Do Möbius Silabenzene and Möbius Phosphabenzene Exist? Ab Initio MO and Density Functional Study of Electrocyclic Ring-Opening Reactions of Hetero-Dewar Benzenes Containing Silicon or Phosphorus

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Ab initio molecular orbital and hybrid density functional calculations have been performed on the electrocyclic ring opening of *cis*-Dewar silabenzenes **1a** and **2a** and *cis*-Dewar phosphabenzenes **1b** and **2b**. Complete structural optimizations at the correlated MP2/6-31G*, CCSD(T)/6-31G*//MP2/6-31G*, B3LYP/6-31G*, and B3LYP//6-311G*/B3LYP/6-31G* levels predict the existence of Möbius silabenzene (**3a**; 1,3,5-*cis,cis,trans*-1-silacyclohexatriene), having an energy 70−76 kcal mol^{-1} higher than that of silabenzene **4a**. Möbius phosphabenzene (**3b**; 1,3,5-*cis,cis,trans*-1-phosphacyclohexatriene) is predicted to exist 80−85 kcal mol^{-1} above phosphabenzene **4b**. Ring opening of *cis*-Dewar silabenzene **1a** involves a barrier of 20−23 kcal mol^{-1} and results in the formation of Möbius silabenzene (**3a**). Ring opening of **1b** produces the analogous Möbius phosphabenzene (**3b**) by overcoming a barrier of 26−31 kcal mol^{-1}. These potential energy barriers are very close to the experimental enthalpic barrier of 23−25 kcal mol^{-1} for the formation of the parent Möbius benzene. The structures of **3a** and **3b** exhibit one fully trans double bond with dihedral angle H−C−C−H $\approx$ 180°. Bonding considerations reveal that Möbius silabenzene is antiaromatic, while Möbius phosphabenzene is nonaromatic in nature. The rotation of the trans π-bond in **3a** and **3b** results in the lowest energy benzenoid isomers **4a** and **4b**. Calculations also support the existence of higher energy *trans*-Dewar silabenzene (**5a**) and *trans*-Dewar phosphabenzene (**5b**) as potential minima. The ring opening of **5a** yields silabenzene, while that of **5b** results in phosphabenzvalene **6b**. We also characterized two other higher energy phosphabenzvalene isomers, **7b** and **8b**, as potential minima. The phosphabenzvalene **6b** is found to be closer in energy to the benzenoid form **4b** than the Dewar phosphabenzene isomers investigated in this study. The present analysis reveals that a conrotatory mode of ring opening takes place in Dewar silabenzenes and Dewar phosphabenzenes. Progress of the electrocyclic ring-opening reactions is monitored by estimating the extent of bond formation/breakage in the respective transition states. It is found that the extent of π-bond breaking is more pronounced than that of π-bond formation at the transition states.

1. Introduction

Pericyclic ring-opening reactions involving high-energy structures are quite common among isomers of benzene. The ring-opening reactions of *cis*-Dewar benzene (*cis*-bicyclo[2.2.0]hexadiene) and *trans*-Dewar benzene (*trans*-bicyclo[2.2.0]hexadiene) are shown to be orbital symmetry controlled.[1] *cis*-Dewar benzene undergoes a ring-opening reaction to give Möbius benzene (1,3,5-*cis,cis,trans*-cyclohexatriene) in a shallow energy minimum, which is ∼100 kcal mol^{-1} above benzene. The π-orbital basis in 1,3,5-*cis,cis,trans*-cyclohexatriene defines a Möbius topology, and hence, this compound has been referred to as Möbius benzene or as *trans*-benzene (as there is a trans-fused double bond in the ring). Möbius benzene undergoes trans-π-bond rotation to give benzene. The stationary points have been located at various levels of theory using ab initio calculations.[1] Two-configuration SCF (TCSCF) calculations by Johnson and Daoust[1] and complete active space SCF (CASSCF) calculations by Havenith et al.[2] seem to indicate a direct conversion of *cis*-Dewar benzene to benzene. The *trans*-Dewar benzene is predicted to be a possible benzene isomer, which is ∼158 kcal mol^{-1} higher in energy than benzene. This species undergoes a ring-opening reaction to yield benzene.

Substitution of a methine unit (CH) in isomers of benzene by isovalent electronic −SiH or −P produces

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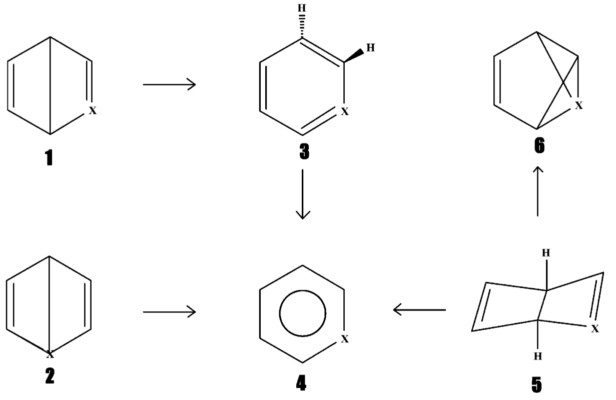
varied isomers, which outnumber those of the parent hydrocarbon. Discussions on silaaromaticity by different groups have stimulated synthetic attempts toward silabenzene.[3−6] Silabenzene eluded synthesis for a long time, and silatoluene was the first closely related molecule to be synthesized and characterized.[7,8] Only after much effort was the parent silabenzene synthesized and subjected to spectral characterization.[9−13] Maier and co-workers[12a] have reported the photochemical isomerizations of silabenzene and Dewar silabenzene in a matrix isolation study. Wakita et al. determined the structure of silabenzene by X-ray crystallography and studied its photochemical valence isomerization into silabenzvalene.[13a] Phosphabenzene and some of its valence isomers have been synthesized and are found to display exciting isomerization reactions and novel binding modes to transition-metal fragments.[14−16]

Several studies have focused on the stability of silabenzene and its isomers using semiempirical and ab initio calculations.[17−23] The recent rigorous ab initio calculations on silabenzene indicate that it is only slightly less aromatic than benzene.[5,24] Priyakumar and Sastry[25] have identified two new valence isomers of silabenzene which are local minima lying only ~20 kcal mol^{-1} above silabenzene, on the basis of MP2, CCSD(T), and hybrid density functional calculations.

