and O···O electrostatic interactions, it is significant that the amino group of anthranilic acid does not participate in any specific interaction.

The difference Fourier map indicated that the carboxyl and amino groups of anthranilic acid and the phenol group of picric acid are neutral. This is also suggested by the bond lengths and angles, and the intermolecular interaction pattern of the complex.

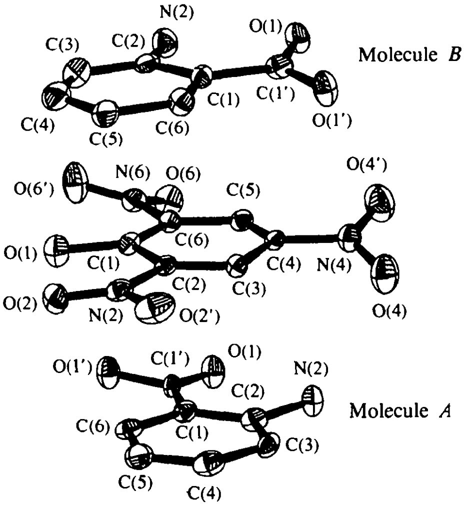


Fig. 1. The stacking interaction between the anthranilic and picric acid molecules. The upper and lower anthranilic acid molecules correspond to molecules *A* and *B*, respectively. H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.

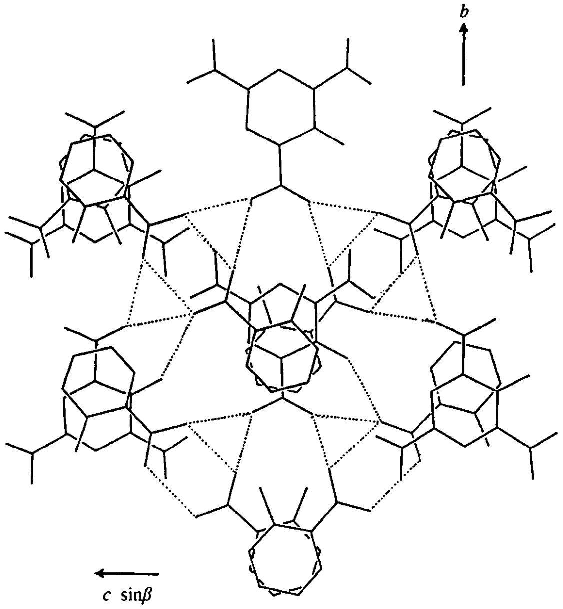


Fig. 2. The crystal packing of the 2:1 anthranilic acid–picric acid complex viewed along the *b* axis. Dotted lines represent hydrogen bonds.

Experimental

Crystals of the title complex were prepared by slow evaporation of an aqueous ethanol solution containing equimolar amounts of anthranilic acid and picric acid at room temperature.

Crystal data

$2C_7H_7NO_2.C_6H_3N_3O_7$
$M_r = 503.81$
Monoclinic
Cc
$a = 10.356\,(2)$ Å
$b = 15.350\,(3)$ Å
$c = 13.394\,(3)$ Å
$\beta = 96.38\,(4)°$
$V = 2116.0\,(8)$ Å^3
$Z = 4$
$D_x = 1.580\,(2)$ Mg m^{-3}
$D_m = 1.579$ Mg m^{-3}
D_m measured by flotation in a CCl_4–C_6H_6 mixture

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 23$–$26°$
$\mu = 1.14$ mm^{-1}
$T = 293$ K
Plate
0.40 × 0.20 × 0.10 mm
Red

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
2342 measured reflections
1808 independent reflections
1454 reflections with $F > 3\sigma(F)$

$R_{int} = 0.018$
$\theta_{max} = 65.1°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -16 \rightarrow 16$
4 standard reflections every 100 reflections intensity decay: <2%

Refinement

Refinement on *F*
$R = 0.059$
$wR = 0.067$
$S = 1.7187$
1454 reflections
323 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.001291F^2]$

$(\Delta/\sigma)_{max} = 0.07$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Picric acid			
C(1)—O(1)	1.395 (9)	N(4)—O(4′)	1.19 (2)
C(2)—N(2)	1.47 (2)	C(6)—N(6)	1.51 (2)
N(2)—O(2)	1.19 (1)	N(6)—O(6)	1.22 (2)
N(2)—O(2′)	1.23 (2)	N(6)—O(6′)	1.20 (2)
N(4)—O(4)	1.22 (2)		
C(2)—N(2)—O(2)	122.3 (7)	O(4)—N(4)—O(4′)	118.7 (9)
C(2)—N(2)—O(2′)	113.1 (7)	C(6)—N(6)—O(6)	116.2 (7)
O(2)—N(2)—O(2′)	124.4 (8)	C(6)—N(6)—O(6′)	116.8 (7)
C(4)—N(4)—O(4)	121.1 (8)	O(6)—N(6)—O(6′)	126.9 (8)
C(4)—N(4)—O(4′)	120.2 (8)		
C(1)—C(2)—N(2)—O(2′)	−179 (1)		
C(3)—C(4)—N(4)—O(4′)	−162 (1)		
C(5)—C(6)—N(6)—O(6′)	−160 (1)		

Anthranilic acid	Molecule *A*	Molecule *B*
C(1)—C(1′)	1.44 (2)	1.48 (2)
C(1′)—O(1)	1.21 (2)	1.28 (2)
C(1′)—O(1′)	1.31 (2)	1.29 (2)
C(2)—N(2)	1.41 (2)	1.32 (2)
C(1)—C(1′)—O(1)	127.2 (8)	118.5 (7)
C(1)—C(1′)—O(1′)	114.9 (7)	117.8 (7)
O(1)—C(1′)—O(1′)	117.7 (7)	123.6 (7)
C(1)—C(2)—N(2)	126.4 (7)	118.5 (8)
N(2)—C(2)—C(3)	116.1 (7)	123.6 (9)
C(2)—C(1)—C(1′)—O(1)	1 (1)	7 (1)
C(2)—C(1)—C(1′)—O(1′)	−173 (1)	−174 (1)

