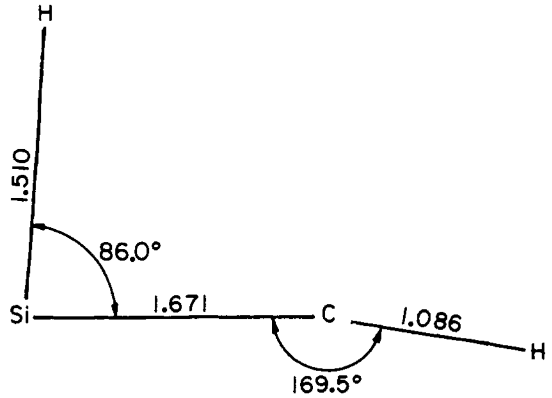

Figure 7. Transition state for the rearrangement of trans-bent silaacetylene to its silylidene isomer. The level of theory used was double-ζ plus d function (DZ+d) configuration interaction (CI), as in Figure 6.

typically lowers the harmonic frequencies by the order of perhaps 4%.

If the above reduction of 7.5% is applied to our DZ+d CI prediction of the silicon–carbon stretching frequency, an empirical result of 1092 cm^{-1} is obtained. By comparison with the experimental values of 1001 and 1003 cm^{-1} for the Si=C double-bond stretching frequency in dimethylsilaethylene,[21,22] it is seen that the silaacetylene frequency is somewhat higher. This is consistent with the characterization of the silicon–carbon linkage in trans-bent silaacetylene as an exceptionally strong double bond. Should a silaacetylene be prepared in the laboratory (perhaps with two very bulky substituents such as adamantyl replacing the hydrogen atoms in Figure 6), one would thus expect to observe a notably higher Si–C stretching frequency than for the analogous silaolefin.

Since the geometry optimization for trans-bent silaacetylene was carried out in point group C_s, it is not obvious that a nonplanar C_1 geometry might not be preferred. However, Table III shows that the planar structure is a genuine relative minimum of the DZ+d CI energy surface; i.e., all harmonic vibrational frequences are real.[30] Moreover, the out-of-plane a″ frequency is 665 cm^{-1}, which is actually higher than the in-plane C–Si–H bend at 420 cm^{-1}. The magnitude of this torsional frequency at 665 cm^{-1} is not surprising when one appreciates that this corresponds to internal rotation about a silicon–carbon bond of order approximately $2^1/_2$.

Next, an attempt was made to locate a cis-bent equilibrium geometry for silaacetylene. Given the HSiC and HCSi trans bond angles of 128.8 and 150.1°, is not an implausible possibility. However, the search proved fruitless. Starting from a cis structure obtained essentially via rotation of the trans geometry by 180° about the Si=C axis, no adjacent stationary point could be located. Gradient values in this region of the energy hypersurface were substantial, and the total energy was above that of the constrained linear structure. Thus it appears that there is no cis-bent isomer of silaacetylene.

Finally, the transition state from trans-bent silacetylene to the silylidene isomer was located at the DZ+d CI level of theory. This is shown in Figure 7 and corresponds to an energy of −327.98936 hartrees, or 4.2 kcal above the DZ+d CI energy of silaacetylene. When the Davidson correction is appended, the classical barrier increases somewhat, to 5.7 kcal. The latter result, of course, is consistent with the finding that correlation effects provide the origin of the barrier; i.e., the barrier vanishes within the Hartree–Fock approximation.

Concluding Remarks

Vibrational frequencies have been predicted for five different nondissociative stationary points on the $SiCH_2$ potential energy hypersurface. Among these the silylidene isomer **1** is the lowest lying energetically and therefore the most likely to be observed experimentally. Silaacetylene itself has a trans-bent equilibrium geometry, corresponding to a silicon–carbon bond order of approximately $2^1/_2$.

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Note Added in Proof. The DZ SCF transition state for the unimolecular reaction of **3** was eventually found by using analytic *second* derivative methods. It is a nonplanar C_1 symmetry structure lying 17.8 kcal above **3**.

