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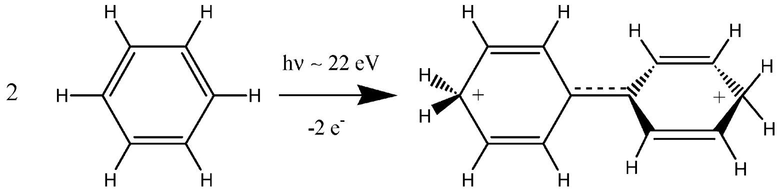
J. Am. Chem. Soc., **2005**, 127 (48), 16824-16834• DOI: 10.1021/ja042238j • Publication Date (Web): 12 November 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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The Fate of Dicationic States in Molecular Clusters of Benzene and Related Compounds

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Abstract: Calculations employing density functional theory indicate that, rather than undergoing fragmentation, dicationic clusters of benzene, hexafluorobenzene, and naphthalene produced by sequential one-electron or sudden double-ionization experiments on the neutrals can relax via the formation of inter-ring covalent C−C bonds, along with a series of proton transfers that enable a substantial reduction of inter- and intramolecular Coulomb repulsions. The theoretically predicted chemically bound structures correspond to deep local energy minima on the potential energy surface pertaining to the lowest electronic state of the dications and can therefore be regarded as metastable (kinetically long-lived) species. This discovery invalidates on theoretical grounds the liquid-droplet model of multiply charged clusters and sheds very unexpected light on possible consequences in chemistry of the intermolecular Coulombic decay (ICD) mechanism [Cederbaum, L. S.; et al. *Phys. Rev. Lett.* **1997**, *79*, 4778; Jahnke, T.; et al. *Phys. Rev. Lett.* **2004**, *93*, 163401] for deep inner-valence ionized states. Propagation of charge rearrangement reactions and proton transfers to several monomers may eventually lead to the formation of rather extended dicationic assemblies.

1. Introduction

Benzene (Bz) is the most representative aromatic molecule and certainly one of the cornerstones of theories of chemical reactivity. Benzene clusters are prototype systems to study $\pi-\pi$ intermolecular interactions, a fundamental topic in chemistry and biology.[1] Quite naturally therefore, a wealth of experimental and theoretical studies has focused on neutral clusters of benzene, primarily on their structural and spectroscopic properties.[2] In contrast, despite the evolution of techniques and theories for probing and analyzing the structure and properties of ions of molecular clusters,[3] much less experimental and computational studies have been conducted on charged clusters of benzene Bz_n^{Z+}.[4] The simplest example is the benzene cation radical ($n = 1$, $Z = 1$) which has attracted considerable interest, both experimentally and theoretically, as a typical Jahn−Teller system.[5] The next simple charged clusters in this series are the benzene dimer cation ($n = 2$, $Z = 1$) and the benzene dication ($n = 1$, $Z = 2$). Although the last two decades have witnessed a steady increase of experimental and theoretical interest in the gas-phase physics and chemistry of ions of molecular clusters, or molecular dications (see ref 6 for reviews and references therein), most studies on charged benzene clusters have mainly focused on the benzene dimer cation. Very little is known about the dicationic states of benzene, both in isolated form and in clusters. Recent advances in this fairly rapidly evolving field have led us to undertake the present study of doubly charged clusters of benzene and related molecules, such as naphthalene and hexafluorobenzene.

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(4) There is no evidence for the existence of negatively charged clusters of benzene molecules in the gas phase. Notice also that in the gas phase, the electron affinity of benzene in its ground state is negative, $EA(C_6H_6) = -1.12$ eV.; see, e. g.,: Frasinsky, L. J.; Codling, K.; Hatherly, P.; Barr, J.; Ross, I. N.; Toner, W. T. *Phys. Rev. Lett.* **1987**, *58*, 2424.

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10.1021/ja042238j CCC: $30.25 © 2005 American Chemical Society

Recent theoretical works have demonstrated that, compared with isolated molecules, atomic or molecular clusters must behave in a fundamentally drastically different way under inner-valence ionization. This finding stems from the observation that, in a cluster environment, the double-ionization threshold lies much below the ionization energies pertaining to the innermost valence levels, as a result of strong intermolecular electron correlation effects and of the delocalization of charges on different molecules. Therefore, excited (more specifically, shake-up) electronic states that result from ionization of deep enough inner-valence electrons are naturally prone to stabilization via efficient electronic processes referred to as intermolecular Coulombic decays (ICD).[7] These involve first a drop of an outer-valence electron of the monomer carrying the initial vacancy into the inner-valence electron hole, whereas the released energy is transferred via virtual photon exchange to a neighboring monomer. This ultrafast energy transfer results in turn into autoionization of another outer-valence electron from that monomer, leaving two positive charges at different locations in the cluster. In simpler words, ICD is a route for electric charge migration without the assistance of nuclear dynamics. Since the dispersion and electrostatic forces accounting for the cohesion of molecular clusters are usually very weak, the ultimate fate of the cluster after ICD is normally to decay via Coulomb explosion[8] into smaller units.

The ICD mechanism originally predicted by Cederbaum and et al.[7a] has only very recently been experimentally inferred from the electron spectra of photoexcited Ne clusters,[7i] and explicitly assessed through synchrotron experiments on 2s ionized neon dimers, along with three-particle detection in coincidence of the autoionized electron and of the two neon cations,[7k] or from a determination of the 2s vacancy lifetime in surface and bulk atoms of free Ne clusters.[7l] The consequences of this mechanism for chemistry and biology have yet to be explored in detail. For instance, with regards to the intensity of the radiation field present in such an environment, it is quite clear that ICD processes must play an important role in the stellar and interstellar chemistry of clusters. Also, studies of electron transfers in the condensed phase are essential in research focusing on biological radiation damages.[9]

Obviously, the Coulomb repulsion between positive charges on different monomer sites decreases as the distance between these sites increases and is thus expected to scale inversely to system size. On the contrary, the cohesion forces ensuring the stability of the neutral cluster increase with system size. There must therefore exist some threshold size[10] for a multiply charged cluster below which fragmentation into two distinct charged fragments is energetically and kinetically favorable and above which the short-range intermolecular interactions may create, together with the strong long-range Coulomb repulsion, an energy barrier on the pathway leading to fragmentation. This barrier is often sufficiently high[11] to confer a substantial lifetime to thermodynamically unstable multiply charged cations. It has been experimentally demonstrated,[12] for instance, that, in the gas phase, the smallest cluster of benzene molecules that can bear two positive charges must contain at least 23 units.

To simply predict the threshold size $n_0(Z+)$ of a given cluster bearing Z units of charge (e), and containing n_0 molecules, a crude liquid-droplet model, which resembles that of the Coulomb instability of liquid droplets proposed at the end of the nineteenth century by Lord Rayleigh,[13] and further developed by Meitner and Frisch,[14] and Bohr and Wheeler,[15] has often been invoked (see also refs 10a, 16−19, and ref 20 for current review and references therein). According to this model, $n_0(Z+)$ is obtained by equating the electrostatic energy $\cong Z^2e^2/R$ of a charged sphere of radius R with Z positive charges to its surface energy $\cong \gamma R^2$ where γ is the surface tension. Therefore, the threshold radius is proportional to $(Z^2e^2/R)^{1/3}$. The volume of the sphere being proportional to n_0, it follows that, according to this model, $n_0(Z+)$ must scale like Z^2. Despite the crudeness of the model, such estimates of n_0 in general fairly agree with the experimental data available for multiply charged van der Waals clusters: if their size $n \ll n_0$, they are intrinsically unstable and their fragmentation is exothermic.[17] As an example, the liquid-droplet model predicts that for Bz, $n_0(2+) = 18$ (see Table 2 in ref 17), to compare with an experimental value of $n_0(2+) = 23$ (see above).

However, the liquid-droplet model was invalidated by Martrenchard et al.[21] in 1991 who experimentally inferred the existence of doubly charged clusters of *p*-difluorobenzene (*p*-

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difluoroBz$)_n^{2+}$ with $3 \leq n \leq 15$ and estimated their lifetimes to be larger than 40 μs.[21] This family has been further extended to a hybrid series of small but stable clusters such as (p-difluoroBz$_3$·Bz$_n$)$_n^{2+}$ and (p-difluoroBz·Bz$_n$)$_n^{2+}$.[21b] It must be noted nonetheless that (p-difluoroBz)$^{2+}$ was not observed.[21b] So far, the structures of all these dications remain unknown. The semiempirical calculations conducted in ref 21b led to the conclusion that these doubly positively charged clusters are simply tightened by electrostatic and dispersion forces. As shall be seen, it is actually much more reasonable to suggest that the liquid-droplet approximation breaks down because it does not account for quantum chemical effects, more specifically the formation of additional chemical bonds, but rather crudely assumes that the excess charge (hole) spreads over the whole cluster surface and that the constituting molecules are arranged in a way that the total surface energy is minimized.

