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Multicenter Bonding in Carbocations with Tetracoordinate Protons

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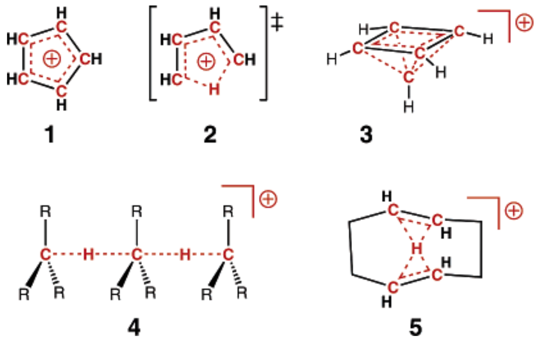
The nature of the bonding in a set of nonclassical carbocations with tetracoordinated protons “sandwiched” between two C═C π bonds was scrutinized using the new computational methodology of generalized population analysis. The results of this theoretical analysis strongly corroborate the conclusions of a previous study in which the occurrence of delocalized 5-center 4-electron (5c−4e) bonding in the C−C−H−C−C fragments of such cations was anticipated.

Introduction

Organic molecules with putative 5-center 4-electron (5c−4e) bonding arrays are of great interest, both because of their highly delocalized nature and because such molecules contain substructures with unusual geometries. The most commonly encountered organic species with 5c−4e bonding are derivatives of the simple pentadienyl cation. Other, more exotic, species for which the possibility of 5c−4e bonding has been discussed previously are shown in Chart 1. Structure **1** is the cyclopentadienyl cation.[1] On the basis of orbital considerations, 5c−4e bonding in a fully delocalized, D_{5h}, π-system constructed from five parallel p-orbitals should not be favorable, however, as it would involve a ground state with a degenerate pair of singly occupied orbitals. Structure **2** is the transition state structure for a cationic [1,4] sigmatropic shift of hydrogen.[2,3] If such a shift is suprafacial with respect to the 4-carbon substructure, then the reaction should be orbital symmetry-forbidden[2,4,5] and delocalized 5c−4e bonding should again be unfavorable. However, if such a shift is antarafacial with respect to the 4-carbon substructure, then delocalized 5c−4e bonding should be favorable and the reaction should be orbital symmetry-allowed. Structure **3**, protonated “pyramidane”,[6] contains a square pyramidal, delocalized 5c−4e bonding array involving five carbon atoms. The geometries and bonding in this and a variety of related structures that possess 5-coordinate carbons[7,8] with pyramidal geometries have been discussed previously.[6,9] Structures of type **4**[10] represent rare examples with acyclic 5c−4e arrays. For these structures, trigonal bipyramidal 5-coordinate carbons have been predicted. Structure **5** appears to possess a bicyclically delocalized 5c−4e array at whose center resides a 4-coordinate hydrogen.[11] This structure and its derivatives (Chart 2)[12] are the focus of this report. Note that though the pentadienyl cation and cyclopentadienyl cation (**1**) have π-delocalized 5c−4e bonding arrays, cations **2**−**5** have arrays that involve at least some σ-delocalization.

CHART 1



In the work described herein, the proposal that delocalized 5c−4e bonding exists in structures such as **5** is tested using generalized population analysis (GPA),[13−16] and the effects of substituents and overall charge on the bonding and geometry of the 5-center C−C(B)−H−C−C(B) cores of these structures (which can be thought of as protons “sandwiched” between two π-bonds[11]) are explored.

