in germabenzene is predicted to be nearly the same as that in silabenzene by both types of reaction, while one observes a sharper drop from germabenzene to stannabenzene. The similar behavior of compounds containing third- and fourth-period atoms has been noted previously.[48]

Both bond separation and superhomodesmic reactions predict pyridine to be about as aromatic as benzene. Phosphabenzene is predicted to be 88% (bond separation) or 90% (superhomodesmic) as aromatic as pyridine. There is generally a small steady decrease in the delocalization stabilization of these rings as the size of the heteroatom increases. Even stibabenzene is 79% (72%) as aromatic as pyridine according to the bond separation (superhomodesmic) reactions. These group IV versus group V trends parallel those already discussed with regard to π bond strengths in an earlier paper.[49]

The bond separation reactions for the group V five-membered rings suggest that the delocalization stabilization for pyrrole is much greater than that for the other members of the series. In fact, the superhomodesmic reaction energies for all species except pyrrole are slightly negative. This implies that the stabilization exhibited by the bond-separation reactions for the latter compounds is already contained in butadiene before the ring is formed. This is consistent with the structures discussed earlier: Only in pyrrole is the delocalization in the butadienyl backbone greater than that in isolated butadiene. Clearly, this overcomes whatever strain is introduced due to the small CCC and CCX angles.

As for the group V five-membered rings, the superhomodesmic reactions for the group VI analogues provide a more direct analysis of the effect of the heteroatom on the delocalization in isolated butadiene. As expected from the earlier discussion of structures, both thiophene and selenophene are predicted to be more stabilized than furan according to this measure, while that for tellurophene is about the same as that for furan. This is qualitatively consistent with the order of reactivity noted earlier for these compounds. The positive superhomodesmic reaction energies for these compounds reflect the fact that, in contrast with the group V analogues, the delocalization in the butadienyl backbone does increase relative to isolated butadiene (see Table II, Figure 4, and section IIIA).

IV. Conclusions

This study has presented a characterization of the aromaticity of a series of metal-substituted benzene and cyclopentadiene compounds in terms of their structures and bond separation and superhomodesmic reactions. The predicted structures of these compounds are in general in good agreement with the available experimental structures. The structures of the six-membered rings suggest substantial delocalization. The structures of the five-membered rings indicate that strain due to small bond angles must be weighed against structural delocalization in determining stabilization due to formation of the ring. Of the group V five-membered rings, pyrrole has the most strained butadiene backbone but also is much more delocalized than the other structures. On the other hand, furan is the most strained and least delocalized of the group VI five-membered rings.

Although there is a sharp drop in "aromaticity" (delocalization energy) from benzene to silabenzene, those of sila- and germabenzene are almost the same. Another sharp drop is predicted from germa- to stannabenzene. For the six-membered group V rings, there is a small steady decrease in delocalization energy with increase in size of the heteroatom. On the basis of superhomodesmic reactions, pyrrole is the only group V five-membered ring to exhibit delocalization stabilization. All four group VI five-membered rings exhibit significant stabilization due to delocalization, with thiophene being much more delocalized than furan. This is consistent with the observed relative reactivities of these compounds.

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Registry No. C_6H_6, 71-43-2; NC_5H_5, 110-86-1; PC_5H_5, 289-68-9; AsC_5H_5, 289-31-6; SbC_5H_5, 289-75-8; OC_4H_4, 110-00-9; SC_4H_4, 110-02-1; SeC_4H_4, 288-05-1; TeC_4H_4, 288-08-4; silabenzene, 289-77-0; germabenzene, 75920-32-0; stannabenzene, 289-78-1; pyrrole, 109-97-7; phosphole, 288-01-7; arsole, 287-77-4; stibole, 288-04-0.

