Inorg. Chem. **2005**, *44*, 7184–7188

Inorganic Chemistry
Article

Condensed Two- and Three-Dimensional Aromatic Systems: A Theoretical Study on the Relative Stabilities of Isomers of $CB_{19}H_{16}^{+}$, $B_{20}H_{15}Cl$, and $B_{20}H_{14}Cl_2$ and Comparison to $B_{12}H_{10}Cl_2^{2-}$, $C_6H_4Cl_2$, $C_{10}H_7Cl$, and $C_{10}H_6Cl_2$

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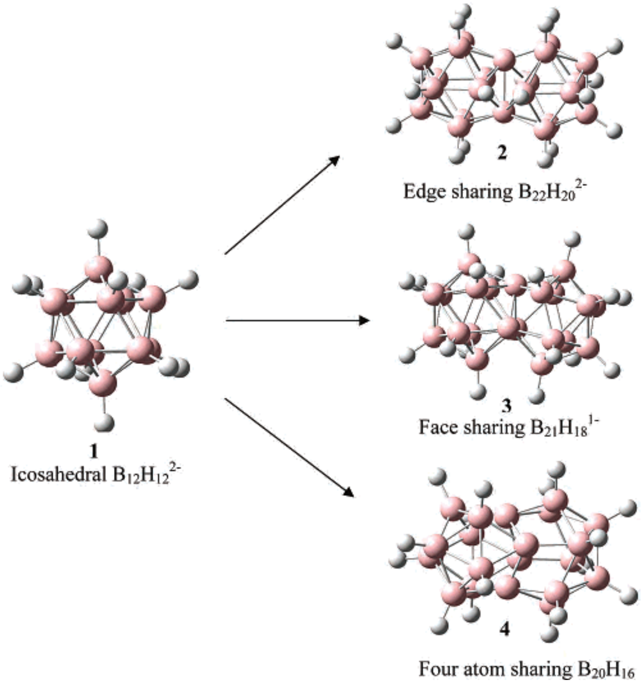
Received May 9, 2005

DFT studies (B3LYP/6-31G*) on mono- and dichloro derivatives of benzene, naphthalene, $B_{12}H_{12}^{2-}$, four-atom-sharing condensed systems $B_{20}H_{16}$, and monocarborane isomers of $B_{20}H_{16}$ are used to compare the variation of relative stability and aromaticity between condensed aromatics. The trends in the variation of the relative energies and aromaticity in these two- and three-dimensional systems are similar. Aromaticity, estimated by NICS values, does not change considerably with condensation or substitution. The minor variation in the relative energies of the isomers of chloro derivatives is explained by the topological charge stabilization rule of Gimarc. The compatibility of the cap and ring orbitals decides the relative stability of $CB_{19}H_{16}^{+}$.

Introduction

Benzene and $B_{12}H_{12}^{2-}$ are important prototypes of two- and three-dimensional aromatic compounds in the carbon and boron families.[1] Condensation of two benzenes sharing an edge gives naphthalene, which has a well-developed chemistry of its own. The properties of benzene and naphthalene were contrasted frequently in the early days of aromaticity.[2] The variation of aromaticity and reactivity has been especially noted. In contrast, the chemistry of condensed polyhedral borane is only being developed.[3] Among the possible condensation products of $B_{12}H_{12}^{2-}$ (**1**), such as the edge-sharing $B_{22}H_{20}^{2-}$ (**2**), face-sharing $B_{21}H_{18}^{-}$ (**3**), and four-atom-sharing $B_{20}H_{16}$ (**4**) (Scheme 1), the latter is synthesized and characterized.[4] The electronic requirements of these condensed products are now understood by the *mno* rule.[5] Though $B_{20}H_{16}$ is one of the borane equivalents of naphthalene, there is limited information available on $B_{20}H_{16}$.[6] A major part of the development in the chemistry of polyhedral boranes came from the study of carboranes.[7] While borane

