Which Electron Count Rules Are Needed for Four-Center Three-Dimensional Aromaticity?

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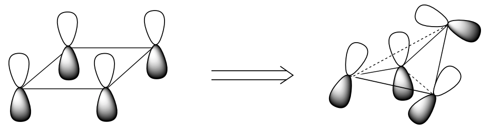
Abstract: A series of charged and neutral four-center *n*-electron (4c – *n*e, $n = 1-4$) molecules based on the adamantane framework, but which include combinations of boron, nitrogen, and phosphorus atoms at bridgehead positions, were studied computationally at the B3LYP/6–31G* level of density functional theory (DFT). The three-dimensional aromaticity, observed earlier for the 1,3,5,7-bisdehydroadamantane dication (**1**), is found to be general for 4c – 2e electron systems. The degree of electron delocalization, evaluated by energetic, geometric, and various magnetic criteria, is quite independent of the molecular symmetry (point groups vary from T_d to C_s), the degeneracy of the orbitals, the molecular charges, and the nature of the atoms participating in the delocalized bonding. Although the multiple positive (e.g., in **1** and some of the heteroatom systems) and multiple negative charges are strongly repulsive, the rigid adamantane frameworks help hold the bridgehead atoms within bonding distances with the fewer available electrons. The corresponding 4c – 1e doublets are approximately half as aromatic as the 4c – 2e singlets based on the same criteria. However, the three-electron systems may either adopt distorted but still four-center delocalized structures, or alternative 3c – 2e two-dimensional arrangements in which the fourth bridgehead atom is more distant. There is no need to derive special rules for each point group for 4c – *n*e systems. Although the three-dimensional stabilization is computed to be quite appreciable, ranging between 10 and 50 kcal mol^{-1}, this delocalization energy is generally not sufficient to overcome distortion due to strain in higher homologues of **1** and in analogous noncage systems. Among the various 4c – 2e homoadamantanedehydro dications studied, only the 1,8-dehydrohomoadamandiyl-3,6-dication forms a three-dimensional aromatic system.

Keywords: aromaticity · boron · density funtional calculations · heteroadamantanes · nucleus-independent chemical shifts

Introduction

Aromaticity, a manifestation of cyclic electron delocalization,[1] is not confined to two dimensions; many species exhibit three-dimensional aromaticity.[2] This paper is concerned with basic cases that involve the interaction of four orbitals in essentially tetrahedral symmetry. The most basic system that might exhibit such delocalization, H_4^{2+} (T_d), is not bound at adequately high levels of ab initio theory.[3] However, four-center two-electron (4c – 2e) bonding was demonstrated for both Li_4^{2+} and Na_4^{2+} in T_d symmetry,[4] although the dissociation barriers are small due to the large Coulomb repulsion. Indeed, otherwise unsupported species like $(CH_3)_4^{2+}$ are not bound.[4]

Four-center bonding can be realized in tetrahedral or quasitetrahedral systems, provided a molecular framework helps hold the interacting atoms together. For example, *cyclo*-$(CH)_4^{2+}$ favors D_{2d} over D_{4h} symmetry energetically by 8.1 kcal mol^{-1}.[5]



$C_4H_4^{2+}$, D_{4h} $C_4H_4^{2+}$, D_{2d}

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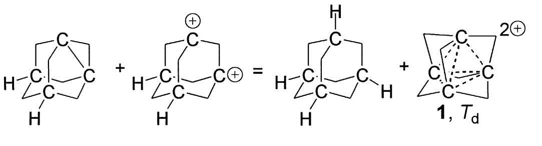
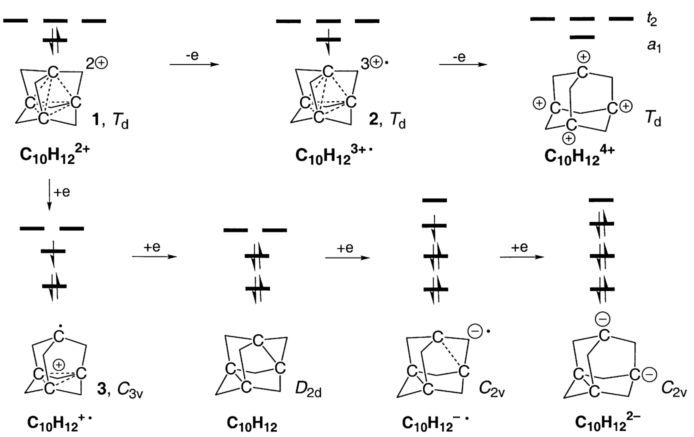
The anticipated Hückel planar two-dimensional $4n+2\pi$-electron D_{4h} arrangement is not even a minimum.[6] The extra 1,3-overlap on both faces of the D_{2d} ring, which points towards a T_d-like arrangement, confers extra stability.[6] Experimentally, tetrahedral 4c–2e delocalization was first realized in the 1,3,5,7-bisdehydroadamantane dication **1** (Scheme 1).[7, 8, 9] The T_d structure of **1** was established by comparing the experimental NMR chemical shifts with those computed ab initio and the stabilization energy of **1** computed for Equation (1) is quite large ($-47.0\ \text{kcal mol}^{-1}$ at MINDO/3). More recent high-level theoretical studies have further confirmed the three-dimensional aromaticity of **1**.[9, 10]



(1)

$\Delta E = -35.1\ \text{kcal mol}^{-1}$

The relevant molecular orbital patterns in **1**[6, 7] and its analogues with more or with fewer electrons are shown in Scheme 1. Inside-cage interactions between the four bridgehead atomic orbitals in T_d symmetry result in a bonding a_1 and an antibonding t_2 set of molecular orbitals; only the favorable a_1 orbital is occupied in **1**.



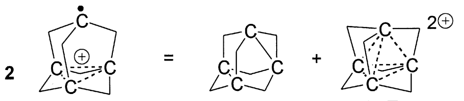
Scheme 1. Orbital occupancies resulting from the sequential removal or addition of electrons to **1**.

Abstract in Ukrainian:

Обчислювальними методами, на рівні B3LYP/6-31G* теорії функціоналу густини (ТФГ), проведені дослідження ряду заряджених і нейтральних молекул, що містять чотирьохцентрову n-електронну систему (4c-ne, n=1-4) та базуються на адамантановому каркасі, який включає комбінацію атомів бору, азоту і фосфору у вузлових положеннях. Знайдено, що тривимірна (3D) ароматичність, що спостерігалась раніше в 1,3,5,7-бісдегідроадамантильному катіоні (**1**), є загальною властивістю 4c-ne електронних систем. Рівень делокалізації, визначений за енергетичними, геометричними та різноманітними магнітними критеріями, виявився досить незалежним від симетрії молекули (групи симетрій від T_d до C_s), виродженості орбіталей, заряду молекули та природи атомів, що приймають участь у делокалізованому зв’язку. Хоч в багатозарядних молекулах з позитивними (як в **1** і деяких гетероатомних молекулах) і негативними зарядами спостерігається значне відштовхування, жорсткий адамантановий каркас допомогає утримувати вузлові атоми на відстанях, що забезпечують зв’язування з меншою кількістю електронів. Відповідні 4c-1e дублети приблизно вдвічі менш ароматичні ніж 4c-2e синглети на основі тих же критеріїв. Проте, триелектронні системи можуть або відповідати деформованим, але ще чотирицентровим делокалізованим структурам, або альтернативним 4c-ne 2D системам, в яких четвертий вузловий атом знаходиться на більшій відстані. Для 4c-ne 3D ароматичних систем немає необхідності розробляти окремі правила для кожної групи симетрії молекули. Хоч обчислена енергія 3D стабілізації є досить значною і коливається в межах від 10 до 50 ккал/моль, вона недостатня для компенсації енергії напруження, що виникає в циклічних гомологах **1** та в аналогічних некаркасних системах. Серед досліджених різноманітних 4c-2e гомоадамантанових дегідродикатіонів лише 1,8-дегідроадамантил-3,6-дикатіон утворює 3D-ароматичну систему.

Hence, the single-electron occupancy in the 1,3,5,7-bisdehydroadamantane trication **2** also should be favorable. However, partial occupation of the triply degenerate t_2 orbital of **1** (as shown by the four cases at the bottom of Scheme 1) leads to Jahn–Teller distortion.[11] The energetic and structural changes when electrons are added to **1** sequentially were studied recently by Chan and Arnold.[10] With one more electron added to **1**, the 1,3,5,7-bisdehydro-adamantane radical cation (**3**) favors a C_{3v} structure with a tris-homoaromatic cation unit (at C^3, C^5, C^7) and a separated radical center (at C^1). If two electrons are added to **1**, neutral 1,3,5,7-bisdehydroadamantane $C_{10}H_{12}$ results; this has two localized three-membered rings and the symmetry is lowered from T_d to D_{2d}. With yet another electron, the 1,3,5,7-bisdehydroadamantane radical anion $C_{10}H_{12}^-$ prefers C_{2v} symmetry and has one localized three-membered ring and spin/charge located on the remaining two bridgehead carbons. The 1,3,5,7-bisdehydroadamantane dianion $C_{10}H_{12}^{2-}$, which has four more electrons than **1**, was shown to have two localized carbanion moieties. Thus, the addition of electrons to **1** results in localized arrangements because of the occupied antibonding orbitals (t_2 for **1**). However, one *cannot* expect that the "*..next member of this series would contain eight delocalized electrons*".[10] The 1,3,5,7-adamantetrayl tetraanion $C_{10}H_{12}^{4-}$ and, more realistically, its neutral lithium salt, $C_{10}H_{12}Li_4$, have fully occupied sets of relevant a_1 and t_2 orbitals and prefer *localized* structures in T_d symmetry. Such 4c–8e occupancy is exemplified by the classical molecule, urotropine $C_6N_4H_{12}$ (isoelectronic with $C_{10}H_{12}^{4-}$), which was the first cage molecule to be recognized (1895).[12] Eight *delocalized* electrons cannot be expected in the adamantane framework.

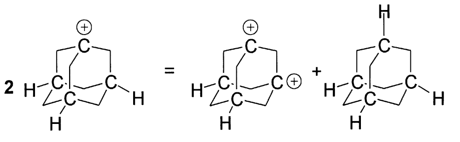
We consider bonding rules for four-center three-dimensional aromaticity in this paper and clarify other statements[10] we feel are misleading. We also take issue with the energetic analysis, based on Equation (2) which led Chan and Arnold to conclude that **1** "*..is highly unstable compared to the radical cation (3).*" While being highly endothermic, Equation (2) is not balanced coulombically and includes a highly strained[13] 1,3,5,7-bisdehydroadamantane as a reference compound. This influence can be shown by Equation (3), which models the Coulomb effect, and by Equation (4), which evaluates the "extra strain" due to the presence of two cyclopropane rings in the same molecule.



