JOC Note

# Evidence for 5-Center 4-Electron Bonding in (C···H···C···H···C) Array

Robert Ponec* and Gleb Yuzhakov

*Institute of Chemcial Process Fundamentals,*
*Czech Academy of Sciences, Prague 6, Suchdol,*
*165 02 Czech Republic*

*rponec@icpf.cas.cz*

*Received May 21, 2003*

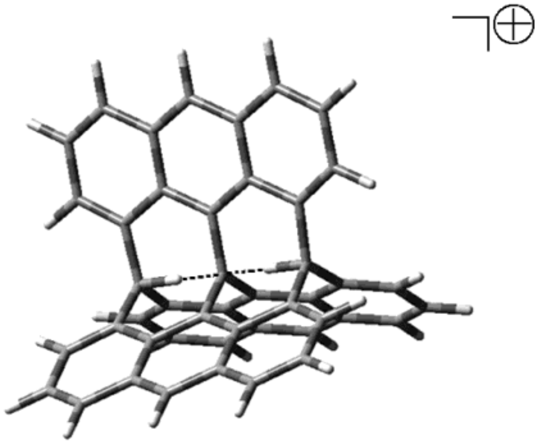
**Abstract:** This paper brings new independent evidence for 5-center 4-electron bonding, whose existence in (C···H···C···H···C) fragment of the molecule I was anticipated in the recent study by Tantillo and Hoffmann. The evidence is based on the applications of the so-called multicenter bond indices, recently proposed as new efficient tool for the detection and localization of multicenter bonding in molecules.

## Introduction

The idea of multicenter bonding, introduced in late 1940s by Longuet-Higgins,[1] represents an example of this successful auxiliary concept allowing the rationalization of the structure of the molecules violating ordinary valence and stoichiometry rules known from classical structural theory. An example in this respect is the broad class of electron-deficient molecules and Lipscomb's seminal application of the concept of 3-center 2-electron (3c-2e) bond in the field of boron chemistry[2−4] is a cornerstone which undoubtedly contributed to wide acceptance of this concept as a new nonclassical paradigm of structural chemistry. Although it is true that (3c-2e) bonding represents the most ordinary type of multicenter bonding, it is likely that the existence of nonclassical bonds involving more than three centers cannot be completely excluded. The eventual existence of such bonds thus still represents an interesting challenge for contemporary chemistry. Into the framework of efforts for the detection of this type of nonclassical bonding can be included the recent study by Tantillo and Hoffmann,[5] who claim the discovery of the system containing 5c-4e bonding localized in the central (C···H···C···H···C) fragment of cation I (Chart 1).

Intrigued by this report, we decided to check the anticipated existence of 5c-4e bonding in this molecule using the theoretical approach specifically designed for the detection and localization of multicenter bonding known under the name generalized population analysis.[6−11] The term generalized population analysis is a generic name for the whole family of approaches based on the partitioning of the identity (1) into mono- di-, tri-, and generally $k$-atomic contributions, which can be attributed appropriate chemical or physical meaning according to actual value of $k$.

**CHART 1**



$$\frac{1}{2^{k-1}}\,\mathrm{Tr}(\mathrm{PS})^k = N = \sum_{A} \Delta_{A}^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \ldots \sum_{A<B<\ldots K} \Delta_{AB\ldots K}^{(k)} \quad (1)$$

Thus, for example, the diatomic contributions resulting from the partitioning of the identity (1) for $k = 2$ are identical to the well-known Wiberg or Wiberg−Mayer indices,[12−14] which are widely accepted as the theoretical counterpart of the classical concept of bond order. Similarly, the triatomic contributions from the partitioning of the identity (1) for $k = 3$ have been widely used, as the so-called 3-center bond indices, for the detection and the localization of the eventual presence of 3-center bonding in the molecules.[15−20] The usefulness of these indices for structural elucidations arises from the interesting nontrivial finding that their values sensitively mimic the presence and/or absence of bonding interactions between individual atoms in a molecule. Thus, for example, in the case of molecules well described by classical Lewis model of localized 2c-2e bonds, the corresponding 2-center bond indices attain non-negligible values only between classically bonded atoms, while for

---

* To whom correspondence should be addressed.

[1] Longuet-Higgins, H. C. *J. Chim. Phys.* **1949**, *46*, 275.

[2] Lipscomb, W. *J. Chem. Phys.* **1954**, *22*, 985.

[3] Lipscomb, W. N. *Science* **1977**, *196*, 1047.

[4] Lipscomb, W. N. *Acc. Chem. Res.* **1973**, *8*, 257.

[5] Tantillo, D. J.; Hoffmann, R. *J. Am. Chem. Soc.* **2003**, *125*, 4042.

[6] Mundim, K. C.; Giambiagi, M.; Giambiagi, M. S. *J. Phys. Chem.* **1994**, *98*, 6118.