Scheme 1



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10.1021/ic050730d CCC: $30.25

cations are not common, we compare here the isomers of $C_2B_{10}H_{12}$ and $CB_{19}H_{16}^+$. We find that such cross comparisons between two- and three-dimensional structures are very useful. A recent comparison of the benzyl cation−tropylium cation system to the corresponding carboranes[8] led to the report of synthesis of $CB_9H_{10}^-$ derivatives.[9] We also study here the structure and stability of the chloro derivatives of $B_{12}H_{12}^{2-}$ and of the condensed product $B_{20}H_{16}$ and compare them to the benzenoid systems. The present results will also trigger new experiments in the area.

Methods

We have optimized the structures of mono- and dichloro derivatives of benzene, naphthalene, $B_{12}H_{12}^{2-}$, and $B_{20}H_{16}$ at the B3LYP/6−31g* level[10] using the Gaussian 03 program package.[11] All the monocarborane isomers ($CB_{19}H_{16}^+$) of four-atom-sharing condensed $B_{20}H_{16}$ are studied at the same level of theory. Nucleus-independent chemical shift (NICS)[12] values are calculated at ring centers for benzene and naphthalene, at cage centers for $B_{12}H_{12}^{2-}$ and $B_{20}H_{16}$, and at the centroid of $B_{20}H_{16}$ at the GIAO-HF/6-31+g*//B3LYP/6-31g* level.[12]

Results and Discussions

Comparison of $C_2B_{10}H_{12}$ and $CB_{19}H_{16}^+$. The most studied disubstituted boranes are the carboranes. Three isomers of the icosahedral carborane $C_2B_{10}H_{12}$ are known. Thermal isomerization and equilibrium studies involving the three isomers 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), *o*-, *m*-, and *p*-carborane, respectively, established their relative stability. The 1,2- isomer is the least stable one and isomerizes to the next stable 1,7- isomer (meta) at 500 °C. This in turn goes to the most stable 1,12- isomer (para) above 615 °C.[13] Theoretical studies at various levels have confirmed these experimental trends (Table 1).[14]

Table 1. Relative Energies of Isomers of $CB_{19}H_{16}^+$ and $C_2B_{10}H_{12}$

compound	relative energy (kcal/mol)	compound	relative energy (kcal/mol)
1-$CB_{19}H_{16}^+$	0.00	1,12-$C_2B_{10}H_{12}$	0.00
2-$CB_{19}H_{16}^+$	5.71	1,7-$C_2B_{10}H_{12}$	2.82
3-$CB_{19}H_{16}^+$	16.01	1,2-$C_2B_{10}H_{12}$	18.70
4-$CB_{19}H_{16}^+$	33.10		

There is only one monosubstituted carborane possible, viz. $CB_{11}H_{12}^-$. There are three isomers possible for $C_2B_{10}H_{12}$. There have been several attempts at explaining the stability of positional isomers of carboranes, such as Gimarc's topological charge index, Williams rule, and optimization of ring−cap overlap.[15] According to Gimarc's rule of topological charge index of carboranes, more electronegative incoming atoms prefer to be located at sites of higher electron density, while more electropositive elements prefer sites of lower electron density. The Mulliken atomic charges in $CB_{11}H_{12}^-$ are B12 (−0.079), B7 (−0.005), and B2 (0.005), respectively. Therefore, the topological charge index explains their relative stability. The propensity of the chemistry of $C_2B_{10}H_{12}$ in comparison to that of $B_{12}H_{12}^{2-}$ comes from the lack of charge. However, there are some unique characteristics of $B_{12}H_{12}^{2-}$ and $CB_{11}H_{11}^-$ that arise from the negative charge.[16] In contrast, $B_{20}H_{16}$ is neutral. Replacement of one B by C^+ leads to $CB_{19}H_{16}^+$, with four isomers. A stable large carborane with a positive charge is sure to generate unique chemistry of its own.

