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Does 4-Iodoniacyclopentene Exist?

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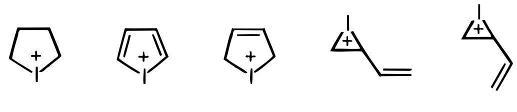
Cyclic and acyclic halonium ions represent a class of organic onium compounds with a considerable chemical interest and utility as reagents in organic synthesis.[1] A broad number of them can be isolated as stable salts or prepared *in situ* for further reactions, and they have been postulated as reaction intermediates in electrophilic halogenations.[1] Special attention has been paid to cyclic ions, and, in particular, the theoretical interest in three-membered-ring cyclic halonium ions shows a substantial increase in recent years.[2−4] In regard to five-membered-ring cyclic halonium ions (Chart 1), iodoniacyclopentane, **1**, and 5-iodoniacyclopenta-1,3-diene, **2**, have been observed,[1] but this has not been possible for 4-iodoniacyclopentene, **3**, which could participate in electrophilic additions of positive iodine to conjugated dienes. In fact, we have observed that bis(pyridine)iodonium(I) tetrafluoroborate allows the regioselective functionalization of conjugated dienes to give both 1,2- or 1,4-addition products depending on the reaction conditions,[5] which suggests an equilibriun between intermediates species like **3**−**5** (Chart 1). We have recently described the *ab initio* calculations on the potential energy hypersurfaces for $C_2H_2I^+$ isomers.[4] The agreement between our experimental results for the iodofunctionalization of alkynes[6] and *ab initio* calculations prompted us to study the existence of 4-iodoniacyclopentene (**3**). As far as we know, no theoretical study has been carried out on this ion. We report here the *ab initio* study of the $C_4H_6I^+$ species.

All calculations were carried out with the Gaussian94 program package.[7] The molecular geometries were first optimized without any molecular symmetry constraints at the Hartree−Fock self-consistent field (HF) level of theory and reoptimized by the Møller−Plesset perturbation theory[8] with second-order corrections (MP2), using Schlegel's analytical gradient procedure.[9] Regarding the atomic basis set, the standard split-valence 6-31G(d,p) basis,[10,11] with six d-functions for C and three p-functions for H, and the split-valence M4(d) basis,[12] with one set of six d-functions ($\zeta_d = 0.266$) for I (4,3,3,3,21/4,3,3,21/4,3,1), appeared to be a good choice because of the nice agreement between ab initio calculations and experimental results.[4,11,13] This basis set will be hereafter referred to as DZV(d,p). The optimized structures were characterized as minima or saddle points by analytic frequency calculations which also yielded zero-point vibrational energy and thermochemical analysis.

Chart 1



1 **2** **3** **4** **5**

In order to assess the importance of higher level correlated methods, additional single-point calculations on the MP2/DZV(d,p) geometries were performed with incorporation of correlation energy using Møller−Plesset perturbation theory with fourth-order corrections (MP4SDTQ),[14] configuration interaction including all single and double excitations,[15] corrected with quadruple excitation, by using Davidson's formula (CISD+Q),[16] and coupled cluster theory with single and double substitutions (CCSD)[17] with the DZV(d,p) basis set.

Furthermore, the existence of ionic species may require functions of higher angular momentum. Thus, we have carried out single-point calculations at the MP2 level using the uncontracted pseudorelativistic effective core potential (ECP) of Hay and Wadt,[18] augmented by two sets of d functions ($\zeta_d = 0.105$ and 0.334)[12] and one set of f functions ($\zeta_f = 0.433$)[13a] for I (111/111/11/1) in conjunction with a 6-311G(2df)[19] basis set for C and H. This basis set will be hereafter referred to as TZV(2df).

The relevant geometrical parameters of the optimized structures with the MP2/DZV(d,p) wave function are given in Figure 1. The **3**, **4**, and **5** structures were characterized as minima on the potential energy hypersurface, and they are intermediates resulting from attack of positive iodine on butadiene. The 4-iodoniacyclopen-

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[1] Olah, G. A. *Halonium Ions*; J. Wiley: New York, 1975.

[2] Menéndez, M. I.; Suárez, D.; Sordo, J. A.; Sordo, T. L. *J. Comput. Chem.* **1995**, *16*, 659. Herges, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 51. Bloemink, H. I.; Hinds, K.; Legon, A. C.; Thorn, J. C. *Chem. Eur. J.* **1995**, *1*, 17. Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448. Rodriquez, C. F.; Bohme, D. K.; Hopkinson, A. C. *J. Am. Chem. Soc.* **1993**, *115*, 3263. Reynolds, C. H. *J. Am. Chem. Soc.* **1992**, *114*, 8676.

