J. Am. Chem. Soc. **1991**, *113*, 417-423

Ab Initio Electronic Structure Calculations on the Benzene Dication and Other $C_6H_6^{2+}$ Isomers

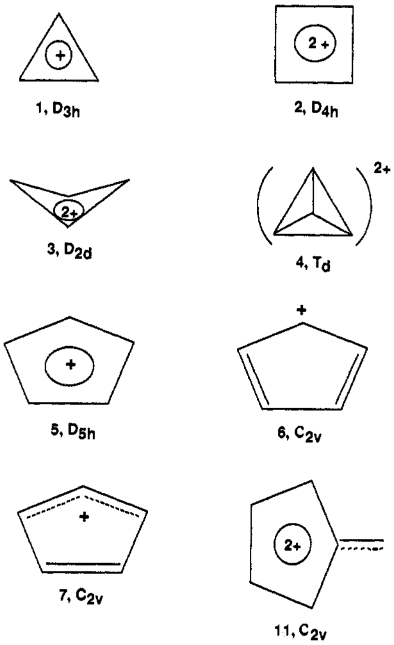
Karsten Krogh-Jespersen

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. *Received March 30, 1990*

Abstract: High-level ab initio molecular orbital calculations have been carried out on a series of $C_6H_6^{2+}$ isomers. Optimized geometrical structures have been obtained, and characterized via normal mode and frequency analysis, at the single-determinant Hartree-Fock level with a basis set of split valence plus polarization function quality (HF/6-31G*//6-31G*). Relative energies were derived from calculations including correlation energy corrections at the third-order Moller-Plesset level (MP3/6-31G*//6-31G*) and the zero-point vibrational energy contributions. Both singlet and triplet states were investigated for the benzene dication and only one minimum was located on each potential energy surface. The singlet benzene dication is distorted from planarity (D_{6h} (**10(S)**) or D_{2h} (**16**, **19**) symmetry) to a chair-like conformation (C_{2h}, **17**). The triplet benzene dication is in D_{6h} symmetry (**10(T)**) unstable at the Hartree-Fock level toward distortion to a planar structure of C_{2v} symmetry, ~0.4 kcal/mol lower in energy. However, at the correlated level **10(T)** is 3.5 kcal/mol lower in energy than the C_{2v} triplet structure and 6.6 kcal/mol more stable than the singlet benzene dication structure (**17**). Considerably lower in energy (~10 kcal/mol) than **10(T)** is a singlet pentagonal pyramid (C_{5v}, **9**). Pyramid ⟨−⟩ benzene dication interconversion on the singlet surface is opposed by barriers of 40.3 and 23.7 kcal/mol, respectively, for the forward and reverse reactions. Other potentially low energy $C_6H_6^{2+}$ isomers, such as allylcyclopropenyl dications (**12**, **13**) or the fulvene dication (**11**), are 3-14 kcal/mol higher in energy than **9**. The nonclassical pyramidal ion (**9**) is predicted to be the global $C_6H_6^{2+}$ minimum energy structure. This contention is supported by selective calculations with a larger basis set (6-311G*) at the MP3 level (MP3/6-311G*//6-31G*), which show a preferential increase in the stability of **9** relative to **12**, **13**, **10(T)**, and **17** by ca. 2 kcal/mol compared to the results obtained at the MP3/6-31G*//6-31G* level.

Numerous calculations have been carried out to determine the molecular structures and energetics of hydrocarbon mono-[1] or dications,[2] often with surprising results for even small and, presumably, simple species. The monocyclic rings and pyramidal structures formed by plain polymethine units with formulas $(CH)_m^+$ or $(CH)_m^{2+}$ are particularly interesting for electronic structure studies. Molecules featuring $4n + 2$ electrons ($n = 0, 1, 2, ...$) as π-electrons conjugated along the perimeter of planar (or nearly planar) rings or as interstitial electrons in three-dimensional, pyramidal arrangements are often attributed special, "aromatic" stabilization;[3a-g] conversely, species containing $4n$ interstitial or π-type electrons are destabilized and considered "antiaromatic".[3h] Transformation of an annulenic ring to a pyramid with a hypervalent carbon at the apex liberates two electrons to add to the already available π-electrons, thus formally changing a planar molecule with $4n$ π-electrons into an isomer with $4n + 2$ interstitial electrons, or vice versa. Nonclassical species featuring carbon atoms with a coordination number larger than four are common among singly charged hydrocarbons[1] and in organoboranes,[3e-g] and the electronic structure and reactivity of such half-sandwich systems provide a noteworthy link between inorganic and organic chemistry.[1d,3c,4] General structural or stability rules cannot be based on simple electron-counting schemes, however, due to a number of complicating factors.

Chart I



1, D_{3h}
2, D_{4h}
3, D_{2d}
4, T_d
5, D_{5h}
6, C_{2v}
7, C_{2v}
11, C_{2v}

One significant complication arises through the patterns exhibited in highly symmetrical structures by the molecular orbitals containing the π or interstitial electrons.[3b] A ring of formula $(CH)_m^+$ or $(CH)_m^{2+}$, or its isoelectronic pyramidal counterpart, with more than two such electrons (i.e., $n > 0$) must in maximum symmetry (D_{mh} for the ring, $C_{(m-1)v}$ for the pyramid) possess a partially filled set of degenerate orbitals and it will therefore, on the basis of the Jahn-Teller (JT) theorem,[5] be highly susceptible to geometrical distortions introduced by coupling of the electronic and nuclear motions. The magnitudes of these distortions and their energetic consequences are not readily predicted, however. Additional factors that may influence the structures and relative

