Potentially Aromatic Metallocycles

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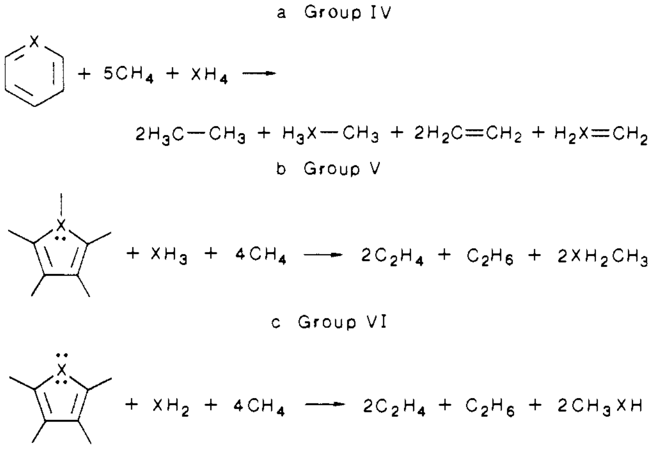
Abstract: Ab initio molecular orbital theory is used to characterize a series of metal-substituted benzene and cyclopentadiene structures, with the heteroatom taken from the block in the periodic table bounded by groups IV-VI and periods 2-5. Structures are predicted with the 3-21G* basis set and SCF wave functions. The calculated bond lengths and bond angles are in general within 0.04 Å and 2°, respectively, of the available experimental values. As a measure of the delocalization stabilization, ΔE and ΔH_0 values for the appropriate bond separation and superhomodesmic reactions are calculated with 3-21G* Hartree-Fock energies for these compounds and some smaller acyclic structures.

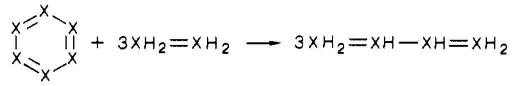
I. Introduction

Considerable efforts have gone into the study of five- and six-membered ring compounds.[1-38] The theoretical and experimental work involving benzene, substituted silabenzene, and the various isomers of disilabenzene have recently been reviewed.[1,2]

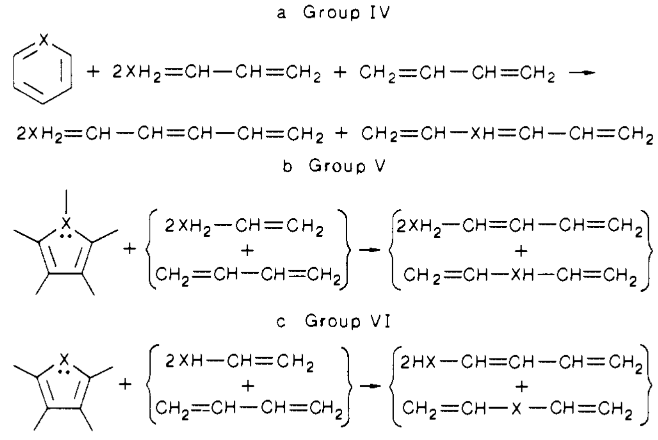
Scheme I. Bond Separation Reactions



Scheme II. Homodesmic Reaction



Scheme III. Superhomodesmic Reactions



Scheme IV. Superhomodesmic Reaction

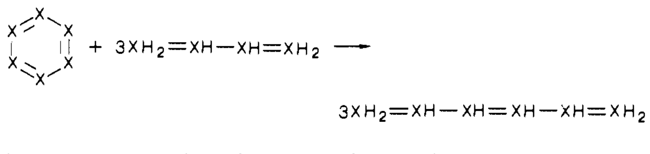


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Table I

C	N	O
Si	P	S
Ge	As	Se
Sn	Sb	Te

In addition, several theoretical and experimental papers have appeared in the literature relating to other metal-substituted benzenes. Included in these studies are those that focus on aromatic character and the various methods by which aromaticity may be defined.[14-37] In particular, significant attention has been given to the comparison of the properties of pyridine with benzene.[15-19] Initial concepts of aromaticity have been derived from these studies. George et al.[15] calculated empirical resonance energies for benzene and pyridine from experimental $\Delta H_f°$ data and from 6-31G(d)[38] self-consistent field (SCF) calculations. These results predict the aromatic stabilization of pyridine and benzene to be essentially the same. Among the studies performed on phosphabenzene,[20-24] Lohr et al.[20] theoretically determined gas-phase proton affinities in a series of phosphorus compounds, including phosphabenzene and three protonated forms of phosphabenzene, using a variety of basis sets. It was inferred from this study, in agreement with experiment, that P-site protonation is favored.[24]

