

The Question of Reversible Formation of Bromonium Ions during the Course of Electrophilic Bromination of Olefins. 2. The Crystal and Molecular Structure of the Bromonium Ion of Adamantylideneadamantane

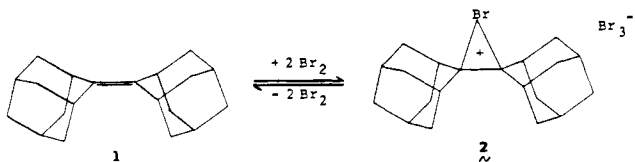
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Abstract: Single-crystal X-ray analysis of the material produced when adamantylideneadamantane (**1**) is brominated in CH_2Cl_2 ($\text{C}_{20}\text{H}_{28}\text{Br}_4$) reveals it to be a stable three-membered cyclic bromonium ion tribromide (**2**). The structure shows a slightly asymmetric three-membered ring with lengths of 2.116 (6) and 2.194 (6) Å for the Br-C bonds and 1.497 (8) Å for the C-C bond. The internal angles of the ring are 40.6 (2)° at Br and 72.5 (3) and 66.9 (3)° at the C atoms. The dihedral angle between the substituent planes of the carbons connecting the adamantyl rings is 32.9°. The associated Br_3^- counterion forms a close contact with the Br^+ suggestive of an intimate ion pair which may be the cause of the asymmetry in the three-membered ring. The overall structure reveals that there is severe crowding at the side opposite to the Br atom which prevents access of a nucleophile to the ion. This unusual feature is the likely source of the stability of the ion pair. It is also shown that **2** is formed in a completely reversible manner from **1**.

In 1937, Roberts and Kimball first proposed that a cyclic three-membered bromonium ion was formed as an intermediate during the electrophilic addition of Br_2 to an olefinic double bond.¹ Subsequently these ions have been quite generally invoked in related instances because they provide a ready explanation for both the product stereochemistry and effects of substituents.² Although Olah has provided NMR evidence for the existence of cyclic bromonium ions under stable ion conditions,^{3a} there is virtually no structural evidence about such species^{3b,c} since they apparently react to produce products more rapidly than they are formed.

Some 15 years ago, Wynberg and co-workers^{4a,b} reported that adamantylideneadamantane (**1**), when treated with Br_2 in CCl_4 ,

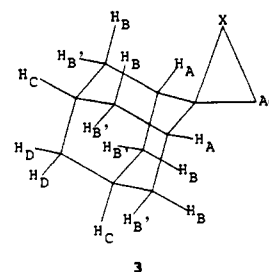


yielded a yellow precipitate having an empirical formula and properties consistent with bromonium ion tribromide **2**. The unusual aspects of **2** indicative of its ionic character included insolubility in nonpolar media, reappearance of molecular Br_2 and **1** upon attempted recrystallization from polar solvents, and a mass spectrum of **2** yielding peaks no higher than those corresponding to the molecular ion of **1** additional peaks for Br^+ and Br_2^+ .⁴ Nugent^{4c} has also reported that **1**, when treated with SbCl_5 , yields a complex analyzing correctly for the corresponding chloronium ion of **1** with an associated SbCl_6^- .

Table I. ^1H NMR Data^a for **1** and **2**^b

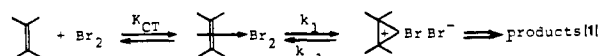
1 (X = —)	2 (X = Br^+)
H_A 2.92 (s, 4 H)	H_A 3.11 (s, 4 H)
H_B 1.90 (d, 8 H, $J_{\text{BB}'} = 12$ Hz)	H_B^c 2.51 (d, 8 H, $J = 13$ Hz)
$\text{H}_{B'}$ 1.66 (d, 8 H, $J_{\text{BB}'} = 12$ Hz)	$\text{H}_{B'}^c$ 2.23 (d, 8 H, $J = 13$ Hz)
$\text{H}_{C,D}$ 1.83 (br s, 8 H)	H_C 2.19 (s, 4 H)
H_D 2.04 (s, 4 H)	

^a 400 MHz, room temperature in $(\text{CD}_2\text{Cl}_2)_2$. ^b Saturated solution. ^c Tentative assignments for **B** and **B'**.