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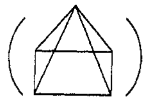
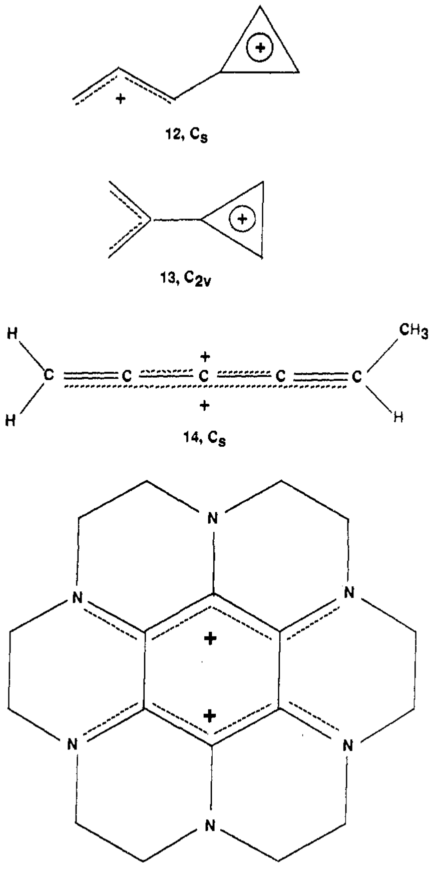
stabilities include the extent of cap–base overlap in a pyramid or the presence of destabilizing nonbonded interactions in small rings. The necessity to disperse the net positive charge effectively may, in particular for the dications, lead to unusual structures with unique bonding situations which will often be subject to large substituent effects.

Consider as examples a few of the smaller cations assembled by methine units. The cyclopropenyl cation ($C_3H_3^+$, **1**) is the smallest Huckel-aromatic monocation with two π-electrons fully conjugated in an equilateral triangle (D_{3h} symmetry).[6] However, there is ample computational evidence that the cyclobutadienyl dication (**2**), which also features two π-electrons in a conjugated carbon framework and hence serves as the smallest Huckel-aromatic dication, is actually not a planar molecule (D_{4h}).[7] This ion prefers a puckered (D_{2d}) structure (**3**) with a significant barrier (~8–10 kcal/mol) to ring inversion. The puckering has been interpreted in terms of relief from destabilizing, antibonding 1,3-interactions occurring in the plane of the ring in combination with favorable orbital interactions engendered by the lowering in molecular symmetry, but the puckered geometry could also be viewed as a severely Jahn–Teller distorted structure originating in a pyramidal tetrahedrane dication, **4**. The cyclopropenyl cation and the cyclobutadienyl dication are computed to be the most stable isomers of their respective chemical formulas,[8] indicating the strongly stabilizing influence exerted by the two π-electrons. The cyclopentadienyl cation ($C_5H_5^+$, **5**)[9,10] has four π-electrons, two of which must occupy a degenerate molecular orbital in D_{5h} symmetry. Singlet coupling of these two electrons induces JT distortions to a butadiene-like π-system (**6**) or to a structure with a localized double bond and an allyl cation type unit (**7**); the latter structure is perhaps slightly nonplanar.[9b] An alternative, square-pyramidal structure (**8**) with a pentacoordinate carbon and six interstitial electrons is higher in energy than **7** but perhaps only by some 10 kcal/mol.[9a] However, triplet coupling of the two π-electrons constitutes the ground state for **5**.[10] A triplet ground state has been experimentally verified for **5**[11a] and also for $C_5Cl_5^+$,[11b] but other substituents are known to alter the ground state of cyclopentadienyl cations. Thus, the pentaphenyl and various aryl-substituted cyclopentadienyl cations have singlet ground states in solution[11c,d] and may even be pyramidal, although definitive experimental confirmations have not been made.[11e,f] Substituent effects appear less dramatic in the smaller, more rigid cyclopropenyl cations and cyclobutadienyl dications. For example, substantial evidence has been presented to demonstrate that fully methylated cyclobutadienyl dications are also puckered with significant barriers to inversion.[7c] X-ray crystallographic analysis of several fully substituted cyclopropenyl cations shows the persistence of the central equilateral unit, and even unsymmetrical substitution has generally only small structural effects on the C_3 unit.[12]



8, C_{4v}

Chart II



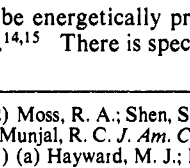
12, C_s

13, C_{2v}

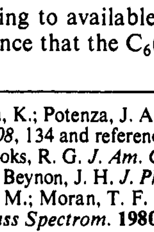
14, C_s

15, C_{2h}

There are many reports describing the gas-phase formation and fragmentation of $C_6H_6^{2+}$ ions,[13] but detailed geometrical structures for these ions are not available from experimental data. Certainly, a pyramidal species (**9**) with six interstitial electrons should be a viable candidate as the most stable $C_6H_6^{2+}$ species, but the four-π-electron benzene dication (**10**) and other isomers (**11–14**) may be energetically preferred according to available calculations.[14,15] There is spectroscopic evidence that the $C_6(CH_3)_6^{2+}$



9, C_{5v}



10 (S,T), D_{6h}

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Table I. Ab Initio Total Energies (au) and Zero-Point and Relative Energies (kcal/mol) of $C_6H_6^{2+}$ Isomers at HF/6-31G*//6-31G* Geometries

species[a]	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	ZPE[b]	ΔE^{HF}	ΔE^{MP3}	ΔE^{c}
9(S)	−229.886 95	−230.614 75	−230.640 54	66.8 (0)	0.0	0.0	0.0
10(T)	−229.898 52	−230.580 04	−230.620 22	63.7 (0)[d]	−7.3	12.8	10.0
17(S)	−229.872 11	−230.575 21	−230.612 09	65.3 (0)	9.3	17.9	16.6
16(S)	−229.867 46	−230.561 05	−230.599 82	64.5 (1)	12.2	25.6	23.6
19(S)	−229.865 91	−230.552 09	−230.595 36	63.9 (2)	13.2	28.4	25.8
18(S)	−229.832 72	−230.536 33	−230.572 52	64.1 (1)	34.0	42.7	40.3
12(S)	−229.905 56	−230.593 08	−230.631 17	64.0 (0)	−11.7	5.9	3.4
13(S)	−229.910 48	−230.590 31	−230.629 17	64.1 (0)	−14.8	7.1	4.7
11(S)	−229.892 65	−230.572 48	−230.614 21	64.6 (0)	−3.6	15.9	13.9
14(S)	−229.842 47	−230.531 19	−230.569 28	60.2 (0)	27.9	44.7	38.8