More extensive studies have been carried out by several groups.[25-28] Ashe[25] considered the series of compounds MC_5H_5, M = CH, N, P, As, Sb. In this experimental study of a family of aromatic compounds in which carbon is bonded to an entire column of elements, the concept of aromaticity was addressed by a comparative study of their NMR spectra, structural data, and chemical behavior. This work will be considered in more detail below. An investigation by Campos-Vallette and Clivijo[26] involved the calculation of the force field and mean amplitudes of vibration and experimental determination of relative reactivities of the furan-like series MC_4H_4, M = O, S, Te, Se. The ground-state aromaticity order thiophene > tellurophene > selenophene > furan was determined by considering force fields and mean amplitudes of vibration of the compounds. In the same work, the reactivity toward electrophilic substitution was determined to be in the order furan > selenophene > tellurophene > thiophene.

Various methods have been employed to determined aromaticity. One method used[4,6] to provide a quantitative measure of the delocalization stabilization in potentially aromatic compounds is the calculation of the energy difference ΔE for the appropriate bond separation reaction.[39] This type of reaction measures the stability of a parent molecule relative to isolated prototypical bonds. Examples of these bond separation reactions are given in Scheme I. The aromaticities of benzene, silabenzene,[2] and the three isomers of disilabenzene[8] using such isodesmic reactions have previously been considered in this laboratory with 3-21G[40] energies at STO-2G[41] geometries (hereafter denoted 3-21G//STO-2G). These reactions measure the stability of the parent molecule relative to its *simplest* isolated prototypes (Scheme I), such that each bond type is formally conserved. Such a reaction minimizes the importance of correlation error in the calculation.

Two types of isodesmic reactions that have been used by Nagase et al.[11] are the homodesmic[42] (Scheme II) and the superhomodesmic[43] (Scheme IV) reactions. Note that these latter two types of reactions conserve successively larger fragments of the parent ring compounds. In particular, superhomodesmic reactions directly measure the effect of "cyclizing" an already delocalized structure. Comparisons of the ΔE for these two types of reactions were performed for benzene, silabenzene, and hexasilabenzene at both the SCF/3-21G and SCF/6-31G(d) levels for both systems.[11] The results for the homodesmic reactions differed from those of the superhomodesmic reactions by less than 2 kcal/mol. The numerical results indicated that hexasilabenzene has approximately half the aromatic stabilization energy of benzene.[11] More general examples of superhomodesmic reactions are given in Scheme III.

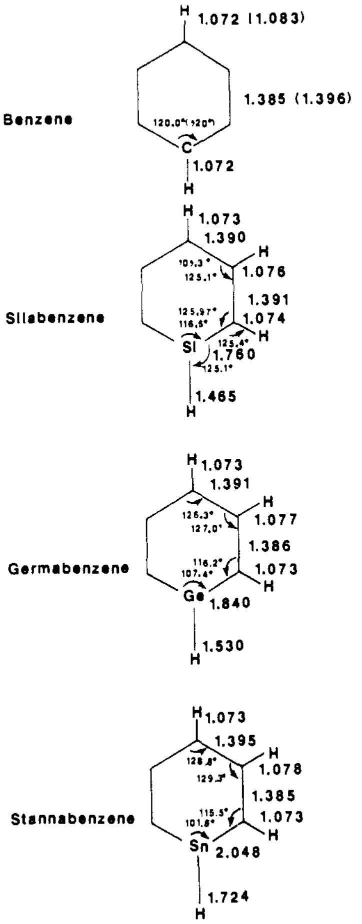

Figure 1. SCF/3-21G* geometries for group IV six-membered rings. Angles are in degrees, and bond lengths are in angstroms. Experimental values are given in parentheses.

The present study considers the potential aromaticity in various ring structures containing the block of elements from the periodic chart in Table I. Only the planar isomers of the six-membered ring structures have been considered. Group IV elements (Si, Ge, Sn) all form analogues that are isovalent with benzene. In these structures (Figure 1), the $(4n + 2)\pi$ network may be directly compared with this reference molecule. Group V analogues of benzene are slightly different in that the heteroelement has a nonbonding electron pair, which is not used in the aromatic sextet (Figure 2). For this group, analogues of the five-membered ring cyclopentadiene, such as pyrrole, are also potentially aromatic heterocycles. These compounds (Figure 3), in contrast to their six-membered ring counterparts, could delocalize the lone pair of electrons into the butadienyl backbone.