Subsequently Olah and co-workers⁵ suggested that the atypical behavior of **2** (which included its loss of Br_2 under vacuum, and irreversible transfer of Br_2 to cyclohexane and tetramethylethylene to give the corresponding dibromides and **1**)^{5b} indicated that **2** had "more the character of a two-electron, three-centered π -complex and not a three-membered ring σ -complex (alkylene bromonium ion)."

Recently we have reported that it is quite likely that the bromonium ion intermediates formed during the course of electrophilic addition of Br_2 to olefins are generated reversibly as in eq 1 and



that differences in the propensity to reverse could account in part for the differences in the observed rate constants for the bromination of various olefins.⁶

While this seems reasonable, it is based upon measuring the scavenging of Br_2 from bromonium ions produced solvolytically in the presence of Br^- .⁶ Clearly more direct observation of re-

(1) Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.*, **1937**, *59*, 947-948.

(2) For extensive recent reviews of electrophilic bromination, see: (a) de la Mare, D. P.; Bolton, R. "Electrophilic Additions to Unsaturated Systems", 2nd ed.; Elsevier: New York, 1982; pp 136-197. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 151-163. (c) Freeman, F. *Chem. Rev.* **1975**, *75*, 439-490. (d) Schmid, G. H.; Garratt, D. G. "The Chemistry of Double Bonded Functional Groups", Suppl. A, Part 2; Patai, S., Ed.; Wiley: New York, 1977; p 725.

(3) (a) Olah, G. A. "Halonium Ions"; Wiley: New York, 1975. (b) Stable bromonium ions are known, but these are of the cyclic five-membered type (Sandin, R. B.; Hay, A. S. *J. Am. Chem. Soc.* **1952**, *74*, 274-275) or complex type (Blair, L. K.; Parris, K. D.; Hii, P. S.; Brock, C.P. *Ibid.* **1983**, *105*, 3649-3653).

(4) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907-908 (bromination). (b) Wieringa, J. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579-4582 (chlorination). (c) Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 4533-4534.

(5) (a) Olah, G. A.; Hockswender, T. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3574-3580. (b) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *Ibid.* **1974**, *96*, 3581-3589.

(6) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. *J. Am. Chem. Soc.* **1984**, *106*, 4515-4521.

versibility would be desirable. It would seem that the bromination of **1** to produce **2** represents one of the few promising opportunities to directly confirm our proposals since the reverse reaction of **2** → **1** is well documented.^{4,5} The major question to be resolved prior to such confirmation rests on whether **2** is best described as an atypical π complex⁵ or a bona fide cyclic bromonium ion. Herein we report the X-ray structure of **2** which indicates for the first time the nature of a three-membered cyclic bromonium ion.

Experimental Section

Materials. Acetonitrile was purified by distillation of reagent grade material from P_2O_5 , the middle fraction (bp 81 °C) being collected. 1,2-Dichloroethane was purified by washing with concentrated H_2SO_4 , saturated $NaHCO_3$, and then H_2O . Drying was effected by azeotropic removal of H_2O , with the residual material being distilled from P_2O_5 (bp 83.5 °C). Br_2 was purified as previously described.⁶

Adamantylideneadamantane (**1**) was prepared according to the procedure of Geluk,⁷ the product being recrystallized from CH_3CN and finally sublimed to yield colorless crystals: mp 184–186 °C (lit.⁷ 184–187 °C); 400 MHz 1H NMR ($CICD_2CD_2Cl$) as in Table I.