[a] Spin state is indicaed in parentheses (S = singlet, T = triplet). [b] Unscaled zero-point energies computed at the HF/6-31G*//6-31G* level. The number of imaginary frequencies is given in parentheses. [c] Best values for the relative energies obtained by taking the MP3/6-31G*//6-31G* relative energies corrected for the differences in zero-point energies; the latter were scaled by a factor of 0.89 for this purpose; see Computational Details. [d] As discussed in the text, the triplet benzene dication does not possess a minimum of D_{6h} symmetry at the HF/6-31G*//6-31G* level. We report the total energies at the D_{6h} geometry and use the zero-point energy for the distorted triplet structure of C_{2v} symmetry; see text for details.

species prepared in solution by Hogeveen and Kwant has the pyramidal structure and exists as a singlet,[16] whereas the $C_6Cl_6^{2+}$ species studied by Wasserman et al. at liquid nitrogen temperature is known to possess a triplet ground state as a benzene dication-like species.[17] Molecules based on the triplet benzene dication nucleus have been proposed as candidates for organic molecular ferromagnets.[18] A particularly promising system, the dodecahydrohexaazacoronene dication ($HOAC^{2+}$, **15**), does have a triplet ground state in a CH_2Cl_2/CH_3CN mixture, but the ESR spectra indicate that in pure CH_3CN the triplet state lies 0.9 kcal/mol above a singlet ground state.[19] In the solid state, the dication is a singlet with a thermally accessible triplet state present for several different counterions. Single-crystal X-ray analysis shows a strongly JT distorted, planar benzene nucleus with ab initio calculations (HF/STO-3G//STO-3G) demonstrating that the positive charge is significantly delocalized over the nitrogen atoms, effectively forming two cyanine dye cations connected by C–C single bonds in the central ring.[19] Similar features are observed in the related hexakis(dimethylamino)benzene dication ($C_6(Me_2N)_6^{2+}$) with additional distortions to nonplanarity occurring in the central C_6 and C_6N_6 moieties.[20] Thus, the electronic states in these $C_6R_6^{2+}$ species not only depend strongly on the substituent (R) but may in addition be very sensitive to the nature of the solvent, phase, and counterion.

An additional facet to the electronic structure of $C_6R_6^{2+}$ species was added by Sagl and Martin, who prepared a $C_6I_6^{2+}$ ion with a singlet ground state in triflic acid.[21] They proposed, primarily on the basis of magnetic susceptibility and NMR experiments as well as results from a qualitative molecular orbital calculation (EHT), that this species was of the benzene dication type except that the electron deficiency was not in the π-framework but in the σ-framework. The ion was predicted to have ten σ-electrons conjugated via iodine in-plane 5p orbitals and still possess six π-electrons in carbon out-of-plane orbitals, therefore being Huckel-aromatic in two orthogonal electronic systems ($n = 2$ and 1, respectively) and presumably preserving the planar, hexagonal symmetry (D_{6h}) appropriate for a fully substituted benzene.

Inspired by the discovery of Sagl and Martin, we have been carrying out ab initio molecular orbital computations on $C_6I_6^{2+}$ isomers and related halogenated benzene dications.[22] It became evident during the course of that study that in-depth questions regarding the structures and energetics of even the parent species could not be answered decisively on the basis of the published literature. The available experimental data on $C_6H_6^{2+}$ provide no structural and only very limited energetic information.[13] The data presented from previous theoretical calculations are suggestive but neither complete nor mutually supportive,[14,15] and these calculations are, in addition, outdated in terms of current computational capabilities. In the present work we use results from high-level ab initio calculations to (a) discuss the geometrical structures and relative energies of the singlet and triplet states in the benzene dication, (b) assess the energy difference between the ground state of the singlet benzene dication and the pyramidal species, as well as locate the transition state for their interconversion, and (c) briefly present data on other low-energy isomers in an attempt to elucidate the global minimum on the singlet $C_6H_6^{2+}$ surface.

Computational Details

All ab initio electronic structure calculations[23] were carried out with the GAUSSIAN86 and GAUSSIAN88 program packages[24] on a Convex C220 minisupercomputer or on Digital Equipment Corporation VAX computers. Stationary points on the potential energy surfaces were located at the single-determinant Hartree–Fock level (restricted for singlets, unrestricted for triplets) with the 6-31G* split valence plus polarization function basis set (HF/6-31G*//6-31G*). The nature of a particular stationary point (minimum, transition state, or general saddle point) was determined by normal mode and frequency analysis at the HF/6-31G*//6-31G* computational level. The calculated vibrational zero-point energies (ZPE) were scaled by 0.89 for use in determinations of relative energies. Further improvements to the total energies were obtained by including correlation energy corrections through third-order perturbation theory at the Moller–Plesset level (MP3/6-31G*//6-31G* or MP3/6-311G*//6-31G*). Total and relative energies for the important structures may be found in Table I. Unless specifically stated otherwise, relative energies quoted in the text refer to data obtained at the MP3/6-31G*//6-31G* level and do not include the vibrational ZPE corrections. Any additional calculations will be noted at the relevant places in the discussion of the results.

Results and Discussion

Prior Computational Work. A discussion of the electronic structure and bonding in pyramidal $C_6H_6^{2+}$ (**9**) on the basis of ab initio calculations[25] was published simultaneously with the

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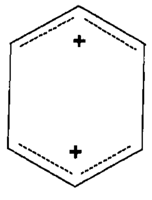
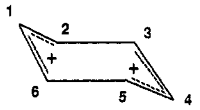
report of the successful preparation and characterization of $C_6(CH_3)_6^{2+}$.[16b] Later work at the semiempirical MINDO/3 level focussed on the benzene dication and the fragmentation processes of $C_6H_6^{2+}$ ions in the gas phase.[26] Systematic computational investigations that are most pertinent to the present study have been published by Lammertsma and Schleyer (LS)[14] and by Dewar and Holloway (DH).[15]

LS carried out ab initio calculations on a number of $C_6H_6^{2+}$ isomers and some likely fragmentation ions ($C_5H_3^+$ and CH_3^+). The calculations were at the Hartree–Fock level with a 3-21G basis set and included geometry optimizations but not normal mode analyses. They identified the fulvene dication (**11**) as the lowest energy structure, followed by two allylcyclopropenyl ions (**12**, **13**) 5–6 kcal/mol higher in energy. They were unable to determine with their computational techniques whether the ground state of the benzene dication would be a singlet, planar but distorted structure (D_{2h} symmetry, **16**) or a planar triplet of hexagonal symmetry (D_{6h}, **10(T)**). An energy separation between the fulvene and benzene singlet dications of nearly 20 kcal/mol was obtained. A cumulene-type structure (**14**) was of similar relative energy as **16**, but the pyramid (**9**) was computed an additional 10 kcal/mol higher in energy. LS pointed out that d-type polarization functions and correlation energy corrections were likely to be important for accurate predictions of the relative energies. These authors also presented heats of formation data for the various ions computed with the semiempirical MINDO/3 and MNDO methods. They concluded that results obtained with the MNDO method overall resembled the ab initio data best but that both methods showed limitations in studies of carbodications. Finally, LS also noticed the prediction of a chair-like structure (**17**) for the benzene dication from both of these semiempirical methods but did not pursue the issue at the ab initio computational level.