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Ab Initio Study of Coupled Cages

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Abstract: The structure and energetics of carborane and borane coupled cages were investigated by means of ab initio calculations. In general, the structure of a carborane and borane linked together by a boron–boron bond or a pair of hydrogen bridges is only slightly perturbed from the corresponding isolated carborane or borane. Fusion into a larger single cage is thermodynamically favored. From model calculations of 1,6-$C_2B_4H_6$ and 1,5-$C_2B_3H_5$ with BH_3, activation barriers were estimated for exchange of terminal hydrogens between the carborane and B_2H_6. In contrast to 1,6-$C_2B_4H_6$/B_2H_6, a low barrier (about 10 kcal/mol) is predicted for the exchange in 1,5-$C_2B_3H_5$/B_2H_6.

Coupled cages in the boron hydrides and carboranes have attracted recent attention[1–9] due to their possible use in the synthesis of larger cages via cage-condensation reactions as well as their possible involvement as transition states or intermediates in

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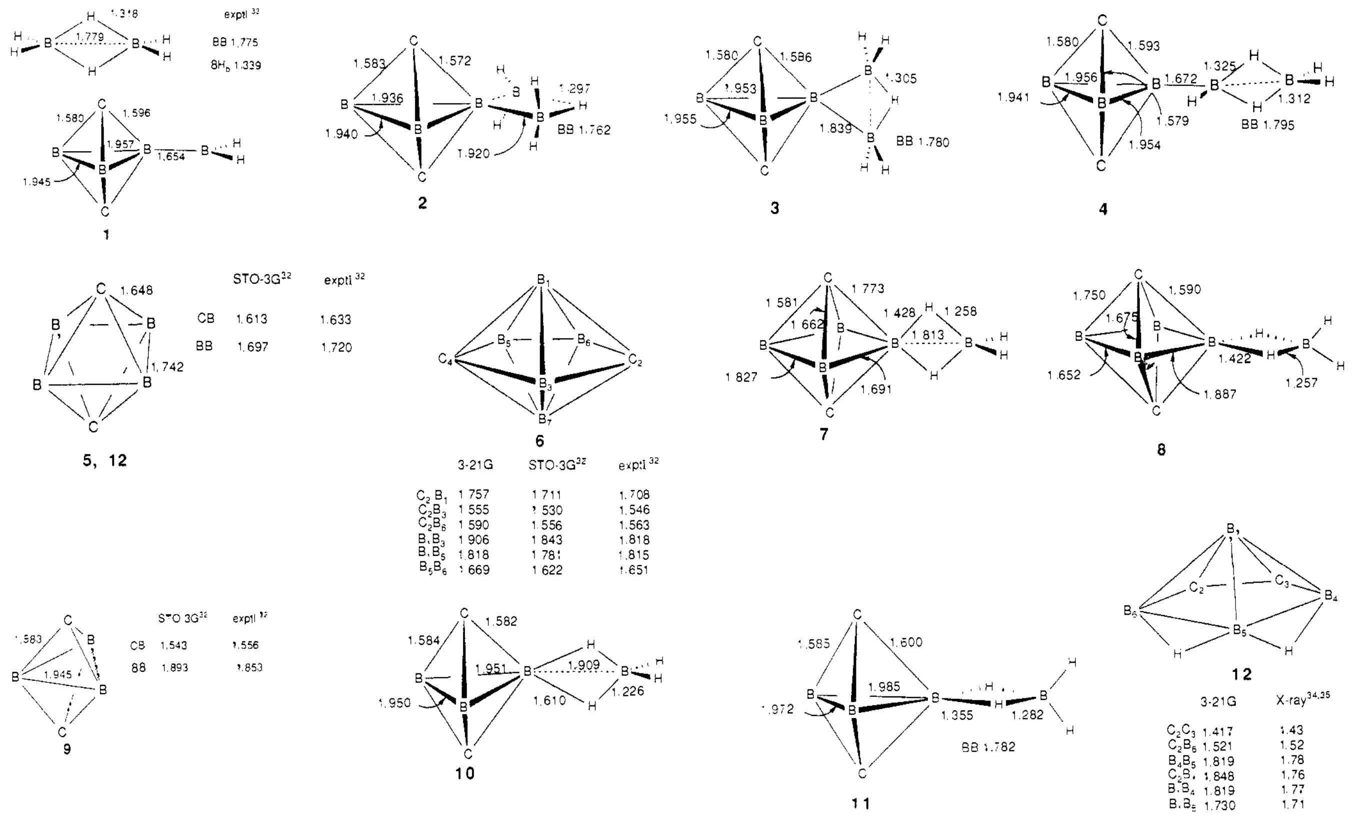

