On the Structure of Phenonium Ions: The Important Role of Back-Bonding Interaction in Carbocation Chemistry

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Received: November 16, 1999; In Final Form: March 16, 2000

Binding in phenonium ions $[C_6H_5{-}C_2(OH)_4]^+$, $[C_6H_5{-}C_2(CH_3)_4]^+$, $[C_6H_5{-}C_2F_4]^+$, $[p\text{-}NC{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}OHC{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2H_4]^+$, $[p\text{-}F{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}H_3C{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}HO{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2(CHO)_4]^+$, and $[C_6H_5{-}C_2(CN)_4]^+$ was investigated with the B3LYP/6-31G* method. The analysis of the Kohn−Sham orbitals and a Bader analysis of the computed electron density of the phenonium ion, $[C_6H_5{-}C_2H_4]^+$, clearly show that back-bonding from the phenyl cation moiety to the ethylene fragment determines the formation of the three-membered cycle, rendering the shielding of the ipso carbon atom similar to that for an sp^3 C, while an extension of the conjugation occurs as both π systems merge with each other. The important stabilization gained from this process determines the orthogonal conformation of the phenonium ion.

Introduction

Since the postulation of the bridged phenonium ion by Cram in 1949[1] the structure of this carbocation has been extensively investigated. The phenonium ion was initially a major subject of the classical−nonclassical carbocation debate, and has been considered nonclassical in nature for years.

In 1970, Olah et al.[2] first reported that long-lived phenonium ions could be prepared under superacid stable ion conditions. The proton−proton coupling constants observed for the methylene carbons established the bisected structure of phenonium ions, and ^{13}C chemical shift for the ipso carbon atom established its sp^3 nature. This indicated the classical nature of these cations which has been generally accepted since. In 1993, a theoretical study of the structure of the phenonium ion concluded that this ion is nonclassical with considerable 6π-aromatic character.[3] In 1995, Olah et al.[4], on the basis of their experimental NMR studies and theoretical calculations, claimed that Cram's phenonium ion is a spirocyclopropyl benzenium ion containing a 4π cyclohexadienyl system which cannot be characterized as a nonclassical ion. The point under debate is important since it is related to the very nature of bonding in phenonium ions, and without its knowledge the structure of these species and the influence of different factors on it (e.g., substituents) could not be adequately explained.

Very recently,[5] back-bonding has been shown to play a fundamental role in carbocation chemistry. In the case of phenonium ions, the importance of this interaction had already been suggested previously.[6] We present here a theoretical analysis which makes possible a rationalization of binding in phenonium ions clearly showing that the conformation and nature of their structure is determined by back-bonding from the phenyl cation moiety to the ethylene fragment.

Methods

We performed full optimization by means of the Schlegel's algorithm[7] with the B3LYP DFT method[8] and the 6-31G* basis set using the *Gaussian 94* program.[9] The nature of the stationary points was further checked by frequency calculations.

The Kohn−Sham orbitals were analyzed by means of a theoretical method proposed by Fukui's group[10] using the ANACAL program.[11] This method is based on the expansion of the MOs of a complex system A−B in terms of those of its constituent fragments. A configuration analysis is performed by writing the MO wave function built with the Kohn−Sham orbitals corresponding to the combined system in terms of various electronic configurations

$$\Psi = C_0\Psi_0 + \sum_q C_q\Psi_q \qquad (1)$$

where Ψ_0 (zero configuration, AB) is the state in which neither electron transfer nor electron excitation takes place and Ψ_q stands for monotransferred configurations (A^+B^- and A^-B^+), monoexcited configurations (A*B and AB*), and so on. This type of analysis has proved useful for understanding the chemical features of complex formation from chemically interacting systems.

