(ppm, $CDCl_3$) 168.80, 147.25, 142.34, 139.09, 70.74, 52.09, 51.46, 34.08, 18.25; mass spectrum, *m/e* ($M^+$) calcd 288.1361, obsd 288.1369.

Anal. Calcd for $C_{17}H_{10}O_4$: C, 70.81; H, 6.99. Found: C, 70.83; H, 7.05.

**1,4,5,8-Tetrahydro-*N*,1,4-trimethyl-5,8-methanophthalazine-2,3-dicarboximide (17 and 18).** A solution of **5** (410 mg, 2.80 mmol) in dichloromethane (10 mL) was stirred under nitrogen at -70 °C while a solution of *N*-methyltriazolinedione in dichloromethane was introduced via syringe until a slight color persisted. The resulting solution was allowed to warm to room temperature and the solvent was evaporated to give a quantitative yield of adducts **18** (45%) and **17** (55%). This mixture was separated by HPLC on a Waters Prep 500 instrument with petroleum ehter-ethyl acetate (3:1) as eluent. The individual isomers were subsequently recrystallized from ether-petroleum ether and obtained as colorless crystalline solids.

For **18**: mp 138-140 °C; IR ($cm^{-1}$, KBr) 3020, 2980, 2940, 1760, 1720, 1690, 1475; $^1H$ ($CDCl_3$) $\delta$ 6.8 (m, 2 H), 4.3 (q, $J = 6$ Hz, 2 H), 3.5 (m, 2 H), 3.05 (s, 3 H), 2.1 (m, 2 H), 1.55 (d, $J = 6$ Hz, 6 H); $^{13}C$ NMR (ppm, $CDCl_3$) 153.17, 147.15, 142.83, 73.31, 52.48, 49.86, 24.81, 18.06; mass spectrum; *m/e* ($M^+$) calcd 259.1321, obsd 259.1325.

Anal. Calcd for $C_{14}H_{17}N_3O$: C, 64.87; H, 6.61. Found: C, 64.84; H, 6.61.

For **17**: mp 131-132 °C; IR ($cm^{-1}$, KBr) 3060, 2950, 2930, 2860, 1760, 1715, 1465; $^1H$ NMR ($CDCl_3$) $\delta$ 6.8 (m, 2 H), 4.7 (q, $J = 6$ Hz, 2 H), 3.5 (m, 2 H), 3.05 (s, 3 H), 2.1 (m, 2 H), 1.25 (d, $J = 6$ Hz, 6 H); $^{13}C$ NMR (ppm, $CDCl_3$) 153.07, 146.38, 142.73, 71.27, 51.85, 50.83, 24.81; mass spectrum, *m/e* ($M^+$) calcd 259.1321, obsd 259.1327.

**Catalytic Hydrogenation Experiments. General Procedure.** A sample of the appropriate triene adduct was dissolved in ethyl acetate and a small quantity of platinum oxide or 5% palladium-carbon was added. With vigorous stirring, the mixture was hydrogenated at atmospheric pressure and reduction was arrested upon uptake of 1 mol of hydrogen. The solution was filtered through Celite and the filtrate was evaporated. The residual solid in every case proved identical by mixture melting point and $^1H$ NMR with the corresponding diene adduct.

**Acknowledgment.** Financial support for the research carried out at The Ohio state University was provided by the National Cancer Institute (Grant CA-12115).

**Supplementary Material Available:** Tables of final atomic parameters, bond lengths, bond angles, torsion angles, and final anisotropic thermal parameters for **6**, **8**, **9**, **13**, and **18** (Tables II-XXV) (21 pages). Ordering information is given on any current masthead page.

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# A Stable $Br^+$ Complex. A Twisted Bicyclo[2.2.2]octane Derivative. Synthesis and Structure of Bis(quinuclidine)bromine(I) Tetrafluoroborate