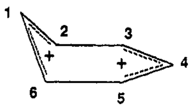


16, D_{2h}



17, C_{2h}

DH studied $C_6R_6^{2+}$ isomers (R = H, CH_3, OH, F, and Cl) closely related to the pyramid or the benzene dication, preferring the MINDO/3 method above MNDO. For the parent $C_6H_6^{2+}$ system, they found pyramidal **9** to be 0.6 kcal/mol more stable than chair-like **17**. Furthermore, **17** was 11.3 kcal/mol more stable than **16**, and these three structures were all identified as minima on the potential energy surface. DH also identified the transition state (**18**) for the interconversion of **17** and **9**, 31 kcal/mol above either species. Minima on the triplet potential energy surface were located corresponding to both planar (**10(T)**) and nonplanar (**17**) benzene dications, with the triplet chair-like form 7.8 kcal/mol lower in energy. The singlet–triplet energy differences between the individually optimized minima were small with the triplet state computed higher in energy than the singlet state for **17**, but slightly lower in energy for the planar structures (**10(T)** vs **16**).



18, C_s

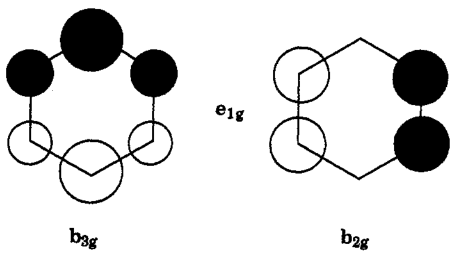


Figure 1. Schematic representation of the $e_{1g}(\pi)$ set of molecular orbitals in **10** (D_{6h} symmetry). The symmetry labels in the D_{2h} point group are also given.

Thus, although not always fully comparable, the results obtained from the two sets of methods, ab initio all-electron vs semiempirical valence-electron only, differ with respect to the number of predicted minima as well as the relative energies of the spin states for the benzene dication, and also in the predicted energy of this ion relative to the pyramidal carbocation. The detailed MINDO/3 study by DH predicts two distinct minima for both the singlet and triplet benzene dication. The singlet benzene dication **17** and the pyramidal structure **9** are isoenergetic and lower in energy than any triplet structures. Conversely, the ab initio study by LS found that **9** was higher in energy than **16**, which was estimated to be of similar energy as the triplet benzene dication (**10(T)**).

The Singlet Benzene Dication. In D_{6h} symmetry, the benzene dication HOMO is a doubly degenerate π-type orbital of e_{1g} symmetry containing two electrons. Proper spin coupling of the electrons yields one triplet state ($^3A_{2g}$) and two singlet states ($^1A_{1g}$, $^1E_{2g}$). The expectation is that all these states will be close in energy. Following Hund's rule, the triplet state will presumably be the ground state, followed by the $^1E_{2g}$ and $^1A_{1g}$ states, but the anticipated energetic proximity of the singlet states has special consequences. The spatially doubly-degenerate $^1E_{2g}$ state ought not possess a minimum at the hexagonal geometry but should undergo a "first-order" JT distortion along in-plane normal modes of e_{2g} symmetry to relieve the spatial degeneracy.[27] In addition, a "pseudo" or "second-order" JT effect could mix the $^1A_{1g}$ and $^1E_{2g}$ states via vibronic coupling to e_{2g} modes,[28] structurally distorting the ion even further. On the basis of the well-known nodal pattern for the e_{1g} set of π-orbitals (Figure 1), the distortions from perfect hexagonal symmetry are likely to be primarily skeletal in nature and include either an expansion of two opposite C–C bonds and concomitant contraction of the other four C–C bonds or the reverse scenario.[29] Such distortions along e_{2g} modes lower the point group symmetry to D_{2h} and break the degenerate e_{1g} set of π-orbitals into b_{2g} and b_{3g} orbitals.[30] The electronic state labels change from D_{6h} to D_{2h} as follows: $^3A_{2g} \rightarrow {}^3B_{1g}$; $^1A_{1g} \rightarrow {}^1A_g$; $^1E_{2g} \rightarrow {}^1A_g + {}^1B_{1g}$. Doubly occupying either π-orbital (b_{2g}^2 or b_{3g}^2) gives rise to a ^1A_g state; the $^3B_{1g}$ and $^1B_{1g}$ states have one electron in each of these nondegenerate orbitals ($b_{2g}^1b_{3g}^1$), triplet or singlet coupled. The two ^1A_g states can interact strongly with each other in geometries near D_{6h} symmetry and will produce two geometrically distorted structures. The $^3A_{2g}$ state can be represented as a single Slater determinant. A proper treatment of the singlet states at (or near) the D_{6h} geometry requires a multideterminantal (MCSCF) treatment,[31] which is outside the scope of the present work. The importance of an MCSCF treatment for the description of the singlet states will diminish as the states split apart and should be minimal near the equilibrium geometries

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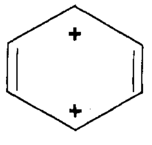
(29) Raghavachari, K.; Haddon, R. C.; Miller, T. A.; Bondybey, V. E. *J. Chem. Phys.* **1983**, *79*, 1387.

(30) We use a coordinate system where the molecule lies in the *xy* plane with the *x* axis bisecting opposite C–C bonds.

