Pergamon

Tetrahedron Letters 40 (1999) 3503–3506

TETRAHEDRON LETTERS

Reinvestigation of σ-Allyl Cations: High Level Ab Initio Quantum Mechanical Predictions

Kim K. Baldridge, [1a] James Leahy, [1b] and Jay S. Siegel[1c]

San Diego Supercomputer Center, P.O. Box 85608, San Diego, CA 92186-9784. Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720 Department of Chemistry, University of California, San Diego, La Jolla, CA 92093-0358.

Received 8 February 1999; accepted 26 February 1999

Abstract: The question of stability of sigma-delocalized allyl cations is reinvestigated by hybrid HF-DFT quantum mechanical calculations. These computations predict that the existing molecular proposals, for such effects, are not symmetrically delocalized systems.

The three-center-two-electron bonding associated with the allyl cation can be depicted in two extreme orientations:[2-4] the common π-allyl cation, constructed from an olefin and a parallel empty p orbital;[5] and what has been called a σ-allyl cation, constructed from a carbon-carbon sigma bond and a colinear empty p orbital (Figure 1).[2] The latter arrangement of three p orbitals has never been realized experimentally, but a candidate structure, a capped triquinane **1**, has been postulated.[6-8] It was anticipated that a σ arrangement of p orbitals could delocalize similarly to the π-allyl cation, and thus display a new type of non-classical cation.[2] Such a structure could be envisioned as a reactive intermediate in an S_E2 process,[9] or during the protonation of a hydrocarbon in super acidic media.[10,11] Given the strength of the carbon-carbon sigma bond, one might question whether a compensating gain of cation stability could be strong enough to induce a fully delocalized structure. Prior to synthesis, computational methods should be able to shed some light on the structure and energetics of such species. Unfortunately, early studies took place at a time when only constrained geometry optimizations could be done and only on model systems such as **2** (C_3H_9+).[2] After close to 20 years this fundamental question remains unanswered by any means. Herein we revisit this question through the ab initio quantum mechanical prediction of the structure and energetics of **1**, **2** (C_3H_9+), and **3** (Figure 2).

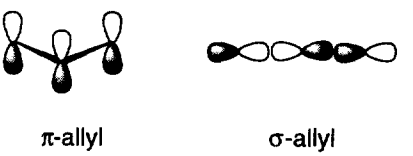

Figure 1. Two depictions of the allyl system.

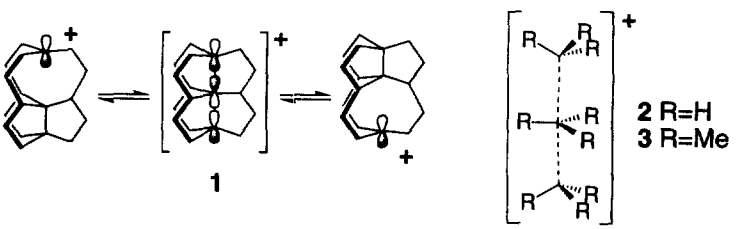

Figure 2. Proposed σ-allyl delocalized systems, **1**, **2**, and **3**.

PII: S0040-4039(99)00542-0

Simple orbital diagrams give a qualitative picture for the symmetric form of the σ-allyl cation (Figure 3).[12] The balance between how much bond strength is lost and how much cation stabilization is gained will determine if the potential energy along the sigma coordinate is single or doubled-welled.