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**Abstract:** A stable complex of $Br^+$, bis(quinuclidine)bromine(I), has been prepared, and the structure of its tetrafluoroborate salt has been determined by single-crystal X-ray diffraction techniques. Bis(quinuclidine)bromine(I) tetrafluoroborate crystallizes in the chiral space group $T^4$-$P2_13$ of the cubic system with four formula units in a cell of dimension $a = 12.029$ (4) Å; the ions are situated on $C_3$ axes. The structure was described by 84 variables, and at convergence of the full-matrix, least-squares refinement the values of $R$ and $R_w$ (on $F$, 453 data for which $F_o^2 > 3\sigma(F_o^2)$) are 0.024 and 0.027. The N-Br-N grouping of the cation is strictly linear, but the two Br-N bond lengths, 2.156 (2) and 2.120 (2) Å, are quite different. The conformation of the quinuclidines around the Br atom is neither staggered nor eclipsed; one quinuclidine is rotated relative to the other about the $C_3$ axis by about 30°. The quinuclidine cages are themselves twisted so that the two N-C-C-C torsion angles are 12.8 (4)° and -4.8 (5)°. The rms libration of the quinuclidine cages about the $C_3$ axis, estimated from a rigid-body thermal-motion analysis, is between 5.2° and 6.2°.

Since the discussions of Noyes and Stieglitz,[2] halogen cations of the type $X^+$ have received a great deal of attention, particularly as electrophiles in halogenation reactions; there is, however, no strong evidence for their existence as discrete ions in condensed phases. This is not surprising if one considers $X^+$ to be analogous to $H^+$, which is generally situated on some basic site. The $X^+$ ions have been the subject of several critical reviews.[3]

Although $I^+$ and $Br^+$ cannot be prepared as discrete ions, they can be stabilized in amine complexes with coordination number II. Several bis(amine)iodine(I) and -bromine(I) complexes have been investigated by various spectroscopic techniques,[4-8] and the evidence supports a linear N-X-N arrangement.

Bis(amine)halogen(I) complexes are important practically as new, stable sources of active halogen and theoretically as probes of the electronic structure about the central halogen.[9,10] These

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(1) (a) Berea College. (b) University of Kentucky.

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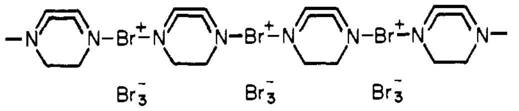
cations can be considered, in a simple approach, to have an $X^+$ central ion electrostatically coordinated by nitrogen lone pairs as in **1** or to be a hypervalent[11] species with an "expanded octet" of 10 electrons about the central halogen as in **2**. An intermediate, asymmetric representation as in **3** and **4** having an octet of electrons about X and a "no-bond" contribution is also possible.

$$\underset{\mathbf{1}}{N{:}\;X^+\;{:}N} \qquad \underset{\mathbf{2}}{{}^+N{-}X^-{-}N^+} \qquad \underset{\mathbf{3}}{{}^+N{-}X\;{:}N} \qquad \underset{\mathbf{4}}{N{:}\;X{-}N^+}$$

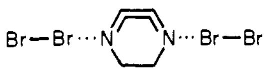
Collectively, all four representations can contribute to the electronic structure in a Mulliken-type model.[12] The bonding can also be described by a three-center molecular orbital treatment analogous to that for the trihalides.[5c]

We became interested in the bis(quinuclidine)bromine(I) complex when it occurred to us that the Dabco–$2Br_2$ complex[13] might have the structure (**5**) of a cationic polymer of alternating



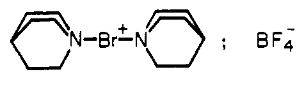
5

Dabco (1,4-diazabicyclo[2.2.2]octane) and $Br^+$, with $Br_3^-$ counterions. Alternatively, the structure of Dabco–$2Br_2$ might be that of the molecular complex **6**, a type seen by Hassel and characterized by a linear N–X–X arrangement.[14]



6

Since strong evidence exists for both types of complexes, both **5** and **6** are reasonable structures for Dabco–$2Br_2$; interconversion of the molecular and ionic complexes is also possible.[5c-i,6] However, because Dabco–$2Br_2$ is formed as an amorphous solid and is insoluble in a variety of solvents, its structure is not readily probed by conventional techniques. Thus, we chose to approach this problem by preparing and characterizing related complexes of quinuclidine that mimic local features of Dabco–$2Br_2$. Herein, we report the structure of bis(quinuclidine)bromine(I) tetrafluoroborate (**8**), which confirms that the local coordination of



8

$Br^+$ in **5** is reasonable. This is the first crystallographic study of a bis(amine)bromine(I) complex containing an aliphatic amine; the only other bromine(I) complex so investigated, bis(quinoline)bromine(I),[4a] contains an aromatic amine.

