J. Phys. Chem. A **1999,** *103,* 8491−8495

Ab Initio Topological Analysis of the Electronic Density in Isobutonium Cations

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Received: April 26, 1999; In Final Form: August 3, 1999

Studies performed on isobutonium cations at the ab initio level show that five different stable structures can be characterized. The two structures most energetically favored correspond to van der Waals complexes, one of them between CH_4 and i-$C_3H_7^+$ and one of smaller energy between H_2 and the $C_4H_9^+$ cation. Among the isobutonium cations, the most stable structure corresponds to the C-isobutonium cation where a three-center two-electron bond is formed. The isobutonium cations on the H are significantly higher in energy. The topology of the electronic density charge of the isobutonium cations is studied, at ab initio level, using the theory of atoms in molecules (AIM) developed by Bader. The electronic delocalization that operates through the σ bonds in saturated molecules and specifically in protonated alkanes can be studied by means of the analysis of the charge density and of the Laplacian of the electronic charge density at the bond critical points.

1. Introduction

Protonation of an alkane molecule conceptually gives a carbonium ion[1,2] where a three-center two-electron bond[3] is formed, preserving the electronic octet of the carbon atom. The existence of these species in superacid media was established by Olah and are of great importance, at the present time, for understanding the chemistry of petrochemical processes.[4]

Previous studies[1] in isobutonium cations, at the ab initio level, show that five different stable structures could be characterized from the structural and energetic point of view. Among the isobutonium cations, the most stable structure corresponds to the C-isobutonium ion, structure **1** (Figure 1). The H-isobutonium cations, structures **2** and **3** (Figure 1), are significantly higher in energy. In **2**, the three-center bond involves $C_{(2)}$−H*−H *, where the $C_{(2)}$ corresponds to a tertiary carbon atom. On the other hand, in **3**, the bond is formed among $C_{(1)}$−H*−H**,** where $C_{(1)}$ is a primary carbon atom. The two energetically most favored structures correspond to van der Waals complexes: one between CH_4 and i-$C_3H_7^+$, structure **4** (Figure 1), and other, of lower energy, between H_2 and the t-$C_4H_9^+$ cation, structure **5** (Figure 1). At the MP4(SDTQ)/6-311++G**//MP2-(full)/6-31G** level, **5** is 4.26 kcal/mol lower in energy than **4** and about 5.5 kcal/mol more stable than **1**.[5] The order of stability among the isobutonium cations is in good agreement with the experimental results of isobutane protonation in the gas phase, where formation of methane and isopropyl cations is preferred, suggesting protonation in the C−C bond.[6] On the other hand, in liquid superacid, the main products are the *tert*-butyl carbenium ion and hydrogen,[7] in agreement with calculations of **5** being the most stable i-$C_4H_{11}^+$ species. The reasons for the great stability of the C-isobutonium compared to the H-isobutonium is believe to be related to the charge distribution among the atoms and groups participating in the three-center bond. Hence, in **1**, the positive charge is better delocalized among the three atoms, thus lowering the energy.

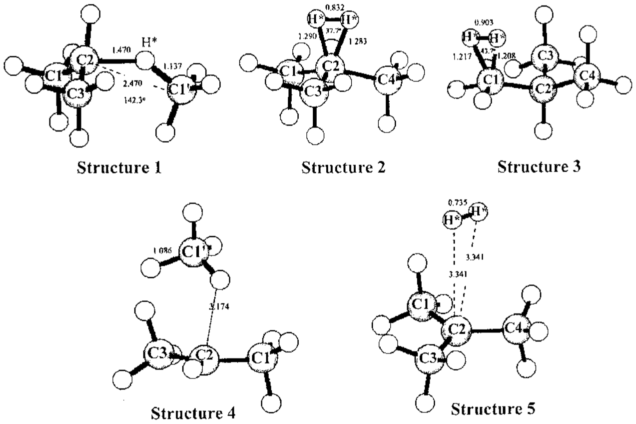

Figure 1. Structures **1**−**5.** MP2 (full)/6-31G** geometries of i-$C_4H_{11}^+$ isomers.

