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

O5—C5	1.206 (2)	C2—C21	1.448 (2)
O6—C6	1.210 (2)	C3—C31	1.449 (2)
C1—C11	1.508 (2)	C4—C5	1.526 (2)
C1—C3	1.515 (2)	C4—C6	1.528 (2)
C1—C2	1.516 (2)	C5—C51	1.473 (2)
C1—C4	1.536 (2)	C6—C61	1.467 (2)
C2—C3	1.297 (2)		
C3—C1—C2	50.66 (8)	C2—C3—C1	64.72 (10)
C3—C1—C4	120.39 (11)	C5—C4—C6	106.37 (10)
C2—C1—C4	119.67 (11)	C5—C4—C1	113.53 (10)
C3—C2—C1	64.62 (10)	C6—C4—C1	111.66 (11)

Friedel opposites were collected (6559 reflections) and merged to give 4608 symmetry-independent reflections. From the systematic absences ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$) the only possible space group is $P2_1/n$ (No. 14). All H atoms were refined with distance restraints for the C—H distances. Disorder was detected in one cyclopropane ring. Therefore, atoms C62 and C63 were each split over two positions with occupancies of 0.5 for each site. In Fig. 1, only positions C62*A* and C63*A* are drawn.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADSHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL-Plus* (Sheldrick, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1296). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaazatriphenylenehexacarboxamide Solvate Exhibiting π-Complexation in the Solid State

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Abstract

1,4,5,8,9,12-Hexaazatriphenylene-2,3,6,7,10,11-hexacarboxamide [HAT-(amide)$_6$], $C_{18}H_{12}N_{12}O_6$, has been crystallized from Me_2SO/water solutions. The unit cell contains two HAT-(amide)$_6$ molecules, four dimethyl sulfoxide (Me_2SO) molecules and one water molecule (formula unit: $C_{18}H_{12}N_{12}O_6.2C_2H_6OS.0.5H_2O$). Pairs of overlapping HAT-(amide)$_6$ molecules form dimers having a one-half ring offset which permits HOMO–LUMO overlap. The C and N atoms of the core rings of one member of the dimer are separated from the best least-squares plane of the core rings of the other member of the dimer by an average distance of 3.31 (9) Å, which is smaller than the sum of the relevant van der Waals radii and is consistent with the π-complexation described by Beeson, Fitzgerald, Gallucci, Gerkin, Rademacher & Czarnik [*J. Am. Chem. Soc.* (1994), **116**, 4621–4622]. Adjacent dimers are separated by a mean distance of 3.69 (9) Å. Some of the amide hydrogen bonds act in concert with the π-complexation in the formation of the dimers. The bond lengths and angles of the HAT core are not uniform. The C—C bonds fall into two distinct groups with means of 1.457 (6) and 1.405 (10) Å; the C—N bonds also fall into two distinct groups with means of 1.350 (2) and 1.322 (7) Å. The 18 atoms comprising the HAT core have a mean deviation of 0.08 (5) Å from the best least-squares plane describing the core. Dihedral angles between the amide-group planes and the least-squares plane of the HAT core range from 10 to 78°. The complex pattern of hydrogen bonding includes intermolecular N—H···O and N—H···N bonds as well as intramolecular N—H···N interactions. Only one cyclic dimer hydrogen-bond is formed. Me_2SO and water molecules are involved in the hydrogen-bonding scheme and act also to complete the packing around the HAT-(amide)$_6$ molecules. The mean values of the 16 intermolecular N—H···O hydrogen bond parameters are: N···O 2.99 (19), H···O 2.02 (24) Å, N—H···O 159 (15)°.

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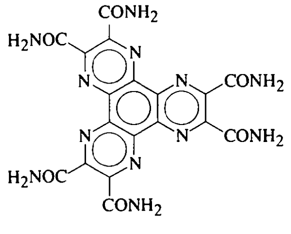
Comment

Various substituted hexaazatriphenylene (HAT) molecules have been synthesized (Kanakarajan & Czarnik, 1986, 1988) and characterized (Kanakarajan & Czarnik, 1989) in order to determine their usefulness in polymers having high thermal and oxidative stability. A number of the substituted HAT molecules studied contain six substituents capable of hydrogen bonding, hexaazatriphenylenehexacarboxamide [HAT-(amide)$_6$] among them.



HAT-(amide)$_6$

The combination of a large aromatic ring system with six symmetrically substituted hydrogen-bonding groups provides a potential opportunity to observe the role of hydrogen bonding and π-complexation in producing a crystalline structure. This report presents full structural results for a HAT-(amide)$_6$ solvate; selected results were presented in an earlier report (Beeson, Fitzgerald, Gallucci, Gerkin, Rademacher & Czarnik, 1994).