## Experimental Section

**Preparation of Bis(quinuclidine)bromine(I) Bromide (7).**[15] To a 50-mL flask containing a Teflon-covered magnetic stirring bar and 4.048 g (39.64 mmol) of quinuclidine (Aldrich) was added 15 mL of dichloromethane (Aldrich Gold Label) to dissolve the quinuclidine. To another flask containing 2.307 g (14.43 mmol) of $Br_2$ (A.C.S. reagent) was added 5 mL of dichloromethane. The $Br_2$ solution was added dropwise to the stirred solution of quinuclidine at room temperature. Some white crystals formed during the latter stages of addition of $Br_2$. After addition of $Br_2$, the mixture was stirred for about 10 min. Then, to the mixture was added an equal volume of ethyl ether (anhydrous, A.C.S. reagent) to precipitate additional white solid. This mixture was stirred for 15–30 min. Then the white solid was collected via vacuum filtration on a sintered glass frit in an adaptor with a ground glass joint that could be attached to a vacuum line. The solid was dried in this adaptor for 1–3 h by pumping on a vacuum line. The yield of solid **7** was 5.493 g (99.6%). No well-defined melting point for **7** was observed. Instead, when **7** was heated in a capillary, a red-brown coloration with decomposition commenced at 137 °C and became most apparent in the 150–160 °C range.

Table I. Summary of Crystal Data and Details of Intensity Collection and Refinement

| | |
|---|---|
| formula | $C_{14}H_{26}BBrF_4N_2$ |
| formula weight, amu | 389.1 |
| space group | $T^4$-$P2_13$ |
| *a*, Å | 12.029 (4) |
| *Z* | 4 |
| temp, °C | 22.5 |
| crystal volume, mm$^3$ | 0.0635 |
| bounding planes | $\{111\}, \{\bar{1}11\}, \{110\}$ |
| radiation | Mo Kα (graphite monochromator) |
| linear absorption coefficient, cm$^{-1}$ | 23.72 |
| transmission factors | 0.456–0.515 |
| decomposition, % | 3.7 |
| takeoff angle, deg | 2.5 |
| scan information | 0.8° 2θ (θ/2θ scan) each side of Kα doublet extended 25% for backgrounds; 120-s maximum scan time (target signal-to-noise ratio 50:1) |
| maximum 2θ, deg | 65.0 (0.756 Å$^{-1}$) |
| data collected | $h, k \geq 0; l > 0; k, l \geq h$ |
| *p* factor | 0.02 |
| unique data | 1183 |
| unique data with $F_o^2 > 3\sigma(F_o^2)$ | 453 |
| final number of variables | 84 |
| $R$, $R_w$ on $F$ ($>3\sigma$) | 2.4, 2.7 |
| error in observation of unit weight, e$^-$ | 1.60 |

**Preparation of Bis(quinuclidine)bromine(I) Tetrafluoroborate (8).**[15,16] To a 100-mL round-bottom flask with stirring bar and 3.130 g (8.190 mmol) of **7** was added 37 mL of dichloromethane to dissolve **7**. To another flask containing 1.667 g (8.562 mmol) of $AgBF_4$ (Alfa) was added 31 mL of acetonitrile (Aldrich Gold Label) to dissolve the $AgBF_4$. The solution of $AgBF_4$ was transferred to an addition funnel and added slowly dropwise to the stirred solution of **7**. The resulting precipitate of AgBr was collected and dried on a vacuum line as described above. The yield of AgBr was 98.8%. To the stirred filtrate was added an equal volume of ethyl ether to precipitate **8** as a white solid. After 30 min of additional stirring, **8** was collected and dried for 3 h on a vacuum line as described above. The yield of **8** was 2.785 g (87.3%). Samples of **8** have been stored for 3 years with no sign of decomposition.

**Crystals for Structure Determination.** Crystals were obtained by dissolving 1.40 g of **8** in 20 mL of acetonitrile. This solution was allowed to stand in an unstoppered flask for 11 days. Then, from this solution 0.561 g of crystals were collected. Anal. Calcd for $C_{14}H_{26}N_2BrBF_4$: C, 43.22; H, 6.74; N, 7.20; Br, 20.54; F, 19.53. Found: C, 43.39; H, 6.58; N, 7.10; Br, 20.37; F, 19.31.

Routinely recrystallized **8** can be obtained by cooling a saturated, warm solution of **8** in acetonitrile, or an acetonitrile solution of **8** can be concentrated by slowly removing the acetonitrile at reduced pressure to yield crystals of **8**. When crude or recrystallized **8** is heated in a capillary, decomposition begins at about 130 °C with the appearance of a red-brown color and becomes most apparent in the 160–165 °C range.