Figure 1. Geometric parameters of various species calculated at the 3-21G level. Terminal hydrogens on carbon and boron are usually not shown for clarity.

Table I. Total Energies (Hartrees) of Species on the $C_2B_5H_9$ (**1**–**8**) and $C_2B_4H_8$ (**9**–**13**) Potential Energy Surfaces

	molecule	sym	3-21G	6-31G	MP2/6-31G	6-31G*	ZPE (NEV)[a]
1	1,5-$C_2B_3H_4$ (BH_2) + BH_3	C_{2v}, D_{3h}	−203.161 66	−204.225 48	−204.662 43	−204.320 17	72.85 (0)
2	1,5-$C_2B_3H_4$ (B_2H_5)	C_{2v}	−203.179 36	−204.238 96	−204.711 42	−204.342 51	79.03 (0)
3	1,5-$C_2B_3H_4$ (B_2H_5)	C_{2v}	−203.159 46	−204.220 64	−204.695 51	−204.326 79	77.98 (1)
4	1,5-$C_2B_3H_4$ (B_2H_5)	C_s	−203.181 36	−204.240 92	−204.705 97	−204.346 82	78.91 (0)
5	1,6-$C_2B_4H_6$ + BH_3	D_{4h}, D_{3h}	−203.215 42	−204.215 42	−204.695 50	−204.333 17	74.17 (0)
6	2,4-$C_2B_5H_7$ + H_2	C_{2v}, $D_{\infty h}$	−203.205 06	−204.260 46	−204.758 39	−204.368 86	73.92 (0)
7	1,6-$C_2B_4H_5$ (BH_4)	C_{2v}	−203.113 26	−204.171 36	−204.678 72	−204.293 11	77.19 (1)
8	1,6-$C_2B_4H_5$ (BH_4)	C_{2v}	−203.109 77	−204.168 32	−204.673 61	−204.289 29	76.92 (2)
9	1,5-$C_2B_3H_5$ + (BH_3)	D_{3h}, D_{3h}	−178.056 33	−178.985 94	−179.374 00	−179.073 79	65.00 (0)
10	1,5-$C_2B_3H_4$ (BH_4)	C_{2v}	−177.990 50	−178.919 48	−179.336 55	−179.014 12	66.84 (2)
11	1,5-$C_2B_3H_4$ (BH_4)	C_{2v}	−178.046 14	−178.973 43	−179.383 84	−179.068 67	70.06 (0)
12	1,6-$C_2B_4H_6$ + H_2	D_{4h}, $D_{\infty h}$	−178.040 58	−178.965 45	−179.407 96	−179.069 97	63.54 (0)
13	2,3-$C_2B_4H_8$	C_s	−178.060 64	−178.991 93	−179.430 08	−179.086 40	71.07 (0)

[a] Zero-point energies are given in kilocalories/mole while the number of imaginary frequencies (NEV) is given in parentheses.

the halogen transfer between carborane polyhedra and in the formation of 5,6-$C_2B_6H_{12}$ from 1,5-$C_2B_3H_5$ and B_2H_6. Very few theoretical calculations have been reported for this unique class of compounds. The first well-characterized coupled cage was 1:1′-$[B_5H_8]_2$, which was described in 1961.[10,11] Since then others have been reported.[12-28]

An interesting aspect of several coupled cages is their ability to undergo a coupled-cage to single-cage fusion under suitable