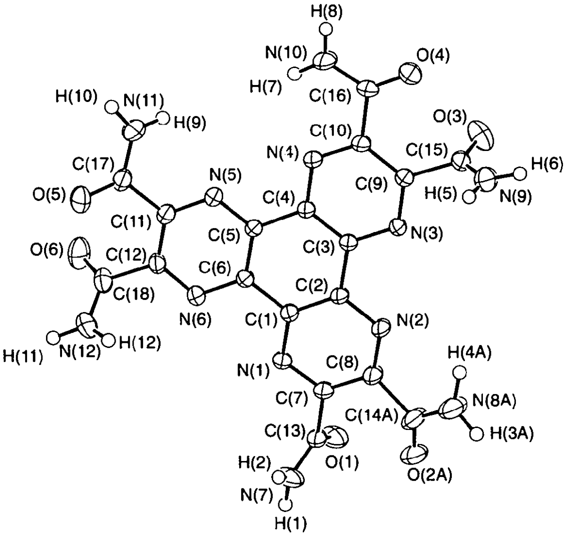
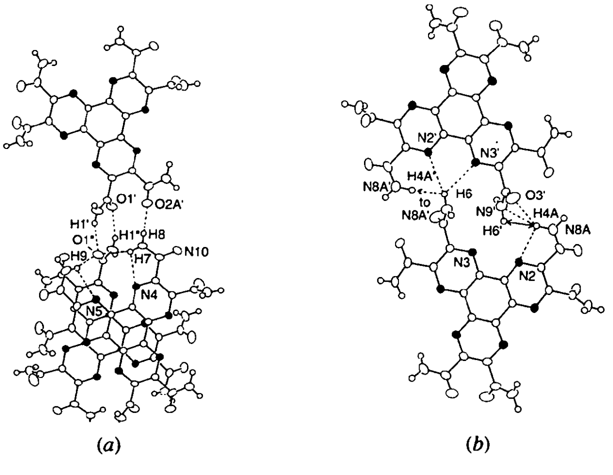


Fig. 1. An *ORTEP*II (Johnson, 1976) view of HAT-(amide)$_6$, showing the atom-numbering scheme. For clarity, one of the (disordered) amide groups at C(8) has been omitted. Displacement ellipsoids are drawn at 50% probability for all atoms except the H atoms, which are of arbitrary size.

The unit cell was found to contain two HAT-(amide)$_6$ molecules, four disordered Me_2SO molecules and a water molecule near an inversion center. The HAT-(amide)$_6$ molecules stack in a closely packed arrangement, with molecules related by inversion and translation along **z**. The spacing of the molecules in the stack is not uniform; rather, the molecules form closely spaced dimers. The C and N atoms of the core rings of one member of each dimer are separated from the best least-squares plane of the core rings of the other member of the dimer by distances that range from 3.16 to 3.51 Å, with an average of 3.31 (9) Å, somewhat less than the expected van der Waals separation of aromatic rings. The corresponding separations between adjacent dimers in the stack range from 3.49 to 3.84 Å, with an average of 3.69 (9) Å. Fig. 2(*a*) shows the overlap of the HAT-(amide)$_6$ molecules in a view down the stack direction. The molecules are offset so that three atoms of one HAT molecule project onto the centers of three of the rings of an adjacent HAT molecule. The pairing of the HAT-(amide)$_6$ molecules and the pattern of overlap indicate that π-system interactions are significant.



(*a*) (*b*)

Fig. 2. *ORTEP*II (Johnson, 1976) views of (*a*) the hydrogen bonding involving H(1), H(7), H(8) and H(9) [symmetry codes: (′) *x*, 1+*y*, *z*; (″) 1−*x*, −*y*, 1−*z*] and (*b*) the hydrogen bonding involving H(4*A*) and H(6) [symmetry code: (′) −*x*, −*y*, 1−*z*]. For clarity, only the amide group *A* at C(8) has been depicted. Ring N atoms have been shaded. Dashed lines indicate the hydrogen-bond interactions.

For structural comparisons we have selected the structure of a closely related compound, 1,10-phenanthroline, which has been reported both as the pure substance (Nishigaki, Yoshioka & Nakatsu, 1978) and as a complex with ammonium picrate (Jones, Milburn, Sawyer & Hughes, 1981). In the present study, the nine C—

C bonds of the HAT core demonstrate a distinct pattern such that three of them [C(2)—C(3), C(4)—C(5) and C(6)—C(1)] are longer, with an average value of 1.457 (6) Å, than the remaining six C—C bonds, that have an average value of 1.405 (10) Å. These values are consistent with those reported for similar bonds in the 1,10-phenanthroline molecules cited above: the long C—C bonds averaged 1.453 (2) Å, the other corresponding C—C bonds averaged 1.400 (26) Å. The 12 C—N bonds of the HAT core are also of two distinct lengths: six have a mean length of 1.350 (2) Å and the remaining six have a mean length of 1.322 (7) Å. Again, this is consistent with the two 1,10-phenanthroline structures in which the C—N bond lengths can be described by the two mean values 1.359 (6) and 1.318 (9) Å. The interior angles of the HAT core have mean values 117.2 (4)° for the six angles centered on N and 120.9 (8)° for the 18 centered on C. The bond lengths of the amide groups are normal, excepting those in the disordered amide group at C(8). The average C—N bond length for the five ordered amides is 1.321 (4) Å, while the average C—O bond length is 1.219 (11) Å. Both averages are in agreement with typical values for amides (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The bond angles of the ordered amide groups are internally consistent except for those of C(13), O(1), N(7). Here the C—C—N and C—C—O angles are nearly equal (see Table 2) whereas the others differ on average by 4.9°. The C(13), O(1), N(7) amide group is also the only one involved in a cyclic-dimer hydrogen bond.

