

L-Shaped Three-Center Two-Electron (C–C–C)⁺ Bonding Array

Naohiko Yoshikai, Salai Cheettu Ammal, and Eiichi Nakamura*

Contribution from the Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

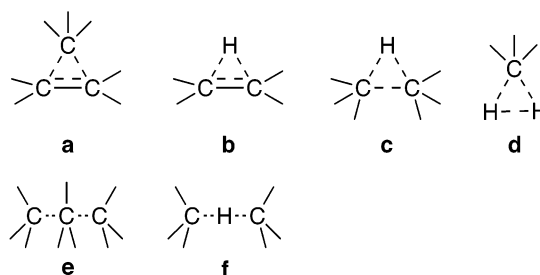
Received May 20, 2004; E-mail: nakamura@chem.s.u-tokyo.ac.jp

Abstract: The structures and reactivities of the complexes between carbenium ions (R⁺) and acetylene or propyne have been investigated with the aid of electron-correlated quantum mechanical calculations (hybrid density functional, perturbation theory, and coupled cluster methods). Depending on the R group, the acetylene/carbenium ion interaction can produce either an “open” 3c-2e structure or the conventional vinyl cation structure. The “open” 3c-2e C–C–C bonding geometry exists as a minimum for R = methyl and primary/secondary/tertiary alkyl, and hence is the most notable. The alignment of three carbon centers is neither bridged nor linear, but L-shaped, and represents a new type of “open” 3c-2e bonding that has so far escaped proper attention.

Bonding is a central subject in chemistry. In the chemistry of neutral hydrocarbons, two atoms share two electrons to form a bond. The case where three atoms share two electrons to form a three-atomic bonding array (3c-2e) is much less common, but occupies an important position in carbocation chemistry.¹ The geometry of such a 3c-2e bonding may be classified into two categories by the nature of the C–C (or C–H) bond involved in the bonding, “closed” and “open”. The “closed” 3c-2e bonding is found in a “bridged” cation where the geometry is triangular so that there is a bonding interaction among all three atoms (Chart 1, **a–d**). The “open” 3c-2e bonding is typically found in a “linear” array where there is no direct bonding interaction between the two terminal atoms (Chart 1, **e** and **f**).

The “bridged” structure is exemplified by a 2-norbornyl cation² (**a**), H-bridged ethyl cation³ (**b**), and protonated methane⁴ (**d**). The bonding in these species has been the subject of interest for a long time. On the other hand, the “open” structures are much less common: While the linear C–H–C 3c-2e bonding (**f**) can exist when the central proton is fixed by a rigid carbon framework,^{1,5} none of the “open” C–C–C array (**e**) has been known to date. The hypothetical symmetric arrays **e** and **f** do not exist as stable minima without any structural constraint.^{6,7} Ideally, both the bridged (**a–d**) and the linear (**e, f**) 3c-2e bonds

Chart 1



are symmetric. The three atomic centers of the bridged bond form an isosceles triangle, while the structure of the linear bonds is symmetric with respect to the central atom.

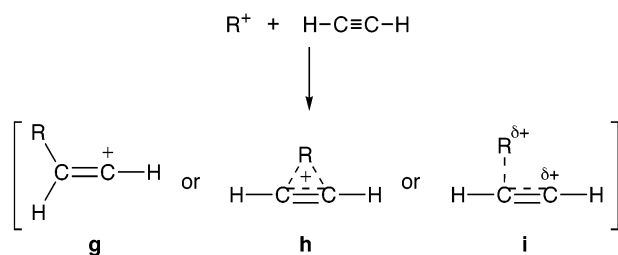
The bridged cations **a** and **b** can be illustrated as complexes of an olefin with a carbenium ion and a proton, respectively. The carbenium ion or the proton is positioned above the center of the C=C double bond to maximize the electrostatic interaction as well as the overlap of their vacant orbital and the C=C π orbital. Note that such a symmetric structure is one of the two extreme cases of olefin–cation complexes: It has been discussed that they often take structures that lie between the symmetric extreme and another extreme, that is, “classical” carbocation.⁸

How does acetylene interact with a carbenium ion or proton? The structure of a protonated acetylene C₂H₃⁺ has been extensively studied (Chart 2, R = H).⁹ The global minimum is a bridged 3c-2e structure **h** (R = H), which is more stable than

- (1) Saunders, M.; Jimenez-Vazquez, H. A. *Chem. Rev.* **1991**, *91*, 375. Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432. McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, *25*, 47.
- (2) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440. Schleyer, P. v. R.; Sieber, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *32*, 1606. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393.
- (3) Krishnan, R.; Whiteside, R. A.; Pople, J. A.; Scheleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.
- (4) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716. Müller, H.; Kutzelnigg, W.; Noga, J.; Klopner, W. *J. Chem. Phys.* **1997**, *106*, 1863. Schreiner, P. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3239.
- (5) Protonated ethane (C₂H₇⁺) may be represented as an intermediary structure between **c** and **f**: Carneiro, J. W. D.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F., III; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483. East, A. L. L.; Liu, Z. F.; McCague, C.; Cheng, K.; Tse, J. S. *J. Phys. Chem. A* **1998**, *102*, 10903.

- (6) When optimized at the B3LYP/6-311G(d,p) level with symmetry assumption, structures **e** and **f** (substituents: hydrogen) have three and two imaginary frequencies, respectively.
- (7) Theoretical prediction of stable, linear 5c-4e C---H---C---H---C bonding array with structural constraint: Tantillo, D. J.; Hoffmann, R. *J. Am. Chem. Soc.* **2003**, *125*, 4042.
- (8) Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875.

