Acta Cryst. (1996). C**52**, 936–940

Arene–Arene Stacking in 6,6′-Diphenyl-3,3′-bi-1,2,4,5-tetrazine and 6-Phenyl-1,2,4,5-tetrazine-3-carbaldehyde Benzoylhydrazone Monohydrate

JOSEF BREU,[a]* KLAUS-JÜRGEN RANGE,[a] NORBERT BIEDERMANN,[b] KONRAD SCHMID[b] AND JÜRGEN SAUER[b]

[a]*Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany, and* [b]*Institut für Organische Chemie, Universität Regensburg, D-93040 Regensburg, Germany. E-mail: josef.breu@chemie.uni-regensburg.de*

(*Received 1 September 1995; accepted 6 November 1995*)

Abstract

Despite the demands of the stronger hydrogen-bonding interactions present in the crystal structures of the title compounds, $C_{16}H_{10}N_8$ and $C_{16}H_{12}N_6O.H_2O$, T-shaped and shifted π-stacked arrangements of aromatic moieties are preferred, leading to herringbone and/or π-stacked crystal-packing motifs. Therefore, in both these compounds the crystal packing is in accordance with the theory of arene–arene interactions being dominated by electrostatics.

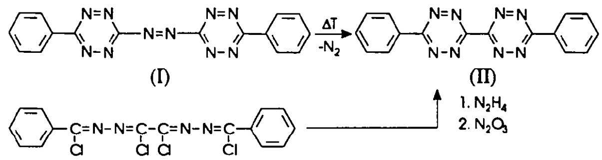
Comment

Non-covalent interactions between aromatic molecules control many molecular recognition and self-assembly processes both in solution and in the solid state (Hunter, 1993), and thus determine the structures and properties of molecular assemblies in biology, chemistry and materials science. These interactions, however, are not well understood. Analyzing crystal-packing patterns of aromatic compounds, extracting common geometric motifs and generalizing from large amounts of crystallographic data is one approach to developing a better understanding of arene–arene interactions (Desiraju & Gavezzotti, 1989).

Recent experimental (Cozzi, Cinquini, Annuziata & Siegel, 1993) and simulation (Jorgensen & Severance, 1990) work shows that most so-called π–π interactions are dominated by electrostatics. The inherent polarity of aromatic systems stems from the electron-rich core being surrounded by an electron-poor torus of H atoms. This electrostatic description accounts for the energetic preference for T-shaped and shifted π-stacked arrangements, leading to herringbone and/or π-stacked crystal-packing motifs (Desiraju & Gavezzotti, 1989), depending on the relative size of the surface areas having opposite sign to the molecular electrostatic potential (MEP).

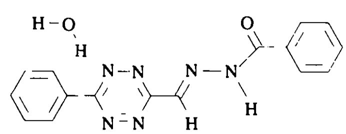
When the aromatic group is only part of the molecule or the MEP is altered by, for example, substitution in the ring, the requirements of the very weak π–π interactions are easily overridden by other forces. The title compounds, 6,6′-diphenyl-3,3′-bi-1,2,4,5-tetrazine, (II), and 6-phenyl-1,2,4,5-tetrazine-3-carbaldehyde benzoylhydrazone monohydrate, (IV), represent examples of this case.

The synthesis of compound (II), by pyrolysis of azocompound (I) with loss of nitrogen, was first reported by Russian workers (Kovalev, Anufriev & Rusinov, 1990). In a straightforward synthetic path, the bitetrazine (II) was obtained, using the tetraimidechloride (III), by ring closure with hydrazine and subsequent oxidation (Biedermann & Sauer, 1994). As the isolated products turned out to be different, proof of the final structure was established by X-ray analysis, which showed that only the compound isolated *via* the second pathway corresponded to structure (II).



(III)

On crystallizing compound (II) without protection from moisture, the tetrazine derivative (IV) was obtained as a degradation product; ring-opening reactions of this type are well documented for 1,2,4,5-tetrazine rings (Neunhoeffer, 1984).



(IV)

The molecular structures of compounds (II) and (IV) are shown in Figs. 1 and 2, respectively. Bond distances and angles for both structures show normal values within experimental error compared with related structures deposited in the Cambridge Structural Database (Allen *et al.*, 1987).