The 18 atoms comprising the HAT core have a mean deviation of 0.08 (5) Å from the best least-squares plane describing these atoms. The mean value is consistent with considerable puckering of the ring system, as is the large standard deviation of the values from the mean. The deviation of the non-H atoms in 1,10-phenanthroline from the best least-squares plane describing these atoms is 0.021 (13) Å for the pure substance (Nishigaki *et al.*, 1978) and 0.026 (18) Å for the complex with ammonium picrate (Jones *et al.*, 1981). Both the means and the standard deviations are notably smaller than for the title compound. A major factor in the non-planar conformation of the present molecule is the interaction of the six amide groups. Three of the four amide pairs have O···O approaches of 3 Å or less: O(1)···O(2*A*) 2.95 (2), O(3)···O(4) 3.000 (3) and O(5)···O(6) 2.981 (3) Å. The dihedral angles of the seven amides groups cover a broad range (10–78°, Table 4). However, the amide N atom is always closer than the amide O atom to the neighboring ring N atom. This can be seen in the N—C—C—N torsion angles, whose magnitudes are all less than 90° (Table 4). The arrangement of the amide groups thus causes the close intramolecular approaches to be between the O atoms as described above. Other nitrogen-containing aromatic ring systems having primary amide substituents *ortho* to the ring N atom, such as quinoline-2-carboxamide, have been found to adopt orientations in which the amide N atoms are rotated toward the ring N atom (Gdaniec, Jaskolski & Kosturkiewicz, 1977, and references therein).

The hydrogen bonding involved in HAT-(amide)$_6$ is complex and is characterized by the absence of arrangements typically found in amide hydrogen bonds. Table 5 lists the hydrogen-bond parameters for the amide H atoms. Only one amide group is found to participate in a cyclic dimer hydrogen bond, N(7)—H(1)···O(1$^{\text{i}}$) [symmetry code: (i) $1-x$, $-1-y$, $1-z$], shown in Fig. 2(*a*). The O(1) atom also intrudes into the bay region of an adjacent amide molecule, thus participating in bifurcated hydrogen-bonding arrangements with H(7) and H(9); the second interaction for H(7) and H(9) is an internal hydrogen bond with N(4) and N(5) as respective acceptors. Among the amide O atoms, O(1), O(2), O(2*A*), O(3) and O(6) accept amide H atoms to form hydrogen bonds. O(4) accepts only water H atoms, forming hydrogen bonds with H(18) and H(17) [*D*—H = 1.00 and 0.93, *D*···*A* = 2.818 (5) and 2.924 (5), H···*A* = 1.84 and 2.33 Å, and *D*—H···*A* = 164 and 121°, for acceptor *A* at $x+1$, y, z and $1-x$, $1-y$, $1-z$, respectively].

The rigid framework of the HAT core to which the amide groups are attached prohibits proper orientation for multiple cyclic hydrogen-bonded dimers to be formed or for all the amide O atoms to be involved as acceptors. The solvent molecules can accommodate the HAT-(amide)$_6$ structure as acceptors for hydrogen bonds [H(2), H(3), H(3*A*), H(10) and H(11)] and to complete packing. The mean values for the intermolecular N—H···O hydrogen bonds formed, given in Table 5, are similar to those reported by Taylor & Kennard (1984) [N···O 2.99 (19), H···O 2.02 (24) Å; N—H···O 159 (15)°]. Amide H atoms H(4), H(4*A*), H(6) and H(12) do not have single strong interactions. Rather, each has multiple weak interactions, with H(6) and H(12) interacting with nitrogen acceptors only. H(6) intrudes into the bay region of the neighboring HAT-(amide)$_6$ molecule related by inversion to form a three-centered bond with ring N atoms N(2$^{\text{v}}$) and N(3$^{\text{v}}$) [symmetry code: (v) $-x$, $-y$, $1-z$; see Fig. 2*b*]. There is also a weak interaction of H(6) with N(8$^{\text{v}}$). Two of the interactions of H(4*A*) can also be seen in Fig. 2(*b*): those with N(2) and N(9$^{\text{v}}$). Also apparent is the close approach of H(4*A*) to H(6$^{\text{v}}$) (1.97 Å). The crowded environment of H(4*A*) [and similarly of H(4), which was omitted from the drawing for clarity] together with a lack of strong hydrogen-bonding interactions may account for the disorder of this amide group. The six intramolecular hydrogen bonds with a mean H···*A* value 2.55 (22) Å (shown in Table 5) are weaker than those described by Gdaniec *et al.* (1977) for which the mean H···*A* value was 2.24 (8) Å. However, the values reported by Gdaniec *et al.* (1977) were for structures more nearly planar than the HAT-(amide)$_6$ molecule reported here.