Chart 2



the primary vinyl cation structure **g** ($R = H$) by ~ 4 kcal/mol at the correlated level of calculation (experiment: 6 kcal/mol).¹⁰ The corresponding carbenium ion ($R = \text{alkyl}$) complex has not been studied systematically in depth. Earlier (Hartree–Fock) studies reported that, for $R = \text{alkyl}$, a 3c-2e structure **h** is no longer a minimum and exists instead as what has been assigned as a primary vinyl cation (**g**).¹¹

We have been interested in this issue for some time and studied carefully, by electron-correlated quantum mechanical calculations, the interaction of acetylene with various carbenium ions.^{12–15} In this Article, we report that, depending on the R group, the acetylene/carbenium ion interaction can produce either an “open” 3c-2e structure **i**, or the conventional cation **g** (Chart 2). The structure **i** exists as a minimum for $R = \text{methyl}$ and primary/secondary/tertiary alkyl. It is neither bridged nor linear, but L-shaped, and represents a new type of “open” 3c-2e bonding that has so far escaped proper attention. While 1,2-dimethyl-2-norbornyl cation and a related compound have been known to take a similar L-shaped framework,¹⁶ it is notable that such an open 3c-2e structure exists as a minimum on the potential surface of such a simple system without any structural constraints. The conventional vinyl cation structure **g** results when $R = CF_3$, a highly electron-withdrawing group. Interaction with phenyl cation gives a symmetric structure like **h**, where the triangular moiety is a spirocyclopropenyl structure rather than a 3c-2e system. When $R = \text{vinyl}$, a geometry intermediary between **h** and **i** results.

Computational Details

All calculations were performed with Gaussian 98 and 03 packages.¹⁷ Three electron-correlated methods were employed for geometry optimization: the density functional theory (DFT) method using B3LYP hybrid functional,¹⁸ the Møller–Plesset (MP) perturbation theory with single, double, and quadruple substitutions (MP4(SDQ)),¹⁹ and the coupled cluster method using single and double substitutions (CCSD).²⁰

- (9) Lindh, R.; Rice, J. E.; Lee, T. J. *J. Chem. Phys.* **1991**, *94*, 8008. Klopner, W.; Kutzelnigg, W. *J. Phys. Chem.* **1990**, *94*, 5625. Liang, C.; Hamilton, T. P.; Schaefer, H. F., III *J. Chem. Phys.* **1990**, *92*, 3653.
- (10) Crofton, M. W.; Jagod, M. F.; Rehffuss, B. D.; Oka, T. *J. Chem. Phys.* **1989**, *91*, 5139.
- (11) Apeloig, Y.; Müller, T. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley & Sons: New York, 1997.
- (12) Some of the carbocation species described here were previously studied at electron-correlated levels such as MP2 and B3LYP: see refs 13–15.
- (13) $R = \text{methyl}$: López, R.; Sordo, J. A.; Sordo, T. L.; Schleyer, P. v. R. *J. Comput. Chem.* **1996**, *17*, 905.
- (14) $R = \text{vinyl}$: Cunje, A.; Rodriguez, C. F.; Lien, M. H.; Hopkinson, A. C. *J. Org. Chem.* **1996**, *61*, 5212.
- (15) $R = \text{phenyl}$: (a) Rappoport, Z.; Kobayashi, S.; Stanger, A.; Boese, R. *J. Org. Chem.* **1999**, *64*, 4370. (b) Gronheid, R.; Zuilhof, H.; Hellings, M. G.; Cornelisse, J.; Lodder, G. *J. Org. Chem.* **2003**, *68*, 3205.
- (16) (a) Olah, G. A.; Demember, J. R.; Lui, C. Y.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 1442. (b) Saunders, M.; Telekowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (c) Myhre, P. C.; McLauren, K. L.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 5294. (d) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560. (e) Muchall, H. M.; Werstuijk, N. H. *J. Phys. Chem. A* **1999**, *103*, 6599.

For comparison, we also used Hartree–Fock (HF) calculations that tend to converge on the two-center two-electron bonding, familiar to organic chemists. The HF structures are denoted as **1a'**, **1b'**, etc., because they may differ very much from the electron-correlated structures (**1a**, **1b**, etc.) For all calculations, the 6-311G(d,p) basis set was employed,²¹ and the results were always compared with those obtained with a smaller basis set 6-31G(d), which generally gave similar structures.²² No symmetry assumption was made unless otherwise noted. The B3LYP and the HF stationary points were characterized by normal-mode analysis. Stationary points of the MP4(SDQ) and CCSD calculations were characterized by eigenvalues of Hessian matrices. The Boys localization procedure²³ was performed to obtain localized Kohn–Sham orbitals.²⁴ Natural population analysis and natural bond orbital (NBO) analysis²⁵ were performed at the same level as the one used for geometry optimization. All charge distribution analyses discussed in this Article are made on the basis of the natural population analysis. Natural resonance theory (NRT) analysis was performed to obtain a resonance picture of the studied systems.²⁶ Bond critical points were obtained by the atoms in molecules (AIM) method.²⁷

Results and Discussion

When a carbenium ion R^+ is allowed to approach either to the C^1 atom or to the center of an acetylene molecule, an addition complex **1** is formed, which was optimized at the

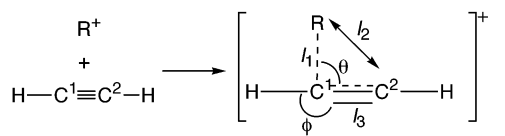
- (17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (18) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (19) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.
- (20) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 7382. Scuseria, G. E.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, *90*, 3700.
- (21) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- (22) The smallest case (**1a**) was optimized at higher levels (CCSD/cc-pVTZ and CCSD(T)/6-311G(d,p)) to obtain very similar structures. Geometries are given in the Supporting Information.
- (23) (a) Boys, S. F. In *Quantum Theory of Atoms, Molecules, and the Solid State*; Lowdin, P. O., Ed.; Academic Press: New York, 1968; pp 253–262. (b) Haddon, R. C.; Williams, G. R. *J. Chem. Phys. Lett.* **1976**, *42*, 453.
- (24) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
- (25) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 3.1*; University of Wisconsin: Madison, WI, 1990.
- (26) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593. Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610. Glendening, E. D.; Badenhop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628. Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; University of Wisconsin: Madison, WI, 1996.
- (27) Bader, R. F. *Atoms in Molecules – A Quantum Theory*; Oxford University Press: Oxford, 1990.