Adamantylideneadamantane Bromonium Ion Tribromide (2). To 1.0 g of **1** dissolved in 50 mL of CH_2Cl_2 was added a 10% excess of Br_2 (1.32 g, 0.44 mL) in 50 mL of CH_2Cl_2 . The immediately formed yellow precipitate was filtered, washed with 3 × 5 mL of CH_2Cl_2 and then vacuum dried for about 15 min to yield 2.15 g of product, mp 160–163 °C. Recrystallization from purified acetonitrile yielded yellow plates (mp 160–162 °C) having an infrared spectrum identical with the unrecrystallized material: IR (Nujol) 2850, 1453, 1376, 1352, 1328, 1232, 1112, 1085, 1052, 1029, 1005, 942, 935, 875, 865, 700, 590, 421, 403 cm^{-1} ; 1H NMR ($CICD_2CD_2Cl$) as in Table I. Anal. Calcd for $C_{20}H_{28}Br_4$: C, 40.83; H, 4.80. Found: C, 41.08; H, 4.78. Crystals of **2** suitable for X-ray diffraction were grown as follows. A 5-mm diameter glass tube was fashioned having a lower compartment (~1–2 cm) separated from the upper part by a constriction (i.d. < 1 mm). Into the lower compartment up to the midpoint of the constriction was placed a solution of **2** in CH_3CN (saturated at room temperature) containing a 100% excess of Br_2 . On top of this solution was carefully placed a second solution (saturated at 60 °C) of **2** in acetonitrile. In order to avoid too rapid a crystallization, the upper part of the tube was gently warmed to about 60 °C. The entire mixture was capped and allowed to stand at room temperature for 12–24 h, after which time a few clear golden crystals had formed.

X-ray Crystallography. An orange, block-shaped crystal of $C_{20}H_{28}Br_4$, having approximate dimensions of 0.23 × 0.15 × 0.31 mm, was mounted in a nonspecific orientation inside a capillary on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using Mo $K\alpha$ radiation (λ 0.71073 Å) with a graphite crystal, incident beam monochromator.

The automatic peak search and reflection indexing programs⁸ in conjunction with a cell reduction program showed the crystal to be monoclinic, and from the systematic absences of:

$$h0l, l \text{ odd}; 0k0, k \text{ odd}$$

the space group was determined to be $P2_1/c$ (no. 14).⁹

Cell constants were obtained from a least-squares refinement of the setting angles of 18 reflections in the range $11 < 2\theta < 25^\circ$. The various crystal parameters are given in Table II.

The intensity data were collected at room temperature using an ω - 2θ scan ranging in speed from 10.1 to 1.1 deg/min (in ω). The variable scan rate was chosen to give $\sigma(I)/I \leq 0.05$ within a time limit of 40 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1 - α_2 wavelength dispersion:

$$\omega \text{ scan width (deg)} = 0.30 + 0.35 \tan(\theta)$$

Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range to give a peak to background counting time of 2:1. Intensity measurements were made to a maximum 2θ of 54°. There were two reflections which were chosen as standard reflections, and these were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection.

(7) Geluk, H. W. *Synthesis*, **1970**, 652–653.

(8) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.

(9) "International Tables for X-ray Crystallography"; Kynoch Press, Birmingham, England, 1969; Vol. I.

Table II. Experimental Details

A. Crystal Data	
$C_{20}H_{28}Br_4$	
FW = 588.08	
crystal dimensions: 0.23 × 0.15 × 0.31 mm	
monoclinic space group $P2_1/c$	
$a = 7.404$ (3), $b = 7.320$ (1), $c = 37.354$ (8) Å	
$\beta = 95.49$ (3)°	
$V = 2015$ Å ³ , $Z = 4$	
$d_c = 1.938$ g/cm ³ , $\mu = 79.13$ cm ⁻¹	
B. Intensity Measurements	
radiation	Mo $K\alpha$ (λ 0.71073 Å)
monochromator	incident beam, graphite crystal
take-off angle	3.0°
detector aperture	2.00 mm horizontal 4.0 mm vertical
crystal-to-detector distance	205 mm
scan type	ω - 2θ
scan rate	10.1–1.1 deg/min
scan width	0.30 + 0.35 tan(θ) deg
data collection 2θ limit	54.00 deg
reflections measured	4389 unique, 2097 with $I > 3.0\sigma(I)$
corrections applied	absorption correction

A linear regression analysis of these standards showed a mean change in intensity of -4.7 (2.6) % over the time of data collection, which was considered negligible.

