Ion Chemistry of *anti-o,o′*-Dibenzene

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Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

Abstract: The ion chemistry of *anti-o,o′*-dibenzene (**1**) was examined in the gaseous and the condensed phase. From a series of comparative ion cyclotron resonance (ICR) mass spectrometry experiments which involved the interaction of Cu^+ with **1**, benzene, or mixtures of both, it was demonstrated that **1** can be brought into the gas phase as an intact molecule under the experimental conditions employed. The molecular ions, formally $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{\cdot-}$, were investigated with a four-sector mass spectrometer in metastable-ion decay, collisional activation, charge reversal, and neutralization–reionization experiments. Surprisingly, the expected retrocyclization to yield two benzene molecules was not dominant for the long-lived molecular ions; however, other fragmentations, such as methyl and hydrogen losses, prevailed. In contrast, matrix ionization of **1** in freon (77 K) by γ-radiation or in argon (12 K) by X-irradiation leads to quantitative retrocyclization to the cationic dimer of benzene, $\mathbf{2}^{\cdot+}$. Theoretical modeling of the potential-energy surface for the retrocyclization shows that only a small, if any, activation barrier is to be expected for this process. In another series of experiments, metal complexes of **1** were investigated. **1**/Cr^+ was formed in the ion source and examined by metastable ion decay and collisional activation experiments, which revealed predominant losses of neutral benzene. Nevertheless, comparison with the bis-ligated $[(C_6H_6)_2Cr]^+$ complex provided evidence for the existence of an intact **1**/Cr^+ under these experimental conditions. No evidence for the existence of **1**/Fe^+ was obtained, which suggests that iron mediates the rapid retrocyclization of **1**/Fe^+ into the bis-ligated benzene complex $[(C_6H_6)_2Fe]^+$.

Keywords: dibenzene · cycloreversions · gas-phase chemistry · mass spectrometry · transition metals

Introduction

Since the first synthesis of *anti-o,o′*-dibenzene (**1**) in 1969,[1] there has been a great deal of scientific interest in this molecule.[2] In particular, the propensity of **1** to exothermically dissociate into two benzene molecules has been a focus of attention. Most of this work has dealt with the nature of the symmetry-forbidden retrocyclization.[3] In this context, photoinduced, thermally-induced, concerted and stepwise mechanisms have been discussed.[4] In very recent work, a model has been proposed which involves electron transfer (ET) catalysis for the [2+2] cycloreversion of **1**.[5] This is of special interest because one of the most important pericyclic reactions of radical cations is the [2+2] cycloreversion of cyclobutane derivatives, which was the first class of pericyclic reactions recognized to be catalyzed by ET.[6] Indeed, ET accelerates the rate of the reaction $\mathbf{1} \rightarrow 2\,C_6H_6$ by at least five orders of magnitude relative to the thermal process.[5]

Inspired by the proposal of a radical-cation intermediate for the [2+2] cycloreversion of **1**, we examined the ion chemistry of *anti-o,o′*-dibenzene by mass spectrometric techniques as well as by matrix isolation in order to probe the behavior of ionized **1** in different environments. In order to understand this process, it is important to realize that, in analogy to cyclobutane, cycloreversion of $\mathbf{1}^{\cdot+}$ does not lead directly to dissociation, because benzene and its radical cation form a complex $\mathbf{2}^{\cdot+}$ that is bound by $\approx 20\,kcal\,mol^{-1}$.[7, 8] Under collisionless conditions in the gas phase, the exothermicity of the cycloreversion and the gain in entropy will provide sufficient driving force for the dissociation of $\mathbf{1}^{\cdot+}$ into the $C_6H_6^{\cdot+}$ ion and neutral C_6H_6; however, at higher pressures, or in the condensed phase, the reaction is likely to stop at the stage of the complex $\mathbf{2}^{\cdot+}$.

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Experimental Section

Compound **1** was synthesized in 13% overall yield from commercially available *cis*-3,5-cyclohexadiene-1,2-diol as reported previously.[3c] After synthesis, the compound was stored and transported at $-78\,^{\circ}C$. Evacuation in the vacuum lock prior to introduction into the mass spectrometer or the vacuum line of the matrix-isolation apparatus is safely assumed to remove any benzene contained in the samples.