Scheme 1. Potential Electrocyclic Ring-Opening Pathways for Substituted Bicyclo[2.2.0]hexadienes[a]



[a] In **1a**−**5a**, X = SiH, and in **1b**−**6b**, X = P.

The high-energy isomers of silabenzene and phosphabenzene, which have not been characterized experimentally so far are expected to be less stable, similar to the high-energy isomers of benzene, and can conveniently be studied theoretically. Theoretical characterization of hitherto unknown valence isomers can enthuse experimentalists, as there has been a surge of interest in the synthesis of several organometallic compounds containing heterocyclic ligands.[14,15,26] It is interesting to note that a novel structure, in contrast to the Dewar, Möbius, and Hückel isomers, has been detected by an ultrafast electron diffraction study of the excited state of pyridine through a ring-opening reaction.[26h] In the present study, we investigated the electrocyclic ring-opening reactions of monosubstituted Dewar benzenes having a silicon or a phosphorus heteroatom by quantum-chemical computations. Ring-opening reactions from the two forms of *cis*-hetero Dewar benzenes **1** and **2** and the trans isomer **5** are studied. Scheme 1 depicts the potential electrocyclic pathways connecting the various isomers of C_5H_6Si and C_5H_5P.

In addition to the Möbius benzenes **3a** and **3b** shown in Scheme 1, where the heteroatom is one bond away from the trans fused bond, two more Möbius benzene analogues are theoretically possible. The heteroatom can either be a part of the trans fused double bond or be two bonds away, as depicted in Chart 1.

2. Methodology

The electrocyclic ring-opening reactions of the hetero-Dewar benzenes have been studied using the GAUSSIAN 94 and GAMESS programs.[27,29] All species involved in the study have been investigated by complete structural optimization using second-order Møller−Plesset (MP2) and hybrid density func-

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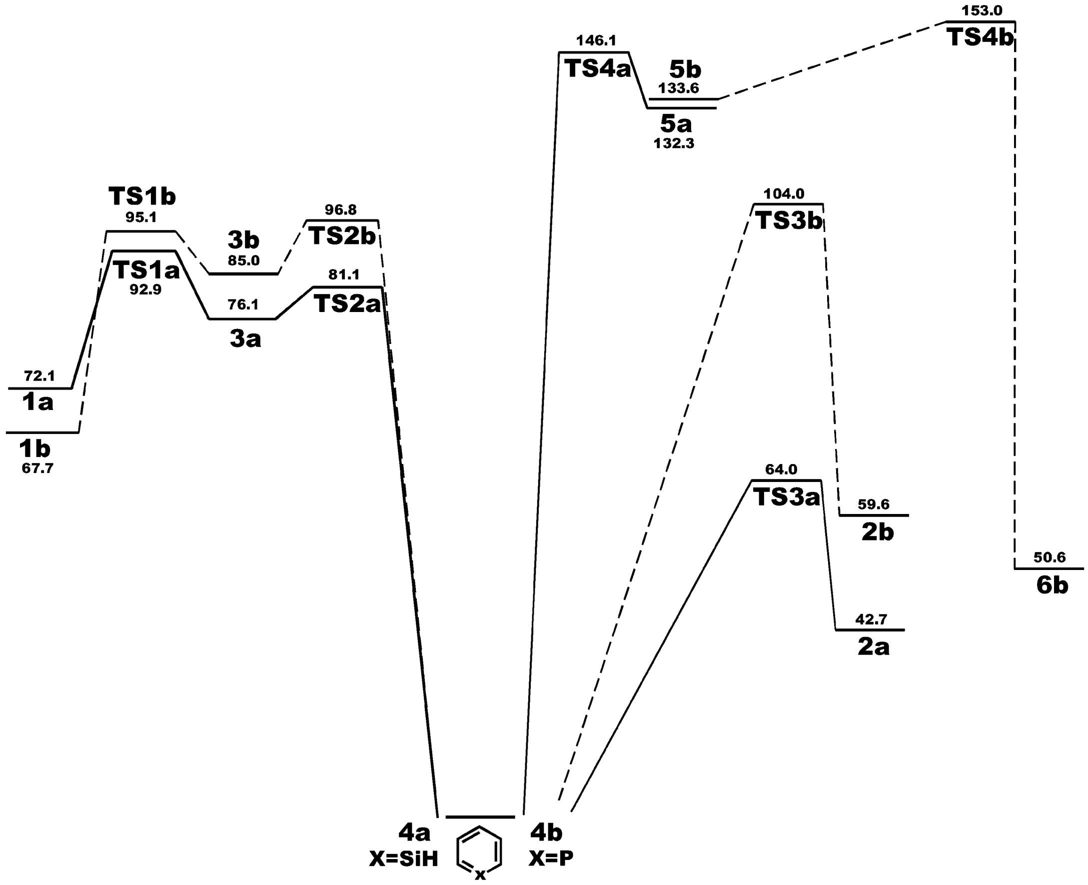
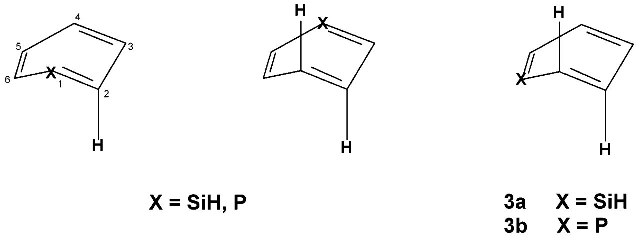


Figure 1. Schematic energy diagram for electrocyclic ring-opening pathways among the isomers of silabenzene and phosphabenzene. Relative energies at the B3LYP/6-31G* level are shown.

