roughly the average of the atomic gauge factors. The greater flexibility of the GIAO wave function results in faster convergence. As the GIAO method can thus employ smaller basis sets, it may be ultimately the more efficient method, in spite of the savings offered by the localized techniques.

Another conclusion emerging from our calculations is that, unless large basis sets are used, the accuracy of individual tensor components is often lower with the localized methods than with the GIAO. This is true even in the cases where the isotropic average is correctly predicted by IGLO and LORG. By contrast, the tensor components are usually fairly well predicted by the GIAO method.

Finally, we would like to emphasize that our implementation of the GIAO method can be routinely used for NMR chemical shift calculations on fairly large molecules, say in the C_{10}–C_{15} range, on departmental workstations and minicomputers. Indeed, all results shown in this paper have been obtained on minicomputers. Our program currently runs on the IBM 4381 under CMS and VS1, on the IBM RT PC workstation under AIX, and on the Celerity 1200 and the Apollo DN10000 workstations under Unix. These versions, including integral, closed-shell SCF, and chemical shift calculations, are available for a nominal fee from the University of Arkansas. The whole TEXAS system, including many other features, some unique, such as a very compact integrals storage, UNO-CAS gradients, and a very efficient geometry optimization using automatically generated internal coordinates, will also be made generally available in the fall of 1990 from the University of Arkansas.

Acknowledgment. We gratefully acknowledge partial support for this project by the National Science Foundation under Grant CHE-8500487. We thank IBM Corp. for financial support and for the loan of an PC-RT workstation. The Apollo DN10000 used for the large calculations was purchased with funds provided by NSF under Grant CHE-8814143. We thank Prof. P. R. v. Schleyer for the ab initio geometry of the adamantyl cation, Prof. G. Fogarasi for the ab initio optimized geometry of stilbene, Profs. N. Allison and W. L. Meyer for the MMX optimized geometry of octahydroparacyclophane, and Mr. P. Taylor for the ab initio geometries of oxocane. We are also grateful to one of our reviewers for careful and constructive criticism.

Structure and Energetics of $C_2H_4Br^+$: Ethylenebromonium Ion vs Bromoethyl Cations

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Contribution No. 91 from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. *Received March 8, 1990*

Abstract: The cyclic and acyclic isomers of $C_2H_4Br^+$ are compared by using ab initio quantum mechanical techniques, including the use of electron correlation and polarization functions. The cyclic bromonium ion is found to be more stable than the acyclic 1-bromoethyl cation by 1.5 kcal/mol, in very good agreement with experiment. A transition state for the interconversion of these two forms is reported, the energy barrier being ~25 kcal/mol. The relative energies of the cyclic and acyclic minima are remarkably insensitive to basis set and electron correlation effects, validating the results of previous low-level studies. The 2-bromoethyl cation does not exist as a minimum on the potential energy surface and spontaneously collapses to the bromonium ion upon torsion.

Introduction

The addition of Br_2 to olefins is usually highly stereospecific, and the postulation in 1937 of a cyclic bromonium ion as an intermediate by Roberts and Kimball[1] was a radical suggestion. The detection of these intermediates was to come 30 years later in the pioneering NMR studies in superacid media from Olah's group.[2] In the interim, the mechanism for addition of Br_2 to double bonds via a bridged intermediate was widely accepted because it neatly accounted for why addition was anti: Br^+ is added to the double bond, forming a 3-membered ring, and attack by the remaining Br^- must come from the other side. The positive charge in the ethylenebromonium ion does not reside on the Br atom at all but primarily on the carbon atoms. Thus there is no attraction between the Br atom in the ring and Br^-, and steric factors are free to exert their full effect. A recent review by Ruasse[3] gives an account of the bromination of olefins, with consideration of whether bromonium ions or β-bromo carbocations are intermediates for various alkenes.

The open 2-bromoethyl cation is expected to be unfavorable because of the positive charge residing on a primary carbon: methyl substitution should stabilize this carbonium center relative to the bridged isomer. The positive charge on the carbon in the 1-bromoethyl cation is stabilized by Br, which is able to back-donate electron density. The global energy minimum should be either the open 1-halo form or the onium ion. The trend among halogens from experiment favors the open 1-halo isomer for F and Cl and bridging for Br and I.[4,5] There may not even be a cyclic ethylenefluoronium ion.

