hydrochloride (Hanic, 1966), but is close to the values observed for vitamin B_6 compounds whose phenolic group is deprotonated (Mosset *et al.*, 1978; K. J. Franklin & Richardson, 1980; Thompson *et al.*, 1980). The pyridine ring is planar.

The $-CH_2NH_3^+$ group forms an intramolecular hydrogen bond to the phenolate oxygen O(2) (Table 3). The resulting ring, O(2)–C(4)–C(3)–C(7)–N(2)–H(9), has the same conformation as the metal chelate rings in the copper and zinc complexes of pyridoxamine (Thompson *et al.*, 1980; K. J. Franklin & Richardson, 1980). The H(9) atom in the $-CH_2NH_3^+$ group also makes a close contact with O(1) in a glide-related molecule, although the interaction seems to be somewhat weaker than the intramolecular one (Table 3).

The HPM^+ cations are stacked with the ring planes parallel (Fig. 2). The stacks are linked by hydrogen bonds from the ammonium group to the phenolate O atom O(2) in screw-related molecules (not shown in Fig. 2), and by hydrogen bonds from the ammonium, hydroxymethyl, and pyridinium groups to Cl^- ions (Table 3).

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Benzotriazolium Hydrogensulphate

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Abstract. $C_6H_6N_3^+.HSO_4^-$, $M_r = 217{\cdot}2$, orthorhombic, *Pbcn*, $a = 12{\cdot}976$ (1), $b = 7{\cdot}892$ (1), $c = 17{\cdot}292$ (1) Å, $Z = 8$, $V = 1770{\cdot}8$ (3) Å^3, $D_c = 1{\cdot}63$ Mg m^{-3}, $F(000) = 896$, Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), μ(Cu $K\alpha$) = $0{\cdot}318$ mm^{-1}. The structure was solved by the heavy-atom method and refined by full-matrix least squares. The final R and R_w for 1239 observed reflexions and 156 parameters are respectively 0·044 and 0·062. The benzotriazolium ions have *mm* symmetry. Two strong N–H···O hydrogen bonds, 2·687 (5) and 2·705 (5) Å, link the benzotriazolium cations to the hydrogensulphate anions, which, in turn, form infinite chains through an O–H···O hydrogen bond of 2·565 (5) Å.

Introduction. Deliquescent crystals of the title compound were obtained by evaporation to dryness on P_2O_5 of an aqueous solution of H_2SO_4 and benzotriazole. A prismatic crystal (0·09 × 0·14 × 0·46 mm), elongated along **b**, was sealed in a Lindemann capillary tube and used for data collection on an Enraf–Nonius four-circle CAD-4 diffractometer. Monochromatized Cu $K\alpha$ radiation was used. Lattice constants were obtained by least squares from the 2θ values of 25 reflexions. Of 1755 independent reflexions measured to $\sin\theta/\lambda \simeq 0{\cdot}60$ Å^{-1} by the ω–θ scan technique, 1239 having $I > 3\sigma(I)$ were taken as observed. During the data collection, the azimuth of each reflexion was adjusted to reach as close as possible the position of the minimum absorption path, so that no correction for absorption was applied. The intensities of three monitor reflexions, periodically remeasured, showed no crystal damage.

The structure was solved using heavy-atom and Fourier synthesis techniques and refined by full-matrix least-squares procedures.

All H atoms were located from a difference electron density map. The final least-squares refinement of atomic parameters with anisotropic thermal factors for the non-hydrogen atoms and isotropic thermal factors for the H atoms included a correction for isotropic extinction [refined G coefficient was 1·8 (0·1) × 10^{-6}] and converged to $R = 0{\cdot}044$ for the observed reflexions. The weighting scheme $w = (1 + |F_o| +$

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Table 1. *Atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and thermal parameters for* H *atoms* ($\times 10$) *with estimated standard deviations in parentheses*

	x	y	z
S	1633·7 (6)	−443 (1)	3639·8 (4)
O(1)	1911 (3)	1026 (4)	3093 (1)
O(2)	1132 (2)	284 (3)	4298 (1)
O(3)	984 (2)	−1520 (4)	3182 (1)
O(4)	2592 (2)	−1283 (4)	3836 (2)
N(1)	3728 (2)	2506 (4)	1709 (1)
N(2)	3661 (2)	3541 (3)	1119 (2)
N(3)	3677 (2)	2561 (4)	506 (1)
C(4)	3829 (2)	−593 (4)	249 (2)
C(5)	3955 (3)	−2061 (4)	656 (2)
C(6)	3993 (3)	−2079 (4)	1475 (2)
C(7)	3907 (3)	−650 (4)	1905 (2)
C(8)	3799 (2)	852 (4)	1492 (2)
C(9)	3760 (2)	881 (4)	688 (2)

