

A hydrocarbon dication with nonplanar hexacoordinated carbon

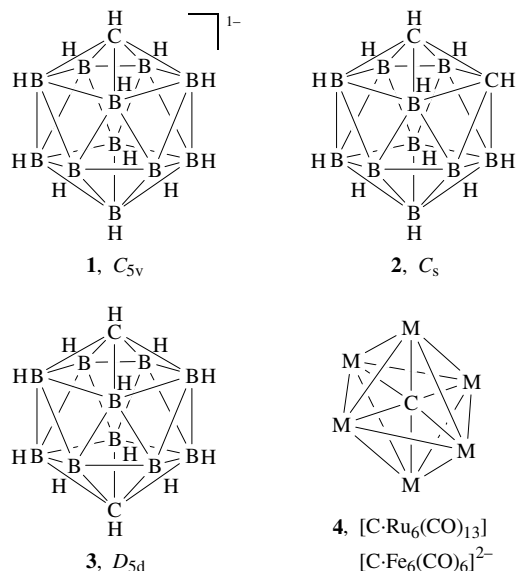
Ruslan M. Minyaev,* Vladimir I. Minkin, Tatyana N. Gribanova and Andrey G. Starikov

Institute of Physical and Organic Chemistry, Rostov State University, Southern Scientific Centre of the Russian Academy of Sciences, 344090 Rostov-on-Don, Russian Federation. Fax: +7 8632 43 4667; e-mail: minyaev@ipoc.rsu.ru

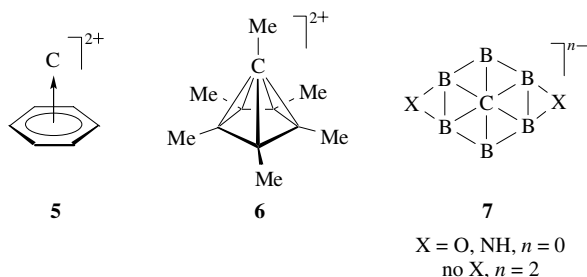
10.1070/MC2004v014n02ABEH001905

Ab initio [MP2(fu)/6-311G**] and DFT (B3LYP/6-311G**) calculations predict a stable hydrocarbon dication containing nonplanar hexacoordinated carbon.

The bonding capabilities of the carbon atoms are of great interest to theoretical chemistry.¹ It was computationally found that the coordination of carbon can be raised to seven and eight by placing it inside an appropriate framework of boron atoms^{2–4} and formally eight-coordinated carbon centres are present in some nickel and cobalt clusters.⁵ The boron and metal atom environments provide for the formation of multicentre bonds of carbon and its nonclassical stereochemistry. Attention was focused on compounds containing hexacoordinated carbon centres such as exemplified by carboranes **1–3**⁶ isoelectronic with the icosahedric borane $B_{12}H_{12}^{2-}$, carbide clusters **4**^{5,7} and the hexa-augmented dication $C(AuPPh_3)_6^{2+}$.⁸



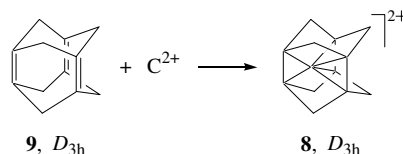
The *ab initio* calculation performed at different levels of approximation predicts the stability of other molecules and ions with hexacoordinated carbon centres: CLi_6^n ($n = 0, 2+$),⁹ CH_6^{2+} ,¹⁰ cation carbene **5**¹¹ and dication **6**, which was the only experimentally observed species with a hexacoordinated carbon atom.¹² Recently, a structural type of organoboron compounds **7** with planar hexacoordinated carbon was extensively studied using *ab initio* and DFT calculations.^{1,4,13,14}



Here we report on a computational finding of stable hydrocarbon dication **8** exemplifying a structural type of compounds containing hexacoordinated carbon atoms. Calculations performed with the aid of *ab initio* MP2(fu)/6-311G** (MP2) and DFT B3LYP/6-311G** (DFT) methods¹⁵ predict that dication **8** corresponds to an energy minimum on the potential energy

surface (PES). The geometry of **8** found by calculations and that for the electrically neutral cage system **9** into which the central carbon atom is immersed are shown in Figure 1. The energy characteristics are summarised in Table 1.