The purity of **7** and **8** were routinely monitored by titration with 0.1 N thiosulfate, according to conventional iodometric techniques. Typically, equivalent weights for **7** and **8** were obtained within 3% of the theoretical value for titrations involving 1 mequiv.

**Crystal Structure Determination.** Crystals grown as described above were mounted in air. Data were collected with an Enraf-Nonius CAD4/F diffractometer; details are summarized in Table I. The

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[15] In most cases, bis(amine)bromine(I) salts have been prepared from the corresponding bis(amine)silver(I) salts (Kauffman, G. B.; Stevens, K. L. *Inorg. Synth.* **1963**, *7*, 173–176).

[16] Bis(quinuclidine)iodine(I) salts have been reported.[5i]

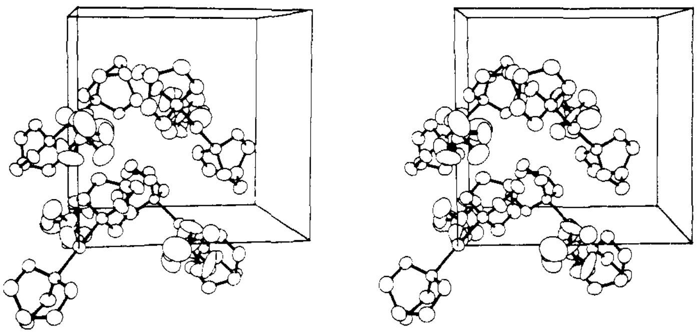

Figure 1. Stereoscopic drawing of the contents of a unit cell of bis(quinuclidine)bromine(I) tetrafluoroborate. Both orientations of the disordered $BF_4^-$ ions are shown. In this and the following drawings the shapes of the atoms correspond to 50% contours of thermal motion. Hydrogen atoms have been omitted for the sake of clarity.

crystals decomposed slightly during irradiation, turning from colorless to pale orange. Unit-cell parameters determined as part of a least-squares fit of the setting angles of 25 reflections having $2\theta > 22°$ indicated that the crystals are cubic, as did the morphology of the crystals and their darkness under crossed polarizers. A comparison of the intensities of the *hkl* and *hlk* reflections established the Laue group as $m3$; the extinctions then uniquely determined the space group to be $P2_13$. Since there are four formula units in the unit cell, both cation and anion are required to conform to $C_3$ symmetry.

The structure was solved by heavy-atom methods. The determination of the relative twists of the quinuclidine cages, which was made more difficult by the nearly face-centered arrangement of the Br atoms, was greatly facilitated by group-refinement techniques. The $BF_4^-$ ions were found to be disordered. The unique B–F vector is directed randomly [fractional occupancy for one position is 0.515 (15)] along the positive and negative directions of the body diagonal; there may also be rotational disorder about this [*xxx*] vector that is not described by the model. Correlation between atoms B(1) and B(2) and F(12) and F(22) was a problem in the least-squares refinement, and, consequently, the parameters of the atoms of the anion have not been determined very precisely. Calculations were carried out by using programs and procedures described previously.[17] Anomalous terms were included for the Br atoms, and it was determined that the enantiomer corresponded to the basic symmetry position $\bar{x}\bar{y}\bar{z}$ rather than $xyz$. The H atoms were added as fixed contributions to the $F_c$'s after idealization ($r_{C-H} = 1.00$ Å; $B$ is 1 Å$^2$ larger than that of the bonded C atom) at a late stage in the refinement. A correction for extinction,[18] with a final value of the extinction parameter of 0.79 (12) $\times 10^{-7}$, improved the agreement significantly. The highest peaks in a final difference Fourier map are less than 0.3 e/Å$^3$ high and are associated with the Br and F atoms. No important trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ [where $w = 4F_o^2/\sigma^2(F_o^2)$] as a function of $|F_o|$, $(\sin\theta)/\lambda$, or the Miller indices. The final coordinates and equivalent $B$'s of the refined atoms are listed in Table II. Tabulations of anisotropic thermal parameters, hydrogen atom parameters, and $10|F_c|$ vs. $10|F_o|$ are available.[19]