Resorting to density functional theory (DFT), and a reliable hybrid and gradient-corrected functional that has been widely employed in studies of reaction pathways, the present work provides theoretical evidences that, in sharp contrast with the expectations of the liquid-droplet model and the Coulomb explosion that has been predicted by high-level computations for small clusters of rare gas atoms (Ne) and molecules such as water or hydrogen fluoride, double-ionization processes on clusters of benzene and related molecules such as hexafluorobenzene and naphthalene may induce the formation of covalently bound dicationic assemblies of two, and possibly more, monomer units.

2. Computational Framework

Most computations, framing the present work, were performed by means of the GAUSSIAN98 package of programs,[22] employing DFT along with the Becke three-parameters Lee−Yang−Parr (B3LYP) functional[23] and Dunning's correlation consistent polarized valence basis sets of double- and triple-ζ quality, in short cc-pVDZ and cc-pVTZ,[24] respectively. These computational levels, B3LYP/cc-pVDZ and B3LYP/cc-pVTZ, are known to be fully adequate for theoretical studies of molecular structures, vibrational spectra, and related properties (see ref 5e and references therein). The pruned integration grid that has been used for performing all geometry optimizations with DFT/B3LYP is the default one, which has 75 radial shells and 302 angular points per shell, and results in about 7000 points per atom. In the present work, harmonic vibrational frequencies and the related zero-point vibrational energies (ZPVEs) have been analytically calculated at all employed computational levels in order to verify whether the identified stationary structures correspond to energy minima or to saddle-points on the potential energy surfaces. Enthalpies and entropies were estimated from the partition functions calculated at room temperature (298 K) using Boltzmann thermostatistics and the rigid-rotor-harmonic-oscillator approximation.[25] The expectation value of the $\mathbf{S}^2$ operator for radicals and closed-shell dications was found to remain always equal to ~0.750 and ~0.00, respectively. It is worth noting that DFT methods are known to be less sensitive to spin contamination problems than post-SCF ab initio approaches such as Møller−Plesset theories. In their unrestricted version, these methods, and the B3LYP functional in particular, are thus better suited for studying bond dissociation processes. We refer in particular to section 11.5 within the text book by F. Jensen[26] for a comparison with the results of benchmark calculations employing a multireference wave function.

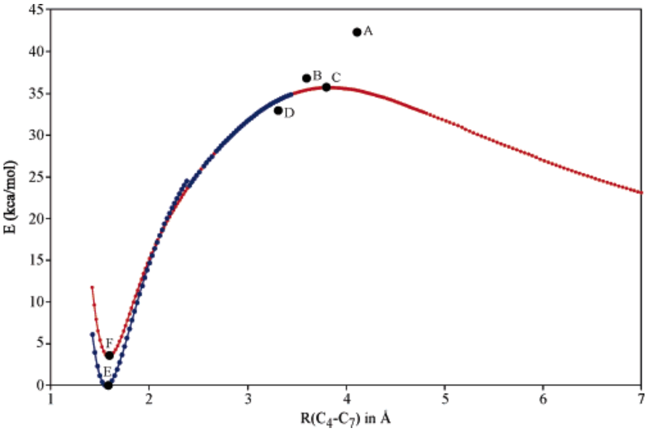

Figure 1. B3LYP/cc-pVDZ study of the dissociation pathway of the Bz_2^{2+}-I species under the constraints of C_{2h} (red curve) or C_2 (blue curve) symmetry point groups. See Figure 2 for an illustration of the **A**−**F** structures.

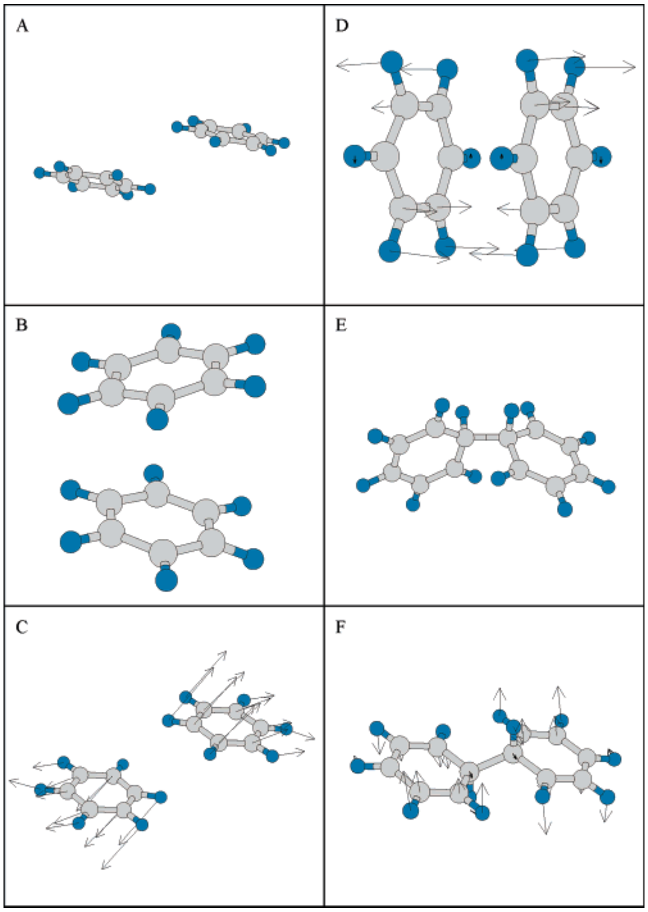

Figure 2. Structures corresponding to stationary or entry points on the potential energy surface of the dicationic dimer of benzene. (A) state produced through vertical double ionization of the neutral sandwich; (B) state produced through vertical ionization of the adiabatically relaxed Bz_2^+ cation; (C) TS_D; (D) TS_I; (E) Bz_2^{2+}-I; (F) Bz_2^{2+}-I_{ts}. Atom displacements in C, D, and F derive from the eigenvectors related to the imaginary frequency characterizing these transition states.

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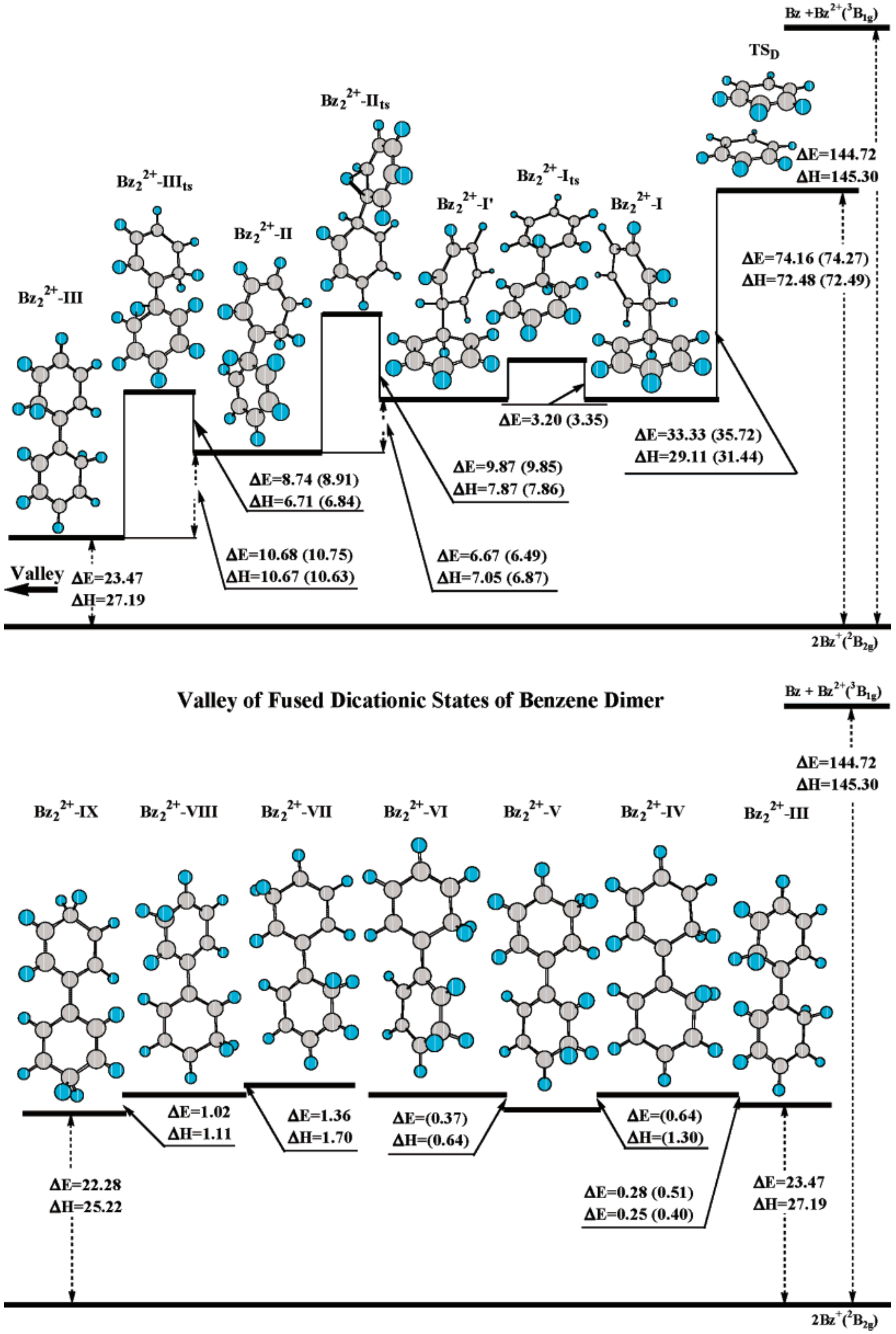