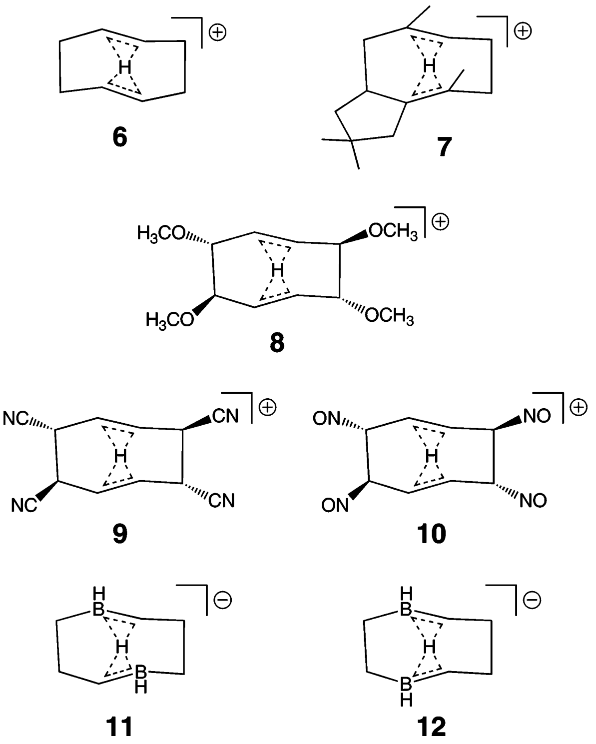
Theoretical

GPA is a sophisticated tool for the detection and localization of multicenter bonding in molecules, and this methodology was previously used to characterize the 5c−4e bonding in **4**.[10,17] As the theoretical background underlying the formalism of generalized population analysis has been described in several previous studies,[15,16,18] we discuss here only the basic ideas to the extent necessary for the purpose of the present study. GPA is a generic name for the procedure allowing for the detection of the presence and/or absence of bonding interactions in a molecule on the basis of the contributions resulting from the partitioning of the powers of the product of the charge-density bond-order density matrix **P** and the overlap matrix **S** (eq 1) into terms that can be attributed certain physical and/or chemical meaning.

$$\frac{1}{2^{k-1}}\mathrm{Tr}(\mathbf{PS})^k = \sum_A \Delta_A{}^{(k)} + \sum_{A<B} \Delta_{AB}{}^{(k)} + ... \sum_{A<B<...<K} \Delta_{ABC...K}{}^{(k)} \tag{1}$$

10.1021/jp0568430 CCC: $33.50

CHART 2



Thus, for example, the existence of localized two-center two-electron bonding can straightforwardly be detected by the values of the contributions $\Delta_{AB}^{(2)}$, resulting from the partitioning for $k = 2$. These terms are identical to the so-called Wiberg indices,[19] later generalized by Giambiagi et al.[20] and independently by Mayer.[21] These values are known to coincide with bond orders in classical structural formulas. For nonconnected atoms the values are negligible. The ability to reflect the existence of bonding interactions is retained also for the indices resulting from the partitioning (1) for higher values of k, and the terms $\Delta_{ABC}^{(3)}$ are widely used as the so-called three-center bond indices for the detection and characterization of three-center bonding.[18,22,23] The same general approach can be used also for the detection of multicenter bonding delocalized over even more centers. For example, the application of such multicenter bond indices to the characterization of homoaromaticity was reported recently.[24] Detecting the 5-center bonding in the central C−C−H−C−C fragment in cations such as **5**[11] involves the scrutiny of the corresponding five-center bond indices resulting from the partitioning of the identity (1) for $k = 5$. The bond indices were calculated using our own program, which is available upon request. The density matrix **P** and the overlap matrix **S** required for the analysis were generated using GAUSSIAN03.[25]

