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Homoconjugation in the Adamantane Cage: DFT/IGLO Studies of the 1,3-Dehydro-5-adamantyl Cation, Its Isoelectronic Boron Analogue 1,3-Dehydro-5-Boraadamantane, and Related Systems[1,†]

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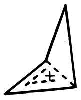
The structure of 1,3-dehydro-5-adamantyl cation and its isoelectronic boron analogue 1,3-dehydro-5-boraadamantane as well as some related adamantane systems, hitherto unknown as persistent long-lived species, were investigated by using the density functional theory (DFT) method. ^{13}C and ^{11}B NMR chemical shifts of the compounds were also calculated using the IGLO method. Stabilization of the systems due to homoconjugation is discussed.

Introduction

The homoaromaticity[2] concept was first introduced by Winstein in the late 1950s,[3] and homoaromatic overlap was studied first in 6π-Hückeloid systems such as the homotropylium cation. The parent monohomoaromatic homocyclopropenium ion[4] **1** and trishomoaromatic trishomocyclopropenium ion[5,6] **2** were successfully prepared and studied as long-lived ions under superacidic conditions. Although the parent bishomoaromatic 4-cyclopentenyl cation **3** has not been observed,[5b] the bishomoaromatic nature of its ethano- and etheno-bridged analogues 7-norbornenyl **4** and 7-norbornadienyl **5** cations was extensively studied[6,7] by NMR and ab initio/IGLO methods.[8] Isoelectronic boron analogues of **4** and **5**, 7-boranorbornene and 7-boranorbornadiene, respectively, were also investigated by the ab initio/IGLO method.[9]



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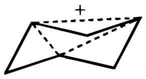

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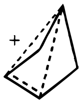

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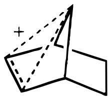

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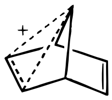

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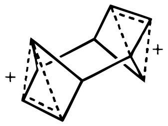
Furthermore, the bishomoaromatic nature of *anti*-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9,10-diyl dication **6** and *anti*-tricyclo[4.2.1.1^{2,5}]deca-3-ene-9-yl cation **7** and the trishomoaromatic nature of trishomocyclopropenium ion **2** were also extensively investigated by the ab initio/IGLO theory.[10]



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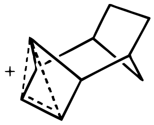

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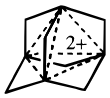

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Schleyer et al. have prepared[11a] and characterized the intriguing 1,3-dehydro-5,7-adamantanediyl dication **8** under long-lived stable ion conditions. The dication **8** is an example of a three-dimensional aromatic system in which the p orbitals of the four bridgehead carbons overlap inward in the cage in a tetrahedral fashion involving two electrons. Schleyer et al. have also calculated[11a] the structures and ^{13}C NMR chemical shift values of the dication **8** ab initio/IGLO methods and the computed results agree very well with the experimental data. The dication **8** can also be considered as a three-dimensional aromatic compound. In neutral hydrocarbon systems, however, the magnitude of homoaromatic overlap decreases with increasing interruption of methylene groups of the otherwise conjugated π-framework.

We now report density functional theory (DFT)/IGLO studies of the 1,3-dehydro-5-adamantyl cation and its isoelectronic boron analogue 1,3-dehydro-5-boraadamantane as well as some related ions, hitherto not yet observed as persistent long-lived species. Since this

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[†] Dedicated to P. v. R. Schleyer on the occasion of his 70th birthday.

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Table 1. Total Energies (−au) and ZPE[a]

no.	B3LYP/6-31G*//B3LYP/6-31G*	ZPE (kcal/mol)
2	233.72778	83.3
9	388.58332	127.7
10	375.59294	124.9
11	220.75331	80.1
12	374.74020	118.3
13	361.75816	115.6
14	375.54280	122.5
15	362.36700	118.8