[3] Rodriquez, C. F.; Bohme, D. K.; Hopkinson, A. C. *J. Org. Chem.* **1993**, *58*, 3344. Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 7147.

[4] Campos, P. J.; Rodríguez, M. A. *J. Chem. Soc., Chem. Commun.* **1995**, 143.

[5] Barluenga, J; González, J. M.; Campos, P. J.; Asensio, G. *Tetrahedron Lett.* **1986**, *27*, 1715. Barluenga, J; González, J. M.; Campos, P. J.; Asensio, G. *Tetrahedron Lett.* **1988**, *29*, 6497.

[6] Barluenga, J; Rodríguez, M. A.; González, J. M.; Campos, P. J.; Asensio, G. *Tetrahedron Lett.* **1986**, *27*, 3303. Barluenga, J; Rodríguez, M. A.; Campos, P. J. *J. Org. Chem.* **1990**, *55*, 3104.

[7] Gaussian 94 (Revision C.3), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1995.

[8] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

[9] Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

[10] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[11] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

[12] Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E. *J. Comput. Chem.* **1984**, *5*, 146.

[13] (a) Gobbi, A.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1162. (b) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448.

[14] Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

[15] Bunge, A. *J. Chem. Phys.* **1970**, *53*, 20. Bender, C. F.; Schaefer, H. F. *J. Chem. Phys.* **1971**, *55*, 4798.

[16] Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974.

[17] Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35. Purvis, G. D.; Barlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382. Scuseria, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *90*, 3700.

[18] Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

[19] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

S0022-3263(96)01266-2 CCC: $12.00

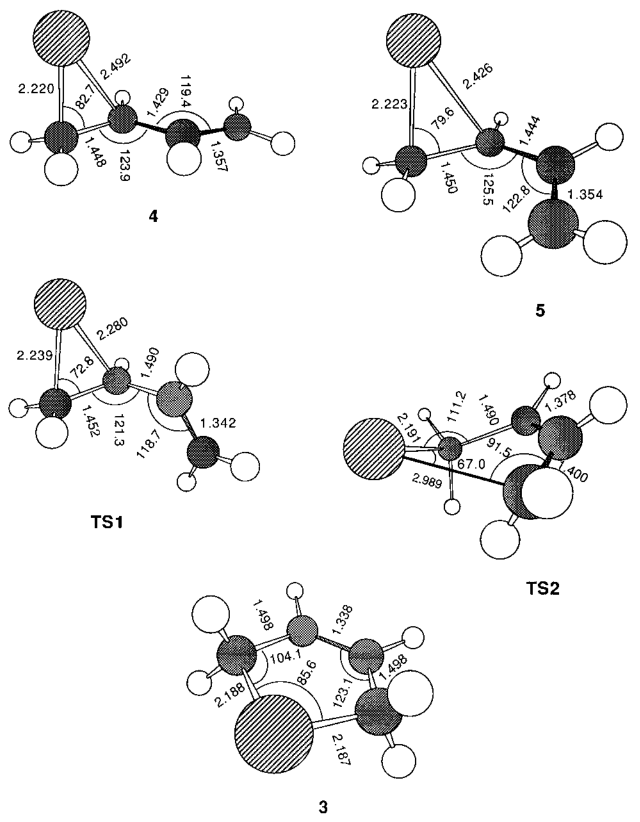

Figure 1. Computer plot of the MP2/DZV(d,p) optimized structures (lengths in Å, angles in deg) for the *s-trans* (**4**) and *s-cis* (**5**) 2-vinyliodoniacyclopropane, the 4-iodoniacyclopentene (**3**), and the transition structures for the interconversion between **4** and **5** (**TS1**) and between **5** and **3** (**TS2**).

tene **3** shows a C_{2v} type symmetry (although no geometry constraints were imposed) with shorter C−I distances (2.187 and 2.188 Å), two C−C single bonds (1.498 Å), one C−C double bond (1.338 Å), bond angles of 85.6° (C−I−C), 104.1° (I−C−C), and 123.1° (C−C−C), and plane−plane angles of 0.0° [both ($C_1-C_2-C_3$)($C_2-C_3-I_4$) and ($C_1-C_2-C_3$)($C_2-C_3-C_4$)]. The equilibrium geometries of the *s-trans*- and *s-cis*-2-vinyliodoniacyclopropane **4** and **5** show a highly nonsymmetric iodonium bridge with C−I distances of 2.220 and 2.492 Å in the former and 2.223 and 2.426 Å in the latter. The observed asymmetry can be explained if one considers the π conjugation with the vinyl group. This effect places the C−C bond between the three-membered-ring and the vinyl group as 1.429 Å for **4** and 1.444 Å for **5**, which are noticeably shorter than those observed (1.463 Å) or calculated (1.465 Å, CASSCF/6-31G*)[20] for *s-trans*-butadiene.