Group VI elements do not have a substituted benzene analogue that has a $(4n + 2)$-π network. One can, however, consider the

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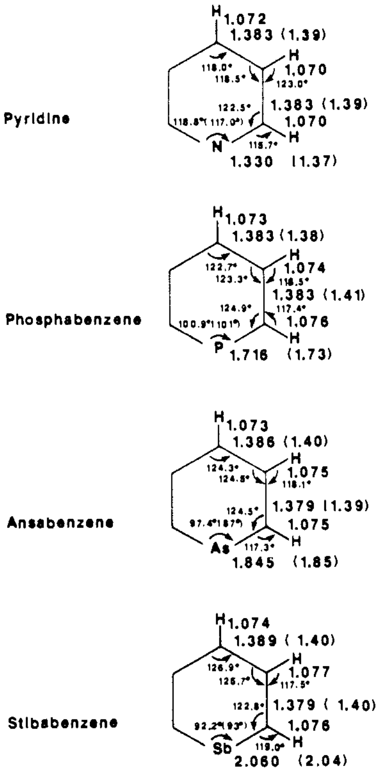

Figure 2. SCF/3-21G* geometries for group V six-membered rings. Angles are in degrees, and bond lengths are in angstroms. Experimental values are given in parentheses.

substituted five-membered rings such as furan and thiophene (Figure 4). These compounds involve heteroatoms with two lone electron pairs, which could delocalize into the butadienyl backbone.

In this work each of the possible structures for the group of elements given in Table I is considered with both bond separation and superhomodesmic reactions as a measure of the delocalization stabilization (aromaticity). After an outline of the theoretical methods in section II, the results of the calculations are presented in section III. A summary and conclusions are presented in section IV.

II. Computational Methods

All geometries have been optimized with the 3-21G* basis set[44] at the SCF level of computation, using the optimization methods in GAUSSIAN82[45a] for compounds containing second- and third-period atoms and GAMESS[45b] for those containing fourth- and fifth-period atoms. The latter program was used because of convergence problems for these elements in GAUSSIAN82. Note that the GAUSSIAN82 and GAMESS calculations utilized five and six d orbitals, respectively, on the third- to fifth-period elements. The d orbital exponents have been given in previous papers.[46]

The corresponding force fields were performed for each structure with the appropriate programs. GAUSSIAN82 provides analytical gradients and energy second derivatives, whereas GAMESS obtains the second derivatives from finite differences of analytical gradients. All structures were verified as minima on their respective potential energy surfaces via their positive definite force constant matrices. The calculations were carried out with the North Dakota State University IBM 3081D and the Quantum Chemistry VAX 11/750 and Celerity C1260D computers.

III. Results and Discussion

A. Structures. The calculated structures for the group IV and V six-membered rings and the group V and VI five-membered rings are compared with the available experimental data in Figures

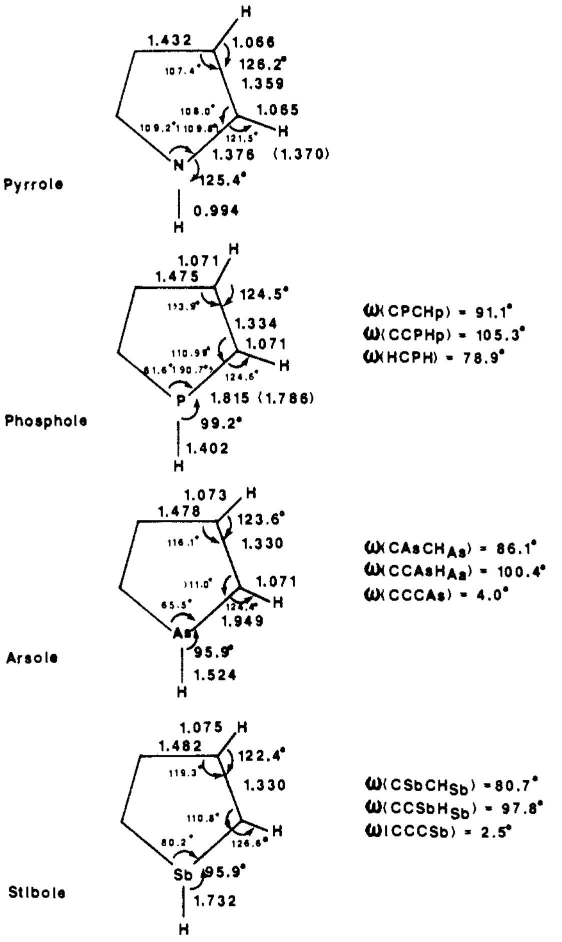

Figure 3. SCF/3-21G* geometries for group V five-membered rings. Angles are in degrees, and bond lengths are in angstroms. Experimental values are given in parentheses.