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Table II. Relative Energies (kcal/mol) of species on the $C_2B_5H_9$ (**1–8**) and $C_2B_4H_8$ (**9–13**) Potential Energy Surfaces

	molecule	3-21G	6-31G	MP2/6-31G	6-31G*	[MP2/6-31G*] (+ZPC)[a]
1	1,5-$C_2B_3H_4$ (BH_2) + BH_3	0.0	0.0	0.0	0.0	0.0 (0.0)
2	1,5-$C_2B_3H_4$ (B_2H_5)	−11.1	−8.5	−30.8	−14.0	−36.3 (−30.1)
3	1,5-$C_2B_3H_4$ (B_2H_5)	1.4	3.0	−20.8	−4.2	−28.0 (−22.9)
4	1,5-$C_2B_3H_4$ (B_2H_5)	−12.4	−9.7	−27.3	−16.7	−34.3 (−28.2)
5	1,6-$C_2B_4H_6$ + BH_3	4.2	6.3	−20.8	−8.2	−35.3 (−34.0)
6	2,4-$C_2B_5H_7$ + H_2	−27.2	−22.0	−60.2	−30.6	−68.8 (−67.7)
7	1,6-$C_2B_4H_5$ (BH_4)	30.4	34.0	−10.2	17.0	−27.2 (−22.9)
8	1,6-$C_2B_4H_5$ (BH_4)	32.6	35.9	−7.0	19.4	−23.5 (−19.4)
9	1,5-$C_2B_3H_5$ + (BH_3)	0.0	0.0	0.0	0.0	0.0 (0.0)
10	1,5-$C_2B_3H_4$ (BH_4)	41.3	41.7	23.5	37.4	19.2 (21.0)
11	1,5-$C_2B_3H_4$ (BH_4)	6.4	7.8	−6.2	3.2	−10.8 (−13.6)
12	1,6-$C_2B_4H_6$ + H_2	9.9	12.9	−21.3	2.4	−31.8 (−33.3)
13	2,3-$C_2B_4H_8$	−2.7	−3.8	−35.2	−7.9	−39.3 (−33.2)

[a] Relative energies are computed using the additivity approximation[36] while zero-point corrected relative energies are given in parentheses.

conditions. The reaction of BX_3 and 1,6-$C_2B_4H_6$ can produce either a cage with an *exo*-BX_2 substituent or a fused cage depending on the identity of X.[4] If X = Br, the product formed is 2-Br_2B-1,6-$C_2B_4H_5$ whereas, if X = Cl, the main product is the closo cage $C_2B_5H_6Cl$ substituted primarily at the 3-position. A possible mechanism in the latter reaction might be the formation of the BX_2-substituted cage followed by incorporation of the boron into an expanded cage. In the case of 1:2-$[B_5H_8]_2$, a coupled cage has been observed[1] to undergo fusion into a larger cage. In addition, a coupled cage has been proposed[2–4] as a possible transition state or intermediate in the exchange of a halogen for hydrogen in the carborane $C_2B_5H_7$.

It is known that the perturbing effect of an exo substituent on cage bonding is small. For instance, in the coupling of two B_5H_9 cages to form a coupled-caged compound, X-ray data[5] indicate only small deviations from normal cage distances.[5] This may be due to the exo/endo separability of the molecular orbitals utilized for cage bonding and exo bonding, which has been demonstrated from photoelectron studies of cages.[12] The major orbital interaction observed is the interaction of the exo substituent with the surface (π) orbitals of the cage. This evidence suggests that coupled cages will not significantly perturb the individual cage-bonding patterns. The purpose of the present study is to determine the perturbing structural effects of coupled cages relative to separated cages and to determine the energetics of coupled cages compared to fusion into larger single-cage compounds.