Figure 3. Lower-energy portion of the potential energy surface of the ground electronic state of Bz_2^{2+} describing the migration of the double hole over the benzene ring. The relative electronic energies and the ZPVE-corrected energies (i.e., enthalpies) are displayed in the following order: B3LYP/cc-pVTZ and B3LYP/cc-pVDZ (in parentheses).

Except for a few situations that will be explicitly mentioned where appropriate, most reaction and activation energies discussed in the sequel account for zero-point vibrational energies and derive from our most thorough B3LYP/cc-pVTZ or B3LYP/6-31+G(d,p) calculations, respectively. Differences on reaction and activation energies between these two models and the B3LYP/cc-pVDZ one are limited: relative overestimations of our best (B3LYP/cc-pVTZ) estimates for these energies by the B3LYP/cc-pVDZ model never exceed 8%. Therefore, with regards to the size of the employed basis sets and the height of the computed energy barriers, we did not deem necessary to systematically account for basis set superposition errors (BSSEs).[27] Some calculations in section 3 illustrate these two methodological issues.

3. Consequences of Double Ionization in Bz_2

Suppose that one electron in the innermost valence level of a dimer of benzene molecules is ionized by interaction with an electron or photon of sufficient energy. All electronic states produced by ionization of the innermost C_{2s} orbitals of Bz, and by extension Bz_2, are shake-up states described as mixtures of singly ionized but electronically excited configurations. These states are found at vertical ionization energies around 27 eV.[28] Since they lie much above the vertical double-ionization threshold of the dimer (21.9 eV, at the B3LYP/cc-pVTZ level), they will, according to the ICD mechanism by Cederbaum and co-workers, very naturally decay within time scales of the order of 1 to 100 fs, through emission of a second electron into the continuum, leaving thereby a doubly ionized cluster bearing two positive charges localized on different monomers. It may then be expected, by analogy with the works reported so far on clusters of Ne, HF, and H_2O,[7] that the ultimate fate of the Bz_2 cluster will be simply to undergo a Coulomb explosion.

From inspection of the potential energy surfaces computed for the electronic ground state of Bz_2^{2+}, of which the main features are summarized in Figures 1−3, it appears however that two reaction channels are opened once Bz_2 has been doubly ionized. As anticipated, the most energetically favorable route leads to a fragmentation of the cluster into two distinct Bz^+ species. From here and henceforth, this reaction pathway will be referred to as the *fission route*. Another route, which is at first glance less competitive from an energy viewpoint, leads on the contrary to the *formation of a covalent C−C chemical bond* between the two rings. This second reaction path will be referred to as the *fusion route*, and this first identified covalently bound structure will be described as the Bz_2^{2+}-I species (structure **E** in Figures 1 and 2, see Figure 4 for atom labeling). In this covalently bound dimer the inter-ring bond connects two carbon atoms bearing four substituents and exhibiting a tetrahedral configuration, thus an sp^3 hybridization state (see Figure 4). At the B3LYP/cc-pVDZ and B3LYP/cc-pVTZ levels, the vertical dicationic state (**A**) produced by the sudden removal of two electrons from the neutral dimer in its displaced parallel form lies at 5.9 and 6.9 kcal/mol, respectively, above the transition state (TS_D) on the reaction pathway that describes (**C**) the dissociation of the Bz_2^{2+}-I dimer into two Bz^+ radical cations (Figure 1). These two states (**A** and **C** in Figures 1 and 2) are very similar from a geometrical viewpoint: the TS_D state is a displaced and perfectly parallel form of C_{2h} symmetry, whereas in neutral form the benzene rings in the dimer of benzene exhibit a twist angle of ∼13°. The inter-ring distance defined by the relative location of the closest carbon atoms in different rings $r(C_4{-}C_7) = 3.80$ Å in the TS_D state (**C**, B3LYP/cc-pVTZ result) is decreased by ∼0.5 Å compared with the geometry of the neutral dimer ($r(C_4{-}C_7) = 4.33$ Å). Values of 3.82 and 4.08 Å are correspondingly found at the B3LYP/cc-pVDZ level. This observation implies that the doubly ionized form of the neutral dimer of benzene (**A**) lies on the side of the TS_D energy barrier leading to Coulomb fragmentation into $2Bz^+$. However, it is worth noting from Figure 1 that the total electronic energy of the Bz_2^{2+} cluster does not vary by more than 0.55 kcal/mol when the inter-ring distance $C_4{-}C_7$ increases from 3.5 to 4.2 Å, an energy difference which is comparable with that associated with thermal fluctuations at room temperature (RT). Therefore, with regards to the above energy difference of ∼6 kcal/mol and the extreme smoothness of the reaction path around TS_D, it seems quite likely that, at energies equal to or slightly above the vertical double-ionization threshold, a nonnegligible fraction of the dications produced by the sudden removal of two electrons should relax through fusion into the Bz_2^{2+}-I species (**E**).

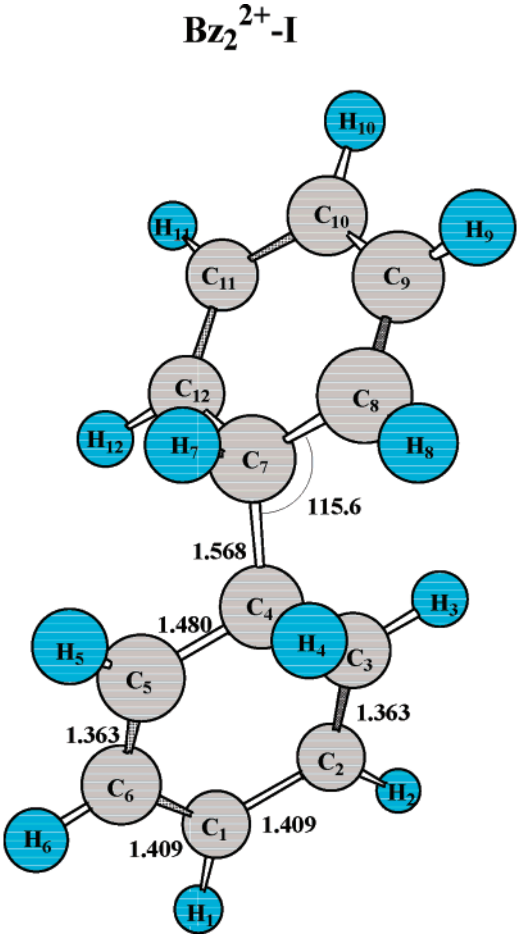

Figure 4. Molecular structure of Bz_2^{2+}-I at the B3LYP/cc-pVTZ level (bond lengths in angstroms). The atomic numbering that has been provided in this figure is used throughout the present work.

