Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 48 (2007) 7266–7268
Tetrahedron Letters

How stable actually is the planar ‘triangular’ benzene dication?

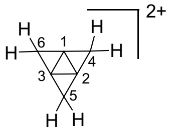
Alexander M. Genaev* and Vyacheslav G. Shubin

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Acad. Lavrentiev Ave. 9, 630090, Russia

Received 15 June 2007; revised 8 August 2007; accepted 13 August 2007

Abstract—Quantum chemical calculations indicate that the kinetic stability of an earlier proposed elegant planar ‘triangular’ benzene dication **1a** is very low. The kinetic stability of its methylated derivative **2a** is even lower.

Species with unusual, nonclassical structures are widespread in carbocation chemistry.[1] Among these is the especially exciting ‘triangular’ carbodication $C_6H_6^{2+}$ (**1a**) recently described by Priakumar and Sastry as a ‘viable’ structure.[2] An important feature of this dication is the presence of planar tetracoordinated carbons. Ab initio (MP2) and density functional theory (B3LYP) calculations indicated that carbodication **1a** was at a minimum on the potential energy surface.[2]



1a

With our rather a wide experience in preparing stable carbocations,[3] it was very tempting for us to consider generating carbodication **1a** as a long-lived species. At first, we decided to estimate the kinetic stability of this dication using quantum chemical methods. We selected the DFT method implemented in the PRIRODA program[4] (PBE potential, 3z basis) based on its fast algorithm and our previously favorable results, consistent with experimental data. As was shown in our recent paper,[5] the energy barrier values for carbocation rearrangements calculated with the use of this program were very close to the experimentally determined values. In addition, the kinetic stability of dication **1a** was estimated by using B3LYP/6-311+G** and MP2/6-311+G** methods (GAMESS program[6]).

As shown by the data presented in Table 1, the kinetic stability of carbodication **1a** is rather low: the energy barrier ($\Delta E + ZPE$) of its transformation into the isomeric fulvene dication **1e** (Fig. 1) is about 10 kcal/mol, which corresponds to an estimated half-lifetime of approximately 10 min at −130 °C.

It is well known that the kinetic stability of methylated carbocations is usually much higher than that of the parent, unsubstituted analogues. For example, while the heptamethylbenzenium ion is stable in CF_3COOH even at +70 °C,[7] the unsubstituted benzenium cation can only be prepared as a long-lived species in a superacid medium at low temperature.[8] Similarly the pyramidal dication **2d** (Fig. 2) is stable at +100 °C,[9] whereas, to the best of our knowledge, its unsubstituted analog **1f** (Fig. 1) has not yet been prepared.

Surprisingly, our calculations indicated that the polymethylated carbodication **2a** is even less stable than its unsubstituted analog **1a**. The energy barrier of its rearrangement into **2c** (Fig. 2) is 1.2 kcal/mol (Table 2, $\Delta E + ZPE$). The lower kinetic stability of dication **2a** compared to that of dication **1a** apparently results from location of the methyl groups at negatively charged carbons in the ground state of the dication and the stabilizing effect of these groups in the transition state of the rearrangement, where charges on these carbons become positive.

From the data obtained, it follows that experimental detection of the ‘viable’ carbodications **1a** and **2a** as

---

Keywords: Carbocations; Quantum chemical calculations; Rearrangement.

* Corresponding author. Tel.: +7 383 330 9386; fax: +7 383 330 9752; e-mail: genaev@nioch.nsc.ru

doi:10.1016/j.tetlet.2007.08.043

Table 1. Calculated relative energies ΔE (kcal/mol) of intermediates and transition states for the rearrangement of dication **1a**

	PBE/3z		B3LYP/6-311+G**		MP2/6-311+G**	
	ΔE	$\Delta E + ZPE$	ΔE	$\Delta E + ZPE$	ΔE	$\Delta E + ZPE$
1a	0.0	0.0	0.0	0.0	0.0	0.0
TS **1a**→**1b**	8.5	6.8	8.4	8.3	12.3	10.3
1b	6.0	4.3	6.0	5.4	10.1	8.1
TS **1b**→**1c**	11.1	9.1	9.2	8.3	13.3	11.2
1c	0.7	−1.0	−6.9	−5.6	3.9	2.2
TS **1c**→**1d**	7.7	5.3	2.9	2.5	8.6	6.5
1d	−37.2	−37.2	−47.5	−46.4	−38.3	−38.0
TS **1d**→**1e**	−17.5	−19.5	−24.7	−25.5	−16.0	−17.9
1e	−79.1	−77.8	−97.7	−95.7	−82.4	−81.9
1f	−94.2	−90.9	−99.7	−95.6	−109.6	−106.6