The electron density computed was analyzed by means of the "atoms in molecules" theory of Bader[12] using the AIMPAC package.[13]

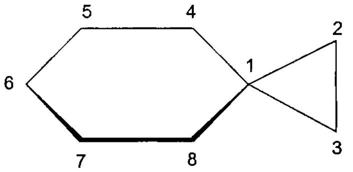
Results and Discussion

The minimum energy structures of $[C_6H_5{-}C_2(OH)_4]^+$, $[C_6H_5{-}C_2(CH_3)_4]^+$, $[C_6H_5{-}C_2F_4]^+$, $[p\text{-}NC{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}OHC{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2H_4]^+$, $[p\text{-}F{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}H_3C{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}HO{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2(CHO)_4]^+$, and $[C_6H_5{-}C_2(CN)_4]^+$ were investigated. Table 1 presents some geometrical and electronic parameters obtained in the present work for various substituted phenonium ions. B3LYP/6-31G* absolute energies and optimized geometries of those phenonium ions are listed in Table 1S and Figure 1S, respectively, available in the Supporting Information. Table 2 displays the relative weight of the most important configurations of phenyl cation and ethylene fragments in the systems studied.

A configuration analysis of the minimum structure $[C_6H_5{-}C_2H_4]^+$ (phenonium ion) shows that the most important com-

10.1021/jp994068g CCC: $19.00

TABLE 1: Geometrical Parameters of Phenyl Cation, $C_6H_5^+$, and Various Substituted Phenonium Ions[a]



	Bond Lengths (Å)								
species	C1−C2	C1−C3	C2−C3	C1−C8	C1−C4	C8−C7	C4−C5	C7−C6	C5−C6
$C_6H_5^+$				1.327	1.327	1.435	1.435	1.395	1.395
$[C_6H_5-C_2(OH)_4]^+$	1.535	2.424	1.535	1.403	1.406	1.394	1.393	1.398	1.398
$[C_6H_5-C_2(CH_3)_4]^+$	1.604	1.967	1.463	1.418	1.418	1.388	1.388	1.399	1.399
$[C_6H_5-C_2F_4]^+$	1.505	2.250	1.508	1.415	1.415	1.386	1.386	1.403	1.403
$[p\text{-NC}-C_6H_4-C_2H_4]^+$	1.634	1.634	1.432	1.429	1.429	1.379	1.379	1.414	1.414
$[p\text{-OHC}-C_6H_4-C_2H_4]^+$	1.634	1.634	1.431	1.431	1.428	1.379	1.382	1.408	1.407
$[C_6H_5-C_2H_4]^+$	1.628 (0.181)	1.628 (0.181)	1.433 (0.284)	1.430 (0.296)	1.430 (0.296)	1.381 (0.322)	1.381 (0.322)	1.406 (0.309)	1.406 (0.309)
$[p\text{-F}-C_6H_4-C_2H_4]^+$	1.615	1.615	1.439	1.436	1.436	1.374	1.374	1.407	1.407
$[p\text{-H}_3C-C_6H_4-C_2H_4]^+$	1.615	1.615	1.439	1.434	1.434	1.375	1.375	1.416	1.416
$[p\text{-HO}-C_6H_4-C_2H_4]^+$	1.598	1.598	1.447	1.443	1.441	1.366	1.368	1.421	1.421
$[C_6H_5-C_2(CHO)_4]^+$	1.634	1.634	1.469	1.444	1.444	1.379	1.379	1.406	1.406
$[C_6H_5-C_2(CN)_4]^+$	1.634	1.634	1.507	1.451	1.451	1.374	1.374	1.411	1.411

[a] In parentheses, electron density at the bond critical point (characterized by two negative and one positive curvatures of the charge density[12a]) of the phenonium ion, $[C_6H_5\text{-}C_2H_4]^+$.

TABLE 2: Relative Weights of the Most Important Electronic Configurations of Fragments in the $[C_6H_5-C_2X_4]^+$ ($A = C_6H_5^+$; $B = C_2X_4$) and $[p\text{-Y}-C_6H_4-C_2H_4]^+$ ($A = p-\text{Y}-C_6H_4^+$; $B = C_2H_4$) Minimum Structures