The manner in which some of the hydrogen bonds act in concert with π-complexation to generate the dimer arrangement is notable. The two HAT-(amide)$_6$ molecules of a dimer share bifurcated hydrogen bonds, H(7) and H(9) being the donor H atoms and O(1^{iii}) [symmetry code: (iii) $1 - x, -y, 1 - z$] being the acceptor, as illustrated by dashed lines in Fig. 2(*a*). There is also a weak interaction of H(4) with O(6^{iii}). Additionally these three H atoms have the strongest intramolecular hydrogen-bonding interactions as evidenced by their N—H···N distances (Table 5) and N—C—C—N torsion angles (Table 4). This cooperative effect among inter- and intramolecular hydrogen bonding must play a major role in helping to create the π-complexation in the present electron-deficient heterocycle which, based on X-ray analysis of other electron-deficient aromatic heterocycles (see Table 1 in Beeson *et al.*, 1994), should be predisposed to avoid π-complexation.

Although the water H-atom coordinates were fixed from a difference map, the geometry is quite satisfactory [O(9)—H(17) 0.93, O(9)—H(18) 1.00 Å, H(17)—O(9)—H(18) 108°]. Moreover, the hydrogen bonding involving the water molecule is plausible (Table 5).

Experimental

Hexaazatriphenylenehexacarboxamide [HAT-(amide)$_6$] (I) was prepared according to the method of Kanakarajan & Czarnik (1986). Crystals were obtained by vapor diffusion of water into Me_2SO solutions. Crystals from undisturbed growths were mainly straw-colored hexagonal rods that decomposed quickly upon removal from the mother liquor. The crystal system of these rods was determined to be trigonal (see Beeson *et al.*, 1994). Crystals from growths which had been disturbed, however, were clear amber plates, rectangular in cross-section, that were stable upon removal from the mother liquor. An experimental sample of the latter type was mounted on a glass pin with epoxy cement and coated with Apiezon L grease. The crystal density D_m was measured by flotation.

Crystal data

$C_{18}H_{12}N_{12}O_6.2C_2H_6OS.0.5H_2O$
$M_r = 657.63$
Triclinic
$P\bar{1}$
$a = 12.723\ (4)$ Å
$b = 13.429\ (2)$ Å
$c = 8.737\ (7)$ Å
$\alpha = 103.54\ (3)°$
$\beta = 99.02\ (5)°$
$\gamma = 92.72\ (4)°$
$V = 1428\ (2)$ Å^3
$Z = 2$
$D_x = 1.529$ Mg m^{-3}
$D_m = 1.56$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.3–14.9°$
$\mu = 0.246$ mm^{-1}
$T = 296$ K
Plate
0.46 × 0.38 × 0.19 mm
Amber

Data collection

AFC-5*S* diffractometer
$\omega–2\theta$ scans
Absorption correction: six ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.955$, $T_{max} = 1.000$
8671 measured reflections
8312 independent reflections
4120 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.016$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 17$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 12$
6 standard reflections monitored every 150 reflections intensity variation: ±3.9% (average max. relative intensity)

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.052$
$S = 1.68$
4120 reflections
536 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974) for C, O, N, S and from Stewart, Davidson & Simpson (1965) for H