Ion cyclotron resonance experiments form Beauchamp's group[4] found two non-interconverting isomers of $C_2H_4Br^+$ and attributed the spectra to the 3-membered ring being 1.4 kcal/mol lower than the 1-bromoethyl cation which was made from a different source. This procedure has been criticized because the two different modes of product production may lead to differing levels of internal energy in the two isomers.[6] Because of its stereoselectivity, it has recently been reported that $C_2H_4Br^+$ has been used as a

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[6] For example, see: Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3792 and ref 14 therein.

0002-7863/90/1512-8260$02.50/0

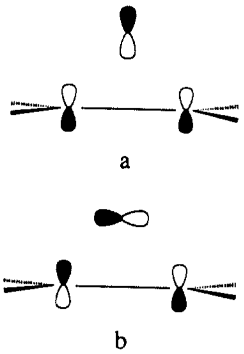

Figure 1. (a) The donor-acceptor interaction between the filled C_2H_4 π orbital and the empty adduct orbital. (b) The interaction between the vacant π^* orbital and a filled adduct orbital.

chemical ionization reagent to distinguish geometrical isomers in mass spectrometry studies.[7]

The X-ray structure of a substituted ethylenebromonium ion with a Br_3^- counterion (formed from bromination of adamantylideneadamantane) has also been determined.[8] The back-side attack by Br^- is sterically impossible, so the bromination stops at the intermediate. The close proximity of the counterion introduces an asymmetry in the bromonium ion: the difference in C–Br distances is 0.078 Å but other effects are smaller. In the comparison of the symmetric theoretical geometry with the corresponding experimental one, average values will be used.

One issue that arises in the discussion of 3-membered rings is whether the ring is a σ-complex or a π-complex. Figure 1 shows the two types of bonding. The relationship between π-complexes and true 3-membered rings has been discussed by Dewar and Ford.[9] Cremer and Kraka[10] also studies this relationship using an analysis of computed electron densities. This complex issue will be addressed later in this paper, keeping in mind that there is no sharp boundary between the two.

The only previous theoretical studies of the $C_2H_4Br^+$ system were performed at the SCF level with small basis sets and incomplete optimization.[11] Also, the characterization of stationary points was not feasible at the time of the study, nor was the search for a C_1 transition state. Given the previous low levels of theory that were used to treat the bromonium ion, the question of Beauchamp's values, and the intervening X-ray structure analysis, we decided to clarify the energetics and structures of the various $C_2H_4Br^+$ isomers. The justification for examining only intermediates rather than including the transition state for $Br_2 + C_2H_4 \rightarrow Br^- + C_2H_4Br^+$ comes from an ab initio study[12] showing that the transition state is essentially a 3-membered ring plus a Br^-. The opposite case was found for F_2, which added in a syn fashion via a nonsymmetrical 4-center transition state.

Theoretical Methods

Geometries were optimized at the SCF and at the configuration interaction (CI) levels of theory with use of analytic gradient methods.[13,14] The configurations in the CI expansion included single and double substitutions with respect to the Hartree-Fock reference determinant (CISD). The core orbitals were kept frozen (1s on C, 1s, 2s, 2p, 3s, 3p on Br) as were the 8 virtual orbitals with energies over 20 hartrees. Harmonic vibrational frequencies at the SCF level were obtained analytically as well.[15] Location of the "transition state" (see Figure 2) from the 2-bromoethyl cation was done by following the eigenvector[16] of the H_4–C_1–H_3 rocking mode.

The smallest basis set employed was of double-ζ (DZ) quality, namely the C(9s5p/4s2p) and H(4s/2s) Huzinaga-Dunning basis set,[17,18] combined with Dunning's Br(15s12p5d/8s6p2d) set that was published in an article by Bauschlicher, Schaefer, and Bagus.[19] The next basis set consisted of the DZ basis plus the addition of d functions to the heavy atoms (DZ+d), with exponents suitable for describing polarization effects: $\alpha_d(C) = 0.75$ and $\alpha_d(Br) = 0.40$. The standard designation of this DZ+d basis is C(9s5p1d/4s2p1d), H(4s/2s), and Br(15s12p6d/8s6p3d). The largest basis utilized a triple-ζ contracted set with two sets of polarization functions (TZ2P) on the heavy atoms and a DZ set for H with a polarizing set of p functions [$\alpha_p(H) = 0.75$]. The exponents of the primitive functions in the TZ and DZ basis sets were the same; the TZ contraction coefficients for C are from ref 18 and those for Br are from ref 20. The pairs of d-function exponents were $\alpha_d(C) = 1.5, 0.35$ and $\alpha_d(Br) = 0.54, 0.19$. The C(9s5p/5s3p), H(4s1p/2s1p), and Br(15s12p7d/10s8p4d) basis set will be referred to as TZ2P for brevity, even though it is only of DZP quality for the hydrogen atoms.

