Br(2)···C(8) = 3·350 (5) Å, are observed as the rings are tilted with respect to the Br atom.

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Structure of the Hydrogensulfate Salt of a Diazaadamantanone, 5,7-Diphenyl-1,3-diazatricyclo[3.3.1.1^{3,7}]decan-6-one

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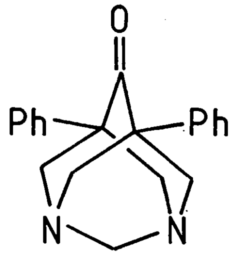
Abstract. $C_{20}H_{21}N_2O^+.HSO_4^-$, $M_r = 402{\cdot}51$, orthorhombic, $Pca2_1$, $a = 21{\cdot}655\ (4)$, $b = 11{\cdot}598\ (3)$, $c = 7{\cdot}392\ (4)$ Å, $V = 1857\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}44$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}21$ mm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0{\cdot}037$ for 2137 reflections with $I > 2{\cdot}5\sigma(I)$. The diazaadamantanone is protonated at only one of the N atoms, N(3), and the N$^+$—C bond lengths, 1·490–1·534 (4), mean 1·508 Å, are longer than the N—C bond lengths at the tertiary N(1) atom, 1·419–1·473 (4), mean 1·452 Å. In the HSO_4^- anion, the S—OH bond length is 1·549 (3) Å and the S=O bond lengths are 1·428–1·447 (4) Å; the HO—S=O angles are 105·2–106·6 (2), mean 106·1°, and the O=S=O angles are 109·5–114·7 (2), mean 112·6°. Hydrogen bonding occurs between the organic cation and the hydrogensulfate anion, N(3)···O(3), 2·799 (4) Å, and between hydrogensulfate anions, O(2)···O(5), 2·536 (4) Å.

Introduction. When sulfuric acid H_2SO_4 reacts with organic bases to form salts, both protons of the acid are generally transferred to the base, *e.g.* adenosine *N*-oxide (Prusiner & Sundaralingam, 1972) and 1-(4-aminobutyl)guanidine (Chandrasekhar, Pattabhi & Raghunathan, 1982). Transfer of one proton to give an acid salt of composition $BH.HSO_4$ is also known however, 3,7-dimethyl-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (Levina, Kurkutova, Potekhin, Struchkov, Palyulin & Zefirov, 1982) and 3-phenoxypyridine (Bandoli, Grassi, Montoneri, Pappalardo & Perly, 1988) providing recent examples. In the course of conformational studies of diazabicyclo[3.3.1]nonane derivatives (McCabe, Milne & Sim, 1985) we had occasion to prepare 5,7-diphenyl-1,3-diazaadamantan-6-one (1) as a synthetic precursor; the sulfuric acid salt of this base can involve the transfer of either one or two protons and an X-ray crystal-structure analysis has established that the former is the case.



(1)

Experimental. 5,7-Diphenyl-1,3-diazatricyclo-[3.3.1.1^{3,7}]decan-6-one (1) (Chiavarelli & Settimj,