Searches for the transition states connecting **3**−**5** were carried out by linear synchronous transit (LST) calculations[21] at the MP2/DZV(d,p) level. The LST procedure locates a maximum along a path connecting two structures but not a proper transition state and, thus, subsequent geometry optimizations were carried out at the same level. These optimizations led to two stationary points, **TS1** and **TS2**, characterized as true transition structures (only one imaginary frequency). By the intrinsic reaction coordinate (IRC) reaction path,[22] it was confirmed that **TS1** and **TS2** are the transition states for the interconversion between **4** and **5** and between **5** and **3**, respectively. An extensive search to find the saddle points connecting **3** and **4** at the MP2/DZV(d,p) level was unsuccessful. All attempts to minimize the corresponding open structures led to **4** or **5**. In the transition structure **TS1**, the absence of the above referred π conjugation causes the internal C−C bond to lengthen (1.490 Å), the vinyl C−C bond to shorten slightly (1.342 Å), and the C−I bonds to equalize (2.239 and 2.280 Å). The transition state for the interconversion between **5** and **3** (**TS2**) can be considered as an open structure (C−I distances 2.191 and 2.989 Å) with the positive charge delocalized along an allylic structure (Mulliken population analysis gave a charge of +0.154 on I, +0.017 on C_α, and +0.354, +0.048, and +0.427 on allylic carbons, with the hydrogen atomic charges summed into heavy atoms).

The total energies, along with the zero-point vibrational energies, of **3**−**5**, **TS1**, and **TS2**, calculated by using the MP2/DZV(d,p) wave function, are given in Table 1. Due to the different nature of the cyclic structures, the entropy contributions might be crucial and, therefore, the free energies derived from the thermochemical analysis for $T = 298$ K are also included in Table 1. Figure 2 shows the relative energies, including the free energies and the ZPE corrections. We have found that, at the MP2/DZV(d,p) level of theory, the five-membered-ring cyclic ion **3** is the global minimum while the structures **4** and **5** should be 3.5 and 6.8 kcal/mol less stable than **3**, respectively; **TS1** and **TS2** lie 13.0 and 22.8 kcal/mol above **3**, respectively.

Table 1 and Figure 2 also give the additional single-point calculations on the MP2/DZV(d,p) geometries at the MP4SDTQ/DZV(d,p), CISD+Q/DZV(d,p) and CCSD/DZV(d,p) levels of theory. These higher correlated level methods also predict that 4-iodoniacyclopentene (**3**) should be the global minimum on the $C_4H_6I^+$ potential energy surface. On the other hand, to assess the importance of basis set quality, calculations with the improved basis set TZV(2df) at the MP2 level (Table 1 and Figure 2) were performed. From the MP2/TZV(2df) level, we derive the same conclusions, which reveals that the obtained results do not depend appreciably on the basis set. Thus, our calculations predict a feasible interconversion from **4** (obtained from the addition of electrophilic iodine to the most stable *s-trans*-butadiene) to the *s-cis* cyclic cation **5** through a first transition structure **TS1** {activation energy from 9.1 [CCSD/DZV(d,p)] to 9.5 kcal/mol [MP2/DZV(d,p)]}; **5** could be transformed into **3** through a second transition structure **TS2** {activation energy from 14.5 [CCSD/DZV(d,p)] to 18.8 kcal/mol [MP2/TZV(2df)]}.

The used level of theory is comparable with previous calculations reported for bridged cation species.[23] Since theoretically predicted geometries and relative energies are in good agreement with experimental ones,[23] we can assume that our calculations are accurate enough to obtain valid conclusions.

Finally, because of dealing with ionic species, solvent might also considerably affect the relative energies of

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(20) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.

(21) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

(22) Truhlar, D. G.; Kuppermann, A. *J. Am. Chem. Soc.* **1971**, *93*, 1840. Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(23) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley: New York, 1986. (b) Carneiro, J. W. de M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 4064. Buzek, P.; Schleyer, P. v. R.; Sieber, S.; Koch, W.; Carneiro, J. W. de M.; Vancik, H.; Sunko, D. E. *J. Chem. Soc., Chem. Commun.* **1991**, 671.