The anisotropic thermal parameters determined in this study for the atoms of the cation are reasonably precise. The esd's for the $U^{ij}$'s average $2 \times 10^{-4}$, $16 \times 10^{-4}$, and $29 \times 10^{-4}$ Å$^2$, and $\langle U^{ii}/\sigma(U^{ii})\rangle$ is 215, 29, and 20, respectively, for the Br, N, and C atoms. We therefore analyzed the $U^{ij}$'s of the cation according to the rigid-body model,[20] using Trueblood's program THMI.[21] The fit (see Table III) is only moderately good. The agreement factors $R = \{\sum[w(U_o^{ij} - U_c^{ij})]^2/\sum[wU_o^{ij}]^2\}^{1/2} = 0.042$ and $\Delta = \{\sum[w(U_o^{ij} - U_c^{ij})]^2/\sum w^2\}^{1/2} = 13 \times 10^{-4}$ [where $w = \sigma^{-2}(U^{ij})$] are acceptable, especially considering the sizes of the observed $\sigma(U^{ij})$'s, but the fit and agreement factors are dominated by the Br atom contributions. For the C atoms, $\langle(U_o^{ij} - U_c^{ij})^2\rangle^{1/2} = 52 \times 10^{-4}$, not quite twice the average $\sigma(U^{ij})$. The contributions to the thermal motion of the very low frequency modes described as Q–Br–Q (Q = quinuclidine) stretches and bends may render the rigid-body model inappropriate. Consequently, we repeated the analysis for the two quinuclidine cages taken individually. The agreement factors $R = 0.072$ and 0.058 and $\Delta = 25 \times 10^{-4}$ and $22 \times 10^{-4}$ increased slightly owing to the absence of the Br atom contributions, but $\langle(U_o^{ij} - U_c^{ij})^2\rangle^{1/2}$ for the C atoms was reduced to $40 \times 10^{-4}$ and $35 \times 10^{-4}$. The important difference between the two types of fit is the expansion of the libration tensor when the quinuclidine cages are considered independently.

Table II. Positional and Thermal Parameters for the Atoms of Bis(quinuclidine)bromine(I) Tetrafluoroborate

| atom | $x^a$ | $y$ | $z$ | $B$, Å$^2$ [b] |
|---|---|---|---|---|
| Br | −0.00164 (4) | −0.00164 | −0.00164 | 3.6 |
| F(11) | 0.5519 (7) | 0.5519 | 0.5519 | 6.9 |
| F(12) | 0.3815 (12) | 0.5304 (14) | 0.4780 (18) | 9.7 |
| F(21) | 0.4018 (7) | 0.4018 | 0.4018 | 9.4 |
| F(22) | 0.4052 (17) | 0.5552 (14) | 0.491 (3) | 11.6 |
| N(1) | 0.1019 (2) | 0.1019 | 0.1019 | 3.0 |
| N(2) | −0.1034 (2) | −0.1034 | −0.1034 | 3.5 |
| C(1) | 0.0415 (4) | 0.2059 (3) | 0.1283 (4) | 4.2 |
| C(2) | 0.1071 (4) | 0.2733 (4) | 0.2146 (4) | 4.7 |
| C(3) | 0.2234 (6) | 0.2234 | 0.2234 | 4.6 |
| C(4) | −0.0322 (4) | −0.1681 (4) | −0.1797 (4) | 4.7 |
| C(5) | −0.1034 (5) | −0.2382 (4) | −0.2588 (4) | 5.1 |
| C(6) | −0.2247 (5) | −0.2247 | −0.2247 | 4.8 |
| B(1) | 0.479 (4) | 0.479 | 0.479 | 7.4 |
| B(2) | 0.476 (2) | 0.476 | 0.476 | 7.8 |

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The equivalent $B$'s are calculated from the anisotropic thermal parameters $\beta$ and the direct metric $G$ as $^4/_3\mathrm{Tr}(\beta G)$.

