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Computational studies of benzyl-substituted halonium ions

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Abstract—Density functional computations were carried out whose objectives were to quantify the interactions of chlorine and bromine with neighboring cationic centers in a series of 1-aryl-2-haloethyl cations. Analysis of structural changes and bonding interactions gave rise to linear correlations with σ^+ values of the aryl substituents. Electron-donating groups diminished bridging and electron-withdrawing groups gave rise to stronger bridging.

1. Introduction

Halonium ions, involving iodine, bromine or chlorine, are well-documented species formed as intermediates in various chemical processes, for example, in the electrophilic addition of halogens to alkenes.[1] The electrophilic addition of halogens to unsymmetrical alkenes can lead to carbocations in which the cationic center is stabilized by partial halogen bridging, or to dipole-stabilized carbocations, resulting in restricted rotation about the C=C bond.[2] For example, calculations have established that the cationic center–bromine distance increases with weaker bridging in alkyl substituted unsymmetrical bromonium ions.[3] Stabilization of the halogen-substituted cationic center by conjugation with vinyl or aryl substituents might be expected to further reduce the extent of halogen bridging. Density functional theory and ab initio calculations have shown that halogen bridging in vinyl stabilized chloronium and bromonium ions is weaker than in alkyl substituted analogs.[4] Bromonium ion bridging was stronger than chloronium ion bridging in vinyl-stabilized systems,[4] as expected from previous experimental[5] and computational[6] studies.

The addition of bromine to aryl-substituted alkenes has been studied experimentally in solution, mainly with substituted styrenes and stilbenes.[7] These addition reactions generally show lower stereoselectivities (*anti* addition) than bromine addition to alkyl-substituted alkenes. Phenyl ring substituents affect stereoselectivities and electron donating *para* substituents show lower stereoselectivities in styrene derivatives.[8] Rate studies of bromine addition to ring-substituted styrenes were consistent with the intermediacy of benzylic carbocations[9] on the basis of Hammett correlations. Stereochemical studies of bromine addition to *cis*- and *trans*-β-methylstyrene in acetic acid were interpreted as involving intimate bromocarbocation bromide ion pairs.[10] Rate studies of bromine addition to 4-substituted stilbenes in solution were interpreted as involving competing bridged and unbridged bromocationic intermediates[11] although other interpretations envision intermediates with variable degrees of bridging.[12,13]

In light of the variety of structural possibilities for aryl-substituted β-bromocarbocations and the smaller number of studies available for chlorine substituted cations it was of interest to extend our earlier DFT computational study[4a] to include the structures and energies of halomethyl substituted benzyl cations: Ar–CH(+)–CH_2-X. Because this study involved both chlorine and bromine a comparison of variable bridging interactions was possible. The extent of bridging was assessed by comparing C^+–C–X bond angles and bond index values between halogens (X) and the cationic center. In addition, potential energy plots revealed the relative energies of bridged versus classical ions. Computations were carried out in vacuo to assess the importance of intrinsic interactions. The affect of solvation on geometry and relative stability in selected cases was probed using continuum methodology.

2. Computational methods

All structures were fully optimized by analytical gradient using the Gaussian 98[14] suites. Density functional (DFT)

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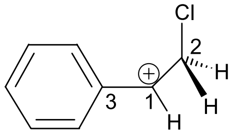
calculations used the exchange potentials of Becke[15a] and the correlation functional of Lee, Yang and Parr.[15b] Frequencies were computed by analytical methods. Reported enthalpies were corrected for zero-point energy differences (ZPVE) (unscaled)[16] and thermal effects at 298.150 K. Conformational searches involved systematic changes (12–20° increments) in the C–C–C–X dihedral angles followed by full optimizations of the maxima and minima. All stationary points gave rise to the correct number of imaginary frequencies. Curves for conformational plots and Hammett plots were fitted using MicrosoftWord Excel routines.

3. Results and discussion

3.1. 2-Chloro-1-phenylethyl cation (1)



1

A plot of the conformational energy versus dihedral angle Cl–C_2–C_1–C_3 for 2-chloro-1-phenylethyl cation **1** at the B3LYP/6-31+G(d) level was used to locate maxima and minima (Fig 1).

The structures 2, 3, 4 and 5 were subjected to full optimization and normal coordinate analysis at the B3LYP/6-311+G(d) level. Relative enthalpies and geometric features are listed in Table1.