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

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

	x	*y*	*z*	U_{eq}
O(1)	0.4726 (2)	−0.3731 (1)	0.5706 (2)	0.0439 (6)
O(2)†	0.225 (1)	−0.429 (1)	0.391 (2)	0.092 (4)
O(2*A*)†	0.241 (1)	−0.418 (1)	0.452 (2)	0.056 (3)
O(3)	0.0863 (2)	0.1969 (2)	0.6908 (3)	0.0591 (7)
O(4)	0.1168 (2)	0.3328 (2)	0.4705 (3)	0.0555 (7)
O(5)	0.6829 (2)	0.1369 (2)	−0.0145 (2)	0.0422 (6)
O(6)	0.8109 (2)	0.0302 (2)	0.2043 (2)	0.0506 (6)
N(1)	0.4567 (2)	−0.2123 (1)	0.3475 (2)	0.0264 (5)
N(2)	0.2570 (2)	−0.1651 (2)	0.4258 (3)	0.0374 (6)
N(3)	0.1965 (2)	0.0311 (1)	0.4568 (2)	0.0257 (5)
N(4)	0.3228 (2)	0.1779 (1)	0.3702 (2)	0.0279 (5)
N(5)	0.4970 (2)	0.1206 (2)	0.2323 (2)	0.0279 (5)
N(6)	0.5731 (2)	−0.0715 (1)	0.2317 (2)	0.0272 (5)
N(7)	0.4634 (2)	−0.4434 (2)	0.3065 (3)	0.0454 (8)
N(8)†	0.1633 (4)	−0.2891 (4)	0.5897 (7)	0.056 (2)
N(8*A*)†	0.1083 (5)	−0.3329 (4)	0.394 (1)	0.095 (3)
N(9)	−0.0183 (2)	0.1105 (2)	0.4623 (4)	0.0473 (8)
N(10)	0.2774 (2)	0.3722 (2)	0.4109 (4)	0.0525 (9)
N(11)	0.6091 (3)	0.2646 (2)	0.1395 (4)	0.0546 (9)
N(12)	0.7318 (2)	−0.1114 (2)	0.0189 (3)	0.0467 (8)
C(1)	0.4193 (2)	−0.1207 (2)	0.3414 (3)	0.0235 (6)
C(2)	0.3216 (2)	−0.0951 (2)	0.3887 (3)	0.0247 (6)
C(3)	0.2876 (2)	0.0079 (2)	0.4000 (3)	0.0234 (6)
C(4)	0.3502 (2)	0.0806 (2)	0.3564 (3)	0.0234 (6)
C(5)	0.4460 (2)	0.0516 (2)	0.2918 (3)	0.0234 (6)
C(6)	0.4820 (2)	−0.0457 (2)	0.2872 (3)	0.0233 (6)
C(7)	0.3950 (2)	−0.2778 (2)	0.3940 (3)	0.0287 (6)
C(8)	0.2925 (2)	−0.2555 (2)	0.4250 (4)	0.0406 (8)
C(9)	0.1712 (2)	0.1272 (2)	0.4734 (3)	0.0258 (6)
C(10)	0.2349 (2)	0.2012 (2)	0.4286 (3)	0.0270 (6)
C(11)	0.5842 (2)	0.0944 (2)	0.1744 (3)	0.0272 (6)
C(12)	0.6244 (2)	−0.0017 (2)	0.1782 (3)	0.0265 (6)
C(13)	0.4458 (2)	−0.3719 (2)	0.4294 (3)	0.0324 (7)
C(14)†	0.2265 (8)	−0.3282 (7)	0.488 (1)	0.040 (2)
C(14*A*)†	0.2069 (9)	−0.3487 (9)	0.407 (1)	0.050 (3)
C(15)	0.0746 (2)	0.1504 (2)	0.5529 (3)	0.0333 (7)
C(16)	0.2040 (2)	0.3096 (2)	0.4390 (3)	0.0361 (7)
C(17)	0.6319 (2)	0.1685 (2)	0.0921 (3)	0.0315 (7)
C(18)	0.7322 (2)	−0.0267 (2)	0.1332 (3)	0.0336 (7)
S(1)	0.9814 (2)	0.1865 (2)	0.0982 (2)	0.0555 (6)
O(7)	1.0850 (8)	0.1560 (7)	0.136 (1)	0.067 (2)
C(19)	0.9237 (3)	0.1095 (4)	−0.0883 (4)	0.085 (1)
C(20)	0.977 (1)	0.3017 (7)	0.028 (1)	0.210 (7)
S(1*A*)†	1.0049 (3)	0.2246 (3)	0.0473 (6)	0.073 (1)
O(7*A*)†	1.100 (1)	0.200 (1)	0.103 (2)	0.097 (5)

C(20*A*)†	0.9154 (8)	0.2668 (8)	0.170 (1)	0.078 (4)
S(2)	0.2936 (2)	0.4623 (1)	0.8657 (3)	0.0781 (7)
O(8)	0.3624 (7)	0.5534 (3)	0.9875 (5)	0.085 (2)
C(21)	0.337 (1)	0.353 (1)	0.923 (2)	0.171 (6)
C(22)	0.1687 (10)	0.4505 (10)	0.945 (2)	0.184 (6)
S(2*A*)†	0.265 (1)	0.4770 (9)	0.954 (3)	0.200 (6)
O(8*A*)†	0.3371	0.5564	0.9881	0.111 (9)
C(21*A*)†	0.328 (2)	0.356 (2)	0.884 (4)	0.092 (8)
C(22*A*)†	0.182 (4)	0.473 (3)	0.826 (5)	0.25 (2)
O(9)	0.9765 (4)	0.4779 (3)	0.3976 (6)	0.073 (2)

† Occupancy factors: 0.53 (1) for O(2), N(8) and C(14); 0.47 (1) for O(2*A*), N(8*A*) and C(14*A*); 0.62 (1) for S(1), O(7) and C(20); 0.38 (1) for S(1*A*), O(7*A*) and C(20*A*); 0.73 (1) for S(2), O(8), C(21) and C(22); 0.27 (1) for S(2*A*), O(8*A*), C(21*A*) and C(22*A*).

