Références

Boileau, J., Emeury, J. M., de Longueville, Y. & Monteagudo, P. (1981). *Internationale Jahrestatung*, Karlsruhe CA, 1–3 juillet 1981, pp. 505–524.

Boileau, J., Emeury, J. M. & Kerhen, J. P. (1973). Brevet Français 73.27038 (24 juillet 1973).

Boileau, J., Wimmer, E., Carail, M. & Gallo, R. (1985). *Propellants Explos. Pyrotechnics*. Soumis.

Chapman, N. B. & Shorter, J. (1978). *Correlation Analysis in Chemistry*. London: Plenum.

Emeury, J. M. & Girardon, H. (1980). Brevet Européen 6782 (9 janvier 1980).

Frenz, B. A. (1978). *Computing in Crystallography*, édité par H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Gallo, R. (1983). *Prog. Phys. Org. Chem.* **14**, 115–163.

Gordon, A. J. & Ford, R. A. (1972). *The Chemist's Companion*, pp. 107–112. New York: John Wiley.

Himes, V. L., Hubbard, C. R., Mighell, A. D. & Fatiadi, A. J. (1978). *Acta Cryst.* B**24**, 3102–3104.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee.

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. de York, Angleterre, et Louvain-la-Neuve, Belgique.

Olofson, G., Stilbs, P., Drakenberg, T. & Forsen, S. (1971). *Tetrahedron*, **27**, 4583–4587.

Petersen, H. (1973). *Synthesis*, pp. 243–292.

Stilbs, P. (1971). *Acta Chem. Scand.* **25**, 2635–2641.

Stilbs, P. (1972). *Tetrahedron Lett.* pp. 227–230.

Acta Cryst. (1985). C**41**, 1683–1685

2,3,4,5,6,7,8,9-Octahydro-2,2,5,5,8,8-hexamethyl-1*H*-benzo[1,2-*c*:3,4-*c′*:5,6-*c″*]-tripyrrolium Tribromide Dihydrate

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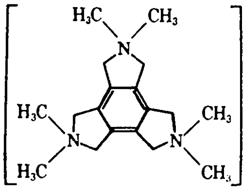
Abstract. $C_{18}H_{30}N_3^{3+}.3Br^-.2H_2O$, $M_r = 564{\cdot}20$, triclinic, $P\bar{1}$, $a = 11{\cdot}097\,(1)$, $b = 13{\cdot}502\,(1)$, $c = 9{\cdot}124\,(1)$ Å, $\alpha = 92{\cdot}87\,(1)$, $\beta = 111{\cdot}37\,(1)$, $\gamma = 66{\cdot}08\,(1)°$, $V = 1156{\cdot}0\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}53$ g cm^{-3} (by flotation in CCl_4/1,2-dichloropropane mixture), $D_x = 1{\cdot}621\,(1)$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 55{\cdot}6$ cm^{-1}, $F(000) = 568$, $T = 297\,(3)$ K, final $R = 0{\cdot}074$ and $wR = 0{\cdot}070$ for 2525 observed reflections. The structure consists of discrete cations with nominal C_3 symmetry. At the nucleus of the cation is a planar six-membered aromatic ring; the bridged and nonbridged C—C bonds in this ring are virtually equivalent in length (1·388 and 1·387 Å, respectively). Attached to the central ring are three appreciably puckered five-membered pyrrolium rings. The bend in each pyrrolium ring, averaging 31°, raises the N atom about 0·47 (10) Å above the plane of the other four atoms; this results in an alignment of the methyl groups to axial and equatorial positions. Two cations are held together electrostatically as a 'sandwich' by a central network of four water molecules and two bromide anions, forming a six-membered ring held together by O—H···Br$^-$ and O—H···O hydrogen bonds; two other Br$^-$ anions link to the ring through O—H···Br$^-$ hydrogen bonds.

Introduction. In the search for novel aromatic systems to use in the synthesis of zeolites, a series of tris- and tetrakis(quaternary ammonium) compounds were investigated. One of these was the title compound, synthesized according to a procedure described elsewhere (Ciric, Lawton, Kokotailo & Griffin, 1978). The cation (I) will be referred to as triquat.



(I)

This material was used to synthesize a new zeolite, ZSM-18 (Ciric, 1976).

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Experimental. Colorless ellipsoidal crystal; minor and major diameters 0·1768 and 0·2577 mm, respectively; Siemens diffractometer equipped with a GE quarter-circle Eulerian cradle; Zr-filtered Mo $K\alpha$ radiation; no monochromator; no balanced filters; unit-cell dimensions by least-squares refinement of 67 strong independent reflections with $12° < \theta < 14{\cdot}5°$; data collected by θ–2θ step scan; index range: h −13 to 13, k −15 to 15, l 0 to 10; three reference reflections measured after every 50 reflections; no significant variation or decay of standards detected; 4540 reflections measured within $2° \leq \theta \leq 25°$; 2525 reflections classified as observed $[F \geq 3\sigma(F)]$; intensities corrected for Lorentz, polarization, and absorption; transmission factors ranged from 0·406 to 0·582, based on a linear absorption coefficient of 55·6 cm^{-1} for Mo $K\alpha$; estimated standard deviation in the intensity assigned on the basis of counting statistics (Corfield, Doedens & Ibers, 1967); estimated standard deviation in F_o calculated by finite-difference method (Williams & Rundle, 1964); structure solved by direct methods.