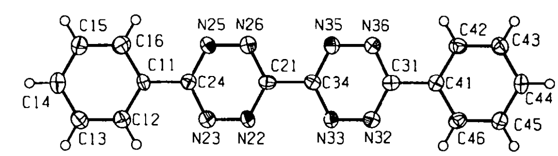


Fig. 1. The molecular structure of compound (II) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

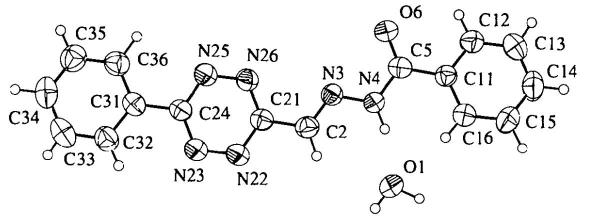


Fig. 2. The molecular structure of compound (IV) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The tetrazine rings in compound (II) are planar, the maximum deviations from the least-squares planes being 0.012 (3), 0.017 (3), 0.032 (3) and 0.034 (3) Å for the pivot atoms C21, C24, C31 and C34, respectively. The dihedral angle between the two tetrazine planes is 7.7 (2)° and that between the phenyl plane and the adjacent tetrazine plane is 2.2 (2)° for the C11–C16 ring and 2.4 (2)° for the C41–C46 ring. The molecule is slightly curved in the line of its long axis.

The tetrazine ring of the decomposition product (IV) is also planar, with maximum deviations from the best least-squares plane of 0.011 (3) and 0.018 (3) Å for the pivot atoms C21 and C24, respectively. The tetrazine ring is almost coplanar with the adjacent phenyl ring, the dihedral angle between them being 2.88 (15)°.

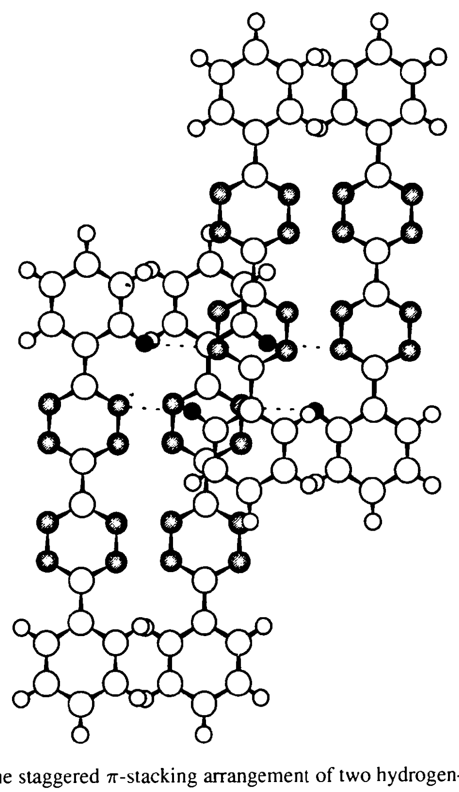


Fig. 3. The staggered π-stacking arrangement of two hydrogen-bonded pairs of (II).

The crystal structure of compound (II) is comprised of C—H···N hydrogen-bonded dimers with a C46···N32^{i} distance of 3.460 (5) Å and a C46—H46···N32^{i} angle of 155.4 (3)° [symmetry code: (i) $1-x$, $1-y$, $-z$] (Fig. 3). The molecules forming the pair are coplanar and shifted by approximately half the length of a molecule along the long axis. The next pair is shifted along the long axis of the molecule and perpendicular to it, yielding a staggered parallel stacking of aromatic rings in the overlapping region, with perpendicular distances from the ring centroids to the parallel plane of between 3.310 and 3.371 Å. Adjacent stacks protrude into the niches apparent in Fig. 3, with a perpendicular orientation of their molecular planes, giving rise to an edge–face arrangement of phenyl rings (Fig. 4).

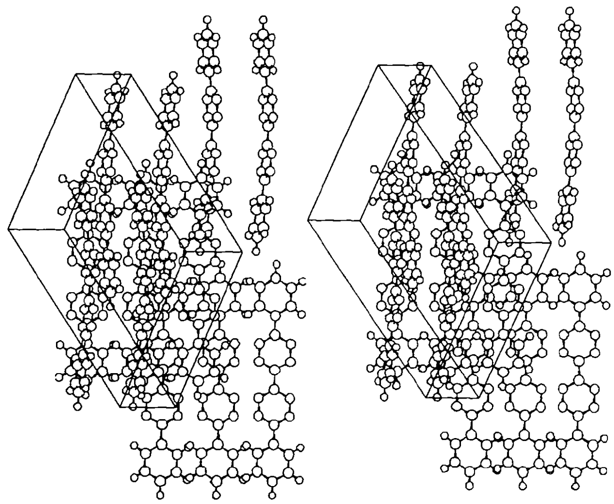


Fig. 4. Stereoscopic view of the unit cell of compound (II).