The molecular charge distribution (ρ) topology yields a single unified theory of molecular structure that defines atoms, bonds, structure, and the mechanisms of structural change.[8,9] The same theory defines all average properties of an atom in a molecule.[10]

One may, unambiguously, assign a chemical structure to a molecule by determining the number and kind of critical points (c.p.) in its electronic charge distribution, i.e., points where $\nabla\rho = 0$. The same information enables one to determine whether the structure is topologically stable with respect to the making or breaking of chemical bonds. If it is unstable, one may predict the possible ensuing structural changes. The determination of

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10.1021/jp991360f CCC: $18.00

TABLE 1: Topological Local Properties at the Critical Points, c.p. (3,−1) or Bond Critical Points, of 1 and 4 (in parentheses)[a]

bond	R	$\rho(r_c)$	$\nabla^2\rho(r_c)$	λ_1	λ_2	λ_3	$\|\lambda_1\|/\lambda_3$	ϵ
$C_{(1')}-H^*$	1.1370	0.2250	−0.6678	−0.4447	−0.4411	0.2179	2.0403	0.0082
	(1.0860)	(0.2805)	(−1.0042)	(−0.7013)	(−0.6944)	(0.3915)	(1.7914)	(0.0100)
$C_{(1')}-H$	1.0840	0.2888	−1.0697	−0.7753	−0.7628	0.4684	1.6552	0.0164
	(1.0860)	(0.2800)	(−1.0017)	(−0.6980)	(−0.6908)	(0.3870)	(1.8035)	(0.0104)
$C_{(2)}-H^*$	1.4700	0.0786	0.0654	−0.0998	−0.0820	0.2471	0.4037	0.2171
	(3.1740)	(0.0054)	(0.0023)	(−0.0025)	(−0.0017)	(0.0272)	(0.0932)	(0.5209)
C_2-H	1.0890	0.3003	−1.1717	−0.8650	−0.8305	0.5238	1.6513	0.0415
	(1.0870)	(0.3035)	(−1.2117)	(−0.8969)	(−0.8599)	(0.5451)	(1.6453)	(0.0429)
C_3-H	1.0850	0.2872	−1.0521	−0.7586	−0.7443	0.4508	1.6829	0.0192
	(1.0860)	(0.2853)	(−1.0441)	(−0.7655)	(−0.7459)	(0.4674)	(1.6379)	(0.0263)
C_1-C_2	1.4750	0.2778	−0.8499	−0.5358	−0.5165	0.2024	2.6476	0.0374
	(1.4380)	(0.2969)	(−0.9586)	(−0.5855)	(−0.5390)	(0.1659)	(3.5293)	(0.0863)
C_2-C_3	1.4750	0.2778	−0.8499	−0.5358	−0.5165	0.2024	2.6476	0.0374
	(1.4360)	(0.2978)	(−0.9634)	(−0.5887)	(−0.5421)	(0.1674)	(3.5161)	(0.0858)

[a] Bond distances are expressed in angstroms, and $\rho(r_c)$ and $\nabla^2\rho(r_c)$ are expressed in au.

the kind and number of critical points and thereby the structure of a molecule is, computationally, a straightforward procedure, being comparable in its simplicity of implementation and computer time requirements to a Mulliken population analysis.[11] It is shown that chemical information about a molecular system is usefully summarized and economically extracted from its charge distribution in terms of the properties of ρ at its critical points.

In this work, the topology of the electronic density charge is studied for all of the i-$C_4H_{11}^+$ species shown in Figure 1, at the ab initio level, using the theory of atoms in molecules (AIM) developed by Bader.[8,9] The electronic delocalization that operate through the σ bonds in saturated molecules and specifically in protonated alkanes can be studied by means of the analysis of the charge density and the Laplacian of the electronic charge density at the bond critical points.

The ellipticity provides a sensitive measure of the susceptibility of a system to undergo a structural change. Therefore, predictions of structural changes in the geometry of the isobutonium cations will be presented on the basis of the properties of bond ellipticity and the curvature of the bond path, with all of them defined in terms of a system's charge distribution.[12,13]

2. Calculation Method

Calculations of Hartree−Fock, single-reference second-order Møller−Plesset perturbation theory (MP2) were performed for the isobutonium cations and the van der Waals complexes. The fully optimized molecular geometries were characterized as minima in the potential energy surface by the absence of imaginary vibrational frequencies. Calculations were carried out with the *Gaussian 94*[14] package of molecular orbital programs using the 6-31G** basis sets.