Most of the gas-phase experiments were performed with a modified VG-ZAB-HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B and E stand for magnetic and electric sector, respectively), which has been described elsewhere.[9] The ions of interest were generated by electron ionization (EI, 70 eV) or chemical ionization (CI) of appropriate precursors; $[Cr(CO)_6]$ and $[Fe(CO)_5]$ acted as the metal sources. On account of the volatility of **1** at 10^{-6} mbar, its thermal instability,[3c] and the need to gently warm the sample in the probe tip to $\approx 35\,^{\circ}C$ by the ion-source heating ($200\,^{\circ}C$), useful ion intensities lasted only for a few minutes. During this period, a signal at m/z 156, which formally corresponds to the radical cation $\mathbf{1}^{\bullet+}$, was observed under EI conditions. The subsequent disappearance of this particular signal provides strong evidence for the origin of the m/z 156 from **1** rather than from any possible (less volatile) impurity of the sample. After acceleration to 8 keV, the ions of interest were mass-selected by using B(1)/E(1) at a resolution of $m/\Delta m \geq 4000$, which was sufficient to resolve most of the other isobaric species. In some cases, for example $\mathbf{1}/[Cr(C_6H_3D_3)]^+$, isobaric interferences were present; however, their contributions to the spectra could be deconvoluted by comparison with the spectra of isotopologues and background signals that remained after decomposition of **1**. Note that contributions that result from the natural abundance of ^{13}C were fully acknowledged in all experiments.

The ion structures were probed by various MS/MS experiments.[10] Unimolecular dissociations of metastable ions (MI) in the field-free region preceding B(2) were monitored by scanning this sector. Collisional activation (CA) spectra were obtained similarly, with helium as a target gas (80% transmission, *T*) in the field-free region preceding B(2). Likewise, charge stripping (CS) experiments were performed with oxygen (80% *T*) instead of helium. For neutralization–reionization of cations via neutrals to cations ($^+NR^+$), two collision cells in the field-free region preceding B(2) were used, of which the first contained xenon (80% *T*) for neutralization, and—after deflection of the remaining ions—the second contained oxygen (80% *T*) for reionization. Neutralization–reionization of anions via neutrals to cations ($^-NR^+$) was performed in a similar manner, except that oxygen was used in both collisions (80% T, each). For charge reversal of B(1)/E(1) mass-selected anions ($^-CR^+$) oxygen (80% T) was also used as a collision gas. In all cases, the resulting mass spectra were recorded by scanning B(2).

Additional gas-phase studies were performed with a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an external ion source and a superconducting magnet (max. 7.05 T).[11, 12] The aim of these studies was to investigate whether **1** can be brought into the gas phase as an intact molecule or if it decomposes before it reaches the analyzer region under the experimental conditions employed (see below). To this end, experiments were performed with mass-selected $^{63}Cu^+$, which was generated by laser desorption/laser ionization[13] of a copper target followed by transfer of the ions to the ICR cell and mass selection. Cu^+ was treated with a pulsed-in $\approx$100:1 mixture of argon and cyclohexane in order to generate the $[Cu(c\text{-}C_6H_{12})]^+$ association complex,[14] which can serve as a probe for the neutral gases present in the FTICR cell from ligand-exchange reactions.[15] Neutral **1** and $[D_6]$benzene were introduced through leak valves at pressures in the range of 10^{-8} to 10^{-7} mbar; the vial containing solid **1** was kept in an ice bath during the measurements.

For the matrix experiments, **1** was either dissolved to a concentration of 10^{-2} M in a mixture of $CFCl_3$ and CF_2BrCF_2Br ("freon mixture") or co-deposited with an equimolar amount of CH_2Cl_2 (acting as an electron scavenger) and a $\approx$1000-fold excess of Ar on a CsI plate held at 20 K (because of the low volatility of **1**, this was effected by passing a stream of Ar/CH_2Cl_2 over a sample of **1** held at $-28\,^{\circ}C$ in a U-tube attached to the inlet system of the cryostat). Ionization of the solvents was effected by exposure of the freon solutions to 0.5 Mrad of MeV ^{60}Co γ-rays, or by exposure of the Ar matrices to keV X-irradiation as described in detail earlier.[16] Subsequent hole transfer from the matrix leads to ionization of the substrate **1**, whereas electrons are trapped by the freon, or by CH_2Cl_2 in the case of the Ar matrix experiments. Electronic absorption spectra were recorded with a Perkin–Elmer Lambda 900 instrument.

In the computational studies, geometry optimizations of $\mathbf{1}^{\bullet+}$ and its rearrangement products were carried out by the B3LYP hybrid density functional method[17] with the 6-31G* basis set to model the one-electron density and/or by the CASSCF method with an ANO basis set. All stationary points located by B3LYP were subjected to analysis by second-derivative calculations. The DFT calculations were carried out with the Gaussian 98 program.[18] CASSCF geometry optimizations and subsequent CASPT2 single-point calculations[19] were performed with an active space of nine electrons in ten molecular orbitals (MOs), to ensure that the same type of MOs always remained in the active space to ascertain continuity of the potential-energy surfaces. These calculations were carried out with the MOLCAS program,[20] with the DZ[C]3s2p1d/[H]2s ANO basis set of Widmark et al.[21]