The four isomers generated by carbon substitution are 1-$CB_{19}H_{16}^+$, 2-$CB_{19}H_{16}^+$, 3-$CB_{19}H_{16}^+$, and 4-$CB_{19}H_{16}^+$. Out of these, 1-$CB_{19}H_{16}^+$ is the most stable (Table 1). The least stable, 4-$CB_{19}H_{16}^+$, is 33.10 kcal/mol higher in energy. This is indeed a large range, compared to that in the $C_2B_{10}H_{12}$ series. The Mulliken charges calculated on the four different boron atoms in $B_{20}H_{16}$ [B1 (−0.059), B2 (−0.012), B3 (−0.035), and B4 (−0.019)] allow the prediction of the relative stability of the carborane cations, $CB_{19}H_{16}^+$, as

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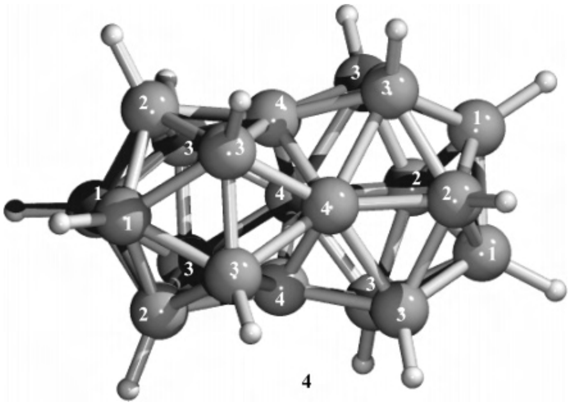

Figure 1. Molecular structure of four-atom-sharing condensed $B_{20}H_{16}$, showing the numbering used.

substitution at B1 > B3 > B4 > B2 (Figure 1). However, this is not supported by the results. The relative stability of these carboranes could be explained by the ring−cap orbital compatibility used in explaining the relative stability of $C_2B_{10}H_{12}$ isomers.[15c] According to this, caps with less diffuse orbitals prefer small rings. Thus three- and four-membered rings prefer the CH group as a cap. The interaction of the CH cap with a four-membered boron ring requires orbital reorientation by tilting B−H groups toward the cap. The interaction between a CH cap and B5 ring is even less favorable. The CH group in carborane ($CB_{19}H_{16}^+$) isomers can be considered as a case of a CH cap on different five-membered rings of the skeleton.

The redirection of orbitals of the five-membered rings toward carbon by tilting the B−H bonds toward the C−H cap helps in increasing the overlap between the ring and CH cap. This flexibility is maximum when all the substituents on the B5 rings are hydrogens as in 1-$CB_{19}H_{16}^+$. This is calculated to be the most stable isomer. One boron atom (B4) of the five-membered ring that interacts with CH in 2-$CB_{19}H_{16}^+$ bridges the two polyhedra and hence cannot be effective in redirecting the orbitals as much as in 1-$CB_{19}H_{16}^+$. Therefore, 2-$CB_{19}H_{16}^+$ is less stable by 5.71 kcal/mol. Similarly, the CH in 3-$CB_{19}H_{16}^+$ has to interact with a B5 ring, two borons of which bridge the two polyhedra. Thus, positional isomers 2-$CB_{19}H_{16}^+$ and 3-$CB_{19}H_{16}^+$ are higher in energy than 1-$CB_{19}H_{16}^+$. The fourth isomer, 4-$CB_{19}H_{16}^+$, where carbon forms a part of a bridge and is heptavalent, is expected to be the least stable one as indeed is calculated (Table 1).