The topological calculations of the charge density distribution were carried out using 6-311++G** basis sets. The local topological properties of the electronic charge density in the bonds critical points were obtained with the AIMPAC package of programs.[15] The critical points of the charge distribution (points of the distribution where $\nabla\rho = 0$) are classified by their rank and signature, analyzing the Hessian matrix of ρ. Four types of c.p. can be characterized. The critical points that present three non-null eigenvalues, two of these (λ_1 and λ_2) being negative and one positive (λ_3), correspond to bond critical points (3, −1) and they will be analyzed in this study.

In this paper, bond ellipticity ($\epsilon = (\lambda_1/\lambda_2) - 1$) is defined in terms of the charge density value and its principal curvature at a bond critical point. The ellipticity measures the deviation of the charge distribution of a bond path from axial symmetry. In terms of the orbital model of electronic structure, the ellipticity provides a quantitative measure of the bond character and the direction of its major axis.[9]

The Laplacian $\nabla^2\rho(r)$ is associated with the charge density. It is the sum of the curvatures in the electron density along any orthogonal coordinate axes at the point (r). The sign of $\nabla^2\rho(r)$ indicates whether the charge density is locally depleted [$\nabla^2\rho(r) > 0$] or locally concentrated [$\nabla^2\rho(r) < 0$].

A molecular graph is the network of bond paths linking pairs of neighboring nuclei. The molecular graph for a molecule at an equilibrium geometry is identified with the corresponding network of chemical bonds.

3. Results and Discussion

Structures 1 and 4. Table 1 shows the more significant topological local properties at the c.p. (3, −1) or bond critical points for **1** and **4** (in parentheses). We have also included the bond distances.

The topological distribution of the electronic charge density on the C-isobutonium cation **1** shows significant differences with respect to the van der Waals complex, **4**. In the first one, the electronic density at the two c.p. of the C−H bond found in the three-center bond $C_{(2)}-H^*-C_{(C1')}$ is very different. In fact, the density in the bond c.p. of $C_{(1')}-H$ * of the methyl group is greater than the density in the $C_{(2)}-H^*$ of the isopropyl group. Both c.p. show very different topological characteristics in function of the values that adopt the curvatures, and they allow us to characterize the first c.p. $C_{(1')}-H^*$ as a covalent bond, where the Laplacian of the density $\nabla^2\rho(r_c) < 0$ and $|\lambda_1|/\lambda_3$ is > 1 ($\rho(r_c) = 0.2250$ au and $\nabla^2\rho(r_c) = -0.6678$ au). On the other hand, the bond c.p. between $C_{(2)}-H^*$ corresponds to a closed shell interaction, as does that of the van de Waals interaction. If we compare the local properties of the $C_{(1')}-H^*$ bond with the other carbon hydrogen bonds of the methyl group (taken as reference bonds), we can see that both the density and the Laplacian values are diminished, indicating a weaker interaction.

It can be observed in Table 1 that the distance between the $C_{(2)}$ and the H* in the three-center bond is 1.470 Å in **1** and 3.174 Å in **4**. In a similar way, the bond c.p. $C_{(2)}-H^*$ in **1** and **4** exhibits the characteristics of a closed shell interaction, where $\rho(r_c)$ takes a small value (0.0786 au) in the first structure and a much smaller one in the second structure (0.0054 au) and the Laplacian of the density, $\nabla^2\rho(r_c)$, is positive, (0.0654 and 0.0023 au, respectively). It is also proven in both cases that the relationship, $|\lambda_1|/\lambda_3$ is < 1, (0.4037 and 0.0932), as generally happens in a van der Waals interaction. It is interesting to note that the ellipticity, ϵ, in both cases is greater than that in the other C−H bonds ($\epsilon = 0.2171$ in the cation **1** and $\epsilon = 0.5209$