Chart 1. Structures of the Three Possible Möbius Silabenzenes (X = SiH) and Möbius Phosphabenzenes (X = P)



tional calculations at the 6-31G* level. The hybrid density functional calculations include Becke's three-parameter exchange and correlation components of the electron−electron interaction and the gradient-corrected nonlocal correlation functional of Lee, Yang, and Parr[28] (B3LYP). At the optimized geometries frequency calculations were performed to confirm the potential minima and saddle points. Intrinsic reaction coordinate (IRC) calculations have been carried out by starting from the transition states, and the reaction paths connecting a given transition state (TS) in both directions, leading to the reactant and the product, were verified. The extent of bond formation/cleavage along the reaction paths was examined using Wiberg's bond orders obtained by natural bond orbital (NBO) analysis using the NBO program[30] at the B3LYP/6-31G* level. To examine the role of more accurate correlation corrections to the relative energies along the potential energy surface (PES), coupled cluster calculations including singles, doubles, and triples terms at the CCSD(T)/6-31G*//MP2/6-31G* level were performed. We also carried out single-point calculations using the triple split valence basis set at the B3LYP/6-311G*//B3LYP/6-31G* level and compared the energetics.

3. Results and Discussion

Figure 1 depicts the relative energies in the electrocyclic ring-opening reactions in both silabenzene and phosphabenzene isomers at the B3LYP/6-31G* level. Similar trends in the relative energies are obtained by B3LYP/6-311G*//B3LYP/6-31G*, MP2/6-31G*, and CCSD(T)/6-31G*//MP2/6-31G* calculations. The total energies of the isomers of silabenzene and phosphabenzene and the transition states for the interconversions among the isomers at the various levels of theory are shown in the Supporting Information. The relative energies shown in Figure 1 are not corrected for zero-point vibrational energy (ZPVE), as comparison is also made with the results of other methods such as CCSD(T)/

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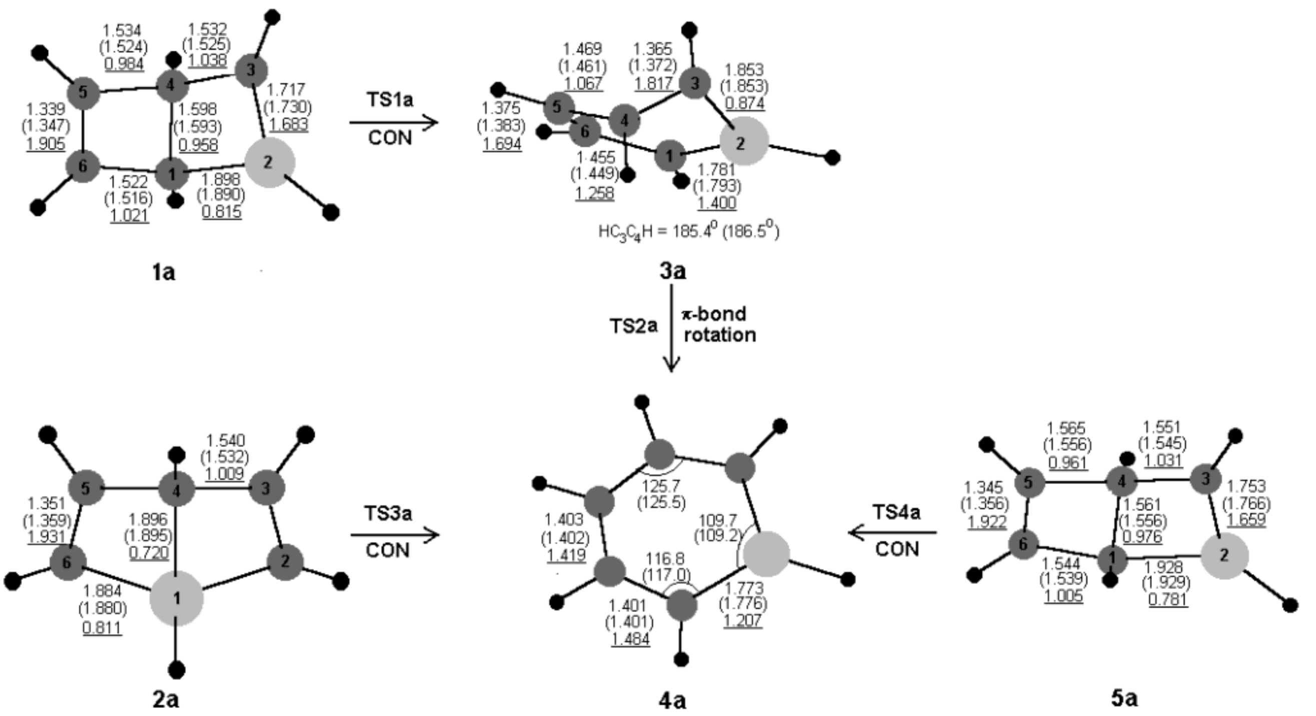

Figure 2. B3LYP/6-31G* and MP2/6-31G* (in parentheses) optimized structures of the isomers of C_5H_6Si and their interconversion pathways. The underlined values are the Wiberg bond orders at the B3LYP/6-31G* level.

6-31G*//MP2/6-31G*, for which ZPVE was not calculated. The ZPVE values of the different isomers at the B3LYP/6-31G* level are listed in the Supporting Information. The relative energies predicted by the B3LYP/6-31G* and B3LYP/6-311G*//B3LYP/6-31G* calculations vary within 1 kcal mol^{-1}. MP2/6-31G* calculations show a lowering of ~2−6 kcal mol^{-1} in the relative energies as compared to the B3LYP/6-31G* values in silabenzene isomers, while the lowering is less marked in phosphabenzene isomers. However, the transition states other than **TS1a** and **TS1b** are predicted to have slightly higher relative energies at the MP2/6-31G* level. As expected, the CCSD(T)/6-31G*//MP2/6-31G* calculations lower the relative energies more than in the MP2/6-31G* method, due to the additional correlation effects being taken into account. However, in the transition states the changes in relative energies are less, according to CCSD(T)/6-31G*//MP2/6-31G* calculations. Consequently, the potential energy barriers for the different ring-opening reactions under study are the lowest in the B3LYP method.