Table III. Results of the Thermal Motion Analysis

| crystal system | complete cation | individual quinuclidines[a] |
|---|---|---|
| $L_c^{11} = L_c^{22} = L_c^{33}$, deg$^2$ | 10.7 (16) | 25.4 (29), 21.3 (26) |
| $L_c^{12} = L_c^{13} = L_c^{23}$, deg$^2$ | 8.3 (17) | 4.7 (17), 8.6 (14) |
| $T_c^{11} = T_c^{22} = T_c^{33}$, $\times 10^{-4}$ Å$^2$ | 450 (2) | 395 (8), 448 (7) |
| $T_c^{12} = T_c^{13} = T_c^{23}$, $\times 10^{-4}$ Å$^2$ | −25 (2) | −7 (8), −11 (7) |
| $S_c^{12} = S_c^{23} = S_c^{31}$, $\times 10^{-2}$ deg Å | 5 (3) | 12 (5), 2 (5) |
| $S_c^{13} = S_c^{21} = S_c^{32}$, $\times 10^{-2}$ deg Å | 1 (3) | −7 (5), 2 (5) |
| internal system ($C_3 \parallel x$) | complete cation | individual quinuclidines[a] |
| $L_i^{11}$, deg$^2$ | 27.4 | 34.8, 38.4 |
| $L_i^{22} = L_i^{33}$, deg$^2$ | 2.4 | 20.6, 12.7 |
| $T_i^{11}$, $\times 10^{-4}$ Å$^2$ | 400 | 381, 425 |
| $T_i^{22} = T_i^{33}$, $\times 10^{-4}$ Å$^2$ | 475 | 402, 460 |
| $S_i^{11} = -2S_i^{22} = -2S_i^{33}$, $\times 10^{-2}$ deg Å | 6 | 6, 4 |
| $S_i^{23} = -S_i^{32}$, $\times 10^{-2}$ deg Å | 3 | 16, 1 |

[a] Center of libration at N atom.

## Results and Discussion

The crystal structure determination confirms the synthesis of the surprisingly stable bis(quinuclidine)bromine(I) cation. The linear geometry expected for a 10-electron system is exact as a result of the symmetry requirements of the cubic space group. Figure 1 shows that the ions of the $BF_4^-$ salt form an arrangement reminiscent of the ionic rock-salt structure, with the Br and B atoms taking, approximately, the $M^+$ and $X^-$ positions, and the

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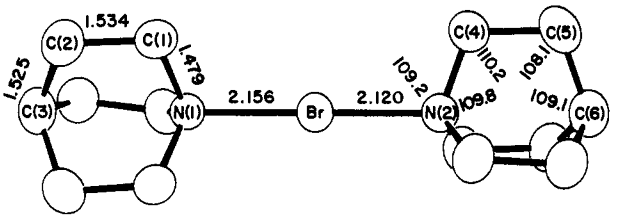

**Figure 2.** Drawing of the non-hydrogen atoms of the bis(quinuclidine)bromine(I) cation showing atom numbering and some bond lengths and angles. The bond lengths and angles involving C atoms have been averaged over the two halves of the cations. Estimated standard deviations for the individual Br–N, N–C, and C–C bond lengths are 2 × $10^{-3}$, 4 × $10^{-3}$, and 6 × $10^{-3}$ Å, respectively, and for the Br–N–C, C–N–C, and C–C–C bond angles are 0.2, 0.3, and 0.4°. The esd's for the means shown average 0.002 Å and 0.2°.

Table IV. Torsion Angles (deg) for the Bis(quinuclidine)bromide(I) Cation

| | |
|---|---|
| N(1)–C(1)–C(2)–C(3) | 12.8 (4) |
| N(2)–C(4)–C(5)–C(6) | −4.8 (5) |
| C(1)–N(1)–C(3)–C(2) | 7.8 (3) |
| C(4)–N(2)–C(6)–C(5) | −2.9 (3) |
| C(4)–N(2)–N(1)–C(1) | 27.8 (3) |
| C(5)–N(2)–N(1)–C(1) | 24.9 (3) |
| C(4)–N(2)–N(1)–C(2) | 35.5 (3) |
| C(5)–N(2)–N(1)–C(2) | 32.6 (3) |

**Figure 3.** Stereoscopic drawing of the cation showing the calculated hydrogen positions and the anisotropic thermal ellipsoids of the non-hydrogen atoms. In this drawing only, the hydrogens have been drawn with arbitrary isotropic thermal parameters of 2.0 Å$^2$.

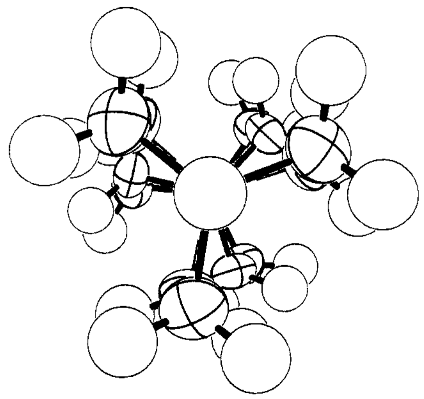

**Figure 4.** The bis(quinuclidine)bromine(I) cation viewed along the $C_3$ axis. The more twisted quinuclidine, which contains N(1), is in the rear of the drawing.

quinuclidines located, although asymmetrically, in the tetrahedral holes.