(31) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69.

of the separate distorted structures.[32]

Three stationary points have been located on the singlet potential energy surface. Previous studies have only reported on one of the possible structures with D_{2h} symmetry, **16**, corresponding to $b_{3g}^2b_{2g}^0$ occupancy, and have seemingly ignored **19** with $b_{2g}^2b_{3g}^0$ occupancy.



19, D_{2h}

Our single-determinant ab initio calculations show that, although being stationary points, neither structure is a minimum on the singlet surface. **19** has two short C–C bonds (1.335 Å) of near double bond length and four longer C–C bonds of near single bond length (1.474 Å). For comparison, the optimized C–C bond length in neutral benzene is 1.386 Å (HF/6-31G*/6-31G*), close to the experimental value of 1.397 Å.[33] However, **19** has two imaginary vibrational frequencies with one normal mode (366i cm^{-1}, b_{2g}) being in-plane and the other (210i cm^{-1}, b_{3g}) corresponding to an out-of-plane distortion toward a chair-like structure. The other stationary point, **16**, with two long central C–C bonds (1.533 Å) of single bond length and four much shorter terminal ones (1.374 Å) in a double allyl cation type arrangement,[34] is 2.8 kcal/mol lower in energy than **19** but it still has an imaginary frequency for the out-of-plane distortion (314i cm^{-1}, b_{3g}). **17**, a chair-like conformation of C_{2h} symmetry, is indeed a minimum (lowest vibrational frequency = 262 cm^{-1}) on the singlet $C_6H_6^{2+}$ ab initio energy surface, in agreement with the results from the semiempirical methods. The dihedral angle between the two planes formed by a terminal allyl cation fragment ($C_1C_2C_6$ or $C_3C_4C_5$) and the central four carbon atoms ($C_2C_3C_5C_6$) is 20.7°. The allyl cation bond lengths are preserved at 1.377 Å in **17**; however, relative to **16** the central C–C bond lengths (C_2C_3 and C_4C_5) decrease by almost 0.04 Å to 1.495 Å. **17** is only 2.9 kcal/mol below **16** at the HF/6-31G*/6-31G* level, but the energetic preference for **17** increases substantially to 7.7 kcal/mol at the correlated level. Thus, **17** will most likely also be the minimum structure if geometry optimization was carried out at a correlated level (e.g. MCSCF). We conclude that structure **17** represents the geometry of the singlet state of the benzene dication and that the planar structure **16** with one imaginary frequency corresponding to out-of-plane motion may be viewed as the transition state for interconversion of the two possible equivalent chair structures.

It is also of interest to analyze the distortion energies for the investigated benzene dication structures in some detail. The two components of the degenerate $e_{1g}(D_{6h})$ π-orbital can be chosen so they transform as b_{2g} and b_{3g}, respectively, in D_{2h} symmetry (Figure 1). We can then obtain approximate values for the relative state energies even at a geometry with D_{6h} symmetry by carrying out conventional restricted single-determinant HF calculations on the closed shell ^1A_g singlets (b_{2g}^2 or b_{3g}^2), followed by calculations for the correlation energy contributions. At the neutral benzene geometry, we find that the two ^1A_g states created in the above manner are nearly degenerate (0.1 kcal/mol difference in energy, MP3/6-31G*//6-31G*). Geometry optimization with D_{6h} symmetry imposed leads to a C–C bond length for both closed shell singlets of 1.422 (1) Å, very close to the bond length computed for the $^3A_{2g}$ state (1.420 Å, vide infra) and only 0.036 Å longer than the computed C–C bond length in neutral benzene (vide supra). At the MP3/6-31G*/6-31G* level, relaxation with hexagonal symmetry imposed stabilizes the closed shell states by an average of 7.1 kcal/mol; the corresponding value at the HF level is slightly smaller (4.7 kcal/mol). In an ab initio computational study of $C_6H_6^+$, Raghavachari et al.[29] found a C–C distance of 1.405 (1) Å (HF/6-31G//6-31G) for the two doublet states when D_{6h} symmetry was imposed. We find a similar bond length of 1.403 (1) Å for $C_6H_6^+$ at the HF/6-31G*//6-31G* level, giving a structural distortion of 0.019 Å relative to neutral benzene and an energetic lowering by only 1.0 kcal/mol relative to the monocation at the neutral benzene geometry. The C–C bond length increase in the dication is thus twice as large as that in the monocation, but the decrease in energy is only slightly more than four times as large (5 kcal/mol vs 1 kcal/mol). The effective force constant for the totally symmetric C–C stretch is thus very similar in both cations.

Table II. Orbital Energies ϵ (eV) of Planar (**16**) and Chair-like (**17**) Benzene Dications (HF/6-31G*//6-31G*)

16, D_{2h}		**17**, C_{2h}		difference[a]
orbital	ϵ	orbital	ϵ	ϵ(**16–17**)
$3b_{1g}(\sigma)$	−26.46	$3b_g$	−26.78	0.32
$6a_g(\sigma)$	−25.43	$6a_g$	−25.99	0.55
$1b_{1u}(\pi)$	−24.58	$6b_u$	−24.44	−0.14
$1b_{3g}(\pi$, HOMO)	−21.74	$7a_g$(HOMO)	−21.76	0.02
$1b_{2g}(\pi^*$, LUMO)	−13.75	$4b_g$(LUMO)	−12.81	−0.89
$1a_u(\pi^*)$	−8.50	$5a_u$	−8.69	0.19
$2b_{1u}(\pi^*)$	−7.04	$7b_u$	−7.64	0.60

[a] A positive value means that the orbital has been stabilized upon the out-of-plane geometry distortion.

The benzene monocation ($C_6H_6^+$) undergoes first-order JT distortions from D_{6h} symmetry ($^2E_{1g}$) to structures of D_{2h} symmetry ($^2B_{2g}$, $^2B_{3g}$). Raghavachari et al. defined the JT stabilization energy as the energy difference between the geometry optimized but symmetry constrained (D_{6h} vs D_{2h}) structures, and they obtained a mean value for the two monocation structures of 2.4 kcal/mol at a π(CISD) level of calculation with the 6-31G basis set. Following their approach, the JT stabilization energy ($D_{6h} \rightarrow D_{2h}$) at the MP3/6-31G*//6-31G* level is 9.5 kcal/mol for **19**, but the energy gained by the alternative D_{2h} structure **16** is larger at 13.9 kcal/mol. Of course, **16** then distorts further ($D_{2h} \rightarrow C_{2h}$), gaining an additional 7.7 kcal/mol for a full JT stabilization of 21.6 kcal/mol. The total distortion energies are considerably larger in the dication than in the monocation.