3, C_{3v} 1, T_d

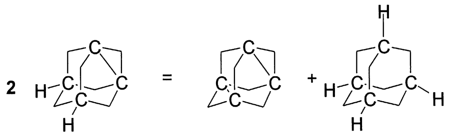
(2)

ΔE = + 135.6 kcal mol^{-1}
(at B3LYP/6-31G*)
+ 131 kcal mol^{-1}
(at B3PW91/6-31G*)[10]



(3)

ΔE = + 131.0 kcal mol^{-1}



(4)

ΔE = + 39.9 kcal mol^{-1}

Abstract in German: *Aufbauend auf dem Adamantangerüst wurde eine Serie geladener und neutraler Vierzentren-n-Elektronensystemen (4c–ne, n = 1–4), die auch Kombinationen von Bor-, Stickstoff- und Phosphoratomen in den Brückenkopfpositionen enthalten, rechnerisch auf dem B3LYP/6-31G* Dichtefunktionaltheorie (DFT)-Niveau untersucht. Dreidimensionale Aromatizität, wie sie schon früher für das 1,3,5,7-Bisdehydroadamantyldikation (**1**) gefunden wurde, hat allgemeine Gültigkeit für 4c–2e-Systeme. Der Grad der Elektronendelokalisation, quantifiziert durch energetische, geometrische und verschiedene magnetische Kriterien, ist weitgehend unabhängig von der molekularen Symmetrie (die untersuchten Punktgruppen variierten von T_d bis C_s), der Entartung der Orbitale, der molekularen Ladungen und der Natur der in den delokalisierten Bindungen involvierten Atome. Obwohl mehrfach positive (z. B. in **1** und einigen heterosubstituierten Systemen) und negative Ladungen sich stark abstoßen, hilft das rigide Adamantangrüst dabei, die Brückenkopfatome trotz weniger zu Verfügung stehender Elektronen auf Bindungsabstand zusammenzuhalten. Basierend auf den gleichen Kriterien sind die entsprechenden 4c–1e Dublettzustände etwa halb so aromatisch wie die 4c–2e Singuletts. Allerdings nehmen die Dreielektronensysteme entweder verzerrte, aber dennoch delokalisierte, oder alternative 3c–2e 2D-Strukturen an, in denen das vierte Brückenkopfatom weiter entfernt ist. Es besteht keine Notwendigkeit, für jede Punktgruppe besondere Regeln für 4c–ne-Systeme aufzustellen. Obwohl die 3D-Stabilisierung mit 10 bis 50 kcal/mol rechnerisch ziemlich groß ist, ist diese Delokalisation im allgemeinen nicht ausreichend, um die aufgrund von Ringspannung verursachten Verzerrungen in höheren Homologen von **1** und analogen nicht-käfigartigen Verbindungen zu kompensieren. Von allen untersuchten 4c–2e Homoadamantyldehydrodikationen bildet nur das 1,8-Dehydroadamadiyl-3,6-dikation ein 3D-aromatisches System.*

We argue that when these very large total Coulomb and strain imbalances [which total +170.9 kcal mol^{-1}, Eqs. (3) and (4)] are taken into account, **1** is considerably more stabilized than **3** (35.3 kcal mol^{-1}) from the internal electron delocalization.

Our computational studies include a large set of 4c–*n*e (*n* = 1–4) molecules based on the adamantane framework with boron, nitrogen, and phosphorus heteroatoms at the bridgehead positions. This allows us, inter alia, to model Equation (2) isoelectronically with neutral systems which avoid the Coulombic imbalance. We also report on a series of higher homologues of **1** probing the scope of 4c–2e bonding in the larger dehydrohomoadamantane dications.

Computational Methods

Geometries were fully optimized at the HF/6–31G* and B3LYP/6–31G* levels of theory (UHF and UB3LYP for open-shell species) as implemented in the Gaussian 94[14] and Gaussian 98[15] program packages. Harmonic vibrational frequencies were computed at the HF level to ascertain the nature of the stationary points. All structures discussed below are energy minima without imaginary frequencies (NIMAG = 0), unless noted otherwise. As we are using mostly isodesmic or homodesmotic equations,[16] systematic errors should largely cancel,[17] and ZPVE corrections were not applied in energy evaluations. Nucleus-independent chemical shifts (NICS),[18] based on the magnetic shieldings computed at the centers of ring or of cage systems, were computed with the continuous set of gauge transformations (CSGT) method at B3LYP/6–31G* level as implemented in the Gaussian 98 program. Like the ^{3}He chemical shifts inside fullerenes (He@C$_{60}$),[19] the negative (upfield) NICS values indicate electron delocalization (in our case three-dimensional aromaticity).

Results and Discussion

The parent systems: Large aromatic stabilization energies [ASE, −35.1 kcal mol^{-1}, Eq. (1)] and large negative nucleus-independent chemical shifts (NICS) values (−43.0 ppm, Table 1) at the geometric center clearly indicate the aromatic nature of **1**; this is consistent with our earlier report which used the gauge-independant atomic orbital (GIAO) method.[20] Removal or addition of an electron from or to **1** leads to the radical trication **2** and the radical cation **3**, respectively. How does the change in electron occupancy affect the aromaticity? While **2** is a minimum in T_d symmetry (Figure 1), **3** prefers C_{3v} symmetry owing to Jahn–Teller distortion. Bond lengths between bridgehead carbon atoms are only slightly elongated in **2** relative to **1** (2.16 vs. 2.10 Å). The HOMO of **1** and the SOMO of **2** are similar (Figure 1) and describe the 4c bonding between the bridgehead carbon atoms: 4c–2e in **1** and 4c–1e in **2**. In contrast, the SOMO of **3** has C_{3v} symmetry and describes the antibonding interaction between the basal, positively charged CCC unit and the apex carbon radical. The highest doubly occupied orbital represents the apex carbon, which is highly pyramidalized and does not participate significantly in this three-dimensional bonding: three C–C bonds are elongated (2.35 Å) and another three are shortened (1.98 Å).

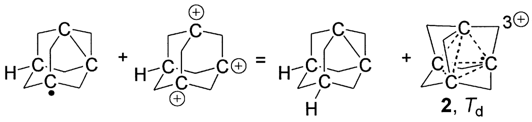
The difference in the electronic structures of **1**–**3** result in changes of the NICS values (Table 1) computed in the center

Table 1. Energies and NICS values of structures **1**–**33** at the B3LYP/6–31G* level.

	Formula	Electronic system	Point group	B3LYP/6–31G* energy [au]	NICS [ppm] mid-point[a]	NICS [ppm] center three-membered rings[b]
1	$C_{10}H_{12}{}^{2+}$	4c–2e	T_d	–387.50908	–43.0	–37.5
2	$C_{10}H_{12}{}^{\cdot 3+}$	4c–1e	T_d	–386.78011	–26.0	–21.8
3	$C_{10}H_{12}{}^{+\cdot}$	4c–2e+1e	C_{3v}	–387.90459	–30.2	–42.5; –16.5
4	$C_9H_{12}B^+$	4c–2e	C_{3v}	–374.74020	–37.8	–13.7, –13.4
5	$C_9H_{12}B^{\cdot 2+}$	4c–1e	C_{3v}	–374.25448	–22.2	–19.8, –18.4
6	$C_9H_{12}B^{\cdot}$	4c–3e	C_s	–374.91189	–14.6	–7.9, –19.2, –9.2
7	$C_8H_{12}B_2$	4c–2e	C_{2v}	–361.75815	–34.8	–29.9, –28.6
8	$C_8H_{12}B_2{}^{\cdot +}$	4c–1e	C_{2v}	–361.49384	–20.3	–17.9, –16.2
9	$C_8H_{12}B_2{}^{\cdot -}$	4c–3e	C_{2v}	–361.72798	–16.6	–
		3c–2e+1e	C_s	–361.73422	–23.3	–11.8, –18.8, –14.1, –31.4
10	$C_7H_{12}B_3{}^-$	4c–2e	C_{3v}	–348.57713	–33.2	–29.2, –25.8
11	$C_7H_{12}B_3{}^{\cdot}$	4c–1e	C_{3v}	–348.52331	–19.2	–16.9, –15.1
12	$C_7H_{12}B_3{}^{\cdot 2-}$	3c–2e+1e	C_{3v}	–348.34596	–22.9	–17.1, –30.5
13	$C_6H_{12}B_4{}^{2-}$	4c–2e	T_d	–335.20564	–33.3	–28.1
14	$C_6H_{12}B_4{}^{\cdot -}$	4c–1e	T_d	–335.35426	–19.6	–16.8
15	$C_6H_{12}B_4{}^{\cdot 3-}$	4c–3e	C_{2v}[c]	–334.74699	–8.4	–
		3c–2e+1e	C_{3v}	–334.77174	–17.2	–13.5, –1.4, –31.8, –10.1
16	$C_7H_{12}B_2N^+$	4c–2e	C_s	–378.15995	–29.3	–26.7, –25.8, –22.9
17	$C_7H_{12}B_2N^{\cdot 2+}$	4c–1e	C_s	–377.67248	–13.2	–11.2, –10.3, –9.1
18	$C_7H_{12}B_2N^{\cdot}$	3c–1e+2e	C_s	–378.37673	–20.6	–16.0, –16.2, –23.8
19	$C_7H_{12}B_2P^+$	4c–2e	C_s	–664.81307	–25.5	–24.6, –23.5, –19.3
20	$C_7H_{12}B_2P^{\cdot 2+}$	4c–1e	C_s	–664.32641	–10.0	–9.0, –7.6, –6.1
21	$C_7H_{12}B_2P^{\cdot}$	3c–1e+2e	C_s	–665.02350	–16.6	–13.8, –13.3, –19.9
22	$C_6H_{12}B_3N$	4c–2e	C_{3v}	–365.18253	–24.5	–22.3, –19.3
23	$C_6H_{12}B_3N^{\cdot +}$	4c–1e	C_{3v}	–364.90724	–11.1	–9.2, –8.1
24	$C_6H_{12}B_3N^{\cdot -}$	3c–1e+2e	C_{3v}	–365.18795	–17.4	–12.9, –22.4
25	$C_6H_{12}B_3P$	4c–2e	C_{3v}	–651.83588	–20.5	–19.3, –15.7
26	$C_6H_{12}B_3P^{\cdot +}$	4c–1e	C_{3v}	–651.54815	–7.8	–6.6, –5.6
27	$C_6H_{12}B_3P^{\cdot -}$	3c–1e+2e	C_{3v}	–651.84008	–15.9	–11.8, –19.8
28	$C_{11}H_{14}{}^{2+}$	4c–2e	C_2	–426.82165	–33.2	–24.7, –32.2
29	$C_{12}H_{16}{}^{2+}$	2c–2e	D_2	–466.11702	–26.5	–22.7
30	$C_{13}H_{18}{}^{2+}$	3c2e+1e	C_3	–505.48584	–23.5	–35.6, –15.4
31	$C_{14}H_{20}{}^{2+}$	2c–2e	C_2	–544.78010	–11.3	–14.1
32	$C_{15}H_{22}{}^{2+}$	2c–2e	C_2	–583.11210	–6.0	–7.7
33	$C_{16}H_{24}{}^{2+}$	2c–2e	C_2	–623.42148	–1.8	–2.8