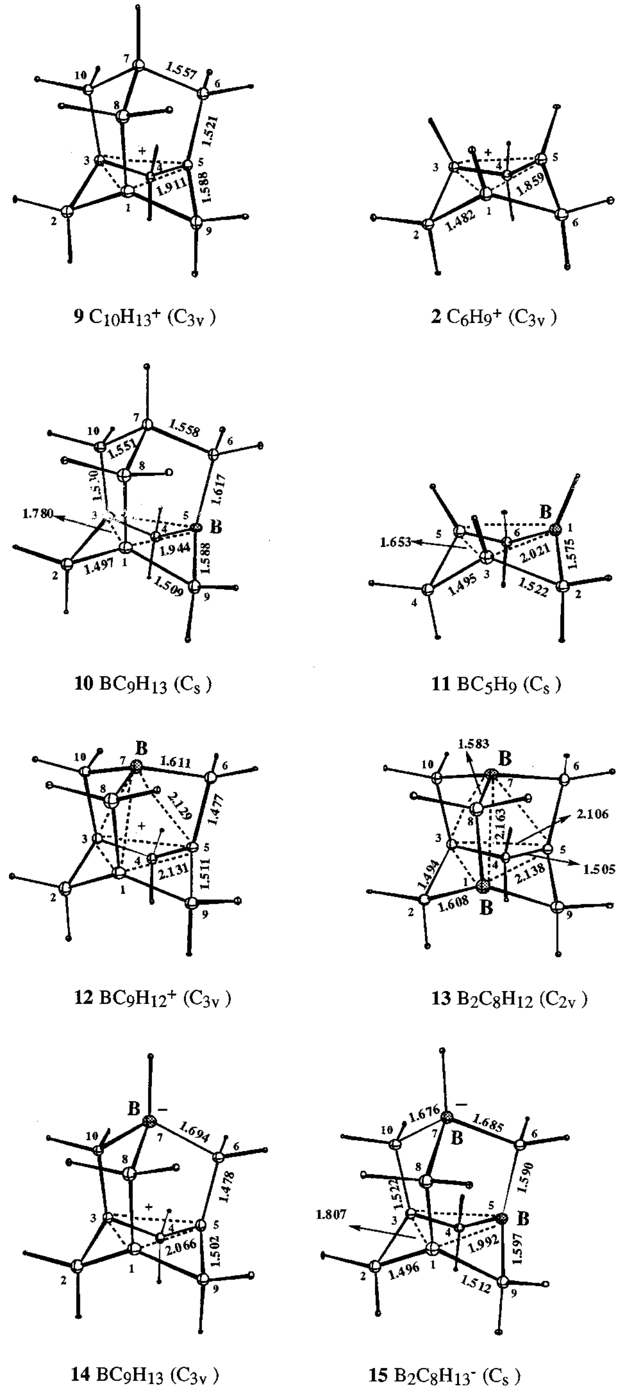
[a] Zero point vibrational energies (ZPE) at B3LYP/6-31G*//B3LYP/6-31G* scaled by a factor of 0.98.

manuscript was written, Schleyer et al. have reported[11b] the structures of **12** and **13** calculated at the B3LYP/6-31G* level focusing on four-center three-dimensional aromaticity.

Calculations

Calculations were carried out with the Gaussian 98 program system.[12] The geometry optimizations were performed using the DFT[13] method at the B3LYP[14]/6-31G* level.[15a] Vibrational frequencies at the B3LYP/6-31G*//B3LYP/6-31G* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.98.[15b] Final energies were calculated at the B3LYP/6-31G*//B3LYP/6-31G* + ZPE level. Calculated energies are given in Table 1. B3LYP/6-31G* geometrical parameters and final energies will be discussed throughout, unless stated otherwise. ^{13}C and ^{11}B NMR calculations were performed according to the reported method using IGLO programs[16] at the IGLO DZ levels using B3LYP/6-31G* geometries. Huzinaga[17a] Gaussian lobes were used as follows; Basis DZ: C, B: 7s 3p contracted to [4111,21], H, 3s contracted to [21]. The ^{13}C NMR chemical shifts were referenced to TMS. The ^{11}B NMR chemical shifts were first computed using B_2H_6 as reference. The ^{11}B NMR chemical shifts were finally referenced to BF_3/OEt_2 (δ (B_2H_6) 16.6 vs BF_3/OEt_2).

Results and Discussion



9 $C_{10}H_{13}^+$ (C_{3v}) **2** $C_6H_9^+$ (C_{3v})

10 BC_9H_{13} (C_s) **11** BC_5H_9 (C_s)

12 $BC_9H_{12}^+$ (C_{3v}) **13** $B_2C_8H_{12}$ (C_{2v})

14 BC_9H_{13} (C_{3v}) **15** $B_2C_8H_{13}^-$ (C_s)

Figure 1. B3LYP/6-31G*-optimized structures of **2** and **9**−**15**.