Whereas the benzene monocation remains planar, the presence of an additional positive charge in the π-system of the dication engenders larger geometrical changes and a further descent in molecular symmetry. A strong driving force for the structural distortions would appear to arise from the necessity to effectively disperse the excess positive charge. Even the small degree of nonplanarity computed in **17** effectively breaks the σ–π separation and allows hyperconjugation between the allylic π-bonds and the central long C–C σ-bonds. According to the Mulliken population analysis of the wave functions,[23] this does lead to a slightly more balanced distribution of the excess positive charge, but the absolute changes are actually very small. The net charges on the various carbon atoms (summing the hydrogen charges into the charges of their respective carbon atoms) are +0.40 (four times) and +0.20 (two times) in **16**, and they are only adjusted to +0.38 (four times) and +0.23 (two times) in **17**. An additional and most likely major driving force for distortion toward nonplanarity can be deduced from a detailed analysis of the higher lying occupied and lower lying unoccupied molecular orbitals.

Relevant molecular orbital energies for **16** and **17** are presented in Table II. There is an increase in the HOMO–LUMO energy gap from 7.99 eV in **16** to 8.95 eV in **17**, but this is not due to direct mixing between these two orbitals. Although the decrease in molecular symmetry generally allows greater mixing among the orbitals, the two frontier orbitals remain of different symmetries. In fact, the HOMO is virtually unchanged in energy, and it is the LUMO that is destabilized by nearly 1 eV upon out-of-plane bending and hence solely responsible for the increased HOMO–LUMO separation. The two highest occupied orbitals in **16** are both π-orbitals, and they are essentially unaffected in both orbital energy and coefficients by the relatively small deviations from overall planarity exhibited by **17**. Two occupied molecular orbitals of σ-symmetry are strongly stabilized in **17**

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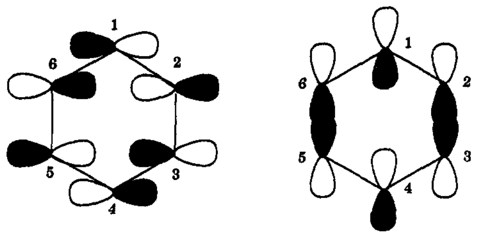
[32] Nakamura, K.; Osamura, Y.; Iwata, S. *Chem. Phys.* **1989**, *136*, 67.

[33] Langseth, A.; Stoicheff, B. P. *Can. J. Phys.* **1956**, *34*, 350.

[34] The optimized C–C bond length in the allyl cation is 1.373 Å at the HF/6-31G*//6-31G* level.



3 b_{1g} 6 a_g

Figure 2. Schematic representation of the $3b_{1g}$ and $6a_g$ σ-orbitals in **16**.

relative to **16** (Figure 2). One of these, the $3b_{1g}(\sigma)$ orbital, is stabilized by 0.32 eV upon distortion. In **17**, this orbital transforms according to the same irreducible representation (b_g) as the LUMO, a π^*-orbital, thus inducing σ–π^* mixing. The σ-orbital consists in **16** primarily of in-plane C(2p) orbitals, out-of-phase along the periphery of the ring and across the ring between carbons 2–6 and 3–5 (Figure 2). The π^*-orbital in question is the orbital shown in Figure 1 as the b_{2g} orbital. Trans bending of carbon atoms 1 and 4 relieves some 1–2(1–6) and 3–4(4–5) antibonding, and the concomitant motion of the hydrogens on carbons 2, 3, 5, and 6 toward pseudo-axial positions reorients the p-orbitals and makes it possible for them to mix strongly with the π^*-orbital, an effect very clearly shown in both the orbital energies and coefficients. This relieves antibonding across the ring and also increases 2–3 and 5–6 bonding, since the π^*-orbital is bonding between these atoms. In fact, the Mulliken overlap population across the ring between atoms 2–6(3–5) increases from −0.08 in **16** to 0.04 in **17**, and the distance decreases from 2.340 Å in **16** to 2.257 Å in **17**. This σ–π^* orbital interaction also explains the decrease in central (2–3 and 5–6) C–C bond lengths by 0.04 Å from **16** to **17**. The largest decrease in orbital energy (0.55 eV) is observed for the $6a_g$ orbital, however (Figure 2). This orbital is also primarily composed of in-plane C(2p) orbitals, strongly 2–3 and 5–6 bonding but weakly 1–2(1–6) and 3–4(4–5) antibonding. Trans bending of carbons 1 and 4 again relieves some terminal antibonding, and the shortened 2–3 and 5–6 bond lengths in **17**, largely induced through the σ–π^* interaction just described, stabilize this orbital strongly. The molecular orbital coefficients in **17** are essentially unchanged from those in **16**, and the stabilization of the $6a_g$ orbital is attributed to increased atomic orbital overlap, not orbital mixing.

The overall picture of the distortion mechanism in **16** therefore shows strong resemblance to one of the interpretations for the puckering in **3**.[7] Destabilizing 1,3-interactions in the σ-system of the ring may be relieved by σ-π^* orbital mixing in a nonplanar geometry of lower symmetry without any significant loss of stability occurring to the π-system. Note, finally, that the direct product symmetry of the two decisive interacting orbitals is b_{3g} ($b_{1g}(\sigma) \otimes b_{2g}(\pi^*) = b_{3g}$ in D_{2h} symmetry), fully consistent with the result obtained from the normal mode analysis that the symmetry of the out-of-plane mode inducing the **16** → **17** distortion was indeed also of b_{3g} symmetry.[3c,28] Thus, the chair-like structure **17** may be viewed as arising from both first- and second-order JT effects present in the planar singlet benzene dication.

