An MNDO Approach to the Symmetry of Bromine Bridging in Substituted Bromonium Ions

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Calculated energy profiles for the opening of six methyl bromonium ions show single, shallow or very flat minima corresponding to symmetrical or highly asymmetrical bridged structures depending on the symmetry of the substitution but not on the number of methyl groups.

Bromine bridging in alkene bromination intermediates is currently believed to be more or less symmetrical depending on the substituents at the double bond.[1,2] However, there is no consensus as to the magnitude of this bridging. This arises from the fact that only indirect data, such as the stereo-

chemistry of bromine addition to cis- or trans-disubstituted ethylenes[1d,3] or the similarity of kinetic effects of the substituents on one or the other carbon atom,[1c,e] are available. Even the interpretation of the ^{13}C NMR spectra of 'frozen' bromonium ions is not certain.[2] A unifying view involving equilibration between bridged and open bromocarbocations has, therefore, been suggested (Scheme 1).[1b,2]

Ab initio calculations have only been performed on the ion derived from ethylene itself, at the SCF level using small basis sets.[4] We report here results obtained using a semi-empirical method, MNDO,[5] on several methyl-substituted bromonium ions (1)–(6).
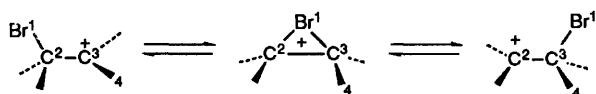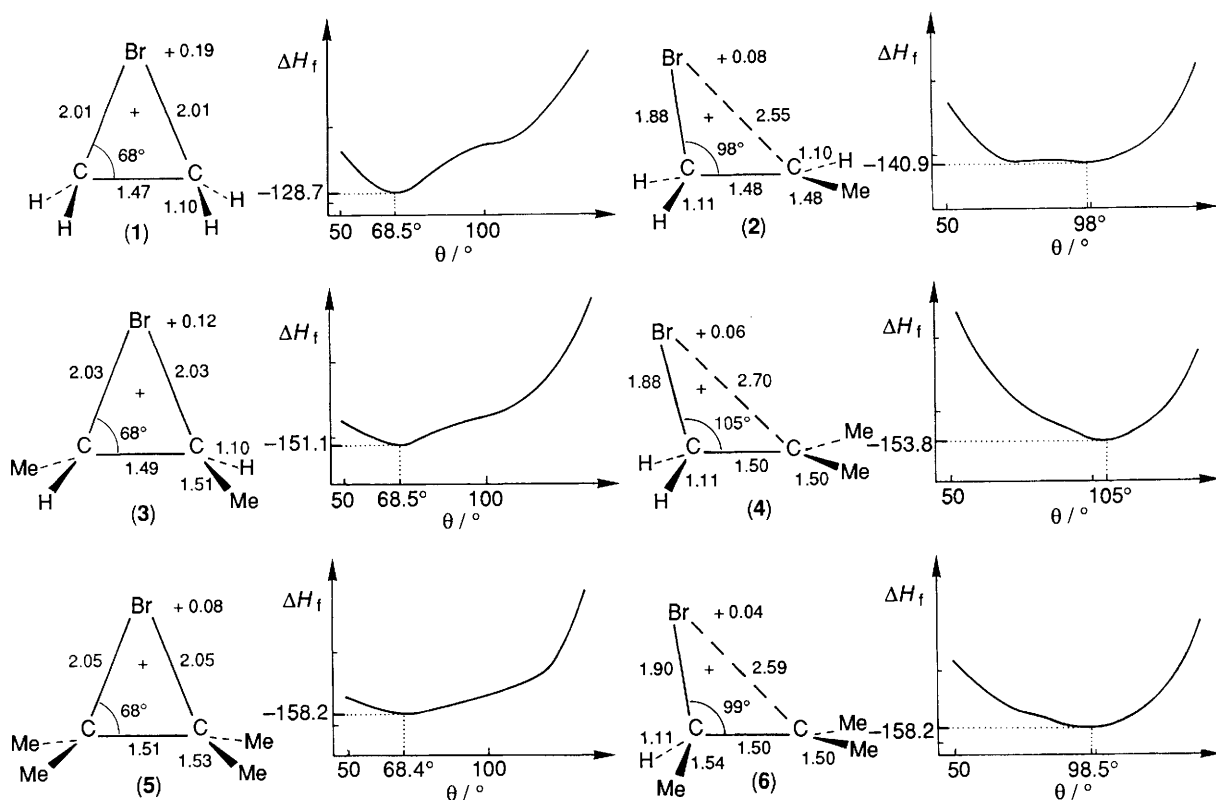