In contrast with the relative location of the vertically doubly ionized state (**A**), the fusion route is *readily* reached when using as inputs for optimizations of the geometry of Bz_2^{2+} the adiabatically relaxed structure of the monocation, Bz_2^+, in its sandwich form. Indeed, according to the B3LYP/cc-pVTZ model, the latter π-stack structure (**B** in Figures 1 and 2) is characterized by a significantly shorter (by ∼0.5 Å) inter-ring distance of $r(C_4{-}C_7) = 3.34$ Å (3.60 Å at the B3LYP/cc-pVDZ level). In its lowest doubly ionized state this structure lies at only ∼1 kcal/mol above the TS_D state. Therefore, in this case, if a Coulomb explosion cannot be entirely ruled out after further ionizing an adiabatically relaxed monocationic dimer, the dications produced this way through sequential ionization events should predominantly decay via fusion into the Bz_2^{2+}-I species. At inter-ring $r(C_4{-}C_7)$ distances below ∼2 Å, these covalently bound dimers have C_2 symmetry (Figure 1) in their most stable conformation. At the B3LYP/cc-pVTZ level and for the energy minimum (**E**) encountered on the reaction path which describes

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Table 1. NPA Charges of the Selected Structures of the Covalently Bound Benzene Dimer Dication (see Figure 1) and in the Dicationic Closed-Shell State (A in Figure 1) Produced by a Sudden (Vertical) Double Ionization of the Neutral D-Sandwich[a]

atom	Bz_2^{2+}-I[b]	Bz_2^{2+}-II	Bz_2^{2+}-III	Bz_2^{2+}-IV	Bz_2^{2+}-VII	Bz_2^{2+}-VIII	Bz_2^{2+}-IX	D-sandwich[c]
C_1	0.083	0.079	−0.220	−0.220	0.108	0.100	−0.574	−0.126
C_2	−0.218	−0.222	0.062	0.100	−0.569	−0.564	0.094	−0.093
C_3	0.028	0.041	−0.187	−0.543	0.086	0.062	−0.233	−0.209
C_4	−0.329	−0.405	0.120	0.125	−0.141	−0.109	0.131	−0.143
C_5	0.029	0.039	−0.547	−0.190	0.052	0.046	−0.233	−0.077
C_6	−0.219	−0.222	0.113	−0.065	−0.226	−0.227	0.094	−0.216
C_7	−0.329	0.216	0.120	0.125	0.171	−0.109	0.131	−0.093
C_8	0.029	−0.557	−0.547	−0.543	−0.223	0.046	−0.233	−0.126
C_9	−0.219	0.101	0.113	0.100	0.070	−0.227	−0.094	−0.216
C_{10}	0.083	−0.232	−0.220	−0.220	−0.229	0.100	−0.574	−0.077
C_{11}	−0.218	0.084	0.062	0.065	0.090	−0.564	0.094	−0.143
C_{12}	0.028	−0.237	−0.187	−0.190	−0.544	0.062	−0.233	−0.209
H_1	0.256	0.256	0.270	0.270	0.254	0.252	0.355	0.226
H_2	0.269	0.269	0.254	0.251	0.354	0.349	0.253	0.224
H_3	0.238	0.244	0.238	0.322	0.241	0.237	0.252	0.229
H_4	0.352	0.360	0.323(H_5')	0.317(H_3')	0.352(H_2')	0.349(H_2')	0.355(H_1')	0.228
H_5	0.243	0.244	0.323	0.248	0.234	0.238	0.252	0.225
H_6	0.268	0.269	0.251	0.255	0.268	0.266	0.252	0.233
H_7	0.352	0.323(H_8')	0.323(H_8')	0.319(H_8')	0.326(H_{12}')	0.349(H_{11}')	0.355(H_{10}')	0.224
H_8	0.243	0.322	0.323	0.322	0.245	0.238	0.252	0.226
H_9	0.268	0.251	0.251	0.251	0.253	0.266	0.253	0.233
H_{10}	0.256	0.270	0.270	0.270	0.268	0.252	0.355	0.225
H_{11}	0.269	0.255	0.254	0.255	0.250	0.349	0.253	0.228
H_{12}	0.238	0.249	0.238	0.248	0.313	0.237	0.252	0.229

[a] B3LYP/cc-pVTZ results from an NBO analysis. [b] Alias **E** in Figure 1. [c] Alias **A** in Figure 1.

under the constraint of C_2 symmetry the fusion of two Bz^+ species into Bz_2^{2+}-I, $r(C_4-C_7) = 1.568$ Å and the dihedral angle between the Bz rings amounts to 71.1°. This state lies at ~3.3 kcal/mol below a first-order saddle-point of C_{2h} symmetry (**F**) with $r(C_4-C_7) = 1.59$ Å and which connects two conformational enantiomers of C_2 symmetry (Bz_2^{2+}-I and Bz_2^{2+}-I′, see also Figure 3). The related transition mode has an imaginary vibrational frequency of ~45 i cm^{-1} and describes therefore the rotation of Bz rings about the central C−C bond (Figure 2). According to elementary transition state theory,[29] this low-energy barrier determines a rate constant of the order of 10 interconversions per nanosecond at room temperature.

Passing by, another transition state (**D**) could be found upon exploring the potential energy surface of the Bz_2^{2+} species. At the B3LYP/cc-pVDZ and B3LYP/cc-pVTZ levels, this structure lies at ~30.0 and ~31.6 kcal/mol above the Bz_2^{2+}-I energy minimum, respectively (ZPVEs included). At the latter level, this stationary point is characterized by an imaginary frequency of 95 i cm^{-1} and an inter-ring $r(C_4-C_7)$ distance of 3.32 Å. As a parallel π-stack, it is thus structurally very close (Figure 2) to the sandwich and most stable form of the benzene dimer monocation (**B**) but lies slightly *below* (Figure 1) the reaction path leading to fission. This transition state connects the Bz_2^{2+}-I species reported in Figures 1−3 to another structurally identical energy minimum which differs only by the labels of the carbon atoms involved in the inter-ring bond. In other words, this first-order saddle-point describes an intramolecular rearrangement (TS_I) of the Bz_2^{2+}-I species through a cleavage of the central C_4-C_7 bond. Also, under the constraint of the C_2 symmetry point group, a very sudden rotation of the benzene rings into a coplanar conformation is observed at an inter-ring separation $r(C_4-C_7)$ of ~2.40 Å (Figure 1). C_2 being a subgroup of the C_{2h} symmetry point group, the reaction paths calculated at larger separations under the constraints of both symmetries therefore very naturally coincide.

As the highest lying point (**C**) on the C_{2h} reaction path displayed in Figure 1, TS_D actually determines the barrier that, on one hand, governs the fusion of rings and on the other hand, the Coulomb explosion of the Bz_2^{2+} cluster. Each ring in TS_D is characterized by a "local" C_{2v} symmetry point group and exhibits a structure which is very similar to that of the benzene radical cation in its $^2B_{1g}$ state.[5e] TS_D is placed at ~72.5 kcal/mol above the final product of the fission route (Figure 3), which obviously implies that the latter pathway is an absolutely irreversible one. In contrast, the first identified local energy minimum (Bz_2^{2+}-I) on the left-hand-side of the barrier is the doorway to a complex series of configurational rearrangements via proton transfers (structures Bz_2^{2+}-I to Bz_2^{2+}-IX in Figure 3). In comparison with the reaction pathway describing the dissociation of Bz_2^{2+}-I into $2Bz^+$, these are characterized by much more limited energy barriers. The extent of the barrier seen from Bz_2^{2+}-I along this reaction pathway makes us believe that, once they are formed in vacuum, the covalently bound Bz_2^{2+} species should be very easy to detect experimentally. Indeed, according to elementary transition state theory,[29] an activation enthalpy of the order of 30 kcal/mol typically corresponds, at room temperature, to a dissociation rate constant and, thus, half-lifetime $T_{1/2}$ of the order of 6×10^{-10} s^{-1} and ~36 years, respectively.

Evaluations, according to the counterpoise method by Boys and Bernardi,[30] of basis set superposition errors[27] on the energy of the TS_D and TS_I states (**C**, **D**) relative to the dissociation limit into $2Bz^+$ give corrections of the order of −0.1 kcal/mol at the B3LYP/cc-pVDZ level and are expected to be much smaller when using the larger cc-pVTZ basis set.