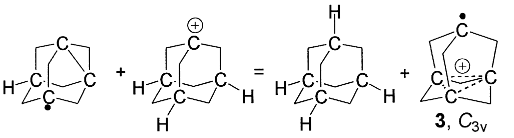
[a] Geometrical center formed by four bridgehead atoms. [b] The NICS values are given in decreasing order of sum of the atomic weights of atoms in different 3-membered rings. [c] NIMAG = 1 at UB3LYP/6–31G*.

of the molecule and in the center of the three-membered rings formed by the bridgehead carbons. The NICS values in the centers of **1** (–43.0) and **2** (–26.0) are more negative than those at the centers of three-membered rings formed by quaternary carbons (–37.5 and –21.8, respectively). In **3**, the largest negative NICS was found in the center of one of the three-membered rings (–42.5); the value in the geometric center of the molecule is less negative (–30.2). From NICS comparisons we find that **1** is approximately twice as aromatic as **2**; this is consistent with ASE evaluations from Equations (1) and (5). The removal of an electron from the 4c–2e system (**1**) does not perturb the overall delocalization: a tetrahedral 4c–1e system results in **2** with reduced aromaticity. In contrast, addition of one electron to **1** leads to partial occupancy. As shown by Chan and Arnold,[10] the two-dimensional 3c–2e tris-homoaromatic[21] moiety and an additional radical center at the apical carbon form, and we denote this situation as 3c–2e+1e. Correspondingly, the ASE computed based on Equation (6) is also half of that of **1** [Eq. (1)].



(5)

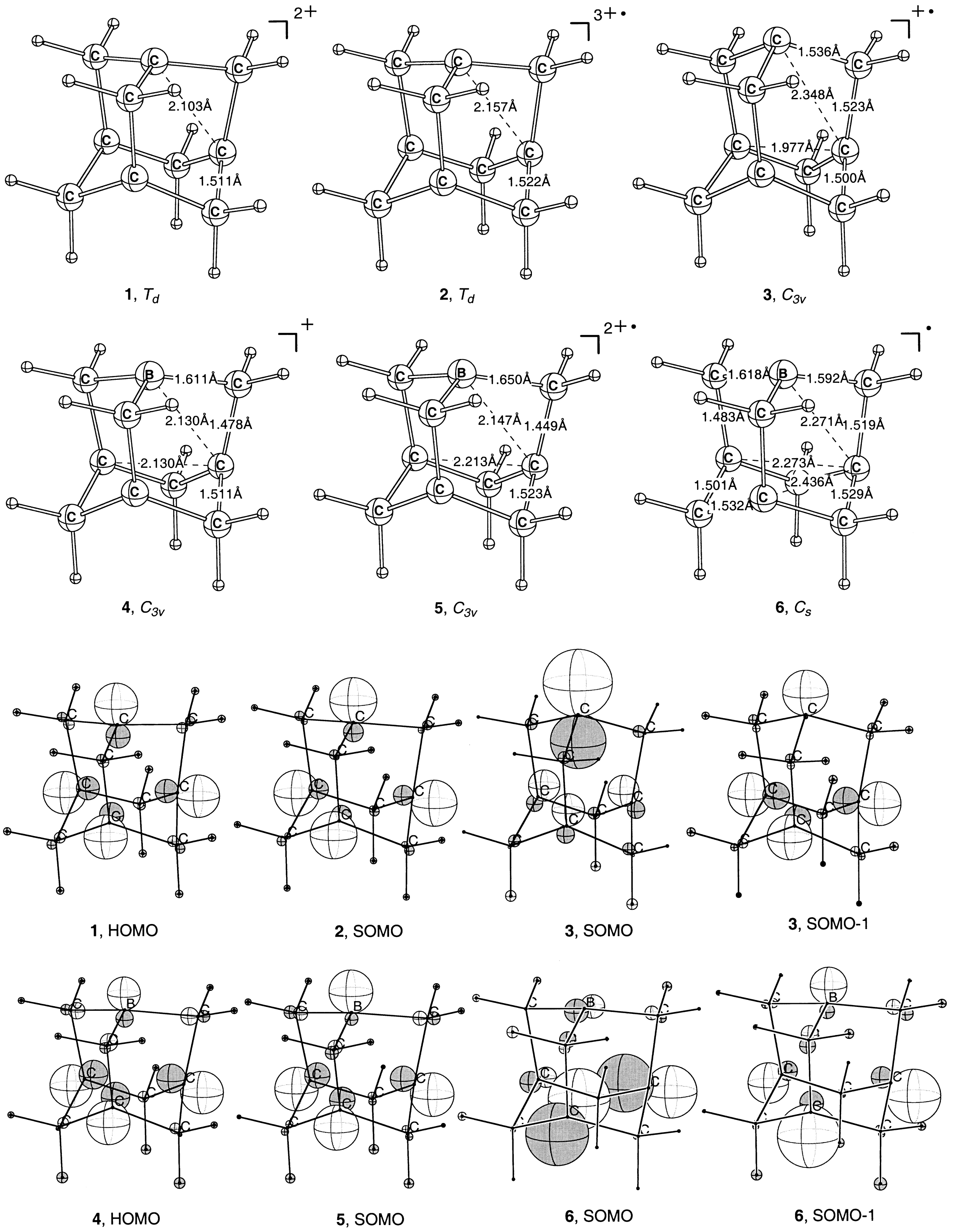
ΔE = -16.8 kcal mol^{-1}



(6)

ΔE = -16.7 kcal mol^{-1}

On this basis and the result from Equations (2)–(4), we disagree with the earlier claim of Chan and Arnold[10] that the stability of **3** is higher than that of **1**. Their conclusion was based on Equation (2) which compared **1** and **3** directly, but without proper charge and strain compensation. Coulomb repulsion in multiply charged species is very large and must be balanced in an energy evaluation by a reference molecule with the same charge. In our Equations (1), (5), and (6), the charge is accounted for with the inclusion of the corresponding di- or trication reference molecules. While only "localized" reference compounds are used, our calculated ASEs show the change of aromaticity when the number of electrons in the 4c system is varied. Instead of using Equation (2), compounds **1** and **3** can be compared *directly*, by means of Equation (7) [just



1, T_d **2**, T_d **3**, C_{3v}

4, C_{3v} **5**, C_{3v} **6**, C_s

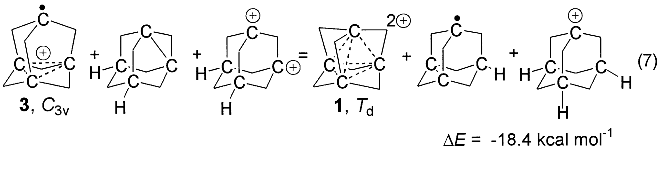
1, HOMO **2**, SOMO **3**, SOMO **3**, SOMO-1

4, HOMO **5**, SOMO **6**, SOMO **6**, SOMO-1

Figure 1. B3LYP/6–31G* optimized geometries and important orbitals of structures **1**–**6**.

the difference between Eqs. (1) and (4)], which takes charge compensation into account and is balanced with respect to strain.

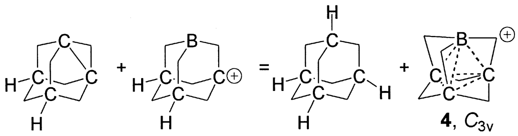
The exothermicity of Equation (7) clearly shows that the 4c–2e system in **1** is more stable than the 3c–2e tris-



ΔE = -18.4 kcal mol^{-1}

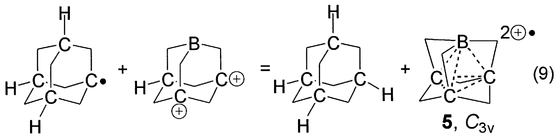
homoaromatic system in **3**. In supporting their assertion that the reverse is true Chan and Arnold argue[10] that "*the effectiveness of delocalization in **1** is reduced*" because of the longer C–C bond lengths and because "*the total overlap between the bridgehead atoms in **1** is only half the magnitude between the bridgehead atoms in the cyclohexyl moiety of **3***". While we agree that each bonding interaction involving the three bridgehead atoms in **3** is somewhat larger in magnitude than each interaction in **1** {Wiberg bond indices[22] (WBI) are 0.28 in **1** vs. 0.38 in **3** from our ab initio NBO[23] analysis}, there are twice as many bonding interactions in **1** as there are in **3**. The effective total internal bonding in **1** leads to higher stabilization than in **3**.

Boraadamantanes: Can our findings about the aromaticity of **1**–**3** be applied to other heteroatomic systems with lower charges? Replacing one of the tertiary cationic carbons in **1**–**3** by a neutral boron atom gives compounds **4**–**6** (Figure 1). Equations (8) and (9) show that the behavior of **4** and **5** is quite comparable with that of **1** and **2**, that is, the 4c–2e system in **4** is more aromatic than the 4c–1e system in **5**. The NICS values in the geometrical centers of **4** –37.8 and **5** –22.2 are higher than in the middle of any of the three-membered rings formed by bridgehead atoms.


(8)

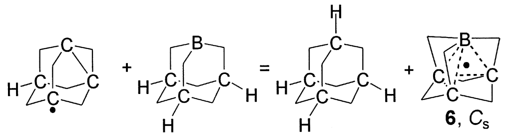
4, C_{3v}

ΔE = -32.9 kcal mol^{-1}


(9)

5, C_{3v}

ΔE = -22.4 kcal mol^{-1}

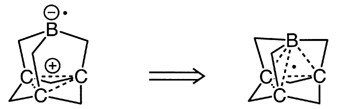

(10)

6, C_s

ΔE = -10.3 kcal mol^{-1}

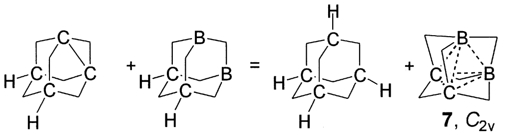
The changes in ASE and NICS also are reflected in the corresponding geometries: the distances between bridgeheads (Figure 1) are elongated in **5** (C–C 2.21 Å and C–B 2.15 Å) relative to **4** (C–C and C–B 2.13 Å), that is, the differences in geometries of the monobora-adamantane 4c–2e (**4**) and 4c–1e (**5**) systems are similar to those of the *all*-carbon cases (**1** and **2**). However, the situation with the three-electron systems is quite different. Reflecting the differences in electron delocalization, structure **6** is a minimum in C_s rather than in C_{3v} symmetry found for isoelectronic **3**.