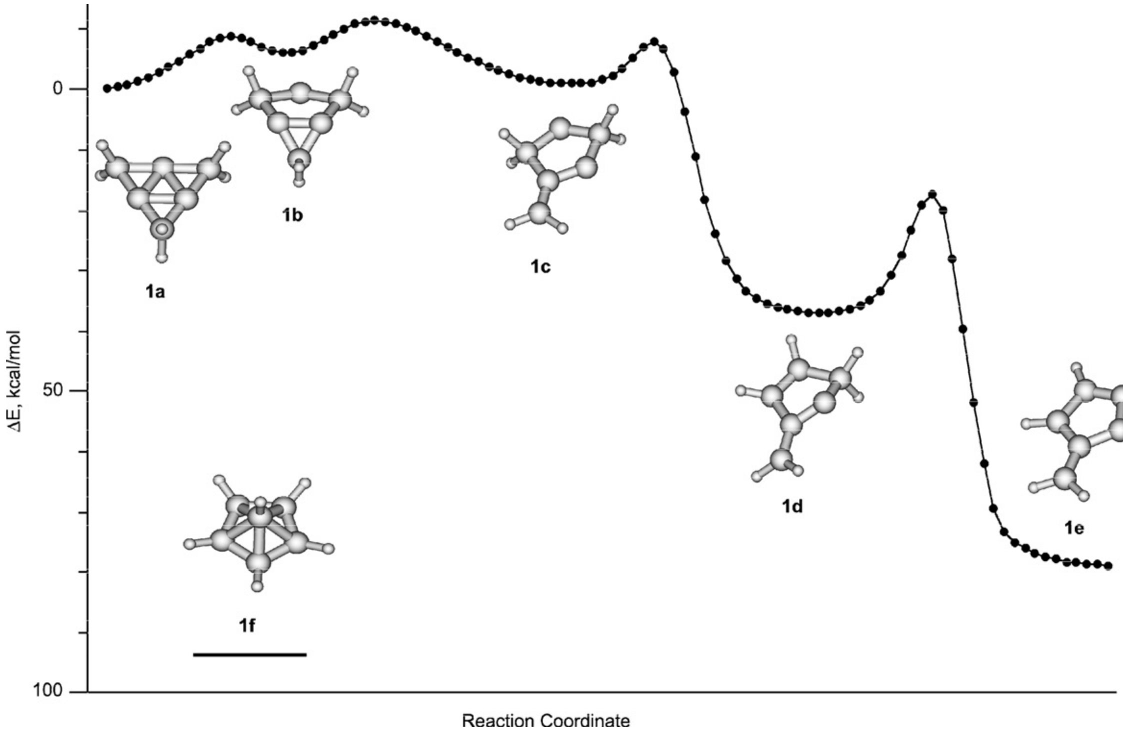


Figure 1. Energy profile obtained from IRC calculations (PBE/3z).

Table 2. Calculated (PBE/3z) relative energy ΔE (kcal/mol) of isomeric dications and transition states for the rearrangement of dication **2a**

	ΔE	$\Delta E + ZPE$	Charge on atoms C^{4-6}
2a	0.0	0.0	−0.085
TS **2a**→**2b**	1.9	1.2	+0.219
TS **2b**	−21.1	−23.9	+1.349
2c	−111.6	−111.9	+1.571
2d	−121.1	−119.6	

persistent species is hardly possible, and may remain one of the elusive goals in carbocation chemistry.

