On the $C_2H_2I^+$ Potential Energy Hypersurface. An *ab initio* Study

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The study of the $C_2H_2I^+$ cation at several levels of *ab initio* theory reveals the existence of four stationary points, three of them are characterized as minima and another as a transition state; the 1-iodovinyl cation is the global minimum, the cyclic iodonium ion is very close in energy to the 1-iodovinyl cation and the transition state connecting the 1-iodovinyl cation and the cyclic iodonium ion is very high in energy.

Vinyl cations are important reactive intermediates in organic reaction mechanisms.[1] The electrophilic addition of halogens and other halogenated reagents to alkynes generate cationic species with a halogen atom in either bridged or open structures. The nature of the intermediate determines the final product. Therefore, it is of great interest to know the relative stabilities of such structures because they are involved in the first step of many important synthetic processes.[2] Despite the recent theoretical interest in $C_2H_2X^+$ species,[3] as far as we know, no extensive theoretical study has been devoted to $C_2H_2I^+$ or reactions between alkynes and iodine. We have described the iodofunctionalization of alkynes with bis(pyridine)iodo(I) tetrafluoroborate.[4] Based on our experimental results, we have postulated a cyclic iodonium ion intermediate in electrophilic additions of positive iodine to alkynes[4c] in agreement with previous reports.[5] At this point it is of interest to calculate the stabilities of various possible intermediates. This paper reports on the performed *ab initio* study of the potential energy hypersurface for $C_2H_2I^+$ species.

All calculations were carried out by using the Gaussian 92 program package.[6] The molecular geometries of the $C_2H_2I^+$ isomers were initially optimized, within appropriate molecular symmetry constraints, at the Hartree–Fock self-consistent field (HF) level of theory, and electron correlation, keeping the core orbitals frozen, was included in further optimizations by using Møller–Plesset perturbation theory[7] with second-order corrections (MP2) or configuration interaction including all Hartree–Fock interacting[8,9] singly and doubly excited configurations (CISD) relative to the SCF reference configuration, employing Schlegel's analytical gradient procedure.[10] Harmonic vibrational frequencies of the optimized structures were calculated to characterize these stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energy corrections (ZPC) to the relative energies, by diagonalizing the mass-weighted Cartesian force-constant matrix computed analytically by second derivatives (SCF and MP2) or numerically by finite differences (CISD) of analytical gradients. The contribution to the CISD correlation energy from quadruple excitations was obtained by using Davidson's formula to estimate the energy correction due to the effect of unlinked clusters (simultaneous pair correlation)[11] and is denoted by CISD(+Q).

The following basis sets have been employed. For C and H, the standard split-valence 6-31G and 6-31G** (with six d-functions for C and three p-functions for H) basis sets,[12,13] and for iodine, the M4 (43333/4333/43), the M4* (43333/4333/431), where the M4 was augmented by a set of six d-functions with an exponent of 0.266, and the SV* (433321/43321/431), where it was also splitting the outer contracted Gaussian s- and p-type orbitals, basis sets.[14]

Table 1 shows the absolute and relative energies for the 1-iodovinyl cation **1**, the 2-iodovinyl cation **2**, the cyclic iodonium ion **3**, and the transition structure, **ts**, from **3** to **1**. All attempts to minimize the cyclic structure with a proton bridge led to structure **1**. Initially, the transition structure, **ts**, connecting **1** and **3** was located by a linear synchronous transit calculation[15] and, it was then optimized.

At all levels of theory, the 1-iodovinyl cation **1** is the global minimum, which is expected if one considers the π donation

Table 1 Absolute energies (+6989.0) in hartrees, relative energies in kcal mol^{-1} (in parentheses, 1 cal ≈ 4.184 J) and zero point energies in kcal mol^{-1} for $C_2H_2I^+$

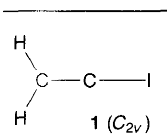
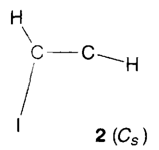
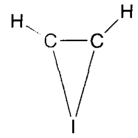
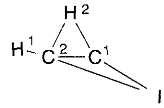
	HF/ 6-31GM4	HF/ 6-31G**M4*	HF/ 6-31G**SV*	MP2/ 6-31G**M4*	MP2/ 6-31G**SV*	CISD/ 6-31G**SV*	CISD(+Q) 6-31G**SV*
 **1** (C_{2v})	- 0.328945 (0.0) min, 18.6	−0.546405 (0.0) min, 18.5	−0.569954 (0.0) min, 18.7	−0.872626 (0.0) min, 17.4	−0.914526 (0.0) min, 17.6	−0.900093 (0.0) min, 18.0	−0.950756 (0.0)
 **2** (C_s)	- 0.325791 (2.0) min, 18.8						
 **3** (C_{2v})	- 0.320956 (5.0) min, 18.8	−0.538865 (4.7) min, 18.5	−0.556148 (8.7) min, 18.6	−0.872245 (0.2) min, 17.4	−0.908778 (3.6) min, 17.6	−0.888508 (7.3) min, 17.9	−0.938535 (7.7)
 **ts** (C_s)		−0.520229 (16.4) **ts**(393.9i), 16.8	−0.538079 (20.0) **ts**(404.4i), 16.8	−0.841584 (19.5) **ts**(286.3i), 16.2	−0.875361 (24.6) **ts**(288.1i), 16.3	−0.864522 (22.3) **ts**(310.6i), 16.4	−0.912405 (24.1)