The SOMO of **6** (Figure 1) mainly describes the antibonding interactions between two bridgehead carbons; as a consequence, the critical C–C distances increase to 2.27 Å and 2.44 Å. The *doubly* occupied C_{3v}-like SOMO-1 of **6** shows substantial contributions of *all* bridgehead atoms as also observed in **4** and **5**. The NICS at the centers of *two* CCB rings of **6** (–19.2) are more negative than those in the center of remaining CCB (–9.2) and CCC (–7.9) moieties. This provides strong evidence for three-dimensional delocalization in the 4c–3e system of **6**; this is due to the large contribution of the doubly occupied HOMO to the three-dimensional bonding interactions. NBO analysis shows five of the bonding interactions between all bridgehead atoms to be comparable (WBI = 0.15–0.22) and to be reduced only for the one long C–C bond (WBI = 0.03). The ASE values show that the aromaticity of **6** [Eq. (10)] is approximately half of that in **5** [Eq. (9)]. The formation of C_{3v} symmetric **6** with the radical center located on the boron atom (3c–2e+1e system) is hampered by the intramolecular charge separation; hence, this structure favors C_s symmetry with 4c–3e bonding.


3c-2e + 1e
6, C_{3v}

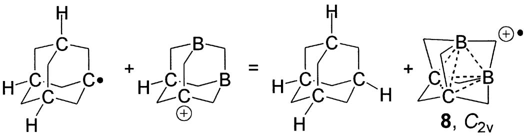
4c-3e
6, C_s

The same trend found in **1**–**3** is exhibited by the dibora-adamantanes **7**–**9** (Figure 2)[24] with 4c–*n*e bonds [Eqs. (11)–(14)]. For instance, **7** (4c–2e) is more aromatic than **8** (4c–1e) based on Equations (11) and (12). Two forms of **9** in C_s and C_{2v} symmetry were located, the latter is less stable by 3.9 kcal mol^{-1}. The NICS value computed in the center of the basal CBB ring of **9** in C_s (–31.4) is much larger than in the geometrical center of the molecule (–23.3). This indicates that **9** prefers 3c–2e+1e bonding, and the C_{2v} structure with 4c–3e bonding is less favorable.


(11)

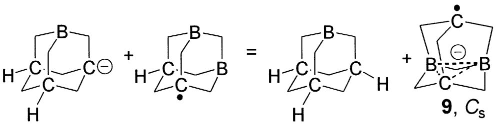
7, C_{2v}

ΔE = -30.0 kcal mol^{-1}


(12)

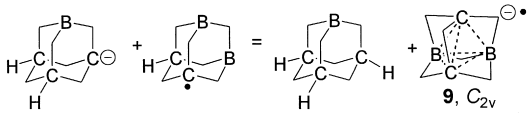
8, C_{2v}

ΔE = -24.8 kcal mol^{-1}


(13)

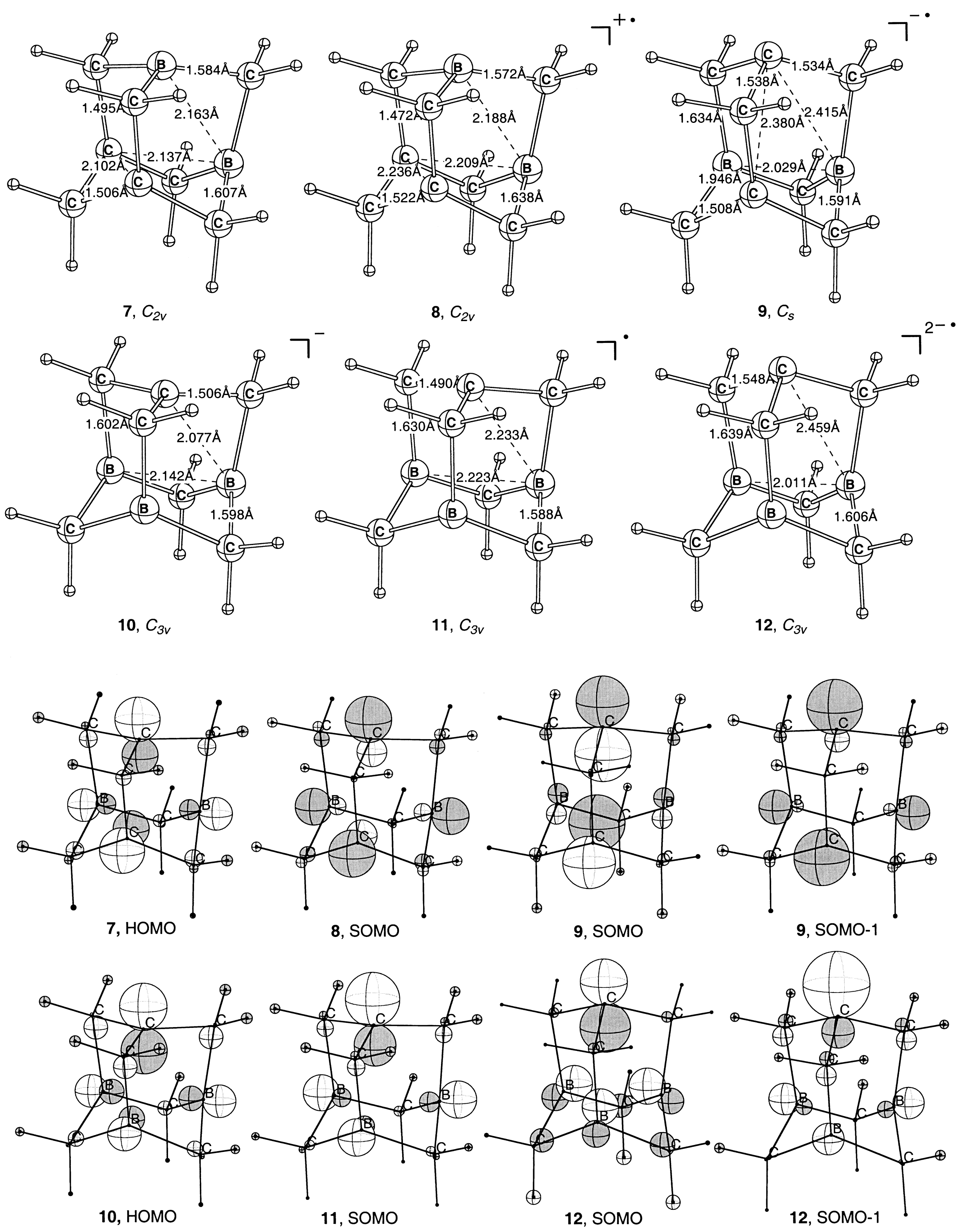
9, C_s

ΔE = -17.4 kcal mol^{-1}


(14)

9, C_{2v}

ΔE = -13.5 kcal mol^{-1}



7, C_{2v} **8**, C_{2v} **9**, C_s

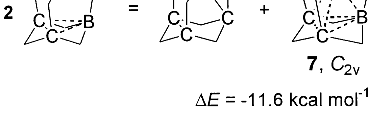
10, C_{3v} **11**, C_{3v} **12**, C_{3v}

7, HOMO **8**, SOMO **9**, SOMO **9**, SOMO-1

10, HOMO **11**, SOMO **12**, SOMO **12**, SOMO-1

Figure 2. B3LYP/6–31G* optimized geometries and important orbitals of structures **7**–**12**.

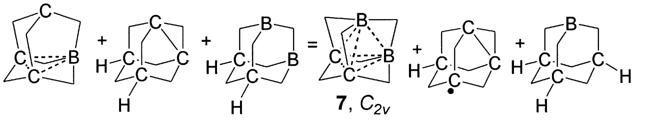
As carbocations structurally are similar to isoelectronic trivalent boron compounds,[25] **7** represents the uncharged analogue of dication **1**. This allows us to model Equation (2)[10] by a coulombically balanced neutral system [Eq. (15)].



7, C_{2v}

ΔE = -11.6 kcal mol^{-1} (15)

Equation 15 is exothermic even without strain correction [see Eq. (4)]! Hence, the greater stability of the 4c–2e **7** over the 3c–2e structure clearly shows again the bias arising from the lack of charge compensation in Equation (2). Strain-compensated Equation (16) reveals that the true stabilization energy of **7** is even higher.



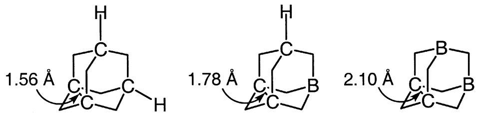
7, C_{2v}

(16)

ΔE = -19.4 kcal mol^{-1}

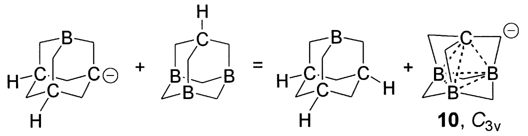
The geometries of **1** and its analogues result from a balance between in-cage through-space σ bonding and the strain imposed on the adamantane framework. Due to lack of "internal" bonding electrons, stable minima in 4c–2e and 4c–1e systems could be achieved at larger bond lengths, than normally found in dehydroadamantanes with 2c–2e bonds (1.56 Å).[26] The stepwise inclusion of boron atoms in the 1,3-dehydroadamantane cage leads to remarkable C–C bond elongations.

In 1,3-dibora-5,7-dehydroadamantane **7** the 2.1 Å distance between bridgehead carbon atoms probably is the longest in noncharged molecules ever reported.[27] The WBI (0.33) for this C–C bond still shows an appreciable bonding interaction.



7

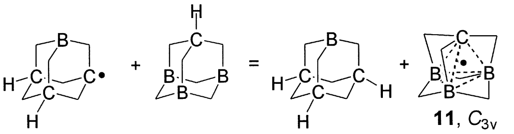
The aromatic character of the triboraadamantanes (**10**–**12**, Figure 2), also parallels those of the parent *all*-carbon cases [Eqs. (17)–(19)]. While **10** and **11** prefer fully delocalized structures with differing magnitudes of aromaticity, the dianion radical **12** prefers the partially localized 3c–2e+1e structure with NICS values of −22.9 at the mid-point and −30.5 in the center of the BBB ring, as found for **3**. The C_{3v}-symmetric SOMO of **12** (Figure 2) clearly reflects this type of delocalization.