The d functions in the SCF calculations were the 5-component spherical harmonic functions, whereas the 6-component Cartesian d functions were used in the CISD calculations due to current program limitations. This should not affect the comparison of the SCF and CISD results in any significant way.

Results and Discussion

Figure 2 displays the various stationary points studied. The selected bond lengths and angles are those that are deemed the most reliable, i.e., DZ+d CISD optimized parameters. Table I includes all of the optimized bond distances and angles for the DZ+d SCF, TZ2P SCF, and DZ+d CISD levels of theory. The only noteworthy change in bond angles with respect to level of theory is the increase in the CCBr angle of 1.8° in the 2-bromoethyl cation upon inclusion of electron correlation. As a result there is a concomitant closing of the H_5–C_2–H_6 angle by 1.9°.

The primary differences with respect to level of theory are in bond lengths: the increase of about 0.01 Å for CISD over SCF for C–H bonds is uniform and quite expected, whereas the C–C and C–Br distances exhibit more variability. Electron correlation decreases the C–Br distance in all cases, indicating a significant contribution to the bonding since correlation usually lengthens bonds. This effect is particularly noticeable in the bromonium ion because electron correlation is generally needed for the description of bridging systems anyway. The improvement of the basis set at the SCF level shortened the C–C bonds by about 0.01 Å, again as expected, but the effect of CISD is the shortening of the C–C bond by varying amounts. This is probably due to a hyperconjugative interaction between the empty p orbital on the carbocation center and a "pseudo π" bonding MO of the same symmetry on the methyl group. This same interaction is that which is also used to explain why double bonds are eclipsed with respect to a methyl group hydrogen[21] (see Figure 3).

The structure of bridged $C_2H_4Br^+$ can be compared with that of 3-membered rings and π-complexes in an attempt to label it. In the bromonium ion, the C–Br distance of 2.025 Å is a bit longer than a typical single bond length[22] of 1.94 Å. The C–Br distance from the X-ray determination[8] is 2.155 Å, which is 0.13 Å longer than the theoretical structure for the parent. The difference is

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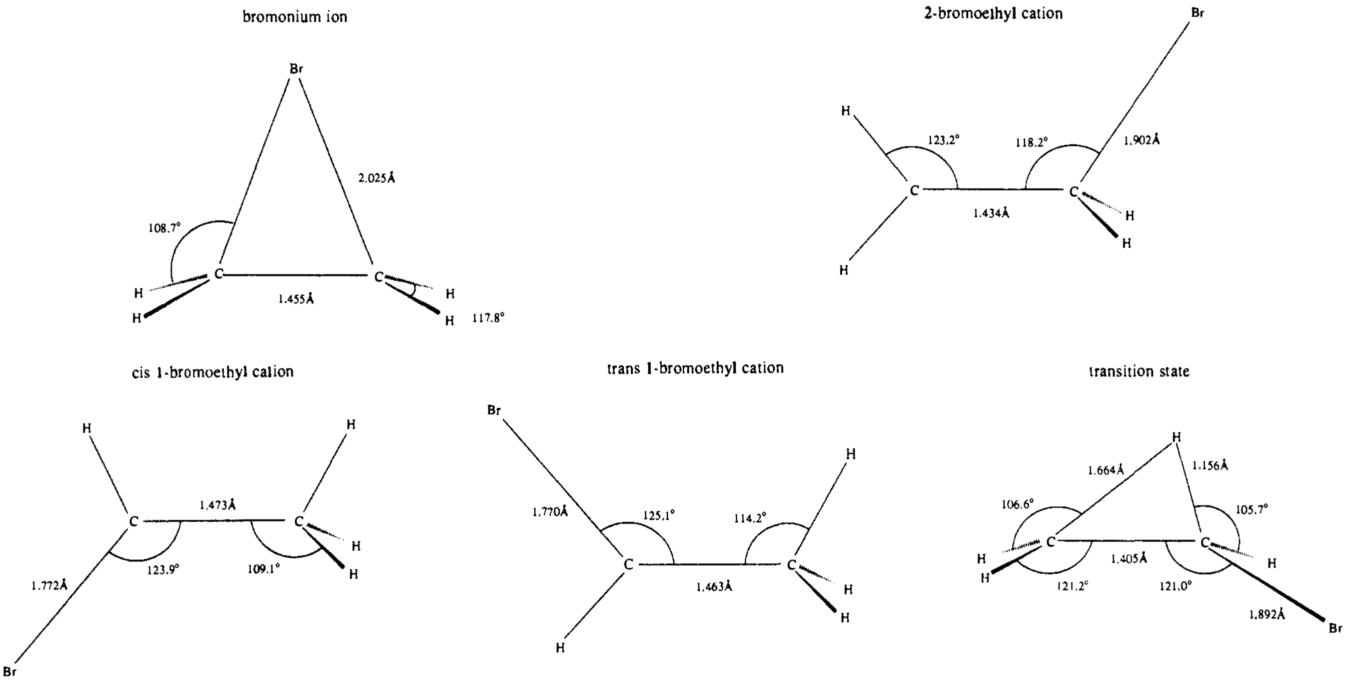