The central carbon atom forms six ordinary bonds with peripheral carbon atoms with the bond lengths typical of usual aliphatic hydrocarbons. The C–C bond lengths in the six-membered rings (~ 1.6 Å) are only slightly elongated as compared to those in cyclohexane. The cage system of **9** formed by two cyclohexane-like chairs bonded to each other by three double C–C bonds (~ 1.35 – 1.36 Å) has considerably shorter C–C distances (~ 1.54 – 1.55 Å). The hexacoordinated carbon atom in dication **8** accumulates a negative Mulliken charge of -0.156 e (DFT) or -0.336 e (MP2), which allows us to consider **8** as the charge-transfer complex of cage system **9** with C^{2+} . The intrusion of C^{2+} into the centre of **9** leads to the elongation of all C–C bonds in the two six-membered cycles, particularly double C–C bonds. However, the significant strain of thus formed system **8** is compensated by the formation of six multicentre C–C bonds so that the reaction



is exothermic. The energy effect is estimated at 460.1 (DFT) or 458.7 kcal mol^{–1} (MP2), respectively. Our preliminary calculations showed that any structural distortions followed the vibration mode directions led to significant increases in energy.

The six multicentre C–C bonds of the hexacoordinated carbon in **8** are formed as a result of the interaction of s and p valence orbitals of the central carbon atom with π and π^* molecular orbitals (MOs) of three double bonds of the cage structure of **9**. The orbital interaction diagram is schematically illustrated in Figure 2.

In contrast with the diprotonated methane $(CH_6)^{2+}$ in which the hexacoordinated carbon forms two 2c–2e and two 3c–2e bonds,¹² all six CC bonds in **8** are fully equivalent. As can be seen in the diagram, the principal contribution to stabilization of **8** is brought by the interaction of e' MO of **9** with p_x, p_y AOs of C^{2+} and unoccupied a_2'' MO with p_z AO, which leads to the formation of two bonding MOs of e' and a_2' symmetries. As

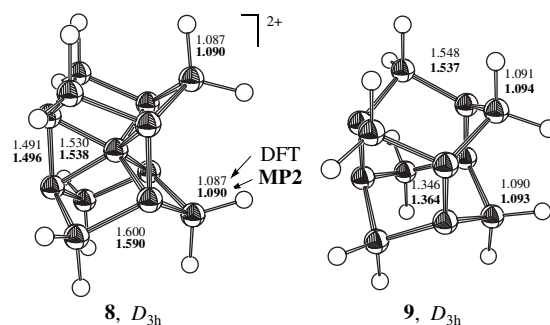


Figure 1 Geometry parameters of compounds **8** and **9** calculated by DFT (B3LYP/6-311G**) and *ab initio* [MP2(full)/6-311G**] methods. The bond lengths and angles are indicated in angstrom units and degrees, respectively.

Table 1 *Ab initio* [MP2(fu)/6-311G**] and DFT (B3LYP/6-311G**) data for compounds **8**, **9** and C²⁺.^a

Structure, symmetry	Method	E_{tot}	$E_{\text{tot}} + \text{ZPE}$	ΔE	ΔE_{ZPE}	ω_1
8 , D_{3h}	DFT	-501.630105	-501.422278	460.1	458.8	359
	MP2	-500.438754	-500.229551	458.7	464.0	270
9 , D_{3h}	DFT	-464.384413	-464.178651	0	0	373
	MP2	-463.243484	-463.035837	0	0	361
C ²⁺	DFT	-36.512510	-36.512510	0	0	—
	MP2	-36.464256	-36.464256	0	0	—

^a E_{tot} (a.u.) is the total energy (1 a.u. = 627.5095 kcal mol⁻¹); ZPE (a.u.) is the harmonic zero-point correction; ΔE (kcal mol⁻¹) is the relative energy; ΔE_{ZPE} (kcal mol⁻¹) is the relative energy including a harmonic zero-point correction; ω_1 (cm⁻¹) is the smallest harmonic vibration frequency. No imaginary frequencies were found for structures **8** and **9**.

can be seen in Figure 2, the LUMO of **8** has the antibonding character for the central carbon and filling it with electrons would strongly destabilise the system. Indeed, calculations of the electrically neutral system of **8** showed that the structure