Table 1. Structural Parameters (Bond Lengths in Å and Bond Angles in deg) of Acetylene/Carbenium Ion Complexes **1a–g**

R	method	<i>l</i> ₁	<i>l</i> ₂	<i>l</i> ₃	θ	φ
Me (1a)	B3LYP	1.611	2.061	1.242	91.6	145.7
	MP4(SDQ)	1.639	1.976	1.244	85.4	152.0
	CCSD	1.634	1.993	1.246	86.5	150.9
	HF	1.521	2.530	1.260	130.7	109.7
Et (1b)	B3LYP	1.647	2.106	1.238	92.6	146.8
	MP4(SDQ)	1.664	2.005	1.241	86.0	153.1
	CCSD	1.659	2.016	1.243	86.8	152.1
	HF	1.541	2.509	1.259	127.0	113.7
<i>i</i> -Pr (1c)	B3LYP	1.690	2.199	1.235	96.2	146.4
	MP4(SDQ)	1.685	2.065	1.240	88.4	152.6
	CCSD	1.680	2.073	1.241	89.1	151.7
	HF	1.565	2.479	1.256	122.6	118.4
<i>t</i> -Bu (1d)	B3LYP ^a	3.096	3.122	1.202	80.0	176.2
	MP4(SDQ)	1.777	2.282	1.235	96.8	150.1
	CCSD ^b					
	HF	1.570	2.532	1.257	126.8	114.7
CF ₃ (1e)	B3LYP	1.626	2.522	1.252	121.9	124.6
	MP4(SDQ)	1.589	2.520	1.267	123.5	120.1
	CCSD	1.591	2.518	1.268	123.1	120.9
	HF	1.556	2.488	1.259	123.8	117.3
Ph (1f)	B3LYP	1.616	1.616	1.252	67.2	161.0
	MP4(SDQ)	1.612	1.612	1.261	67.0	161.3
	CCSD	1.614	1.614	1.260	67.0	161.5
	HF	1.598	1.598	1.237	67.2	160.5
CH=CH ₂ (1g)	B3LYP	1.571	1.760	1.249	76.3	153.5
	MP4(SDQ)	1.590	1.735	1.254	74.2	156.3
	CCSD	1.598	1.726	1.253	73.4	157.5
	HF	1.595	1.701	1.229	72.8	158.1

^a The structure depended on the basis set used. See ref 28. ^b Not calculated.

B3LYP, MP4(SDQ), and CCSD levels as well as at the HF level. The cationic carbon atom of the R⁺ cation is denoted by “C^R” in the following discussion. We studied methyl (Me), ethyl (Et), *i*-propyl (*i*-Pr), *tert*-butyl (*t*-Bu), CF₃, phenyl, and vinyl groups as the R group (**1a–g**). All three correlated methods gave essentially the same structure,²⁸ but the HF calculations afforded totally different structures in some cases. Table 1 summarizes the structural parameters of these complexes at all theoretical levels examined.



1
R = Me (**a**), Et (**b**), *i*-Pr (**c**), *t*-Bu (**d**)
CF₃ (**e**), Ph (**f**), CH=CH₂ (**g**)

Complexes with Alkyl (Me, Et, *i*-Pr, and *t*-Bu) Cations.

The cases where R = Me, Et, *i*-Pr, and *t*-Bu groups are discussed first. The structures of the MP4(SDQ)-optimized complexes (**1a–d**) and the HF-optimized complexes (**1a'–d'**) are shown in Figure 1. Inspection of Figure 1 immediately makes it apparent that the MP4(SDQ) structures, which are essentially the same as the CCSD structure (Table 1), are very different from the HF structures, indicating the necessity of electron-correlation in the description of these structures. The (theoretically insufficient) HF calculations indicate that the R group and the C¹ atom are fully bonded to make the C¹ atom trigonal, sp²-hybridized while the C² atom remains to be digonal, sp-hybridized. This structural feature as combined with the positive

C²H charge of ca. +0.7 (and the NBO and NRT analyses described later) indicate that the HF structure conforms to the formalism of **g** (Chart 2), a primary vinyl cation.

On the other hand, the structures obtained by the correlated calculations are characterized by several unique structural properties: First, the unusual C²–C¹–C^R angle of ca. 90° is incompatible with the conventional vinyl cation structure **g**. Second, the C¹–C^R bond length is short enough to consider that it is a C–C σ-bond, that is, only ca. 8% longer (except for **1d** (R = *t*-Bu), 13% longer) than the true C¹–C^R σ-bond found in the corresponding HF structure. Third, the C²–C^R distance is about 2 Å, too far to be considered as a bond: In addition, the linear HC¹C²H acetylene bonding is bent into a zigzag array (cf. Figure 1), whose geometry makes the bonding between C² and C^R very unlikely. The complexes **1a–d** are apparently not bridged cations **h** (Chart 2).

The above discussions based on structural features were further supported by electronic analyses at different levels. First, bond critical points (i.e., saddle points of electron density) of complexes **1a–c** were searched by the AIM method (indicated as **cp1** and **cp2** in Figure 2). It was found that critical points exist between C¹ and C² atoms (**cp1**), and C¹ and C^R atoms (**cp2**), but not between C² and C^R. Thus, it is clear that there is a bond between the C¹ and C^R atoms but not between the C² and C^R atoms. The C¹–**cp2** distance (0.87–0.91 Å) is longer than the C^R–**cp2** distance (0.77–0.78 Å) in all structures, which indicates that the C¹ atom takes more electrons in the C¹–C^R bond than the C^R atom (supported by the NBO analysis, see below).

