in each case showed maxima consistent with one major and one minor orientation; this was allowed for in the refinement during which all H atoms were treated as riding atoms (C—H 0.96 and N—H 0.86 Å). The methyl-H-atom occupancies refined to 0.85 (3)/0.15 (3), 0.84 (3)/0.16 (3) and 0.68 (3)/0.32 (3) for the C511, C512 and C62 methyl-H atoms, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PREP*8 (Ferguson, 1998).

We thank Dr J. F. Gallagher and Dublin City University for the funds to purchase the X-ray tube used in the data collections. While no direct support for the research described here was provided by NSERC (Canada), we do thank that organisation for the partial funding of the 1992 upgrade of the CAD-4 diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1260). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 751–754

2,2′-Biphenol–1,10-phenanthroline (1/1): a two-dimensional structure built up from three types of hydrogen bond and π–π stacking interactions

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Abstract

In the title compound, $C_{12}H_{10}O_2\cdot C_{12}H_8N_2$, there is an intramolecular O—H···O hydrogen bond within the 2,2′-biphenol component which is linked to the 1,10-phenanthroline component *via* a three-centre hydrogen bond involving both N atoms as acceptors. The bimolecular aggregates are linked by C—H···O hydrogen bonds into spiral chains along [010], and these, in turn, are linked into a sheet parallel to (101) by π–π stacking interactions between pairs of 1,10-phenanthroline units related by centres of inversion.

Comment

The heterocyclic diamine 2,2′-bipyridyl has been widely used as a chelating ligand for metal ions (Reedijk, 1987); in such an application, the two N atoms are necessarily located on the same edge of the near planar ligand. However, in pure 2,2′-bipyridyl, the molecules lie across centres of inversion, so that the N atoms lie on opposite edges (Merritt & Schroeder, 1956; Chisholm *et al.*, 1981). The ease of rotation about the central C—C bond is illustrated by the values of the dihedral angle between the two heteroaryl rings in hydrogen-bonded adducts of 2,2′-bipyridyl. In the 1:1 adduct with 4,4′-sulfonyldiphenol, the 2,2′-bipyridyl molecule has a conformation close to *trans*-planar, with a dihedral angle of 8.4 (1)° (Lavender *et al.*, 1998*a*), while in the 1:2 adduct with 1,3,5-trihydroxybenzene, the two independent 2,2′-bipyridyl molecules are again close to *trans*-planar in conformation, with dihedral angles of 15.0 (1) and 14.7 (1)° (Lavender *et al.*, 1998*b*). In contrast, when 2,2′-bipyridyl molecules are captured in the cavity formed by paired C-methylcalix[4]resorcinarene molecules, the dihedral angle is 40.4 (1)° (Ferguson *et al.*, 1998).

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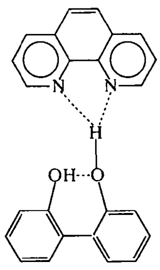
In the related diamine 1,10-phenanthroline, the arrangement of the two N atoms is fixed by the presence of the C5—C6 bridge, affording control of the mutual orientation of the hydrogen-bond acceptor sites. Hence, it may be expected that the action of 1,10-phenanthroline as a hydrogen-bond acceptor might reflect its behaviour as a chelating ligand (Reedijk, 1987), with a single donor H atom mimicking the role of the metal centre. The 1:1 adduct formed between 2,2′-biphenol and 1,10-phenanthroline, $C_{12}H_{10}O_2{\cdot}C_{12}H_8N_2$, (I), whose structure is reported here, provides a simple test of these ideas.



(I)

The asymmetric unit of (I) contains one molecule of each component. Within the 2,2′-biphenol component, the dihedral angle between the two aryl rings is 42.7 (1)°, no doubt determined in large part by the geometric requirements of the intramolecular O—H···O hydrogen bond (Table 2), which forms an *S*(7) motif (Bernstein *et al.*, 1995). This biphenol molecule thus has a free hydroxyl group, and this acts as a hydrogen-bond donor to both N atoms of the 1,10-phenanthroline component, in an $R_1^2(5)$ motif, so that the complete graph-set descriptor for the hard hydrogen bonds can be written as $S(7)R_1^2(5)$. The three-centre hydrogen bond is rather asymmetric, with significantly different O···N and H···O distances for the two N atoms (Table 2); nonetheless, 1,10-phenanthroline can be regarded here as a chelating ligand to hydrogen. The sum of angles around this H atom is very close to 360°.