A total of 5118 reflections were collected and these were corrected for Lorentz, polarization, and background effects according to the following formulas:

$$I = SR(SC - R*B) / Lp$$

$$\sigma^2(I) = \{SR(SC + R^2B) + (pI)^2\} / Lp^2$$

where SR is the scan rate, SC is the total scan count, R is the ratio of scan time to background time, B is the total background count, p is a factor to down-weight intense reflections (chosen as 0.040 in this experiment), and Lp is the Lorentz and polarization correction term.

The data were corrected for absorption effects using an empirical correction based on the absorption surface method for Walker and Stuart.¹⁰ The maximum and minimum correction coefficients applied to F_o were 1.3316 and 0.7227, respectively. After averaging equivalent forms and rejecting any systematically absent data, there were 4389 unique reflections of which 2097, having $I > 3.0\sigma(I)$, were used in the structure solution and refinement.¹¹

The structure was solved using the RANTAN procedure in the direct methods program MULTAN¹² which gave the positional parameters for three of the four Br atoms. The remaining nonhydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement of atomic parameters was carried out by using full-matrix least-squares techniques on F_o minimizing the function:

$$\sum w(|F_o| - |F_c|)^2$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively, and the weighting factor w is given by:

$$w = 4F_o^2 / \sigma^2(F_o^2)$$

The neutral atom scattering factors were calculated from the analytical expression for the scattering factor curves.^{13a} The f' and f'' components of anomalous dispersion^{13b} were included in the calculations for all nonhydrogen atoms.

Positions were calculated for all 28 H atoms assuming C–H of 1.05 Å and regular sp^3 geometry. These calculated positions were compared to peaks observed in a difference Fourier and were found to coincide quite

(10) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *39*, 158–166.

(11) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by Frenz, B. A. ("Computing in Crystallography"; Delft University Press, Delft, Holland, 1978; pp 64–71) and several locally written or modified programs.

(12) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. MULTAN 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.

(13) (a) "International Tables for X-ray Crystallography"; Kynoch Press, Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) *Ibid.*, Table 2.3.1.

Table III. Selected Interatomic Distances in Ångströms^a

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Br1	C1	2.116 (6)	C3	C4	1.51 (1)	C12	C13	1.546 (9)
Br1	C11	2.194 (6)	C4	C5	1.51 (1)	C12	C20	1.534 (9)
Br1	Br3	3.097 (1)	C4	C9	1.548 (9)	C13	C14	1.51 (1)
Br2	Br3	2.718 (1)	C5	C6	1.526 (9)	C14	C15	1.54 (1)
Br2	Br4	2.412 (1)	C6	C7	1.535 (9)	C14	C19	1.54 (1)
C1	C2	1.508 (8)	C6	C10	1.53 (1)	C15	C16	1.53 (1)
C1	C8	1.513 (8)	C7	C8	1.550 (9)	C16	C17	1.54 (1)
C1	C11	1.497 (8)	C8	C9	1.524 (9)	C16	C20	1.52 (1)
C2	C3	1.548 (9)	C11	C12	1.516 (8)	C17	C18	1.545 (9)
C2	C10	1.542 (9)	C11	C18	1.514 (8)	C18	C19	1.545 (9)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Interatomic Angles in Degrees^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C1	Br1	C11	40.6 (2)	C5	C6	C7	110.7 (5)	C13	C12	C20	108.7 (5)
Br3	Br2	Br4	177.46 (5)	C5	C6	C10	110.3 (6)	C12	C13	C14	110.9 (6)
Br1	Br3	Br2	75.23 (3)	C7	C6	C10	108.3 (5)	C13	C14	C15	110.4 (6)
Br1	C1	C2	110.7 (4)	C6	C7	C8	109.2 (5)	C13	C14	C19	108.2 (5)
Br1	C1	C8	108.1 (4)	C1	C8	C7	105.8 (5)	C15	C14	C19	110.0 (6)
Br1	C1	C11	72.5 (3)	C1	C8	C9	110.3 (5)	C14	C15	C16	108.9 (5)
C2	C1	C8	113.1 (5)	C7	C8	C9	109.7 (5)	C15	C16	C17	108.9 (5)
C2	C1	C11	121.2 (5)	C4	C9	C8	109.9 (5)	C15	C16	C20	110.4 (6)
C8	C1	C11	121.4 (5)	C2	C10	C6	109.6 (5)	C17	C16	C20	109.5 (5)
C1	C2	C3	108.8 (5)	Br1	C11	C1	66.9 (3)	C16	C17	C18	109.8 (6)
C1	C2	C10	106.7 (5)	Br1	C11	C12	109.8 (4)	C11	C18	C17	110.6 (5)
C3	C2	C10	109.3 (5)	Br1	C11	C18	108.6 (4)	C11	C18	C19	106.2 (6)
C2	C3	C4	110.5 (5)	C1	C11	C12	122.9 (5)	C17	C18	C19	108.7 (5)
C3	C4	C5	110.8 (6)	C1	C11	C18	122.4 (5)	C14	C19	C18	109.7 (5)
C3	C4	C9	108.2 (6)	C12	C11	C18	112.7 (5)	C12	C20	C16	110.4 (5)
C5	C4	C9	109.5 (6)	C11	C12	C13	105.5 (5)				
C4	C5	C6	109.5 (6)	C11	C12	C20	110.5 (5)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