The Triplet Benzene Dication. The triplet benzene dication ($^3A_{2g}$) gains 4.2 kcal/mol upon geometry optimization from a neutral benzene geometry with D_{6h} symmetry imposed, but the stationary point reached is seemingly not a minimum at the unrestricted Hartree–Fock level. A doubly degenerate, in-plane mode (e_{1u}) has an imaginary frequency of an unusually large magnitude (~2500i cm^{-1}). Distorted structures of D_{2h} or C_{2h} symmetry analogous to the singlet benzene dication structures discussed above (**16**, **17**, **19**) all reverted to the D_{6h} stationary point upon energy minimization. At the geometry of singlet **17**, for example, the lowest triplet state is 23.5 kcal/mol above the singlet ground state, in contrast to the predictions from the semiempirical models (vide supra). Distortions to C_{2v} symmetry revealed a stationary point with just one low imaginary frequency (104i cm^{-1}), when the C_2 axis passed through two opposite sides in the hexagon. Finally, a minimum of C_{2v} symmetry was located with the C_2 axis passing through two opposite carbon atoms. The optimized structure for this species is actually only 0.4 kcal/mol lower in energy than the D_{6h} structure at the HF level, and after correlation energy corrections have been included then the triplet state is 3.5 kcal/mol more stable at the D_{6h} structure. In accordance with the very modest energy lowering computed at the HF level is a maximum distortion of only 0.020 Å in any of the C–C bond lengths. The symmetrical D_{6h} structure **10(T)** has C–C bond lengths of 1.420 Å while the distorted structure contracts in one end (C–C = 1.402 Å) and extends in the opposite end (C–C = 1.440 Å), leaving the central bonds essentially unchanged (C–C = 1.427 Å). The spin contamination in the UHF wave function developing from mixing with other spin states has increased slightly from $S^2 = 2.009$ (D_{6h}) to $S^2 = 2.015$ (C_{2v}), perhaps contributing to the decrease in energy.

Our conclusion regarding the triplet benzene dication is that the global minimum is actually formed by the symmetrical hexagon. The large magnitude of the imaginary frequency is associated with a symmetry-breaking instability of the unrestricted Hartree–Fock wave function at the D_{6h} geometry, which probably leads to instabilities in the solution of the coupled perturbed Hartree–Fock equations used in computing vibrational frequencies.[23] The miniscule decrease in energy upon reoptimization at the HF level shows that the potential energy surface is very flat at this computational level. Correlation energy corrections apparently increase the curvature of the surface around the hexagonal geometry. The triplet state lies more than 25 kcal/mol below the singlets near the neutral benzene geometry, but this estimate is based on incorrect wave functions for the singlets and is likely to be too high. Comparing the singlet and triplet dications at their respective optimal geometries, the separation is diminished to only 5.1 kcal/mol.

The Pyramidal Dication. The orbital interaction diagram rationalizing the stabilized configuration formed by the interstitial electrons in **9** has been presented elsewhere.[3,4,15] The present geometry is characterized by a C–C in-plane bond length of 1.425 Å, a (CH)$^+$–cap to $C_5H_5^+$ basal plane distance of 1.137 Å corresponding to cap–ring C–C bond lengths of 1.662 Å, and a tilt of the hydrogens by 12.4° toward the cap. The structure is more compact with polarization functions in the basis set than without, e.g. the previously published HF/3-21G geometry[14] shows C–C bond lengths of 1.442 and 1.740 Å and the HF/6-31G C–C bond lengths are 1.437 and 1.713 Å, respectively. The pyramid lies in a steep minimum on the potential energy surface with the lowest vibrational frequency, a degenerate (e_2) ring–hydrogen mode, computed at 496 cm^{-1}. As anticipated by LS,[14] the energy of the pyramid relative to that of the benzene dication is very sensitive to both the inclusion of polarization functions and electron correlation. **17** is computed as considerably more stable than **9** at the HF level with unpolarized basis sets, in fact the difference is more than 20 kcal/mol at the HF/6-31G//6-31G level. Adding the set of cartesian d-functions to the basis set preferentially stabilizes **9** by a substantial amount (~30 kcal/mol) even at the HF level and places it 9.3 kcal/mol below **17**. Correlation energy corrections increase the energy difference further to 17.9 kcal/mol in favor of the pyramidal structure.

Benzene Dication–Pyramid Interconversion. The pyramidal cation **9** has both a degenerate HOMO and LUMO with a large separation in orbital energy (18.1 eV) and thus no low-lying triplet state, ruling out interconversion with, say, the triplet benzene dication **10(T)**. The interconversion of **17** and **9** is, however, allowed on the singlet surface under C_s symmetry. The transition state, **18**, was located 24.7 kcal/mol above **17**, or 34.0 kcal/mol above **9**, at the HF level. Correlation energy contributions do not alter the barrier (24.8 kcal/mol) relative to **17**, but it is increased to 42.7 kcal/mol relative to **9**. The structure of the transition state is "early and tight" with most internal coordinates achieving values in **18** that are more similar to those of **17** than those of **9**. For example, the computed C_2–C_3 (C_5–C_6) bond length in **18** is 1.511 Å, a small decrease from the value of 1.533 Å in **17** and still considerably longer than the 1.425 Å found in **9**. The terminal C_3–C_4–C_5 unit in **18** is still allylic with C–C bond lengths of 1.377 Å (1.374 Å in **17**), but the dihedral angle between the $C_3C_4C_5$

and $C_2C_3C_5C_6$ planes is down to 7.1° in **18** from 20.7° in **17**. The position of the migrating carbon (C_1) in the transition state is characterized by bond lengths of 1.443 Å to its nearest neighbors C_2 and C_6 (1.374 Å in **17**, 1.662 Å in **9**) and a dihedral angle between the $C_1C_2C_6$ and $C_2C_3C_5C_6$ planes of 69.5°, so this carbon atom is still well outside the periphery of what will become the basal plane of **9**. The C_2–C_6 distance has decreased dramatically in **18** (1.536 Å) relative to **17** (2.257 Å), however, in preparation for the new carbon–carbon bond that will be formed between these atoms in the product (**9**).

