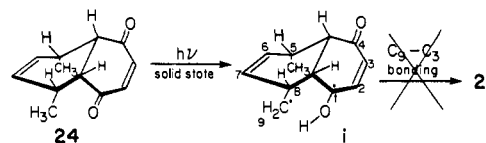


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- (32) Cookson, Crundwell, Hill, and Hudec^{33a} have reported that irradiation of crystals of tetrahydro-1,4-naphthoquinone **25** yields a dimer of unknown stereochemistry assumed to have the gross structure of **27b**. No melting point was reported for this material. Similarly, Dekker, Martins, Kruger, and Goosen^{33b} have reported the formation of a dimer of unknown stereochemistry from the photolysis of substrate **26** (Pyrex-filtered sunlight, phase unspecified). Its reported melting point (265–268 °C dec) corresponds to that of **27c**, mp 265 °C dec.
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- (34) Note in addition that diketone **28**, which is formed from **24** in solution via γ -hydrogen abstraction followed by C_9 to C_3 bonding and ketonization, cannot be formed in the solid state since the required biradical collapse

is impossible from the twist conformation **i**. Formation of **28** requires an intervening half-chair–half-chair ring flip of biradical **i** which is possible in solution but not in the solid state.



- (35) Assuming only cis stereochemistry at the four ring junctions, six diastereomeric dimers of substrate **25** are possible. They are anti-anti-anti, anti-anti-syn, syn-anti-syn, anti-syn-anti, anti-syn-syn, and syn-syn-syn. Of these, the anti-anti-anti dimer **27b** is clearly the least sterically congested and the syn-syn-syn isomer the most.
- (36) It is interesting to note that the relative carbonyl double bond geometry shown in Figure 4 appears to favor involvement of the oxygen double bond $2p$ atomic orbital rather than its n orbital in interacting with and bonding to C_7 . This is in contrast to the commonly accepted notion that the mechanism of oxetane formation between carbonyl compounds and electron-rich olefins involves the oxygen n orbital in exciplex and/or initial biradical formation. See N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975), and references cited therein.
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Synthesis and Crystal Structure of 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, $C_{18}H_{30}N_3^{3+} \cdot 3Br^- \cdot 2H_2O$ ¹

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Abstract: A new trisquaternary ammonium compound, referred to as triquat tribromide dihydrate, has been synthesized from a mixture of hexabromomethylbenzene and anhydrous dimethylamine in anhydrous ethanol. The colorless product crystallizes in the centrosymmetric triclinic space group $P\bar{1}-C_1$, with lattice parameters $a = 11.097 \pm 0.001$, $b = 13.502 \pm 0.001$, $c = 9.124 \pm 0.001$ Å, $\alpha = 92.87 \pm 0.01^\circ$, $\beta = 111.37 \pm 0.01^\circ$, and $\gamma = 66.08 \pm 0.01^\circ$. The structure consists of discrete cations of nominal C_3 symmetry, two of which are held together electrostatically as a sandwich by a central network of bromide anions and water. The two halves of the resulting dimer are related by a crystallographic center of symmetry. At the center of the triply charged cation is a planar six-membered aromatic ring to which are attached three appreciably puckered five-membered (pyrrolium) rings. There are two methyl groups per nitrogen atom.

Introduction

There are very few tris- and tetrakisquaternary ammonium salts reported in the literature in which the charged nitrogen atoms are relatively close to each other in a molecule possessing

rigidity and high symmetry.^{4a,b} We wish to report the synthesis and characterization of 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.