Table III. Comparison of Calculated Orbital Energies (eV) of the Coupled Cage (**2**) to 1,5-$C_2B_3H_5$ and B_2H_6

sym	coupled cage	1,5-$C_2B_3H_5$/B_2H_6[a]
a_2	−11.48	−11.05
b_2	−11.81	−11.05
a_1	−12.03	−12.52
a_2	−12.58	−12.82 (B_2H_6)
b_1	−12.74	−12.52
a_1	−13.53	−14.07 (B_2H_6)
b_2	−14.21	−13.80
b_1	−14.54	−14.64 (B_2H_6)
a_1	−15.41	−15.11[b]/−15.73[c]
b_2	−17.37	−17.34 (B_2H_6)
a_1	−17.61	−18.59
b_1	−18.24	−17.83
a_1	−19.05	−17.83
a_1	−23.38	−24.12 (B_2H_6)
b_2	−24.14	−23.60
a_1	−30.30	−29.72

[a] Orbital energies of B_2H_6 are indicated; other orbital energies are of 1,5-$C_2B_3H_5$. [b] Bridging hydrogen orbital on diborane. [c] Terminal B–H orbital in 1,5-$C_2B_3H_5$.

All calculations were carried out with the GAUSSIAN 82 program package.[30] Energies were determined at 3-21G-optimized geometries[31] (Figure 1), and single-point calculations were carried out at several higher levels (Table I). Vibrational frequencies were determined analytically (at the 3-21G level) in order to characterize the stationary points as minima (0 imaginary frequencies), saddle points (1 imaginary frequency), or stationary points of higher order (>1 imaginary frequency) and to determine zero-point corrections. Calculations at the MP2/6-31G and HF/6-31G* levels were used to approximate relative energies at the MP2/6-31G* level by using the additivity approximation[36] (Table II). This method generates relative energies, which are usually within 5 kcal/mol of the full basis set plus correlation results.

Cage compounds are characterized by strong coupling of internal coordinates, which makes geometry optimizations difficult. Without an estimate of the off-diagonal elements of the Hessian matrix (force constant matrix), the optimization algorithm often steps in unreasonable directions. A practical solution to this problem, which usually leads to an optimum geometry after only a few iterations, is first to optimize the geometry using the MNDO method[37] and then to calculate the Hessian matrix analytically at the first point at the ab initio level.

Results

A coupled cage between 1,5-$C_2B_3H_5$ and B_2H_6 can be formed through the condensation of a terminal BH of the carborane with either a bridging hydrogen or a terminal hydrogen of diborane. Considering the former case first, two orientations of the diborane moiety were explored. The molecular plane including the borons of 1,5-$C_2B_3H_4$ can either include the two borons of diborane (**2**) or bisect the two borons (**3**). The bisected geometry is higher in energy at all levels (Table II) and is predicted to be 7.2 kcal/mol less stable at the [MP2/6-31G*] + ZPC level. The preferred

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orientation can be rationalized as resulting from reduced steric repulsion between the BH_2 groups of the B_2H_5 moiety and the carbons in **2** as compared to **3**.

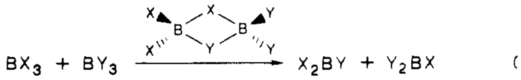
An inspection of the vibrational frequencies of **2** and **3** reveals an imaginary frequency in **3** ($135i$ cm^{-1}), which interconverts equivalent **2** structures. Relative to the 1,5-$C_2B_3H_5$ carborane with a substituted BH_2 group and BH_3 (**1**), **2** is 30.1 kcal/mol lower in energy, which is similar to the 29.5 kcal/mol stabilization calculated at the same level for the association of two BH_3 units. Hence, a $C_2B_3H_4$ unit has an effect similar to hydrogen in the predicted association of two boranes.

When orbital energies of the coupled cage are compared with 1,5-$C_2B_3H_5$ plus B_2H_6, remarkably little effect is seen. Both $C_2B_3H_4$ and B_2H_5 appear to each other like a hydrogen orbital with one electron in it. A demonstration of the small perturbing effect is given in Table III. If a terminal hydrogen from the carborane and a bridging hydrogen from diborane are removed with no orbital relaxation allowed, the orbitals match almost perfectly the orbitals of the coupled cage. The orbital at 15.11 eV is primarily a BH orbital of 1,5-$C_2B_3H_5$ while the orbital at 15.73 eV is the out-of-phase combination of the two bridge hydrogens in diborane. The average value of 15.42 eV is nearly the same energy as the orbital of B–B character in the coupled cage.