	x	y	z	B (Å^2)
H(N1)	378 (3)	306 (5)	215 (2)	65 (10)
H(N3)	361 (2)	311 (4)	10 (2)	44 (7)
H(C4)	379 (3)	−44 (4)	−31 (2)	48 (8)
H(C5)	403 (3)	−318 (5)	39 (2)	54 (8)
H(C6)	408 (3)	−317 (5)	171 (2)	55 (8)
H(C7)	390 (3)	−56 (4)	251 (2)	51 (8)
H(O1)	235 (4)	206 (7)	344 (3)	101 (15)

$0{\cdot}001|F_o|^2)^{-1}$ was used and the final R_w was 0·062.* A PDP 11/34 computer and the Enraf–Nonius structure determination package (SDP) were used throughout.

Final atomic parameters and their estimated standard deviations are listed in Table 1.

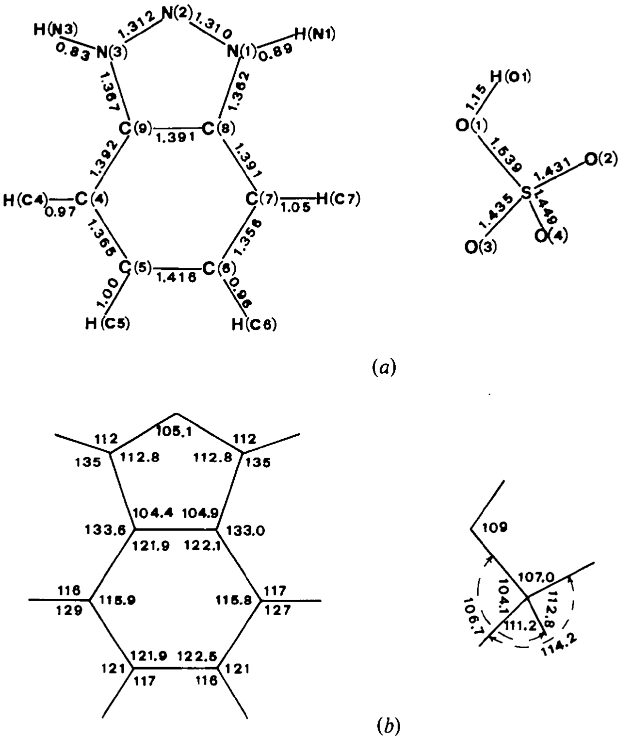
Atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and for the H atoms from Moore (1963).

Discussion. This work is a part of a comparative investigation on the structure of benzotriazole systems (Giordano & Zagari, 1977, 1978).

The dimensions of the benzotriazolium cations and hydrogensulphate anions are shown in Fig. 1, which also gives the atomic numbering scheme.

As in solution (Dal Monte, Mangini, Passerini & Zauli, 1958), the benzotriazolium cation appears protonated in position 3 so that it displays *mm* symmetry, which is exact within experimental error.

The bond-order–bond-length curves of Burke-Laing & Laing (1976) were used to derive Pauling's bond orders, which are shown in Fig. 2 together with the estimated contributions of the predominant resonance forms. Lengths of the chemically equivalent bonds were averaged. Comparison of the geometries of the benzotriazolium cation and the 1- and 2-benzotriazolyl neutral residues reveals that significant differences occur only in the five-membered heterocycle (Giordano & Zagari, 1978). In the cation, the replacement of a



(*a*)

(*b*)

Fig. 1. (*a*) Bond lengths (Å) and numbering scheme. (*b*) Bond angles (°). Taking into account also the e.s.d.'s of the cell parameters, the ranges for the e.s.d.'s are: 0·005–0·012 Å (mean 0·009 Å) for bonds involving non-hydrogen atoms, 0·09–0·15 Å (mean 0·10 Å) for bonds involving H atoms, 0·4–0·8° (mean 0·7°) for angles involving non-hydrogen atoms, 5–7° (mean 6°) for angles involving H atoms.