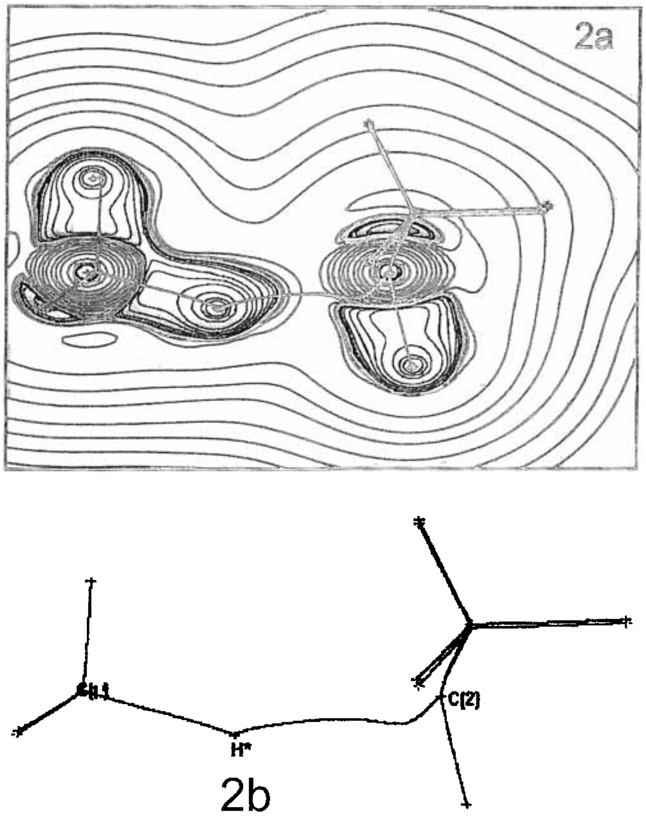

Figure 2. (a) Contour map of the Laplacian distribution $\nabla^2\rho$ in **1**. This is shown in the plane that contains the three-center two-electron bond $C_{(1')}-H^*-C_{(2)}$. (The black contour lines correspond to negative values of $\nabla^2\rho$ and display the regions of the space where the electronic density is concentrated. In addition, the gray lines indicate the regions where the density is depleted and correspond to positive values of $\nabla^2\rho$). (b) Molecular graph of the C-isobutonium **1** where the c.p. are indicated.

in the van der Waals complex). Because the ellipticity arises from the relationship among the negative curvatures along axes perpendicular to the bond path, its increase is a measure of how far the density distribution is from the axial symmetry in the bond ($\lambda_1 \neq \lambda_2$).

In Table 1, it can be observed that the $C_{(2)}-H$ bond (where the considered hydrogen does not interact with the methyl group) is the one that presents the highest density (0.3035 au) and Laplacian (−1.2117 au) values. The ellipticities between $C_{(2)}-C_{(1)}$ and $C_{(2)}-C_{(3)}$, as seen in the Table 1, are $\epsilon = 0.086$, which is much higher than the value found for the propane molecule ($\epsilon = 0.009$).

Figure 2a shows the contour map of the Laplacian distribution $\nabla^2\rho$ for the C-isobutonium ion **1,** in the plane that contains the $C_{(1')}-H^*-C_{(2)}$ bond (the molecular graph is superimposed). The black contour lines correspond to negative values of $\nabla^2\rho$ and display the regions of the space where the electronic density is concentrated. In addition, the gray lines indicate the regions where the density is depleted and correspond to positive values of $\nabla^2\rho$. This figure allows one to differentiate both types of bonds because the critical point at the covalent bond $C_{(1')}-H^*$ is located in a region of charge accumulation whereas the critical point between $C_{(2)}-H^*$, corresponding to the van der Waals complex, is in an area of charge depletion. Figure 2b shows the molecular graph of the C-isobutonium ion **1** where the c.p. are indicated. The three-center two-electron bond $C_{(1')}-H^*-C_{(2)}$ is observed. The bond trajectory $C_{(2)}-H^*$ in **1** corresponds to the van der Waals interaction between the carbon atom of the isopropyl group and the methyl hydrogen.