The differences in relative stabilities that arise on replacing a by an isoelectronic −BH −CH group are quite interesting. We have used isodesmic equations (eqs 1 and 2) to estimate the relative stability of various boranes ($B_nH_n^{2-}$, $B_{20}H_{16}$) and their carboranes ($CB_{19}H_{16}^+$).

$$CB_{11}H_{12}^{-} + B_{20}H_{16} \rightarrow 1\text{-}CB_{19}H_{16}^{+} + B_{12}H_{12}^{2-} \qquad \Delta H = 217.33\ \text{kcal/mol} \quad (1)$$

$$CB_5H_6^{-} + B_{20}H_{16} \rightarrow 1\text{-}CB_{19}H_{16}^{+} + B_6H_6^{2-} \qquad \Delta H = 277.68\ \text{kcal/mol} \quad (2)$$

Table 2. Data for $B_nH_n^{2-}$ (n = 5−7, 12), $B_{20}H_{16}$, and for Their Most Stable *closo*-Carborane Derivatives[17]

molecule	total energy[a]	ZPE[b]	TE + ZPE[c]
$B_5H_5^{2-}$	−127.09272	36.67	−127.03428
$B_6H_6^{2-}$	−152.65161	47.10	−152.57656
$B_7H_7^{2-}$	−178.14319	56.30	−178.05348
$B_{12}H_{12}^{2-}$	−305.69026	105.00	−305.52293
$B_{20}H_{16}$	−506.90851	154.28	−506.66264
1-$CB_{19}H_{16}^+$	−519.86261	155.80	−519.61433
1,5-$C_2B_3H_5$	−153.77382	44.86	−153.70234
1,6-$C_2B_4H_6$	−179.24479	54.44	−179.15804
2,4-$C_2B_5H_7$	−204.73130	63.93	−204.62942
1,12-$C_2B_{10}H_{12}$	−318.99437	108.82	−318.82096
$CB_4H_5^-$	−140.53863	41.33	−140.47277
$CB_5H_6^-$	−166.05271	51.42	−165.97076
2-$CB_6H_7^-$	−191.53405	60.54	−191.43757
$CB_{11}H_{12}^-$	−318.99437	108.82	−318.82096

[a] Total energies (hartrees). [b] Zero-point energy (ZPE) (kcal/mol): calculated at the B3LYP/6-31g* level. [c] Total energy + zero-point energy (TE + ZPE) (hartrees): calculated at theB3LYP/6-31g* level.

The large endothermicity of these reactions is a reflection of the high separation of charges in the products. The lower endothermicity of eq 1 may be a reflection of the inherent extra stability of $B_{12}H_{12}^{2-}$ or the extra stability of an octahedral carborane, $CB_5H_6^-$. This is further estimated using eq 3, obtained by subtracting eq 2 from eq 1.

$$B_6H_6^{2-} + CB_{11}H_{12}^{-} \rightarrow CB_5H_6^{-} + B_{12}H_{12}^{2-} \qquad \Delta H = -60.35\ \text{kcal/mol} \quad (3)$$

The preference of carbon for a smaller polyhedron is obvious. Thus, there is no major inherent difference in the stability of $CB_{11}H_{12}^-$ and $CB_{19}H_{16}^+$ (Table 2).

$B_{12}H_{11}Cl^{2-}$, $B_{12}H_{10}Cl_2^{2-}$, C_6H_5Cl, and $C_6H_4Cl_2$. Chlorinated derivatives ($B_{12}H_{11}Cl^{2-}$, $B_{12}H_6Cl_6^{2-}$, and $B_{12}Cl_{12}^{2-}$) of $B_{12}H_{12}^{2-}$ have been prepared in the early 1970s by reaction with chlorine.[18] The dianion $B_{12}H_{12}^{2-}$ reacts smoothly in aqueous or alcoholic solutions with chlorine to give derivatives in which all hydrogen atoms have been replaced sequentially by halogens. Conversion of $B_{12}H_{12}^{2-}$ to chlorinated derivatives can also be effected with the addition of hydrogen chloride.