Table 1. Calculated Total Energies (Hartrees), Zero-Point Vibrational Energies (kcal/mol), and Free Energies (kcal/mol) for 4-Iodoniacyclopentene (3), *s-trans*-2-Vinyliodoniacyclopropane (4), *s-cis*-2-Vinyliodoniacyclopropane (5), and the Transition States for the Interconversion between 4 and 5 (TS1) and between 5 and 3 (TS2)[a]

species	MP2/DZV(d,p)	MP4SDTQ/DZV(d,p)	CISD+Q/DZV(d,p)	CCSD/DZV(d,p)	MP2/TZV(2df)	ZPE	ΔG^b
3	−7068.331442	−7068.403726	−7068.382296	−7068.376852	−166.623770	56.3	37.1
4	−7068.322488	−7068.395609	−7068.372772	−7068.367814	−166.614967	55.8	35.5
5	−7068.317318	−7068.390643	−7068.367624	−7068.362572	−166.610303	55.8	35.5
TS1	−7068.306642	−7068.380081	−7068.357486	−7068.352431	−166.599676	55.2	35.6
TS2	−7068.290476	−7068.365176	−7068.342486	−7068.338143	−166.579005	55.2	35.3

[a] All calculations at the MP2/DZV(d,p)-optimized geometries. [b] Thermochemical analysis for $T = 298$ K.

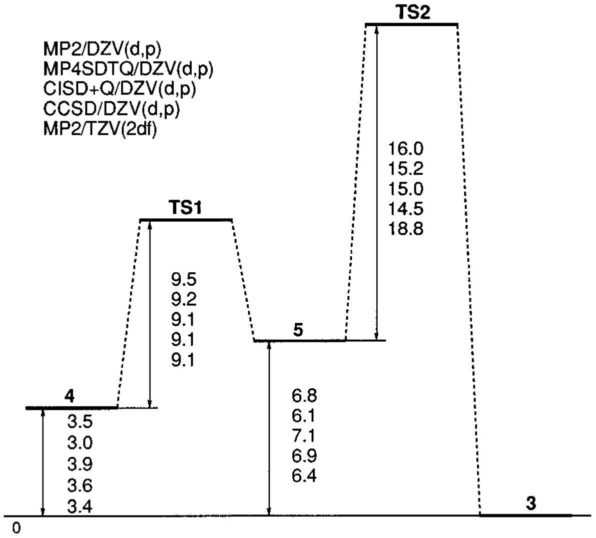

Figure 2. Relative energies (kcal mol^{-1}) of $C_4H_6I^+$ isomers (see Figure 1), including free energies and ZPE corrections. All calculations at the MP2/DZV(d,p)-optimized geometries.

$C_4H_6I^+$ isomers. We have carried out an exploratory study with a continuum solvation model,[24] as implemented in Gaussian94,[7] but, unfortunately, we obtained inconsistent results. However, taking into account the calculated dipole moments (2.3, 6.1, 5.3, 3.9, and 7.1 debyes for **3**, **4**, **5**, **TS1**, and **TS2**, respectively), it can be deduced that an increase in solvent polarity should stabilize **4** more than **3** while in a nonpolar solvent **3** should remain as the global minimum.

In summary, the addition of electrophilic iodine to the most stable *s-trans*-butadiene may occur with the initial formation of **4**. Direct nucleophilic attack on **4** would give the 1,2-product, while the 1,4-product with trans configuration could be formed by attack at the 4 position (S_N2'-type mechanism), favored by π conjugation from the vinyl group. The barriers for the interconversion between **4** and **3** (through **5**) are high and, thus, equilibration to the more stable 4-iodoniacyclopentene (**3**) is prevented and the 1,4-products with cis configuration have not been observed experimentally.[5] However, because **3** is the global minimum, the existence of 4-iodoniacyclopentene still remains open. These results should encourage experimentalists to search for this species by an alternative method. In this sense, Table 2 shows the calculated vibrational frequencies (scaled by 0.94)[23a] and IR intensities for **3**.

Table 2. Calculated [MP2/DZV(d,p)] Vibrational Frequencies (cm^{-1}, scaled by 0.94) and IR Intensities (km mol^{-1}) for 4-Iodoniacyclopentene (3)

ν	inten	ν	inten	ν	inten
3044	21.9	1291	17.6	862	0.0
3035	13.7	1220	13.2	830	4.5
3034	0.0	1184	13.1	746	9.9
3029	8.6	1110	0.9	643	55.3
2963	0.1	1082	8.0	567	20.0
2962	3.2	1069	0.0	439	9.7
1616	10.2	946	5.3	319	0.0
1413	9.6	889	1.9	305	3.1
1410	5.5	876	0.0	112	3.5

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(24) Cramer, C. J.; Truhlar, D. G. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York; Vol. 6, 1995.