Intermediacy of 1,3-dehydro-5-adamantyl cation was invoked in the solvolysis studies of 5-bromo-1,3-dehydroadamantane.[17b] However, the cation has not yet been characterized under long-lived stable ion condition. Now we have investigated the ion using DFT/IGLO method. B3LYP/6-31G* optimized geometry of 1,3-dehydro-5-adamantyl cation **9** (C_{3v} symmetrical) is given in Figure 1. For comparison, structure of homocyclopropenium ion **2** (C_{3v} symmetrical) was also calculated at the same B3LYP/6-31G* level and displayed in Figure 1. B3LYP/6-31G* calculated structure of **2** agrees very well with the previously reported ab initio MP2/6-31G* structure.[10] The relevant C1−C3 bond length of **9** (1.911 Å) is only 0.052 Å longer than the C1−C3 bond length of **2** (1.859 Å). This indicates similar stabilizing trishomoaromatic nature of **9** and **2**. In cation **9**, the p orbitals of the three tertiary bridgehead sp2-carbons (C1, C3, C5) overlap

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(12) Gaussian 98 (Revision A.5): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; 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.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon, M.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

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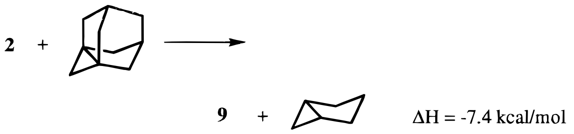
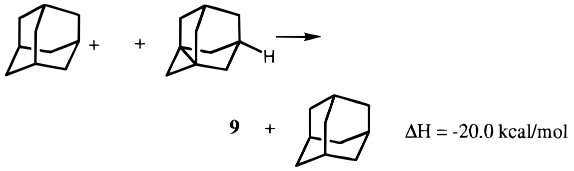
involving 2 electrons whereas in cation **2** the p orbitals of the three secondary sp2-carbons (C1, C3, C5) overlap also involving 2 electrons. The C1−C8 and C8−C7 bond lengths of **9** are 1.521 and 1.557 Å. These are only 0.0.23 Å shorter and 0 013 Å longer than the C−C bond length of adamantane (1.544 Å) calculated at the same B3LYP/6-31G* level. This shows that the positive charge of the ion **9** is extensively delocalized among three C1, C3 and C5 sp^2 type carbons and thus involving little additional C−C (e.g.C8−C7) hyperconjugation.

The stabilization energies of the ions **2** and **9** due to trishomoaromatic interaction were compared by the isodesmic eq 1. The reaction is exothermic by 7.4 kcal/mol indicating more stabilization of **9** compared to **2** probably due to large skeletal size.



(1)

To further investigate the relative stabilities of **9** we also considered isodesmic eq 2 where reaction of 1-adamantyl cation and 1,3-dehydro-adamantane leads to **9** and adamantane. The reaction is exothermic by 20.0 kcal/mol indicating significant stabilization of **9** due to trishomoaromatic interaction.



(2)

^{13}C NMR chemical shifts of **2** and **9** were calculated by the IGLO method. The calculated ^{13}C NMR chemical shifts of C1 and C2 of **2** were found to be $\delta^{13}C$ 4.7 and 16.1, respectively, closely matching the experimentally observed[5a] values of 4.7 and 17.3. The calculated ^{13}C NMR chemical shifts of the relevant C1 and C2 of **9** are $\delta^{13}C$ 43.8 and 37.9, respectively. The $\delta^{13}C$ 43.8 of carbocationic centers is significantly more deshielded than that of the corresponding carbocationic centers of **2** ($\delta^{13}C$ 4.7). Also the $\delta^{13}C$ 70.4 of tertiary C7 carbon is unusually deshielded compared to that of tertiary carbon of neutral adamantane ($\delta^{13}C$ 15.4) computed at the same level.

Isoelectronic boron analogues of **9** and **2**, structures **10** and **11**, respectively, were also calculated (Figure 1). The calculated structures also show the stabilizing trishomoaromatic natures in both **10** and **11**. The C1−C3 and C1−B5 bond lengths of **10** are 1.780 and 1.944 Å, respectively, also close to the related C3−C5 and C3−B1 bond lengths of **11** (1.653 and 2.021 Å). In cation **10** the p orbitals of the two bridgehead sp2-carbons (C1, C3) and the bridgehead sp2-boron (B5) overlap involving 2 electrons. The calculated $\delta^{13}C$ value of the bridgehead sp2-carbon C1 of **10** is 19.5. On the other hand, related C3 carbon of **11** is very shielded at $\delta^{13}C$ −10.5. The calculated $\delta^{11}B$ value of **10** and **11** are −19.6 and −4.4, respectively.