10, C_{3v}

(17)

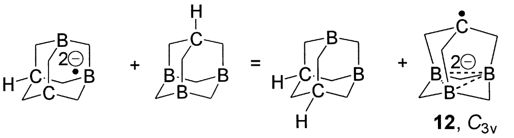
ΔE = -47.2 kcal mol^{-1}



11, C_{3v}

(18)

ΔE = -23.9 kcal mol^{-1}

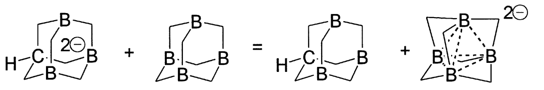


12, C_{3v}

(19)

ΔE = -32.3 kcal mol^{-1}

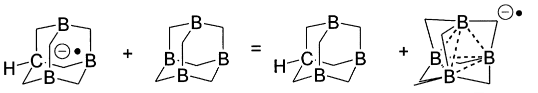
Tetraboraadamananes (**13** and **14**, Figure 3) also behave like the di- and triboraadamantanes **7**, **8**, **10**, and **11** with three-dimensional-electron delocalization [Eqs. (20) and (21)]: compound **13** (4c–2e) is more aromatic than **14** (4c–1e). The trianion radical **15** prefers C_{3v} rather than C_{2v} symmetry [Eqs. (22) and (23)].



13, T_d

(20)

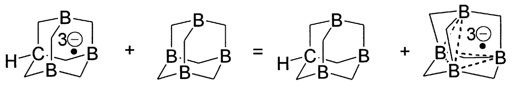
ΔE = -30.3 kcal mol^{-1}



14, T_d

(21)

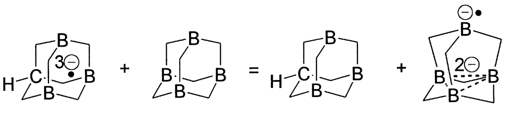
ΔE = -17.5 kcal mol^{-1}



15, C_{2v} (NIMAG=1)

(22)

ΔE = -26.7 kcal mol^{-1}



15, C_{3v}

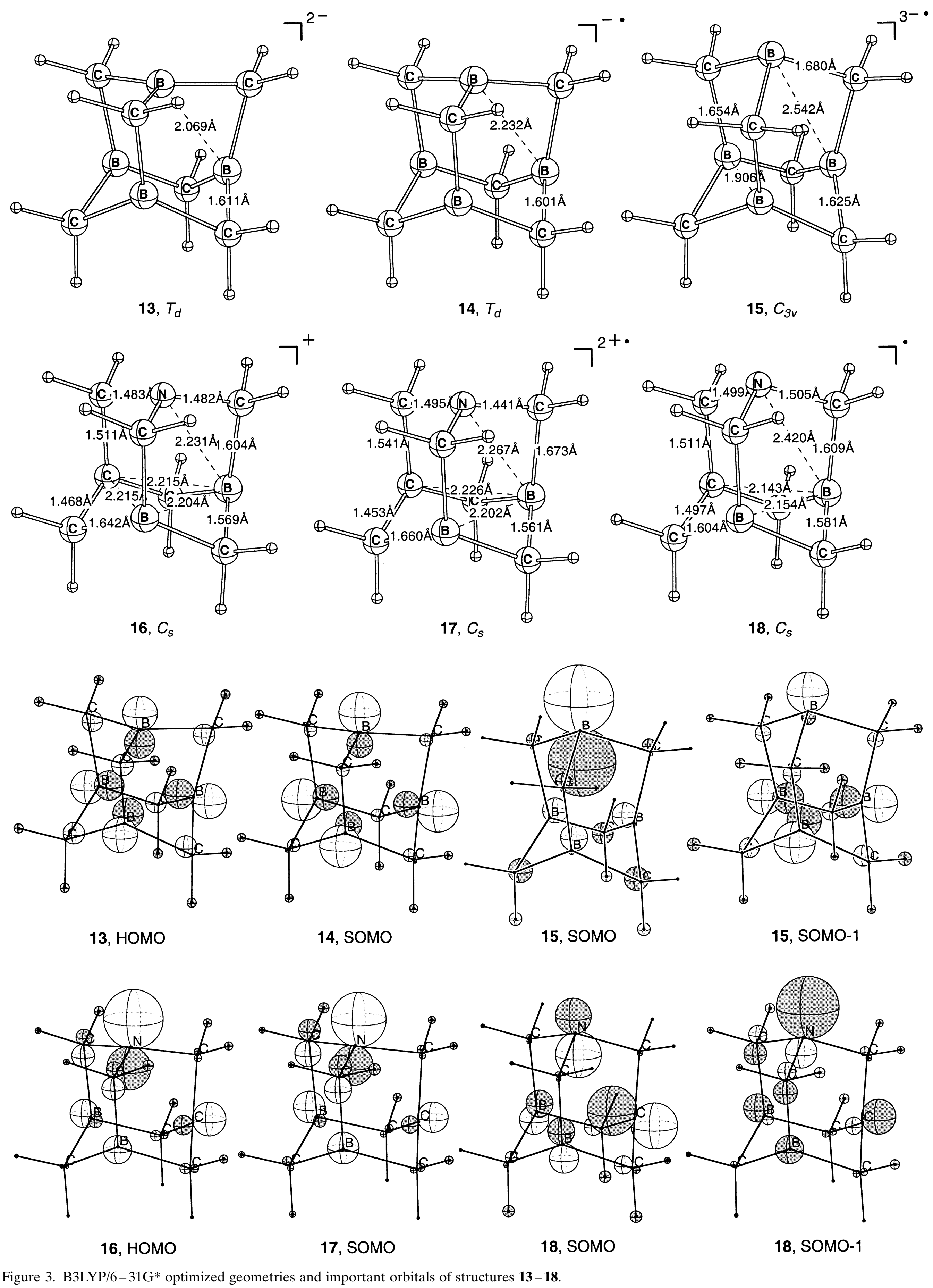
(23)

ΔE = -42.3 kcal mol^{-1}

Compound **15** with C_{2v} symmetry has one negative vibrational mode and one of the BB bonds (2.71 Å) is much longer than the other BB bonds (2.22 and 2.46 Å) due to strong antibonding interactions in the SOMO. In contrast, three B–B distances in C_{3v} symmetrical **15** (Figure 3) are shortened (1.91 Å). The largest negative NICS, computed in the center of the small BBB ring (−31.8), is higher than at the midpoint of the molecule (−17.2) or in the middle of any other BBB ring (−10.1); this is an indication of the 3c–2e+1e bonding in **15**.

Other heteroadamantanes containing boron, nitrogen, and phosphorus: We have also computed structures with nitrogen (**16**–**18** and **22**–**24**) and with phosphorus (**19**–**21** and **25**–**27**) atoms included in the 4c–*n*e systems (Figures 4 and 5). These compounds follow the same pattern described above: 4c–2e systems are more aromatic than either 4c–1e or 4c–3e structures [Eqs. (24)–(29)].

Due to the highly pyramidal character,[28] the contribution of the phosphorus heteroatom to the HOMO in **19** (Figure 4) is small, but increases in the more electron deficient system **20**. These findings are reflected in the ASEs, which are comparable, 22.0 kcal mol^{-1} [Eq. (24)] versus 20.7 kcal mol^{-1} [Eq. (25)] for phosphorus-containing 4c–2e (**19**) and 4c–1e (**20**) structures, respectively. The differences in ASEs between triboraheteroadamantanes **22** and **25** versus **23** and **26** are again similar to the all-carbon case: 4c–2e systems are twice



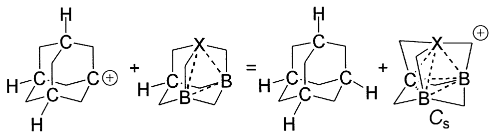
13, T_d **14**, T_d **15**, C_{3v}

16, C_s **17**, C_s **18**, C_s

13, HOMO **14**, SOMO **15**, SOMO **15**, SOMO-1

16, HOMO **17**, SOMO **18**, SOMO **18**, SOMO-1

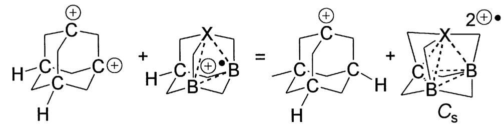
Figure 3. B3LYP/6–31G* optimized geometries and important orbitals of structures **13**–**18**.



(24)

16, X = N, ΔE = -17.0 kcal mol^{-1}

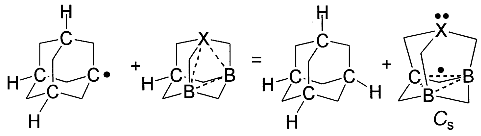
19, X = P, ΔE = -22.0 kcal mol^{-1}



(25)

17, X = N, ΔE = -5.5 kcal mol^{-1}

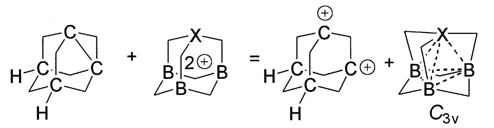
20, X = P, ΔE = -20.7 kcal mol^{-1}



(26)

18, X = N, ΔE = -15.0 kcal mol^{-1}

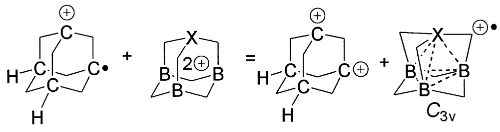
21, X = P, ΔE = -16.8 kcal mol^{-1}



(27)

22, X = N, ΔE = -56.5 kcal mol^{-1}

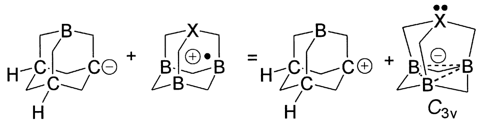
25, X = P, ΔE = -51.3 kcal mol^{-1}



(28)

23, X = N, ΔE = -26.4 kcal mol^{-1}

26, X = P, ΔE = -27.4 kcal mol^{-1}



(29)

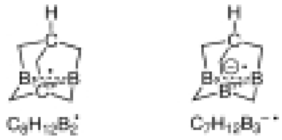
24, X = N, ΔE = -33.0 kcal mol^{-1}

27, X = P, ΔE = -40.9 kcal mol^{-1}

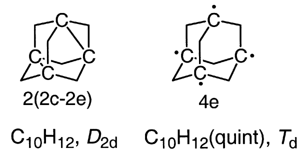
as aromatic as 4c–1e systems. The NICS values in the geometrical center of all these structures are larger than in the middle of any three-membered ring (Table 1).

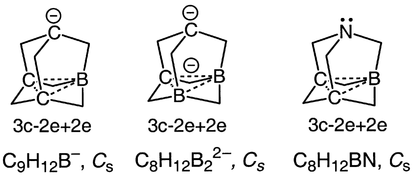
The major differences again concern the 3e systems. Removal of an electron from the nitrogen and phosphorus lone pair requires energy and the formation of 3c–2e+1e systems is unfavorable. Instead, the 3e structures (**18**, **21**, **24**, and **27**) prefer 3c–1e+2e delocalization, comprised of 3c–1e CBB and BBB rings with the lone pair on nitrogen or phosphorus. The contribution of the phosphorus atom to the three-dimensional bonding SOMO-1 of **21** and **27** is negligible (Figures 4 and 5).