Table 2 shows the mean local topological properties at the bond critical points of **2** and **5**. The bond distances are also reported.

It can be observed the changes in bond electronic distribution of **2** to give the van de Waals complex, **5**. In t-$C_4H_9^+$, the three primary carbon atoms resemble each other. On the other hand, in **2**, one C−C bond is longer than the other two. In **5**, the three bonds are shortened, and the density in the bond c.p. of the three C−C bonds increase compared to **2**. This is explained by the hyperconjugation that takes place to stabilize the *tert*-butyl cation. It can be seen that in **2** $\lambda_2 = -0.0526$ (the value approaches to zero) whereas the other two eigenvalues are $\lambda_1 = -0.1793$ and $\lambda_3 = 0.1554$, which represents a topological characteristic indicating an unstable critical point. The high ellipticity found for the C_2-H^* bond in **2** suggests that this species will undergo a structural change.[12,13] This is in agreement with the calculated potential energy surface of the i-$C_4H_{11}^+$ that shows that the interconversion of **2** in the van der Waals complex **5** occurs with a negative activation energy. For practical reasons, one must suppose that **2** spontaneously decomposes to **5** and, by this way, cannot be formally considered a discrete intermediate.

The toplogical study of the charge density reveals that an electronic delocalization takes place on the three C−C bonds in **5**. In this way, the van der Waals complex between the H_2 and the *tert*-butyl cation is stabilized, and it is the energetically most-favored i-$C_4H_{11}^+$ structure. The Laplacian of the density distribution in the plane that contains the four carbon atoms of the planar *tert*-butyl cation shows (Figure 3) that each of the hydrogen atoms in the H_2 molecule is located symmetrically in an area where the Laplacian is negative, i.e., the concentration of the electronic charge density along the trajectory of the bond between C−C where the density is maximum. The molecular graph is superimposed.

In Table 3, we display the most significant local topological properties at the bond critical points for the 1-H-isobutonium cation, **3**. The bond distances are also reported.

TABLE 2: Mean Local Topological Properties at the Bond Critical Points of 2 and 5 (in parentheses)[a]

bond	R	$\rho(r_c)$	$\nabla^2\rho(r_c)$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	ϵ
C_2-H^*	1.2900	0.1712	−0.0764	−0.1793	−0.0526	0.1554	0.1535	2.4080
	(3.3410)	(0.0021)	(0.0078)	(−0.0005)	(−0.0004)	(0.0088)	(0.0592)	(0.2046)
H^*-H^*	0.8320	0.2354	−0.7780	−0.6831	−0.4763	0.3814	1.7911	0.4343
	(0.7350)	(0.2667)	(−1.1255)	(−0.9090)	(−0.9082)	(0.6917)	(1.3141)	(0.0008)
C_1-C_2	1.5200	0.2560	−0.7150	−0.4807	−0.4735	0.2393	2.0095	0.0152
	(1.4590)	(0.2885)	(−0.9082)	(−0.5682)	(−0.5361)	(0.1962)	(2.8966)	(0.0599)
C_2-C_3	1.5200	0.2560	−0.7148	−0.4806	−0.4734	0.2393	2.0086	0.0152
	(1.4590)	(0.2885)	(−0.9081)	(−0.5682)	(−0.5361)	(0.1962)	(2.8965)	(0.0599)
C_2-C_4	1.5410	0.2430	−0.6406	−0.4486	−0.4337	0.2417	1.8563	0.0343
	(1.4570)	(0.2900)	(−0.9156)	(−0.5735)	(−0.5381)	(0.1960)	(2.9258)	(0.0659)

[a] Bond distances are expressed in angstroms, and $\rho(r_c)$ and $\nabla^2\rho(r_c)$ are expressed in au.