At the B3LYP/cc-pVTZ level, the electronic energy released by relaxation of the molecular geometry of the most stable form

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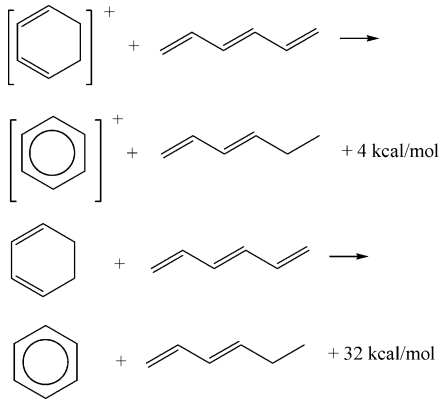
of the dimer monocation (**B**) into Bz_2^{2+}-I (**E**) is large (∼34.0 kcal/mol) and is very comparable to the electronic energy barrier (∼33.3 kcal/mol, **C**) pertaining to the dissociation of the latter species into two noninteracting Bz^+ molecules. The relaxation energy released by double ionization of the most stable form of the neutral dimer (Bz_2) into Bz_2^{2+}-I, i.e., the energy difference between states **A** and **E** in Figure 1, is correspondingly found to amount to ∼39.2 kcal/mol. In the same order, energy differences of 36.7, 35.7, and 42.6 kcal/mol were found at the B3LYP/cc-pVDZ level (Figure 1). These energies corroborate the idea that the formation of the inter-ring C−C bond more specifically relates to a single-electron adiabatic ionization process on the dimer monocation, which then simply enables the *pairing of two free electrons with opposite spins*. The energy released by the formation of an inherently strongly localized C−C bond between the two benzene rings is obviously sufficient to overcome the Coulomb repulsion between the positively charged monomers. In agreement with the r^{-1} scaling that is expected for the Coulomb interaction energy between electric charges localized on two identical molecular fragments at large distances, we note that the energy of the dicationic cluster decreases inversely to the interdistance [$r(C_4{-}C_7)$] between rings, according to linear regressions ($R^2 > 0.9997$) of these energies over about 100 points in scans by steps of 0.04 Å, at inter-ring distances comprised between 4.5 and 9 Å (in these scans, all geometry parameters were optimized except $r(C_4{-}C_7)$).

It is worth noting that, at the geometry pertaining to structure **F** (C_{2h} point group), the lowest singlet-to-triplet one-electron excitation energy amounts to 62.9 or 63.2 kcal/mol at the B3LYP/cc-pVDZ or B3LYP/cc-pVTZ levels, respectively. Geometry optimizations show, that, unlike the lowest singlet electronic ground state, the lowest triplet state is fully dissociative. *These results also confirm the suggestion that the formation of the additional C−C bond simply relates to the pairing of electrons with opposite spin*. In this chemical process, aromaticity[31] does apparently not play a very substantial role. Indeed, according to the Hückel rules for aromatic and antiaromatic rings, the radical cation of benzene is, with five π-electrons, a nonaromatic system. The benzene radical cation in its $^2B_{2g}$ ground state and the benzene molecule are characterized by aromatic stabilization energies[31,32] of ∼4.0 and ∼32.0 kcal mol^{-1}, respectively (B3LYP/cc-pVTZ results, ZPVEs included), according to the following isogyric chemical reactions:



Also in line with the interruption of π-ring currents by two C atoms in sp^3 hybridization states, the Bz_2^{2+}-I species display, at the B3LYP/cc-pVDZ level, NICS[33] indices[31,34] of the order of 0.01 and can thus also be described as a nonaromatic species. The same observation essentially prevails for all dicationic dimers studied in the sequel.

A few more remarkable features of Bz_2^{2+}-I deserve to be emphasized and discussed in detail. Bz_2^{2+}-I is structurally very distinct from the benzene dimer cation (Bz_2^+). The formation of the inter-ring $C_4{-}C_7$ bond induces substantial elongations of the neighboring C−C and C−H bonds, by ∼0.06 and ∼0.03 Å, respectively, along with a downshift of the corresponding C−H stretching vibrations by ca. 170 cm^{-1} in comparison with those in the cationic sandwich [$\upsilon^{\mathrm{asym}}(C_4{-}H_4, C_7{-}H_7) = 2837$ cm^{-1} and $\upsilon^{\mathrm{sym}}(C_4{-}H_4, C_7{-}H_7) = 2839$ cm^{-1}]. These elongations and frequency shifts obviously reflect the change in the hybridization state of C_4 and C_7, from sp^2 to sp^3. The additional $C_4{-}C_7$ bond results also more specifically into the appearance in the IR spectrum of Bz_2^{2+}-I of a C−C stretching mode at $\upsilon(C_4{-}C_7) = 1115$ cm^{-1} (IR activity = 3 km/mol).

Conducting a natural bond orbital (NBO) analysis[35] upon Bz_2^{2+}-I allows us to approximately locate the two holes that are present in the covalently bound dication (Figure 4). The charges determined by the natural population analysis (the so-called NPA charges) from the NBOs are collected in Table 1. Examination of the NPA charges of Bz_2^{2+}-I demonstrates that charge increases are greatest on the hydrogen atoms H_4 and H_7 attached to the carbon atoms C_4 and C_7 involved in the fusion process. Quite naturally, the NPA charges on the other hydrogens and carbons also vary, but to a lesser extent. These changes demonstrate the relatively strong localization of the two holes around C_4 and C_7. The implication of such double-hole localization is 3-fold, to say the least.

First, the excess charges on the hydrogen atoms H_4 and H_7 are congruent with a lengthening of the $C_4{-}H_4$ and $C_7{-}H_7$ bonds by 0.03 Å compared to other C−H bonds. This in turn allows the C_4 and C_7 atoms, which are both characterized by NPA charges of −0.329 *e*, to share partially an electron pair and therefore to form the observed additional and rather robust inter-ring covalent single bond ($r(C_4{-}C_7) = 1.57$ Å).

Second, since the excess charges are mainly localized on the hydrogen atoms H_4 and H_7, the two bonds $C_4{-}H_4$ and $C_7{-}H_7$ are twisted relative to each other in order to limit the extent of Coulomb repulsion. This induces a relative rotation of two benzene rings with respect to each other by a dihedral angle $\tau(C_5C_3C_8C_{12})$ of ±62.9°. The fact that the Bz_2^{2+}-I structure possesses an isoenergetic and enantiomeric conformer of C_2 symmetry, Bz_2^{2+}-I′ (see Figure 3), implies that the series of proton transfers starting from Bz_2^{2+}-I is also doubly degenerate (in Figure 3, only the branch starting from Bz_2^{2+}-I′ is shown).

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Table 2. Overview of Some Basic Structural and Electronic Properties of the Identified Bz_2^{2+}-I to -IX Species[a]

species	migrating protons on	$r(C_4–C_7)$	$\angle C_3–C_4–C_5–C_8$	ΔE	ΔH(298 K)	ΔE(S→T)
Bz_2^{2+}-I	C_4, C_7	1.568	68.0	18.5	19.5	63.2
Bz_2^{2+}-II	C_4, C_{12}	1.526	67.6	11.9	12.6	49.9
Bz_2^{2+}-III	C_3, C_{12}	1.472	0.0	1.2	2.0	23.0
Bz_2^{2+}-IV	C_3, C_8	1.477	30.6	1.5	2.2	26.4
Bz_2^{2+}-V	C_2, C_9	1.500	51.0	1.0	1.7	38.5
Bz_2^{2+}-VI	C_3, C_9	1.489	37.7	1.2	1.7	38.4
Bz_2^{2+}-VII	C_2, C_{12}	1.484	40.1	1.4	1.8	37.8
Bz_2^{2+}-VIII	C_2, C_{11}	1.496	48.1	1.0	1.1	38.1
Bz_2^{2+}-IX	C_1, C_{10}	1.489	49.2	0.0	0.0	36.6

[a] Inter-ring bond length $r(C_4-C_7)$ in angstroms; twist angle $\angle C_3-C_4-C_5-C_8$ in degrees; relative energy ΔE, enthalpy difference (ΔH) at room temperature, and first singlet−triplet excitation energy ΔE(S→T) in kcal/mol (B3LYP/cc-pVTZ results).

Third, the C−C bonds in the vicinity of the C_4-C_7 fusion bond, specifically $r(C_4-C_3) = r(C_4-C_5) = r(C_7-C_8) = r(C_7-C_8) = 1.48$ Å, are significantly longer (by 0.12 Å) than the bonds that are located further, namely $r(C_2-C_3) = r(C_5-C_6) = r(C_8-C_9) = r(C_{11}-C_{12}) = 1.36$ Å. In view of their lengths these bonds can obviously be described as single and double C−C bonds, respectively. The remaining C−C bonds have a length equal to $r(C_1-C_2) = r(C_1-C_6) = r(C_9-C_{10}) = r(C_{10}-C_{11}) = 1.41$ Å, which is consistent with a bond order around 1.5 and reflects the delocalization of two unpaired π-electrons over the [C_6,C_1,C_2] and [C_9,C_{10},C_{11}] segments, respectively.