The NICS values (Table 1) provide verification of 3c–1e+2e delocalization in three-electron systems. The largest negative NICS values are found at the centers of the CBB (−23.8 and −19.8 for **18** and **21**, respectively) and BBB rings of **24** (−22.4) and **27** (−19.8). This agrees with the NICS values computed for model tris-homoaromatic 3c–1e systems (−21.2 in the center of the CBB ring of 1,3-diboraadamant-5-yl radical $C_8H_{12}B_2^{\bullet}$, and −19.5 in the center of the BBB ring of 1,3,5-triboraadamantane radical anion $C_7H_{12}B_3^{\bullet-}$).

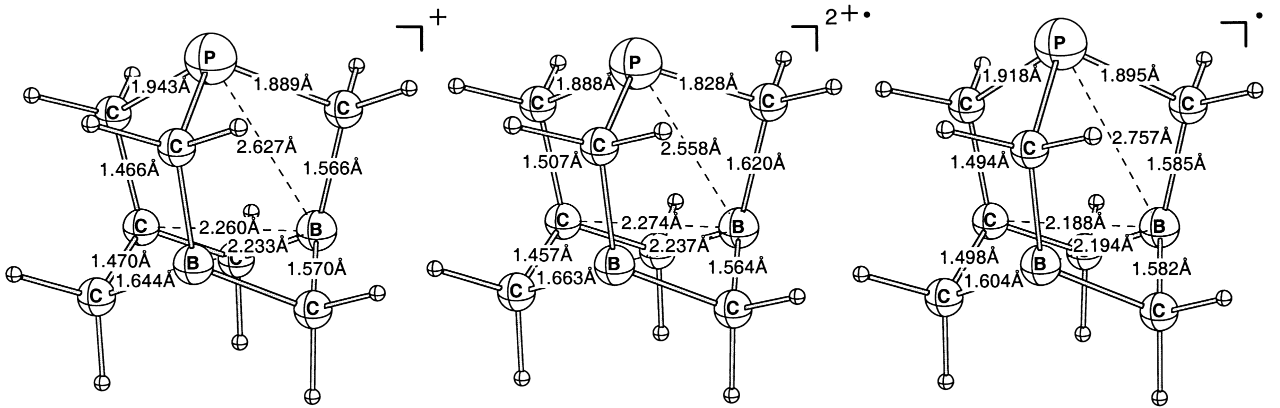


Related cage systems: We have also studied some four-electron systems to complete this series. The stable D_{2d} form of the *all*-carbon structure (1,3,5,7-bisdehydroadamantane, $C_{10}H_{12}$, Scheme 1) has localized C–C single bonds. The NICS value at the mid-point (+5.5) clearly shows the nonaromatic character of this molecule. Its higher spin state, $C_{10}H_{12}$(quintet), is a minimum in T_d symmetry and has singly occupied set of a_1 and t_2 orbitals. This "high-spin"[29] tetra-radical is fully localized (NICS = −1.4 in the molecule center). However, some four-electron heteroadamantanes, such as the 1,3,5,7-bisdehydro-1-boradamantane anion $C_9H_{12}B^-$, the 1,3,5,7-bisdehydro-1,3-diboradamantane dianion $C_8H_{12}B_2^{2-}$, and 1,3,5,7-bisdehydro-1-bora-3-azaadamantane $C_8H_{12}BN$ prefer structures with 3c−2e+2e bonding with a lone pair on the carbon or heteroatom (but 4c–4e delocalization is never observed).

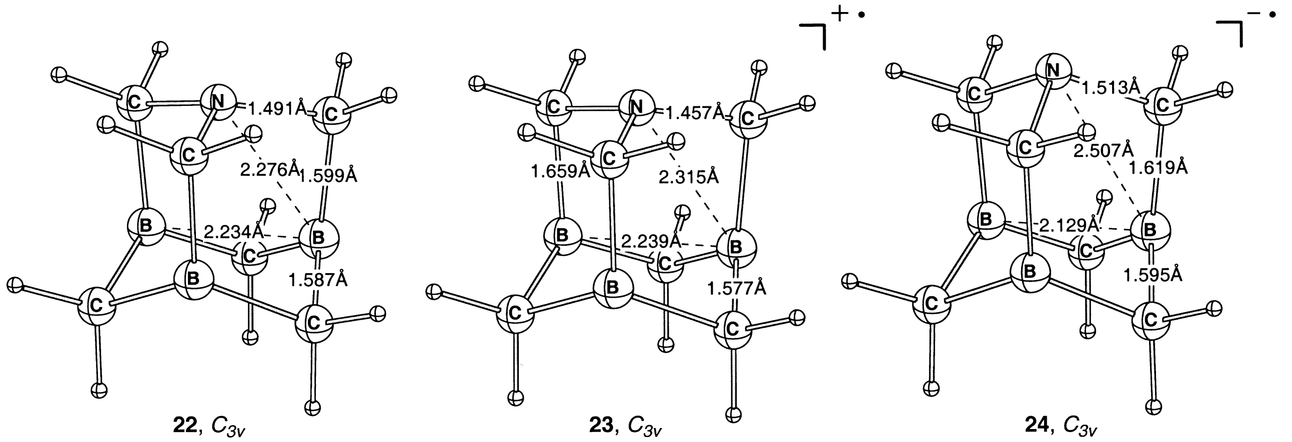




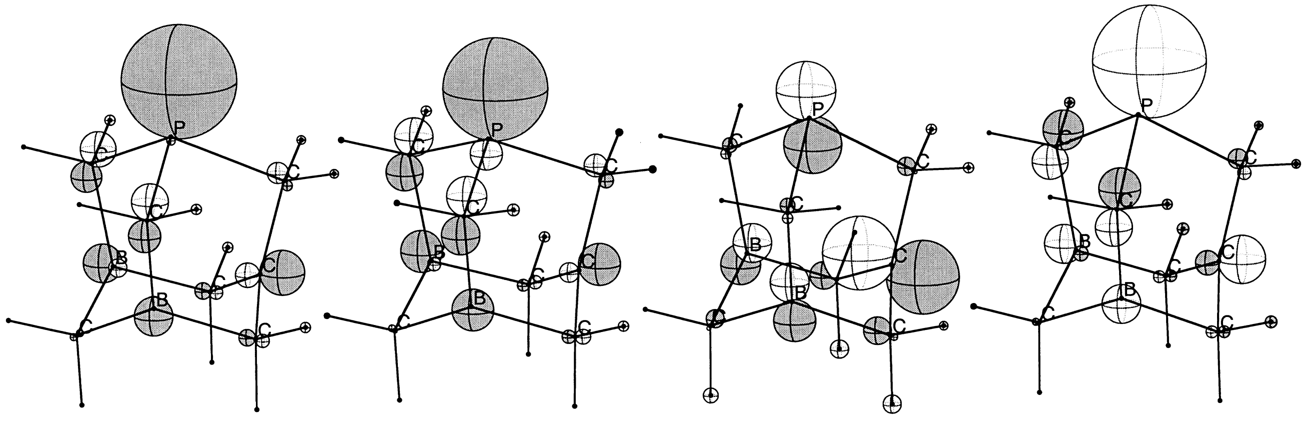
The exceptional stability of **1** clearly shows that highly energetically favorable three-dimensional 4c–2e bonding can overcome the strain in the deformed dehydroadamantane framework. Dication **1** can be viewed as being composed of a central tetrahedron (C^1–C^4) and six edges (n–r) that consist of methylene units. Stepwise replacement of the CH_2 units in **1** by CH_2CH_2 groups will change the strain in the system and reduce the overlap of the p-type orbitals in the HOMO of **1**. To probe the strength of the 4c–2e bonding, we carried out computations of geometries and stabilization energies according to Equation (30) on a series of homologues of dication **1**, with the corresponding derivatives of the 1,3-adamantyl dication, 1,3,5,7-bisdehydroadamantane, and 1,3-dehydroadamantane as reference compounds. From this it should be possible to assess the nature of the four-center two-electron bond as a balance of three-dimensional aromatic stabilization and the strain in the series of dications **28**–**33** (Table 1 and Figure 6).