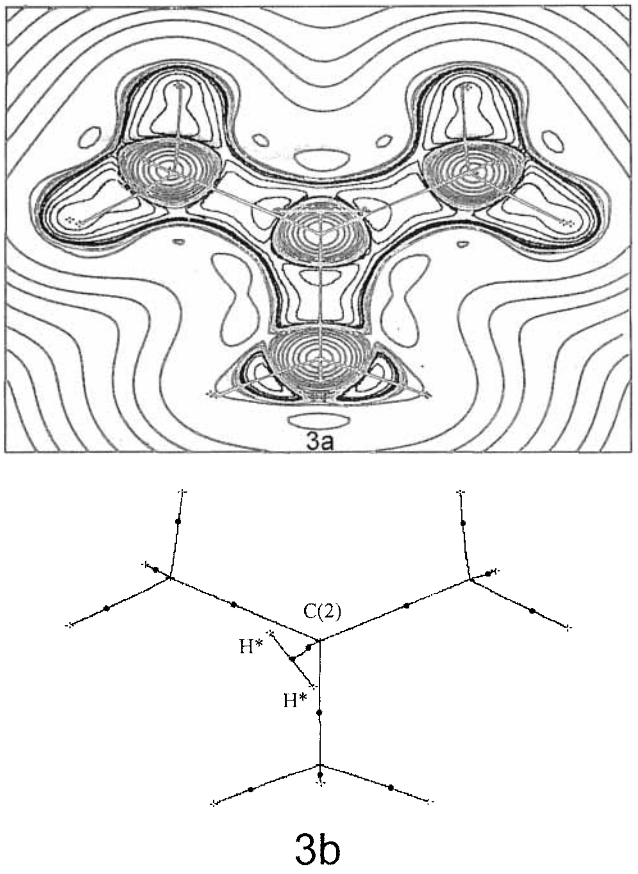

Figure 3. (a) Contour map of the Laplacian distribution $\nabla^2\rho$ of the van der Waals **5** in the plane that contains the four carbon atoms. (The black contour lines correspond to negative values of $\nabla^2\rho$ and display the regions of the space where the electronic density is concentrated. In addition, the gray lines indicate the regions where the density is depleted and correspond to positive values of $\nabla^2\rho$.) The molecular graph is superimposed. (b) Molecular graph of **5** where the c.p. are indicated.

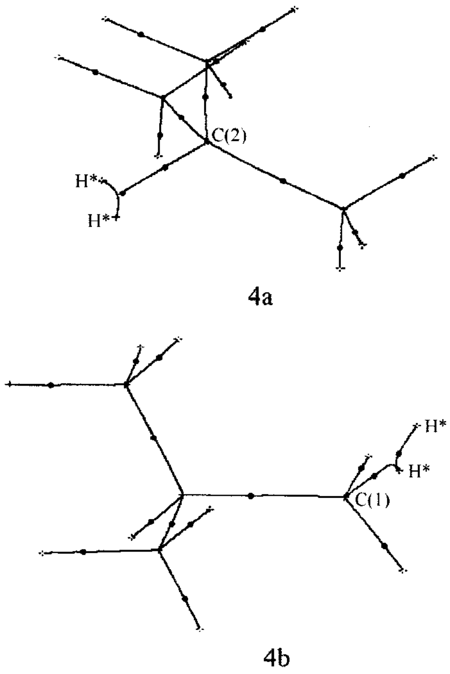

Figure 4. (a) Molecular graph of the 2-H-isotunonium cation (**structure 2**). The bond trajectories and the three-center bond on the tertiary carbon is shown. (b) Molecular graph of the 1-H-isotunonium cation (**structure 3**). The bond trajectories and the three-center two-electron bond $C_{(1)}-H^*-H^*$ on the primary carbon are also shown.

The three-center bond C−H*−H* in the primary carbon is less energetically favored than that in the tertiary carbon atom of **2**, the 2-H-isobutonium cation. It is also remarkable that in these two structures a bond c.p is found between the H*−H* and can be characterized as covalent. In **2**, the H*−H* distance is shorter, ($d = 0.832$A), and the density in the bond c.p. ($\rho(r_c) = 0.2354$ au) is greater than that in **3** ($d = 0.9030$A and $\rho(r_c) = 0.2200$ au).