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

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
S	0·71057 (3)	0·36505 (5)	0·24830	0·038
C(2)	0·59875 (16)	0·15086 (27)	0·98831 (40)	0·045
C(4)	0·59558 (12)	0·28068 (20)	0·72410 (39)	0·036
C(5)	0·54259 (11)	0·20818 (19)	0·64309 (38)	0·032
C(6)	0·57193 (10)	0·11079 (18)	0·53128 (33)	0·027
C(7)	0·61555 (10)	0·03474 (18)	0·64278 (36)	0·030
C(8)	0·57728 (13)	−0·01314 (21)	0·80406 (38)	0·037
C(9)	0·50857 (13)	0·14929 (21)	0·80373 (38)	0·038
C(10)	0·66632 (11)	0·11469 (21)	0·72230 (39)	0·035
C(11)	0·64529 (10)	−0·05955 (20)	0·52934 (37)	0·032
C(12)	0·68076 (12)	−0·03094 (22)	0·37888 (43)	0·038
C(13)	0·70914 (14)	−0·11536 (31)	0·27620 (53)	0·051
C(14)	0·70301 (14)	−0·23126 (29)	0·32284 (62)	0·057
C(15)	0·66741 (16)	−0·25995 (25)	0·47002 (60)	0·057
C(16)	0·63890 (13)	−0·17582 (23)	0·57305 (48)	0·043
C(17)	0·50147 (12)	0·28494 (21)	0·52751 (42)	0·039
C(18)	0·52595 (16)	0·34337 (24)	0·38045 (52)	0·050
C(19)	0·48816 (23)	0·41068 (27)	0·26953 (63)	0·070
C(20)	0·42631 (22)	0·42140 (27)	0·30670 (78)	0·080
C(21)	0·40178 (19)	0·36646 (31)	0·45286 (91)	0·076
C(22)	0·43896 (15)	0·29816 (29)	0·56329 (62)	0·055
N(1)	0·55131 (11)	0·08123 (19)	0·91359 (32)	0·040
N(3)	0·63664 (10)	0·20628 (18)	0·83614 (34)	0·037
O(1)	0·56103 (8)	0·09506 (15)	0·37308 (27)	0·035
O(2)	0·68307 (11)	0·44619 (18)	0·39397 (35)	0·050
O(3)	0·66782 (11)	0·36920 (22)	0·10004 (36)	0·058
O(4)	0·71682 (18)	0·25435 (23)	0·33092 (55)	0·090
O(5)	0·77106 (13)	0·41008 (36)	0·20455 (40)	0·097

1958) (1·022 g, 3·36 mmol) and conc. sulfuric acid (0·19 ml of 18*M*, 3·4 mmol) were dissolved in ethanol (15 ml) and stirred overnight; solvent was removed under suction and the residue crystallized from methanol–water to yield the salt (0·796 g, 59% yield), m.p. 430–431 K.

Colourless crystal, dimensions 0·14 × 0·18 × 0·38 mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 11–16°; 2510 intensities surveyed in range θ 2·0–28·0°, h 0–28, k 0–15, l 0–8; max. counting time 120 s; scan width 0·96° + 0·14°tanθ; 2137 independent reflections with $I > 2{\cdot}5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity ($< \pm 2\%$). No absorption correction. S atom located from sharpened Patterson synthesis and *MITHRIL* (Gilmore, 1984). The C, N, and O atoms were located in successive difference Fourier syntheses and after preliminary least-squares adjustment of the parameters of these atoms, the H atoms were located in a difference Fourier synthesis. No attempt was made to assign the handedness of the chosen crystal, because of the small value of f'' for S. Full-matrix least-squares calculations on F with anisotropic thermal parameters for the S, C, N, and O atoms and isotropic parameters for the H atoms. Convergence at $R = 0{\cdot}037$, $wR = 0{\cdot}049$, $S = 2{\cdot}66$ for 340 parameters, $\Delta/\sigma < 0{\cdot}2$, $w = 1/\sigma^2(|F|)$. Final $\Delta\rho$ max. 0·41, min. −0·22 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Table 2. *Interatomic distances* (Å) *and angles* (°)

S–O(2)	1·549 (3)	S–O(3)	1·435 (3)
S–O(4)	1·428 (4)	S–O(5)	1·447 (4)
C(2)–N(1)	1·419 (5)	C(2)–N(3)	1·534 (4)
C(4)–C(5)	1·543 (4)	C(4)–N(3)	1·490 (4)
C(5)–C(6)	1·537 (4)	C(5)–C(9)	1·555 (4)
C(5)–C(17)	1·522 (4)	C(6)–C(7)	1·533 (4)
C(6)–O(1)	1·207 (4)	C(7)–C(8)	1·554 (4)
C(7)–C(10)	1·554 (4)	C(7)–C(11)	1·521 (4)
C(8)–N(1)	1·473 (4)	C(9)–N(1)	1·463 (4)
C(10)–N(3)	1·500 (4)	C(11)–C(12)	1·392 (4)
C(11)–C(16)	1·394 (4)	C(12)–C(13)	1·383 (5)
C(13)–C(14)	1·394 (5)	C(14)–C(15)	1·374 (6)
C(15)–C(16)	1·383 (5)	C(17)–C(18)	1·386 (5)
C(17)–C(22)	1·388 (5)	C(18)–C(19)	1·397 (6)
C(19)–C(20)	1·373 (7)	C(20)–C(21)	1·362 (8)
C(21)–C(22)	1·394 (7)		