Computations

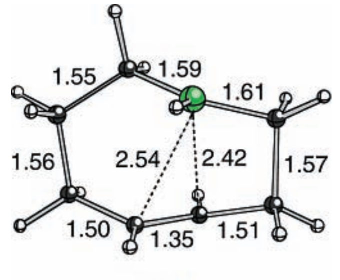
To obtain reliable structures for molecules **5**−**12**, their geometries were optimized at the B3LYP/6-31+G(d,p)[26−28] level of theory. Structures **5**−**10** were characterized as minima and structures **11** and **12** as transition structures by analysis of their vibrational frequencies. Because GPA, as a representative of the broader family of Mulliken-like population analyses, is known to exhibit some weaknesses with diffuse basis functions,[29] the multicenter bond indices were calculated using the smaller but still sufficiently reliable 6-31G(d) basis set with the geometries reoptimized at the B3LYP/6-31G(d) level (unless otherwise noted). Reoptimization with this smaller basis set was found to have only small effects on most of the molecular geometries. For all molecules except **7**, **10**, and **11**, no changes to C−C, C−H, or B−H distances greater than 0.01 Å were observed. For structure **11**, the B−H distances were 0.02 Å shorter when the 6-31G(d) basis set was used. For structure **10**, the potential energy surface involving rotation of the NO groups was extremely flat at the B3LYP/6-31+G(d,p) level and no discrete minimum could be located. Bond distances in various structures on this flat region were similar to those in the B3LYP/6-31G(d) minimum. The B3LYP/6-31G(d) minimum is shown in Figure 1. The only molecule for which the change of basis set resulted in significant geometrical changes was structure **7**. At the B3LYP/6-31+G(d,p) level, structure **7** resides on a relatively flat plateau and has only small barriers for rearrangement to structures with localized protons. Reoptimization of structure **7** with the smaller basis set led to structures with localized protons. The multicenter indices reported for structure **7** are therefore computed using the 6-31G(d) basis set on the geometry optimized using the 6-31+G(d,p) basis set.

Results and Discussion

Figure 1 shows the geometries of structures **5**−**12**. The geometries of **5**−**8** have been discussed previously.[11] Comparison of the C−C−H−C−C core of **5**, **8**, **9**, and **10** reveals that the geometry of this substructure is not very sensitive to the presence of substituents—be they electron donors or acceptors—on the ethylene tethers connected to the 5-center core, although the symmetry of the core is reduced for non-D_2-symmetric conformations (i.e., with OCH_3 and NO substituents, but not with linear CN substituents).[30] This suggests that 9-center 8-electron delocalization, suggested as a possibility in a previous study,[11] probably does not contribute significantly to the structure of these molecules. The lengths of the C−C bonds in the CR_2CR_2 tethers do vary slightly with substitution but the C−C bonds that connect the CH_2CH_2 units to the C−C−H−C−C core do not shorten as the tethers are elongated, as might be expected if 9-center 8-electron bonding contributed significantly (in fact, they lengthen slightly).[11]

Replacement of carbon atoms of the C−C−H−C−C core with boron atoms was also examined. For each carbon-to-boron replacement the overall charge of the molecule changes by −1. For example, structures **11** and **12**, each containing two boron atoms, have overall charges of −1. The delocalization in these structures appears to be disrupted somewhat compared to **5**. In both **11** and **12**, contacts between the central hydrogen and the sites of boron substitution are considerably longer than when carbon atoms were present.

Both **11** and **12** are actually transition state structures, apparently for hydrogen transfer between the two carbons of each C−B−H−C−B core. When only a single carbon atom is substituted by a boron atom, thus producing a system with an overall charge of zero, only structures with normal C−H and B−H bonds could be located (e.g., **13**). This suggests that it is