	Type of Configuration						
		A^-B^+		$A^{2-}B^{2+}$		A^+B^-	
species	AB	HOMO−LUMO	(HOMO-2)−LUMO	HOMO−LUMO	(HOMO-2)−LUMO	HOMO−LUMO	(HOMO-1)−LUMO
$[C_6H_5-C_2(OH)_4]^+$	0.45	1.00		0.39			0.02
$[C_6H_5-C_2(CH_3)_4]^+$	0.53	1.00	0.03	0.35	0.02		0.09
$[C_6H_5-C_2F_4]^+$	0.44	1.00		0.41			0.11
$[p\text{-NC}-C_6H_4-C_2H_4]^+$	0.58	1.00	0.06	0.29		0.12	
$[p\text{-OHC}-C_6H_4-C_2H_4]^+$	0.52	1.00	0.06	0.33			0.15
$[C_6H_5-C_2H_4]^+$	0.60	1.00	0.06	0.29		0.21	
$[p\text{-F}-C_6H_4-C_2H_4]^+$	0.59	1.00	0.07	0.28		0.22	
$[p\text{-H}_3C-C_6H_4-C_2H_4]^+$	0.60	1.00	0.07	0.28		0.22	
$[p\text{-HO}-C_6H_4-C_2H_4]^+$	0.62	1.00	0.08	0.27		0.25	
$[C_6H_5-C_2(CHO)_4]^+$	1.00	0.19	0.88		0.15	0.37	
$[C_6H_5-C_2(CN)_4]^+$	1.00	0.98		0.20		0.70	

ponents of its electronic density come basically from the monotransfer A^-B^+ ($A=C_6H_5^+$; $B=C_2H_4$) and the ditransfer $A^{2-}B^{2+}$ from the HOMO of C_2H_4 to the LUMO of $C_6H_5^+$, the zero configuration AB and the monotransfer A^+B^- from the HOMO of $C_6H_5^+$ to the LUMO of C_2H_4, with smaller participation of the monotransfer A^+B^- from the HOMO-3 of $C_6H_5^+$ to the LUMO of C_2H_4. As a result, there is a net natural bond orbital (NBO) charge transfer of 0.48 e from C_2H_4 to $C_6H_5^+$. The monotransfers A^+B^- determine the presence of an important back donation from the cation to the ethylene moiety. This back-bonding interaction leads to the cleavage of the π C2−C3 bonding in ethylene and makes possible the formation of the two bonds C1−C2 and C1−C3 (see Table 1 for atom numbering). Figure 1 displays the computer plots of the HOMO-1, HOMO-2, and HOMO-4 of the phenonium ion system reflecting the interaction between the HOMO of $C_6H_5^+$ and the LUMO of C_2H_4, the HOMO of C_2H_4 and the LUMO of $C_6H_5^+$, and between the HOMO-3 of $C_6H_5^+$ and the LUMO of C_2H_4, respectively. These plots clearly show that the back donation from $C_6H_5^+$ to C_2H_4 determines an electron density corresponding to the formation of two C−C bonds, whereas the HOMO-(C_2H_4)-LUMO($C_6H_5^+$) interaction would lead rather to a three-center bonding between the two fragments. It has already been found that back donation plays an analogous role in the benzenium ion, the H_2 elimination from it taking place through deactivation of this interaction.[5a]

The importance of this back donation becomes apparent by three different features of our results. First, there is a ring critical point (characterized by two positive and one negative curvatures of the charge density[12a]) in the middle of the cyclopropyl moiety with a value of the electron density of 0.174. Second, the ellipticity of C1−C2 and C1−C3 bonds, which provides a measure of the extent to which charge is preferentially accumulated in a given plane,[12a] is 1.83, indicating that charge is preferentially accumulated in the plane defined by C1, C2, and C3. Third, the geometry of the benzene ring reflects the depletion of the HOMO of $C_6H_5^+$ which is bonding between atoms C1−C4, C1−C8, C6−C7, and C5−C6 (the corresponding bonds stretch), and antibonding between atoms C4−C5 and C7−C8 (the corresponding bonds shorten) (see Table 1 and Figure 1).