As a doorway state on the potential energy surface of Bz_2^{2+}, the Bz_2^{2+}-I structure opens a deep and large rift with minor ridges that enable a very substantial energy stabilization of the cluster, by as much as ∼19.5 kcal/mol, through a series of hydrogen transfers around the benzene rings (in straightforward analogy with ref 36), until the strength of the Coulomb repulsion between holes is minimized (see Figure 3 and Table 2). The internal energy barriers associated to these hydrogen “jumps” range from 8 to 11 kcal/mol. In particular, the reaction path which connects Bz_2^{2+}-I and Bz_2^{2+}-II is characterized by an internal energy barrier and an activation enthalpy of 9.9 and 7.9 kcal/mol, respectively. This barrier is the highest on the reaction pathway leading to the most stable form of Bz_2^{2+} and is the rate-determining step therefore for the decay of the Bz_2^{2+}-I species via the fusion route. At room temperature, according to transition state theory, this activation enthalpy corresponds to a rate constant of the order of 10^7 s^{-1}. The latter value implies that the Bz_2^{2+}-I complex has a sufficiently long lifetime ($T_{1/2} \sim 0.1$ μs) to be detectable experimentally.

The reduction of Coulomb forces at the origin of this cascade of proton transfers is consistent with the NPA charges that are reported in Table 1 (the two migrating protons are reported with primed labels). We take as a main example the very first hydrogen jump $H_7 \rightarrow H_{8'}$ from C_7 to C_8 and over the Bz_2^{2+}-II$_{ts}$ saddle-point characterized by an activation barrier of 9.9 kcal/mol (Figure 3). At the B3LYP/cc-pVTZ level, upon taking into account the ZPVE corrections, this proton migration alone suffices to lower the energy of the dicationic dimer by 7.1 kcal/mol relative to the initial Bz_2^{2+}-I energy minimum form. This stabilization can be ascribed to the fact that one of the two electron holes, that was originally mainly localized on H_7, has migrated to the $C_8H_8H_{8'}$ group, whereas the other one has remained mainly localized on H_4 (see the NPA charges on H_4, H_8, and $H_{8'}$ in Table 1). The excess of positive charges on the $C_8H_8H_{8'}$ group considerably weakens the C_8-C_9 bond, as is reflected by a very substantial elongation of this bond, by 0.10 Å, compared to that in Bz_2^{2+}-I. This hole migration leads obviously to an increase of the hole−hole separation and, thus, a reduction of Coulomb repulsion forces. Quite naturally, this hole migration and release of Coulomb repulsions thereby result also into a contraction of the C_4-C_7 bond by 0.04 Å. We also observe an elongation of the C_8-H_8 bond by 0.02 Å and an increase of the twist angles between the two rings by about 10° [$\tau(C_5C_3C_{12}C_8) = 76.7°$)]. Regarding the MO pattern of Bz_2^{2+}-II, it is worth mentioning that the HOMO−LUMO gap of the latter species is only slightly larger, by ∼0.05 eV, than that of Bz_2^{2+}-I.

The next local energy minimum Bz_2^{2+}-III in this cascade of rearrangements is placed at only 27.2 kcal/mol above the dissociation limit into $2Bz^+$. This minimum is separated from the dissociation limit by a global energy barrier of ∼50 kcal/mol (see Figure 3). A considerable energy stabilization, by ∼10.6 kcal/mol, of Bz_2^{2+}-III with respect to Bz_2^{2+}-II stems from a further proton transfer, this time from the C_4 to the C_5 carbon atoms. This charge repositioning induces the formation of an inter-ring double bond [$r(C_4-C_7) = 1.47$ Å] and quite naturally, therefore, the coplanarity of benzene rings, which also helps to minimize the hole−hole Coulomb repulsion [in the Bz_2^{2+}-III structure, the twist angle $\tau(C_1C_3C_8C_{12})$ amounts to −0.1° only]. In line with the enhanced π-conjugation of rings, the HOMO−LUMO gap of Bz_2^{2+}-III is equal to 3.10 eV only, to compare with a value of 4.10 eV for Bz_2^{2+}-I. This band gap is in fact the smallest one for all studied dicationic Bz_2^{2+} dimers—as further proton transfers result again into significant deviations from coplanarity and release therefore of inter-ring π-conjugation (Figure 3, Table 2). Unsurprisingly therefore, Bz_2^{2+}-III exhibits an extremely limited singlet-to-triplet one-electron excitation energy (1.00 eV at the B3LYP/cc-pVTZ level).

Many more proton transfers and hole migrations (Figure 3, Table 2) yield the global energy minimum form, Bz_2^{2+}-IX, along the fusion reaction pathway. Before characterizing in detail the latter species, let us outline some general trends we observe in some basic properties of the dicationic states of the dimer of benzene as the two electron holes migrate around benzene rings. The first one pertains to the fusion bond C_4-C_7. The longest one (1.58 Å) is found in Bz_2^{2+}-I. It is then shortened to 1.53 Å in Bz_2^{2+}-II and 1.47 Å in Bz_2^{2+}-III, reflecting the decrease of Coulombic repulsion and enhancement of inter-ring π-conjugation. This obviously corroborates a drastic reduction of the HOMO−LUMO band gap, and first one-electron excitation energy thereby (Table 2). The shortest C_4-C_7 bond lengths are predicted for the Bz_2^{2+}-III and Bz_2^{2+}-IV species. The largest HOMO−LUMO gaps amount to 4.16 and 4.11 eV and are correspondingly calculated for the Bz_2^{2+}-I and Bz_2^{2+}-II species, whereas the narrowest ones (3.10 and 3.24 eV) are identified for Bz_2^{2+}-III and Bz_2^{2+}-IV, respectively. The latter two dicationic structures exhibit minimal deviations from coplanarity. While Bz_2^{2+}-III, as mentioned above, exhibits an almost planar carbon backbone, Bz_2^{2+}-IV is characterized by a still rather limited twist angle $\tau(C_3C_5C_5C_8)$ of 30.6° between the two rings. Beyond this point, we note that the energies of the Bz_2^{2+}-III to -IX species do not differ by more than 1.5 kcal/mol (Table 2), due to a subtle balance between the release of Coulombic repulsions, as the protons migrate further away, and partial

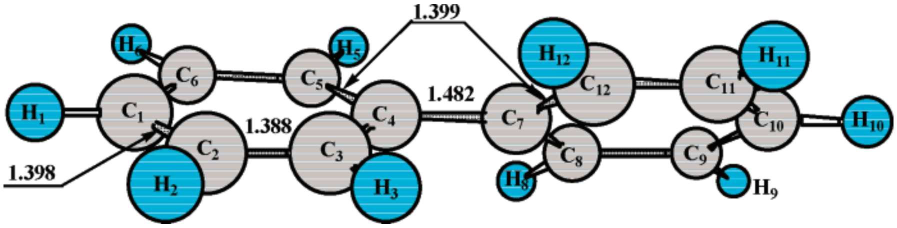

Figure 5. B3LYP/cc-PVTZ-optimized structure of the biphenyl molecule in its ground electronic state. See Table 3 for detailed geometrical parameters.

Table 3. Comparison of the Molecular Structure of the Bz_2^{2+}-IX Species and of the Biphenyl Molecule (B3LYP/cc-pVTZ Results, D_2 Symmetry Point Group)

	Bz_2^{2+}-IX	biphenyl
$r(C_1-C_2)$	1.459	1.390
$r(C_1-H_1)$	1.109(H_1')	1.082
$\angle C_2C_1H_1$	109.9(H_1')	120.3
$r(C_2-C_3)$	1.369	1.388
$r(C_3-C_4)$	1.413	1.399
$r(C_4-C_7)$	1.489	1.482
$\angle C_6C_1C_2$	117.1	119.4
$\angle C_1C_2C_3$	121.0	120.3
$\angle C_2C_3C_4$	119.7	121.0
$\angle C_3C_4C_5$	121.6	118.0
$\angle C_3C_2H_2$	120.5	119.7
$\angle C_4C_3H_3$	120.2	119.4
$\angle C_2C_6C_{11}C_9$	49.2	38.9

interruptions of inter-ring π-conjugation due to further departures from planarity. All these species will be therefore simultaneously observed at room temperature in experiments employing spectroscopic techniques with time scales larger than 1 μs.