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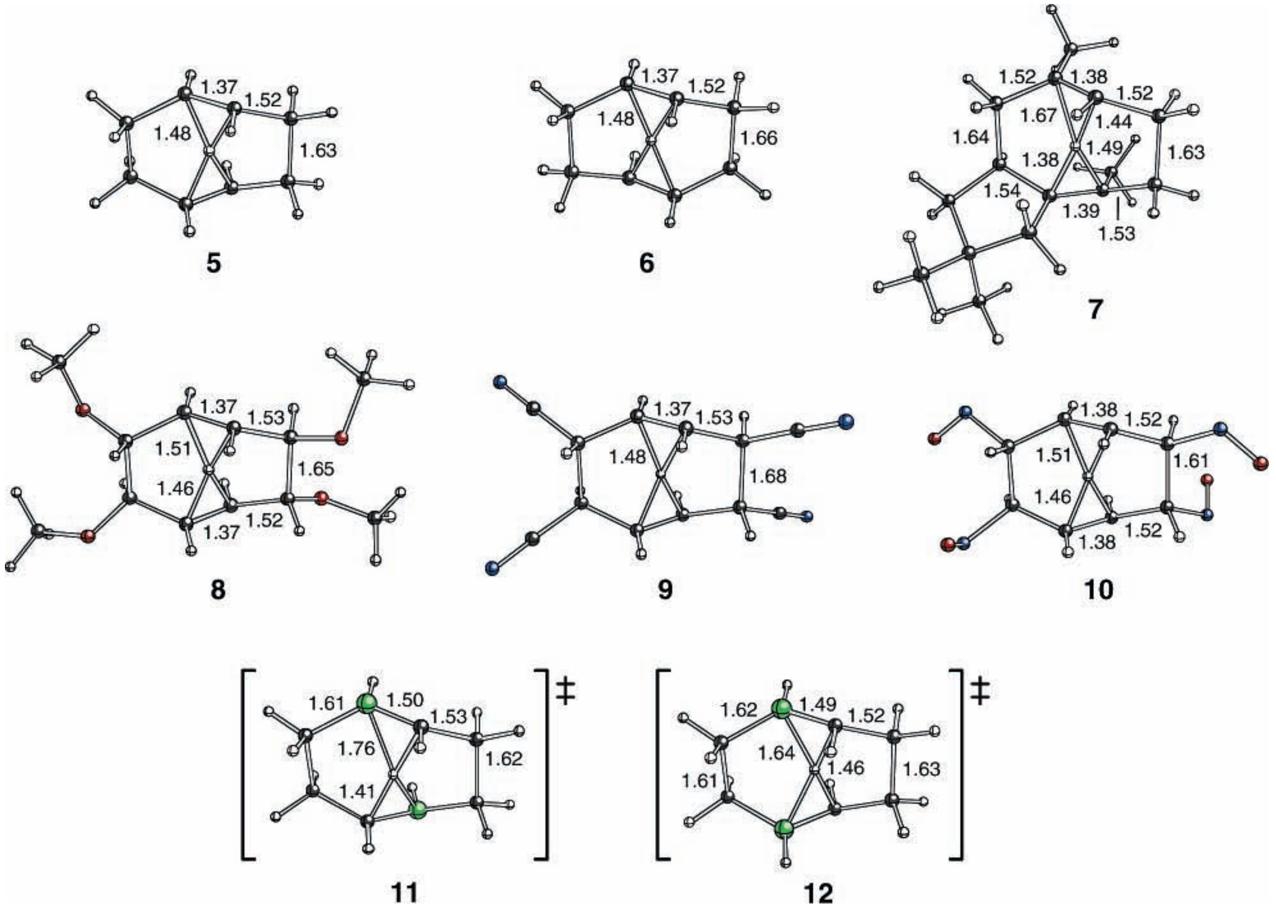


Figure 1. Geometries of structures **5**−**12** optimized at the B3LYP/6-31+G(d,p) level (the geometry shown for structure **10** is that obtained with B3LYP/6-31G(d); see Computations section for details). Selected distances are shown in Å.

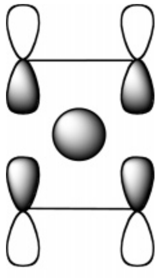
TABLE 1: Calculated Values (B3LYP/6-31G(d)) of 5-Center Bond Indices for Structures 5−12

molecule	5-center bond index
5	−0.0476
6	−0.0462
7	−0.0411[a]
8	−0.0456
9	−0.0465
10	−0.0429
11	−0.0345
12	−0.0304

[a] The index for **7** is based on the geometry optimized with B3LYP/6-31+G(d,p). See Computations section for details.

not only the delocalization of electron density but also charge that promotes the formation of C−C(B)−H−C−C(B) cores with bridging hydrogens.[9]

Let us address now the issue of 5c−4e bonding in these molecules. Before discussing our calculated values of multicenter bond indices for **5**−**12**, however, it is useful to remind readers briefly of the results of our previous study[16] in which a simple analytical model of multicenter bonding was introduced. In that study it was found that bond indices can be used not only to detect the existence of multicenter bonding in a molecule and to characterize its "strength", but also, as claimed in previous studies,[31,32] to obtain important chemically relevant information from the sign of these indices. Thus, for example, a positive 3-center index is observed for 3c−2e bonding whereas a negative 3-center index is observed for 3c−4e bonding. In the case of 5c−4e bonding, with the bonding topology anticipated for cations such as **5** and exemplified by the delocalized molecular orbital shown schematically as **14**, the analytical model yields an idealized value of the 5-center bond index equal to −0.060.