It had been recognized by Backer^{4c} that hexabromometh-

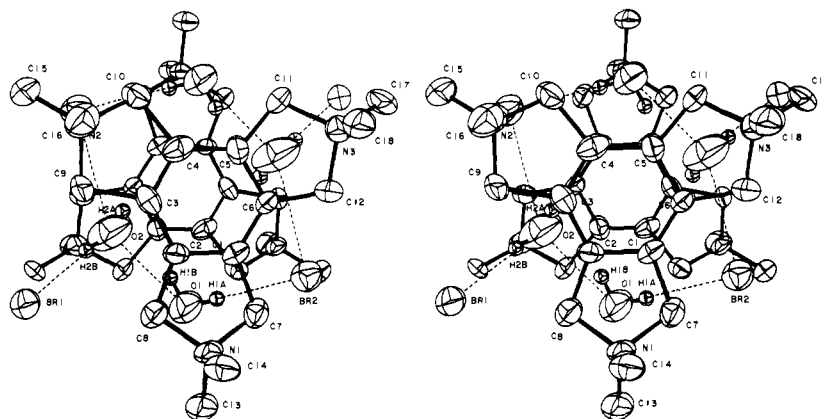
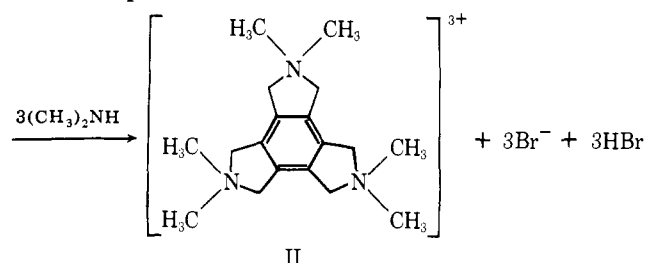
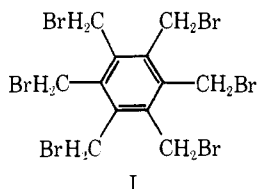
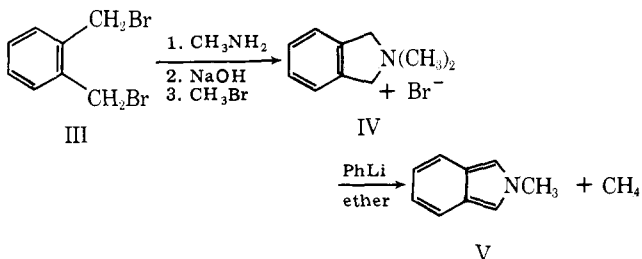


Figure 1. Stereoview of the $[C_{18}H_{30}N_3]^{3+} \cdot 2Br^- \cdot 2H_2O$ dimer *normal* to the aromatic rings. For simplicity, hydrogen atoms in the cation are not shown. Ellipsoidal boundaries (except water hydrogens) are at the 60% probability level.

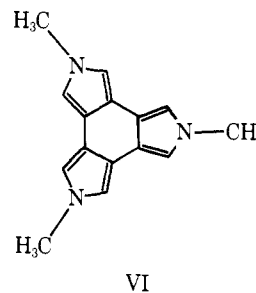
ylbenzene (I), prepared by direct bromination of hexamethylbenzene in ethylene dibromide, reacts with 3 mol of an amine such as *N*-methylaniline, but the structures of the resulting products were not established. Our curiosity regarding the structures of these products was stimulated by our continuing interest in and search for potential precursors for unusual aromatic systems.



As suspected, the amine adducts proved to be tripyrrolium salts as confirmed by NMR spectroscopy conducted on the hexamethyl derivative II obtained from I upon heating with dimethylamine in nitromethane. It had been demonstrated by Wittig and co-workers that the corresponding dimethylisoin-dolinium bromide (IV) prepared from *o*-xylylene dibromide (III) gives the methyl isoindole V upon treatment with phen-



yllithium in ether.^{4d} It is our hope that by analogy II will give the fused tris-*N*-methylpyrrole VI under similar conditions. Quaternary ammonium compounds have been used in the synthesis of a number of zeolites.⁵ In the continuing search for other such compounds triquat dibromide dihydrate was recognized as a candidate and was used to synthesize zeolite ZSM-18.⁶ This significant and unusual property prompted us to initiate an x-ray study of the structure of triquat tribromide dihydrate.