The crystal structure of (IV) consists of hydrogen-bonded infinite one-dimensional chains of (IV) and water molecules of crystallization (Fig. 5). Two chains are arranged head-to-tail in a staggered parallel stack, these pairs in turn forming a herringbone-like packing pattern (Fig. 6).

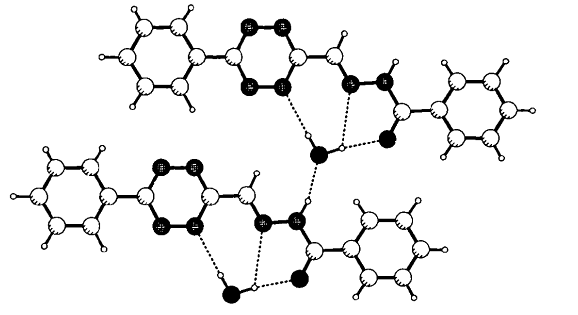


Fig. 5. A view of the one-dimensional infinite hydrogen bonding in compound (IV).

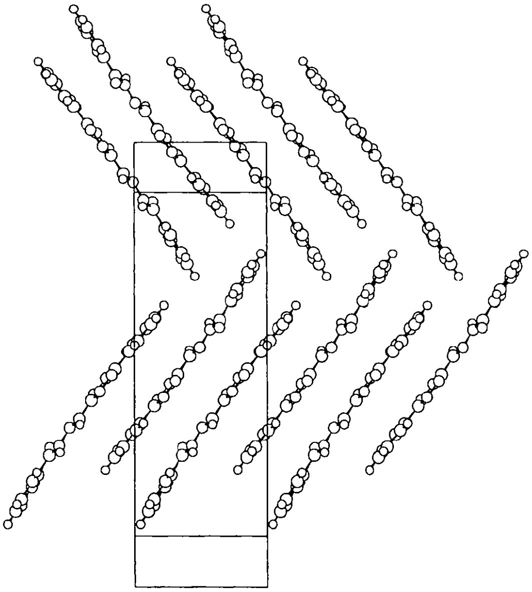


Fig. 6. The molecular packing of compound (IV) showing the herringbone-like arrangement.

Despite the demands of the stronger hydrogen-bonding interactions present in the crystal structures of compounds (II) and (IV), T-shaped and shifted π-stacked arrangements of aromatic moieties are preferred, leading to herringbone and/or π-stacked crystal-packing motifs. The crystal packings of (II) and (IV) are therefore in accordance with the theory of arene–arene interactions being dominated by electrostatics.

Experimental

Compound (II)

Crystal data

$C_{16}H_{10}N_8$
$M_r = 314.31$
Monoclinic
$P2_1/c$
$a = 14.063\,(3)$ Å
$b = 5.2670\,(5)$ Å
$c = 18.941\,(3)$ Å
$\beta = 98.387\,(14)°$
$V = 1388.0\,(4)$ Å^3
$Z = 4$
$D_x = 1.504$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1187 reflections
$\theta = 2.17–23.79°$
$\mu = 0.10$ mm^{-1}
$T = 173\,(2)$ K
Coffin
$0.16 \times 0.12 \times 0.09$ mm
Red

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction: none
3638 measured reflections
1668 independent reflections