We have selected the mono- and dichloro derivatives to make a comparison between $B_{12}H_{12}^{2-}$ and $B_{20}H_{16}$ vis-à-vis C_6H_6 and $C_{10}H_8$. The relative stabilities of the 1,2-, 1,7-, and 1,12- isomers of $B_{12}H_{10}Cl_2^{2-}$ are given in the Table 3. The relative stabilities of these may be related to the charge distribution in the monochlorinated species. Thus, the preference for the replacement of the second hydrogen by chlorine will be for the hydrogen that has maximum negative charge. Calculated charges (Table 4) indicate the order para > meta > ortho as is seen in Table 3.

The energy difference between the ortho isomer and the para and meta isomers is similar to that for the corresponding dichlorobenzenes. In both cases the para and meta isomers

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(17) The relative energies of all the positional isomers of the *closo*-monocarboranes, $CB_{n-1}H_n^-$ (n = 5−12), and the *closo*-dicarboranes, $C_2B_{n-2}H_n$ (n = 5−12), are discussed at the RMP2(fc)/6-31G* level of theory in: (a) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454. (b) Jemmis, E. D.; Ramalingam, M.; Jayasree, E. G. *J. Comput. Chem.* **2001**, *22*, 1542.

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Table 3. Relative Energies and NICS[a] Values of Dichloro Derivatives of $B_{12}H_{12}^{2-}$ and C_6H_6

molecule	relative energy (kcal/mol)	NICS	compound	relative energy (kcal/mol)	NICS
$B_{12}H_{12}^{2-}$		−34.4	C_6H_6		−11.5
1,2-$B_{12}H_{10}Cl_2^{2-}$	1.38	−35.9	1,2-$C_6H_4Cl_2$	2.50	−12.5
1,7-$B_{12}H_{10}Cl_2^{2-}$	0.00	−35.8	1,3-$C_6H_4Cl_2$	0.08	−12.8
1,12-$B_{12}H_{10}Cl_2^{2-}$	0.11	−35.5	1,4-$C_6H_4Cl_2$	0.00	−12.7

[a] NICS values at the center of the cage/ring.

Table 4. Mulliken Atomic Charges in 1-Chloro-$B_{12}H_{11}^{2-}$ and 1-Chlorobenzene

atoms	B2	B7	B12	atoms	C2	C3	C4
charges at B	0.0025	0.0032	−0.0001	charges at C	−0.128	−0.127	−0.126
charges at H	−0.1378	−0.1601	−0.1621	charges at H	0.155	0.140	0.137

Table 5. Relative Stabilities and NICS[a] Values of Monochloro Isomers of $B_{20}H_{16}$ and $C_{10}H_7Cl$

molecule	relative energy (kcal/mol)	NICS1	NICS2	NICS3
$B_{20}H_{16}$		−30.9	−30.9	−68.3
1-$B_{20}H_{15}Cl$	0.00	−31.7	−31.0	−68.3
3-$B_{20}H_{15}Cl$	0.74	−31.3	−31.7	−68.3
2-$B_{20}H_{15}Cl$	1.29	−30.3	−30.7	−67.7
$C_{10}H_8$		−11.4	−11.4	
2-$C_{10}H_7Cl$	0.00	−12.0	−11.4	
1-$C_{10}H_7Cl$	0.93	−11.9	−11.6	

[a] NICS1 = values at the center of the first cage/ring, NICS2 = values at the center of the next cage/ring, NICS3 = values at the center of the four-atom-sharing ring.

Table 6. Mulliken Atomic Charges in $B_{20}H_{16}$ and $C_{10}H_8$

B4	B1	B2	B3	atom	C1	C2
charges at B	−0.059	−0.012	−0.035	charges at C	−0.1910	−0.1350
charges at H	0.033	0.035	0.046	charges at H	0.1290	0.1295

are close to each other in energy. The charges on the hydrogens in C_6H_5Cl are indicators of the preferred positions for second chlorine substitution. Though there is a basic difference between the two- and three-dimensional aromaticity of having a definite σ and π framework in the former, substitution effects are comparable. Similarly, the substituent positions do not affect the extent of aromaticity as indicated by NICS values. The differences in energy between the para and meta isomers are so small that we do not attempt any interpretation.

