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 $U_{\rm iso}$ 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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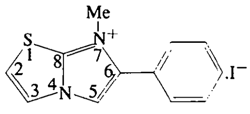
Abstract

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 donated by Dr E. V. Babaev. For the method of preparation and spectral characteristics see O'Daly, Hopkinson, Meakins & Raybould (1991).



(I)

A comparison of the neutral (Cavalca, Domiano & Musatti, 1972) and cationic forms of 6-phenylimidazo[2,1-*b*]thiazole shows that the insertion of the positive charge causes noticeable changes in the imidazole part of the bicyclic unit. Conjugation of the S atom with the imidazole ring increases while it decreases with the C(4)═C(5) double bond. 1-Methyl-2-phenylimidazo[1,2-*a*]pyridinium iodide and 1-methyl-6-nitro-2-phenylimidazo[1,2-*a*]pyridinium iodide, investigated by us previously (Tafeenko, Schenk & Paseshnichenko, 1995), also contain an imidazolium ring. Comparison of the structural data and the results of MNDO calculations for imidazopyridinium and imidazothiazolium cations shows that bond orders and bond lengths in the imidazolium rings are almost the same, whereas the electron-density distribution in these two bicyclic units differs due to the presence of the S atom, with a large positive charge in the imidazothiazolium cation. As a result, the crystal packing of these salts is also different. In the structures of imidazopyridinium iodides, the I^- anion forms its main contacts with the N and C atoms of the cation. In the title structure, the anion forms contacts with the S and N atoms of the three neighbouring cations, the shortest distance being I···S(1) of 3.722 (1) Å (Table 3).

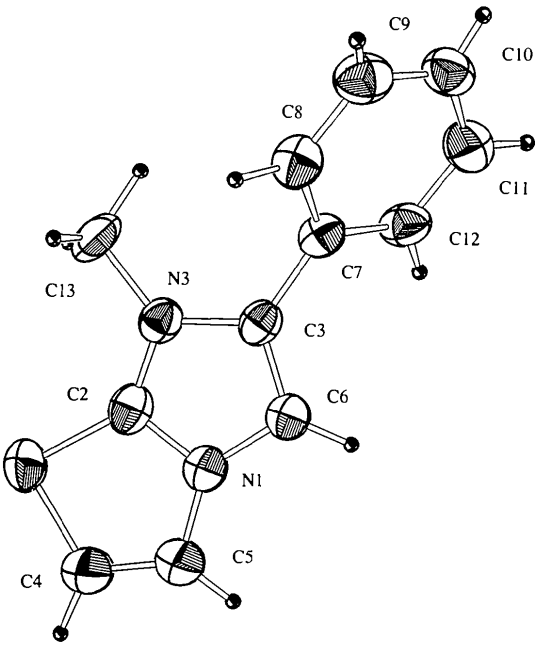


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

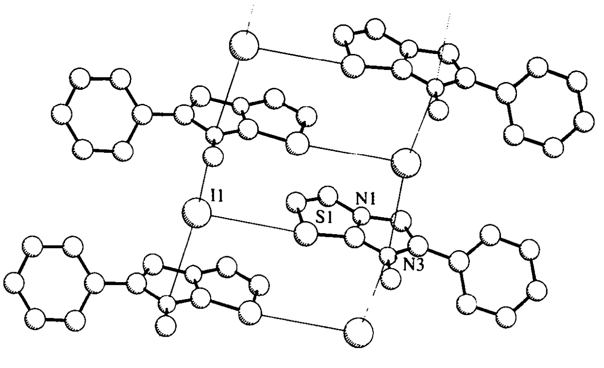


Fig. 2. The crystal packing within the unit cell projected onto the (011) plane. Cation–anion contacts are shown as dotted lines.

Experimental

7-Methyl-6-phenylimidazo[2,1-*b*]thiazolium iodide was crystallized from ethanolic solution.

Crystal data

$C_{12}H_{11}N_2S^+.I^-$
$M_r = 342.2$
Monoclinic
Cc
$a = 6.255\,(1)$ Å
$b = 30.059\,(4)$ Å
$c = 7.425\,(1)$ Å
$\beta = 113.95\,(2)^\circ$
$V = 1276$ Å^3
$Z = 4$
$D_x = 1.782$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 15$–18°
$\mu = 2.615$ mm^{-1}
$T = 295$ K
Approximate prism
0.40 × 0.25 × 0.20 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.82$, $T_{\max} = 0.99$
1761 measured reflections
1521 independent reflections

1480 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.013$
$\theta_{\max} = 28^\circ$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 39$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 90 min
intensity decay: <1.2%

Refinement

Refinement on *F*
$R = 0.019$
$wR = 0.021$
$S = 1.62$

$w = 4F^2/[\sigma^2(I) + (0.015F^2)^2]$
$(\Delta/\sigma)_{\max} = 0.12$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

1480 reflections
183 parameters
All H-atom parameters refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1962, Vol. III)