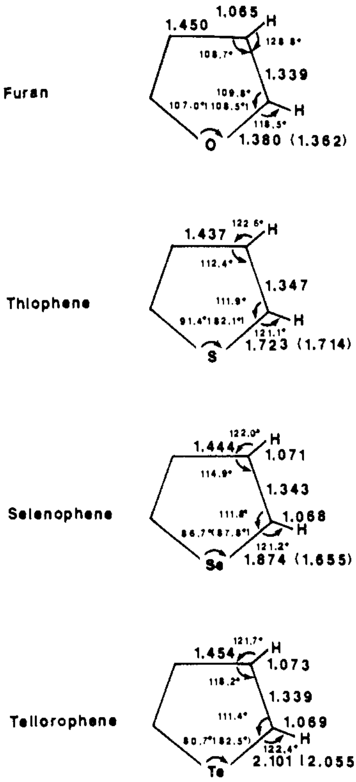

Figure 4. SCF/3-21G* geometries for group VI five-membered rings. Angles are in degrees, and bond lengths are in angstroms. Experimental values are given in parentheses.

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Table II. SCF/3-21G* Bond Lengths for Isolated Single and Double Bonds (Å)

X	XH_3—CH_3 X—C	XH_2—CH_2 X=C
C	1.542	1.315
Si	1.885	1.692
Ge	1.979	1.773
Sn	2.187	1.982
X	XH_2—CH_3 X—C	XH=CH_2 X=C
N	1.471	1.256
P	1.857	1.644
As	1.985	1.770
Sb	2.192	1.986
X	XH—CH_3 X—C	
O	1.441	
S	1.825	
Se	1.965	
Te	2.182	

Table III. Energetics and Enthalpies (kcal/mol) for Bond Separation and Superhomodesmic Reactions

	bond separation		superhomodesmic	
X	ΔE	ΔH^a	ΔE	ΔH^a
	Six-Membered Rings			
C	60.18^b	61.27	25.99	23.29
Si	46.44^b	46.84	17.97	16.02
Ge	45.57	46.32	16.75	
Sn	42.16	42.82	12.20	
N	64.19^b	63.96	25.78	21.89
P	56.56^b	56.63	23.30	20.89
As	53.49	53.87	21.58	
Sb	50.49	50.52	18.56	
	Five-Membered Rings			
N	42.70	43.80	5.16	5.62
P	12.23	16.49	-1.53	-0.20
As	12.86	16.81	-0.18	
Sb	11.05	14.33	-1.92	
O	32.37	35.19	5.01	5.01
S	30.21	32.54	10.07	9.80
Se	24.90	27.78	7.89	
Te	19.11	22.19	4.31	

^{a}Corrected for scaled zero-point vibrational energies (see text). ^{b}Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. In *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 375.

1-4, respectively. For comparison purposes, the isolated single- and double-bond lengths, calculated at the same level of theory, are summarized in Table II. All other structural data for the reference molecules in Schemes I and III are available from the authors upon request.

The structures of benzene and silabenzene (Figure 1) have been discussed previously[2]. The CX bond lengths in the group IV six-membered rings are 0.03-0.04 Å shorter than the average of their isolated singly and doubly bonded analogues (see Table II), indicating substantial delocalization. Note that the rings become successively distorted as the size of the heteroatom increases. In particular, the increasing length of the CX bond and the near-constancy of the CC bond lengths result in a steady decrease in the CXC angle from 120° in benzene to 101.6° in stannabenzene.

The SCF/3-21G* structures of the group V six-membered rings (Figure 2) are in good agreement with the experimental geometries, the calculated bond lengths and angles being within 0.01 Å and 1° of the experimental values, respectively. The CX and CC bond lengths are again 0.03-0.04 Å shorter than the average of the corresponding single- and double-bond lengths, suggesting significant delocalization. The phenomenon of decreasing CXC bond angle with increasing size of the heteroatom is observed here as well. The CSbC angle in stibabenzene is 92.2°, in good agreement with the experimental value of 93°.[15]

The calculated structure of pyrrole is in excellent agreement with experiment, while the calculated CPC angle in phosphole is 9° greater than the experimental value (Figure 3). The experimental structures of arsole and stibole are apparently not known.