Table 2. *Selected bond lengths (Å) and angles (°)*

O(1)—C(13)	1.231 (3)	C(1)—C(6)	1.463 (3)
O(2)—C(14)	1.41 (2)	C(2)—C(3)	1.455 (3)
O(2*A*)—C(14*A*)	1.17 (2)	C(3)—C(4)	1.389 (3)
O(3)—C(15)	1.202 (3)	C(4)—C(5)	1.453 (3)
O(4)—C(16)	1.221 (3)	C(5)—C(6)	1.399 (3)
O(5)—C(17)	1.225 (3)	C(7)—C(8)	1.406 (3)
O(6)—C(18)	1.219 (3)	C(7)—C(13)	1.519 (3)
N(1)—C(1)	1.349 (3)	C(8)—C(14)	1.512 (10)
N(1)—C(7)	1.325 (3)	C(8)—C(14*A*)	1.58 (1)
N(2)—C(2)	1.347 (3)	C(9)—C(10)	1.415 (3)
N(2)—C(8)	1.313 (3)	C(9)—C(15)	1.515 (3)
N(3)—C(3)	1.352 (3)	C(10)—C(16)	1.512 (3)
N(3)—C(9)	1.326 (3)	C(11)—C(12)	1.416 (3)
N(4)—C(4)	1.351 (3)	C(11)—C(17)	1.513 (3)
N(4)—C(10)	1.321 (3)	C(12)—C(18)	1.516 (3)
N(5)—C(5)	1.351 (3)	S(1)—O(7)	1.411 (10)
N(5)—C(11)	1.319 (3)	S(1)—C(19)	1.740 (4)
N(6)—C(6)	1.353 (3)	S(1)—C(20)	1.79 (1)
N(6)—C(12)	1.331 (3)	C(19)—S(1*A*)	1.862 (5)
N(7)—C(13)	1.318 (3)	S(1*A*)—O(7*A*)	1.32 (2)
N(8)—C(14)	1.32 (1)	S(1*A*)—C(20*A*)	1.71 (1)
N(8*A*)—C(14*A*)	1.27 (1)	S(2)—O(8)	1.548 (5)
N(9)—C(15)	1.326 (4)	S(2)—C(21)	1.74 (1)
N(10)—C(16)	1.317 (4)	S(2)—C(22)	1.84 (1)
N(11)—C(17)	1.322 (3)	S(2*A*)—O(8*A*)	1.322 (9)
N(12)—C(18)	1.324 (4)	S(2*A*)—C(21*A*)	1.86 (3)
C(1)—C(2)	1.403 (3)	S(2*A*)—C(22*A*)	1.40 (4)
C(1)—N(1)—C(7)	116.9 (2)	N(5)—C(11)—C(17)	116.1 (2)
C(2)—N(2)—C(8)	117.1 (2)	C(12—C(11)—C(17)	122.6 (2)
C(3)—N(3)—C(9)	117.0 (2)	N(6)—C(12)—C(11)	121.7 (2)
C(4)—N(4)—C(10)	117.3 (2)	N(6)—C(12)—C(18)	116.6 (2)
C(5)—N(5)—C(11)	117.7 (2)	C(11)—C(12)—C(18)	121.6 (2)
C(6)—N(6)—C(12)	117.1 (2)	O(1)—C(13)—N(7)	124.9 (2)
N(1)—C(1)—C(2)	121.1 (2)	O(1)—C(13)—C(7)	117.7 (2)
N(1)—C(1)—C(6)	119.8 (2)	N(7)—C(13)—C(7)	117.3 (2)
C(2)—C(1)—C(6)	119.1 (2)	O(2)—C(14)—N(8)	130 (1)
N(2)—C(2)—C(1)	120.9 (2)	O(2)—C(14)—C(8)	108.4 (10)
N(2)—C(2)—C(3)	118.2 (2)	N(8)—C(14)—C(8)	118.6 (7)
C(1)—C(2)—C(3)	120.9 (2)	O(2*A*)—C(14*A*)—N(8*A*)	122 (1)
N(3)—C(3)—C(2)	118.8 (2)	O(2*A*)—C(14*A*)—C(8)	114 (1)
N(3)—C(3)—C(4)	121.6 (2)	N(8*A*)—C(14*A*)—C(8)	119.0 (9)
C(2)—C(3)—C(4)	119.6 (2)	O(3)—C(15)—N(9)	125.1 (3)
N(4)—C(4)—C(3)	121.2 (2)	O(3)—C(15)—C(9)	120.0 (3)
N(4)—C(4)—C(5)	119.1 (2)	N(9)—C(15)—C(9)	114.8 (3)
C(3)—C(4)—C(5)	119.7 (2)	O(4)—C(16)—N(10)	125.4 (2)
N(5)—C(5)—C(4)	117.7 (2)	O(4)—C(16)—C(10)	120.3 (2)
N(5)—C(5)—C(6)	121.2 (2)	N(10)—C(16)—C(10)	114.4 (2)
C(4)—C(5)—C(6)	121.0 (2)	O(5)—C(17)—N(11)	125.0 (3)
N(6)—C(6)—C(1)	119.8 (2)	O(5)—C(17)—C(11)	120.2 (2)
N(6)—C(6)—C(5)	121.0 (2)	N(11)—C(17)—C(11)	114.7 (2)
C(1)—C(6)—C(5)	119.2 (2)	O(6)—C(18)—N(12)	125.6 (3)
N(1)—C(7)—C(8)	121.4 (2)	O(6)—C(18)—C(12)	118.6 (2)
N(1)—C(7)—C(13)	116.3 (2)	N(12)—C(18)—C(12)	115.8 (2)
C(8)—C(7)—C(13)	122.0 (2)	O(7)—S(1)—C(19)	107.4 (4)
N(2)—C(8)—C(7)	122.0 (2)	O(7)—S(1)—C(20)	114.8 (6)
N(2)—C(8)—C(14)	116.6 (4)	C(19)—S(1)—C(20)	92.7 (4)
N(2)—C(8)—C(14*A*)	117.4 (5)	C(19)—S(1)—C(20*A*)	115.3 (4)
C(7)—C(8)—C(14)	120.4 (4)	C(19)—S(1*A*)—O(7*A*)	110.6 (8)
C(7)—C(8)—C(14*A*)	118.0 (5)	C(19)—S(1*A*)—C(20*A*)	99.4 (4)
N(3)—C(9)—C(10)	121.4 (2)	O(8)—S(2)—C(21)	104.7 (6)
N(3)—C(9)—C(15)	114.2 (2)	O(8)—S(2)—C(22)	105.0 (6)
C(10)—C(9)—C(15)	124.3 (2)	C(21)—S(2)—C(22)	91.5 (7)
N(4)—C(10)—C(9)	121.5 (2)	O(8*A*)—S(2*A*)—C(21*A*)	109 (1)
N(4)—C(10)—C(16)	116.5 (2)	O(8*A*)—S(2*A*)—C(22*A*)	115 (2)
C(9)—C(10)—C(16)	121.9 (2)	C(21*A*)—S(2*A*)—C(22*A*)	102 (2)
N(5)—C(11)—C(12)	121.1 (2)		