Figure 2. The isomers of $C_2H_4Br^+$ considered in this study with DZ+d CISD optimized geometry parameters of note. The values for the transition-state structure are from the DZ+d SCF optimized geometry.

Figure 3. The hyperconjugative interaction between the empty p orbital on the cation center with the occupied methyl group MO of π symmetry.

due to the fact that the adamantyl derivative is expected to allow less distortion of the ethylenic plane, which results in the intermediate resembling a π-complex more, with an attendant weaker bonding and larger C–Br distance. The bromonium C–C distance of 1.455 Å is between the usual values of 1.34 Å for C=C and 1.54 Å for C–C. The adamantyl substituted C–C bond length of 1.497 Å is rather extreme for a π-complex (the C–C bond in cyclopropane is 1.497 at the 6-31G* SCF level![10]). Our first thought was that this long distance could be explained by steric repulsion, but the unbrominated adamantylideneadamantane C–C distance is 1.336 Å.[23] This is an increase of 0.161 Å upon bromination, which is more indicative of a σ–complex. The X-ray structure thus sheds no light on the nature of the ethylene-bromonium ion. The ab initio C–C length for $C_2H_4Br^+$ upon bromination is 1.455 Å, which is slightly above the upper bound for π-complexes given by Ittel and Ibers (1.36–1.44 Å).[24] The bending of the CH_2 groups away from the former C_2H_4 plane by about 17.4° is intermediate between ethylene (0°) and cyclopropane (30°). The typical distortion of C_2H_4 for planarity for π-complexes is 16–20°.[24] Even the strained adamantyl compound shows an out-of-plane bend of 16.4°.

The last indicator of σ or π character to be considered is charge transfer. The bonding in π-complexes is primarily from the ethylene π orbital to an empty adduct orbital. The stronger σ–complexes form with back-donation of electron density from the adduct orbital of proper symmetry to the π^* MO, with little net charge transfer. From a charge analysis derived from the dipole moment derivatives,[25] the positive charge does not reside on the Br atom at all, but on the C atoms. This is also qualitatively the same charge distribution that comes from a Mulliken population analysis. This means that very little back-donation of electron density has occurred, if any. If forced to choose, it seems that the bridged $C_2H_4Br^+$ is a strong π-complex rather than a σ-complex.

At first glance the 2-bromoethyl cation (which will turn out to be a transition state) has a little more multiple bond character than the bromonium ion, but it must be realized that the bond arises from the overlap of sp^2 and sp^3 orbitals. The C–Br bond is significantly shortened to the point where it is even a little shorter than the typical C–Br bond. There is a great deal of repulsion between the eclipsed C–H and C–Br bonds: the CCBr angle is 9.7° larger than the sp^3 value of 109.5°! This results in more p character in the bonds to the CH_2 group and the HCH angle decreases 8.5° from the tetrahedral ideal. The bending of the CH_2 group is enhanced by the interaction of the pseudo-π orbitals with the empty p orbital on the cation center. The resulting loss of electron density in the C–H bonding MO gives rise to an increase in the C–H bond distance of about 0.015 Å. The large amount of s character remaining in the bond to the Br atom explains why it is shortened so much.