The global energy minimum (Bz_2^{2+}-IX) along the fusion pathway is placed at about 25.2 kcal/mol above the dissociation limit into $2Bz^+$. In line with the axial symmetry of this configuration, and due to steric repulsions, the twist angle between the two rings amounts to 46.6°. In this species, the inter-ring C_4-C_7 bond length amounts to 1.49 Å only, a value which, despite the above twist angle and the remaining Coulomb repulsion, is still significantly smaller than that expected for a single C−C bond (1.53 to 1.55 Å) and reflects therefore a bond order between 1 and 2. As Table 1 shows, in Bz_2^{2+}-IX the two holes are mainly localized on CH_2 groups that are located at maximal distance from each other. With a first singlet-to-triplet excitation energy of 1.6 eV (36.6 kcal/mol) only, this cluster can also be regarded as a *highly reactive biradical species* with two free electrons on C_1 and C_{10}.

The geometrical characteristics of Bz_2^{2+}-IX bear great similarities (Table 3) with that of the biphenyl molecule (Figure 5), except for the bond lengths and angles describing the near-environment of the C_1 (or C_{10}) carbon atoms bearing the migrating protons ($H_{1'}$ or $H_{10'}$). This similarity suggests immediately another route for producing the Bz_2^{2+}-III to -IX dimers by simply considering diprotonation experiments on biphenyl, similar to the well-known protonation experiments on benzene.[36,37] It is worth mentioning that such experiments on biphenyl have been reported very recently and this for the very first time by Meinel et al.[38] According to our best (B3LYP/cc-pVTZ) model, the diprotonation energy of biphenyl (biphenyl $+ 2H^+ \rightarrow Bz_2^{2+}$-IX) in vacuum amounts theoretically to −299 kcal/mol. Because diprotonotion is a so highly exothermic process in vacuum, it is therefore obvious that, in the absence of neighboring molecules, the Bz_2^{2+}-III to -IX species will not spontaneously further relax through proton emissions. We therefore believe that we have identified the most important reaction channels on the potential energy surface of the benzene dimer cation in vacuum.

To summarize and conclude the present section, a key aspect of the potential energy surface of Bz_2^{2+} pertains to the relative thermochemical stability of the covalently bound dicationic Bz_2^{2+}-III to -IX species with respect to the asymptotic dissociation limits defined by $2Bz^+$, and by $Bz + Bz^{2+}$. To our knowledge, this has never been reported so far in the scientific literature, either experimentally or theoretically. Upon examining Figure 3, the former is clearly the lowest energy asymptote, and the latter is energetically unreachable. Therefore, according to the classification proposed in ref 39, *the Bz_2^{2+}-III to -IX species are kinetically metastable with respect to the dissociation limit into $2Bz^+$ but stable relative to the dissociation limit into $Bz + Bz^{2+}$*. Considering that from Bz_2^{2+}-IX the total barrier against dissociation into $2Bz^+$ amounts to 49.6 kcal/mol, these theoretically predicted covalently bound Bz_2^{2+} species can thus be regarded as the first identified examples of a novel family of small, metastable but very long-lived dicationic aromatic clusters in vacuum. Considering the expected time scale of the electronic ICD decay relative to that of the motions of molecules as large as benzene, the calculated barriers toward charge fragmentation and the location of ionized states relative to the transition state on this reaction path, it seems legitimate to conclude that the Bz_2^{2+}-III to -IX species will be ultimately produced by sequential ionization experiments on the neutral dimer of benzene and possibly also from more classical photon or electron impact ionization experiments.

4. Consequences of Double Ionization in $(C_6F_6)_2$

We have mentioned in the Introduction that, despite the expectations drawn from the liquid-droplet model, there are firm experimental evidences for the existence of small doubly positively charged fluoro-substituted benzene clusters, the structure of which remain completely unknown so far. It is thus quite natural to extend our investigation of the consequences of double ionization in aromatic clusters to the case of hexafluorobenzene (C_6F_6) clusters. The vertical double-ionization potential of the dimer of C_6F_6 in its most stable form amounts to ∼23.4 eV at the B3LYP/6-31G+(d,p) level.

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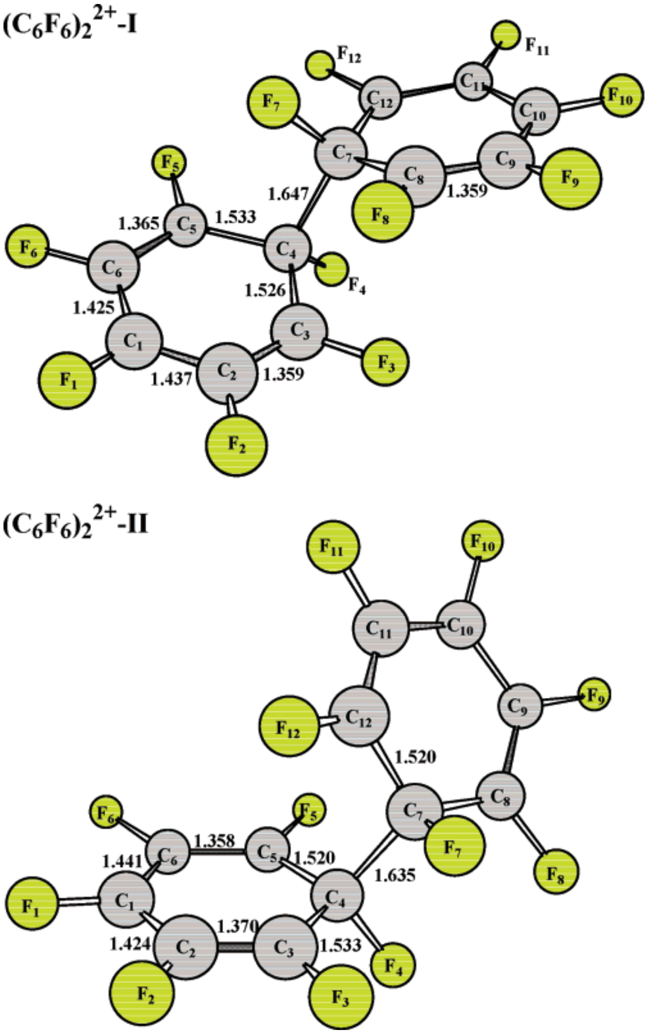

Figure 6. Identified and optimized structures of the dicationic dimer assembly of hexafluorobenzene (the B3LYP/6-31+G(d,p) level). Bond lengths are given in angstroms.

Hexafluorobenzene is a key molecule in studies on $\pi-\pi$ stackings,[40] anion$-\pi$ interactions,[41] and protonation processes.[42]

The presence of electron-withdrawing fluorine substituents tends to impede the coordination of cationic species to the aromatic ring by partly depriving it of its electrons while the F atoms can themselves coordinate with cations. Such induction effects probably explain the T-shaped structure of the hexafluorobenzene dimer radical cation $(C_6F_6)_2^+$. In contrast to the benzene dimer cation, the sandwich-like structure of $(C_6F_6)_n^+$ is unstable against dissociation when $n \geq 2$.[40] In straightforward analogy with benzene, on the other hand, the removal of the electron from the HOMO of C_6F_6 yields a doubly degenerate electronic state whose degeneracy is lifted by a Jahn−Teller distortion of the molecular radical cation. Such distortion lowers the D_{6h} symmetry of C_6F_6 to D_{2h}. With regards to this symmetry lowering, the electronic and molecular structures of $C_6F_6^+$ can be discussed in terms of two nearly isoenergetic (acute or obtuse[5e]) geometrical configurations, associated to $^2B_{2g}$ and $^2B_{1g}$ electronic states, respectively.