Table 3. *Bond lengths (Å) and angles (°) involving amide H atoms in HAT-(amide)$_6$*

H(3), H(4), H(3*A*) and H(4*A*) are fixed due to disorder. The tabulated means are based on refined values only.

	N—H	C—N—H	H—N—H
C(13)—N(7)—H(1)	0.83 (3)	119 (2)	
C(13)—N(7)—H(2)	0.90 (3)	122 (2)	118 (3)
C(14)—N(8)—H(3)	0.96	120	
C(14)—N(8)—H(4)	0.95	120	120
C(14*A*)-N(8*A*)-H(3*A*)	0.95	125	
C(14*A*)-N(8*A*)-H(4*A*)	0.95	108	120
C(15)—N(9)—H(5)	0.87 (4)	120 (2)	
C(15)—N(9)—H(6)	0.89 (4)	118 (2)	122 (3)
C(16)—N(10)—H(7)	0.91 (3)	121 (2)	
C(16)—N(10)—H(8)	0.83 (3)	119 (2)	119 (3)
C(17)—N(11)—H(9)	0.89 (4)	120 (2)	
C(17)—N(11)—H(10)	0.87 (4)	123 (2)	115 (3)
C(18)—N(12)—H(11)	0.96 (4)	118 (2)	
C(18)—N(12)—H(12)	0.87 (3)	115 (2)	127 (3)
Mean	0.88 (4)	120 (3)	120 (5)

Table 4. *Conformation (°) of amide groups in HAT-(amide)$_6$*

The dihedral angle is given for each amide group with respect to the least-squares plane of the HAT core.

Amide group	Dihedral angle	N—C—C—N	Torsion angle
C(13),O(1),N(7)	66.7 (6)	N(1)—C(7)—C(13)—N(7)	−72.2 (3)
C(14),O(2),N(8)	34.2 (6)	N(2)—C(8)—C(14)—N(8)	24.0 (9)
C(14*A*),O(2*A*),N(8*A*)	26.5 (6)	N(2)—C(8)—C(14*A*)-N(8*A*)	0.3 (12)
C(15),O(3),N(9)	78.0 (6)	N(3)—C(9)—C(15)—N(9)	−73.2 (3)
C(16),O(4),N(10)	10.0 (6)	N(4)—C(10)—C(16)—N(10)	−9.8 (4)
C(17),O(5),N(11)	26.1 (6)	N(5)—C(11)—C(17)—N(11)	25.3 (3)
C(18),O(6),N(12)	54.7 (6)	N(6)—C(12)—C(18)—N(12)	59.8 (3)