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Coordination in Benzene Dimer Cation Radical

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Abstract: Ab initio MO calculations are used to characterize coordinations in benzene dimer cation. Binding occurs for all arrangements which allow π overlap between parallel rings. Parity (orbital symmetry) is approximately conserved, and two manifolds which correspond to opposite parities are predicted. Stable species in either manifold exhibit slippery, spongy bonds. In the odd (even) manifold, these are 1-coordinate-like (6-coordinate-like) dimers which are bound by $\sim$12 (11) kcal/mol at inter-ring distances of $\sim$0.26 (0.32) nm. Analysis of the results suggests that such parity manifolds are generally expected of alternant aromatic dimer cations, and also to some extent of their oxidomer analogues. Application to the mechanism of benzene polymerization by aluminum chloride–cupric chloride is discussed.

Aromatic cation radicals have been suggested as intermediates for the oligomerization of polynuclear aromatic hydrocarbons[1,2] and the synthesis of poly(p-phenylene) from benzene–aluminum chloride–cupric chloride.[3-5] They may also be involved in the

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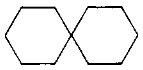
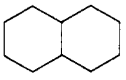
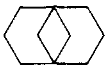
solid-phase synthesis of poly(*p*-phenylene) from the lower *p*-phenylene oligomers, such as *p*-terphenyl.[6] Compared to ordinary electrophilic aromatic substitution, the corresponding reaction mechanisms involve π electrons in novel and imprecisely specified ways. We decided to investigate this, beginning with the simplest prototype, benzene dimer cation radical. This species has been extensively studied,[5,7–24] and most results suggest and/or suppose a symmetrical 6-coordinate sandwich structure (6-C) which has the same symmetry as the monomer. In this work, we report the results of ab initio MO calculations which show that the benzene dimer cation exhibits surprisingly many coordinations.

We used ALIS[25] to carry out frozen ring calculations on 6-C and the structures


1-C


2-C


2-C′

(The rings lie one above the other in parallel planes, and the symmetry group of each structure is S_2. The notation 1-C, etc., means 1-coordinate, etc.) MO energy curves for 6-C were computed for five different minimal basis sets of contracted Gaussians (MIN's): (5s2p2s) or (522);[26] (632);[26,27] (733);[26] (743);[26] and one double-ζ basis set (DZ), (954).[26] (DZ uses one orbital per C 1s, and is otherwise generally contracted in the recommended way.[28]) (522) predicts a lowest energy inter-ring distance (LED) of 0.317 nm, and all other MIN's predict 0.304 nm; DZ predicts 0.349 nm. A value of 0.3 nm has been estimated.[16] Binding energies (BE's) are calculated as the differences between the minima of the aforementioned energy curves and the corresponding energies of the asymptotes (monomer neutral + ion); these are 9(522) − 13(743) kcal/mol for the MIN's, and 5 kcal/mol for DZ. Experimental enthalpies of dissociation are in the range 8–17 kcal/mol.[13,15–18] Therefore, (522) was used for the (frozen ring) 1-C, 2-C, and 2-C′ calculations. LED's (nm) are 0.271 (1-C), 0.284 (2-C), and 0.304 (2-C′); BE's (kcal/mol) are 12 (1-C) and 9 (2-C and 2-C′).

BE's of this magnitude could be strongly influenced by basis set superposition errors. Since an appreciable superposition error in the dimer ion will also appear in the neutral dimer, we used the latter to investigate the error. This is convenient because exact MO calculations would predict strictly repulsive interactions between neutral benzene rings in parallel planes, and appreciable superposition errors in approximate MO calculations for the neutral dimer will thus produce spurious attractions. Since neutral dimers at inter-ring distances near the ionic LED are weakly repulsive, spurious attractions there will be obvious. (522) MO energy curves for $(C_6H_6)_2$ in the four coordinations described above are monotonically decreasing functions of the inter-ring distance: there is no evidence for binding, local minima, etc. At the ionic LED's, the (522) neutral energies are repulsive by 11 (6-C), 13 (1-C), and 8 (2-C and 2-C′) kcal/mol. DZ predicts 9 kcal/mol for 6-C. Based on these results, superposition errors cannot account for a significant part of the binding in the dimer ions.