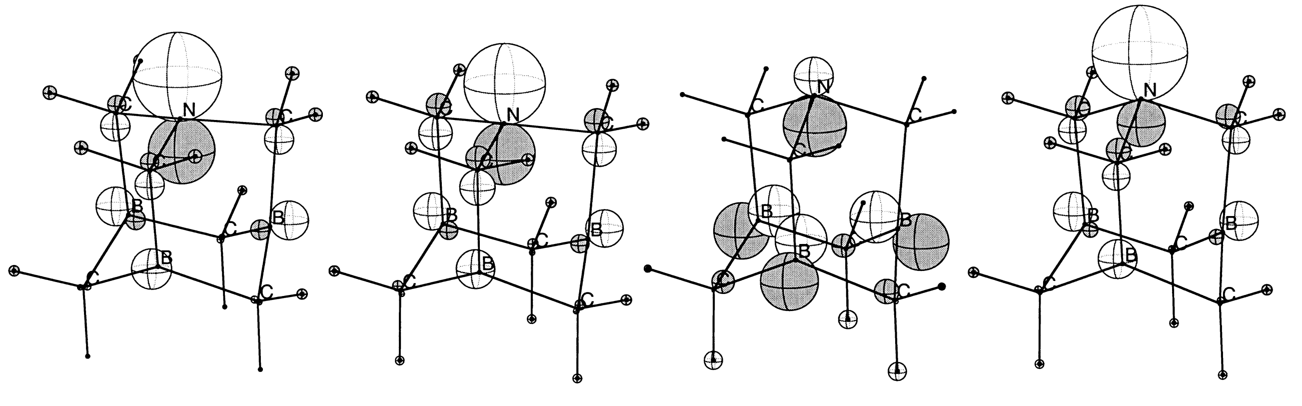
19, C_s **20**, C_s **21**, C_s



22, C_{3v} **23**, C_{3v} **24**, C_{3v}

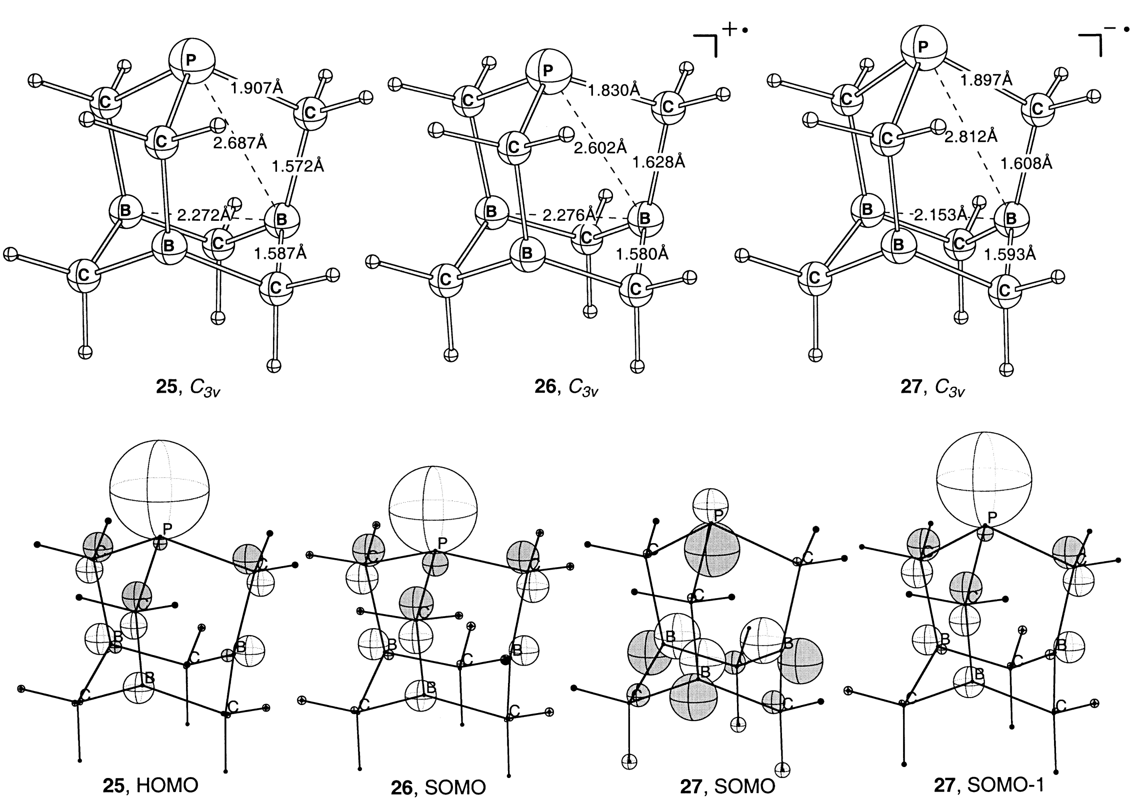


19, HOMO **20**, SOMO **21**, SOMO **21**, SOMO-1



22, HOMO **23**, SOMO **24**, SOMO **24**, SOMO-1

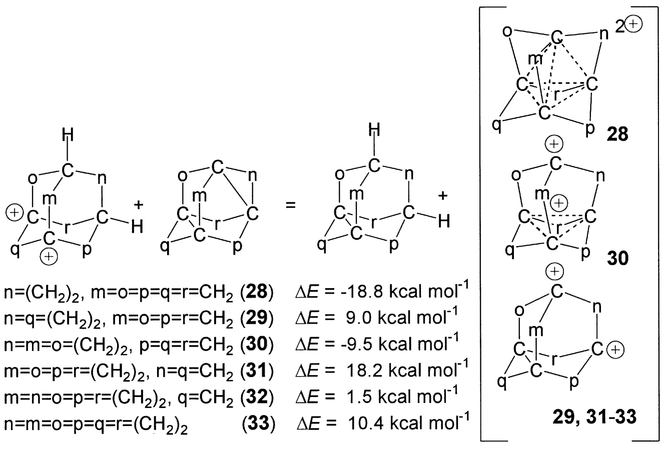
Figure 4. B3LYP/6–31G* optimized geometries of and important orbitals of structures **19**–**24**.



25, C_{3v} **26**, C_{3v} **27**, C_{3v}

25, HOMO **26**, SOMO **27**, SOMO **27**, SOMO-1

Figure 5. B3LYP/6–31G* optimized geometries and important orbitals of structures **25**–**27**.



(30)

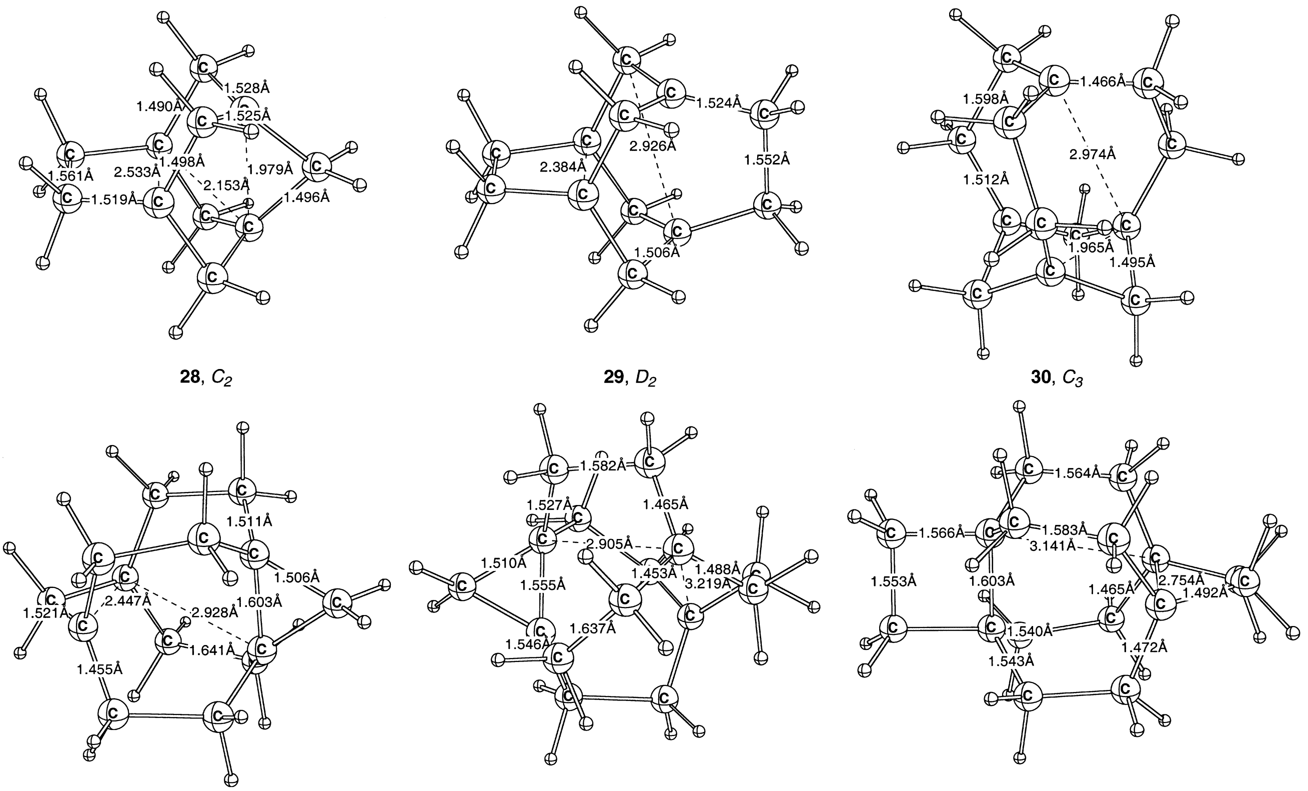
n=$(CH_2)_2$, m=o=p=q=r=CH_2 (**28**) ΔE = -18.8 kcal mol^{-1}
n=q=$(CH_2)_2$, m=o=p=r=CH_2 (**29**) ΔE = 9.0 kcal mol^{-1}
n=m=o=$(CH_2)_2$, p=q=r=CH_2 (**30**) ΔE = -9.5 kcal mol^{-1}
m=o=p=r=$(CH_2)_2$, n=q=CH_2 (**31**) ΔE = 18.2 kcal mol^{-1}
m=n=o=p=r=$(CH_2)_2$, q=CH_2 (**32**) ΔE = 1.5 kcal mol^{-1}
n=m=o=p=q=r=$(CH_2)_2$ (**33**) ΔE = 10.4 kcal mol^{-1}

We have attempted to impose higher symmetries on these systems (e.g., point group T for **33**, D_2 for **31** and **29**); however, we were unable to locate minima under these constraints. At B3LYP/6–31G*, D_2–**29** has one small imaginary frequency (43*i*). It appears that charge separation and formation of a 1,4-dication is favored over three-dimensional delocalization in higher homologues of **1**. As is already apparent in the bis-homo system **29**, the stabilizing effect of four-center two-electron bonding is lost and charge separation is the ultimate structure-determining force.

Exothermic values were computed only for the monohomo-**28** and tris-homo-adamantane **30** systems [Eq. (30)]. The ASE of **28** is approximately half of that of **1** (18.8 vs. 35.1 kcal mol^{-1}). In **30**, a relatively small stabilization (−9.5 kcal mol^{-1}) is achieved by the formation of the homoaromatic 3c–2e tris-homocyclopropenium ion and a separate mono-cationic center. There are no three-dimensional bonding interactions (WBI = 0.02) between the bridgehead and apex carbons as the distances between that atoms are almost 3 Å. The largest negative NICS values in **28** are observed (Table 1) in the middle of the molecule (−33.2); in **30** this value is less negative (−23.5) than in the geometrical center of the three-membered ring (−35.7). This indicates 4c–2e of bonding in **28** and 3c–2e+0e bonding in **30**. The tetra- **31**, penta- **32**, and hexa- **33** polyhomoadamantane dehydro dications are classical dications without significant three-dimensional delocalization. The C−C bond lengths in the cyclopropane (**31** and **32**) and cyclobutane (**33**) moieties are typical for structurally related, uncharged monodehydroadamantanes and dehydrohomo-adamantanes.[30] The formation of two separated classical cationic centers in the bridgehead positions and intact three- or four-membered rings are the structure-determining principles for these systems.

Conclusion

The aromatic stabilization energy of the three-dimensional two-electron system in **1** is higher than that of the two-dimensional 2e system in **3** owing to the larger total number of bonding interactions (6 vs. 3). The three-dimensional aromaticity of **1** appears to be a general property of 4c–2e electron systems in essentially tetrahedral topology and is qualitatively independent of the molecular point group, the degeneracy of the orbitals, the charges, and the nature of the participating atoms. Removing one electron leads to 4c–1e systems; these are approximately half as aromatic as 4c–2e systems, as



28, C_2 **29**, D_2 **30**, C_3

31, C_{2v} **32**, C_2 **33**, C_2

Figure 6. B3LYP/6–31G* optimized geometries of **28**–**33**.

shown by energetic and magnetic analyses. Highly delocalized a_1 HOMOs and SOMOs describe the three-dimensional bonding in 4c–2e and 4c–1e systems, respectively. There is no need to derive any special rules for each point group for such four-center three-dimensional systems.