Experimental Section

Preparation of Hexabromomethylbenzene (I).^{4c} Hexamethylbenzene (39 g) (Aldrich Chemical Co.) was dissolved in 900 mL of dibromoethane (Aldrich) and vigorously stirred in a 3000-mL flask equipped with reflux condenser, stirrer, thermometer, and dropping funnel. The top of the condenser was connected to a Rashig ring scrubber in order to remove HBr vapors. A photoflood light (Type 2911, "Nolequartz Nooklite", Mole-Richardson Co., Hollywood, Calif.) was used as a light source to facilitate the rate of the reaction. Bromine (104 mL, 2 mol) was added slowly from the dropping funnel and the reaction was complete in 2–3 h, yield 140 g (95%), mp 298 °C. The crystals were dried under vacuum at 50 °C overnight and used without further purification for preparation of triquat tribromide.

Preparation of Triquat Tribromide Dihydrate. A suspension of 254.4 g (0.39 mol) of hexabromomethylbenzene in 800 mL of anhydrous ethanol was vigorously stirred in a 3-L flask equipped with stirrer, reflux condenser, thermometer, and gas inlet. Anhydrous dimethylamine was introduced at 70 °C and periodically a sample of the suspension was removed and diluted with water. When the reaction was nearly complete, a sample of the suspension could be completely dissolved by adding a few milliliters of water. The time required depends on crystal size of hexabromomethylbenzene, rate of stirring, dimethylamine addition, etc., and may range from 5 to 20 h. The reaction conditions were maintained for an additional 2–3 h beyond this point, yield 200–220 g (theory 216 g), purity, by Mohr bromide titration, 70–90%. The low purity is attributed to the formation of a solvate complex between the trisquaternary cation and dimethylamine. Purification was achieved by recrystallization from an ethanol–water mixture.

Anal. Calcd for $C_{18}H_{30}N_3Br_3$ (fw 528.19): C, 40.93; H, 5.72; N, 7.96; Br, 45.39. Calcd for $C_{18}H_{30}N_3Br_3 \cdot 2H_2O$ (fw 564.22): C, 38.32; H, 6.07; N, 7.44; Br, 42.49. Found (twice recrystallized): C, 39.0; H, 6.10; N, 7.32; Br, 44.0.

Preparation of Anhydrous Triquat Tribromide (II).^{4d} To a slurry of 3.18 g (6.0 mmol) of hexabromomethylbenzene in 100 mL of nitromethane, maintained at the reflux temperature, was added gaseous dimethylamine through a gas dispersion tube. The color of the slurry turned from yellow to orange within 2–3 min and heating and stirring were continued for an additional 0.5 h. The solid which deposited (0.75 g) was then collected on a filter and subsequently recrystallized twice from ethanol and water and dried for an extended period at 77 °C under vacuum. As expected the trisquaternary salt is soluble in water,

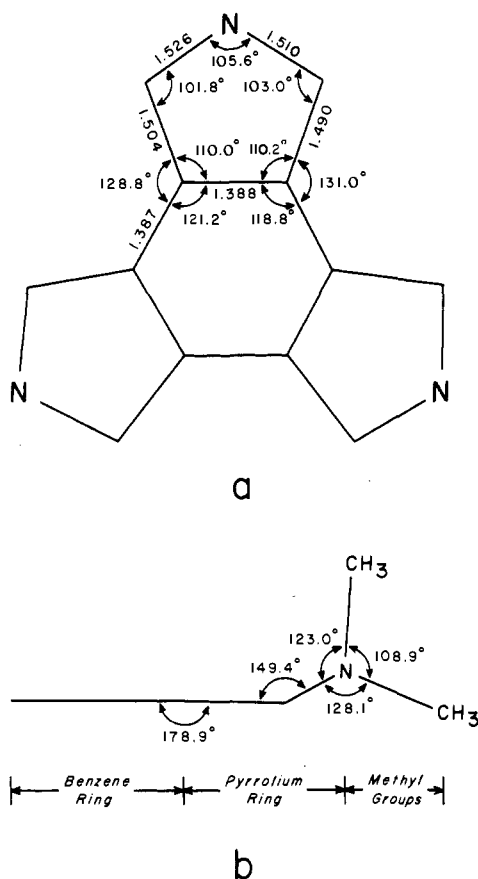


Figure 2. (a) View normal to the cation showing the ring structure and the average C_3 -symmetry related bond lengths and angles. (b) Side view of the cation illustrating average deviations from planarity and the C-N-CH₃ angles.