closely. Hence these atoms were included in subsequent refinement cycles as fixed atoms constrained to "ride" with the attached C atom. Their thermal parameters were isotropic and fixed at values 20% greater than that of the attached C atom.

In the final cycle 217 parameters were refined using 2097 observations having $I > 3\sigma(I)$. The final agreement factors were:

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.041$$

$$R_2 = \frac{(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{0.5}}{\sum w F_o^2} = 0.050$$

The largest shift in any parameter was 0.01 times its estimated standard deviation, and the error in an observation of unit weight was 1.38 e. An analysis of R_2 in terms of F_o , $\lambda^{-1} \sin \theta$, and various combinations of Miller indices showed no unusual trends. The highest peak in the final difference Fourier, 0.5 (1) e Å⁻³, is located near Br1 but is not of chemical significance.

Tables of root-mean-square thermal vibration amplitudes torsion angles, least-squares planes, and observed and calculated structure factors are available as supplementary material, as well as tables of the positional and thermal parameters for all atoms.¹⁴

Results and Discussion

(a) Structure and Properties of 2. Bromination of **1** in chlorinated hydrocarbons immediately yields a bright yellow solid which can easily be handled without special precautions. Although **2** is unstable in polar protic solvents and tends to lose Br₂, it has both stability and modest solubility in CH₃CN, CH₃NO₂, and dichloroethane. Recrystallization of **2** from these solvents yields a purified material which exhibits identical IR spectrum, melting point, and microanalysis with those of the unrecrystallized material.

Given in Table I are the ¹H NMR data for **1** and **2** obtained at 400 MHz in (CD₂Cl)₂. In both cases the spectrum is quite simple and is indicative of (at least) a twofold plane of symmetry with the major couplings being between H_B H_{B'} (defined as in 3). In this solvent, formation of the sparingly soluble **2** produced a downfield shift in all resonances as is expected, although it does

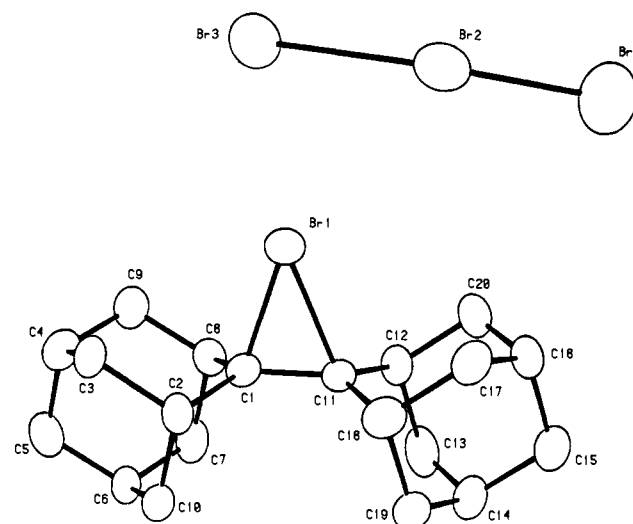


Figure 1. Perspective view of an ion pair showing the atom numbering scheme. Atoms are represented by thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

not appear from the spectrum that the H_{B,B'} and H_C resonances from the top side of the molecule are significantly altered relative to the bottom ones. The limited solubility of **2** precludes obtaining its ¹³C NMR spectrum in (CD₂Cl)₂.