Structure assumed, initially, to be centrosymmetric; an E map based on 240 phased reflections (Long, 1965) revealed the three bromide ions; an electron density synthesis, phased by these ions, revealed the cation positions; positional and isotropic thermal parameters of Br$^-$ and nonhydrogen atoms of the cations refined by full-matrix least squares (*NUCLS*; R. J. Doedens and J. A. Ibers, undated) using F_o magnitudes weighted by $1/\sigma^2(F_o)$; anisotropic thermal parameters for Br$^-$, C and N then introduced. A difference (ΔF) synthesis [*FOUR*; L. J. Guggenberger, undated (a modification of a program by C. J. Fritchie)] revealed two previously unidentified maxima at electron density levels equivalent to C and separated by about 2·7 Å; these maxima attributed to the O atom of water molecules; presence of two water molecules confirmed by mass spectrometric analysis. Positions of the H atoms in the cations, based on C—H = 1·0 Å and normal tetrahedral geometry, included in the subsequent refinement as fixed parameters with isotropic thermal parameters of 3·0 and 3·5 Å^2 for those attached to the pyrrolium rings and in the methyl groups, respectively; water O atoms then refined with anisotropic thermal parameters; H positions at O(1) and approximate positions at O(2) revealed on ΔF synthesis; final set of fixed H positions derived by treating the water molecules as rigid groups with an O—H distance of 0·85 Å and an H—O—H angle of 104·5°. Atomic scattering factors for Br$^-$ ions from Cromer & Waber (1965), for neutral C, N and O from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965); effects of anomalous scattering by bromine included in F_c, using values of f' and f'' given in *International Tables for X-ray Crystallography* (1962); final discrepancy values $R = 0{\cdot}074$ and $wR = 0{\cdot}070$ for all 2525 reflections above $3\sigma(F_o)$; final error-of-fit, based on the 2525 reflections (m) and 235 variables (n), was 1·81; m/n ratio 10·7; final $\Delta/\sigma < 0{\cdot}02$; final difference electron density synthesis essentially featureless; no correction for secondary extinction.

Table 1. *Positional parameters with B_{eq} values*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Anions				
Br(1)	0·49841 (14)	0·72423 (13)	0·00780 (16)	5·13 (6)
Br(2)	0·28533 (14)	0·05132 (10)	0·30687 (15)	4·34 (5)
Br(3)	0·18767 (13)	0·48389 (10)	0·39464 (13)	3·54 (5)
Cation				
C(1)	0·0314 (10)	0·7243 (7)	1·0507 (11)	2·3 (3)
C(2)	0·1767 (10)	0·6990 (8)	1·1094 (11)	2·2 (4)
C(3)	0·2344 (10)	0·7344 (8)	1·2523 (12)	2·5 (3)
C(4)	0·1534 (12)	0·7930 (8)	1·3358 (12)	2·9 (4)
C(5)	0·0092 (10)	0·8165 (8)	1·2775 (12)	2·6 (4)
C(6)	−0·0529 (10)	0·7813 (7)	1·1344 (11)	2·1 (3)
C(7)	−0·0104 (10)	0·6838 (8)	0·8947 (11)	2·7 (4)
C(8)	0·2410 (11)	0·6366 (9)	1·0002 (12)	3·2 (4)
C(9)	0·3881 (11)	0·7198 (9)	1·3391 (13)	3·3 (4)
C(10)	0·2440 (11)	0·8209 (8)	1·4868 (13)	3·2 (4)
C(11)	−0·1010 (11)	0·8797 (9)	1·3461 (12)	3·2 (4)
C(12)	−0·2070 (11)	0·8157 (8)	1·0993 (12)	2·8 (4)
C(13)	0·1354 (12)	0·5855 (10)	0·7337 (13)	3·9 (4)
C(14)	0·1576 (12)	0·4911 (9)	0·9686 (13)	3·4 (4)
C(15)	0·5009 (12)	0·7838 (10)	1·5942 (13)	3·9 (4)
C(16)	0·4290 (12)	0·6363 (9)	1·5947 (13)	3·6 (4)
C(17)	−0·3626 (11)	0·9293 (9)	1·2395 (13)	3·8 (4)
C(18)	−0·1919 (13)	0·7409 (10)	1·3504 (13)	3·8 (5)
N(1)	0·1306 (9)	0·5987 (7)	0·8954 (9)	2·9 (3)
N(2)	0·3917 (9)	0·7415 (7)	1·5056 (9)	2·6 (3)
N(3)	−0·2192 (8)	0·8418 (7)	1·2582 (9)	2·7 (3)
Water molecules				
O(1)	−0·0430 (13)	1·1156 (10)	1·2722 (11)	6·0 (4)
O(2)	−0·2235 (14)	1·9571 (9)	1·0263 (14)	7·4 (8)
H(1*a*)	0·036 (13)	1·110 (11)	1·271 (16)	
H(1*b*)	−0·068 (13)	1·075 (11)	1·204 (16)	
H(2*a*)	−0·203 (21)	1·069 (17)	0·950 (25)	
H(2*b*)	−0·300 (21)	1·113 (17)	1·017 (25)	