Whatever the state to which each of the monomers initially relates, the fusion of two positively charged $(C_6F_6)^+$ molecular radical cations into a dicationic dimer cluster, $(C_6F_6)_2^{2+}$, yields only two different covalently bound structures, $(C_6F_6)_2^{2+}$-I and $(C_6F_6)_2^{2+}$-II (Figure 6), depending on the relative location of the two fluorine atoms bonded to the C_4-C_7 fusion bond formed upon hole repositioning [$r(C_4-C_7) \sim 1.64$ Å]. These $(C_6F_6)_2^{2+}$-I and $(C_6F_6)_2^{2+}$-II structures are characterized by dihedral angles $\tau(F_4C_4C_7F_7)$ of 145.6° and −80.1°, respectively. The most stable species is $(C_6F_6)_2^{2+}$-I, which lies at 1.9 kcal/mol below $(C_6F_6)_2^{2+}$-II. Both carbon rings are structurally identical in each dicationic species and exhibit in both cases four stretched (~1.42 to 1.44 Å) and two compressed (~1.36 to 1.37 Å) C−C bonds. It also appears that ionization of $(C_6F_6)_2^+$ strengthens the C_6-F_6 and $C_{10}-F_{10}$ bonds, lying in meta and para location respective to the extra C_4-C_7 bond. On the other hand, the bonds C_4-F_4 and C_7-F_7 that are immediately adjacent to the fusion bond are considerably weakened, which an elongation by about 0.05 Å reflects.

In straightforward analogy with the dicationic dimer assembly of benzene molecules, the dissociation energy of $(C_6F_6)_2^{2+}$ into $(C_6F_6)^{2+} + (C_6F_6)$ amounts to 49.0 kcal/mol at the B3LYP/6-31G+(d,p) level (ZPVEs included), which shows that $(C_6F_6)_2^{2+}$ is thermodynamically not prone at all to a dissociation process involving hole localization on one monomer unit only. On the other hand, the dissociation reaction pertaining to the fragmentation of $(C_6F_6)_2^{2+}$ into two monocations is characterized at the same level by an activation barrier of 7.9 kcal/mol and a reaction energy of −78.2 kcal/mol. $(C_6F_6)_2^{2+}$ is thus also a metastable and relatively long-lived species on electronic and vibrational time scales, with a half-lifetime of the order of 0.1 μs with regards to Coulomb fragmentation. This lifetime is rather comparable to that (40 μs) of doubly charged clusters of *p*-difluorobenzene $(p\text{-difluoroBz})_n^{2+}$ [$3 \leq n \leq 15$].[21]

5. Toward Extended Dicationic Assemblies of Benzene, Hexafluorobenzene, and Naphthalene

Section 3 demonstrates that two sequential one-electron ionization events on dimers of benzene molecules should result in the formation of covalently bound structures that are equivalent to diprotonated forms of biphenyl. The latter species still contain two active sites that can in turn be involved in further charge-transfer reactions in order to minimize hole repulsions and enable therefore the formation of covalent bonds with additional aromatic molecules. Since at each step of the charge relaxation process, two reactions sites are preserved, one may then also wonder whether the ICD mechanism for the electronic decay of high-lying shake-up ionization states generates species that are reactive enough to induce the formation of larger diprotonated chains or networks such as Bz_3^{2+}, or $(C_6F_6)_3^{2+}$, via a two-directional dicationic polymerization mechanism. Such dicationic polymerization reactions could also be of relevance to clusters of other aromatic molecules such as naphthalene ($C_{10}H_8$)—they may even result into the formation of larger and/or hybrid assemblies such as $(C_{10}H_8)_2^{2+}$, $(C_{10}H_8)_3^{2+}$, or $[Bz-C_{10}H_8-Bz]^{2+}$, and $[Bz-Bz-(C_{10}H_8)-Bz-Bz]^{2+}$ (see

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the Supporting Information, along with refs 43 and 44). The fact that, despite strong hole repulsions, such chemically counterintuitive structures exist at various quantum chemical levels (B3LYP/6-31+G(d,p) or HF/6-31G) as local energy minima is per se a quite astonishing fact, recalling that all that is known at present for multiply charged molecular clusters has been interpreted using the liquid-droplet model.

6. Conclusions and Prospects for the Future

In the present work, we have inferred from density functional theory a so far completely unexpected consequence of double-ionization processes in molecular aromatic clusters. Whereas the fate of states lying above the double-ionization threshold in these clusters is normally to decay electronically via the intermolecular Coulombic mechanism proposed by Cederbaum and co-workers, before undergoing an ultrafast Coulomb fragmentation as a consequence of the localization of holes in different monomers, the present work demonstrates that dications of molecular clusters of benzene, hexafluorobenzene, and naphthalene can stabilize through the formation of rather robust covalent bonds between aromatic rings, along with a complex series of proton migrations that help to minimize Coulombic repulsions. The electronic and structural properties of the most stable dimer structures that can be produced this way indicate that these chemical reactions associated to hole repositioning processes can propagate to further rings and may therefore ultimately lead to rather large polymer chains or networks. With regards to the depletion of the ozone layer and ubiquity of benzene and PAH contaminants in the environment,[45] we believe that the finding that photoionization of aromatic clusters by far-UV radiations may generate long and doubly charged biradical chains should be of importance in cancer research.

This finding obviously completely invalidates the liquid-droplet model which only accounts for electrostatic effects for explaining the relative stability of multiply charged atomic or molecular clusters and thus implies that only sufficiently large clusters may avoid a Coulomb explosion. This model is clearly unsuited for treating situations where doubly charged clusters exhibit, as here, one or several chemical bonds between monomers. This was the case, for instance, in rare gas trimers $(Ne_2Xe)^{2+}$ and $(Ar_2Xe)^{2+}$ [46,47] and transition metal dimers Cr_2^{2+} and Mo_2^{2+}.[48] The first exception to the liquid-droplet model was reported in 1989 by Peifer and Garvey[49] in studies involving electron impact ionization experiments on molecular clusters of 1,1-difluoroethylene. Although the liquid-droplet model predicts that doubly positively charged clusters with less than n_0 ∼25−30 molecules are unstable against Coulomb fragmentation, Peifer and Garvey[49] observed that dicationic clusters of (1,1-difluoroethylene)$_n^{2+}$ with $n \geq 9$ are very long-lived and stable species. One may thus also wonder whether the stability of these species relates to additional covalent bonds due to hole relocations following ICD processes.

Therefore, proving experimentally the existence of dicationic dimers and other small dicationic assemblies of benzene and related compounds in vacuum conditions (such as for instance in interstellar space) would unequivocally demonstrate that chemical bonding can overcome the strong electrostatic repulsion that normally prevails between charged monomers. In general, the formation of a small dicationic dimer is indeed associated with an exceedingly large Coulomb barrier due to the repulsion forces that normally prevail between approaching singly positively charged atoms or molecules. On the other hand, sizable Coulomb barriers confer also substantial kinetic stability to covalently fused dicationic clusters. Large organic molecules are more suitable than small molecules or atoms for accommodating and dissipating positive charges, and thus the metastability of large and covalently bound dicationic assemblies of benzene and related molecules is to be expected. This is especially true for benzene because the benzene radical cation is not aromatic, and thus, forming an C(sp^3)−C(sp^3) inter-ring bond at the expense of cyclic π-conjugation does not require energy. Without any extra penalty, the inter-ring σ-bond is thus expected to result into the formation of a metastable species, corresponding to a local but deep energy minimum.

To confirm this finding experimentally, we suggest specifically to study the decay of dicationic states produced by two sequential one-electron ionization events in clusters of for instance benzene, hexafluorobenzene, or PAH molecules, as well as by photon or electron impact experiments at electron binding energies slightly above the vertical double-ionization threshold, to minimize the extent of vibrational excitations. On the side of theory, quantum mechanical dynamical simulations on doubly charged molecular clusters are mandatory for quantitatively evaluating, for both types of experiments, the relative yields of the fission version the fusion reaction channels.

Acknowledgment. The authors thank the FWO_Vlaanderen, the Flemish branch of the National Science Foundation of Belgium, and the "Bijzonder Onderzoeksfonds" (BOF) of the "Universiteit Hasselt" (previously known as "Limburgs Universitair Centrum") for financial support. One of the authors, E.S.K., particularly thanks the Limburgs Universitair Centrum for a six-month guest professor fellowship in 2003, as well as Francoise Remacle, for her hospitality during his stay at the "Université de Liège". This stay in Liège has been supported by a fellowship of the "Région Wallone" (Grant 115012) and by the EC FET-OPEN STREP Project "MOLDYNLOGIC". Most calculations presented in this work have been performed on an ES40 and an Alpha 1200 Compaq workstations at Hasselt University, Belgium.

Supporting Information Available: Preliminary study (Appendix I) of larger and/or hybrid dicationic assemblies of benzene, hexafluorobenzene, and naphthalene; detailed Cartesian coordinates and energies for all structures displayed in Figures 2−12 (Appendix II); complete description of refs 7k, 7l, and 22. This material is available free of charge via the Internet at http://pubs.acs.org.

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