The CNC angle in pyrrole is 109.2°, close to the value typically preferred by saturated nitrogen. This leads to rather small CCC (107.4°) and CCN (108.0°) angles. Since the base butadienyl moiety is formally sp^2 hybridized, these small angles presumably introduce some strain into the ring. The much smaller apex angles in the P, As, and Sb analogues result in larger CCX and (especially) CCC angles, thereby reducing this strain. On the other hand, comparison of the CC bond lengths in these compounds reveals a much greater delocalization in the nitrogen species compared with the other three heterocycles. The base CC bond length in pyrrole (1.432 Å) is 0.035 Å shorter than that in SCF/3-21G* butadiene. In contrast, the base CC bond lengths in phosphole, arsole, and stibole are somewhat longer than the central CC bond in butadiene. Similar comments apply to the lengths of the side CC bonds of the group V five-membered rings, relative to the terminal bond lengths (1.320 Å) in butadiene. A further indication of delocalization in these rings is the shortening of the CX bond, relative to an isolated single bond (Table II). This shortening is 0.095, 0.042, 0.036, and 0.031 Å, respectively, in the N, P, As, and Sb five-membered heterocycles.

The calculated geometries for the group VI five-membered rings (Figure 4) are generally in excellent agreement with experiment, the general deviation being less than 0.01 Å for bond lengths and 2° for angles. An exception to this is the CTe bond length, which is calculated to be 0.05 Å longer than the experimental value. The COC apex angle in furan is 107°, similar to that in typical divalent oxygen compounds. As for the nitrogen ring discussed in the previous paragraph, this leads to strained CCC and CCX angles relative to the preferred 120°. The much smaller apex angles for the S, Se, and Te rings lead to larger CCX and (especially) CCC angles, with an expected concomitant decrease in ring strain. In contrast with the group V rings, however, the oxygen ring has not only the most strained but also the least delocalized structure. This may be seen from the CC bond lengths (Figure 4) and from the shortening of the CX bond relative to the analogous isolated CX single-bond lengths (Table II). This shortening is 0.060, 0.101, 0.091, and 0.081 Å for the O, S, Se, and Te rings, respectively. Thus, one does not expect significant delocalization stabilization in furan.

B. Energetics. The energy differences (ΔE) for the bond separation and superhomodesmic reactions are summarized in Table III. For all of the bond separation reactions and the homodesmic reactions for periods 2 and 3, these energy differences have also been corrected for zero-point vibrational energies (ZPE), scaled by a factor of 0.89 to correct for the overestimation of vibrational frequencies by SCF calculations,[47] to yield zero-point enthalpy differences ($\Delta H_0°$). The ZPE corrections increase the bond separation $\Delta H_0°$ values by a nearly constant 1-3 kcal/mol relative to the analogous ΔE's, so the trends for the two sets of energies are the same. Because the superhomodesmic reactions yield a much less drastic change in the molecular and electronic structures than do the bond separation reactions, the ZPE corrections for the former are much smaller—on the order of 1 kcal/mol or less for the second- and third-row heterocycles. Because of this, the vibrational analyses of the *reference compounds* for the fourth- and fifth-period rings were omitted to save computer time.

As has been noted previously,[6] the bond separation reactions predict silabenzene to be roughly 75% as aromatic as benzene. The superhomodesmic reactions predict a similar value of 70%. As expected, the absolute values for the superhomodesmic energy differences are much smaller than those for the bond separation reactions, since the latter constitute a much greater change in molecular and electronic structure. The delocalization stabilization

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J. Am. Chem. Soc. 1988, 110, 4208-4212

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.

Acknowledgment. This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by grants from the National Science Foundation (CHE86-40771) and the Air Force Office of Scientific Research (87-0049). The calculations were performed on the North Dakota State University IBM 3081-D32 computer, on a VAX 11/750 purchased by AFOSR Grant 84-0428, and on the Celerity C1260D purchased by NSF Grant CHE-8511697. We are indebted to Prof. Michael W. Schmidt and Jerry Boatz for several helpful discussions.

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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Received November 12, 1987

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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