Table 7. Relative Energies (RE) and NICS[a] Values of All Dichloro of $B_{20}H_{16}$

molecule	RE (kcal/mol)	NICS1	NICS2	NICS3
1,1′a-$B_{20}H_{14}Cl_2$	0.00	−31.8	−31.8	−68.3
1,1a-$B_{20}H_{14}Cl_2$	0.14	−32.6	−31.0	−68.7
1,3′b-$B_{20}H_{14}Cl_2$	0.68	−31.5	−31.3	−67.9
1,3′a-$B_{20}H_{14}Cl_2$	0.74	−31.5	−31.3	−67.9
1,3b-$B_{20}H_{14}Cl_2$	0.83	−32.0	−30.7	−67.8
1,3a-$B_{20}H_{14}Cl_2$	1.21	−31.9	−30.7	−67.9
1,2′b-$B_{20}H_{14}Cl_2$	1.29	−31.4	−30.3	−67.6
3,3′d-$B_{20}H_{14}Cl_2$	1.41	−31.0	−30.7	−67.3
3,3′b-$B_{20}H_{14}Cl_2$	1.46	−31.0	−30.9	−67.4
3,3′c-$B_{20}H_{14}Cl_2$	1.46	−32.6	−31.0	−67.4
3,3b-$B_{20}H_{14}Cl_2$	1.51	−31.5	−30.5	−67.4
1,2a-$B_{20}H_{14}Cl_2$	1.68	−30.8	−30.8	−67.7
3,3a-$B_{20}H_{14}Cl_2$	1.68	−31.5	−30.5	−67.4
3,3c-$B_{20}H_{14}Cl_2$	1.96	−31.1	−30.4	−67.2
2,3′b-$B_{20}H_{14}Cl_2$	2.01	−30.0	−31.0	−67.2
2,3b-$B_{20}H_{14}Cl_2$	2.05	−30.6	−30.5	−67.2
2,3′a-$B_{20}H_{14}Cl_2$	2.16	−30.0	−31.0	−67.2
2,3a-$B_{20}H_{14}Cl_2$	2.36	−30.6	−30.5	−67.4
2,2b-$B_{20}H_{14}Cl_2$	2.47	−30.0	−30.5	−67.2
2,2′a-$B_{20}H_{14}Cl_2$	2.58	−30.0	−30.0	−67.1
3,3′a-$B_{20}H_{14}Cl_2$	2.94	−30.9	−30.9	−67.2

[a] NICS1 = values at the center of the first cage, NICS2 = values at the center of the next cage, NICS3 = values at the center of the four-atom-sharing ring.

Table 8. Relative Energies, C−Cl Bond Lengths and NICS[a] Values of Dichloro Derivatives of Naphthalene

molecule	relative energy (kcal/mol)	C−Cl bond length (Å)	NICS1	NICS2
2,6-$C_{10}H_6Cl_2$	0.00	1.76	−12.0	−12.0
2,7-$C_{10}H_6Cl_2$	0.00	1.76	−12.0	−12.0
1,6-$C_{10}H_6Cl_2$	0.88	1.76	−11.9	−11.9
1,7-$C_{10}H_6Cl_2$	1.00	1.76	−11.9	−11.9
1,3-$C_{10}H_6Cl_2$	1.45	1.76	−12.5	−12.5
1,5-$C_{10}H_6Cl_2$	2.13	1.76	−12.1	−12.1
1,4-$C_{10}H_6Cl_2$	2.28	1.76	−12.3	−11.9
2,3-$C_{10}H_6Cl_2$	3.25	1.75	−12.5	−11.3
1,2-$C_{10}H_6Cl_2$	4.02	1.75	−12.0	−11.7
1,8-$C_{10}H_6Cl_2$	10.49	1.76	−12.2	−12.2

[a] NICS1 = values at the center of the first ring, NICS2 = values at the center of the the next ring.