but insoluble in organic solvents such as ethanol and acetonitrile, and shows signs of decomposition at 250 °C. The NMR spectrum of II in D₂O shows singlet signals at δ 4.97 (2 H) and 3.41 (3 H) assigned to the methylene and methyl protons, respectively; the DHO signal occurs at δ 5.32.

Anal. Calcd for $C_{18}H_{30}N_3Br_3$: C, 40.93; H, 5.72; N, 7.96; Br, 45.39. Found: C, 40.87; H, 5.89; N, 8.05; Br, 45.48.

Description of the Structure. The structure of triquat tribromide dihydrate was solved by direct methods using three-dimensional x-ray diffraction data collected on an automated three-circle diffractometer. The details of the structure and its determination will be published elsewhere.⁷

The triply charged triquat cation, illustrated in Figure 1, consists of a central planar six-membered aromatic ring to which are attached three appreciably puckered five-membered (pyrrolium) rings. There are two methyl groups per nitrogen. The bridged and nonbridged C-C bonds of the aromatic ring are virtually equivalent in length (1.388 and 1.387 Å, respectively). Systematic variations, albeit small, in the bond lengths and bond angles throughout the cation, however, indicate that it is slightly deformed from C_{3v} to C_3 symmetry. A summary of these parameters for the C_3 configuration is presented in Figure 2. The central aromatic ring is rigid but the five-membered pyrrolium ring is puckered. The bend, averaging 31°, raises the nitrogen about 0.47 Å above the plane of the other four atoms. This results in an alignment of the methyl groups to axial and equatorial positions, as illustrated in Figure 2b.

The two triquat cations are held together electrostatically by a central network of bromide ions and water. Four water molecules and two bromine ions are bonded so as to form a planar six-membered ring (VII). As illustrated in Figure 1, each member of this ring is situated

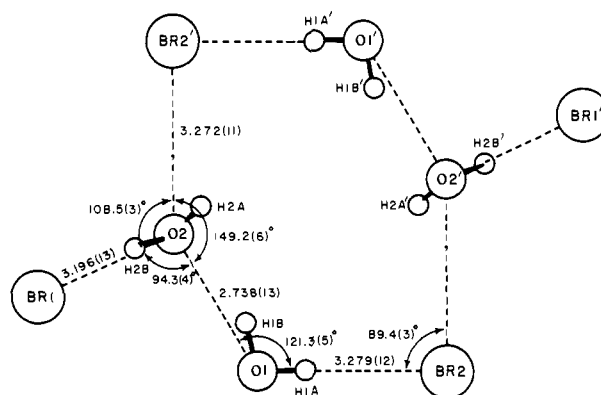
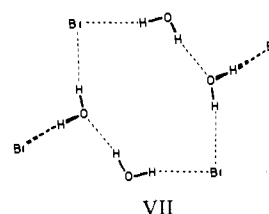


Figure 3. Schematic illustration of the Br...water network at the center of the dimer. Distances and angles, plus their associated standard deviations, are shown with respect to the bromine and oxygen atomic centers. Br(1) and Br(1') are 1.893 (2) Å above and below the plane defined by the other six nonhydrogen atoms.



above or below a pyrrolium ring. Orientation of water hydrogens and distances and angles are shown in Figure 3. The O-O separation is exactly that (2.75 Å) in the low-pressure forms of ice at 100 K,⁸ but longer than those in proton hydrates (H₂O₅⁺, H₂O₃⁺, and H₉O₄⁺)⁹. 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.¹⁰⁻¹²

The top and bottom triquat cations are at normal van der Waals distances from the central 4(Br...H₂O) network indicating that the forces holding the dimer together are primarily electrostatic in nature.

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