The presence of the back-bonding interaction is crucial for explaining the orthogonal conformation of phenonium ions. In effect, while the interaction between the HOMO of C_2H_4 and the LUMO of $C_6H_5^+$ is compatible with both planar and orthogonal conformations, the interactions of the HOMO and the HOMO-3 of $C_6H_5^+$ with the LUMO of C_2H_4 is possible only for nonplanar conformations and is maximum for the

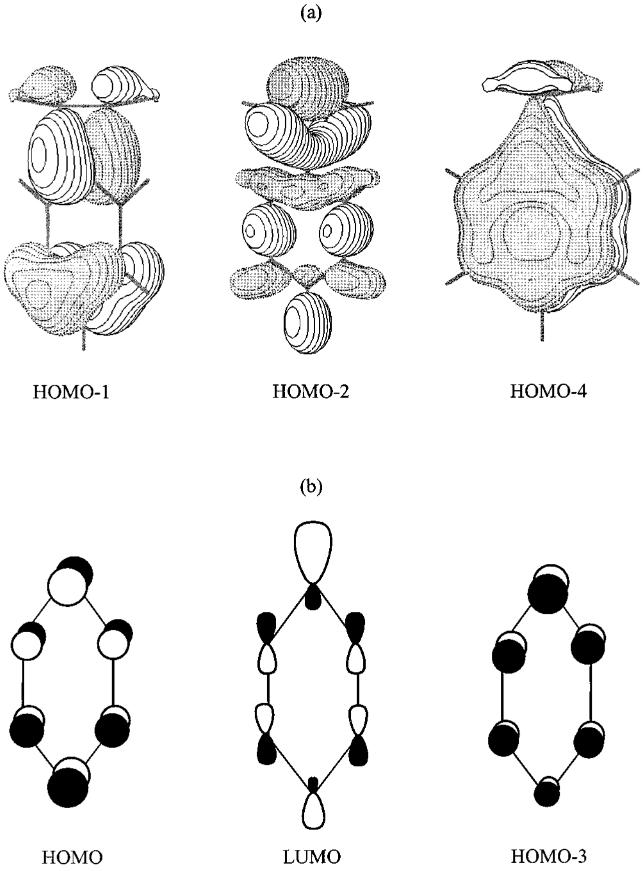
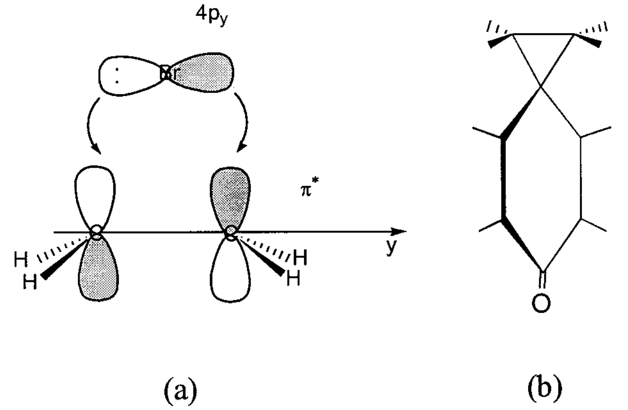


Figure 1. (a) Computer plots of the main frontier molecular orbitals involved in the interaction between phenyl cation and ethylene to form the phenonium ion. (b) Molecular orbitals of $C_6H_5^+$ involved in (a).

SCHEME 1



orthogonal conformation. Accordingly, as the back donation becomes sufficiently small by the effect of substituents, either on ethylene or on the benzene ring, the minimum energy conformation of the $[p\text{-}Y{-}C_6H_4{-}C_2X_4]^+$ system is no more orthogonal but presents only one C$-$C σ bonding between the two fragments. This is the case for the systems $[C_6H_5{-}C_2F_4]^+$, $[C_6H_5{-}C_2(CH_3)_4]^+$, and $[C_6H_5{-}C_2(OH)_4]^+$ (the relative weight of the A^+B^- ((HOMO-1)$-$LUMO) configuration in these systems is 0.11, 0.09, and 0.02, respectively (see Table 2)) in which the steric repulsion between the benzene ring and the substituents on ethylene exceeds the stabilization gained through back bonding. On the contrary, when the back donation is sufficiently important as in $[p\text{-}NC{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}OHC{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2H_4]^+$, $[p\text{-}F{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}H_3C{-}C_6H_4{-}C_2H_4]^+$, $[p\text{-}HO{-}C_6H_4{-}C_2H_4]^+$, $[C_6H_5{-}C_2(CHO)_4]^+$, and $[C_6H_5{-}C_2(CN)_4]^+$ (with a value of the relative weight of the A^+B^- (HOMO$-$LUMO) or ((HOMO-1)$-$LUMO) configuration of 0.12, 0.15, 0.21, 0.22, 0.22, 0.25, 0.37, and 0.70, respectively (see Table 2)), the minimum energy structure is a spirocyclopropyl benzenium ion with an orthogonal conformation.