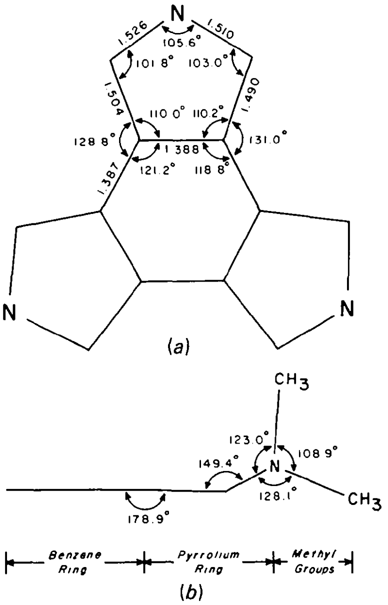
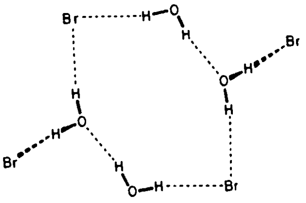


Fig. 1. (*a*) View normal to the cation showing the ring structure and the *average* C_3-symmetry-related bond lengths (Å) and angles (°). (*b*) Side view of the cation illustrating average deviations from planarity and the C—N—CH$_3$ angles. Standard deviations are in the ranges 0·012–0·013 Å and 0·7–0·9°.

Discussion. Atomic coordinates are listed in Table 1.* Systematic variations in bond lengths and angles (Fig. 1) indicate that the cation is slightly deformed from C_{3v} to C_3 symmetry. The pyrrolium ring is puckered with the N atom raised 0·47 (10) Å above the plane defined by the other four atoms in the ring (Fig. 1). The stereochemical consequence is a rotation of one set of methyl groups to an axial position and the other set to a nearly equatorial position relative to the plane of the cation. Two triquat cations are held together electrostatically by a central network of bromide ions and water molecules. Four water molecules and two bromide ions in this central network are hydrogen bonded so as to form a planar six-membered ring (II).



(II)

Each member of this ring is situated above or below a pyrrolium ring. The O···O separation is exactly that (2·75 Å) in the low-pressure forms of ice at 100 K (Kamb, 1968); the O···Br separations range from 3·20 to 3·28 Å and are consistent with distances found in other crystalline hydrates where hydrogen bonding occurs (Lundgren, 1970; Lundgren & Olovsson, 1968; Johnson, Maier & Paul, 1973; Johnson, Frank & Paul, 1973). The top and bottom halves of this dimer approach the central $4(Br^-.H_2O)$ network at normal van der Waals distances, indicating that forces holding the dimer together are primarily electrostatic in nature. The only remaining anion, Br(3), fills interstitial holes between dimers, also at normal van der Waals distances.

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* Lists of structure factors, H-atom positional parameters, anisotropic thermal parameters, bond lengths and angles, root-mean-square thermal amplitudes of vibration, torsion angles within the cation, and weighted least-squares-plane calculations through sets of atoms in the cation, and stereoscopic views of the dimer and the packing have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42327 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ciric, J. (1976). US patent 3 950 496.

Ciric, J., Lawton, S. L., Kokotailo, G. T. & Griffin, G. W. (1978). *J. Am. Chem. Soc.* **100**, 2173–2175.

Corfield, P. W. R., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 215, 216. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, P. L., Frank, J. K. & Paul, I. C. (1973). *J. Am. Chem. Soc.* **95**, 5377–5385.

Johnson, P. L., Maier, C. A. & Paul, I. C. (1973). *J. Am. Chem. Soc.* **95**, 5370–5377.

Kamb, B. (1968). *Structural Chemistry and Molecular Biology*, 1st ed., edited by A. Rich & N. Davidson, p. 507. San Francisco: Freeman.

Long, R. E. (1965). *A Program for Sign Determination by Reiterative Application of Sayre's Equation.* Univ. of California.

Lundgren, J. O. (1970). *Acta Cryst.* B**26**, 1893–1899.

Lundgren, J. O. & Olovsson, I. (1968). *J. Chem. Phys.* **49**, 1068–1074.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Williams, D. E. & Rundle, R. E. (1964). *J. Am. Chem. Soc.* **86**, 1660–1666.