14

The computed 5-center indices for structures **5**−**12** are shown in Table 1. Cations **5**−**10** all have negative 5-center indices between −0.04 and −0.05. Although these values are smaller than the idealized value, the difference is not very dramatic and probably can be attributed to the simplicity of the analytical model, which assumes that each atom contributes to bonding through just one orbital. Thus the anticipated existence of 5c−4e bonding in cations such as **5**−**10**[11] is strongly corroborated by our GPA calculations.

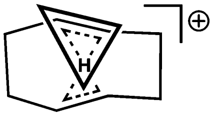
The existence of 5c−4e bonding is also indicated for transition structures **11** and **12**, although the values of their 5-center indices are a bit smaller than in molecules **5**−**10** (Table 1). This decrease in magnitude is, however, consistent with the changes in geometry observed upon replacement of C by B (i.e., B- - -H distances that are considerably longer than the C- - -H distances in **5**−**10**).

TABLE 2: Calculated Values (B3LYP/6-31G(d)) of 3-Center Bond Indices for Structures 5−12

molecule	3-center bond index
5	0.275
6	0.281
7[b]	0.226[a]
	0.247
8[b]	0.284
	0.261
9	0.274
10	0.267
11	0.194
12	0.223

[a] The index for **7** is based on the geometry optimized with B3LYP/6-31+G(d,p). See Computations section for details. [b] Reduction of the symmetry of the 5-center core for molecules 7 and 8, results in the nonequivalence of C−H−C subfragments and this nonequivalence is reflected also in the values of 3-center bond indices.

CHART 3



Multicenter bonding in molecules **5**−**12** is not, however, limited to 5c−4e bonds. GPA analysis reveals also the existence of nonnegligible 3-center bonding in the C−H−C fragments of cations **5**−**10** highlighted in Chart 3. The values of these indices are summarized in Table 2.

The values of such 3-center indices consistently range from 0.223 to 0.284, which can be compared with the idealized value of 0.444 suggested by the analytical model for cyclic 3c−2e bonding.[16] The values for structures **5**−**10** are likely lower than the idealized value because these substructures are part of larger 5-center arrays that are composed of two overlapping 3-center substructures (i.e., the hydrogen atom of each 3-center array is shared with the other).

Although the calculated bond indices from Table 1 seem to suggest that boron substitution does reduce 5c−4e bonding (see structures **11** and **12**), GPA analysis still indicates the existence of 3c−2e bonding in these molecules. In both **11** and **12**, 3-center bonding is again present in substructures of the type indicated in Chart 3 (which in this case correspond to C−H−B arrays). The computed 3-center indices for **11** and **12** are 0.223 and 0.194, respectively, smaller than those for the C−H−C arrays in **5**−**10** due to the general weakening of multicenter bonding upon boron-for-carbon replacements (as described above in regards to geometries and 5-center indices).

Conclusions

The GPA results described above, along with geometric considerations, clearly indicate that the C−C−H−C−C cores of cations such as **5**−**10** feature delocalized 5c−4e bonding. Moreover, the same methodology also indicates that 3c−2e bonding in C−H−C substructures contributes to the bonding in the larger C−C−H−C−C cores. Substitution of carbon by boron was found to slightly reduce the “strength” of multicenter bonding. This and several previous studies[17,22,23] indicate that generalized population analysis is a useful tool for characterizing multicenter bonding in nonclassical structures.

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Supporting Information Available: Coordinates and energies for structures **8**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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