The alternative condensation of 1,5-$C_2B_3H_5$ and B_2H_6 is through two terminal BH bonds. The resulting structure (**4**, Figure 1) indicates very little change of either the carborane or diborane skeleton. The coupled-cage formed through terminal BH condensation is only slightly less stable than condensation through a bridge BH condensation. Thus, as a free borane approaches, one of its hydrogens interacts with the empty orbital of the exocyclic BH unit while the p orbital interacts nearly equivalently with a hydrogen of the exocyclic BH_2 unit or with the exposed boron of the carborane cage.

The question arises as to what the energetics are of coupled-cage fusion into a single-cage structure. Two possibilities were considered. Either the exocyclic BH_2 unit could be incorporated to form a $C_2B_4H_6$ carborane or two borons could be incorporated to form a $C_2B_5H_7$ carborane with loss of H_2. Somewhat surprising is the fact that 1,6-$C_2B_4H_6$ plus borane (**5**) is of similar energy to that of **2** and **4**. If **1** and **5** are compared, it is seen that incorporation becomes 34.0 kcal/mol exothermic. Incorporating two borons to form 2,4-$C_2B_5H_7$ plus H_2 (**6**) yields the most stable form of $C_2B_5H_9$ and is 67.7 kcal/mol exothermic with respect to **1**.

Coupled cages can also serve as transition states for terminal exchange reactions. It is generally accepted[38] that substituent exchange between two borane species, BX_3 and BY_3, proceeds via a cyclic intermediate or transition state as shown in eq 1. A

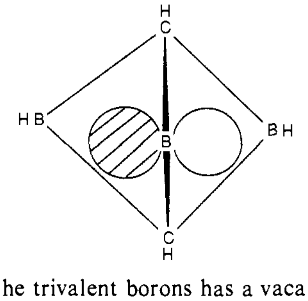


$$BX_3 + BY_3 \longrightarrow X_2BY + Y_2BX \qquad (1)$$

slow side reaction between 2,4-$C_2B_5H_7$ and B,B'-Cl_2-2,4-$C_2B_5H_5$ involving intermolecular chlorine exchange has been proposed[2] to occur by this type of mechanism. The transition state for exchange of terminal hydrogens in 1,6-$C_2B_4H_6$ with BH_3 can be thought of as a coupled cage in which the cage replaces the BX_2 or BY_2 unit in eq 1. Two structures of the coupled cage were explored corresponding to the bridging hydrogens perpendicular to (**7**) or in the same plane (**8**) as the four borons of the carborane (Figure 1). Both structures are of similar energy, and at the highest level ([MP2/6-31G*]), **7** is 3.5 kcal/mol more stable than **8**.

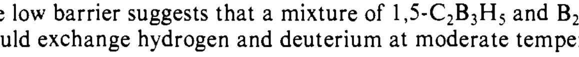
The barrier for hydrogen exchange can be calculated as the difference between **5** and **7** (11.1 kcal/mol). Of course an actual scrambling experiment would not involve BH_3 but rather B_2H_6, and the barrier for hydrogen exchange between 1,6-$C_2B_4H_6$ and B_2H_6 would be higher. Recent theoretical work[39] has suggested that full dissociation of B_2H_6 is not required before BH_3 can react. Instead, if the source of BH_3 is complexed as B_2H_6, an additional activation of 24 kcal/mol is required rather than full dissociation, which is 35 kcal/mol. Therefore, the terminal hydrogen exchange with B_2H_6 instead of BH_3 would require about 35 kcal/mol (11.1 + 24) of activation. This barrier is higher than the known pyrolysis barrier[40-42] for diborane (27 kcal/mol) and therefore should not be observed.