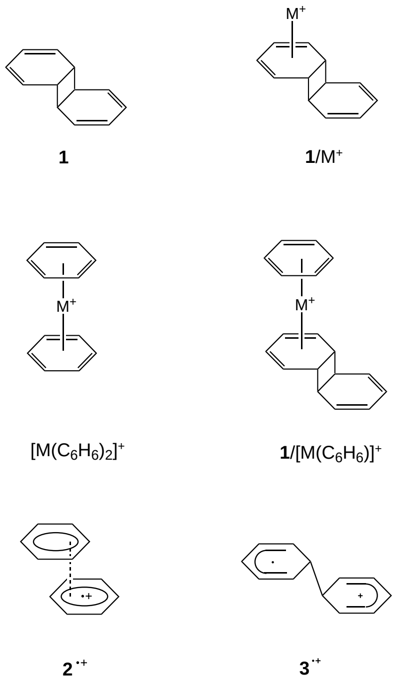
Abstract in German: *Die Ionenchemie von anti-o,o'-Dibenzol* ***1*** *wurde sowohl in der Gasphase als auch in kondensierter Phase untersucht. Ionen-Cyclotron-Resonanz-Massenspektrometrie mit Hilfe von* Cu^+*-Ionen zeigten, dass* ***1*** *unter den experimentellen Bedingungen als intaktes Molekül in der Gasphase existiert. Die Molekülionen, formal* $\mathbf{1}^{\bullet+}$ *und* $\mathbf{1}^{\bullet-}$*, wurden mit einem Viersektor-Massenspektrometer untersucht und verschiedenen Stoßexperimenten unterworfen. Erstaunlicherweise war die erwartete Retrocyclisierung, die zu zwei Benzolmolekülen führen sollte, nicht der Hauptprozess, sondern andere Fragmentierungen, wie Methyl- und Wasserstoffverluste überwogen. Im Gegensatz dazu führte die Matrixionisierung von* ***1*** *durch* γ*-Strahlung in freon (77 K) oder durch Röntgenstrahlung in Argon (12 K) zu quantitativer Retrocyclisierung unter Bildung des kationischen Benzoldimers,* $\mathbf{2}^{\bullet+}$*. Die theoretische Modellierung der Retrocyclisierungs-Potentialenergiefläche zeigt, dass eine nur geringe Barriere für diesen Prozess erwartet werden kann. In einer weiteren Reihe von Experimenten wurden kationische Metallkomplexe von* ***1*** *untersucht. Gasphasenexperimente ergaben, dass im Falle des Chroms der Komplex* $\mathbf{1}/Cr^+$ *erzeugbar war, während für Eisen eine schnelle Retrocyclisierung zum bisligierten Benzolkomplex* $[(C_6H_6)_2Fe]^+$ *vorherscht.*

Results and Discussion

Inspired by the dramatic acceleration of the [2+2] retrocyclization of **1** upon electron transfer in solution,[5] we choose to examine the stability of $\mathbf{1}^{\bullet+}$ by two different spectroscopic methods as well as with ab initio theory.

Stability of 1: A fundamental prerequisite for the investigation of **1** was to prove that it reaches the analyzing volume as an intact molecule under the experimental conditions chosen. This concern is by no means trivial, and three aspects require serious consideration: i) Compound **1** is a thermolabile compound and decomposes at room temperature with a free energy of activation of $24.8 \pm 1.6\ kcal\,mol^{-1}$.[3c] As typical storage temperatures of the sample in the inlet systems were $-28\,^{\circ}C$ in the matrix experiments, $0\,^{\circ}C$ in the FTICR, and $35\,^{\circ}C$ in the sector mass spectrometer, partial thermal degradation is thus to be expected. ii) The inlet systems of the mass spectrometers used are made of stainless steel, which could potentially induce retrocyclization by surface catalysis.[22] iii) By definition, **1** is isobaric with the dimer of two benzene molecules, that is, the product of a [2+2] cycloreversion. A prime topic was therefore to establish that the experimental methods indeed sampled intact **1**, rather than benzene.

