Structure of 1,3-Bis(1-pyrazinio)propane Dibromide*

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Abstract. $C_{11}H_{14}Br_2N_4$, $M_r = 362.1$, orthorhombic, *Pbca*, $a = 13.883$ (4), $b = 19.030$ (4), $c = 9.992$ (3) Å, $V = 2639.7$ Å^3, $Z = 8$, $D_x = 1.822$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 60.7$ cm^{-1}, $F(000) = 1424$, $T = 292$ K, final $R = 0.030$ for 1106 observed reflections. The bis(pyrazinium) dication is fairly extended [N(1)$\cdots$N(3) = 4.415 Å] with the non-H substituents on one of the C—C bonds of the propanediyl chain in a *gauche* conformation and the other in a *trans* conformation. The planes of the two pyrazinium rings are at an angle of 115.0° with respect to each other.

Introduction. A series of 1,1'-(α,ω-alkanediyl)bis(pyrazinium) dications [pyz—$(CH_2)_n$—pyz^{2+}, $n = 2$–8] has been prepared from the reaction of pyrazine (pyz) with the two equivalents of the appropriate α,ω-dibromoalkane, by the synthetic method reported for the analogous 4,4'-bipyridinium compounds (Attalla, McAlpine & Summers, 1984). During the preparation of the bromide salts for use as bridging ligands between moieties such as Fe(CN)$_6^{3-}$, Ru(NH$_3$)$_5^{2+}$, and Co(NH$_3$)$_5^{3+}$, colorless crystals of the title compound were obtained. An interest in the conformation of these dications and an absence of literature reports of structural analyses of free *N*-alkylpyrazinium cations prompted a structural investigation of the present compound.

Experimental. The title compound was obtained by heating 1,3-dibromopropane with an excess of pyrazine in dimethylformamide for 12 h at 323 K. The resulting solid was filtered and recrystallized from ethanol/water. Colorless crystal, specimen $0.02 \times 0.10 \times 0.75$ mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; unit-cell parameters obtained by least-squares analysis of 25 centered reflections with $14 < 2\theta < 25°$; 1715 unique reflections in the range $1 < 2\theta < 45°$, 1106 considered observed at $3\sigma(I)$ level, $h\ 0\rightarrow14$, $k\ 0\rightarrow20$, $l\ 0\rightarrow10$, θ–2θ scan technique, three standard reflections measured every 7200 s of radiation time, max. variation in intensity -1.7%, corrected for Lorentz and polarization effects. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull,

Lessinger, Germain, Declercq & Woolfson, 1980), difference Fourier map calculations revealed positions of all H atoms. Full-matrix least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0.04F^2)^2]$, anisotropic thermal parameters for non-H atoms. H atoms, included in calculations but not refined, assigned isotropic thermal parameters equal to that of parent C atom. Scattering factors: those of Cromer & Waber (1974), anomalous-dispersion coefficients from Cromer (1974). Correction for isotropic secondary-extinction effect included in refinement, $g = 1.47 \times 10^{-7}$. Final $R = 0.030$, $wR = 0.036$, $S = 1.308$ for all observed reflections. Final max. Δ/σ 0.04, final max. and min. $\Delta\rho$ excursions 0.460 and -0.352 e Å^{-3}; calculations performed on a PDP 11/23 computer using Enraf–Nonius *SDP* (Frenz, 1979) and *ORTEP* (Johnson, 1965).

Discussion. The atomic parameters are given in Table 1,‡ and a view of the molecule with the atomic numbering scheme is shown in Fig. 1; the H atoms are omitted to simplify the drawing. Bond lengths and angles for the compound are given in Table 2. A stereoscopic view of the unit cell is shown in Fig. 2.

The two pyrazinium rings are very similar to one another in their molecular dimensions (within 0.02 Å and 2°). Both rings are very close to planar, with deviations of -0.009 to 0.008 Å in the ring containing N(1) and -0.011 to 0.012 Å in the ring containing N(3). The N(2)—C(5) and N(4)—C(9) bond distances at 1.302 (7) and 1.308 (9) Å, respectively, are somewhat shorter (0.03 Å) than the corresponding N(2)—C(7) and N(4)—C(11) distances. The other ring bond distances and angles, including the geometry about the quaternarized N atoms, are similar to those determined for the *N*-methylpyrazinium cation in the ruthenium complexes [(NH$_3$)$_5$Ru(pyzCH$_3$)]I$_3$ and [(NH$_3$)$_5$-Ru(pyzCH$_3$)](tos)$_4$.5H$_2$O (Wishart, Bino & Taube, 1986). The conformation of the propanediyl chain is

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* 1,1'-Trimethylenedipyrazinium dibromide.