Scheme 1

Figure 1. MNDO optimised minimum energy surfaces for the ring opening, as a function of the $Br-C^2-C^3$ bond angle, θ; the x-axis is the $Br-C^2-C^3$ angle (C^2, the most substituted carbon atom). The interval between the two short bars on the y-axis (ΔH_f) is 10 kcal mol^{-1}. The structures give some critical bond distances and angles as well as the net charge on the bromine atom; they correspond to the most stable configuration. The surfaces for structures (1), (3), and (5) were computed in C_s geometry using the 'precise' option; those for (2), (4), and (6) used no symmetry restraints. (1 cal = 4.184 J).

Large variations in the symmetry of the most stable structures (Figure 1) are observed. Symmetrically substituted ions [(1), (3), (5)] exhibit exactly symmetrical structures with two equal θ angles, regardless of the number of methyl groups. However, on going from (1) to (5) there is a significant decrease in the dihedral angle† θ and in the charge on bromine, showing that the substitution increases the cationic character of the carbon atoms. When the ion is asymmetrically substituted [(2), (4)], (6)], its structure is highly asymmetric. The least substituted carbon atom approaches sp^3 hybridisation whereas the most substituted is close to sp^2. However, even ions (4) and (6) cannot be viewed as fully open β-bromocarbocations since the θ angles and C–C bonds do not correspond to those expected in the absence of any bromine–sp^2 carbon interaction [in 2-bromopropane, d(C–Br) = 1.944 Å and θ (Br–C–C) = 116.2°].

The most striking feature of the calculations is the absence of any secondary minimum in the energy profiles in Figure 1.

In the symmetrical series [(1), (3), (5)], increasing methylation markedly flattens the potential well. For (1) in the region of the more open ion (θ ca. 100°), there is a clear inflection point which is 8.1 kcal mol^{-1} higher than the minimum. The energy difference between the most stable configuration and that which would correspond to an open form falls to 6.4 and 3.4 kcal mol^{-1} for (3) and (5), respectively. For the asymmetric ions, (2) exhibits a broad minimum. Relatively open forms are computed for (4) and (6) but large amplitudes of bromine motion are predicted.

The results reported above are qualitatively the same using the AM1 method.[6] The reliability of the semi-empirical calculations is supported by the close resemblance between the structure and the energy profile of ion (1) obtained either by MNDO and AM1, or by ab initio computations.[4a] The energy required to open fully the bridged ion (1) to give the twisted form is 12 kcal mol^{-1} by MNDO, ca. 30 kcal mol^{-1} at the STO-3G level,[4b] but 15 kcal mol^{-1} using a larger basis set.[4b]

In conclusion, the expected double minima energy profiles are not observed in any kind of substitution pattern and the frequently postulated equilibrium between bridged and open carbocationic structures has no current theoretical support. In order to characterise better these ions, correlated ab initio

† Dihedral angles $Br-C^2-C^3R^4$ (R = H or Me) are 115.9, 96.3, 107.7, 94.7, 103.1, and 89.1° in ions (1), (2), (3), (4), (5), and (6), respectively.

studies using a newly developed 6-31G* bromine basis set[7] are in progress.

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