The electron ionization (EI) mass spectrum of **1** shows a $[C_{12},H_{12}]^{\cdot+}$ radical cation at m/z 156. While the EI spectrum of benzene does not show a signal at m/z 156, its mere observation cannot be regarded as proof for the existence of genuine $\mathbf{1}^{\cdot+}$ because the sample might undergo retrocyclization either before or upon ionization to yield the ionized benzene dimer $\mathbf{2}^{\cdot+}$ (Scheme 1).[23, 24] A more specific mass-spectrometric probe must therefore apply an ionization method which is as soft as possible. For this purpose, metal-ion chemistry was applied, in particular, the reactions of the cyclohexane $[Cu(c\text{-}C_6H_{12})]^+$ complex.[15] Copper was chosen because of its good propensity for the formation of association complexes,[14] while it is rather unreactive as far as ligand activation is concerned because of its closed 3d shell.[25] This is essential because in probing the presence of **1** in the gas phase, cationization should not enforce the exothermic [2+2] cycloreversion of **1** to two benzene molecules. In order to lower the internal energy content of putative **1**/Cu$^+$, instead of the bare copper cation, its complex with cyclohexane was used so that **1**/Cu$^+$ could only be formed by the exchange of the cyclohexane ligand present in $[Cu(c\text{-}C_6H_{12})]^+$. Thus, part of the binding energy $D(\mathbf{1}\text{-}Cu^+)$ is consumed by decomplexation of the cyclohexane ligand. In consequence, $[Cu(c\text{-}C_6H_{12})]^+$ can be regarded as a very soft agent for the cationization of neutral molecules, provided that these are able to replace cyclohexane as a ligand.[15b]



Scheme 1. Structures of the radical cations and complexes discussed.

When $[Cu(c\text{-}C_6H_{12})]^+$ is treated with the vapor over solid **1** under ICR conditions, $[Cu,C_6,H_6]^+$ and $[Cu,C_{12},H_{12}]^+$ are initially formed in a ≈9:1 ratio. The former ion is most certainly the benzene complex $[Cu(C_6H_6)]^+$, formed by ligand exchange of $[Cu(c\text{-}C_6H_{12})]^+$ with the neutral benzene formed prior to association with copper and/or generated by Cu$^+$-mediated retrocyclization of **1**. The $[Cu,C_{12}H_{12}]^+$ ion could be intact **1**/Cu$^+$ and/or the bis-(benzene) complex $[Cu(C_6H_6)_2]^+$. Formation of the latter is indeed indicated by the fact that $[Cu(C_6H_6)]^+$ yields $[Cu,C_{12},H_{12}]^+$ at longer reaction times, which could be explained by the association of $[Cu(C_6H_6)]^+$ with another benzene molecule. Similar consecutive associations of arene ligands to metal cations in the gas phase have been observed repeatedly and appear to be quite general.[26] Note, however, that in none of these previous studies more than two benzene ligands, namely $[M(C_6H_6)_n]^+$ with $n > 2$, were found to attach to the metal center; not even in flow-tube experiments that involve typical operating pressures in the mbar regime.[26a] Nevertheless, kinetic analysis and double-resonance experiments reveal that some fraction of $[Cu,C_{12},H_{12}]^+$ is formed directly from $[Cu(c\text{-}C_6H_{12})]^+$; this indicates that intact **1** was present as a neutral species. However, even if **1** is present as a neutral species, the $[Cu,C_{12},H_{12}]^+$ species may entirely consist of $[Cu(C_6H_6)_2]^+$ formed by ligand exchange followed by retrocyclization, rather than intact **1**/Cu$^+$. The subsequent reactions of $[Cu,C_{12},H_{12}]^+$ provided further information: $[Cu,C_{18},H_{18}]^+$ and $[Cu,C_{24},H_{24}]^+$ were formed at longer reaction times. If these products were benzene ligands formed by retrocyclization, they would correspond to the tris- and tetrakis-benzene complexes $[Cu(C_6H_6)_n]^+$ ($n = 3, 4$), which have no precedents in the gas phase with copper or any other transition metal.[26] If intact **1**/Cu$^+$ were indeed formed, these signals are easily rationalized as $\mathbf{1}/[Cu(C_6H_6)]^+$ and $(\mathbf{1})_2/Cu^+$, respectively. While these assignments are still based on the assumption that $[Cu(C_6H_6)_n]^+$ ions with $n > 2$ are unlikely to exist, isotopic labeling provides more direct proof for the presence of **1**/Cu$^+$. Thus, when [D$_6$]benzene was added, in addition to the benzene complexes $[Cu(C_6D_6)_n]^+$ ($n = 1, 2$), only $[Cu,C_{18},H_{12},D_6]^+$, and not $[Cu,C_{18},H_6,D_{12}]^+$ nor $[Cu,C_{18},D_{18}]^+$ were observed in the mass range of the formal tris-benzene complexes. Moreover, when these ions were trapped in a large excess of C_6D_6 for 40 seconds, no $[Cu,C_{18},D_{18}]^+$ (i.e., $[Cu(C_6D_6)_3]^+$) was observed, while the $[Cu,C_{18},H_{12},D_6]^+$ species persisted. This result unambiguously demonstrates that, under FTICR conditions, the $[Cu,C_{18},H_{12},D_6]^+$ ion—or any isotopologue—cannot be formed by association of the bis-benzene complex with another benzene ligand, but its formation can only be rationalized if an intact $C_{12}H_{12}$ unit is present in the copper complex, namely $\mathbf{1}/[Cu(C_6D_6)]^+$.