NBO analysis of complexes **1a–c** was performed for both the MP4(SDQ) and the HF structures. The analysis was performed by using a primary vinyl cation representation as a reference Lewis structure. The results are summarized in Tables 2 and 3. The most striking difference of bonding in the MP4

(28) For **1d** (R = *t*-C₄H₉), the B3LYP calculation gave much different structures depending on the basis set used. For example, the *t*-C₄H₉ cation dissociated from the acetylene at the B3LYP/6-311G(d,p) level, but formed an L-shaped 3c-2e structure when the 6-31G(d) set was employed.

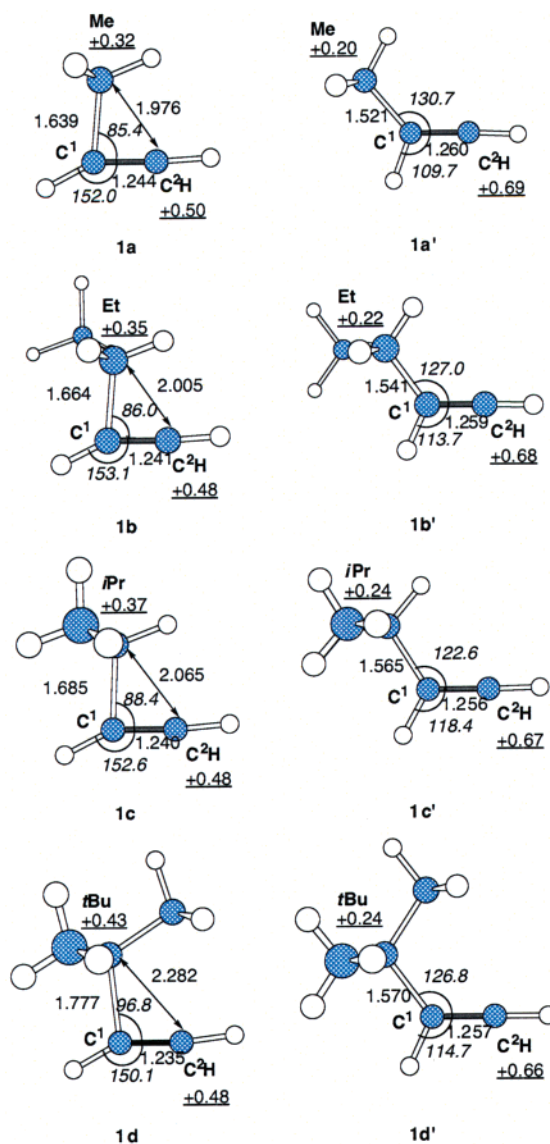


Figure 1. Structures of acetylene–alkyl cation complexes optimized at the MP4(SDQ)/6-311G(d,p) level (**1a–1d**, left) and at the HF/6-311G(d,p) level (**1a'–1d'**, right) (see the details of the structural parameters in Table 1). C¹, C², and C^R atoms are placed on the plane of the paper. Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.

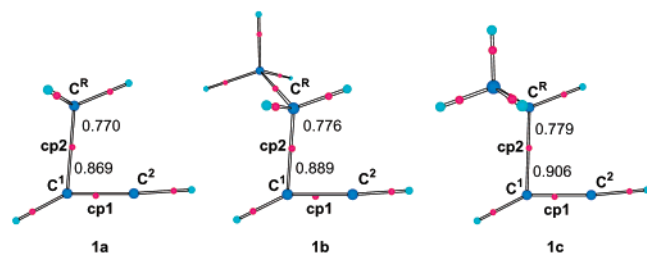


Figure 2. Structures of complexes **1a–c** optimized at the MP4(SDQ)/6-311G(d,p) level, together with the bond critical points (**cp1** and **cp2**) shown as pink dots) obtained by atoms in molecules (AIM) analysis. Distances (Å) between **cp2** and C¹, C^R atoms are shown.

and the HF structures was found in the C¹–C^R σ -bond orbital and C² p(π^*) orbital. While the C¹–C^R bond in the HF structure is almost fully occupied (occupancy larger than 1.9), the occupancy in the MP4 structure is smaller (<1.7). The occupancy of the C² p(π^*) orbital is much larger in the MP4

Table 2. Summary of NBO Analysis of Acetylene/Alkyl Cation Complexes **1a–c** at the MP4(SDQ)/6-311G(d,p) Level

compound	bond orbital	occupancy	orbital coefficients and hybrids
1a	C ¹ –C ^R	1.66	C ¹ : 0.721; s (22.5%), p (77.5%) C ^R : 0.693; s (24.8%), p (75.0%)
	C ¹ –C ² (σ)	1.96	C ¹ : 0.709; s (38.8%), p (61.0%) C ² : 0.706; s (49.3%), p (50.7%)
	C ¹ –H	1.93	C ¹ : 0.811; s (38.5%), p (61.5%) H: 0.586; s (100%)
	C ² –H	1.96	C ² : 0.803; s (48.3%), p (51.6%) H: 0.596; s (100%)
1b	C ² (p π^*)	0.45	s (2.2%), p (97.4%)
	C ¹ –C ^R	1.63	C ¹ : 0.726; s (22.5%), p (77.3%) C ^R : 0.688; s (20.7%), p (79.2%)
	C ¹ –C ² (σ)	1.96	C ¹ : 0.708; s (39.1%), p (60.7%) C ² : 0.706; s (49.4%), p (50.5%)
	C ¹ –H	1.93	C ¹ : 0.810; s (38.2%), p (61.8%) H: 0.587; s (100%)
1c	C ² (p π^*)	0.48	s (2.3%), p (97.4%)
	C ¹ –C ^R	1.61	C ¹ : 0.735; s (23.3%), p (76.5%) C ^R : 0.678; s (16.8%), p (83.0%)
	C ¹ –C ² (σ)	1.96	C ¹ : 0.708; s (39.0%), p (60.8%) C ² : 0.706; s (50.1%), p (49.8%)
	C ¹ –H	1.93	C ¹ : 0.809; s (37.5%), p (62.4%) H: 0.588; s (100%)
1c	C ² –H	1.96	C ² : 0.800; s (47.8%), p (52.1%) H: 0.600; s (100%)
	C ² (p π^*)	0.48	s (1.9%), p (97.8%)