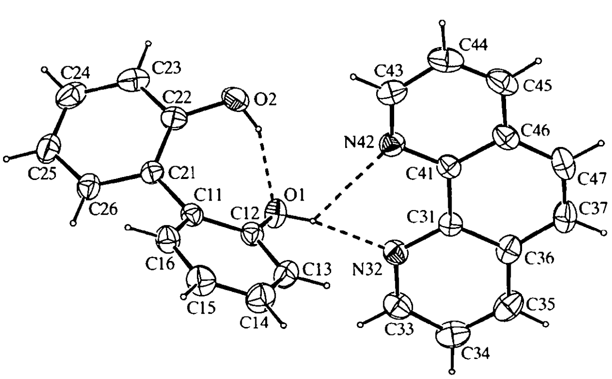


Fig. 1. A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The O2 atom is not used as an acceptor of a hard hydrogen bond; the excess of hard acceptors over donors leads not only to the formation of a three-centre hydrogen bond with two acceptors and one donor, but also to the formation of soft hydrogen bonds. C—H···O hydrogen bonds link the bimolecular aggregates formed by the hard hydrogen bonds into spiral chains running parallel to the [010] direction. Atom C16 in the biphenol at (*x*, *y*, *z*) acts as donor to oxygen O2 at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$), and C16 at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$), in turn, acts as donor to O2 at (*x*, $-1 + y$, *z*), so generating a *C*(6) spiral around the 2_1 axis along ($\frac{1}{4}$, *y*, $\frac{1}{4}$) (Fig. 2). Two such spiral chains run through each unit cell; the second lies around the 2_1 axis along ($\frac{3}{4}$, *y*, $\frac{3}{4}$). Each spiral takes the form of a 'stem-and-leaves' motif, with the 2,2′-biphenol molecules generating the stem and the 1,10-phenanthroline components acting as leaves in alternate habit.

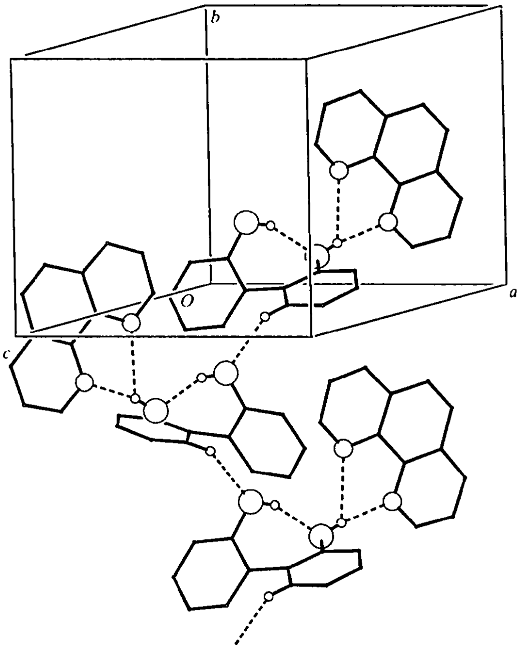


Fig. 2. A view of part of the crystal structure of (I), showing one of the [010] spirals.

These spiral chains are themselves linked by π–π interactions between neighbouring 1,10-phenanthroline units. The phenanthroline units in the aggregates at (*x*, *y*, *z*) and ($1 - x$, $1 - y$, $-z$) are parallel, with an interplanar separation of only *ca* 3.5 Å (Fig. 3), and this interaction serves to link the chains around ($\frac{1}{4}$, *y*, $\frac{1}{4}$) and ($\frac{3}{4}$, *y*, $-\frac{1}{4}$); the π–π interaction between the phenanthroline units at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) and ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$) similarly serves to link the chains around ($\frac{1}{4}$, *y*, $\frac{1}{4}$) and ($-\frac{1}{4}$, *y*, $\frac{3}{4}$). In this manner, each spiral chain is linked to two neighbouring chains, so forming a sheet parallel to [101].

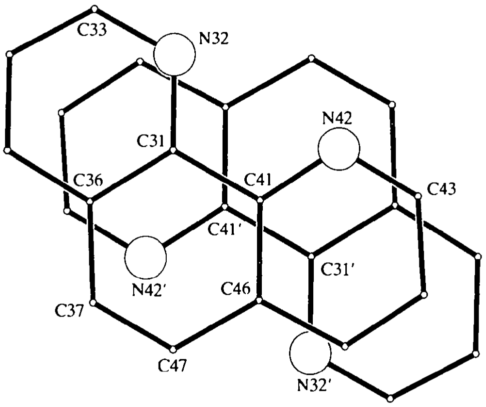


Fig. 3. A view of part of the crystal structure of (I) showing the overlapping 1,10-phenanthroline units at (x, y, z) and ($1 - x$, $1 - y$, $-z$); primed atoms are at ($1 - x$, $1 - y$, $-z$).

The bond distances within the 1,10-phenanthroline component show marked bond fixation, consistent with the presence of two hetero-aromatic rings, together with an essentially isolated double bond in the central ring. The bond lengths and angles are otherwise all typical of their types, and each hydrogen bond is strong for its type.