The optimized geometries of the isomers of silabenzene and phosphabenzene along the electrocyclic conversion pathways are shown in Figures 2 and 3, respectively. The transition-state geometries for the electrocyclic reactions are depicted in Figure 4. From Figures 2−4, it can be seen that the structural parameters predicted by both B3LYP/6-31G* and MP2/6-31G* levels of theory are very similar. Hessian calculations yielded positive vibrational frequencies for all the species given in Figures 2 and 3, indicating that they correspond to minima in the potential energy surface. Each transition state shown in Figure 4 is found to have only one imaginary vibrational frequency, confirming that it is a first-order saddle point in the PES. The values of the imaginary and first real vibrational frequencies obtained for the transition states from the B3LYP/6-31G* calculations are shown along with the optimized geometries in Figure 4. In the discussions that follow, we use the structural parameters and the bond orders obtained at the B3LYP/6-31G* level, as several recent works have shown that reliable results are predicted by this method.

Do Möbius Silabenzene (3a) and Möbius Phosphabenzene (3b) Exist? Both theory and experiment have provided convincing evidence for the existence of *trans*-cyclohexene.[31,32] The structural similarity between *trans*-cyclohexene and 1,3,5-*cis*,*cis*,*trans*-cyclohexatriene has led to the investigation of the latter. The Si and P analogues, 1,3,5-*cis*,*cis*,*trans*-1-silacyclohexatriene (**3a**) and 1,3,5-*cis*,*cis*,*trans*-1-phosphacyclohexatriene (**3b**), are referred to as Möbius silabenzene and Möbius phosphabenzene.

Our calculations have characterized Möbius silabenzene and Möbius phosphabenzene by conrotatory ring opening of *cis*-Dewar benzene analogues **1a** and **1b**, respectively. They are readily located as minima on the RHF, MP2, and B3LYP potential energy surfaces. The dihedral angle HC_3C_4H is close to 180° (185.4° in **3a** and 170.8° in **3b**), indicating that both **3a** and **3b** possess one fully trans $C_3{=}C_4$ double bond, similar to that in Möbius benzene.[1] The trans π-bonds $C_3{=}C_4$ in Möbius silabenzene and Möbius phosphabenzene are substantially pyramidalized, as in *trans*-cyclohexene.[32]

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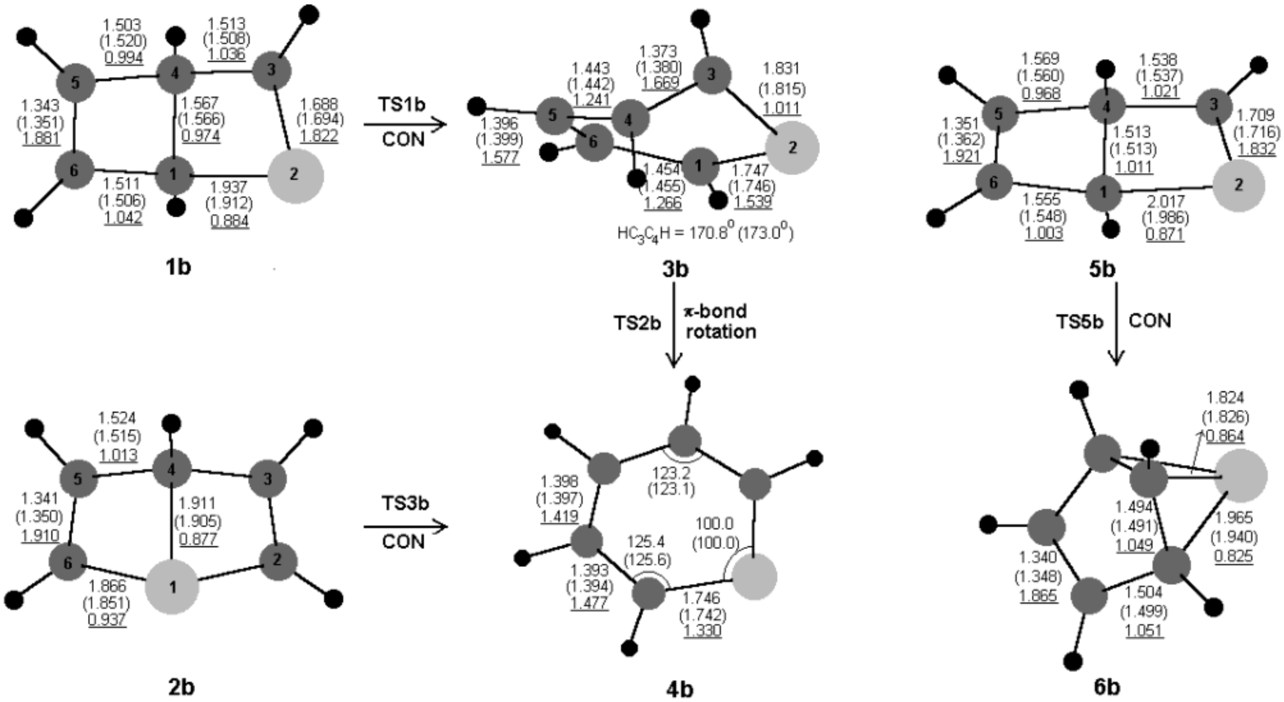

Figure 3. B3LYP/6-31G* and MP2/6-31G* (in parentheses) optimized structures of the isomers of C_5H_5P and their interconversion pathways. The underlined values are the Wiberg bond orders at the B3LYP/6-31G* level.

The calculated bond orders show that in Möbius silabenzene the trans double bond $C_3{=}C_4$ has a higher bond order of 1.817, as compared to that of 1.669 in Möbius phosphabenzene. Although one can identify bond alternation in **3a** and **3b**, there is partial delocalization of π-electrons along the ring bonds $X_2{=}C_1$, $C_1{-}C_6$, and $C_5{=}C_6$, as reflected by the bond orders and bond lengths (Figures 2 and 3). The bond alternation is less marked in Möbius phosphabenzene as compared to that in Möbius silabenzene. The $P_2{-}C_3$ bond that is adjacent to the trans double bond in Möbius phosphabenzene has a bond order of 1.01 and is a typical single bond. The B3LYP/6-31G* method predicts a length of 1.831 Å for the $P_2{-}C_3$ bond, which is close to the experimental values of 1.83−1.85 Å for C−P single bonds.[34,35] However, the bond order of the corresponding $Si_2{-}C_3$ bond (0.874) in Möbius silabenzene is smaller than that of the normal single bond. It is seen that the $X_2{-}C_3$ bond exhibits the lowest bond order in the Möbius benzenes under consideration. According to the ring current definition of Jug,[33] it may be inferred that Möbius silabenzene is antiaromatic, similar to Möbius benzene,[1] while Möbius phosphabenzene is nonaromatic. The presence of the trans double bond in Möbius benzene analogues results in a highly strained structure. The different methods of calculation predict that Möbius silabenzene is 70.3−76.1 kcal mol^{-1} higher in energy than silabenzene. Möbius phosphabenzene is predicted to exist 80.2−85.0 kcal mol^{-1} above phosphabenzene. The present study reveals that, out of the three possible Möbius benzene analogues shown in Chart 1, only **3a** and **3b** correspond to potential minima.