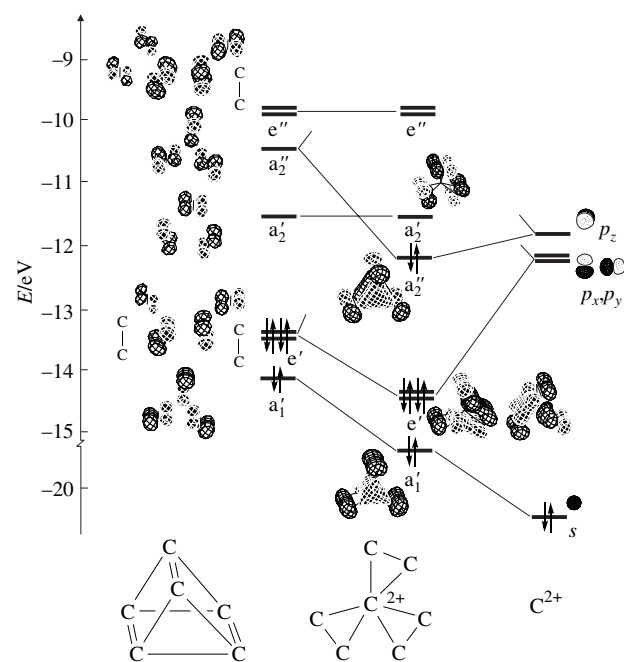


Figure 2 Schematic correlation diagram of the interaction of *s* and *p* valence orbitals of the carbon atom with π and π^* molecular orbitals of three double bonds of the cage structure of **9**. Splitting of the carbon *s* and *p* orbitals and symmetrization of the π and π^* MOs occur according to the D_{3h} symmetry.

corresponded to a top of a hill (two negative force constants) on the PES.

Note that the results of DFT (B3LYP/6-311G**) calculations are in excellent agreement with those obtained using *ab initio* [MP2(fu)/6-311G**] calculations.

In conclusion, the calculations performed demonstrate that dication **8** presents a new structural type for a stable hydrocarbon system containing a hexacoordinated carbon atom linked to six peripheral carbons by multicentre bonds.

This work was supported by the Russian Foundation for Basic Research (grant nos. 04-03-32538 and 02-03-33227), the RF Ministry of Industry and Science (grant no. 945.2003.3), and CRDF (grant no. RC1-2323-RO-02). V.I.M. acknowledges the support of the Foundation for Supporting Russian Science.

References

- 1 V. I. Minkin, R. M. Minyaev and R. Hoffmann, *Usp. Khim.*, 2002, **71**, 989 (*Russ. Chem. Rev.*, 2002, **71**, 869).
- 2 R. M. Minyaev, T. N. Gribanova, A. G. Starikov and V. I. Minkin, *Mendeleev Commun.*, 2001, 213.
- 3 R. M. Minyaev, T. N. Gribanova, A. G. Starikov and V. I. Minkin, *Dokl. Ross. Akad. Nauk*, 2002, **382**, 785 [*Dokl. Chem. (Engl. Transl.)*, 2002, **382**, 41].
- 4 Z.-X. Wang and P. v. R. Schleyer, *Angew. Chem.*, 2002, **114**, 4256.
- 5 P. Chini, *J. Organomet. Chem.*, 1980, **200**, 37.
- 6 J. Casanova, *The Borane, Carborane and Carbocation Continuum*, John Wiley and Son, Chichester, 1998.
- 7 Yu. L. Slovokhotov and Yu. T. Struchkov, *Usp. Khim.*, 1985, **54**, 556 (*Russ. Chem. Rev.*, 1985, **54**, 323).
- 8 H. Schmidbaur, *Pure Appl. Chem.*, 1993, **65**, 691.
- 9 P. v. R. Schleyer and J. Kapp, *Chem. Phys. Lett.*, 1996, **255**, 363.
- 10 G. A. Olah and G. Rasul, *Acc. Chem. Res.*, 1997, **30**, 245.
- 11 V. I. Minkin and R. M. Minyaev, *Dokl. Ross. Akad. Nauk*, 2002, **385**, 502 [*Dokl. Chem. (Engl. Transl.)*, 2002, **385**, 203].
- 12 H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, 1975, **8**, 413.
- 13 R. M. Minyaev and T. N. Gribanova, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 786 (*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 783).
- 14 K. Exner and P. v. R. Schleyer, *Science*, 2000, **290**, 1937.
- 15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.

Received: 18th February 2004; Com. 04/2231