The structure of the cation is illustrated in Figure 2, which also shows the atom numbering scheme and some average bond lengths and angles. The most striking feature is the rather large difference, 0.036 (3) Å, between the two Br–N bond lengths. Such asymmetry has been seen before, however, both in bis(quinoline)bromine(I) perchlorate[4a] and in $Br_3^-$ and $I_3^-$[22] and is perhaps not too unusual in 10-electron systems. Infrared spectra of the bis(pyridine)bromine(I) cation indicate that the pyridines are not equivalent for the perchlorate and $Br_3^-$ salts but are equivalent when the anion is $PF_6^-$;[7b] parallel $^{14}N$ NQR studies support this interpretation.[7b] The dependence of the bonding around the Br atom on the counterion, which is presumably noncoordinating, suggests that the symmetric and asymmetric structures have very similar energies and that the degree of asymmetry observed may be determined by crystal packing considerations.

The average Br–N distances in the bis(quinuclidine)- and bis(quinoline)bromine(I) structures, 2.138 (3) and 2.132 (4) Å, respectively, are very similar, even though the ligands are aliphatic in the former cation and aromatic in the latter. This similarity contrasts with the conclusion[4c] that the average N–I bond length in the aliphatic amine complex bis(hexamethylenetetramine)iodine(I) of 2.30 (1) Å is longer than in the analogous complexes with the aromatic amines pyridine (2.16 (10) Å) and 3-picoline (2.24 (2) Å). The estimated standard deviations of the N–I distances are quite large, however, and the difference is at best barely significant. If, in fact, $\pi$ bonding tends to shorten the N–X bond, then the similarity of the mean N–Br bond lengths in the bis(quinuclidine)- and bis(quinoline)bromine(I) cations requires explanation. One possibility is that quinuclidine is a particularly effective $\sigma$ donor, so that increased $\sigma$ bonding in its complex compensates for the absence of the $\pi$ component that occurs in the quinoline complex. Quinuclidine[23] does have a greater gas-phase basicity (proton affinity) than pyridine[24] and, by extension, than quinoline.

The dimensions of the quinuclidine cage are rather precisely determined in this study and agree well with those found for 4-haloquinuclidinium perchlorates and chlorides.[25] Quinuclidine itself has not been studied in detail because its crystals are disordered.[26] The conformation around the Br atoms of the two quinuclidines is neither staggered nor eclipsed; rather, the quinuclidines are rotated relative to each other by about 30° (see Table IV and Figures 3 and 4). Given the relatively large distance between the two N atoms and the probable absence of non-axially symmetric Br–N bonding, the variation in intramolecular energy with rotation of a quinuclidine about the $C_3$ axis is likely to be very small.

It is interesting to note that each quinuclidine cage is itself very significantly twisted, presumably to relieve eclipsed interactions. The triangle of C(1) atoms is rotated 7.8 (3)° about the $C_3$ axis relative to the triangle of C(2) atoms; the analogous twist of the C(4) relative to the C(5) atoms is −2.9 (3)°. An equivalent description of this deviation from $C_{3v}$ symmetry is given by observing that the torsion angles N(1)–C(1)–C(2)–C(3) and N(2)–C(4)–C(5)–C(6) are opened up from 0 to 12.8 (4) and −4.8 (5)°, respectively. The question of whether or not [2.2.2] ring systems, particularly systems with only axial substituents, are twisted or not in their ground state has been discussed[27,28] with references to spectroscopic, diffraction, and thermodynamic evidence and to force-field calculations. Calculations for bicyclo[2.2.2]octane,[27] which according to the authors may also be applicable to quinuclidine, suggest that the minimum energy conformation is twisted, but that the barrier to interconversion of enantiomers is so low that $C_{3v}$ geometry will usually be observed in crystal structures done at room temperature. This is indeed the case; in bicyclo[2.2.2]octane-1,4-dicarboxylic acid[27] and in nine 4-haloquinuclidinium perchlorates and chlorides[25] the twist angles are all essentially or identically equal to 0. On the other hand, two rather complex quinuclidine derivatives have twist angles between 4 and 6°[29] although in these cases a non-axial substituent

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is a confusing factor; a bicyclo[2.2.2]octane derivative has also been found with a twist angle of 3°.[28] In any event it is clear that the twist of the quinuclidine containing N(1) in the bis(quinuclidine)bromine(I) cation is very large.