The exchange mechanism was also studied for the smaller carborane 1,5-$C_2B_3H_5$ and BH_3. Two orientations of the BH_4 unit were investigated, which were similar to the two orientations of $C_2B_5H_9$ (**7** and **8**). In contrast to **7** and **8** there is a large difference in the energy between the two orientations of $C_2B_4H_8$ (**10** and **11**) where, in the preferred orientation, the bridging hydrogens are in the three-boron plane of the carborane (**11**). A rationalization of the preferred structure can be made with the argument of Andersen et al.[43] The two orientations differ in the degree of utilization of the p orbital on the boron of the carborane, which interacts with the bridging hydrogens of the BH_4 moiety. This is readily apparent from the classical depiction of the bonding in the $C_2B_3H_4$ moiety (below)



where each of the trivalent borons has a vacant orbital. When the bridging hydrogens of the BH_4 moiety approach in the plane containing the three borons (as is the case for **11**), the well-recognized bonding pattern of diborane results. Thus, the similar stability of **7** and **8** can be explained by a similar utilization of the p orbital on boron in the parallel and perpendicular orientations (for the isoelectronic $B_6H_6^{2-}$ the two orientations are identical).

From the relative energies of **9** and **11**, the cage compound is found to be more stable than 1,5-$C_2B_3H_5$ and BH_3 by 13.6 kcal/mol. It is not expected that **11** should be observed since the reaction shown in eq 2, which involves the self-association of BH_3



$$2\ 1,5\text{-}C_2B_2H_4B\overset{H}{\underset{H}{\,}}BH_2 \longrightarrow 2\ 1,5\text{-}C_2B_3H_5 + B_2H_6 \qquad (2)$$

11

(calcd 28.9 kcal/mol; exptl 35 kcal/mol), is exothermic by 1.7 kcal/mol (28.9–(2 × 13.6)). A stable complex between 1,5-$C_2B_3H_5$ and B_2H_6 similar to **11** is also not expected; however, as a transition state, such a structure would serve to exchange terminal hydrogens. If we use 24 kcal/mol as the additional activation required when B_2H_6 is the source of BH_3, a barrier of about 10 kcal/mol (–13.6 + 24) is predicted for hydrogen exchange. The low barrier suggests that a mixture of 1,5-$C_2B_3H_5$ and B_2D_6 should exchange hydrogen and deuterium at moderate temperatures.

The exothermicity of forming a larger cage from 1,5-$C_2B_3H_5$ and BH_3 (**9**) was also calculated. The reaction to form 1,6-$C_2B_4H_6$ and H_2 (**12**) is predicted to be 33.3 kcal/mol exothermic while the reaction to form $C_2B_4H_8$ (**13**) is 33.2 kcal/mol exothermic (Table II). In this regard it is interesting to note the important contributions made by electron correlation and polarization

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functions to relative energies. At the 6-31G level, the reaction **9** → **12** is 12.9 kcal/mol endothermic and the reaction **9** → **13** is 3.8 kcal/mol exothermic. Clearly, reliable results concerning energetics cannot be determined by using only double-ζ or minimal basis set calculations.

Conclusion

Coupled cages have been studied by quantum mechanical methods, which include the effect of both electron correlation and polarization functions. A 1,5-$C_2B_3H_4$ group is nearly equivalent to hydrogen with respect to its interaction as a bridge or terminal group in diborane. This is attributable to the exo/endo separability of the molecular orbitals, which allows the exo orbital on the vacant boron of the $C_2B_3H_4$ group that is outwardly hybridized to interact without significant overlap of the other endo orbitals. In effect these endo orbitals are "folded back" due to their involvement in cluster bonding in the carborane cage.

The terminal hydrogen exchange reaction between BH_3 and the carboranes 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ was studied. From extrapolation of these results it was estimated that the exchange of terminal hydrogens of 1,5-$C_2B_3H_5$ with B_2H_6 takes place with a barrier of about 10 kcal/mol while in 1,6-$C_2B_4H_6$ the barrier is about 35 kcal/mol.