In summary, a considerable amount of intact **1** is present in the gas phase and can be complexed with copper cations. However, it is impossible to quantify exactly how much of **1** decomposed to yield benzene before it reached the analyzer volume. In the extremes, the ≈9:1 ratio of $[Cu(C_6H_6)]^+$ and **1**/Cu$^+$ formed initially could either result from a ≈9:1 mixture of neutral benzene and dibenzene in the gaseous sample or it could be attributed to pure **1**, of which a minor fraction (10%) remains intact upon coordination with Cu$^+$, while the majority

(90%) undergoes metal-ion induced retrocyclization concomitant with expulsion of a benzene ligand to afford $[Cu(C_6H_6)]^+$.

Molecular ions: After confirmation that **1** can remain intact in the gas phase, we now discuss the results obtained with sector-field mass spectrometry. Thermal decomposition of **1** is less likely in this instrument than in FTICR because the solid samples were introduced directly into the high vacuum of the ion source and the overall residence times of the samples in the instrument were a few minutes compared to several hours in the FTICR experiments. The base peak in the EI mass spectrum of **1** corresponds to ionized benzene. The large amount of $C_6H_6^{\bullet+}$ supports the hypothesis of an ET-driven retrocyclization of **1** as a prompt process upon ionization. However, a long-lived $[C_{12},H_{12}]^{\bullet+}$ ion, formally the molecular ion $\mathbf{1}^{\bullet+}$, is also observed. For comparative purposes, we attempted the investigation of the ionized benzene dimer $(C_6H_6)_2^{\bullet+}$ ($\mathbf{2}^{\bullet+}$) as the putative product of [2+2] retrocyclization. However, generation of $(C_6H_6)_2^{\bullet+}$ by chemical ionization of benzene proved impossible under our CI conditions. Failure of this particular experiment is possibly the consequence of the low binding energy of the ionized benzene dimer, which is only ≈7 kcal mol^{-1} at 200 °C.[7, 8] Further gas-phase studies of the $C_6H_6 + C_6H_6^{\bullet+} \rightleftharpoons (C_6H_6)_2^{\bullet+}$ equilibrium[8] and electron ionization of neutral $(C_6H_6)_2$ resulted in the exclusive formation of $(C_6H_6)_2^{\bullet+}$ and $C_6H_6^{\bullet+}$.[27]

For metastable $[C_{12},H_{12}]^{\bullet+}$ ions generated by EI of **1**, a number of fragmentations from the loss of $\Delta m = 1$ up to the loss of $\Delta m = 78$ are observed, among which the latter fragmentation is minor (Table 1). This result suggests that the long-lived $[C_{12},H_{12}]^{\bullet+}$ species formed does not primarily decompose to two benzene molecules by the expected retro-[2+2] route, but that other fragmentation channels are accessible. For example, the loss of a methyl radical (*m*/*z* 15) requires a number of hydrogen shifts prior to fragmentation and thus suggests the occurrence of structural rearrangements, well-known for open-shell hydrocarbon cations.[28] Collisional activation (CA) experiments with $[C_{12},H_{12}]^{\bullet+}$ confirmed the results of the MI experiments (Table 2), as well as the charge stripping (CS) results (not shown), for which the fragmentation patterns are essentially identical to those observed in the CA spectrum. The neutralization–reionization ($^+$NR$^+$) mass spectrum of $[C_{12},H_{12}]^{\bullet+}$ reveals a rich fragmentation pattern of the carbon skeleton, but again ionized benzene is not very prominent.[29] Since NR experiments often involve substantial energy depositions in the molecules involved, this result has two obvious implications. Either the hypothesis of a facile [2+2] retrocyclization of $\mathbf{1}^{\bullet+}$ does not apply to the isolated molecule in the gas phase, or the long-lived $[C_{12},H_{12}]^{\bullet+}$ radical cations sampled in our experiments no longer possess structure $\mathbf{1}^{\bullet+}$. That is to say, genuine $\mathbf{1}^{\bullet+}$ may well undergo retrocyclization, but a minor fraction could undergo skeletal rearrangement after which retrocyclization is less easily achieved and these isomers—instead of $\mathbf{1}^{\bullet+}$—constitute the long-lived ions. Because of the enormous variety of conceivable $[C_{12},H_{12}]^{\bullet+}$ structures, comparative mass spectrometric studies with putative isomers would be circumstantial,[28] and we cannot decide this issue for the time being.

Table 1. Mass differences (Δm [amu]) observed in the unimolecular decomposition of metastable ion complexes.[a]

	−1	−2	−15	−26	−28	−40	−41	−65	−78	−81
$\mathbf{1}^+$	100	23	72	5	16	2	5	7	2	
$\mathbf{1}/Cr^+$				1	1[b]				100	
$[Cr(C_6H_6)_2]^+$									100	
$\mathbf{1}/[Cr(C_6H_3D_3)]^+$									15	100

[a] Intensities are given relative to the base peak = 100%. [b] This minor fragment may also result from an interfering carbonyl complex.