Representations of the four 2-chloro-1-phenylethyl cation stationary points based on fully optimized structures are shown in Figure 2. Numbering used for these structures is also shown, with carbon 1 representing the carbocationic center. Figure 2 shows ion **4** conformation with dihedral angle Cl–C_2–C_1–C_3 = 106.5°. This structure corresponds to the geometry expected for a chloronium ion, that is, chlorine is positioned to bridge to the cationic center on C_1. Figure 2 also shows a higher energy minimum conformation **2** with chlorine C_3 eclipsed: Cl–C_2–C_1–C_3 = 0.0°. The carbon framework of this molecule is planar and the geometry about the carbocationic center C_1 is planar, with angles adding to 360°. An analogous minimum enthalpy eclipsed conformation was observed for 4-chlorobutenyl [4] (Fig. 3).

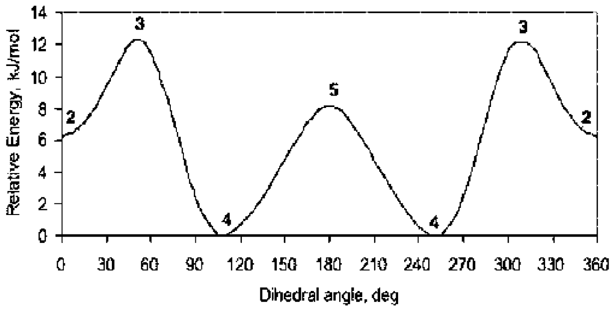


Figure 1. Dependence of relative energy of **1** with dihedral angle Cl–C_2–C_1–C_3: B3LYP/6-31+G(d).

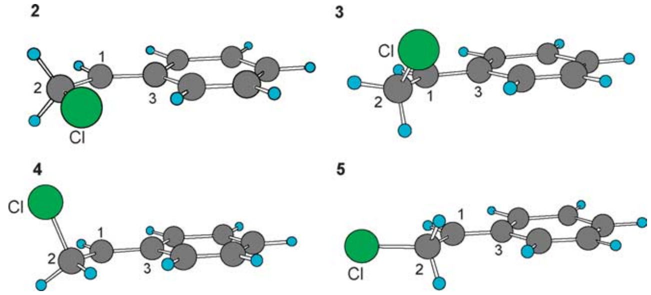
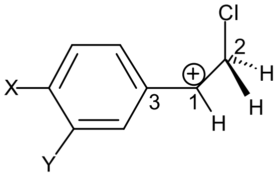


Figure 2. 2-Chloro-1-phenylethyl cation stationary points taken from Figure 1 and optimized at the B3LYP/6-311+G(d) level.

The localized representation of the cation in Figure 3 as well as cations described herein are as shown for convenience as these cations are all delocalized to some extent.

The data in Table 1 show that the Cl–C_2–C_1 bond angle decreases on rotation about the C_1–C_2 bond from a maximum value of 121.6° in conformer **2** to a minimum value of 101.6° in the chloronium ion **4**. The chlorine–carbocationic center C_1 distance also decreases and reaches a minimum value of 256 pm in **4**. The planar geometry about C_1 in **4** suggests that the chlorine bridging is relatively weak. Further evidence for chlorine bridging was obtained by correlations of the Cl–C_2–C_1 bond angle as well as Wiberg bond index (BI)[17] values with electronic properties of phenyl substituents in **1**.

3.2. 2-Chloro-1-arylethyl cations 6



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Optimizations were carried out for a series of 2-chloro-1-arylethyl cations **6** at the B3LYP/6-31+G(d) computational level. The computed structures are minima and correspond to chloronium ion conformations as judged by the Cl–C_2–C_1–C_3 dihedral angles. Important structural parameters are shown in Table 2 along with substituent constants.[18] The Cl–C_2–C_1 bond angle decreases from a value of 106.5° for the *p*-amino substituent to 98.7° for the 5,6-dinitro substituents. Since a smaller Cl–C_2–C_1 bond angle is expected with stronger halogen bridging, this trend correlates with reduced stabilization of the carbocationic center C_1 by the ring containing electron withdrawing substituents. A Hammett plot of the bond angles with σ/σ^+ substituent constants (Fig. 4, data from Table 2) shows an acceptable correlation ($R^2 = 0.964$) and $\rho = -2.86$.

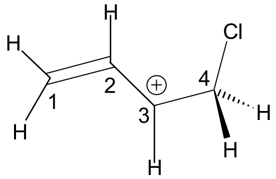

Figure 3. 4-Chlorobutenyl cation: Cl–C_4–C_3–C_2 eclipsed conformation.