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Registry No. 1, 114467-67-3; **2**, 114467-68-4; **5**, 20693-67-8; **6**, 20693-69-0; **7**, 114467-69-5; **9**, 20693-66-7; **10**, 114467-70-8; **13**, 18972-20-8; BH_3, 13283-31-3; B_2H_6, 19287-45-7.

Cis–Trans Energy Difference for the Peptide Bond in the Gas Phase and in Aqueous Solution

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Abstract: Ab initio molecular orbital calculations and Monte Carlo statistical mechanics simulations have been used to study the cis–trans equilibrium for *N*-methylacetamide (NMA) in the gas phase and in dilute aqueous solution. Geometry optimizations were carried out with the 6-31G(d) basis set for the cis and trans forms of NMA. After calculation of the correlation energies with second-order Møller–Plesset theory and the vibrational frequencies, the computed ΔH^{298} and ΔG^{298} favor the trans form by 2.1 and 2.5 kcal/mol in the gas phase. Then, in order to proceed to the simulations in water, the predictions of the OPLS potential functions were compared to results of 6-31G(d) ab initio calculations for complexes of *cis*- and *trans*-*N*-methylformamide (NMF) with a single water molecule. This revealed that the OPLS functions erroneously favor the hydrogen bond to the N–H group in the trans form by ca. 1.3 kcal/mol in comparison to the cis. Compensation requires the use of slightly different charge distributions for the cis and trans forms, which are consistent with the order of the ab initio dipole moments ($\mu_{\text{cis}} > \mu_{\text{trans}}$). Statistical perturbation theory was then applied in Monte Carlo simulations using 216 TIP4P water molecules to compute the difference in free energies of hydration as *trans*-NMA is converted to *cis*-NMA at 298 K. If the OPLS parameters are used for both the cis and trans conformers, the trans isomer is computed to be better hydrated by 2.2 ± 0.3 kcal/mol. However, utilization of the refined charge distributions yields no statistically significant difference in the free energies of hydration (0.1 ± 0.3 kcal/mol favoring trans). These findings emphasize the sensitivity of such results to the details of the intermolecular potential functions. For NMA, the predicted free energy difference of 2.6 ± 0.3 kcal/mol in water is in accord with NMR results (2.5 ± 0.4 kcal/mol), and the negligible solvent effect is consistent with the observed insensitivity of the cis–trans equilibria for NMA and NMF to changes in solvent.

Amides provide the simplest models for the structure and conformational characteristics of the backbones of proteins. Some well-established features for the peptide bond in both amides and proteins are the coplanarity of the groups attached to it, its partial double-bond character that is reflected in shortened C–N distances (ca. 1.34 Å) and substantial rotational barriers (ca. 20 kcal/mol), and preference for the trans rather than cis configuration.[1] The latter bias is sufficiently strong that no more than a few percent of the cis form is detected in experimental studies of secondary amides, and virtually no cis peptide bonds occur in X-ray structures for proteins except when the nitrogen is tertiary, i.e. in a proline residue.[1-9] The low cis population makes accurate experimental determination of the cis–trans energy difference difficult; consequently, it is unclear how the preference for trans peptide bonds in proteins is partitioned between intrinsic and environmental effects. To help elucidate these fundamental questions, the present study has been undertaken to obtain high-level theoretical estimates for the cis–trans energy difference of *N*-methylacetamide (NMA) both in the gas phase and in dilute aqueous solution. The gas-phase results for the enthalpy, entropy, and free energy change at 298 K come from ab initio molecular orbital calculations, with the 6-31G(d) basis set augmented with correlation energy and vibrational frequency calculations. The difference in free energies of hydration for the two conformers is then obtained from statistical perturbation theory in the context of Monte Carlo simulations for the solutes plus 216 water molecules. Analysis of 6-31G(d) results on complexes of *N*-methylformamide (NMF) with a single water molecule indicates the need to use slightly

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