Table 3. Summary of NBO Analysis of Acetylene/Alkyl Cation Complexes (Primary Vinyl Cations) **1a'–c'** at the HF/6-311G(d,p) Level

compound	bond orbital	occupancy	orbital coefficients and hybrids
1a'	C ¹ –C ^R	1.95	C ¹ : 0.753; s (37.9%), p (62.1%) C ^R : 0.658; s (25.6%), p (74.3%)
	C ¹ –C ² (σ)	2.00	C ¹ : 0.712; s (36.3%), p (63.6%) C ² : 0.702; s (51.9%), p (48.1%)
	C ¹ –H	1.90	C ¹ : 0.805; s (26.0%), p (73.9%) H: 0.594; s (100%)
	C ² –H	1.99	C ² : 0.796; s (48.0%), p (52.0%) H: 0.606; s (100%)
1b'	C ² (p π^*)	0.14	s (0.02%), p (99.7%)
	C ¹ –C ^R	1.93	C ¹ : 0.757; s (36.7%), p (63.3%) C ^R : 0.654; s (23.0%), p (76.9%)
	C ¹ –C ² (σ)	1.99	C ¹ : 0.711; s (36.0%), p (63.9%) C ² : 0.703; s (51.8%), p (48.1%)
	C ¹ –H	1.92	C ¹ : 0.805; s (27.4%), p (72.6%) H: 0.594; s (99.9%)
1c'	C ² –H	1.99	C ² : 0.795; s (47.8%), p (52.2%) H: 0.607; s (99.9%)
	C ² (p π^*)	0.14	s (0.0%), p (99.7%)
	C ¹ –C ^R	1.91	C ¹ : 0.761; s (35.3%), p (76.5%) C ^R : 0.678; s (16.8%), p (83.0%)
	C ¹ –C ² (σ)	1.99	C ¹ : 0.710; s (36.0%), p (64.7%) C ² : 0.704; s (52.3%), p (47.6%)
1c'	C ¹ –H	1.93	C ¹ : 0.805; s (28.9%), p (71.0%) H: 0.593; s (99.9%)
	C ² –H	1.99	C ² : 0.794; s (47.6%), p (52.4%) H: 0.608; s (99.9%)
	C ² (p π^*)	0.15	s (0.01%), p (99.7%)

structures (up to 0.5) than in the HF structures (~0.15). Thus, HF structures are best described as primary vinyl cations; that is, most of the original π -electrons of acetylene are used for the formation of the fully fledged C¹–C^R σ -bond upon reaction with the alkyl cations. On the other hand, in the MP4 structures, the hyperconjugation between the C¹–C^R σ -bond and cationic C² 2p-orbital is so strong that the former is no longer a simple σ -bond and the latter is no longer a simple cation.

Chart 3

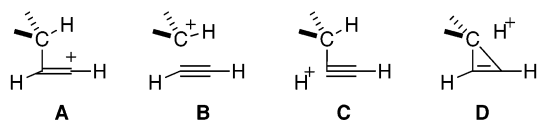


Table 4. Resonance Weight of Lewis Structures **A–D** in Acetylene/Alkyl Cation Complexes **1a–c** (**1a'–c'**) Obtained by NRT Analysis at the B3LYP Level and at the HF Level

entry	compound	resonance weight (%)			
		A	B	C	D
1	1a	75.2	13.3	2.8	3.9
2	1b	58.8	26.5	1.7	1.8
3	1c	54.7	29.1	2.2	1.9
4	1a'	89.1	2.2	4.8	0
5	1b'	86.9	3.0	4.2	0
6	1c'	84.0	4.1	3.7	0

The C² atom is sp-hybridized in both cases, judging from the hybridization of the C² atom in the C²–C¹ σ and C²–H σ orbitals (s:p ~50:50 in each bond). The hybridization of the C¹ atom in the C¹–H bond is much closer to sp in the MP4 structure (s:p ~40:60) than in the HF structure where the geometry does indicate the sp² hybridization (s:p < 30:70). The structural and electronic data indicate that the complexes **1a–c** are neither a simple vinyl cation **g** nor a bridged one **h**, but rather an “open” 3c-2e bonded structure **i** (Chart 2).

To facilitate understanding the nature of the bonding in **1a–c**, natural resonance theory (NRT) analysis was performed to express these molecules as a weighed combination of a series of resonance structures. There are two major Lewis structures for the description of the complexes. One is a classical primary vinyl cation (**A**), and the other is [acetylene + carbenium ion] (**B**) (Chart 3). The formalisms of a protonated, distorted R-substituted acetylene (**C**) and a corner-protonated cyclopropene (**D**) are also possible. The calculated resonance weights (%) of these Lewis structures are shown in Table 4.

The dominant contribution in **1a–c** is the vinyl cation representation (in particular for **1a**, 75.2%, entry 1). However, what must be noted is the cases of **1b** and **1c** (R = Et and *i*-Pr), where there is a significant contribution of the resonance structure **B** (> 25%), indicating that they are indeed “complexes” of R⁺ with acetylene. The contribution of **B** increases significantly as R⁺ becomes more stable, that is, *i*-propyl. With this criterion, too, the L-shaped C^R–C¹–C² array is an “open” 3c-2e bonding. Note that there is little contribution (<4%) of a resonance structure **D** of protonated cyclopropene, a representation previously used to describe **1a**.²⁹

For comparison, the structures obtained by the HF calculations (**1a'–c'**) were also analyzed by NRT (Table 4, entries 4–6). The overwhelming contribution (84–89%) of the resonance structure **A** (as opposed to 2.2–4.1% contribution of **B**) fully supports the conventional vinyl cation (**g**) character of **1a'–c'** that has been suggested by their geometry (Figure 1).