788 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0411$
$\theta_{max} = 23.79°$
$h = -15 \rightarrow 6$
$k = -5 \rightarrow 5$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R(F) = 0.0378$
$wR(F^2) = 0.0886$
$S = 0.745$
1668 reflections
217 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.127$ e Å^{-3}
$\Delta\rho_{min} = -0.137$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N22	0.2912 (3)	0.7335 (5)	0.20176 (14)	0.0324 (16)
N23	0.2171 (3)	0.7420 (5)	0.23762 (14)	0.0362 (16)
N25	0.2842 (3)	1.1089 (5)	0.29904 (14)	0.0323 (16)
N26	0.3585 (3)	1.0988 (4)	0.26384 (13)	0.0330 (16)
N32	0.5053 (3)	0.7311 (5)	0.08287 (12)	0.0309 (16)
N33	0.4386 (3)	0.7229 (5)	0.12495 (13)	0.0302 (13)
N35	0.5048 (3)	1.0928 (5)	0.18505 (13)	0.0310 (16)
N36	0.5723 (3)	1.1010 (4)	0.14294 (12)	0.0294 (12)
C11	0.1303 (3)	0.9517 (6)	0.32127 (15)	0.0252 (14)
C12	0.0576 (4)	0.7740 (6)	0.3086 (2)	0.0344 (16)
C13	−0.0223 (4)	0.7881 (6)	0.3431 (2)	0.0384 (19)
C14	−0.0302 (4)	0.9812 (6)	0.3912 (2)	0.0396 (16)
C15	0.0428 (4)	1.1585 (6)	0.4048 (2)	0.0374 (16)
C16	0.1216 (4)	1.1459 (6)	0.3700 (2)	0.0365 (19)
C21	0.3594 (3)	0.9124 (5)	0.21529 (15)	0.0272 (16)
C24	0.2153 (3)	0.9356 (6)	0.28439 (14)	0.0252 (16)
C31	0.5690 (3)	0.9244 (6)	0.09101 (14)	0.0262 (16)
C34	0.4385 (3)	0.9103 (5)	0.17269 (15)	0.0250 (16)
C41	0.6409 (3)	0.9405 (5)	0.04213 (14)	0.0257 (16)
C42	0.7065 (4)	1.1364 (5)	0.04714 (15)	0.0304 (16)
C43	0.7753 (4)	1.1475 (6)	0.00253 (15)	0.0315 (16)
C44	0.7788 (3)	0.9619 (5)	−0.04905 (15)	0.0323 (16)
C45	0.7122 (4)	0.7673 (6)	−0.0560 (2)	0.0306 (16)
C46	0.6438 (4)	0.7548 (6)	−0.01088 (15)	0.0313 (16)

Table 2. *Selected geometric parameters (Å, °) for (II)*

N22—N23	1.325 (5)	N32—N33	1.317 (5)
N22—C21	1.342 (5)	N32—C31	1.350 (5)
N23—C24	1.353 (4)	N33—C34	1.339 (4)
N25—N26	1.320 (5)	N35—N36	1.327 (5)
N25—C24	1.331 (5)	N35—C34	1.336 (5)
N26—C21	1.346 (4)	N36—C31	1.350 (4)
N23—N22—C21	118.2 (3)	N26—C21—C34	117.7 (3)
N22—N23—C24	116.9 (3)	N23—C24—N25	124.8 (4)
N26—N25—C24	118.2 (3)	N23—C24—C11	116.6 (3)
N25—N26—C21	117.5 (3)	N25—C24—C11	118.6 (3)
N33—N32—C31	118.3 (3)	N32—C31—N36	123.7 (3)
N32—N33—C34	117.1 (3)	N32—C31—C41	118.5 (3)
N36—N35—C34	117.4 (3)	N36—C31—C41	117.8 (3)
N35—N36—C31	117.7 (3)	N33—C34—N35	125.4 (4)
N22—C21—N26	124.4 (4)	N33—C34—C21	116.9 (3)
N22—C21—C34	117.9 (3)	N35—C34—C21	117.7 (3)

Compound (IV)