Although our spectrum of **1** agrees well with that given by Geluk⁷ (CDCl₃), it does not agree with that reported by Olah^{5b} (CCl₄). Nevertheless, our spectrum of **2** does corroborate Olah's reported one obtained in Br₂-HF-SO₂ at -30 °C.^{5b} Such would indicate that **2** and the species obtained by Olah in the latter medium are the same.

Obtaining single crystals of **2** satisfactory for single-crystal X-ray diffraction proved to be a major undertaking and literally required several hundred attempts. Satisfactory crystals were finally obtained from CH₃CN as described in the Experimental Section.

(14) Supplementary material.

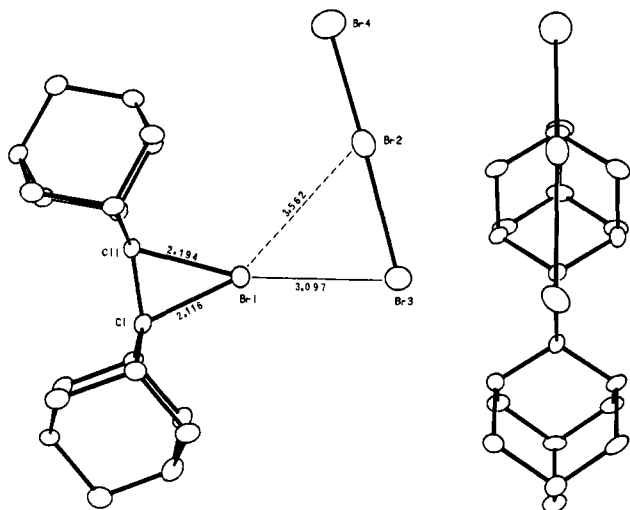


Figure 2. Two perspective views showing the orientation of the Br_3^- ion with respect to the adamantyl rings of the Bromonium ion.

(b) **X-ray Structure Description.** The structure of the adamantylidene-bromine complex is illustrated in Figure 1. It is comprised of an alkene bromonium ion and a closely associated Br_3^- counterion. Tables III and IV list the interatomic distances and angles of importance in the structure. This structure represents the first example of a three-membered bromonium ion complex^{3b} which has been isolated and completely characterized by a single-crystal X-ray structure analysis. The bromine atom is positioned slightly asymmetrically with respect to the two carbon atoms which form the three-membered ring: C1-Br1, 2.116 (6) Å; C11-Br1, 2.194 (6) Å. These distances are slightly longer than normal C-Br single bonds which usually fall in the range 1.93–2.04 Å.¹⁵ The C-C bond of the three-membered ring is 1.497 (8) Å which is slightly shorter than that for a normal C-C single bond (1.54 Å) but very much longer than the double bond in adamantylideneadamantane (1.336 Å).¹⁶ The dihedral angle between the planes C1-C2-C8 and C11-C12-C18 is 32.9° which indicates that the two adamantane moieties are each bent away from the Br1 atom by a significant amount. The bond distances and angles within the two adamantane moieties are normal.¹⁶⁻¹⁸

The Br_3^- counterion differs from that generally observed in other reported structures¹⁹ in that it is not constrained to be symmetric. The ion is essentially linear, Br3-Br2-Br4 177.46 (5)°, but the bond lengths show an almost symmetrical distortion from the usually observed value of ~2.55 Å.¹⁹ This distortion is the result of a close interaction between Br3 and Br1 of the bromonium ion. As shown in Figure 2, the Br_3^- ion sits nearly directly above Br1 with its molecular axis lying over one of the adamantyl rings. The asymmetry is probably the source of the nonequivalent C-Br bond lengths. The van der Waals radius of Br at 1.85 Å²⁰ yields a Br,Br nonbonding contact distance of 3.7 Å. We observe the Br1-Br3 distance in **2** to be 3.097 (1) Å which suggests a nonnegligible interaction between them, perhaps as an intimate ion pair. However, Br1 is clearly associated more with C1 and C11 than it is with Br3. In addition, there is a much weaker Br1-Br2