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N(7)—H(1)···O(1^{i})	2.21 (3)	3.008 (3)	160 (3)
N(7)—H(2)···O(8^{ii})	1.98 (3)	2.870 (6)	169 (3)
N(7)—H(2)···O(8*A*^{ii})	2.12 (3)	2.986 (4)	161 (3)
N(8)—H(3)···O(9^{iii})	2.18	3.062 (6)	154
N(8)—H(4)···O(6^{iii})	2.55	3.494 (6)	176
N(8*A*)—H(3*A*)···O(9^{iv})	2.08	2.988 (7)	160
N(8*A*)—H(4*A*)···O(3^{v})	2.54	3.239 (7)	130
N(9)—H(5)···O(6^{vi})	2.33 (4)	2.840 (4)	118 (3)
N(10)—H(7)···O(1^{iii})	2.32 (3)	3.159 (4)	153 (3)
N(10)—H(8)···O(2^{vii})	2.00 (4)	2.82 (2)	171 (3)
N(10)—H(8)···O(2*A*^{vii})	1.99 (4)	2.82 (2)	174 (3)
N(11)—H(9)···O(1^{iii})	2.11 (4)	2.976 (4)	164 (3)
N(11)—H(10)···O(8^{viii})	2.10 (4)	2.940 (5)	162 (3)
N(11)—H(10)···O(8*A*^{viii})	2.11 (4)	2.971 (3)	171 (3)
N(12)—H(11)···O(7^{ix})	1.97 (4)	2.89 (1)	161 (3)
N(12)—H(11)···O(7*A*^{ix})	1.81 (5)	2.74 (2)	162 (4)
Mean	2.02 (24)	2.99 (19)	159 (15)
N(8)—H(4)···N(9^{v})	2.70	3.167 (5)	111
N(8*A*)—H(4*A*)···N(9^{v})	2.39	3.291 (7)	158
N(9)—H(6)···N(2^{v})	2.54 (4)	3.395 (4)	163 (3)
N(9)—H(6)···N(3^{v})	2.55 (4)	3.159 (3)	126 (3)
N(9)—H(6)···N(8^{v})	2.86 (4)	3.167 (5)	102 (3)
N(9)—H(6)···N(8*A*^{v})	2.90 (4)	3.291 (7)	108 (3)
N(12)—H(12)···N(4^{x})	2.99 (3)	3.258 (4)	100 (2)
N(12)—H(12)···N(5^{x})	2.65 (3)	3.338 (4)	136 (3)
Mean	2.71 (21)	3.26 (9)	126 (25)

N(8)—H(4)···N(2)	2.56	2.776 (5)	93
N(8*A*)—H(4*A*)···N(2)	2.44	2.805 (6)	102
N(9)—H(5)···N(3)	2.91 (4)	2.984 (3)	87 (2)
N(10)—H(7)···N(4)	2.29 (3)	2.654 (3)	103 (2)
N(11)—H(9)···N(5)	2.41 (4)	2.696 (3)	99 (3)
N(12)—H(12)···N(6)	2.70 (3)	2.939 (4)	97 (2)
Mean	2.55 (22)	2.81 (13)	97 (6)
O(9)—H(17)···O(4^{viii})	2.33	2.923 (5)	121
O(9)—H(18)···O(4^{xi})	1.84	2.818 (5)	164

Symmetry codes: (i) $1-x, -1-y, 1-z$; (ii) $x, y-1, z-1$; (iii) $1-x, -y, 1-z$; (iv) $x-1, y-1, z$; (v) $-x, -y, 1-z$; (vi) $x-1, y, z$; (vii) $x, 1+y, z$; (viii) $1-x, 1-y, 1-z$; (ix) $2-x, -y, -z$; (x) $1-x, -y, -z$; (xi) $1+x, y, z$.

Data were collected using graphite-monochromated radiation. Scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. No decay correction was applied but the data were corrected for Lorentz and polarization effects and for absorption. The unit cell was found to be triclinic (since four measurements of the unit-cell parameters of the experimental crystal described here and of a second crystal showed variations greater than the combined e.s.d.'s of the individual values, the mean values were adopted as the best values; no reason for the variation was apparent). The intensity statistics indicated a centrosymmetric space group. $P\bar{1}$ (No. 2) was given initial preference; the refinement proceeded well and it was thus adopted. From the *E* map generated by the direct methods program *SHELXS*86 (Sheldrick, 1985), the initial positions of the C and N atoms comprising the HAT core and the amide C atoms were identified. Difference Fourier methods were used to identify the remaining atoms. The amide group at C(8) was found to be disordered over two sites. In addition, the Me_2SO molecules were found to be disordered. All non-H atoms were refined anisotropically using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989); the coordinates of one of the disordered O atoms [O(8*A*)], however, were fixed in the last least-squares cycles. The populations of the 20 disordered non-H atoms were refined and are listed in Table 1. The population of the water O atom found near an inversion center was fixed at 0.5. H atoms bonded to ordered atoms were refined isotropically. The H atoms of the Me_2SO molecules were generated with fixed methyl geometry after at least one of the set was located in a difference Fourier map. The disordered amide H atoms were generated with fixed geometry. The water H atoms were fixed at positions located in a difference Fourier map following assignment of all other atoms in the structure. In these latter cases, the isotropic displacement parameters of the H atoms were fixed at values 1.5 times the U_{iso} values of their parent atoms.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-Methyl-6-phenylimidazo[2,1-*b*]thiazolium Iodide

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Abstract

The imidazothiazole bicyclic unit of the title compound, $C_{12}H_{11}N_2S^+.I^-$, is planar. The deviation of the C atom of the methyl group from this plane is 0.1 Å and the dihedral angle with the plane of the phenyl ring is 46°. The shortest cation–anion distance is I···S of 3.722 (1) Å.

Comment

The interest in imidazo[2,1-*b*]thiazole derivatives arises from the pharmacological activity of some of these compounds (Pilgram, 1984). Single crystals of 7-methyl-6-phenylimidazo[2,1-*b*]thiazolium iodide, (I), were kindly

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