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‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths to Br and least-squares-planes details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51316 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Br(1)	0·20528 (5)	0·39170 (3)	0·75775 (7)	3·00 (1)
Br(2)	0·92480 (5)	0·37338 (4)	0·37166 (7)	3·41 (1)
N(1)	0·3627 (3)	0·2249 (2)	0·9455 (5)	2·1 (1)
N(2)	0·5590 (3)	0·2212 (3)	0·9215 (5)	3·2 (1)
N(3)	0·1714 (3)	0·0562 (3)	0·7994 (5)	2·3 (1)
N(4)	0·0517 (3)	−0·0254 (3)	0·6474 (6)	3·5 (1)
C(1)	0·2561 (4)	0·2277 (3)	0·9601 (6)	2·2 (1)
C(2)	0·2072 (4)	0·1791 (3)	0·8593 (6)	2·6 (1)
C(3)	0·2356 (4)	0·1028 (3)	0·8788 (6)	2·4 (1)
C(4)	0·4073 (4)	0·2702 (3)	0·8643 (6)	2·7 (1)
C(5)	0·5063 (5)	0·2662 (3)	0·8560 (7)	3·1 (1)
C(6)	0·4131 (4)	0·1779 (3)	1·0153 (6)	2·3 (1)
C(7)	0·5127 (4)	0·1767 (3)	1·0011 (6)	2·9 (1)
C(8)	0·1087 (4)	0·0129 (3)	0·8578 (6)	2·7 (1)
C(9)	0·0492 (4)	−0·0275 (3)	0·7782 (7)	3·5 (2)
C(10)	0·1777 (4)	0·0581 (3)	0·6643 (7)	2·6 (1)
C(11)	0·1173 (5)	0·0166 (3)	0·5910 (6)	3·2 (1)

Table 2. *Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

N(1)–C(1)	1·489 (6)	N(4)–C(9)	1·308 (9)
N(1)–C(4)	1·337 (6)	N(4)–C(11)	1·336 (8)
N(1)–C(6)	1·332 (6)	C(1)–C(2)	1·527 (7)
N(2)–C(5)	1·302 (7)	C(2)–C(3)	1·516 (7)
N(2)–C(7)	1·328 (7)	C(4)–C(5)	1·379 (8)
N(3)–C(3)	1·487 (6)	C(6)–C(7)	1·390 (7)
N(3)–C(8)	1·333 (6)	C(8)–C(9)	1·381 (8)
N(3)–C(10)	1·354 (7)	C(10)–C(11)	1·366 (8)
C(1)–N(1)–C(4)	119·8 (5)	C(1)–C(2)–C(3)	112·3 (4)
C(1)–N(1)–C(6)	119·7 (5)	N(3)–C(3)–C(2)	110·3 (4)
C(4)–N(1)–C(6)	120·5 (4)	N(1)–C(4)–C(5)	117·5 (5)
C(5)–N(2)–C(7)	116·6 (5)	N(2)–C(5)–C(4)	124·5 (6)
C(3)–N(3)–C(8)	121·8 (5)	N(1)–C(6)–C(7)	118·7 (5)
C(3)–N(3)–C(10)	118·5 (5)	N(2)–C(7)–C(6)	122·1 (5)
C(8)–N(3)–C(10)	119·7 (5)	N(3)–C(8)–C(9)	118·9 (5)
C(9)–N(4)–C(11)	117·2 (6)	N(4)–C(9)–C(8)	122·9 (6)
N(1)–C(1)–C(2)	110·8 (4)	N(3)–C(10)–C(11)	118·6 (6)
		N(4)–C(11)–C(10)	122·6 (6)

1973) and [py–$(CH_2)_3$–py](TCNQ)$_2$ (py = pyridine, TCNQ^{2-} = dianion of 7,7,8,8-tetracyanoquinodimethane) (Aswell, Bartlett, Davies, Eley, Wallwork, Willis, Harper & Torrance, 1977). In the nicotinamide complex a similar propanediyl conformation [*gauche* (−64·3°)/*trans* (−166·9°)] to that in the present compound is found. The distance between the quaternary N atoms is 4·452 Å with the rings at an angle of 120·3° with respect to one another. In the pyridinium complex a *trans* propanediyl chain conformation (torsion angles of −174·1 and −179·8°) results in a more extended configuration. The distance between the quaternary N atoms is 4·917 Å and the pyridinium rings have an angle of 66·0° between them. The N(1)–C(1) and N(3)–C(3) bond lengths in the present complex are similar to those found in the nicotinamide complex and about 0·03 Å longer than observed in the pyridine complex.