The close agreement of the (522) results with experiment is probably coincidental. At the (522) accuracy level, calculated BE's should be taken to mean that the ionic moieties are bound by a few kcal/mol. Judging from all computed results, the (522) inter-ring distances are too small by ~10%. However, relative orderings are probably reliable: since the dimer MO's are essentially polarized benzene MO's at these inter-ring distances, dimer-extra effects (e.g., electron correlation, basis set truncation, ring relaxation) are probably comparable among the coordinations, and their incorporation would probably shift the present MO results by similar amounts.

The MO configuration of 6-C is $e_{1u}{}^4 e_{1g}{}^{*3}$, where e_{1u} ($e_{1g}{}^*$) is the bonding (antibonding) combination of the doubly degenerate π HOMO's of benzene. In the other cases, bonding or antibonding with respect to inter-ring coordination lifts the degeneracy (π_x orbitals are largely nonbonding in 1-C); specifically, we find the configurations (using conventional notation): $\pi_{xu}{}^2 \pi_{yg}{}^2 \pi_{yu}{}^{*2} \pi_{xg}{}^{*1}$ (2-C′); $\pi_{xg}{}^2 \pi_{yu}{}^2 \pi_{yg}{}^{*2} \pi_{xu}{}^{*1}$ (2-C); and $\pi_{xg}{}^2 \pi^n{}_{xu}{}^2 \pi^n{}_{xg}{}^2 \pi_{yu}{}^{*1}$ (1-C). The corresponding term symmetries are $^2E_{1g}$ (6-C), ^2A_g (2-C′), and ^2A_u (2-C and 1-C).

Pseudo-Jahn–Teller (PJT) distortions could lead to qualitatively different results.[29–31] Following earlier work,[30,31] we checked this with spatially unrestricted MO's. (All such calculations were started from asymmetric MO's). For all inter-ring distances considered here, the energies of 1-C, 2-C, and 2-C′ are independent of S_2 symmetry constraints (parity constraints). Uniform JT lowering of ~1.5 kcal/mol is found for 6-C, which is half of the $C_6H_6{}^+$ JT lowering (one electron, two rings). [For $C_6H_6{}^+$, (522) gives 2.8 kcal/mol and a π-electron calculation gives 2.7 kcal/mol;[32] related experimental values are 2.9 ($C_6H_3F_3{}^+$),[33,34] 1.6 ($C_6H_3Cl_3{}^+$),[33,34] and 2.3 ($C_6F_6{}^+$)[34] kcal/mol. Intra-ring geometry changes (0.001 nm for bond distances and 2° for bond angles[33,34]) are negligible for our purposes; this is not true of *nonaromatic* ions.[31]] We also calculated energy curves for 16 other coordinations wherein the rings lie in parallel planes. No evidence for PJT distortions was found.

All ground states are bound relative to the asymptotes; i.e., all arrangements which allow π overlap between parallel rings are bound. BE's are typically ~9 kcal/mol. LED's range from ~0.26 nm for coordinations resembling 1-C, to ~0.32 nm for coordinations resembling 6-C. Parity is approximately conserved, so we refer to odd or even dimers. Lowest energies occur for coordinations resembling 1-C (odd) or 6-C (even). A ring of 1-C may be wagged ~15° about the inter-ring bond without increasing the energy. A ring of 6-C may be rotated freely. In addition, one ring of each slides freely for ~0.04 nm to give the coordinations $1C/2C_u$ or $6C/2C_g$, where u (g) refers to odd (even) parity.