Table 2. *Contact distances (Å)*

O(1*A*)···O(1′*B*^{i})	2.62 (1)	O(1′*B*)···O(2^{iii})	3.10 (1)
O(2)···O(1*A*^{ii})	3.07 (1)	O(1*B*)···O(1′*A*^{iv})	2.63 (1)
O(2′)···O(1′*A*^{iii})	3.03 (2)	O(1)···O(1′*B*^{v})	3.06 (1)
O(4)···O(2^{iii})	3.08 (2)	O(1*B*)···O(2′^{vi})	2.95 (2)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (vi) $\frac{1}{2}+x, \frac{1}{2}+y, z$.

Because of (i) the relatively poor crystallinity [scan range in $\omega = (1.85 + 0.15\tan\theta)°$] due to the thin-layered crystal habit, and (ii) the extensive stacking formation of the complex structure, the observed intensities [$F_o \geq 3\sigma(F_o)$] within $2\theta = 130°$ were rather limited, compared with the number of parameters (323) which should be refined. This could be the main cause of the high e.s.d. values for the bonding parameters of the structure. Coordinates of all H atoms were obtained from a difference map during the final stages of refinement and were included as fixed parameters with different isotropic displacement parameters in the final refinement.

Rigaku AFC-5*R* software was used for data collection, cell refinement and data reduction. The structure was determined by direct methods using the program *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Full-matrix least-squares refinement on *F* magnitudes with anisotropic displacement parameters for non-H atoms was performed with *SHELX*76 (Sheldrick, 1976). The molecular graphics were produced with *ORTEP*II (Johnson, 1976).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anhydrous and Hydrated 4-Aminotoluene-3-sulfonic Acid

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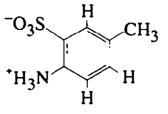
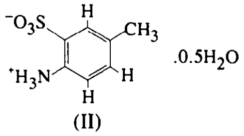
Abstract

The crystal structures of 4-aminotoluene-3-sulfonic acid, $C_7H_9NO_3S$, (I), and its hemihydrate, $C_7H_9NO_3S.0.5H_2O$, (II), are reported. The acid molecules in both crystals exist as zwitterions (ammoniotoluenesulfonate) and pack in layers in which the phenyl rings are nearly parallel. In (I), the ammonium and sulfonate groups are arranged so that a two-dimensional network of intra- and intermolecular N—H···O hydrogen bonds exists on the faces of each layer. Each ammonium H atom is involved in a single hydrogen bond and there are no strong interactions between the layers. In the hydrate (II), the two crystallographically independent molecules adopt a more complicated double-layer structure in which the polar groups and water molecules are located between every other layer. An extensive two-dimensional network of N—H···O and O—H···O hydrogen bonds holds these double layers together, while only weak interactions involving the methyl and phenyl H atoms occur between these slabs. This two-dimensional nature of the intermolecular hydrogen bonding contrasts with that observed in similar sulfonic acids.

Comment

We have recently examined the crystal structures of several amine-substituted arenesulfonic acids (Shubnell & Squattrito, 1994; Gunderman & Squattrito, 1996) in order to compare the stacking patterns in these layered compounds. The present acid, 4-aminotoluene-3-sulfonic acid, is the third isomer of this compound that we have studied and the first for which both anhydrous, (I), and hydrated, (II), forms have been found. All of the compounds exist in the solid state as zwitterions, with the acidic proton on the amine N atom, and all have N—H···$O_{\text{sulfonate}}$ hydrogen bonds as a primary intermolecular interaction. Nonetheless, each compound displays a distinct packing pattern as a consequence of the different arrangement of the hydrogen-bonding groups on the molecule and, in some cases, the differing water content of the crystals. The 4-aminotoluene-3-sulfonic acid molecule is the first isomer in this series to form anhydrous crystals, (I), in water.


(I)


(II)

The structure of the acid molecule, (I), is shown in Fig. 1. The SO_3^- group is staggered with respect to the ring [torsion angle O3—S1—C3—C4 −36.7 (2)°] and there is a strong intramolecular hydrogen bond between H9 and O3 [1.92 (3) Å]. As the packing diagram (Fig. 2) reveals, the molecules are arranged in layers in the *ac* plane that stack in the **b** direction. The phenyl rings are approximately perpendicular to the plane of the layer, while the SO_3^- and NH_3^+ groups are directed towards the faces of the layer, with pairs of molecules in alternating up/down orientations. There are two intermolecular hydrogen bonds linking neighboring mol-

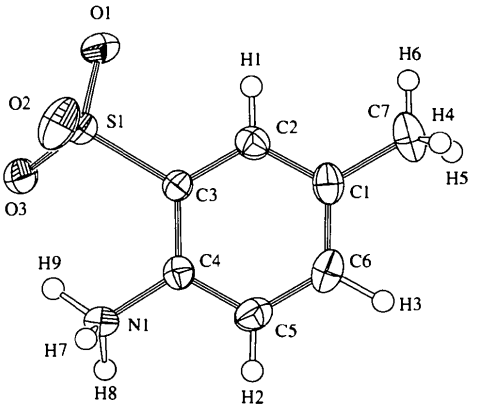


Fig. 1. Molecular diagram of (I) showing the atom-labeling scheme. The displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.