Dewar Silabenzenes and Dewar Phosphabenzenes. *cis*-Dewar heterobenzene can exist in two isomeric forms, which differ from each other in the positioning of the heteroatom. In **1** the heteroatom is substituted in place of one of the sp^2 carbon atoms and possesses the C_1 point group. The isomer **2** exhibits C_s symmetry, as the heteroatom occupies the bridgehead position. The present study shows that the more symmetric species **2** is lower in energy than the isomer **1**. The calculations at the different levels predict that *cis*-1-silabicyclo[2.2.0]hexadiene (**2a**) is 26.2−29.7 kcal mol^{-1} lower in energy than the species *cis*-2-silabicyclo[2.2.0]hexadiene (**1a**). Similarly in the two isomeric forms of the phosphorus analogue, *cis*-1-phosphabicyclo[2.2.0]hexadiene (**2b**) is lower in energy than *cis*-2-phosphabicyclo[2.2.0]hexadiene (**1b**) by about 5.2−8.4 kcal mol^{-1}. These results are consistent with the earlier observation of Liu, Zhou, and Pulay,[36] who found that the C_s form of the Dewar pyridine isomer is lower in energy than the less symmetric C_1 form by 13.6 kcal mol^{-1}.

Similar to the *cis*-Dewar heterobenzenes, the silicon and phosphorus analogues of the *trans*-Dewar benzene can exist in two possible isomeric forms: the heteroatom could be substituted either at the bridgehead or in place of the sp^2 carbon atom. Geometry optimizations lead to a stationary point only when the heteroatom is adjacent to the bridgehead position. Priyakumar and Sastry[25] also arrived at the same conclusion in their study on the valence isomers of silabenzene. *trans*-Dewar sila-

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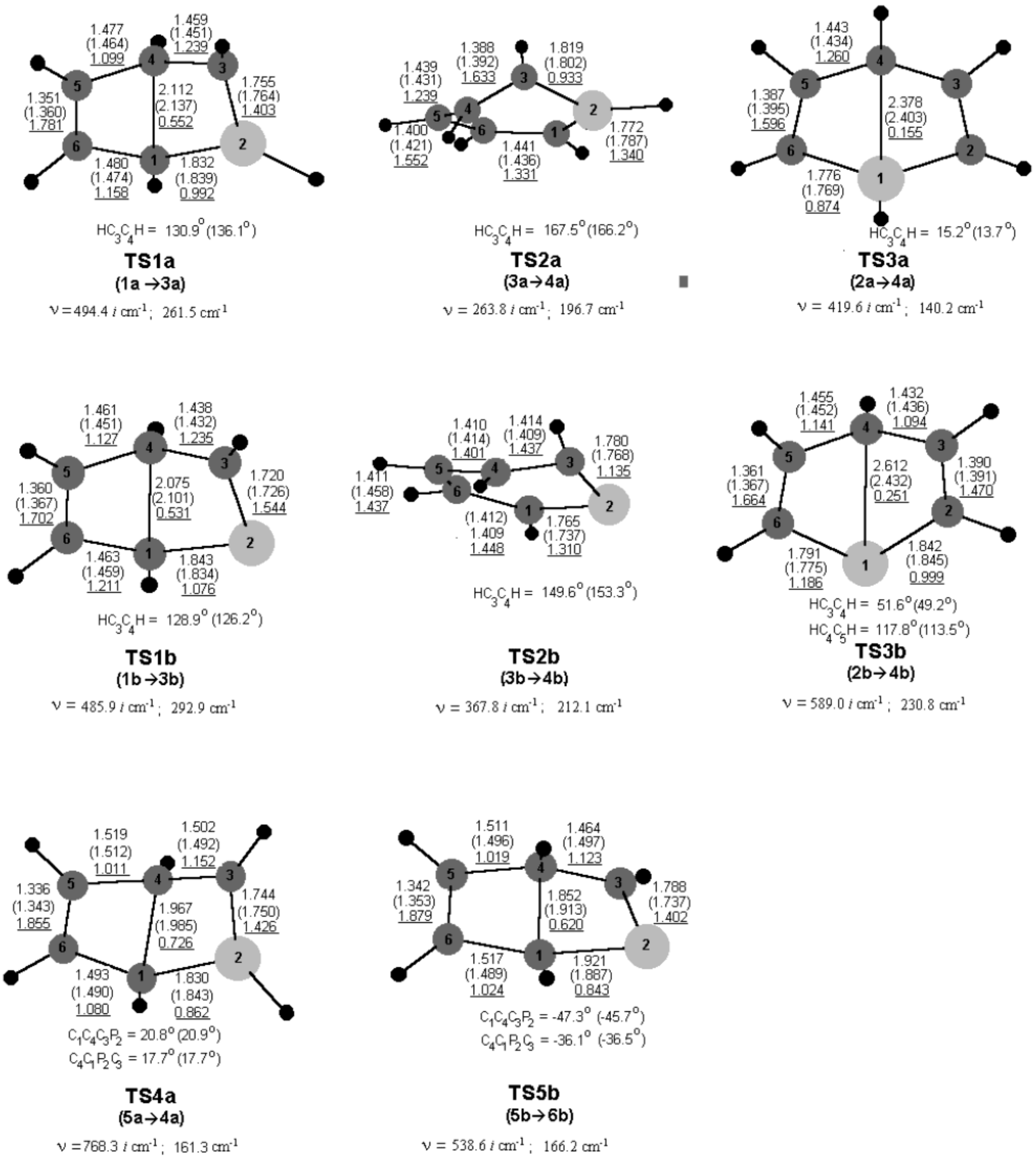
[33] (a) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344. (b) Jug, K.; Köster, A. *J. Phys. Org. Chem.* **1991**, *4*, 163. (c) According to the ring current concept given in refs 33a,b, the lowest ring bond order is used as an index to define the degree of aromaticity. A cyclic system is nonaromatic when the lowest ring bond order is that of a typical single bond. When it is below that of a single bond, the system is classified as antiaromatic. Aromatic systems are characterized by lowest ring bond order values that are intermediate between normal single and double bonds. Wiberg bond orders of C−C bonds predicted by B3LYP/6-31G* in the NAO basis for some standard nonaromatic and aromatic systems are as follows: ethane, 1.04; cyclopentadienyl anion, 1.41; benzene, 1.44.