$B_{20}H_{16}$, $B_{20}H_{15}Cl$, $B_{20}H_{14}Cl_2$, $C_{10}H_8$, $C_{10}H_7Cl$, $C_{10}H_6Cl_2$. The relative stabilities of the monochloro isomers of $B_{20}H_{16}$ are given in Table 5. The Mulliken atomic charges in $B_{20}H_{16}$ are H1 (0.033), H2 (0.035), and H3 (0.046) (Table 6). As we know, substitution of an electronegative atom is more favorable at the site which has larger electron density. In $B_{20}H_{16}$, H1 is more electronegative than H2, which is in turn more electronegative than H3, but that is not the order of their relative stability (Table 5). On the basis of the relative energy values of the monochloro isomers, we try to understand the stability pattern of $B_{20}H_{14}Cl_2$. Substitution at the 1-position is more favorable than at the 3-position, and substitution at the 3-position is more favorable than at the 2-position. The numbering of the dichloro derivatives needs further clarification. We consider the 1,1- isomer when both substitutions take place in the 1-position of the same polyhedron, but if substitution takes place in same position but on different polyhedra then it is the 1,1′- isomer. If these substituents are adjacent to each other in the same polyhedron then it is 1,1a- isomer; if the substituents are far then it is a 1,1b- isomer, and if they are farther then it is a 1,1c- isomer, and so on. Similarly, if substituents are adjacent to each other but in different polyhedra then it is 1,1′a- isomer. Thus, as a first approximation we can predict the stability order as 1,1- > 1,3- > 1,2- > 3,3- > 2,3- > 2,2-. The calculated values show that only two isomers do not follow this order: 1,2- and 3,3′- (Table 7). The 3,3′- isomer has two Cl atoms close to each other, and this is the least stable among all $B_{20}H_{14}Cl_2$ isomers. In general, among the same category the substitution at different cages is more favorable than that at the same cage.

Thus, 1,1′- substitution is more favorable than 1,1-, 1,3′- > 1,3-, 1,2′- > 1,2-, 3,3′- > 3,3-. 1,2a-$B_{20}H_{16}$ is less stable as the steric factor plays a more vital role here than any other factors. In the case of the 1,1a- isomer, the steric interaction is less as the distance between the two boron atoms is more (2.847 Å) than any other normal B−B bond distance (1.780

Table 9. Mulliken Atomic Charges in 1-Chloronaphthalene

atoms	C1	C2	C3	C4	C5	C6	C7	C8
charges at C	−0.141	−0.139	−0.133	−0.185	−0.192	−0.130	−0.134	−0.192
charges at H	−0.019	0.153	0.139	−0.185	0.134	0.134	0.136	0.157

Å) in $B_{20}H_{16}$. The low difference in energy between the chloro- and dichloro-$B_{20}H_{16}$ derivatives is also reflected in the energetics of chloro- and dichloronaphthalenes. Though there is some structural difference between these condensed systems, substitution effects are comparable with those of their parent systems. There are very minor changes in terms of aromaticity when a substitution of this type takes place.

These are to be compared to the chloronaphthalenes (Figure 2). The 2-chloronaphthalene is more stable than 1-chloronaphthalene by 0.9 kcal/mol. The 1-position (also called α-position) is sterically more favorable than the 2-position (β-position) because the Cl−H nonbonded distances are 2.675 and 2.814 Å, whereas in 2-chloronaphthalene these Cl−H distances are 2.854 and 2.861 Å. The relative energies (Table 8) of dichloronaphthalenes follow the order 2,6 = 2,7 > 1,6- > 1,7- > 1,3- > 1,5- > 1,4- > 2,3- > 1,2- > 1,8-. As 2-chloronaphthalene is more stable than 1-chloronaphthalene by 0.93 kcal/mol, it is clear that further substitution on 2-chloronaphthalene will be more favorable than in 1-chloronaphthalene (Table 9). But taking the steric factor in account, further substitution in the same ring is not favorable. Thus, 2,3-dichloronaphthalene is less stable by 3.25 kcal/mol. Similarly, substitution in 1-chloronaphthalene makes 1,6-dichloronaphthalene and 1,7-dichloronaphthalene less stable by around 1.00 kcal/mol. The 1,2-dichloronaphthalene, 1,3-dichloronaphthalene, and 1,4-dichloronaphthalene are less stable due to substitution in the same ring.