Computational methods

Exploration of PES and searching for the rearrangement pathways were carried out using the PRIRODA DFT program.[4] The exchange correlation functional by Perdew, Burke, and Ernzerhof[10] (PBE) was employed. The orbital basis sets of size {3,1,1/1} for H and {6,1,1,1,1,1/4,1,1/1,1} for C were used (3z basis). All stationary points were characterized by analysis of the Hessian matrices. The intrinsic reaction coordinate (IRC) calculations were carried out to describe the reaction paths. In addition, MP2 and B3LYP calculations (the geometry optimization and analysis of the Hessian matrices) were carried out for the stationary points using the GAMESS program[6] with the basis sets 6-311+G** ({3,1,1/1} for H and {6,3,1,1,1/3,1,1,1/1} for C). Charges on carbons C^{4-6} of the dications $C_6Me_6^{2+}$ (Table 2) were calculated by the NBO method[11] at the HF/6-311+G** level of theory.

An animation (created with the MOLDEN program[12]) is available via the Internet at http://limor1.nioch.nsc.ru/quant/dication.

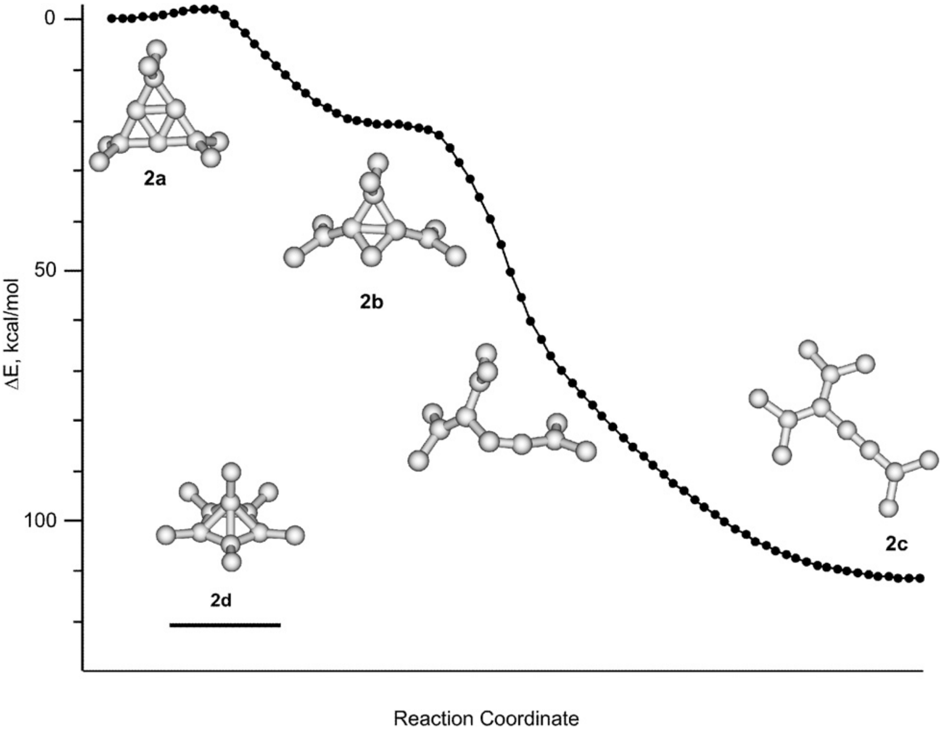


Figure 2. Energy profile obtained from IRC calculations (PBE/3z). Methyl group hydrogens are not shown.

Acknowledgments

We are grateful to the Russian Foundation for Basic Research and to the Russian Academy of Sciences (Project N 06-03-32406 and program N 5.1.9, respectively) for financial support. Helpful discussions with Professor G. K. S. Prakash and Dr. S. Nagy are also gratefully acknowledged.

References and notes

1. *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; Wiley: Hoboken, 2004.
2. Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2004**, *45*, 1515–1517.
3. Borodkin, G. I.; Shubin, V. G. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; Wiley: Hoboken, 2004; pp 125–158.
4. Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151–156; Laikov, D. N.; Ustynyuk, Yu. A. *Russ. Chem. Bull.* **2005**, *54*, 820–826.
5. Genaev, A. M.; Shubin, V. G. *Russ. Chem. Bull.* **2006**, *55*, 1085–1088.
6. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
7. Koptyug, V. A.; Shubin, V. G.; Korchagina, D. V. *Tetrahedron Lett.* **1965**, 1535–1537.
8. Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034–2043.
9. Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413–420.
10. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
11. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.0, University of Wisconsin: Madison, WI, 1990.
12. Schaftenaar, G.; Noordik, J. H. *J. Comput. Aided Mol. Des.* **2000**, *14*, 123–134.