Experimental

Equimolar quantities of 2,2′-biphenol and 1,10-phenanthroline were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, yielding analytically pure (I). Analysis: found C 78.8, H 4.9, N 7.7%; $C_{24}H_{18}N_2O_2$ requires C 78.7, H 5.0, N 7.7%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{12}H_{10}O_2 \cdot C_{12}H_8N_2$
$M_r = 366.40$
Monoclinic
$P2_1/n$
$a = 9.9485\ (6)$ Å
$b = 9.3724\ (6)$ Å
$c = 20.3571\ (11)$ Å
$\beta = 98.605\ (6)°$
$V = 1876.76\ (19)$ Å^3
$Z = 4$
$D_x = 1.297$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.59–19.58°$
$\mu = 0.083$ mm^{-1}
$T = 294\ (1)$ K
Block
0.42 × 0.40 × 0.33 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4407 measured reflections
4296 independent reflections
2555 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 27.42°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 20 min
intensity variation: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.107$
$S = 1.022$
4296 reflections
256 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.0195P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.160$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.144$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0377 (19)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C12	1.3676 (16)	C36—C37	1.426 (2)
O2—C22	1.3665 (17)	C37—C47	1.330 (2)
C31—N32	1.3573 (17)	C41—N42	1.3562 (17)
C31—C36	1.4101 (19)	C41—C46	1.411 (2)
C31—C41	1.4450 (19)	N42—C43	1.3209 (19)
N32—C33	1.3206 (18)	C43—C44	1.392 (2)
C33—C34	1.384 (2)	C44—C45	1.353 (2)
C34—C35	1.360 (2)	C45—C46	1.396 (2)
C35—C36	1.402 (2)	C46—C47	1.426 (2)

C12—C11—C21—C26	136.47 (14)
C16—C11—C21—C26	−40.79 (18)
C12—C11—C21—C22	−45.92 (19)
C16—C11—C21—C22	136.82 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N32	0.82	1.95	2.7468 (15)	165
O1—H1···N42	0.82	2.55	3.0539 (16)	121
O2—H2···O1	0.82	1.87	2.6293 (14)	154
C16—H16···O2$^{\rm i}$	0.93	2.47	3.3250 (18)	153

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

All H atoms were visible in difference maps and were subsequently treated as riding atoms (C—H 0.93 and O—H 0.82 Å).

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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Polysulfonylamines. CIX.† 1,2,4-Triazolium di(methanesulfonyl)amidate

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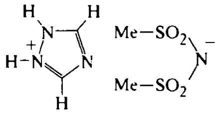
Abstract

The first accurate crystal structure involving the discrete unsubstituted 1,2,4-triazolium cation is reported. In the title salt, $C_2H_4N_3^+\cdot C_2H_6NO_4S_2^-$, the cation is linked to five adjacent anions by a set of N—H···N/O hydrogen bonds and C—H···O interactions, one of the latter being remarkably short and acceptably linear [H···O 2.26 (2), C···O 3.046 (2) Å, C—H···O 161 (2)°]. We suggest on the basis of bond lengths, hydrogen bonding and *U* values that the X-ray structure of $C_2H_4N_3^+\cdot Sb_2F_7^-$ [Udovenko, Gorbunova, Zemnukhova, Mikhailov & Davidovich (1998). *Koord. Khim.* **24**, 655–657; *Russ. J. Coord. Chem.* **24**, 611–613] contains an incorrectly refined cation in which both C atoms have been assigned as N and two N atoms as C.

Comment

The title compound, (I), was investigated as part of a systematic study of hydrogen-bond patterns in crystalline onium di(methanesulfonyl)amidates (Henschel, 1996; Wijaya, 1999). Surprisingly, a search of the October 1998 version of the Cambridge Structural Database (Allen & Kennard, 1993) failed to reveal any crystal structure containing the unsubstituted 1,2,4-triazolium (T^+) cation as a discrete species. Recently we became aware of the X-ray structure of $T^+Sb_2F_7^-$, (II), which mainly focused on the constitution of the fluoroantimonate(III) anion (Udovenko *et al.*, 1998). In this case, published details strongly suggest that the positions of the NH and CH groups in the heterocyclic cation have been erroneously assigned (see below). Thus, in all likelihood, the present result is the first reliable crystal structure of a T^+ salt.



(I)

The formula unit of (I) is shown in Fig. 1. The bond lengths, bond angles and torsion angles of the approximately C_2 symmetric anion are closely similar to those found for the corresponding 1-aza-4-azoniabicyclo[2.2.2]octane salt (Henschel *et al.*, 1997) and will not be rediscussed. Table 1 contains the bond lengths and bond angles of the T^+ heterocyclic ring, which is

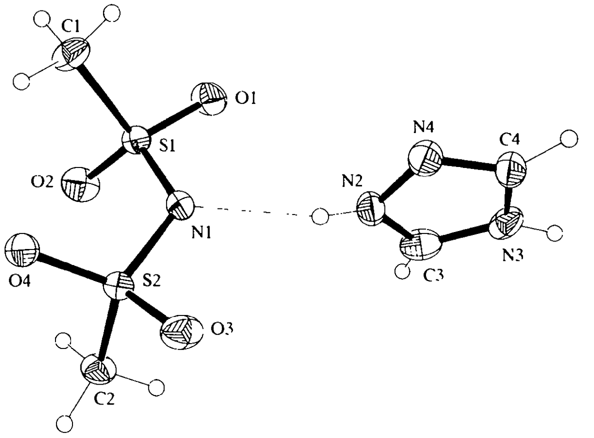


Fig. 1. Structure of the title salt in the crystal. Ellipsoids represent 50% probability levels and H atoms are shown as spheres of an arbitrary radius.

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† Part CVIII: Wirth *et al.* (1998).

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