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Tetrahedron Letters 45 (2004) 1515–1517

Tetrahedron Letters

A system with three contiguous planar tetracoordinate carbons is viable: a computational study on a $C_6H_6^{2+}$ isomer☆

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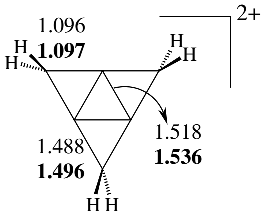
Received 27 October 2003; revised 25 November 2003; accepted 5 December 2003

Abstract—Ab initio and density functional theory calculations indicate that a benzene dication isomer (**1**: $C_6H_6^{2+}$) with three contiguous planar tetracoordinate carbons is at a minimum on the potential energy surface. The remarkable preference for the planar structure for **1** is traced to the aromatic stabilization present in the three membered ring formed by the three planar tetracoordinate carbon atoms.

The van't Hoff–Le Bel tetrahedral arrangement of tetracoordinate carbon is a fundamental paradigm in structural organic chemistry.[1] While rules are framed to agree with observations, exceptions to these established concepts continue to be a part of the enthusiasm and excitement in scientific research. The quest for achieving planar tetracoordinate carbon (ptC) has been triggered by the seminal papers by Hoffmann, Schleyer and co-workers.[2,3] Efforts were made both experimentally and computationally to achieve planar tetracoordination for carbon through electronic stabilization as well as by employing brute force structural constraints.[4–6] The electronic stabilization is achieved in many cases by employing transition metal (Zr, V, W, Ti, Ta) fragments[4d] or suitably varying the charge on the skeleton and embodying other main group elements.[4–6] Most of these strategies are targeted to identify compounds containing one ptC. Reports of compounds containing more than one ptC are scarce; Choukroun and co-workers have reported the synthesis of a two-ptC containing compound.[7] In this letter, we report a dication of a simple hydrocarbon, $C_6H_6^{2+}$ containing three ptCs adjacent to each other which, to our knowledge is the first stable molecule to possess three ptCs. $C_6H_6^{2+}$ has been widely studied; however, to our knowledge, the skeletal arrangement **1** has not previously been explored.[8]

Ab initio (MP2) and density functional theory (B3LYP) calculations indicate that the isomer **1** of benzene dication, where three ptCs are bound to each other, is a local minimum on the $C_6H_6^{2+}$ potential energy surface (Fig. 1).[9,10] The C–C bond lengths in **1** are less than normal C–C single bond lengths indicating that the carbons are tightly bound. Interestingly, all the four bonds connecting to each of the ptC atoms lie within a semicircle, where one of the C–C–C angles is almost linear.

Having shown that **1** is a minimum on the potential energy surface, we went on to examine the factors, which might be responsible for the stabilization of the novel structural arrangement. An examination of the shapes of the frontier molecular orbitals of **1** indicates that the inner three-membered ring is highly delocalized and has aromatic stabilization (Fig. 2).[11] The HOMO corresponds to the π-bonding orbital, which evidences the aromatic stabilization and the LUMO orbitals



1, D_{3h}

Figure 1. The principal geometric parameters (Å) of **1** obtained at the B3LYP and MP2 (bold face) levels of theory using the 6-311+G** basis set.

Keywords: Planar tetracoordinate carbon; $C_6H_6^{2+}$; Calculations; Aromatic stabilization; Singlet–triplet gap.

☆ IICT communication no. 031112.

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doi:10.1016/j.tetlet.2003.12.019

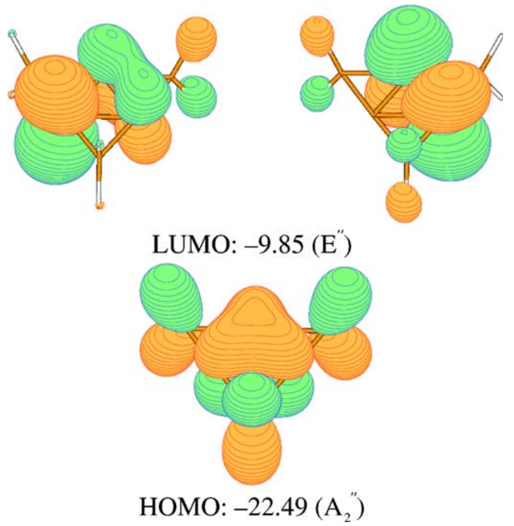
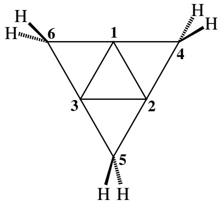


Figure 2. The frontier molecular orbital isosurfaces and the orbital energies (eV) obtained at the HF/6-311+G** level.

correspond to the π* orbital. The overlap among the p-orbitals of the three ptCs could be effective only if the structure is planar. The central three-membered ring with all ptCs represent a 3-centre-2-electron situation in π-as well as σ-frameworks. The HOMO–LUMO energy gap (12.64 eV) and the singlet–triplet energy difference (325.2 kJ/mol) of **1** are found to be substantial indicating high stability. The aromatic character of the central three-membered ring is also supported by the NICS value,[12] which is about −17.7 indicating high aromaticity. Interestingly, the computed NICS value of the central three-membered ring is lower than cyclopropenium ion (−15.9 at the same level), which may be due to the substantial aromatic stabilization in both σ- and π-planes. The bond orders calculated using the NBO method[13] (Fig. 3) confirm tetracoordination for all the carbon atoms (bond order for the C–C bond in ethane is 0.875 at the similar level of theory).

In the present letter, we have shown for the first time that a system with three planar tetracoordinate carbon atoms is viable. The benzene dication isomer **1** was characterized as a minimum on the potential energy surface. The stabilization of the three ptCs is traced to electronic factors, namely aromatic stabilization as reflected in the NICS, HOMO–LUMO gap and singlet–triplet energy differences. Therefore, we propose **1** as a viable candidate for exhibiting a novel structural arrangement and anticipate experimental efforts towards this direction.



NICS(1) = –17.73
Natura l atomic charges: C1 = 0.339
C4 = –0.301
H = 0.314
Bond order: C1 -C2 = 0.811
C1-C4 = 0.865
C4-H = 0.767

Figure 3. The NICS(1) values, charges and bond orders of **1** obtained at the HF/6-311+G** level.

Acknowledgements

U.D.P. thanks UGC, New Delhi for a senior research fellowship. We thank Dr. J. S. Yadav, Director, IICT for his support and encouragement.

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