When considering the crystallographic evidence for the ground-state geometry of [2.2.2] ring systems, it is important to determine whether the structures having twist angles very close to 0 are affected by disorder of mirror-related enantiomers, disorder that may be hidden in the anisotropic thermal parameters if the twist angles are small. In such cases, however, analysis of the thermal motion of the atoms of the [2.2.2] ring system with the TLS rigid-body motion model[20] should reveal an abnormally large libration about the (approximate) $C_3$ axis. The rms value of 5.2–6.2° (depending on the model) found in this study may be used for comparison, since there is no indication that the librational motion is influenced by any kind of double-well potential. This value agrees very well with the corresponding rms value of 5.9 (2)° found for the approximately $C_{3v}$ bicyclo[2.2.2]octane-1,4-dicarboxylic acid by Ermer and Dunitz,[27] who also concluded that their structure was unaffected by disorder.

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**Registry No. 7**, 85282-84-4; **8**, 85282-86-6.

**Supplementary Material Available:** Anisotropic thermal parameters, calculated hydrogen positional parameters, and observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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# Synthesis of Optically Active Pyrrolizidinediols: (+)-Heliotridine

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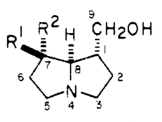
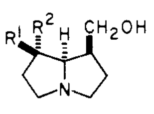
**Abstract:** A practical synthesis of the unsaturated pyrrolizidinediol (+)-heliotridine (**5**) is reported, starting from the readily available (*S*)-malic acid. The azabicyclo[3.3.0]octane ring system has been constructed via a stereoselective acyliminium ion cyclization directed by an acetoxy substituent. A ketene dithioacetal substituent in the cyclization precursor serves both as an efficient cationic cyclization terminator and later as a means of controlling double bond migration regioselectively into the correct position in the pyrrolizidine skeleton.

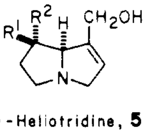
The pyrrolizidines are a group of alkaloids that exhibit remarkably diverse types of biological activity. Various members of this family, which have in common the azabicyclo[3.3.0]octane ring system, have been reported to act as antitumor, hypotensive, local anesthetic, antispasmotic, antiinflammatory, carcinogenic, or hepatotoxic agents.[1] Although a number of substitution patterns and oxidation levels of the basic ring system are known, most common are the diols, either saturated (**1–4**) or 1,2-unsaturated (**5** and **6**). The bases themselves have been isolated from natural sources, but more often they are present as esters, diesters, or macrocyclic bislactones. An intense interest in their synthesis is evident in the recent profusion of new routes to racemic pyrrolizidines,[2] but a practical total synthesis of optically active derivatives had yet to emerge[3] in spite of the deceptive simplicity of the targets. We therefore sought to develop a strategy for preparing unsaturated pyrrolizidinediols from readily available optically active starting materials, and in this paper we report a





R$^1$ = H, R$^2$ = OH (+)-Hastanecine, **1** (−)-Dihydroxheliotridane, **3**

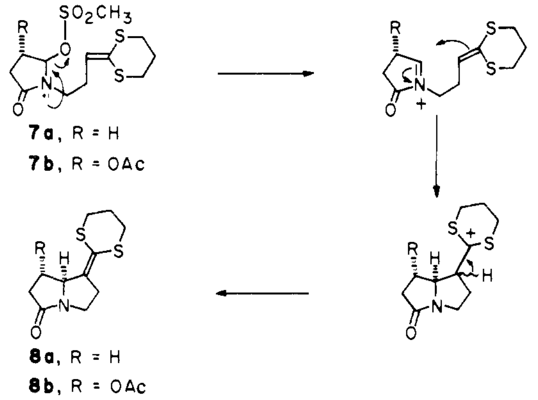
R$^1$ = OH, R$^2$ = H (−)-Turneforcidine, **2** (−)-Platynecine, **4**



R$^1$ = H, R$^2$ = OH (+)-Heliotridine, **5**

R$^1$ = OH, R$^2$ = H (+)-Retronecine, **6**

Scheme I



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