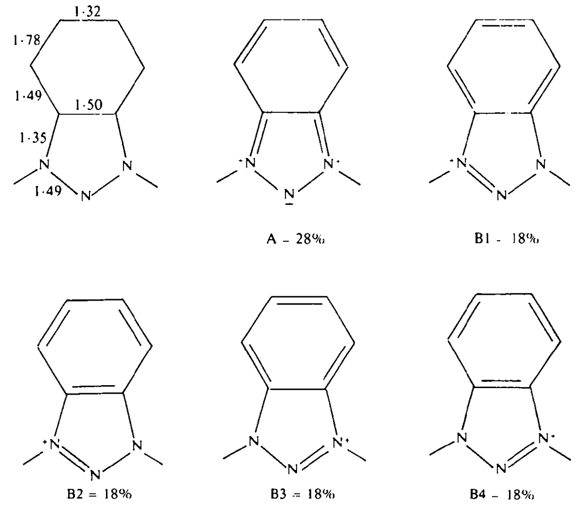


Fig. 2. Bond orders and resonance forms with their % contributions.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35331 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

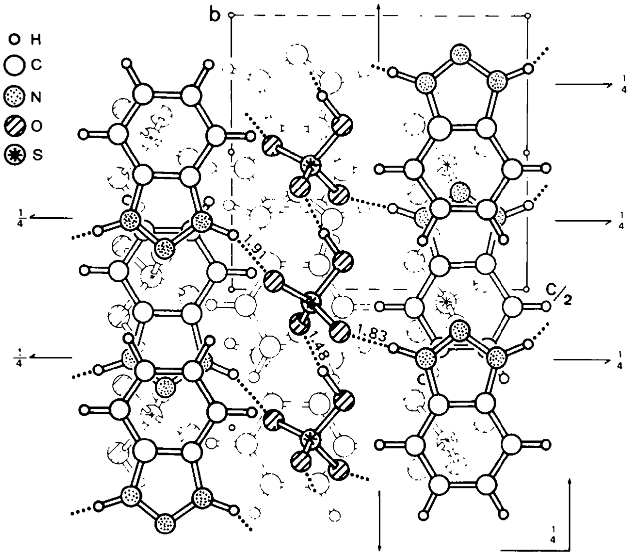

Fig. 3. Projection of the crystal structure along the *a* axis. Dotted lines indicate the hydrogen bonds.

Table 2. *Hydrogen-bond parameters*

A–H···B	A···B (Å)	H···B (Å)	∠A–H···B (°)
O(1)–H···O(4^{i})	2·565 (5)	1·48 (15)	152 (7)
N(1)–H···O(3^{i})	2·687 (5)	1·83 (10)	160 (6)
N(3)–H···O(2^{ii})	2·705 (5)	1·91 (9)	160 (6)

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

'pyridine' nitrogen with a 'pyrrole' nitrogen, characterized by a larger bond angle, causes all the angles in the five-membered ring to rearrange. In turn, the pattern of bond lengths indicates a π-electron delocalization somewhat similar to that found in the 2-benzotriazolyl system.

A view of the crystal structure is shown in Fig. 3. Hydrogensulphate ions are linked by a strong hydrogen bond O–H···O (Table 2) in corrugated chains parallel to **b**. Benzotriazolium ions are also aligned in rows parallel to **b** and alternate with the anion chains with which they are linked by two strong N–H···O hydrogen bonds to form a layer structure normal to **a**.

Table 3. *Displacements* (Å ×10^3) *of the non-hydrogen atoms of the benzotriazolium group from the least-squares best planes*

The mean isotropic positional e.s.d. is 0·004 Å. Asterisks denote atoms not included in the mean-plane calculations.

	Plane I	Plane II	Plane III
N(1)	43*	−4	−1
N(2)	80*	3	23
N(3)	51*	−1	6
C(4)	−8	26*	−14
C(5)	4	81*	18
C(6)	4	84*	19
C(7)	−9	33*	−12
C(8)	5	3	−18
C(9)	4	−1	−20

The dihedral angle between planes I and II is 2·0 (4)°.

The two hydrogen bonds, which involve the protonated nitrogens of the cation and the remaining oxygens of the anion, have the same geometry (Table 2). These hydrogen bonds closely resemble those found in the structures of 1- and 2-benzotriazolylacetic acids where, however, the donor atoms were oxygens.

Analysis of the planarity of the benzotriazolium ion (Table 3) shows that, although essentially planar, the nine-membered heterocycle displays a slight but statistically significant bending about the C(8)–C(9) bond, in such a way that the positively charged five-membered ring approaches the negative ion at ($\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) leaving the benzenoid ring of the benzotriazolium ion on the opposite side.

The packing does not reveal any abnormal van der Waals contacts.

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