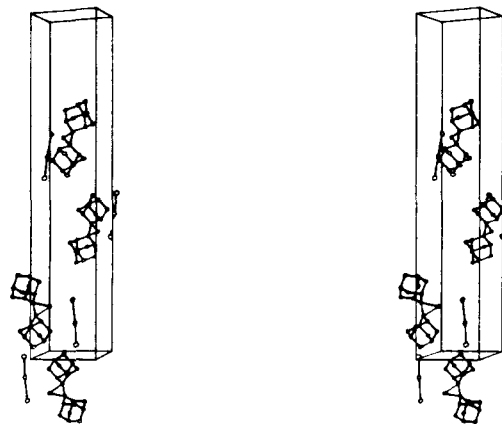


Figure 3. Stereoview showing the molecular packing in a unit cell. The cell axes are oriented with b running left to right, c vertical, and a pointing out of the page.

contact of 3.562 (1) Å. The only other interatomic distances less than the sum of the van der Waals radii are between the H atoms on some of the carbons of the two adamantane groups which lead to a severe crowding on the bottom face. The relevant distances are: 2.01 Å for H10 and H15 on C8 and C12, respectively; 1.97 Å for H1, H24 on C2, C18; 2.17 Å for H9, H17 on C7, C13; and 2.17 Å for H13, H25 on C10, C19.

Figure 3 presents a stereoscopic view of the packing of the ions in a unit cell. All contact distances between the symmetry-related ion pairs exceed the sum of the appropriate van der Waals radii, and only normal crystal packing forces are assumed.

As pertains to the electrophilic bromination of olefins, a distinction has been made between σ complexes and π complexes, and it has been suggested⁵ that **2** resembles the latter. The characteristics of such complexes are suggested to be the following.⁵

(a) π type: formed early in the reaction sequence with little or no change in C or Br_2 hybridization and thus little expected change in the geometry of the individual components. Presumably this can be considered related to a CT complex.

(b) σ type: formed later in the reaction sequence with rehybridization of the C atoms to form σ bonds with the Br^+ , which in turn has an unspecified but reduced degree of interaction with the Br_3^- counterion.

In what are generally accepted to be real π complexes, that is, metal-olefin complexes in which neither component is substituted with strongly electron-donating or -withdrawing groups, one consistently observes two characteristics. The olefinic double bond lengthens from its initial value of 1.33 Å to values of 1.36–1.44 Å.²¹ As well, the substituents on the double bond bend away from the metal by an amount which is highly variable, depending presumably on a complex mixture of steric and electronic effects. Nevertheless, the minimum distortion of each of the olefin substituent planes is some 16–20° from planarity.²¹ (As a point of reference, the distortion of each of the substituent planes in a cisoid sp^3 hybridized ethano unit would be ~55° while that in cyclopropane would be ~30°.)

Contrasting the above description, there are also well-known and characterized species in which a heteroatom forms a three-membered, σ -bonded ring. The closest analogues to the present case are the episulfides which have been characterized both theoretically^{12,22,23} and structurally.^{17,24} These species generally show a central C-C bond length of 1.47–1.50 Å,^{16,23} which is very slightly shorter than the normal 1.54-Å C-C single bond but longer than those observed in the metal-olefin complexes. In addition, the substituents on the central C-C bond of episulfides bend away

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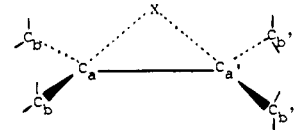
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Table V. Comparison of Adamantylideneadamantane Related Structures^a


X	C _a -X (C _a -X)	C _a -C _a	C _b -C _a -C _b	dihedral angle ^b	C _b -C _a -C _{a'}	ref
-		1.336	110.4	0.0	124.8	17
S	1.85 (1.85)	1.50 (1)	109.0 (8)	45.0	122.6	18
Br	2.11 (2.19)	1.497 (8)	112.9 (5)	32.9	122.0	
O-O	1.47 (1.47)	1.549 (9)	109.0 (5)	62.4	120.4	19a
-N-N-	1.50 (1.514)	1.635 (3)	109.2 (2)	68.5	120.4	19b

^a Angles in deg, bonds lengths in Å. ^b Defined as the dihedral angle between the C_b-C_a-C_b and C_b-C_a-C_{b'} planes.²²

from the sulfur atoms by values similar to the distortion seen in the metal-olefin π complexes, i.e., $\sim 20^\circ$.