[7] Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1990**, *173*, 569.

[8] Sannigrahi, A. B.; Kar, T. *Chem. Phys. Lett.* **1999**, *299*, 518.

[9] Ponec, R.; Uhlik, F. *Croat. Chem. Acta* **1996**, *69*, 941.

[10] Ponec, R.; Mayer, I. *J. Phys. Chem A.* **1997**, *101*, 1738.

[11] Bochicchio, R.; Ponec, R.; Lain, L.; Torre, A. *J. Phys. Chem. A* **1998**, *102*, 7176.

[12] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

[13] Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.

[14] Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73.

[15] Bochicchio, R.; Ponec, R.; Uhlík, F. *Inorg. Chem.* **1997**, *36*, 5363.

[16] Ponec, R.; Roithová, J.; Sannigrahi, A. B.; Lain, L.; Torre, A.; Bochicchio, R. *THEOCHEM* **2000**, *505*, 283.

[17] Sannigrahi, A. B.; Nandi, P. K.; Behera, T.; Kar, T. *THEOCHEM* **1992**, *276*, 259.

[18] Ponec, R.; Jug, K. *Int. J. Quantum Chem.* **1996**, *60*, 75.

[19] Sannigrahi, A. B.; Kar, T. *THEOCHEM* **2000**, *496*, 1.

[20] Kar, T. K.; Marcos, E. S. *Chem. Phys. Lett.* **1992**, *192*, 14.

10.1021/jo034676z CCC: $25.00

the pairs of formally nonbonded atoms the values are practically negligible. A similar situation is the case of multicenter bonding, whose eventual presence in certain molecular fragment is again detected by the non-negligibility of the corresponding multicenter bond index. In this connection, it is also interesting to remark that non-negligible values attain these indices only between very limited set atoms. This implies that similar to the previous case, the multicenter bonding interactions are also localized only between very limited set of centers, and it is important that the regions of nonclassical bonding, detected by the values of the corresponding multicenter bond indices, coincides with the atoms or fragments for which the existence of multicenter bonding is expected by other independent methods. Thus, for example, in the case of diborane, most of the triatomic contributions resulting from the partitioning (1) for $k = 3$ are negligible except two nonvanishing terms which, consistent with the expectations of the *styx* number,[21] are indeed localized in BHB fragments involving borons and the bridging hydrogens.

Straightforward extension of this approach to multicenter bonding involving more than three centers requires, of course, the scrutiny of appropriate polyatomic contributions, resulting from the partitioning of the identity (1), for the corresponding value of $k$. Thus, in the case of the cation I, for which the existence of 5c-4e bonding in the central (C···H···C···H···C) fragment was anticipated, the detection of the eventual existence of such a bond requires the calculation of 5-center bond indices. The calculation of these indices was performed using our program, which is available upon request. The density matrix $P$ and overlap matrix $S$ required for the analysis was generated using Gaussian 98 program[22] at B3LYP level of the theory in 6-31G* basis for completely optimized geometry of the cation I, retrieved from the Supporting Information of the paper.[5]

The results of our analysis are very encouraging and clearly provide a strong theoretical support for the anticipated existence of 5c-4e bonding in the cation I. Consistent with the expectations, the absolute majority of 5-center bond indices in the cation I is practically negligible, and the only nonvanishing term is the one involving just the atoms in (C···H···C···H···C) fragment. The calculated value of the index is equal to $-0.027$. To get a deeper understanding of the meaning the calculated value, the above index can be compared with the "idealized" value of the 5c-4e bond index, which can be derived from a simple analytical model of multicenter bonding analogous to the one proposed in the study.[10] This idealized value, determined for the same bonding topology expected in the study[5] (Chart 2), is equal to $-0.069$.

**CHART 2**

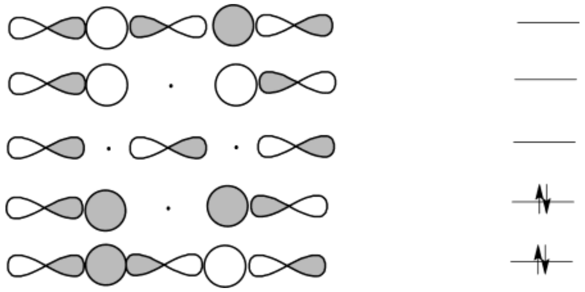
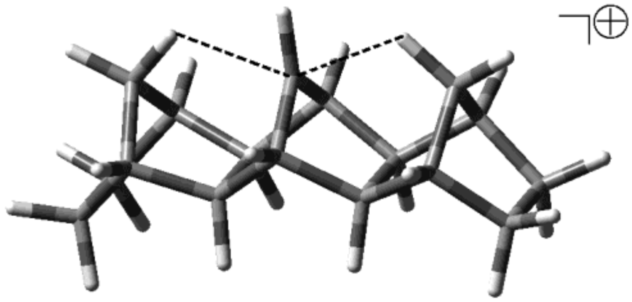