Localized orbital analysis also supports the 3c-2e bonding (Figure 3). One can see the original π -electrons of the acetylene

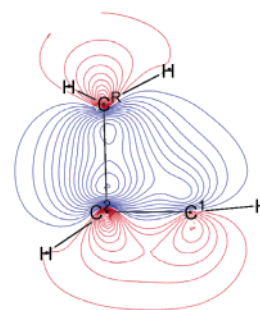
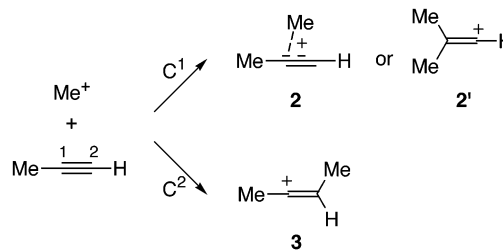


Figure 3. Localized Kohn–Sham orbital of acetylene/Me⁺ complex **1a** at the B3LYP/6-311G(d,p) level.

Scheme 1. Complexation of Propyne with Methyl Cation



are localized along with the L-shaped σ – π framework. The C¹–C^R bond, which, by the first approximation, possesses only one electron due to the C¹ 2p orbital, borrows a part of the π -electrons from the acetylene to form a partial σ -bond (~0.7 electron, vide supra).

Above studies showed that the acetylene/alkyl cation system prefers the L-shaped 3c-2e structure **i** to the conventional vinyl cation **g** because of strong hyperconjugation between the C¹–C^R σ -bond with the cationic C² 2p orbital. This effect cannot be adequately evaluated by the HF calculation.

Why does not the system take the bridged structure **h** like the protonated acetylene (R = H)? One problem is the directionality of the carbon p orbital. While a proton composed of an isotropic 1s orbital can bridge between two acetylenic carbon atoms, the directionality of the alkyl cation p-orbital make the C^{R+} atom form a σ -bond with only one of the two acetylenic carbon atoms. Another related problem is the ring strain of the bridged cyclopropene structure **h**.

To gain further insight into the nature of the 3c-2e bonding in compound **1**, we also examined complexation of methyl cation with propyne (Scheme 1, Figure 4). While complexation with the terminal carbon atom (C²) invariably gave a secondary vinyl cation **3** independent of theoretical methods, complexation with the internal carbon atom (C¹) gave different structures (**2** and **2'**) with the MP4(SDQ) and the HF calculations as in the previous cases. The HF-optimized structure **2'** is a quasi-C_{2v} symmetrical, conventional primary vinyl cation: Here, we may call for equal participation of the two C¹–Me bonds in hyperconjugative interaction with the vacant 2p orbital of the C² atom. The MP4(SDQ)-optimized structure **2**, on the other hand, was completely unsymmetrical, forming the 3c-2e bonding. The linearity of the Me–C¹–C²H in propyne is roughly retained (bond angle: 161.8°) because of the hyperconjugation of only one Me–C¹ σ -bond with the C² 2p orbital.

Complex with Trifluoromethyl Cation. While complexation of acetylene with alkyl cations gave L-shaped 3c-2e structures,

(29) Some time ago, Sordo et al. reported the structure of methyl complex **1a** optimized at the MP2/6-31G(d,p) level, and they denoted it as a “corner-protonated cyclopropene” (ref 13). However, the present analysis clearly shows that such a notation is not adequate.

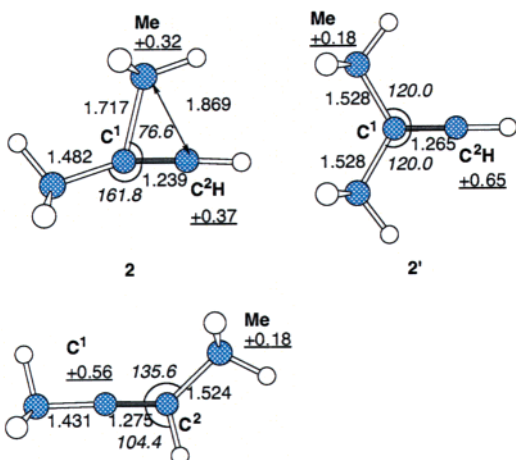


Figure 4. Structures of propyne/methyl cation complexes **2** and **2'** optimized at the MP4(SDQ)/6-311G(d,p) level and **2'** optimized at the HF/6-311G(d,p) level. Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.

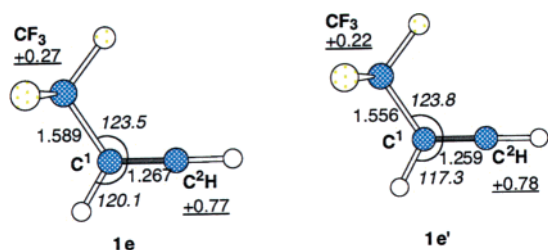


Figure 5. Structures of acetylene/CF₃⁺ complexes (**1e** and **1e'**) optimized at the MP4(SDQ)/6-311G(d,p) level and HF/6-311G(d,p) level, respectively. Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.

complexation with trifluoromethyl cation (CF₃⁺) gave a different result. Structure optimization with the correlated methods gave structures essentially the same as the HF structure (Table 1),³⁰ where the C¹ atom is trigonal and the C² atom is digonal (Figure 5). The positive charge was localized at the digonal center C²H (ca. +0.8). Overall, the structure conforms to the formalism of **g**, a primary vinyl cation. NBO and NRT analyses also supported this picture: The occupancy of the C¹-C^R σ -orbital (~ 1.9) as well as the contribution of the vinyl cation resonance structure (80–90%) are much larger than in the case of the alkyl counterparts (vide supra). The electron-withdrawing CF₃ group “monopolizes” the original π -electrons of acetylene to form a strong C¹-C^R σ -bond, leaving C² as a true cation.