We have also calculated the structure of ion **12** (Figure 1) which can be derived by replacing the CH group (at position C7) of monocation **9** by a boron atom. The monocation **12** is in fact a isoelectronic boron analogue of three-dimensional aromatic 1,3-dehydro-5,7-adamantanediyl dication **8**.[8] The calculated structure of **12** also indicate the existence of three-dimensional aromaticity in which the p orbital of the three carbons (C1, C3, C5) and the p orbital of boron (B7) overlap in a pseudo tetrahedral fashion involving 2 electrons. Thus, the C1−C3 and C1−B7 bond distances of 2.131 and 2.129 Å, respectively, are very close to the related C1−C3 bond distance (2.104 Å) in 1,3-dehydro-5,7-adamantanediyl dication **8** calculated at the same B3LYP/6-31G* level.[18] The calculated $\delta^{13}C$ values of the bridgehead carbon C1 of **12** is 13.7 which is close to that of the experimental value of 6.6 found in **8**.[8] The calculated $\delta^{11}B$ of **12** was computed to be highly shielded at −65.7.

Table 2. IGLO Calculated $^{13}C^{a}$and $^{11}B^{b}$

no.	atom	NMR chemical shifts
2	C1, C3, C5	4.7
	C2, C4, C6	16.1
9	C1, C3, C5	43.8
	C2, C4, C9	37.9
	C6, C8, C10	34.6
	C7	70.4
10	C1, C3	19.5
	C2	35.1
	C4, C9	21.6
	C6	20.5
	C7	50.9
	C8, C10	37.9
	B5	−19.8
11	C3, C5	−10.5
	C4	14.2
	C2, C6	8.7
	B1	−4.4
12	C1, C3, C5	13.7
	C2, C4, C9	35.8
	C6, C8, C10	17.9
	B7	−65.7
13	C3, C5	0.7
	C4	36.8
	C2, C6	20.1
	C8	−0.2
	B1	−49.2
14	C1, C3, C5	76.1
	C2, C4, C9	45.2
	C6, C8, C10	29.4
	B7	6.7
15	C1, C3	23.1
	C2	37.8
	C4, C9	25.3
	C6	12.0
	C8, C10	31.2
	B5	−12.7
	B7	−7.9

[a] ^{13}C shifts are referenced to TMS. [b] ^{11}B shifts are referenced to $BF_3{:}OEt_2$.

For comparison, calculated structure **13**, which can be derived by replacing the C1 carbon of monocation **12** by a boron atom, is also given in Figure 1. Structure **13**, neutral compound with two bridgehead boron atoms, is also an isoelectronic analogue of dication **8**. Structure **13** has been reported previously.[18] Structure **13** also indicate the existence of three-dimensional aromaticity in which the p orbital of the two carbons (C3, C5) and the p orbital of two borons (B1, B7) overlap involving 2 electrons. The C3−C5 and B1−C3 bond distances of **13** are 2.106 and 2.138 Å, respectively, also close to the related C1−C3 bond distance (2.104 Å) of **8**.[18] The calculated NMR

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(18) Prakash, G. K. S., Rasul, G.; Yudin, A. K.; Williams, R. E. *Borane, Carborane, Carbocation Continuum*; Wiley-Interscience: New York, 1998; p 147.

chemical shifts of the bridgehead carbon is δ^{13}C 0.7 and the bridgehead boron is δ^{11}B −49.2.

Although the concept of homoaromaticity was successfully demonstrated in long-lived carbocations, in neutral molecules and carbanions the concept has not been sufficiently established.[19] We have now calculationally probed the Zwitterionic potentially trishomoaromatic compound **14** and its isoelectronic analogue, the negatively charged trishomoaromatic anion **15**. The species **14** is composed of a positively charged trishomoaromatic unit and a negatively charged borate making it overall a neutral compound. On the other hand, **15** is composed of a neutral trishomoaromatic unit (containing a boron atom) and a negatively charged borate making it overall an anion. The calculated structures indicate the presence of trishomoaromatic units in both **14** and **15**. The δ^{13}C and δ^{11}B values of **14** and **15** were also computed using IGLO method and shown in Table 2.

The calculated δ^{13}C of trishomoaromatic carbons (C1, C3, and C5) in **14** at 76.1 ppm is substantially more deshielded than those computed in the case of **9** as well as **12**. However, the calculated bond lengths are comparable (± 0.1 Å). Similar deshieldings are observed in the case of **15** when compared with structure **10**.

Conclusions

DFT calculations at the B3LYP/6-31G* level were carried out to investigate the structures of some of the homoaromatic systems in the adamantane cage, hitherto not yet observed as persistent long-lived species. These are 1,3-dehydro-5-adamantyl cation **9**, isoelectronic boron analogue 1,3-dehydro-5-boraadamantane **10** and related systems **12**−**15**. Stability of the systems due to homoconjugative interactions is discussed. ^{13}C and ^{11}B NMR chemical shifts of the compounds were also calculated using IGLO method.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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