It would appear from the above discussion that there is little, if any, observable structural evidence that would allow a clear distinction to be made between a σ - or π -type complex for a molecule such as **2**, since similar sorts of distortion and central C-C bond lengthening are expected for both types. It is likely that such a distinction is a semantic one and in reality offers no useful chemical insight into the structure or properties of **2**.²⁵

Presented in Table V, for comparison purposes, are selected structural parameters for **1**,^{16, 2} and the related episulfide¹⁸ and dioxetane,¹⁸ and diazetidine^{18b} of **1**. There is a striking similarity between the central C-C bond lengths in the structure of **2** and the episulfide, both of which, at 1.50 Å, are shorter than that in the dioxetane or diazetidine. From the similarity, one must conclude that if the episulfide is to be considered a σ -type heterocyclopropane, then so is brominium ion **2**. The dioxetane, as judged from the dihedral angle of 62.4° , is severely compressed at the bottom side of the molecule which leads to a marked twisting about the central C-C bond. Such is not observed because of

(25) For a pertinent discussion of how the geometries and properties of olefin-metal complexes relate to the σ - π vs. metallocyclopropane bonding models, see: (a) Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc.* **1972**, *94*, 3779-3778. (b) Cramer, R.; Kline, J. B.; Roberts, J. D. *Ibid.* **1969**, *91*, 2515-1524. (c) For a similar conclusion to ours concerning no experimental distinction between π complexes and σ complexes of species such as **2**, see: Olah, G. A.; Bollinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587-2594.

structural restrictions of the three-membered ring in either the episulfide or **2**, although the contacts between the H atoms on the bottom side of the latter are shorter than van der Waals radii. It is this feature which effectively blocks access of a nucleophile to the backside of the C-Br bonds in **2** and leads to its stability.

(c) **1** + 2Br₂ \rightleftharpoons **2** Equilibrium. Having clearly established the character of bromonium ion **2**, a number of qualitative observations indicate that it is capable of regenerating free Br₂ and **1**. Firstly, we have confirmed the observations of Wynberg et al.^{4a} and Olah, et al.^{5b} wherein dissolution of **2** in polar solvents yields after evaporation of the solvent pure **1**. Secondly, **2**, which is stable enough in purified (CH₂Cl)₂ to obtain an ¹H NMR spectrum, is capable of transferring two molecular Br₂ units in this solvent and in CH₃CN to an acceptor olefin such as cyclohexene.^{5b} We have observed that this process is not particularly rapid. The UV-visible spectrum of 1×10^{-3} M **1** and 2×10^{-3} M Br₂ in (CH₂Cl)₂ does not initially match that of 1×10^{-3} M **2**. However, repeated monitoring of both solutions showed that over the course of ~ 200 min, both spectra asymptotically approach the same equilibrium point, with the absorbance of **2** at 272 nm decreasing (due to loss of Br₃⁻) and that of **1** + 2 Br₂ increasing. The latter experiment establishes the equilibrium connection between **1** and **2** in solution.

Conclusion

X-ray crystallographic data presented here for **2** establishes for the first time the nature of a three-membered bromonium ion. The structure of **2** indicates that it is severely crowded at the side opposite to the Br atom which prevents access of a nucleophile. Admittedly, **2** is derived from a unique olefin which is capable of proceeding only partway along the "normal" reaction pathway open to most usual olefins. However, this study does demonstrate the phenomenological importance of reversibility from a bona fide bromonium ion. What remains to be demonstrated unambiguously is whether this is kinetically important in this and other systems.

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Supplementary Material Available: Tables of torsional angles, weighted least-squares planes, root-mean-square amplitudes of thermal vibration, observed and calculated structure factors, positional and thermal parameters for heavy atoms, and derived positional and thermal parameters for hydrogen atoms (28 pages). Ordering information is given on any current masthead page.