Crystal data

$C_{16}H_{12}N_6O.H_2O$
$M_r = 322.33$

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å

Monoclinic
$P2_1/c$
$a = 6.5300$ (3) Å
$b = 8.6338$ (6) Å
$c = 27.7016$ (9) Å
$\beta = 96.052$ (3)°
$V = 1553.08$ (14) Å^3
$Z = 4$
$D_x = 1.378$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 9.38–22.22°$
$\mu = 0.80$ mm^{-1}
$T = 293$ (2) K
Lath
0.2 × 0.06 × 0.03 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2460 measured reflections
2404 independent reflections
1230 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0317$
$\theta_{max} = 64.98°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 31$
3 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0428$
$wR(F^2) = 0.1186$
$S = 0.808$
2404 reflections
263 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.165$ e Å^{-3}
$\Delta\rho_{min} = -0.155$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0016 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (IV)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O6	1.0234 (3)	1.1390 (3)	0.15423 (7)	0.0688 (9)
N3	0.8324 (3)	0.9912 (3)	0.07980 (8)	0.0501 (10)
N4	0.7245 (4)	1.0696 (3)	0.11113 (8)	0.0516 (9)
N22	0.7262 (4)	0.7628 (3)	−0.02503 (8)	0.0640 (11)
N23	0.8202 (4)	0.6728 (3)	−0.05451 (8)	0.0632 (12)
N25	1.1377 (4)	0.7154 (3)	−0.00664 (8)	0.0571 (11)
N26	1.0436 (4)	0.8063 (3)	0.02250 (8)	0.0540 (11)
C2	0.7291 (5)	0.9169 (3)	0.04545 (11)	0.0537 (12)
C5	0.8342 (4)	1.1430 (3)	0.14923 (10)	0.0507 (12)
C11	0.7170 (4)	1.2298 (3)	0.18333 (9)	0.0469 (11)
C12	0.8222 (5)	1.2749 (4)	0.22693 (11)	0.0715 (14)
C13	0.7230 (6)	1.3584 (5)	0.25979 (13)	0.0897 (16)
C14	0.5214 (7)	1.3986 (5)	0.24988 (14)	0.0797 (16)
C15	0.4154 (5)	1.3553 (4)	0.20695 (13)	0.0696 (12)
C16	0.5129 (5)	1.2710 (4)	0.17334 (11)	0.0572 (12)
C21	0.8404 (4)	0.8256 (3)	0.01267 (10)	0.0477 (12)
C24	1.0220 (4)	0.6478 (3)	−0.04408 (9)	0.0480 (12)
C31	1.1275 (5)	0.5427 (3)	−0.07528 (9)	0.0499 (12)
C32	1.0195 (5)	0.4739 (4)	−0.11527 (11)	0.0647 (12)
C33	1.1208 (7)	0.3764 (4)	−0.14439 (13)	0.0807 (16)
C34	1.3257 (7)	0.3456 (4)	−0.13421 (14)	0.0755 (14)
C35	1.4322 (6)	0.4114 (4)	−0.09409 (14)	0.0718 (12)
C36	1.3352 (5)	0.5103 (4)	−0.06505 (12)	0.0624 (12)
O1	0.3048 (3)	0.9593 (3)	0.10778 (8)	0.0729 (10)

Table 4. *Selected geometric parameters (Å, °) for (IV)*

O6—C5	1.229 (3)	N22—C21	1.333 (4)
N3—N4	1.355 (3)	N23—C24	1.337 (4)
N3—C2	1.279 (4)	N25—N26	1.323 (3)
N4—C5	1.367 (4)	N25—C24	1.350 (3)
N22—N23	1.324 (3)	N26—C21	1.337 (4)
N4—N3—C2	117.2 (2)	O6—C5—C11	121.6 (2)
N3—N4—C5	117.4 (2)	N4—C5—C11	117.6 (2)
N23—N22—C21	117.7 (2)	N22—C21—N26	124.8 (3)
N22—N23—C24	118.2 (2)	N22—C21—C2	115.8 (2)
N26—N25—C24	117.8 (2)	N26—C21—C2	119.4 (3)
N25—N26—C21	117.7 (2)	N23—C24—N25	123.7 (2)
N3—C2—C21	118.5 (3)	N23—C24—C31	118.9 (2)
O6—C5—N4	120.8 (3)	N25—C24—C31	117.3 (2)

Table 5. *Hydrogen-bonding geometry (Å, °) for (IV)*

D—H···A	H···A	D—H···A
O1—H1A···O6^{i}	1.84 (4)	174 (3)
O1—H1A···N3^{i}	2.57 (4)	115 (3)
O1—H1B···N26^{i}	2.19 (4)	176 (4)
N4—H4···O11^{i}	2.05 (3)	158 (2)

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

The H atoms of compound (II) were calculated in idealized positions and refined using a riding model, with the isotropic displacement parameters set to 1.2 times the equivalent isotropic parameter of the atom to which they are attached. The H atoms of compound (IV) were calculated in idealized positions and refined with common isotropic displacement parameters for similar groups.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (IV). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984) for (IV). Data reduction: *HELENA* (Spek, 1993) for (IV). For both compounds, program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990) and *INSIGHT*II (Biosym Technologies, 1993) for (II); *PLATON* and *PLUTON* (Spek, 1991) for (IV). For both compounds, software used to prepare material for publication: *PLATON*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Biedermann, N. & Sauer, J. (1994). *Tetrahedron Lett.* **35**, 7935–7938.
Biosym Technologies (1993). *INSIGHT*II. Biosym Technologies, San Diego, USA.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Cozzi, F., Cinquini, M., Annuziata, R. & Siegel, J. S. (1993). *J. Am. Chem. Soc.* **115**, 5330–5331.
Desiraju, G. R. & Gavezzotti, A. (1989). *Acta Cryst.* B**45**, 473–482.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Hunter, C. A. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1584–1585.
Jorgensen, W. L. & Severance, D. L. (1990). *J. Am. Chem. Soc.* **112**, 4768–4774.
Kovalev, E. G., Anufriev, V. A. & Rusinov, G. L. (1990). *Khim. Geterotsikl. Soedin.* **12**, 1691–1692; (1991). *Chem. Abstr.* **114**, 207209.