[34] Scherer, O. J. *Comments Inorg. Chem.* **1987**, *6*, 1.

[35] Corbridge, D. E. C. *Phosphorus*; Elsevier Scientific: Amsterdam, 1980.

[36] Liu, R.; Zhou, X.; Pulay, P. *J. Am. Chem. Soc.* **1992**, *96*, 3669.



TS1a (1a → 3a) ν = 494.4 *i* cm^{-1}; 261.5 cm^{-1}

TS2a (3a → 4a) ν = 263.8 *i* cm^{-1}; 196.7 cm^{-1}

TS3a (2a → 4a) ν = 419.6 *i* cm^{-1}; 140.2 cm^{-1}

TS1b (1b → 3b) ν = 485.9 *i* cm^{-1}; 292.9 cm^{-1}

TS2b (3b → 4b) ν = 367.8 *i* cm^{-1}; 212.1 cm^{-1}

TS3b (2b → 4b) ν = 589.0 *i* cm^{-1}; 230.8 cm^{-1}

TS4a (5a → 4a) ν = 768.3 *i* cm^{-1}; 161.3 cm^{-1}

TS5b (5b → 6b) ν = 538.6 *i* cm^{-1}; 166.2 cm^{-1}

Figure 4. B3LYP/6-31G* and MP2/6-31G* (in parentheses) optimized geometries of transition-state structures of the isomers of C_5H_6Si and C_5H_5P. The frequency values are at the B3LYP/6-31G* level.

benzene (**5a**) and *trans*-Dewar phosphabenzene (**5b**) are higher in energy than the benzenoid isomers by 124.7−132.8 and 126.7−133.6 kcal mol^{-1}, respectively. Hessian calculations show that the stationary points corresponding to the fully optimized geometries of **5a** and **5b** are true minima.

The carbon−carbon single- and double-bond lengths predicted in the different isomers of the hetero-Dewar benzenes are close to the values in *cis*- and *trans*-Dewar benzenes.[1,37] The C=C double-bond lengths are in the range 1.34−1.35 Å and possess bond orders of 1.91−1.93 in the isomers **1a**, **2a**, **5a**, **2b**, and **5b**, while **1b** has a value of 1.88. In the above species the bond lengths around the heteroatom vary significantly. Thus, the Si−C single bond lengths in the isomers **1a**, **2a**, and **5a** are in the range 1.88−1.93 Å. These bonds have bond orders 0.78−0.81 and are thus significantly lower than that of a normal single bond. The Si=C double bonds in the Dewar benzene analogues have lengths of 1.72−1.75 Å and exhibit bond orders in the range 1.66−1.68. In these systems, the Si=C double bonds are predicted to be weaker than the C=C double bonds. The silicon−carbon single- and double-bond lengths are closer to the values reported in the related species.[25] The P−C single

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[37] McNeill, E. A.; Scholer, F. R. *J. Mol. Struct.* **1976**, *31*, 65.

bonds in the Dewar phosphabenzene isomers **1b**, **2b**, and **5b** have lengths in the wide range of 1.87−2.02 Å and are longer than normal P−C single bonds, but the P═C double bonds vary in the narrow range between 1.69 and 1.71 Å.

The intraannular C−C bond in the *cis*- and *trans*-Dewar silabenzenes are 1.598 and 1.561 Å, respectively, and are thus longer than the normal carbon−carbon single bonds. However, in *trans*-Dewar phosphabenzene, the intraannular C−C bond is much shorter, with a value of 1.513 Å, while it is 1.567 Å in the cis isomer. The corresponding values for the parent hydrocarbon are 1.518 and 1.572 Å, respectively. The phosphorus analogue is thus found to be closer to the hydrocarbon system. Wiberg[38] observed a short intraannular C−C bond in *trans*-bicyclo[2.2.0]hexane and attributed this to a twisted σ-bond that attempts to increase overlap.

The predicted dihedral angle between the planes is 121.2° in **1a**, 4° wider than that in Dewar benzene,[37] while it is 118.7° in **1b**. In **2a** and **2b** the planes are separated by 116.5 and 111.3°, respectively.

Electrocyclic Ring Opening of *cis*-Dewar Silabenzenes and Phosphabenzenes. The conrotatory ring opening reaction of **1a** resulted in 1,3,5-*cis*,*cis*,*trans*-cyclosilahexatriene (**3a**) by overcoming an energy barrier of 19.5−23.4 kcal mol^{-1}. The ring opening of **1b** to yield Möbius phosphabenzene **3b** also proceeds in the same manner with a barrier of 26.2−30.7 kcal mol^{-1}. The above potential energy barriers are very close to the experimental enthalpic barrier[39] of 23−25 kcal mol^{-1} for the formation of the parent Möbius benzene and the corresponding theoretical barrier[1] of 24−28 kcal mol^{-1}. The optimized geometry of the transition state **TS1a** (Figure 4) reveals that the C−C central bond is weakened (bond order 0.552) as it is stretched to 2.112 Å. This bridging bond eventually breaks, leading to the product Möbius silabenzene **3a**. In **TS1a**, considerable structural reorganization takes place in the ring containing the silicon atom. The C_1-Si_2 bond length decreases from 1.898 to 1.832 Å, and the $Si_2{=}C_3$ bond increases from 1.717 to 1.755 Å. These structural changes in **TS1a** favor the formation of the product **3a**. The present study reveals that the structure of the transition state **TS1b** also follows the same pattern. Since the major changes in bonding take place in the ring containing the heteroatom, we quantitatively monitor the progress of the reaction using the bond orders of the above bonds. The percentages of bond formation (BF_{ij}) and cleavage (BC_{ij}) at the transition state have been defined by Manoharan and Venuvanalingam[40] as

$$BF_{ij} \text{ or } BC_{ij} = \frac{BO_{ij}^{TS} - BO_{ij}^{R}}{BO_{ij}^{P} - BO_{ij}^{R}} \times 100 \qquad (1)$$

BO_{ij}^{TS} is the bond order at the transition state, while BO_{ij}^{R} and BO_{ij}^{P} represent the bond orders at the reactant and the product stages, respectively.