The 1-bromoethyl cations are very similar to each other. Both have slightly increased C–C bond lengths when compared to all of the other structures. This is due to the C–Br acquiring a fair amount of double bond character. As a matter of fact, the C–C bond may be considered as a single bond in which the short distance arises from overlap of sp^2 and sp^3. There is naturally more repulsion in the form where C–Br and C–H are eclipsed (resulting in larger bond angles) than in the case where C–H and C–H are eclipsing. The pseudo-π orbital of the methyl group is better able to interact with the carbocation center when the partially occupied C–Br π orbital is trans to it; however, this cannot overcome the repulsion to make the trans isomer the lower energy one (see Table II). The partial π bond from the Br to the cation center makes the interaction between the pseudo-π methyl MO and the cation center weaker for both the cis and trans cases. This is reflected in the fact that C–H bonds are shorter and the angles are more reminiscent of sp^3, especially for the trans isomer. We see a definite preference for the partial double bond to eclipse the methyl by 1.5 kcal/mol, an effect that has long been noted.[26]

Finally, the transition state resembles bromoethene with a proton sitting on the π-electron cloud which is polarized toward the bromine-substituted end. The C–C distance exhibits more double bond character by virtue of its length than those in any of the other structures.

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Table I. Optimized Geometrical Parameters for $C_2H_4Br^+$ Stationary Points

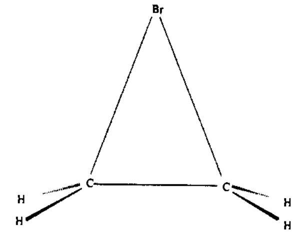
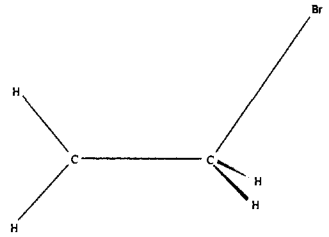
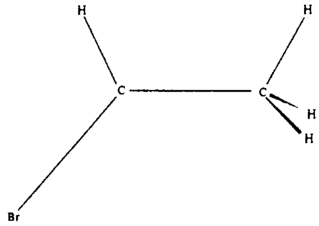
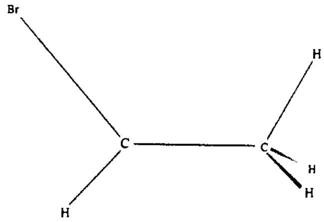
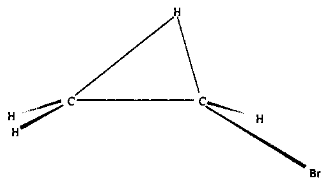
		DZ+d SCF	DZ+d CISD	TZ2P SCF
bromonium ion	C–C	1.442	1.455	1.434
	C–H	1.074	1.084	1.073
	C–Br	2.053	2.025	2.060
	$\angle$H–C–Br	107.7	108.7	107.3
	$\angle$H–C–H	117.9	117.8	118.2
2-bromoethyl cation	C–C	1.447	1.434	1.434
	$C_1{-}H_3$	1.081	1.091	1.081
	$C_1{-}H_4$	1.082	1.092	1.082
	$C_2{-}H_5$	1.094	1.109	1.096
	$C_2{-}Br$	1.909	1.902	1.907
	$\angle C_2{-}C_1{-}H_3$	123.2	123.2	123.1
	$\angle C_2{-}C_1{-}H_4$	119.1	119.0	119.0
	$\angle C_1{-}C_2{-}H_5$	106.2	105.5	106.3
	$\angle H_5{-}C_2{-}H_6$	103.9	101.0	103.6
	$\angle C_1{-}C_2{-}Br$	116.4	118.2	116.6
1-bromoethyl cation (cis)	C–C	1.466	1.463	1.454
	$C_1{-}H_3$	1.091	1.101	1.093
	$C_1{-}H_5$	1.078	1.087	1.077
	$C_2{-}H_6$	1.079	1.090	1.079
	$C_2{-}Br$	1.776	1.770	1.779
	$\angle C_1{-}C_2{-}Br$	125.3	125.1	125.1
	$\angle C_1{-}C_2{-}H_6$	119.1	119.4	119.6
	$\angle C_2{-}C_1{-}H_5$	113.9	114.2	114.2
	$\angle C_2{-}C_1{-}H_3$	107.0	107.1	106.8
	$\angle H_3{-}C_1{-}H_4$	105.7	104.8	105.1
1-bromoethyl cation (trans)	C–C	1.473	1.470	1.462
	$C_1{-}H_3$	1.079	1.088	1.079
	$C_1{-}H_5$	1.089	1.098	1.090
	$C_2{-}C_6$	1.079	1.090	1.079
	$C_2{-}Br$	1.779	1.772	1.782
	$\angle C_1{-}C_2{-}Br$	123.9	123.9	123.7
	$\angle C_1{-}C_2{-}H_6$	121.0	121.1	121.4
	$\angle C_2{-}C_1{-}H_5$	111.3	111.3	111.6
	$\angle C_2{-}C_1{-}H_3$	108.7	109.1	108.4
	$\angle H_3{-}C_1{-}H_4$	106.4	105.7	106.1
transition state	$C_1{-}C_2$	1.405		
	$C_1{-}H_3$	1.664		
	$C_2{-}H_3$	1.156		
	$C_1{-}H_4$	1.080		
	$C_1{-}H_5$	1.079		
	$C_2{-}H_6$	1.078		
	$C_2{-}Br$	1.892		
	$\angle C_2{-}C_1{-}H_4$	119.7		
	$\angle C_2{-}C_1{-}H_5$	121.2		
	$\angle H_3{-}C_1{-}H_4$	106.6		
	$\angle H_3{-}C_1{-}H_5$	110.6		
	$\angle C_1{-}C_2{-}H_6$	117.4		
	$\angle C_1{-}C_2{-}Br$	121.0		
	$\angle H_3{-}C_2{-}H_6$	105.7		
	$\angle H_3{-}C_2{-}Br$	109.5		