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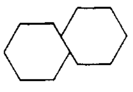
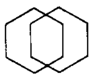


$1C/2C_u$

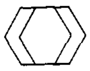
(BE ≈ 12 kcal/mol, LED ≈ 0.26 nm)



$6C/2C_g$

(BE ≈ 11 kcal/mol, LED ≈ 0.32 nm)

Also, the lowest energy dimers may be compressed or expanded by ~0.01 nm without changing the energy (expansions of 6-C and the rotations are free, but compressions require ~1 kcal/mol). Another equally bound coordination is $6C/2C_g'$. In this case,



$6C/2C_g'$ (BE ≈ 11 kcal/mol, LED ≈ 0.31 nm)

displacement away from 6-C (or 2-C′) is 0.03 nm. There appears to be a barrier of ~1 kcal/mol between 6C/2C′ and the other even parity dimers. Apparently, this is because an inter-ring bonding (antibonding) MO at 6-C correlates with an antibonding (bonding) MO of 2-C′. For the same reason, displacing the rings of 6C/2C′ requires $\gtrsim 1$ kcal/mol.

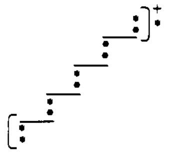
Thus, we conclude that the stable odd (even) dimers are slippery, spongy variants of 1-C (6-C) which are bound by ~12 (11) kcal/mol at inter-ring distances of ~0.26 (0.32) nm. Except (possibily) for 6C/2C′, there are paths on either manifold whereby rearrangements from higher energy coordinations to the slippery forms are unhindered. Abrupt crossings which correspond to symmetry changes occur between the odd and even energy surfaces and involve barriers $\gtrsim 3$ kcal/mol.

Approximate parity conservation arises from the inherent homopolarity of the inter-ring MO's. Whenever there is π-overlap between parallel benzene rings, the inter-ring bonding and antibonding MO's exhibit approximate parity because they are essentially homopolar sums and differences of the benzene π MO's. Thus, the approximate parity of the dimer ion's electronic state is determined by the approximate parity of its singly occupied MO.

The negligible PJT may also be traced to the parity of the inter-ring MO's. When the ground state is odd (even), the lowest energy excited state is even (odd) and is produced by promoting one electron from an even (odd) doubly occupied antibonding MO to the more strongly antibonding odd (even) singly occupied MO: ${\pi_g}^{*2}{\pi_u}^{*1} \rightarrow {\pi_g}^{*1}{\pi_u}^{*2}$ (${\pi_u}^{*2}{\pi_g}^{*1} \rightarrow {\pi_u}^{*1}{\pi_g}^{*2}$). In the cases of 1-C, 2-C, and 2-C′, we calculated MO energy curves and determined that these excited states are unbound. Thus, a PJT effect could mix the odd and even manifolds, and hence weaken inter-ring bonding. Alternatively, a PJT effect would require heteropolar inter-ring MO's, which means that charge would localize, and this would reduce the covalency of the inter-ring bonding. The smaller JT effects break D_{6h} symmetry without destroying parity.

It is possible to conclude from these results that several structures may be expected for most aromatic cations. Firstly, the origin of the binding is charge-spin delocalization, which preserves aromatic character by moderating the intra-ring pπ bonds to form inter-ring pσ bonds; that is, the dimeric bonding does not change the monomeric hybridization. Secondly, the monomeric HOMO's are approximately doubly degenerate in alternant systems. Depending on which "degenerate" MO is ionized, there are several different ways to dimerize and achieve inter-ring coordination. The resultant dimers probably exhibit two "parity" manifolds, and one may be able to exploit their generally different properties. We are currently exploring this.

In relation to the mechanism of polymerization by $AlCl_3$–$CuCl_2$, 1-C is believed to represent the dimeric stage.[5] Subsequent propagation would then occur in a stair-step fashion, yielding **1**



in which the radial cation character is delocalized throughout the chain.[5]

It is pertinent that small amounts of the analogous trimer species have been reported in mass spectrometry.[20] In solid-phase polymerizations,[6] e.g., from *p*-terphenyl, similar 1-coordinate ions are reasonable candidates. Furthermore, the results derived here also hold, to some extent, for oxidomers,[35] since these are formed by partial ionization of the aforementioned monomeric π HOMO's.

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Registry No. Benzene, 71-43-2; benzene dimer cation radical, 34514-15-3.

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[35] Oxidomers are described in ref 1.