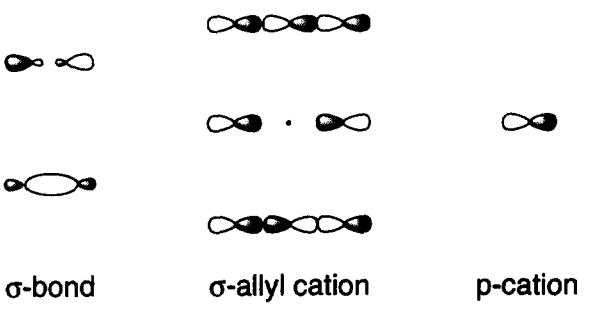

Figure 3. Orbital correlation diagram for the σ-allyl complex

Structural computations of the series **1-3** were performed at the restricted Hartree-Fock (RHF) level of theory using the analytically determined gradients and search algorithms within GAMESS.[13] Additional hybrid density functional methods[14] (HDFT; a known improvement over DFT methods via inclusion of the exact Hartree-Fock exchange based on Kohn-Sham orbitals) were performed using GUASSIAN94[15] to uncover effects of dynamic correlation. More extensive comparison was done on **3** to determine the effects of basis set and correlation. The HDFT methods included Becke's 3 parameter functional[16] in combination with nonlocal correlation provided by Perdew 91 expression,[17] B3PW91. The DZV(2d,p) basis set[18] was employed with the RHF computations, and Dunning's correlation consistent basis sets, cc-pvdz and aug-cc-pvdz[19] were used with the HDFT methods. The former basis set is a [3s2p1d] contraction of a (9s4p1d) primitive set, and the latter is a [4s3p2d] contraction of a (10s5p2d) primitive set.

Computations performed on **1-3** showed convergent properties at b3pw91/cc-pvdz (Figure 4 and Table 1). Starting from a C_{3v} linear structure, **2a** optimizes to a D_{3h} symmetric stationary point (**2b**) which is not a minimum, but has two symmetry-related off-axis negative eigenvalues in its normal mode profile. Following either of these modes leads to stationary point (**2c**), with C_s symmetry and one negative eigenvalue. Continuing down this negative mode leads one finally to a minimum energy structure (**2d**) of C_1 symmetry that can be chemically interpreted as a carbon-hydrogen bond of methane coordinating to ethyl cation.[2,20,21] For **3** the symmetric linear form (**3b**, C_{3h}) is also not a minimum, but this time there is only a single negative mode and it lies along the sigma axis. Following this mode leads to a chiral C_3 symmetric minimum structure (**3a**), that can be chemically interpreted as a t-butyl cation loosely associated with the back end of the central bond in hexamethylethane (C(cat) to C(sp^3) = 5.07Å and C-C = 1.59Å in **3a**). Thus, neither **2** nor **3** can be viewed as an observable symmetric σ-allyl complex. Restricting the analysis to the sigma coordinate, however, one sees that **2** prefers

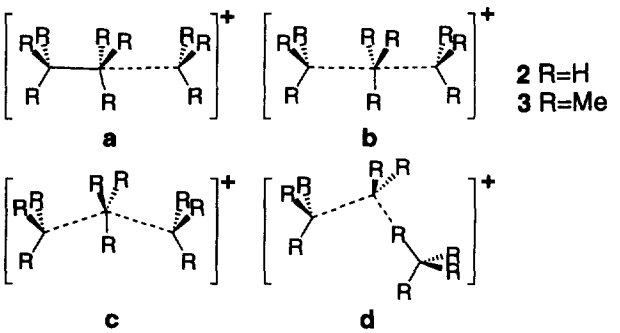

Figure 4. Cationic conformations **a-d**.

to be delocalized whereas **3** does not. This preference can be rationalized by the methyl cation's great instability in the isolated state and unencumbered ability to associate vs the tertiary cations relatively stable character and steric bulk that inhibits intermolecular interaction.[2,20,21]

Table 1. Computational Data on **1**, **2**, and **3** (b3pw91/cc-pvdz)*.

Compound	Symmetry	Character*	R(C-C)	R(C-C to C$^+$)	Relative Energy
1a	C_3	0	1.566	2.989	0.0
1b	C_{3h}	1	2.250	2.250	14.1
2a**	C_{3v}	****	****	****	****
2b**	D_{3h}	2	1.728	1.728	21.6 (20.8)**
2c**	C_s	1	1.664		11.0 (10.7)**
2d**	C_1	0	1.323***	1.484***	0.0 (0.0)**
3a	C_3	0	1.586	5.072	0.0
3b	C_{3h}	1	2.729	2.729	53.1

*Number of negative eigenvalues in the hessian. ** Values in this case differ from those using b3pw91/aug-cc-pvdz by no more than .002 Å, and 0.8 kcal/mol for the relative energies. *** This structure is methane coordinated to ethyl cation. **** Not a stationary point; optimizes to D_{3h} structure.