In **3**, the ellipticity in the bond c.p. between H*−H* is very large ($\epsilon = 1.3855$). The topological properties of the H*−H* bond in the isolated molecule of H_2, $\rho(r_c)$, is 0.2671 au, $\nabla^2\rho(r_c) = -1.1279$ au, and the ellipticity is zero. The large ellipticity value of the H*−H* bond may be an indication that this bond is nearly ready to dissociate.[12,13] In fact, the potential energy surface of the i-$C_4H_{11}{}^+$ shows that **3** undergoes an easy rearrangement to the thermodynamically more favored structure **1**, the C-isobutonium cation. This rearrangement may be associated with the formation of products arising from C−C bond protonation in superacid-catalyzed alkane activation.

Figure 4 represents the molecular graphs for the 1-H-isobutonium and 2-H-isobutonium cations, **3** and **2**, respectively, where the bond trajectories are shown. We also display the three-center bond in the primary and tertiary carbon atoms, respectively.

4. Conclusions

Five different stable structures were studied: three isobutonium cations and two van der Waals complexes. Among the isobutonium cations, the most stable structure corresponds to the C-isobutonium ion. A covalent bond and a van der Waals interaction are characterized because of their topological properties. The H-isobutonium cations are significantly higher in energy. Because of the characterization of an unstable critical point and the larger ellipticity found for the C_2-H^* and H*−H* bonds, these species are capable of suffering a structural change, explaining the easy transformation of **2** in **5** and **3** in **1**.The two most energetically favored i-$C_4H_{11}{}^+$ structures correspond to van der Waals complexes: one involving methane and the isopropyl cation and the other (with the lowest energy) between H_2 and the *tert*-butyl cation. The topological study of the charge density reveals that in the last complex a delocalization of the electronic density takes place on the three carbon

TABLE 3: Most Significant Local Topological Properties at the Bond Critical Points in the 1-H-Isobutonium Cation, 3

bond	R	$\rho(r_c)$	$\nabla^2\rho(r_c)$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	ϵ
C_1-H	1.0890	0.2885	−1.0762	−0.8012	−0.7751	0.5001	1.6019	0.0336
C_2-H	1.0920	0.2879	−1.0515	−0.7500	−0.7393	0.4379	1.7129	0.00143
C_3-H	1.0880	0.2832	−1.0209	−0.7209	−0.7095	0.4095	1.7604	0.0160
C_1-H^*	1.217	0.2090	−0.3783	−0.3362	−0.1285	0.0864	3.8933	1.6174
H^*-H^*	0.9030	0.2200	−0.6002	−0.5608	−0.2351	0.1957	2.8654	1.3855
C_1-C_2	1.5300	0.2425	−0.6627	−0.4347	−0.4246	0.1966	2.2111	0.0237
C_2-C_3	1.5240	0.2563	−0.6951	−0.4883	−0.4824	0.2756	1.7716	0.0123

[a] Bond distances are expressed in angstroms, and $\rho(r_c)$ and $\nabla^2\rho(r_c)$ are expressed in au.

atoms of the methyl group. In this way, **5** is stabilized and happens to be the most energetically favored *i*-$C_4H_{11}^+$ structure. The Laplacian of the density distribution in the plane that contains the four carbon atoms of the *tert*-butyl cation shows that hydrogen atom of the H_2 molecule of the complex is symmetrically located in an area where the Laplacian is negative (concentration of the electronic charge density) along the trajectory of the C−C bond where the $\rho(r_c)$ is maximum.

It is interesting to note that in **4**, the complex between CH_4 and isopropyl cation, the van der Waals interaction takes place with the hydrogen atom of the methyl moiety that is separated by 3.1740 Å from the isopropyl cation. On the other hand, there is no bond critical point with the methyl hydrogen atom that is separated with a distance of 2.889 Å. This seems to indicate that the most distant hydrogen atom presents a more favored stereo electronic arrangement.

Acknowledgment. A.H.J. is a member of the Carrera del Investigador Científico, CICPBA. N.O. and N.M.P. acknowledge SECyT-UNNE for financial support. The authors acknowledge the Centro Nacional de Cálculo Científico, Mérida, Venezuela, for computing time. C.J.A.M. thanks FINEP/PRONEX, CNPq and FAPERJ for financial support. P.M.E. thanks CAPES for a scholarship.

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