The $C_6H_6^{2+}$ ions formed under electron bombardment of benzene possess sufficient excess energy to overcome barriers to rearrangement and fragmentation.[13,26] These ions are most likely formed at the geometry of the neutral benzene molecule (Franck–Condon approximation). Direct computation of the vertical double ionization potential gives 575.8 kcal/mol to the (averaged) singlet dication and 549.5 kcal/mol to the triplet dication. If the measured appearance potential value of 26.0 eV (~599.5 kcal/mol)[13d] is reliable, it would appear that either the calculations overestimate the relative stability of the dication considerably or the experimentally generated ion is in fact formed with substantial internal energy. The barrier to rearrangement to the pyramid (~25 kcal/mol) might well be larger than the barrier(s) for the lowest energy dissociation pathway, even on the singlet surface, and fragmentation rather than rearrangement to **9** proceeds rapidly. Milder preparation conditions should improve the prospects of isolating the benzene dication.

Isomeric Dications. The striking reversal, compared to previously published data,[14,15] in the relative stability of **17** and **9** computed at the higher levels of ab initio theory employed here induced us to take a closer look at some of the other isomers studied by LS.[14] Our final results for the relative energies (MP3/6-31G*//6-31G* + ZPE corrections) of the various species will be briefly presented in this section.

We find that the pyramidal structure **9** is the $C_6H_6^{2+}$ species of lowest energy considered in this study. **9** is 10.0 kcal/mol lower in energy than the triplet benzene dication structure **10(T)**, which in turn is 6.6 kcal/mol more stable than the singlet benzene dication, **17**. With split valence basis sets, the fulvenyl dication **11** is also computed to be far more stable (~30 kcal/mol) than the pyramidal isomer (**9**), but the energy difference is diminished to nearly 3 kcal/mol with the addition of d-functions to the basis set; after correlation and vibrational zero-point-energy contributions have been included, **9** is 13.9 kcal/mol more stable than **11**. The two low-energy allylcyclopropenyl ions, **12** and **13**, fare somewhat better when compared to **9** at higher levels of theory. The perpendicular ion **12** is about 25 kcal/mol more stable than **9** at lower levels of calculation,[14] but at the correlated level employed here, **12** is positioned 3.4 kcal/mol above **9**. The centrally linked allylcyclopropenyl ion **13** prefers a planar geometry at the HF/6-31G* level with the perpendicular orientation, which is preferred at lower levels of calculation (HF/3-21G//3-21G or HF/6-31G//6-31G)[14] being just the transition state for internal rotation ~5 kcal/mol higher in energy. **13** is, however, computed 4.7 kcal/mol above **9** in energy. Finally, the relative energy between the cumulene-type structure **14** and **9** changes by more than 50 kcal/mol between lower and higher computational levels and this ion, estimated 38.8 kcal/mol above **9**, is clearly not competitive as a truly low energy $C_6H_6^{2+}$ isomer.

Concluding Remarks. We have identified the minimum energy structures for the benzene dication on the singlet and the triplet potential energy surfaces. Only one structure representing a minimum could be located for each spin multiplicity. Whereas the triplet state **10(T)** has the anticipated D_{6h} symmetry, the singlet minimum **17** is severely distorted to a chair-like geometry of C_{2h} symmetry. The structural distortions are attributed to a combination of first- and second-order Jahn–Teller effects occurring in the electronic system of a planar benzene dication. The nonplanarity of **17** is attributed specifically to destabilizing nonbonded 1,3-interactions present in the σ-system of **16**, providing a strong analogy with the interpretation for the nonplanarity of another small ring dication, **3**.[7] No boat-like benzene dication structures could be located for either spin multiplicity. The pyramidal cation **9** appears to be situated in a deep minimum with a large barrier separating it from the most obvious rearrangement product, the less stable singlet benzene dication (**17**). Neither ion has been uniquely identified by experimental means, and further experimental work directed toward generating $C_6H_6^{2+}$ ions under milder conditions than previously attempted is strongly encouraged. Substituents are clearly able to influence the relative energetics of these two fundamental structures (viz. the $C_6(CH_3)_6^{2+}$, $C_6Cl_6^{2+}$, and $C_6I_6^{2+}$ ions mentioned above), which will be a topic of our future studies.

These calculations demonstrate again the importance of including polarized basis sets and estimates for the correlation energy when attempts are made to provide relative energies among a set of structurally diverse isomers. We have identified three essentially isoenergetic $C_6H_6^{2+}$ isomers, all containing "aromatic" features. One of these (**9**) is a closed nido structure with six interstitial electrons, and the other two (**12** and **13**) are open structures with a two-π-electron cyclopropenyl ion connected to a delocalized two-π-electron allyl cation. We estimate that differences of ca. 5 kcal/mol are close to the overall reliability of our calculations, in particular since the relative stability of **9** with respect to **12** and **13** diminishes by ca. 10 kcal/mol from the MP2 to the MP3 level (Table I). Although we do also believe that the changes from, say, the MP3 to the MP4 level of perturbation theory would be less than those observed from MP2 to MP3, it seems prudent at this stage only to conclude that these three $C_6H_6^{2+}$ isomers are indeed very close in energy. The "antiaromatic" benzene dication should be somewhat higher in energy.

This does not prevent us from believing, perhaps wishfully and not with complete impartiality, that additional correlation energy corrections (MP4 theory or higher) and basis set expansions (e.g. additional diffuse functions on C) will indeed preferentially favor the pyramidal structure **9**. Encouragingly, correlated calculations with the extended 6-311G* basis set, which includes an additional set of sp-functions on the carbon atoms, do show increased relative stability for **9**. At the MP3//6-311G*//6-31G* level (with ZPE corrections included), **9** is 5.5, 6.7, 11.7, and 18.0 kcal/mol more stable that **12**, **13**, **10(T)**, and **17**, respectively, which represents an average increase in energy separation by ca. 2 kcal/mol relative to the MP3/6-31G*//6-31G* values.[35] These considerations lead us to predict that the pyramidal isomer **9** represents the global $C_6H_6^{2+}$ minimum.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Equipment grants from the National Institutes of Health, the National Science Foundation, and the New Jersey Commission of Science and Technology made this research possible.

Supplementary Material Available: The optimized geometries are available in Z-matrix format as input files to GAUSSIAN88 (11 pages). Ordering information is given on any current masthead page.

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[35] The total energies (au) at the MP3/6-311G*//6-31G* level are the following: **9** (−230.70440); **12** (−230.69172); **13** (−230.68987); **10(T)** (−230.68125); and **17** (−230.67371).