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}
I	0.0000	0.64446 (1)	0.0000	0.04755 (5)
S(1)	0.4974 (4)	0.73177 (3)	0.5139 (3)	0.0541 (3)
N(1)	0.6536 (6)	0.6679 (1)	0.3733 (5)	0.043 (1)
N(3)	0.4592 (5)	0.6379 (1)	0.5282 (4)	0.038 (1)
C(2)	0.5290 (7)	0.6760 (1)	0.4816 (6)	0.042 (1)
C(3)	0.5447 (6)	0.6037 (1)	0.4505 (6)	0.036 (1)
C(4)	0.6621 (9)	0.7425 (2)	0.3768 (8)	0.066 (1)
C(5)	0.7296 (9)	0.7061 (2)	0.3131 (8)	0.061 (1)
C(6)	0.6667 (7)	0.6224 (1)	0.3532 (6)	0.041 (1)
C(7)	0.5025 (8)	0.5565 (1)	0.4703 (5)	0.038 (1)
C(8)	0.2718 (7)	0.5412 (2)	0.4300 (7)	0.047 (1)
C(9)	0.2395 (8)	0.4959 (2)	0.4440 (7)	0.052 (1)
C(10)	0.4197 (8)	0.4664 (1)	0.4884 (7)	0.048 (1)
C(11)	0.6401 (8)	0.4809 (2)	0.5212 (7)	0.052 (1)
C(12)	0.6810 (7)	0.5263 (2)	0.5150 (6)	0.044 (1)
C(13)	0.3360 (7)	0.6355 (2)	0.6580 (6)	0.053 (1)

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

S(1)—C(2)	1.716 (3)	C(3)—C(7)	1.461 (4)
S(1)—C(4)	1.747 (7)	C(4)—C(5)	1.327 (9)
N(1)—C(2)	1.350 (7)	C(7)—C(8)	1.426 (7)
N(1)—C(5)	1.384 (7)	C(7)—C(12)	1.371 (7)
N(1)—C(6)	1.382 (4)	C(8)—C(9)	1.387 (8)
N(3)—C(2)	1.321 (5)	C(9)—C(10)	1.365 (7)
N(3)—C(3)	1.388 (5)	C(10)—C(11)	1.370 (7)
N(3)—C(13)	1.460 (6)	C(11)—C(12)	1.393 (8)
C(3)—C(6)	1.367 (7)		
C(2)—S(1)—C(4)	88.3 (3)	N(1)—C(5)—C(4)	111.6 (6)
C(2)—N(1)—C(5)	113.6 (4)	N(1)—C(6)—C(3)	106.2 (4)
C(2)—N(1)—C(6)	108.5 (4)	C(3)—C(7)—C(8)	120.1 (4)
C(2)—N(3)—C(3)	108.0 (4)	C(3)—C(7)—C(12)	120.3 (4)
C(2)—N(3)—C(13)	122.3 (4)	C(8)—C(7)—C(12)	119.5 (4)
C(3)—N(3)—C(13)	129.3 (4)	C(7)—C(8)—C(9)	117.8 (4)
S(1)—C(2)—N(1)	112.7 (3)	C(8)—C(9)—C(10)	121.7 (5)
N(1)—C(2)—N(3)	109.4 (3)	C(9)—C(10)—C(11)	120.6 (4)
N(3)—C(3)—C(6)	107.9 (3)	C(10)—C(11)—C(12)	119.4 (5)
S(1)—C(4)—C(5)	113.8 (5)	C(7)—C(12)—C(11)	121.0 (4)

Table 3. *Contact distances* (Å)

I···N(3)	3.811 (2)	I···S(1^{i})	3.722 (1)
I···C(4^{i})	3.763 (6)	I···N(3^{ii})	3.759 (2)

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

H atoms were located by difference Fourier synthesis and refined isotropically. Programs used were: *SDP* (Frenz, 1978), *PARST* (Nardelli, 1983), *PLUTO* (Motherwell, 1974) and *ORTEP*II (Johnson, 1976).

The authors are grateful to the Netherlands Organization for Scientific Research (NWO) for the support of this investigation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with the results of MNDO calculations on the cation, have been deposited with the IUCr (Reference: CR1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrogen Bonding in 2-Methyl-1,2,3-propanetricarboxylic Acid, Ammonium Dihydrogen 1,2,3-Propanetricarboxylate Hemihydrate and Tetraammonium 1,2,3,4-Butanetetracarboxylate Monohydrate

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Abstract

The extensive hydrogen-bonded networks of the title compounds, $C_7H_{10}O_6$, (I), $NH_4^+.C_6H_7O_6^-.\frac{1}{2}H_2O$, (II), and $4NH_4^+.C_8H_6O_8{}^{4-}.H_2O$, (III), have been analyzed. In compound (I), layers are formed by eight-membered and 16-membered hydrogen-bonded rings. In compound (II), the anions are arranged into double chains of 30-membered rings through short hydrogen bonds. These chains are cross-linked by weaker hydrogen bonds to H_2O and NH_4^+. In compound (III), stacks of centrosymmetric anions are connected by hydrogen bonds to H_2O and NH_4^+.

Comment

Hydrogen bonding to give supramolecular arrays is a major factor in the design of the crystal structures