Table II. Total and Relative Energies (kcal/mol) of Various $C_2H_4Br^+$ Isomers

	structure				
method	bromonium ion	2-bromoethyl cation	1-bromoethyl cation (cis)	1-bromoethyl cation (trans)	transition state
DZ SCF	-2650.02486	-2650.00137	-2650.02444	-2650.02264	-2649.99134
	0.0	14.7	0.3	1.4	21.0
DZ+d SCF	-2650.11376	-2650.07890	-2650.11037	-2650.10822	-2650.07910
	0.0	21.9	2.1	3.5	21.8
TZ2P SCF	-2650.13325	-2650.09857	-2650.12902	-2650.12666	-2650.09988[a]
	0.0	21.8	2.7	4.1	20.9[a]
DZ+d CISD	-2650.59190	-2650.54740	-2650.58746	-2650.58505	-2650.55137[a]
	0.0	27.9	2.8	4.3	25.4[a]
DZ+d CISD	-2650.64660	-2650.59980	-2650.64227	-2650.63982	-2650.60438[a]
+ Davidson corr	0.0	29.4	2.7	4.3	26.5[a]

[a] Energies at the DZ+d SCF optimized geometry.

Table III. DZ+d SCF Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for $C_2H_4Br^+$ Ssystems

bromonium ion		2-bromoethyl cation		1-bromoethyl cation (cis)		1-bromoethyl cation (trans)		transition state	
3499	45	3454	31	3403	12	3401	14	3463	30
3489	0	3329	6	3378	6	3362	3	3363	16
3368	1	3190	32	3231	9	3259	11	3336	13
3365	18	3153	96	3170	52	3189	41	2710	123
1663	10	1632	0	1609	13	1595	2	1648	10
1596	11	1446	77	1569	23	1574	27	1483	32
1318	0	1424	15	1483	12	1516	63	1439	23
1296	6	1417	4	1455	101	1452	39	1360	10
1222	52	1141	66	1243	17	1193	1	1264	18
1204	1	1113	4	1110	0	1167	35	1101	2
1024	0	1047	11	1058	152	1105	60	985	16
951	1	649	23	831	5	754	76	680	1
896	2	587	10	743	42	718	11	619	16
455	75	334	13	359	7	356	6	355	25
413	40	264i	12	109	1	209i	15	392i	209

Table II records the energies of the isomers at the level of theory in which they were optimized. The only exception was the one labeled as "transition state" in Figure 2, because the optimization in C_1 symmetry past the DZ+d SCF level proved insurmountable. The evaluation of energies at higher levels of theory with DZ+d SCF geometries performed on the other isomers showed that optimization lowered the DZ+d CISD energy by only 0.2–0.4 kcal/mol for the ethyl cations and 4.7 kcal/mol for the bromonium ion. The DZ+d CISD optimized energy will most likely be lower than the single point energy by an amount in this range. Also, the effect of completely optimizing all of the geometry parameters had only a small effect on the DZ SCF results of ref 11.