Complexes with Phenyl and Vinyl Cations. Next, we examined complexation of acetylene with phenyl and vinyl cations (Figure 6). Both correlated and noncorrelated methods gave essentially same results for the acetylene/phenyl cation complex (**1f** and **1f'**, optimized under C_s symmetry with respect to the C^R-C¹-C² plane), which shows features of a vinylnebenzenium ion. This is because the cationic charge is delocalized in the phenyl part to a large extent (+0.49). While the HF calculation gave a primary vinyl cation structure as a stationary point, it was not a minimum at the correlated levels.^{15b} Being similar to Cram’s phenonium ion (i.e., complex between ethylene and phenyl cation), the C^R atom is sp³-hybridized and therefore **1f** is not a 3c-2e bonding system.⁸ In fact, NRT

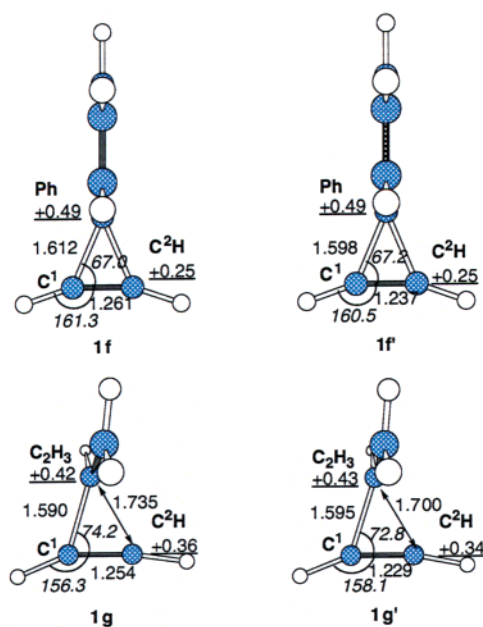
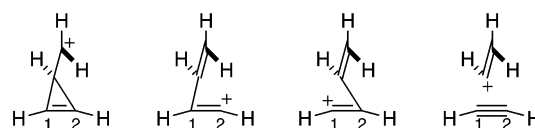


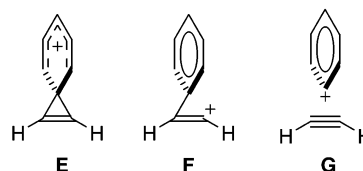
Figure 6. Structures of acetylene/phenyl and vinyl cation complexes optimized at the MP4(SDQ)/6-311G(d,p) level (**1f,g**, left) and at the HF/6-311G(d,p) level (**1f',g'**, right). Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.



	H	I	J	K
B3LYP	31.4	30.8	14.7	10.3
HF	27.6	30.6	13.3	14.9

Figure 7. Resonance weight of Lewis structures **H–K** in the acetylene/vinyl cation complex **1g** (**g'**) obtained from NRT analysis.

Chart 4

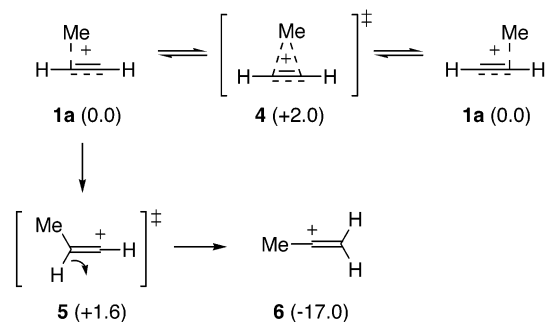


analysis carried out previously by Rappoport and Stanger showed that the resonance structure **E** makes a much greater contribution ($\sim 60\%$) than others such as **F** ($< 20\%$) and **G** (Chart 4).^{15a}

When R is vinyl (**1g**), the structure is halfway between **1a** (R = Me) and **1f** (R = Ph). Being the same as for **1f**, the correlated and the HF calculations gave similar results. The NBO analysis showed that the vacant p-orbital of the C² atom interacts with the C¹-C^R σ -orbital as well as the vinyl π -orbital while C¹ and C^R are σ -bonded.

One can consider four major resonance structures for complex **1g** shown in Figure 7. The resonance structure **H** contributes to the cyclopropene character of the C^R-C¹-C² triangle, and the rest (**I–K**) can be assigned to the unsymmetrical 3c-2e bonding. All four structures have significant contributions. Judging from the resonance weights of **H–K**, one can conclude that **1g** lies electronically between **1a** (3c-2e, **I** and

(30) For HF-optimized structures of C₃H₂F₃⁺ cations: McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Cszizmadia, I. G. *J. Org. Chem.* **1991**, *56*, 575.

Scheme 2. Rearrangement Pathways for **1a**^a

^a Energies relative to **1a** (kcal/mol, MP4(SDQ)/6-311G(d,p)) are shown in parentheses.