Aromaticity in 4c–3e systems strongly depends on the nature of the atoms involved and the relative propensity to form a more stable arrangement that has both two-dimensional 3c–2e aromatic moieties and a separate radical center (3c–2e+1e). If the formation of such 3c–2e+1e systems is hampered by unfavorable intramolecular electronic density separations, the species prefer 4c–3e three-dimensional delocalization owing to the dominating bonding interactions in the highest doubly occupied molecular orbital. In such cases, the antibonding interactions between bridgehead atoms in the SOMO lower the symmetry, but the doubly occupied HOMO contributes to three-dimensional bonding. When nitrogen or phosphorus atoms are present, one- and two-electron systems do not change appreciably, but three-electron systems favor two-dimensional 3c–1e delocalization and a lone pair on the electronegative heteroatom (i.e., 3c–1e+2e arrangements). Four-electron systems prefer 3c–2e+2e delocalization or localized pairs of 2c–2e bonds.

In the present paper, we re-examined **1**–**3** and a number of related systems and show that the energies based on Chan and Arnold's Equation (2) do not evaluate the stability of 4c–2e versus tris-homoaromatic 3c–2e systems correctly. We also differ with their conclusions that "*…for three-dimensional aromaticity different rules are needed to predict the number of delocalized electrons. Furthermore, symmetry dictates that more than one rule is necessary: one for the each point group, which may facilitate electron delocalization in three dimensions*". Their assertion that the "*..next member of the series will contain eight delocalized electrons*" is invalid when only four interacting orbitals (centers) are involved, for example, the eight lone-pair electrons in urotropine, $C_6H_{12}N_4$, are localized. We are not aware of three-dimensional aromatics with only eight delocalized electrons. For example the 26-electron 6c system of *closo*-$(BH)_6^{2-}$ (O_h) has a triply degenerate HOMO, but 14 electrons are involved in delocalized cage B–B bonding. The isoelectronic neutral dicarboranes, *closo*-1,2-$C_2B_4H_6$ (C_{2v}) and *closo*-1,6-$C_2B_4H_6$ (D_{4h}) have lower symmetries and no triply degenerate orbitals, but utilize the same bonding principle.[1, 31, 2b–e] The interstitial electron counting rule of Jemmis and Schleyer[32] may be extended to such three-dimensional aromatics. The clusters are divided conceptually into rings and caps, and electrons are assigned formally to 2e–2c bonds. Thus, $(BH)_6^{2-}$ can be constructed from a central $(BH)_4$ "ring" and two BH "caps".[33] The four-membered ring involves 16 2c–2e bonding electrons (4 B–B and 4 B–H bonds) and the caps include four electrons for the two B–H bonds. The remaining six electrons (four "lone pair" electrons from the two B–H groups and the two electrons representing the negative charges) are involved in binding the rings and caps together. The "six-interstitial-electron rule" is independent of the molecular point groups in three-dimensional aromatics, and can be applied widely.[1, 32]

Four-center delocalized systems are rare examples of three-dimensional radial interactions of p-orbitals, in tetrahedral or quasitetrahedral topologies. Independent of the actual point group of the molecule, in four-centered systems the bonding HOMO formed resulting from in-phase combination of p-orbitals (Figure 1). Aromaticity decreases when electrons are removed from this doubly occupied orbital. Adding electrons to antibonding t_2 orbitals of **1** and its 4c–2e analogues lead to geometrical distortions and reduces the delocalization. We found that this behavior is valid for point groups ranging from T_d to C_s. Hence, *no* special rules are needed to understand the electron delocalization in three-dimensional four-center species: a "two-interstitial-electron rule" is valid in such cases.[34]

In the very rigid, compact adamantane structures like **1**, 4c–2e bonding exists because charge delocalization is effective in cage systems in which the internal distances necessarily are relatively small. Computations show that the three-dimensional delocalization does not generally lead to stabilizing 4c–2e bonding in higher homologues of **1**. Among the various 4c–2e polyhomo-adamantane dehydro dications studied, only the 1,8-dehydrohomoadamantyl-3,6-dication (**28**) is stabilized by three-dimensional delocalization.

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[1] a) V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley, New York, **1994**; b) P. von R. Schleyer, H. Jiao, *Pure. Appl. Chem.* **1996**, *68*, 209.

[2] a) J. Aihara, *J. Am. Chem. Soc.* **1978**, *100*, 3339; b) P. von R. Schleyer, K. Najafian, *Inorg. Chem.* **1998**, *37*, 3454; c) P. von R. Schleyer, G. Subramanian, H. Jiao, K. Najafian, M. Hofmann, in *Advances in Boron Chemistry* (Ed.: W. Siebert), The Royal Society of Chemistry, Cambridge, **1997**; d) E. D. Jemmis, *J. Am. Chem. Soc.* **1982**, *104*, 7017; e) P. von R. Schleyer, K. Najafian, in *The Borane*, *Carborane*, *Carbocation Continuum* (Ed.: J. Casanova), Wiley, New York, **1998**, pp. 169–190.

[3] a) M. N. Glukhovtsev, P. von R. Schleyer, N. J. R. van Eikema Hommes, W. de M. Carneiro, W. Koch, *J. Comput. Chem.* **1993**, *14*, 285; b) M. N. Glukhovtsev, P. von R. Schleyer, K. Lammertsma, *Chem. Phys. Lett.* **1993**, *209*, 207.

[4] M. N. Glukhovtsev, P. von R. Schleyer, A. Stein, *J. Phys. Chem.* **1993**, 97, 5531.

[5] The D_{2d} structure *of cyclo*-$(CH_4)_4^{2+}$ is about 7 kcal mol^{-1} more stable than the D_{4h} form at HF/6–31G* (M. Bremer, P. von R. Schleyer, U. Fleischer, *J. Am. Chem. Soc.* **1989**, *111*, 1147); our re-evaluation at a decisive level of theory, CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ gives 8.1 kcal mol^{-1} in favor of the D_{2d} structure.

[6] M. Pilz, J. Allwohn, M. Bühl, P. von R. Schleyer, A. Z. Berndt, *Z. Naturforsch. B* **1991**, *46*, 1085.

[7] M. Bremer, P. von R. Schleyer, K. Schötz, M. Kausch, M. Schindler, *Angew. Chem.* **1987**, *99*, 795; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 761.

[8] P. von R. Schleyer, in *Cage Hydrocarbons* (Ed.: G. Olah), Wiley, New York, **1990**, p. 31.

[9] G. K. S. Prakash, G. Rasul, A. K. Yudin, R. E. Williams, in *The Borane*, *Carborane* , *Carbocation Continuum* (Ed.: J. Casanova), Wiley, New York, **1998**, pp. 152–167.

[10] M. S. W. Chan, D. R. Arnold, *Can. J. Chem.* **1997**, *75*, 192.

[11] a) H. A. Jahn, E. Teller, *Proc. R. Soc. A* **1937**, *161*, 220; b) A. D. Liehr, *J. Chem. Phys.* **1963**, *67*, 389.

[12] P. Duden, M. Scharff, *Liebigs Ann. Chem.* **1895**, *288*, 218.

[13] The strain energy of 1,3,5,7-bisdehydroadamantane is 155.8 kcal mol^{-1} (B3LYP/6–31G*) evaluated from the homodesmic equation: $C_{10}H_{12} + 14\,H_3CCH_3 = 6\,H_3CCH_2CH_3 + 4\,C(CH_3)_4$

[14] a) J. B. Foresman, Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Pittsburgh, **1996**; b) Density functional theory computations were carried out with the Gaussian 94 program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94, Revision D.3*, Gaussian, Pittsburgh PA, **1995**.

[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, 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, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.5*, Gaussian, Pittsburgh PA, **1998**.

[16] K. B. Wiberg, J. W. Ochterski, *J. Comput. Chem.* **1997**, *18*, 108.

[17] R. L. Disch, J. M. Schulman, *Chem. Phys. Lett.* **1988**, *152*, 402.

[18] a) H. Jiao, P. von R. Schleyer, *Angew. Chem.* **1996**, *108*, 2548; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2383; b) G. Subramanian, P. von R. Schleyer, H. Jiao, *Angew. Chem.* **1996**, *108*, 2824; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2638; c) H. Jiao, P. von R. Schleyer, Y. Mo, M. A. McAllister, T. T. Tidwell, *J. Am. Chem. Soc.* **1997**, *119*, 7075; d) P. von R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669; e) M. K. Cyrański, T. M. Krygowski, N. J. R. van Eikema Hommes, P. von R. Schleyer, *J. Am. Chem. Soc.* **1998**, *37*, 187; f) V. Gogonea, P. von R. Schleyer, P. R. Schreiner, *Angew. Chem.* **1998**, *110*, 2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1945.

[19] M. Bühl, W. Thiel, H. Jiao, P. von R. Schleyer, M. Saunders, F. A. L. Anet. *J. Am. Chem. Soc.* **1994**, *116*, 6005.

[20] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[21] S. Winstein, *J. Am. Chem. Soc.* **1959**, *81*, 6524.

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

[23] A. E. Reed, L. A. Curtiss, F. J. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[24] The B3LYP/6–31G* geometry of **7** was reported previously by Prakash et al. (ref. [25]).

[25] G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field, K. Wade, in *Hypercarbon Chemistry*, Wiley, New York, **1987**.

[26] K. B. Wiberg, *Acc. Chem. Res.* **1984**, *17*, 379.

[27] a) H. F. Bettinger, P. von R. Schleyer, H. F. Schaefer III, *Chem. Commun.* **1998**, 769; b) C. H. Choi, M. C. Kertesz, *Chem. Commun.* **1997**, 2199; c) E. Osawa, K. Kanematsu, in *Molecular Structure and Energetics*, *Vol. 3*, (Eds.: J. F. Liebman, A. Greenberg), VCH, **1986**, pp. 329–369; d) H. Jiao, R. Nagelkerke, H. A. Kurtz, R. V. Williams, W. T. Borden, P. von R. Schleyer, *J. Am. Chem. Soc.* **1997**, *119*, 5291.

[28] E. D. Jemmis, B. Kiran, *Inorg. Chem.* **1998**, *37*, 2110.

[29] M. N. Glukhovtsev, P. von R. Schleyer. *Israel J. Chem.* **1993**, *33*, 455.

[30] A. A. Fokin, P. R. Schreiner, P. von R. Schleyer, P. A. Gunchenko, *J. Org. Chem.* **1998**, *19*, 6494.

[31] a) R. E. Williams. *Inorg. Chem.* **1971**, *10*, 210; b) H. Hogeveen, P. W. Kwant, J. Postma, P. T. Duynen, *Tetrahedron Lett.* **1974**, 4351; c) H. Hogeveen, P. W. Kwant, *Tetrahedron Lett.* **1973**, 1665.

[32] E. D. Jemmis, P. von R. Schleyer, *J. Am. Chem. Soc.* **1982**, *104*, 4781.

[33] T. A. Albright, J. K. Burdett, M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**, p. 426.

[34] M. L. McKee, M. Bühl, O. P. Charkin, P. von R. Schleyer, *Inorg. Chem.* **1993**, *115*, 9659.

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