In the transition state **TS1a**, the cleavage of π-bonding along the $Si_2{=}C_3$ bond is 34.6%, while π-bond formations at the C_1-Si_2 and C_3-C_4 bonds are 30.3% and 25.8%, respectively. Bond order considerations show the extents of π-bond formation at the C_1-P_2 and C_3-C_4 bonds in **TS1b** are 29.3% and 31.4%, respectively, and the π-bond cleavage at the $P_2{=}C_3$ bond is 34.3%.

When a double bond is rearranged into a single bond, the bond order retains a significant value, since the bond is broken only partially. However, when the central σ-bond (intraannular bond) is broken in a bicyclic compound to give a monocyclic species, the bond order of the broken σ-bond may fall below the threshold value for bonding. Hence, the progress of intraannular bond cleavage has been defined in terms of the corresponding interatomic distances:

$$BC = \frac{IAD^{TS} - IAD^{R}}{IAD^{P} - IAD^{R}} \times 100 \qquad (2)$$

IAD^{TS} is the interatomic distance between the atoms at the bridgehead in the transition state, and IAD^{R} and IAD^{P} are the corresponding distances in the reactant and the product stages, respectively. Using the above formula, the percentage of σ-bond cleaved is estimated to be 50.4% in **TS1a** and 51.9% in **TS1b**.

Möbius heterobenzenes **3a** and **3b** undergo π-bond rotation to give the most stable benzenoid isomers, **4a** and **4b**. The energy barrier for the π-bond rotation is predicted to be 4.4−10.2 kcal mol^{-1} in the silicon compound, while it is 11.2−19.1 kcal mol^{-1} in the phosphorus analogue. In comparison to the Wiberg ring bond order of 1.437 in benzene, the values of 1.203 for the Si−C bonds in **4a** and 1.330 for the P−C bonds in **4b** reveal that the heterobenzenes under study are less aromatic than benzene.[33] The transition state **TS2a** has a lowest bond order of 0.933 and is found to be antiaromatic, while **TS2b** has a lowest bond order of 1.135 and comes under the classification of weakly aromatic species.[33] From the changes in the dihedral angles at the transition states **TS2a** and **TS2b**, the extent of the reaction is computed to be 9.6% and 12.5%, respectively. This indicates that the transition state is reached rather early.

Electrocyclic ring opening of Dewar benzene, which was long assumed to be disrotatory,[41] has recently been shown to be conrotatory.[1,2] The present analysis reveals that the conrotatory mode of ring opening takes place in the sila- and phospha-Dewar benzenes.

The barrier for conrotatory ring opening of **2a** to yield **4a** has been computed to be 20.1−28.7 kcal mol^{-1}. The corresponding barrier for **2b** → **4b** is 43.8−48.7 kcal mol^{-1}. The transition state **TS3a** has C_s symmetry, as in the case of the reactant. At the saddle point the Si_1-C_4 central bond is stretched to 2.378 Å and thus has a low bond order of 0.155. The cleavage of π-bonding at the C═C bonds is found to be 74.9%, while the extent of π-bond formation at C_3-C_4 and Si_1-C_2 is 61.2% and 15.9%, respectively.

Unlike **TS3a**, which is symmetric, the analogous transition state **TS3b** is found to be unsymmetrical. The central P_1-C_4 bond length increases from the value of

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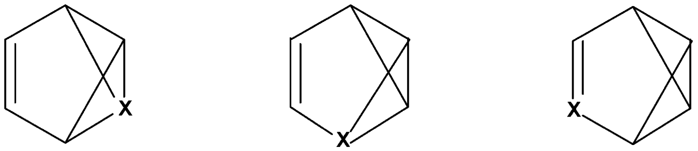
[38] Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *102*, 5679.

[39] (a) Breslow, R.; Napierski, J.; Schmidt, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5906. (b) Leuchtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3025.

[40] (a) Manoharan, M.; Venuvanalingam, P. *J. Mol. Struct. (THEOCHEM)* **1997**, *394*, 41. (b) Manoharan, M.; Venuvanalingam, P. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1799.

[41] (a) Van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1963**, *85*, 3297. (b) van Tamelen, E. E. *Acc. Chem. Res.* **1972**, *5*, 186.

Chart 2. Different Possible Hetero-Benzvalene Isomers[a]



X = SiH **6a** (25.2) **7a** (48.0) **8a** (78.0)

X = P **6b** (50.6) **7b** (57.5) **8b** (67.6)

[a] The relative energies (in kcal mol^{-1}) are shown in parentheses.

1.911 Å in **2b** to 2.612 Å in **TS3b**. This intraannular bond is cleaved by 55.2% at the transition state **TS3b**.

Ring opening of **2a** as well as **2b** yields the heterobenzenes **4a** and **4b**, in apparent violation of the rules of conservation of orbital symmetry. However, an analysis of the movement of the hydrogen atoms attached to the bridgehead atoms (carbon atom and silicon or phosphorus atom) show conrotatory movement in the TS as predicted. In **TS3a**, the hydrogen atoms move such that a trans double bond would be formed including the silicon atom. If a Möbius benzene type compound were to be formed in the ring opening of **2a** as well as **2b**, the trans double bond should include the heteroatom or should be two bonds away (Chart 1). Our attempts to optimize these Mobius benzene analogues (1,3,5-*cis*,*trans*,*cis*-1-silacyclohexatriene, 1,3,5-*trans*,*cis*,*cis*-1-silacyclohexatriene, 1,3,5-*cis*,*trans*,*cis*-1-phosphacyclohexatriene, and 1,3,5-*trans*,*cis*,*cis*-1-phosphacyclohexatriene) could not lead to the corresponding potential minima. The optimization spontaneously resulted in other isomeric forms in the PES. Consequently, the ring opening of **2a** and **2b** leads to the stable benzenoid compounds **4a** and **4b**, which incidentally are the species expected from the disrotatory route.