To overcome the linear instabilities of **2a** and the steric repulsion in **3b**, **1** was designed and set as a target.[2,6] The C_{3h} symmetric form (**1b**) like **3b** optimized to a stationary point with one negative eigenvalue along the sigma axis. Following this mode resulted in a minimum energy structure of C_3 symmetry (**1a**). This structure could be chemically interpreted as a cation-capped triquinane with an intact central carbon-carbon bond of the triquinane (1.566 Å) and a proximal but not-strongly-interacting tertiary cation (C(cation) to C-C bond = 3.0 Å). Thus, from a structural point of view, neither the model nor the designed structures, proposed to display delocalized σ-allyl character, would actually do so.

Looking at the energetics along the sigma coordinate for systems **1** and **3** sheds some additional light on the problem (cf. Table 1). Both are double-welled potentials. In the case of **3**, the delocalized **3b** is predicted to lie as much as 53.1 kcal/mol higher than localized **3a**. In contrast for **1**, **1b** is predicted to be 14.1 kcal/mol higher than **1a**. Thus, on energetic grounds, one can say that **1** comes a long way toward the desired effect, and would have met one of Paquette's criteria: that ionization of a resolved C_3 ion-precursor would racemize quickly by an S_E2 process.[6] From another perspective, **1** would have a dynamic symmetry such that it would appear to have C_{3h} symmetry in the NMR at or slightly above room temperature. Thus, this study claims that the existing targets (for example, **1**) will not fulfill the promise of symmetric σ-allyl interaction, but leaves open the possibility to speculate on potentially better designs. One should look to structures that combine the stabilization gained from interaction of a 1° or 2° carbocation with a σ-bond, with the preorganization in a roughly linear array that is found in **1**. We hope this work will provoke additional computational and/or experimental work[22] and further the discussion of fundamental orbital interactions.

ACKNOWLEDGMENTS: This work was funded by the US National Science Foundation (CHE-9628565; ASC-9212619). Part of this work was carried out in absentia from UCSD; KKB (Fulbright Scholar-Weizmann Institute of Science) and JSS (Meyerhoff Professor-Weizmann Institute of Science).

REFERENCES:

1. (a) SDSC; (b) UC-Berkeley; (c) UC-San Diego.
2. Lipkowitz, K. B.; Larter, R. M.; Boyd, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 85-92.
3. McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, *25*, 47-53.
4. Paquette, L. A. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 106-117.
5. Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *Nouv. J. Chim.* **1985**, *9*, 385-388.
6. Paquette, L. A.; Vazeux, M. *Tet. Lett.* **1981**, *22*, 291-294.
7. Kuck, D.; Paisdor, B.; Grützmacher, H.-F. *Chem. Ber.* **1987**, *120*, 589-595.
8. Alder, R. W. *Tetrahedron* **1990**, *46*, 683-713.
9. (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527-33. (b) Zabka, J.; Farnik, M.; Zdenek, D.; Polach, J.; Herman, Z. *J. Phys. Chem.* **1995**, *99*, 15595-15601.
10. Olah, G. A.; Farooq, O.; Prakash, G. K. S. *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley Interscience: New York, 1989, pp Ch. 11.
11. Olah, G. A.; Prakash, G. K. S. *Electrophilic Reactions on Alkanes*; Patai, S. and Rappaport, Z., Ed.; Wiley Interscience: New York, 1992, pp Ch. 13.
12. Shaik, S. S. *Prog. Phy. Org. Chem.* **1985**, *15*, 197-337.
13. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Albert, S. T. *Quantum Chemistry Program Exchange Bulletin* **1990**, *10*.
14. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
15. 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. 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. *GAUSSIAN94-DFT*; B.1 ed.; Gaussian, Inc.: Pittsburgh, PA, 1994.
16. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
17. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244-13249.
18. Dunning, T.; Hay, P. *Gaussian basis sets for molecular calculations*; Schaefer, H. F., Ed.; Plenum press: New York, London, 1977.
19. Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358-1371.
20. Later studies on C_3H_9+ find similar C_1 symmetric minima but do not consider the C_{3v} to D_{3h} question, nor its relevance to σ-allyl interactions : Collins, S. J.; O'Malley, P. J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4347-4355.
21. Planelles, J.; Sanchez-Marin, J.; Tomas, F. *J. Mol. Struct.* **1984**, *108*, 65-74.
22. See accompanying papers: (a) Paquette, L. A.; Usui, S. *Tetrahedron Lett.* **1999**, *40*, 3499. (b) Usui, S.; Paquette, L. A. *Tetrahedron Lett.* **1999**, *40*, 3495.