O(2)–S–O(3)	105·2 (2)	O(2)–S–O(4)	106·6 (2)
O(2)–S–O(5)	106·5 (2)	O(3)–S–O(4)	114·7 (2)
O(3)–S–O(5)	113·7 (2)	O(4)–S–O(5)	109·5 (3)
N(1)–C(2)–N(3)	109·9 (3)	C(5)–C(4)–N(3)	110·1 (2)
C(4)–C(5)–C(6)	107·6 (2)	C(4)–C(5)–C(9)	107·2 (3)
C(4)–C(5)–C(17)	109·5 (2)	C(6)–C(5)–C(9)	106·5 (2)
C(6)–C(5)–C(17)	111·7 (3)	C(9)–C(5)–C(17)	114·1 (3)
C(5)–C(6)–C(7)	112·9 (3)	C(5)–C(6)–O(1)	123·5 (3)
C(7)–C(6)–O(1)	123·7 (3)	C(6)–C(7)–C(8)	106·8 (2)
C(6)–C(7)–C(10)	107·2 (2)	C(6)–C(7)–C(11)	112·2 (3)
C(8)–C(7)–C(10)	107·5 (3)	C(8)–C(7)–C(11)	113·1 (2)
C(10)–C(7)–C(11)	109·8 (2)	C(7)–C(8)–N(1)	111·1 (2)
C(5)–C(9)–N(1)	111·2 (3)	C(7)–C(10)–N(3)	109·4 (2)
C(7)–C(11)–C(12)	120·2 (3)	C(7)–C(11)–C(16)	121·7 (3)
C(12)–C(11)–C(16)	118·1 (3)	C(11)–C(12)–C(13)	121·0 (3)
C(12)–C(13)–C(14)	120·3 (4)	C(13)–C(14)–C(15)	118·9 (4)
C(14)–C(15)–C(16)	121·0 (3)	C(11)–C(16)–C(15)	120·7 (3)
C(5)–C(17)–C(18)	120·2 (3)	C(5)–C(17)–C(22)	121·9 (3)
C(18)–C(17)–C(22)	117·9 (3)	C(17)–C(18)–C(19)	120·6 (4)
C(18)–C(19)–C(20)	120·3 (5)	C(19)–C(20)–C(21)	119·8 (5)
C(20)–C(21)–C(22)	120·3 (4)	C(17)–C(22)–C(21)	121·0 (4)
C(2)–N(1)–C(8)	111·1 (3)	C(2)–N(1)–C(9)	111·5 (3)
C(8)–N(1)–C(9)	109·7 (3)	C(2)–N(3)–C(4)	109·3 (3)
C(2)–N(3)–C(10)	110·1 (3)	C(4)–N(3)–C(10)	110·7 (3)

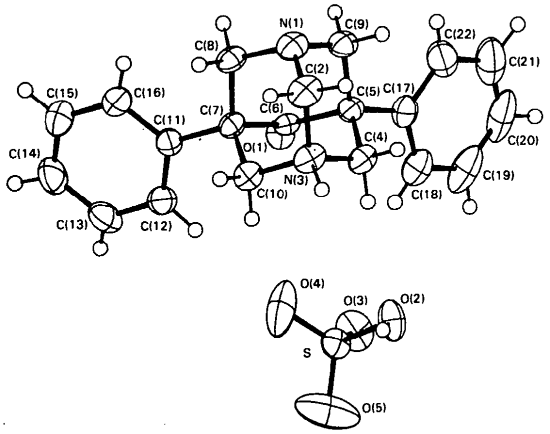

Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C, N, O, and S atoms are drawn at the 50% probability level and the H atoms are represented by spheres of radius 0·1 Å.