Ring-Opening Reactions from *trans*-Dewar Silabenzene and *trans*-Dewar Phosphabenzene. Although the ring-opening reactions proceed in a similar manner in the case of *cis*-Dewar silabenzenes and the analogous *cis*-Dewar phosphabenzenes, we observe a distinct difference in the reaction paths involving the trans isomers. The electrocyclic conrotatory ring opening of *trans*-Dewar silabenzene (**5a**) gives silabenzene, as in the ring-opening reaction of *trans*-Dewar benzene.[1] On the other hand, the ring opening in *trans*-Dewar phosphabenzene leads to phosphabenzvalene **6b**. Attempts to characterize the transition state **TS4b**, which is analogous to **TS4a**, resulted in a second-order saddle point, which eventually crossed into a lower lying path leading to **TS5b**. The same trend is observed with HF/6-31+G* and B3LYP/6-31+G* calculations, which included diffuse functions in the basis set. A tendency for pyramidalization of the phosphorus atom and the adjacent carbon atom C_3 in **TS5b** is evident from the dihedral angles $C_1-C_4-C_3-P_2 = -47.3°$ and $C_4-C_1-P_2-C_3 = -36.1°$. IRC calculations performed at the **TS5b** geometry confirmed that in one direction the search yielded **5b** and on the other the species **6b** was formed smoothly. *trans*-Dewar phosphabenzene (**5b**) has to overcome an energy barrier of 19.4−23.6 kcal mol^{-1} in the formation of phosphabenzvalene **6b** (Chart 2). Attempts to locate the silabenzevalene isomer **6a**, analogous to phosphabenzvalene **6b**, yielded a first-order saddle point, which is 25.2 kcal mol^{-1} higher than silabenzene. This observation was made earlier by Wakita et al.[13a] and Priyakumar and Sastry.[25] These authors could characterize two other silabenzvalene isomers, **7a** and **8a**, as potential minima (Chart 2). Priyakumar and Sastry examined in detail the PES starting from **6a** and succeeded in generating two isomers corresponding to potential minima. Their analysis led to the conclusion that the resulting minima did not correspond to benzvalenes but to bicyclic compounds. We located the phosphabenzevalene isomers **7b** and **8b** as potential minima lying 57.5 and 67.6 kcal mol^{-1} above phosphabenzene at the B3LYP/6-3-1G* level. It should be mentioned that these higher energy phosphabenzevalene isomers **7b** and **8b** are not generated along the electrocyclic reaction paths under study. Only the isomer **6b** was formed by the ring opening of *trans*-Dewar benzene **5b**. From the energetics of the different valence isomers of phosphabenzene investigated in this study, phosphabenzvalene **6b** is found to be closer in energy to the benzenoid form **4b**.

4. Conclusions

We have carried out the electrocyclic ring opening reactions at a level of theory that generally yields reliable results for pericyclic reactions and strained compounds. Our calculations predict the existence of Möbius silabenzene (**3a**), a silabenzene valence isomer, and Möbius phosphabenzene (**3b**), which is a valence isomer of phosphabenzene. These species are formed by conrotatory ring opening of Dewar silabenzene (**1a**) and Dewar phosphabenzene (**1b**), respectively, with predicted barriers of 20−23 and 26−31 kcal mol^{-1}. These barriers are very similar to the experimental enthalpic barrier of 23−25 kcal mol^{-1} for the formation of the parent Möbius benzene. **3a** and **3b** possess a strained trans π-bond. Despite formidable ring constraints in the formation of the extraordinarily strained initial products **3a** and **3b**, orbital symmetry is seen to control the reaction. Because of the fairly small barrier for the trans π-bond rotation to yield the more stable benzenoid isomers (**4a** and **4b**), it may be difficult to detect **3a** and **3b**, though they may be trapped in ultrafast processes. The lowest ring bond orders of 0.874 and 1.011, respectively, in **3a** and **3b** classify Möbius silabenzene as antiaromatic, while Möbius phosphabenzene is nonaromatic according to the bond order criterion.[33]

Ring openings of **2a** and **2b** give silabenzene and phosphabenzene, in apparent violation of the rules of conservation of orbital symmetry. However, an analysis of the movement of the hydrogen atoms attached to the bridgehead atoms (carbon atom and silicon or phosphorus atom) show conrotatory movement, as predicted. In the bicyclic Dewar benzenes, the bond between the heteroatom and the bridgehead carbon exhibits a bond order that is significantly smaller than that of a normal single bond. The transition state **TS2b** involved in the process **3b** → **4b** may be classified as weakly aromatic, having the lowest bond order of 1.135, while **TS2a** has a lowest bond order of 0.933 and is classified as antiaromatic.

Our calculations support the existence of *trans*-Dewar silabenzene (**5a**) and *trans*-Dewar phosphabenzene (**5b**). Species **5a** and **5b** are predicted to be 125−133 and 127−134 kcal mol^{-1} above silabenzene and phosphabenzene, respectively. Unlike the electrocyclic reactions from the *cis*-Dewar benzenes, which follow identical paths for silicon and phosphorus heterosystems, the trans isomers follow different paths. The conrotatory ring opening of **5a** yields silabenzene, while that of **5b** results in phosphabenzvalene.

Analysis of the extent of the reaction at the transition state for the various electrocyclic interconversion processes reveals that the percentage of π-bond breaking is more pronounced than that of π-bond formation.

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Supporting Information Available: Cartesian coordinates of B3LYP/6-31G* and MP2/6-31G* optimized geometries of the species **1a**−**5a** and **1b**−**6b** and their transition states and total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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