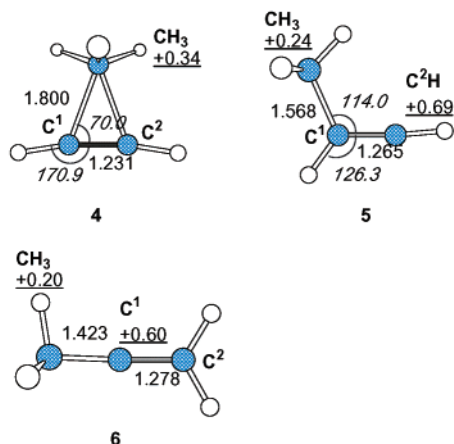
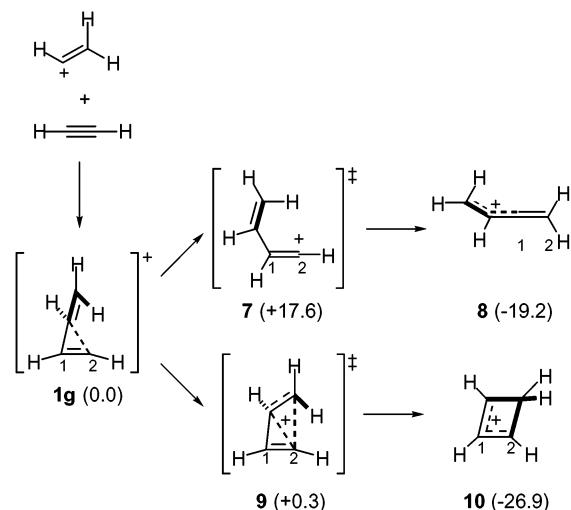


Figure 8. Structures of stationary points along with rearrangement pathways of **1a** optimized at the MP4(SDQ)/6-311G(d,p) level. Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.

K) and **1f** (cyclopropene, **H**), but it has more of the 3c-2e character.

Rearrangement of Acetylene/Cation Complexes. Finally, we describe the stability and reactivity of acetylene/carbenium ion complexes. Expectedly, the methyl complex **1a** is labile and easily rearranges (Scheme 2 and Figure 8). It undergoes 1,2-methyl group migration through a transition state (TS) **4** with only 2 kcal/mol of activation energy.³¹ In TS **4**, the methyl group is symmetrically bridged between the C¹ and C² atoms. 1,2-Hydrogen migration takes place with a small activation energy (1.6 kcal/mol) to give a much more stable secondary propenyl cation (17 kcal/mol more stable). It is interesting that the TS of the hydrogen migration (**5**) looks like a classical primary vinyl cation, where the C¹ and C² atoms are trigonal and digonal and considerable positive charge (+0.69) is localized at the C²H moiety.

Rearrangement reactions of the vinyl complex **1g** were also examined (Scheme 3 and Figure 9).³² The 1,2-hydrogen migration requires much larger activation energy (17.6 kcal/mol) than **1a**, because the complex is thermodynamically much more stable due to the bridging interaction of the vinyl carbon

Scheme 3. Rearrangement Pathways for **1g**^a

^a Energies relative to **1g** (kcal/mol, MP4(SDQ)/6-311G(d,p)) are shown in parentheses.

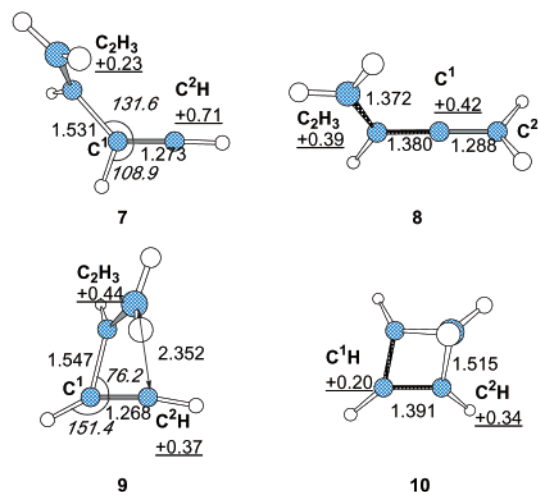


Figure 9. Structures of stationary points along with rearrangement pathways of **1g** optimized at the MP4(SDQ)/6-311G(d,p) level. Bond lengths (Å), bond angles (deg), and natural charges are shown in roman, italics, and underlined, respectively.

(vide supra). The α -vinylvinyl cation product **8** is very stable (by -19.2 kcal/mol) because of the conjugative stabilization of the positive charge.

There is another rearrangement pathway, cyclization to a 2-cyclobutenyl cation **10**. This occurs with a very small barrier (0.3 kcal/mol) via TS **9**, and the resulting cyclobutenyl cation **10** is much more stable than **8** by 7.7 kcal/mol. It is interesting to note that the overall process from the vinyl cation to the cyclobutenyl cation **10** represents a [2 + 2] cycloaddition sequence, a synthetic possibility neglected thus far.

In summary, interaction of a carbenium ion (alkyl or vinyl) with acetylene or propyne forms an L-shaped, “open” 3c-2e C–C–C bonded structure. These intriguing systems have so far remained unnoticed despite extensive investigations about closely related cases.³³ The present studies will provide ideas to experimentalists who are aiming at the observation of primary vinyl cations,³⁴ or designing new synthetic organic reactions.

(31) The barriers for the 1,2-alkyl migration are 1.1, 6.4, 0.4 kcal/mol for **1b**, **1c** (at the MP4(SDQ)/6-311G(d,p) level), and **1d** (at the MP2/6-311G(d,p) level), respectively. For R = CF₃, the symmetrically bridged structure was not a transition state, but a minimum (+8.1 kcal/mol higher than **1e**). Geometries are given in the Supporting Information.

(32) Rearrangement pathways described here are included in a previous study on the potential surface of C₂H₅⁺ at the MP2/6-31G(d,p) level (ref 14), and the results are essentially the same.

(33) van Alem, K.; Lodder, G.; Zuilhof, H. J. *Phys. Chem. A* **2000**, *104*, 2780.

(34) Okuyama, T. *Acc. Chem. Res.* **2002**, *35*, 12.

Given the possibility of a [2 + 2] cycloaddition between acetylene and a vinyl cation, one would suspect that such a 3c-2e species might be able to play some roles in synthetically useful reactions.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science, and Technology for financial support, a Grant-in-Aid for Specially Promoted Research, and the 21st Century COE Program for Frontiers in Fundamental Chemistry. A generous allotment of computational time from the Research

Center of Computational Science, Okazaki National Research Institute and Intelligent Modeling Laboratory, The University of Tokyo, is gratefully acknowledged.

Supporting Information Available: Energies and Cartesian coordinates of stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0470416