**CHART 3**



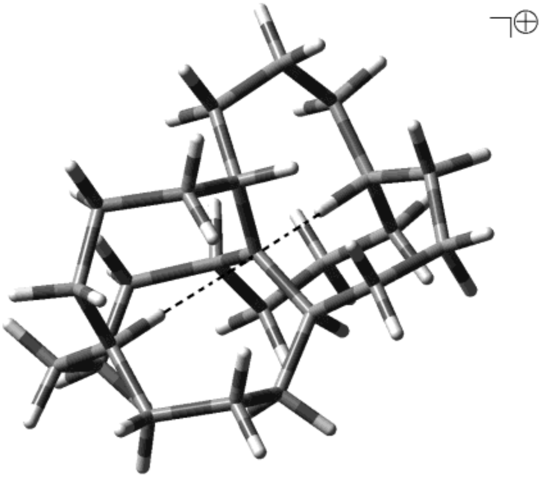
Although this value is a bit higher (in the absolute value) than the one from the real calculations, the difference is not very dramatic and can evidently be attributed to the simplicity of the analytical Hückel-like model. This model namely assumes that each atom contributes to multicenter bonding just by one orbital, which is certainly a dramatic simplification compared to the situation in the real molecule. The observed qualitative agreement between the actual and idealized value of the index is therefore quite plausible. In this connection, is it also interesting to stress once again that the calculated 5-center index for (C···H···C···H···C) fragment ($-0.027$) is in fact the only nonvanishing 5-center index in the whole molecule; all the other 5-center indices are at least 1 order of magnitude smaller. In addition to this, another important factor corroborating the anticipated existence of 5c-4e bonding in the cation I, concerns the coincidence of the sign of actually calculated 5-center bond index with the idealized one derived from the analytical model. The importance of this factor can straightforwardly be demonstrated on the conclusions of the previous study,[10] in which it was shown that the sign of the bond index is dramatically affected by the number of electrons involved in multicenter bonding. Thus, for example, while 3c-2e bonding is characterized by the positive value of the bond index, the analogous index for 3-center 4-electron bond is negative.[10,20] Similar situation exists also in the case of 5-center bonding and solution of the corresponding analytical model shows that negative 5-center bond indices are characteristic just for 5c-4e bonding while 5c-2e and 5c-6e bonding is characterized by the positive values of the corresponding bond indices. An example of the simplest system displaying 5c-6e bonding is, e.g., the cyclopentadienyl anion and consistent with the expecta-

---

(21) Wade, K. *Electron Deficient Compounds. Studies in Modern Chemistry*; T. Nelson and Sons, Ltd.: London, 1971.

(22) Gaussian98, Revision A.9: 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.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

**CHART 4**



tion, the value of the corresponding bond index is indeed positive (0.102).

To further corroborate the above conclusions and to provide another independent support for the ability of bond indices to detect the presence of multicenter bonding in molecules, the above approach was applied also to two cations II and III (Schemes 3 and 4).

These structures were also scrutinized by Tantillo and Hoffmann[5] as the potential candidate for 5c-4e bonding, but unfortunately, no indication of the existence of such a bonding could be found for them. To see whether this absence of 5c-4e bonding will also be reflected in the values of the corresponding indices, the corresponding 5c-bond indices were calculated also for these two structures. The calculations were again performed using the density and overlap matrixes generated, similarly as in the previous case, by the Gaussian 98 program,[22] for the structures completely optimized at B3LYP level of the theory in 6-31G* basis. The results are very encouraging since consistent with the anticipated absence of 5c-4e bonding in these systems, the corresponding (C···H···C···H···C) bond indices are in both case negligibly small and in both cases their values do not exceed 0.001 (in absolute value).

We can thus conclude that the formalism of the generalized population analysis correctly reflected the presence and/or absence of multicenter bonding in the studied systems, and, consequently, it could hopefully be used as an universal auxiliary tool allowing the detection of the eventual presence of such a bonding also in other molecular systems.

An especially interesting example in this respect could be, e.g., the systems studied by McMurry and Sorensen,[23-25] in which the variation of 3c-2e bonding with certain geometrical parameters was reported. Such a study is currently being performed in our laboratory, and the results will be reported elsewhere.

**Acknowledgment.** This study was supported by a grant of the Grant Agency of the Czech Academy of Sciences, No. A4072006. This support is gratefully acknowledged. We also thank professors R. Hoffmann and D. J. Tantillo for providing us with the optimized structures of the cations II and III.

**Supporting Information Available:** Cartesian coordinates of the structures I–III. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034676Z

---

[23] McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, *25*, 47.

[24] McMurry, J. E.; Lectka, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111*, 8867.

[25] Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1990**, *112*, 8135.