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn with *ORTEP* (Johnson, 1965), illustrates the molecular geometry.

The diazaadamantanone molecule is protonated at only one of its N atoms, N(3), and the salt presents an example of the hydrogensulfate ion HSO_4^-. The S—OH bond length is 1·549 (3) Å and the S=O bond lengths are 1·428–1·447 (4), mean 1·437 (8) Å. In both 3-phenoxypyridinium hydrogensulfate (Bandoli *et al.*, 1988) and 3,7-dimethyl-1,5-diphenyl-3-aza-7-azoniabicyclo[3.3.1]nonan-9-one hydrogensulfate (Levina *et al.*, 1982) the hydrogen atom of the HSO_4^- anion is disordered over two oxygen sites and the apparent S—OH bond lengths of 1·502, 1·504 Å in the former and 1·473, 1·498 Å in the latter are effectively averages of S—OH and S=O distances. The mean apparent S—OH distance in these salts, 1·494 Å, is in excellent agreement with the mean of 1·549 (S—OH) and 1·437 Å (S=O) from the diazaadamantanone salt, *viz.* 1·493 Å.

The $C(sp^3)$—N^+ bond lengths at N(3) in the diazaadamantanone cation are 1·490–1·534 (4), mean 1·508 (19) Å, whereas the $C(sp^3)$—N bond lengths at the tertiary N atom, N(1), are 1·419–1·473 (4), mean 1·452 (23) Å. This distinct difference between bond lengths at N^+ and N was noted many years ago in the crystal structures of alkaloids (*e.g.* Hamilton, Hamor, Robertson & Sim, 1962). The mean $C(sp^3)$—$C(sp^3)$ and $C(sp^3)$—$C(sp^2)$ bond lengths in the diazaadamantanone cation are 1·552 (5) and 1·528 (7) Å, respectively. The phenyl C—C distances are 1·362 (8)–1·394 (7), mean 1·385 (10) Å.

The hydrogen bonds in the crystal are N(3)H···O(3) $(x, y, 1+z)$, 2·799 (4) Å, and O(2)H···O(5) $(\frac{3}{2}-x, y, \frac{1}{2}+z)$, 2·536 (4) Å. For the former, N(3)—H, H···O(3), and N(3)—H···O(3) are 1·00 (3), 2·01 (4) Å, and 135 (3)°; for the latter, O(2)—H, H···O(5), and O(2)—H···O(5) are 0·86 (4), 1·75 (5) Å, and 149 (4)°.

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* Lists of coordinates and bond lengths for H atoms, structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51355 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1989). C**45**, 116–119

Structure of the Hydrate Form of 3-Methyl-2-oxo-6,7-dihydro-3*H*-pyrimido-[5,4-*b*][1,4]thiazine-7-carboxylic Acid*

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Abstract. $C_8H_9N_3O_3S.xH_2O$ $(x = 0·862)$, $M_r = 242·771$, monoclinic, $P2_1$, $a = 9·8695\ (5)$, $b = 9·4582\ (6)$, $c = 5·6773\ (4)$ Å, $\beta = 108·995\ (6)°$, $V = 501·10\ (6)$ Å^3, $Z = 2$, $D_m = 1·55\ (2)$, $D_x = 1·609$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1·54056$ Å, $\mu = 28·70$ cm^{-1}, $F(000) = 253·24$, $T = 296\ (1)$ K, final $R(F) = 0·025$ for 955 counter reflections with $F_o^2 > 2\sigma(F_o^2)$. At the beginning of the analysis, the true absorption coefficient was not known. The value used was 28·25 cm^{-1} which is 98·4% of the true value. It is believed that this would not change the results significantly. All H atoms except those of the water molecule were located and their parameters refined. The

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