Neunhoeffer, H. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 3, p. 531. New York: Pergamon Press.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Spek, A. L. (1991). *PLUTON. Molecular Graphics Program*. University of Utrecht, The Netherlands.
Spek, A. L. (1993). *HELENA. Program for Data Reduction*. University of Utrecht, The Netherlands.

Acta Cryst. (1996). C**52**, 940–942

3-Amino-4-hydroxybenzenesulfonic Acid Hemihydrate

Brian J. Gunderman and Philip J. Squattrito*

Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA. E-mail: 3clwp5s@cmuvm.csv.cmich.edu

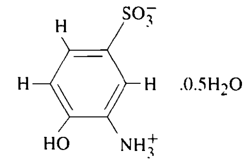
(*Received 10 August 1995; accepted 20 October 1995*)

Abstract

The title compound (3-ammonio-4-hydroxybenzenesulfonate hemihydrate, $C_6H_7NO_4S.\frac{1}{2}H_2O$) crystallizes with two zwitterionic sulfonic acid molecules and one water molecule in the asymmetric unit. The acid molecules pack in layers in which the phenyl rings are nearly coplanar and the polar functional groups are directed towards adjacent layers. These layers stack so that the molecules of one slab are approximately orthogonal to those of the next. There is an extensive network of hydrogen bonds involving the water molecule and the ammonium, hydroxyl and sulfonate groups.

Comment

The present structure is part of a continuing study of the structural patterns in metal arenesulfonate salts (Gunderman & Squattrito, 1994) and sulfonic acids (Shubnell & Squattrito, 1994). These compounds typically form layered structures in which the phenyl rings are in the center of the layer and the sulfonate groups are on the exterior faces. Water molecules and metal ions are found between the layers associated with the sulfonate groups. The exact structure obtained is highly dependent on the nature of the metal ion, if one is present, and on the identity and location of other substituents on the rings. This is certainly true of 3-amino-4-hydroxybenzenesulfonic acid hemihydrate, (I), the first example we have examined to contain three polar substituents.



(I)

As shown in Fig. 1, there are two symmetry-independent molecules, both having the acidic proton on the N atom. The two molecules have nearly identical structural features. The ammonium H atoms are staggered relative to the adjacent hydroxyl group, with the shortest intramolecular H···O contacts being about 2.5 Å. Thus, there does not appear to be strong hydrogen bonding between the hydroxyl and ammonium groups on the same ring, though in both molecules, the C—C—O and C—C—N angles indicate that the two substituents are bent slightly towards one another (Table 2). The most significant difference between the two molecules is that the sulfonate group is rotated approximately 22° about the S—C bond in one relative to the other [torsion angles O(1)—S(1)—C(1)—C(2) 4.2 (3) and O(5)—S(2)—C(7)—C(8) −18.1 (3)°].

Compared to 2-aminotoluene-4-sulfonic acid (Shubnell & Squattrito, 1994), which differs only in having

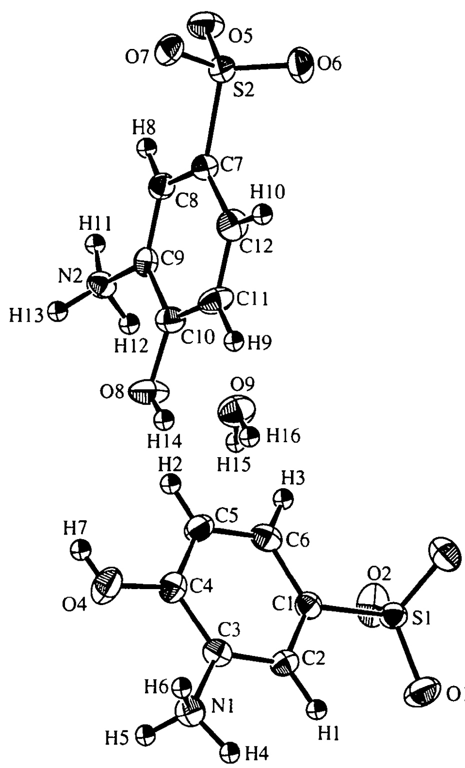


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the two independent sulfonic acid molecules and the water molecule showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.