There is a greater steric interaction in 1,8-dichloronaphthalene, making the Cl−C−C bond angle 124°. The following guidelines emerge from the studies to determine the stability of dichloronaphthalenes: (a) substitution at adjacent carbons is not favorable, (b) the 2-position is more stable than the 1-position, and (c) substitution at different rings is better than that at the same ring. The 1,8-dichloro isomer, where both Cl atoms occupy an α-position, is the least stable. The nonbonded Cl−Cl distance of 3.11 Å here is below the range of the van der Waals radii (3.5 Å), making it the least stable. The next stable isomer is where the chlorine atoms are substituted at adjacent positions, i.e., 1,2- and 2,3-. Among these two isomers, 2,3- is more stable because both the Cl atoms are at β-positions. Then there are two isomers where Cl atoms are at α-positions, i.e., 1,4- and 1,5-. The 1,5- isomer, where substitutions are at different rings, is more stable than the 1,4- isomer where both the Cl atoms are at the same ring. Next, three isomers contain one α-Cl and one β-Cl substituent (1,3- 1,6-, and 1,7-). The 1,3- isomer is the least stable among these three because both Cl atoms are at same ring. The 1,7- isomer is 0.02 kcal/mol more stable than the 1,6- isomer. Most stable isomers are found where the Cl's are substituted at the β-position of the different rings: 2,6- and 2,7-. Substitution does not change the aromaticity considerably as judged from the NICS values. In view of the similarity in energetics, it is anticipated that a chemistry of condensed polyhedral boranes as elaborate as those of naphthalene must be in the realm of the possible.

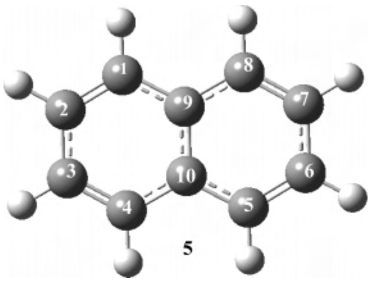

Figure 2. Molecular structure of naphthalene.

Conclusions

We have studied the structures and relative stabilities of all the four monocarborane isomers ($CB_{19}H_{16}^{+}$) of $B_{20}H_{16}$. The relative stability order (1-$CB_{19}H_{16}^{+}$ > 2-$CB_{19}H_{16}^{+}$ > 3-$CB_{19}H_{16}^{+}$ > 4-$CB_{19}H_{16}^{+}$) of these positional isomers are explained based on the ring−cap orbital overlap criterion. Comparisons are made between the mono- and dichloro derivatives of two- and three-dimensional aromatic systems. The stability order of all the chloro isomers is explained based on Gimarc's topological charge stabilization rule. The energy difference between the ortho, para, and meta isomer of dichloro-$B_{12}H_{12}^{2-}$ is similar to that for the corresponding dichlorobenzenes. Though there is a basic difference between two- and three-dimensional aromaticity (of having a definite σ and π framework in the former), substitution effects are comparable. Similarly, we found the substitutent position do not affect the extent of aromaticity significantly.

Acknowledgment. We thank the Department of Science and Technology (DST), Department of Atomic Energy (DAE-BRNS), and Universities with Potential for Excellence (UPE) program of UGC for support of this work. B.P. and A.A. gratefully acknowledge CSIR for senior research fellowships. The High Performance Computing Facility (HPCF) funded under the DST-FIST Program at the University of Hyderabad and Maui High Performance Computing Center (MHPCC) at Hawaii, provided the computational facility.

Supporting Information Available: Listing of total energies and Cartesian coordinates of all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050730D