Table 2. Mass differences [amu] observed in the collisional activation mass spectra.[a]

	−1	−2	−3	−4	−15	−26	−28	−40	−41	−65	−78	−156
$\mathbf{1}^+$	100	18	6	4	54		24		11	8	4	
$\mathbf{1}/Cr^+$						1		1			100	16
$[Cr(C_6H_6)_2]^+$											100	17

[a] Intensities are given relative to the base peak = 100%.

For the sake of completeness, we have subjected **1** to chemical ionization in the negative ion mode with N_2O as the moderating CI gas. Surprisingly, a signal corresponding to the formal anion radical of $\mathbf{1}^{\bullet-}$ was generated under these conditions, even though many closed-shell hydrocarbons do not have positive electron affinities.[30] However, a ring-opened bis-cyclohexadienyl species could well have a positive electron affinity; for comparison, the cyclohexadienyl radical has an electron affinity of 0.6 eV.[30] While collisional activation of $[C_{12},H_{12}]^{\bullet-}$ proved ineffective as electron detachment prevailed, charge reversal to cations revealed abundant fragmentations.[31] However, the formation of benzene, either ionized or neutral, was again not pronounced. Thus, cycloreversion appears to play a minor role for $[C_{12},H_{12}]^{+/0/-}$ species in either charge state.

Proton catalysis: The $C_{12}H_{12}^{\bullet+}$ radical cation generated from **1** does not prefer to undergo a [2+2] retrocyclization to yield ionized benzene; rather, other fragmentation channels prevail. This seems to contradict the previous observation that the ET-catalyzed process is 10^5 times faster than the thermal retrocyclization of **1**.[5] In addition to the conceivable involvement of $C_{12}H_{12}^{\bullet+}$ isomers other than $\mathbf{1}^{\bullet+}$, other explanations are possible. A straightforward one would be a proton- instead of an electron-transfer catalysis, as suggested for other potentially ET-catalyzed reactions.[32–34] Despite several attempts, it was impossible to produce [**1**+H$^+$] by the use of H_2, CH_4, iC_4H_{10}, and H_2O as reagent gases in the CI experiments. Instead, $C_6H_7^+$ was always obtained as the major protonated species in the presence of **1**. This observation might suggest that retrocyclization of [**1**+H$^+$] rather than $\mathbf{1}^{\bullet+}$ is rapid and in fact too fast to allow for the generation of long-lived [**1**+H$^+$] under mass spectrometric conditions; this supports a proton catalysis of the retrocyclization. However, careful control reactions in solution showed that this is not the case. Particularly, the amminium-salt-catalyzed cycloreversion of **1** is not decelerated upon the addition of 2,6-di-*tert*-butylpyr-

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idine as a base.[35] The reaction is also very efficiently catalyzed by photoinduced ET with tris(anisylpyrrylium) tetrafluoroborate as the sensitizer, which does not contain the traces of acids often found as impurities in amminium salts. Further control experiments showed that the efficient [2+2] retrocyclization of **1** under these conditions does not result from a direct photoreaction of neutral **1** or weak Lewis acid properties of the pyrrylium salt. It can therefore be concluded that proton catalysis is not responsible for the rate acceleration in solution. Alternative pathways include the multitude of possible rearrangements of $\mathbf{1}^{\cdot+}$. When the ET-induced reaction was monitored by ^{1}H NMR in deuterochloroform, benzene was the only observable product. Hence, putative sideproducts are formed in less than ≈2% yield.