The SCF vibrational frequencies and IR intensities for the different stationary points are given in Table III and are mainly used to characterize the potential energy surface, since there are no experimental vibrational spectra. For the adamantyl-substituted compound,[8] the lowest two vibrational frequencies of 421 and 403 cm^{-1} may correspond to the C–Br stretch and bend parallel to the C–C bond, as the $C_2H_4Br^+$ harmonic frequencies are 455 and 413 cm^{-1} with respectable IR intensities. After taking into account that SCF frequencies are typically 10% too high, the C–C stretching frequency of 1500 cm^{-1} is a bit below the range of 1640–1680 cm^{-1} observed for double bonds, which is consistent with a π-complex picture.

All energies are reported relative to the cyclic ion which is a global minimum throughout this study. The 2-bromoethyl cation is a transition state that is nearly 30 kcal/mol above the bromonium ion, which by coincidence is the prediction from STO-3G SCF theory.[11] The imaginary vibrational mode of the 2-bromoethyl cation is a torsion; however, all attempts to follow it led to a spontaneous collapse of the C–Br bond toward the middle to give the cyclic ion. This unusual feature has been noted in previous theoretical work on other $C_2H_4X^+$ systems[27] and results in the assertion that the 2-bromoethyl cation will not be observed in the laboratory. This removes the suspicion that it could be a very shallow minimum,[11] the doubt being due to incomplete geometry optimization.

The *cis*-1-bromoethyl cation is indeed a minimum at all levels of theory and is very nearly equal in energy to the bromonium ion. Ab initio agrees amazingly well with experiment on these two dissimilar species. Once the difference in zero-point vibrational energy is taken into account, lowering the *cis*-1-bromoethyl cation by 1.3 kcal/mol relative to the bromonium ion, our best value for the energy difference is 1.5 kcal/mol. The energy difference is remarkably insensitive to basis set or electron correlation, leading to the conclusion that the value of 1.4 kcal/mol given by Berman et al. is accurate.[8] While the Davidson correction negligibly affects the energy differences for the two minima, the actual geometry dependent effects of quadruple excitations may be significant, given the rather small energy difference between the bridged and cis isomers. The *trans*-1-halo isomer is a transition state with an imaginary mode that twists in the direction of the cis isomer and is only slightly higher in energy. Presumably, this indicates that rotation about the C–C bond is nearly unhindered, giving credence to the assertion that the C–C bond is merely a short single bond. Beauchamp's group[8] reported that the cyclic and acyclic minima did not interconvert under their experimental conditions (room temperature), and indeed the structure that is labeled "transition state" presents an energy barrier of 25 kcal/mol for H migration. The vibrational frequency analysis and structure make it clear that this is the previously unreported transition state for the interconversion. The other conceivable pathway that goes through opening the bromonium ion to the 2-bromoethyl ion, followed by H migration via a stationary point with at least 2 imaginary modes, is not feasible.

The final topic of discussion will be on the effects expected when methyl groups are substituted for hydrogen. There has been a great deal of experimental study on this question, and some low level ab initio work on methyl-substituted halonium ions with halogens smaller than bromine.[27,28]

The replacement of an H by CH_3 will induce an asymmetry in the bromonium ion. The methyl will stabilize the positive charge on the α carbon and the Br atom will be shifted toward the unsubstituted carbon atom. This also agrees with Dewar and Ford's[9] argument that the π orbital will be polarized toward the primary carbon, so the Br atom will be shifted that direction in the π-complex. The open ions will all be stabilized by roughly the same amount by a single methyl substitution, whereas the bridged isomer will not benefit to the same degree. Therefore, the 2-bromoisopropyl cation may become the global minimum.

The best chance for observing a methylated derivative of the open 2-bromoethyl cation is to place both methyl groups on the α carbon. This should favor concentrating the charge on the α carbon enough so that the open form *may* be more stable. Given the 30 kcal/mol difference in the parent ion energies this is not likely. The 1,2-dimethyl isomers that arise from bromination of *cis*- and *trans*-2-butenes should be symmetric bridged intermediates. The energy of the open ions produced by ring opening should be decreased relative to the bridged, but not as much as for the 1,1-dimethyl ion. In superacid media, the 1,2-dimethyl isomers undergo H and CH_3 shifts to give the bridged 1,1-dimethylethylenebromonium ion.