From our theoretical analysis of the phenonium ion it is evident that, thanks to the back-bonding interaction, the ^{13}C NMR chemical shift observed for the ipso carbon, indicative of sp^3 hybridization, is compatible with a π system including the six carbon atoms of the aromatic ring. In effect, on one hand the composition of the LUMO of the $C_6H_5^+$ fragment in the phenonium ion includes the participation of s and p_x (along the C_2 axis) atomic orbitals of the ipso carbon atom in a ratio of about 1:2, and the HOMO of the $C_6H_5^+$ fragment includes an important participation of the p_z orbital (perpendicular to the ring plane). Accordingly, the shielding of the ipso carbon atom in the phenonium ion would result similar to that for an sp^3 carbon atom. On the other hand, we see in Figure 1 that the interaction between the HOMO and the HOMO-3 of the cationic moiety and the LUMO of C_2H_4 (in the HOMO-1 and the HOMO-4 of the combined system, respectively) takes place with an important transversal conjugation of the two π systems so that the ipso carbon atom is not cut off the π system of $C_6H_5^+$ but rather this π system is enlarged by incorporating the C_2H_4 fragment.

To further investigate the influence of back donation on bonding in the phenonium ion we have studied the energy change along the twisting distortion of the benzene ring. According to our calculations the energy of the system increases monotonically along the rotation from the orthogonal conformation corresponding to the minimum energy structure of the phenonium ion to the planar conformation which corresponds to a second-order saddle point 39.2 kcal mol^{-1} above the minimum. The distance between C1 and the midpoint of the ethylenic C$-$C bond increases also from 1.461 Å in the minimum to 1.803 Å in the saddle point. These computational facts reflect also the structural and energetic relevance of back-bonding interaction in the phenonim ion.

At this point it is also interesting to note the important role played by back donation in the cyclic bromonium ion (see Figure 2S in the Supporting Information). Although the back-donation interaction is small in this species (relative weight 0.04), the antisymmetric orbital interaction in Scheme 1(a), taking place in the HOMO-1 of the cyclic bromonium ion, fixes the geometry of the system.

Finally, it seems worth mentioning that electron transfer from an aromatic ring to the LUMO of an ethylenic moiety may be very important in some other orthogonal bicyclic systems analogous to those studied above. It has been reported that spiro-[5.2]octa-2,5-dien-4-one in Scheme 1(b) (see Figure 2S in the Supporting Information) has a classical structure with some hyperconjugative involvement of the three-membered ring.[3] A configurational analysis of the Kohn$-$Sham orbitals shows that the most important interactions in this species are the electronic transfers $A^{*+}B^-$ (HOMO$-$LUMO/HOMO$-$LUMO), A^+B^{*-} (HOMO$-$LUMO/HOMO$-$LUMO) and $A^{2+}B^{2-}$ (HOMO$-$LUMO/HOMO$-$LUMO) with relative weights of 0.96, 0.34, and 0.33, respectively, whereas the most important electron transfer from the ethylenic fragment to the ring, $A^{*-}B^+$ (HOMO$-$LUMO/HOMO$-$LUMO) has a relative weight of 0.62.

In summary, back bonding from the phenyl cation moiety to the ethylene fragment determines the formation of the three-membered cycle C1−C2−C3 in the phenonium ion, rendering the shielding of the ipso carbon atom similar to that for an sp^3 carbon atom while there is a gain of conjugation as both π systems merge with each other. The important stabilization from this process determines the orthogonal conformation of the phenonium ion.

Acknowledgment. The authors thank FICYT (Principado de Asturias) for financial support (PB-AMB98-05C1). E. del R. also thanks DGESIC for a grant.

Supporting Information Available: Table 1S, B3LYP/6-31G* absolute energies (hartree) corresponding to the various substituted phenonium ions; Figure 1S, B3LYP/6-31G* optimized geometries for the minimum energy structures of the various substituted phenonium ions; Figure 2S, B3LYP/6-31G* optimized geometries of the cyclic bromonium ion and spiro[5.2]octa-2,5-dien-4-one.

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