The Br$^-$ ions are located in two different environments. Br(1) is associated with the rings containing N(3) with a Br(1)$\cdots$N(3) distance of 3·593 (5) Å. Br(2) is found between two rings containing N(1) [Br(2)$\cdots$N(1) = 3·473 (4) and 3·780 (4) Å] and one ring containing N(3) [Br(2)$\cdots$N(3) = 3·593 (5) Å]. Two short Br$\cdots$C distances, Br(2)$\cdots$C(4) = 3·299 and
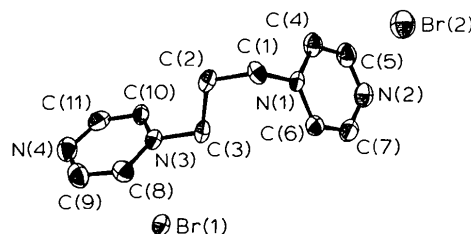
Fig. 1. *ORTEP* diagram (Johnson, 1965) and atomic numbering scheme for title compound.

unsymmetrical with respect to the two pyrazinium rings. The C(1)–C(2) bond is perpendicular (−89·7°) to the plane of the ring containing the N(1) atom, while the C(3)–C(2) bond is twisted only 68·4° with respect to the plane of the ring containing N(3). The N(1)–C(1)–C(2)–C(3) torsion angle is 61·3° while the N(3)–C(3)–C(2)–C(1) angle is 167·8°, such that the non-H substituents are *gauche* with respect to the C(1)–C(2) bond and *trans* around the C(3)–C(2) bond. The distance between the quaternary N atoms N(1)$\cdots$N(3) is 4·415 Å and the planes of the two pyrazinium rings are at an angle of 115·0° with respect to each other.

There have been two other structural analyses of complexes in which two N-heterocycles have been quaternized by a 1,3-propanediyl bridging group, as in the present compound. These are [nic–$(CH_2)_3$–nic]-$Cl_2.H_2O$ (nic = nicotinamide) (Frank, Thayer & Paul,
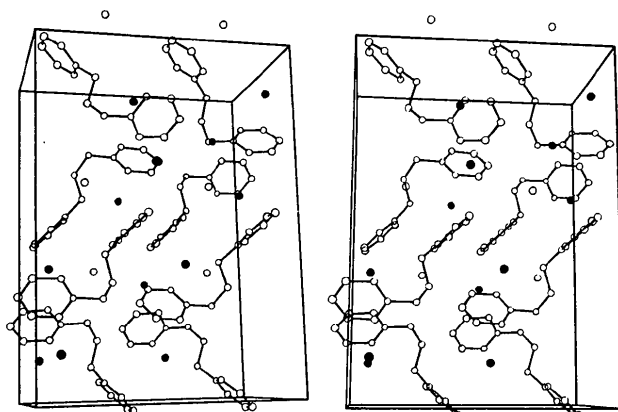

Fig. 2. Stereoscopic view of the unit cell showing the crystal packing. Br(1) is shown as unfilled circles and Br(2) as filled circles. (*a* axis horizontal, *b* axis vertical.)

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

References

ASWELL, G. J., BARTLETT, V. E., DAVIES, J. K., ELEY, D. D., WALLWORK, S. C., WILLIS, M. R., HARPER, A. & TORRANCE, A. C. (1977). *Acta Cryst.* B33, 2602–2607.
ATTALLA, M. I., McALPINE, N. S. & SUMMERS, L. A. (1984). *Z. Naturforsch. Teil B*, 39, 74–78.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
FRANK, J. K., THAYER, N. N. & PAUL, I. C. (1973). *J. Am. Chem. Soc.* 95, 5386–5390.
FRENZ, B. A. (1979). *Enraf–Nonius Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
WISHART, J. F., BINO, A. & TAUBE, H. (1986). *Inorg. Chem.* 25, 3318–3321.

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. $C_{20}H_{21}N_2O^+.HSO_4^-$, $M_r = 402·51$, orthorhombic, $Pca2_1$, $a = 21·655$ (4), $b = 11·598$ (3), $c = 7·392$ (4) Å, $V = 1857$ (1) Å^3, $Z = 4$, $D_x = 1·44$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·21$ mm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0·037$ for 2137 reflections with $I > 2·5\sigma(I)$. 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)
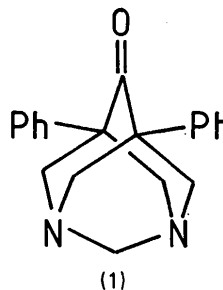
Experimental. 5,7-Diphenyl-1,3-diazatricyclo[3.3.1.1^{3,7}]decan-6-one (1) (Chiavarelli & Settimj,