Metal catalysis: Atomic metal ions could serve as simplistic models for retrocyclization of **1** catalyzed by (closed-shell) Lewis acids or (open shell) metal compounds. Metal ions mediate several formally symmetry-forbidden cycloaddition reactions[36] and may initiate the reversal as well. As far as the choice of the metal (M) is concerned, it should not only act as a mere spectator, unlike copper. If, however, the metal initiates prompt retrocyclization of **1**, the formation of detectable amounts of $\mathbf{1}/\mathrm{M}^+$ may prove impossible. For example, attempts to generate $\mathbf{1}/\mathrm{Fe}^+$ failed in that the ion current for $[\mathrm{Fe,C_{12},H_{12}}]^+$ lasted only for a few seconds after sample introduction to the source. In addition, its reactivity was consistent with that expected for a bis-ligated complex $[\mathrm{Fe(C_6H_6)_2}]^+$.[37] Accordingly, atomic Cr^+ was chosen as it is much less reactive than Fe^+ in terms of hydrocarbon activation, but not as unreactive as Cu^+.[15a, 25, 38] With the use of $[\mathrm{Cr(CO)_6}]$ and **1** as precursors, it was possible to generate a complex of the mass *m*/*z* 208, which may correspond to $\mathbf{1}/\mathrm{Cr}^+$, the ionized bis-benzene chromium complex $[\mathrm{Cr(C_6H_6)_2}]^+$.[39] Therefore, we compared the spectra of putative $\mathbf{1}/\mathrm{Cr}^+$ with those of $[\mathrm{Cr(C_6H_6)_2}]^+$ which was independently generated from $[\mathrm{Cr(CO)_6}]$ and benzene. The MI and CA spectra of putative $\mathbf{1}/\mathrm{Cr}^+$ (Tables 1 and 2) revealed loss of benzene as the major fragmentation channel and are similar to those of $[\mathrm{Cr(C_6H_6)_2}]^+$. Minor differences can be explained by a higher internal energy content of $[\mathrm{Cr(C_6H_6)_2}]^+$ when formed by retrocyclization of transient $\mathbf{1}/\mathrm{Cr}^+$ rather than association of benzene ligands.[40] Similarly, the NR spectrum[41] of putative $\mathbf{1}/\mathrm{Cr}^+$ is very close to the previously reported data for $[\mathrm{Cr(C_6H_6)_2}]^+$ generated independently.[39] Evidence for the formation of intact $\mathbf{1}/\mathrm{Cr}^+$ was, however, provided by ionization of a mixture of $[\mathrm{Cr(CO)_6}]$, **1**, and [1,3,5-$\mathrm{D_3}$]benzene[42] which afforded a $[\mathrm{Cr,C_{18},H_{15},D_3}]^+$ ion. As tris-adducts with benzene appear unlikely for Cr^+,[26f] formation of the bis-ligated complex $\mathbf{1}/[\mathrm{Cr(C_6H_3D_3)}]^+$ is implied. The MI spectrum of this ion showed predominant loss of [1,3,5-$\mathrm{D_3}$]benzene. In the hypothetical case of an ion that has equivalent benzene ligands, a ratio $\mathrm{C_6H_6}$:$\mathrm{C_6H_3D_3}$ of 2:1 is expected if isotope effects are neglected, while the ≈1:7 ratio observed experimentally disproves the presence of three equivalent benzene ligands. Consequently, two pathways compete in the dissociation of metastable $\mathbf{1}/[\mathrm{Cr(C_6H_3D_3)}]^+$: simple ligand loss of the coordinated [1,3,5-$\mathrm{D_3}$]benzene and retrocyclization followed by loss of unlabeled benzene. Accordingly, despite significant occurrence of [2+2] retrocyclization, it is possible to generate $\mathbf{1}/\mathrm{M}^+$ complexes for M = Cr and Cu, while failure with M = Fe is attributed to the better bond-activation capabilities of this metal.[25] In summary, transition metals can indeed affect retrocyclization; however, this property seems to be restricted to the most active metals. With regard to the experimental conditions of the solution studies, complete retrocyclization of **1** as a result of metal catalysis induced by trace impurities therefore appears unlikely.

Matrix experiments: In order to acquire further insight into the stability of the molecular ion $\mathbf{1}^{\cdot+}$, matrix experiments were conducted in which dibenzene **1** was ionized by radiolysis. Figure 1 shows the electronic absorption spectra (400–1200 nm) obtained on ionization of **1** in Ar at 12 K (spectrum a) and in the freon mixture (FM) at 77 K (spectrum b).

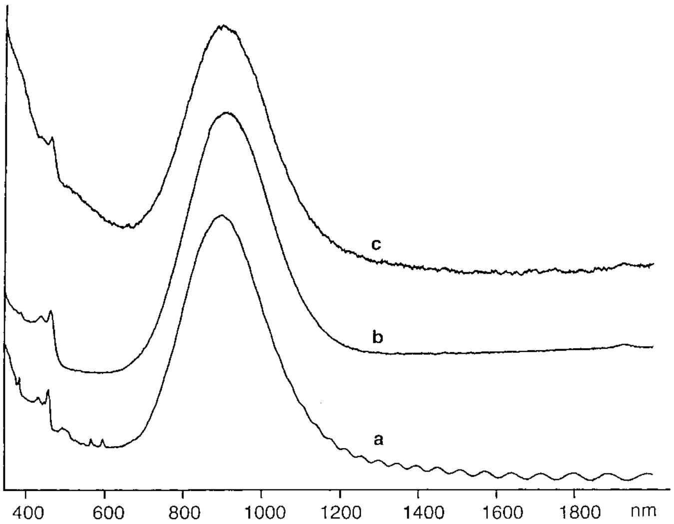

Figure 1. Electronic absorption spectra of ionized **1** a) in argon at 12 K and b) in a freon glass at 77 K. Spectrum c was obtained on ionization of a 0.2 M solution of benzene in a freon glass. All spectra show the charge resonance band of $\mathbf{2}^{\cdot+}$ at $\lambda \approx 900$ nm, but no bands above 1200 nm where $\mathbf{1}^{\cdot+}$ is expected to absorb.