When a third methyl is added, the qualitative trends seen for the 1,1-dimethyl case should be expected, with the Br atom experiencing longer excursions toward the α carbon. The intermediate from the bromination of 2,3-dimethyl-2-butene should be symmetric, with the movement of the Br from the α carbon to the β carbon (and vice versa) being more facile. The experimental observations in superacid media[5] support the proposition that the intermediates are all bridged for the bromine case, whereas

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open 2-halo cations may be possible for chlorine and fluorine.

Conclusions

The two lowest minima of the five structures examined in this study are nearly degenerate, with the bromonium ion coming out lower in energy at all levels of theory. Given the insensitivity of this relative energy to basis set and correlation, we expect that these results, which are in excellent agreement with experiment, will not change substantially upon improving the theoretical treatment. The prediction that there is no bound 2-bromoethyl cation is confirmed conclusively. The rotation about the C–C bond in the 1-bromoethyl cation is nearly free. Since the 1-bromo form is 25 kcal/mol lower in energy than the 2-bromo isomer, protonation of bromoethene will occur only in a Markovnikov fashion. The interconversion of the two minima occurs through a transition-state structure in which a H atom is bridging, with a barrier of 25 kcal/mol. The best description of the bridged ion is as a strong π-complex. It must be reiterated that alkyl substitution can have a great effect on the energetics,[27,28] so the results from this study must be applied to other bromonium systems with great care. The ab initio study of halonium ions in larger alkenes would be highly desirable because of the possible role of these structures in the charge conduction mechanism of doped polyacetylene.[29]

Acknowledgment. This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811.

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^{77}Se NMR and Crystallographic Studies of Selenazofurin and Its 5-Amino Derivative

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Abstract: Studies presented here examine the hypothesis that the close Se–O1′ contact observed in the chemotherapeutic agent selenazofurin is electrostatic in origin. The crystal structure and ^{77}Se spectrum of selenazofurin are compared with those of the 5-amino derivative. The ^{77}Se spectrum of selenazofurin shows a doublet of doublets at 774.2 (5) ppm downfield of dimethyl selenide. A two-bond J coupling of 44.3 Hz is observed between Se and the selenazole heterocycle proton H5. A three-bond J coupling of 3.2 Hz is observed between Se and the furanose proton H1′. These observations are consistent with a positively charged selenium in a partially delocalized selenazole ring, in agreement with earlier X-ray studies. The ^{77}Se signal for the 5-amino derivative appears as a doublet at 687.5 (5) ppm relative to dimethyl selenide and 87 ppm upfield from that observed for the parent compound. A two-bond J coupling between Se and H1′ of 4.2 Hz is observed in the 5-amino derivative. The crystal structure of 5-aminoselenazofurin shows an unusually high glycosidic torsion angle with an increase in the Se–O1′ distance relative to that found in the parent compound. These findings are consistent with a decrease in positive charge on the selenium in the 5-amino derivative, resulting in a decrease in the attractive component of the Se–O1′ interaction and a shift in conformation about the C-glycosidic bond.

Introduction

Selenazofurin (Figure 1a, 2-β-D-ribofuranosylselenazole-4-carboxamide, NSC 340847) is a C-glycosyl selenazole nucleoside demonstrating a wide variety of antitumor[1] and antiviral[2] activities. The crystal structures of both selenazofurin (Figure 1b) and its α anomer show an unusual conformational feature.[3] In each structure, the distance between the selenium atom and the furanose oxygen O1′ is significantly less than the sum of the Se and O van der Waals radii. Similar close intramolecular selenium–oxygen contacts have been noted in crystal structures of two selenophene derivatives,[4,5] and a number of close intermolecular selenium–nucleophile contacts have also been catalogued.[6]

Selenazofurin is the selenium analogue of the antitumor agent tiazofurin. In tiazofurin, the selenium atom of selenazofurin is replaced by a sulfur, forming a C-glycosyl thiazole nucleoside. Crystal structures of tiazofurin and seven analogues also show close heteroatom–oxygen contacts.[7-9] Preliminary computational studies in the thiazole nucleosides suggest that these close S–O contacts result from an electrostatic interaction between a positively charged sulfur and negatively charged furanose oxygen.[10] However, the electronic structure of the selenazole heterocycle has not been widely studied, Crystallographic data on true sel-

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