Table 2 Selected optimized structural parameters for $C_2H_2I^+$ isomers (bond lengths in Å, angles in °)

		HF/6-31GM4	HF/6-31G**M4*	HF/6-31G**SV*	MP2/6-31G**M4*	MP2/6-31G**SV*	CISD/6-31G**SV*
1 (C_{2v})	C–C	1.276	1.272	1.273	1.285	1.288	1.283
	C–I	2.086	1.982	1.951	1.938	1.914	1.931
3 (C_{2v})	C–C	1.232	1.229	1.230	1.267	1.271	1.253
	C–I	2.506	2.344	2.306	2.275	2.246	2.265
ts (C_s)	C^1–C^2		1.225	1.229	1.259	1.260	1.251
	C^1–I		3.251	3.229	3.187	3.162	3.206
	C^2–H^2		1.159	1.153	1.124	1.124	1.133
	I–C^1–C^2		12.3	13.6	24.0	24.8	19.5
	H^2–C^2–C^1		77.9	80.0	101.9	102.6	92.2

from iodine to stabilize the empty p orbital on the carbocation centre. On the other hand, what was surprising was that the 2-iodovinyl isomer **2** is very close in energy to **1** and lower in energy than the cyclic ion **3** at the HF/6-31GM4 level. This however, arises as a consequence of the poor performance of the basis set used in the description of **1** and **3**. With the inclusion of polarization functions, minimization of structure **2** led, in all computed cases, to the cyclic iodonium ion **3**. Related to **3**, the energies at the different levels of calculation are closer to the 1-iodovinyl cation **1** [energy gap ranges from 0.2 (MP2/6-31G**M4*), to 8.7 kcal mol^{-1} (HF/6-31G**SV4*), Table 1] than the previously reported results for the chloro and bromo derivatives.[3] This is in accord with the larger size of iodine and, consequently, a less strained three-membered ring. It can also be noted that electron correlation stabilizes the nonclassical iodonium ion relative to the 1-iodovinyl cation while valence-shell splitting produces the opposite effect, as expected. With regard to the saddle point, **ts**, it was characterized as a true transition state (one imaginary frequency). In addition, at all levels of theory (with the exception of HF/6-31GM4 where no saddle point was found) the energy gaps relative to **3** were very high [from 11.3 (HF/6-31G**SV*), to 21.0 kcal mol^{-1} (MP2/6-31G**SV*), Table 1] and, thus, it does not seem likely that **3** and **1** can interconvert in a dynamic equilibrium. Inclusion of ZPC does not substantially change the energy diagram.

Selected structural parameters of the $C_2H_2I^+$ isomers are given in Table 2. Several features may be observed. The C–C distance in all computed geometries is intermediate between a triple and a double bond, being longer in **1** than in **3** or **ts**. This is the result of the higher stabilizing donation from iodine atom in the former, as confirmed by the short C–I distance in **1**. The introduction of electron correlation produces a shortening of the C–I distance, accompanied by a corresponding lengthening of the C–C distance. In addition, the poor performance of the calculation at the HF/6-31GM4 level is corroborated by the fact that the C–I distances in **1** and **3** are too large. Moreover, the correlation treatment produces a change in the structure of the **ts** to more closely resemble the cyclic structure **3** (higher I–C^1–C^2 and H^2–C^2–C^1 angles, see Table 2). However, this effect is accompanied with an increment in the relative energy between **3** and **ts** (from 11.7–11.3 to 19.3–15.0 kcal mol^{-1}), which indicates that the potential barrier is very high.

The used level of theory is comparable with previous calculations reported for species containing iodine.[14,16] Since theoretically predicted geometries and energies are in good agreement with experimental ones,[14,16] we can assume that our calculations are accurate enough to obtain valid conclusions.

In summary, the addition of electrophilic iodine to acetylene may occur with the formation of a cyclic iodonium ion intermediate. Taking into account the performed calculations, it can be postulated that participation of the 2-iodovinyl isomer does not occur. Furthermore, equilibration to the more stable 1-iodovinyl cation is prevented by the high barrier of the transition state connecting both species. Thus, the cyclic intermediate must be the reagent species in this reaction. This conclusion is in accord with our previous experimental results in iodofunctionalization of alkynes[4] and heterosubstituted alkynes.[17] Further improvement of basis set or correlation treatment will not lead, in our opinion, to qualitatively different results.

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