Both spectra are dominated by intense bands of very similar shapes peaking at 890 nm in Ar or 900 nm in FM. These bands are indicative of the so-called charge-resonance transition in the benzene dimer radical cation, $\mathbf{2}^{\cdot+}$.[43] Spectrum c in Figure 1 was obtained by the ionization of a 0.2 M solution of benzene in FM. Such high concentrations are generally used to observe dimer cations of aromatic compounds, and the NIR band obtained in this way is indeed identical in position and shape to that obtained from the ionization of **1** in FM. This indicates that at least some decomposition has taken place during this process.

In the case of the Ar matrix experiments, UV and IR spectra indicated the complete absence of benzene before ionization, and we assume that the same is true in the FM experiments in which the temperature of **1** was never raised above 0 °C during the preparation of the samples. The question is whether any residual intact $\mathbf{1}^{\cdot+}$ might still be present after ionization of **1**. To answer this question, we need to consider the electronic structure of $\mathbf{1}^{\cdot+}$. According to Gleiter et al.,[2b] **1** may be considered to be a pair of butadiene moieties that interact through space through the C–C σ MOs of a cyclobutane ring. Since only the bonding combination of the butadiene π HOMOs is of the proper symmetry to interact with one of the cyclobutane σ MOs, this leads to a splitting of the highest two π MOs which amounts to 0.67 eV according to the photoelectron spectrum.[2b] It is to be expected that this energy difference increases on relaxation of the geometry of the radical cation. Indeed, CASPT2 calculations of $\mathbf{1}^{\cdot+}$ (see below) predict a $^2A_u \rightarrow {}^2B_g$ electronic transition at 0.9 eV (which corresponds to $\lambda = 1380$ nm) that carries a large oscillator strength. However, as documented in Figure 1, we did not detect any band that peaked above the band at $\lambda = 900$ nm (1.37 eV), even in the freon matrix experiments (Figure 1b) where excess energy is rapidly dissipated.

Although the CASPT2 method usually predicts the first few electronic transitions of radical cations to within ±0.25 eV of experiment, we wanted to exclude the possibility that the prediction is inaccurate by nearly 0.5 eV in this case, and that the $^2A_u \rightarrow {}^2B_g$ transition is hidden under the charge resonance band of $\mathbf{2}^{\cdot+}$. Based on the expectation that $\mathbf{1}^{\cdot+}$ would be converted to $\mathbf{2}^{\cdot+}$ photochemically, we exposed the samples which gave the spectra in Figure 1, to light of various wavelengths (1200–300 nm). However, even prolonged irradiation through a Pyrex filter did not lead to any changes in spectrum a or b. As even minor spectral changes would have been detected in the corresponding difference spectra, we estimate an upper limit for $\mathbf{1}^{\cdot+}$ that will not exceed the lower percent range.

These results appear to contradict the observation that the long-lived (i.e., microseconds) $C_{12}H_{12}^{\cdot+}$ parent ion is accessible in the mass spectrometric experiments described above. In order to resolve this discrepancy one must, however, realize that the hole transfer from the solvent, by which ionization occurs in these matrix experiments, is exothermic by several eV in Ar. Furthermore, the excess energy which is thus imparted to the incipient parent cation can only be dissipated with difficulty. This may prevent the observation of metastable parent cations in Ar matrices.

The effect is much less pronounced in FM in which the hole transfer is less exothermic and excess energy is much more readily dissipated. For example, rather unstable primary cations, such as ionized Dewar benzene,[44] have been observed in FM. The fact that the FM experiments yielded no indication of the presence of parent $\mathbf{1}^{\cdot+}$ implies that either i) decomposition to $\mathbf{2}^{\cdot+}$ takes place upon ionization, ii) decomposition takes place in a matter of minutes at 77 K, or iii) that $\mathbf{1}^{\cdot+}$ is present after ionization, but that it does not manifest itself in the 400–1200 nm range, and that this ion is entirely photostable. In view of the above-mentioned electronic structure calculations, the last possibility seems very unlikely and therefore we conclude that cycloreversion of $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ must be a low-barrier process. From the activation energy of ≈14 kcal mol^{-1} for the analogous cycloreversion of the parent cyclobutane radical cation (which is *endothermic* by ≈5 kcal mol^{-1}),[45] and in view of the high exothermicity of the cycloreversion of $\mathbf{1}^{\cdot+}$, a very low barrier for this process is indeed not unexpected.

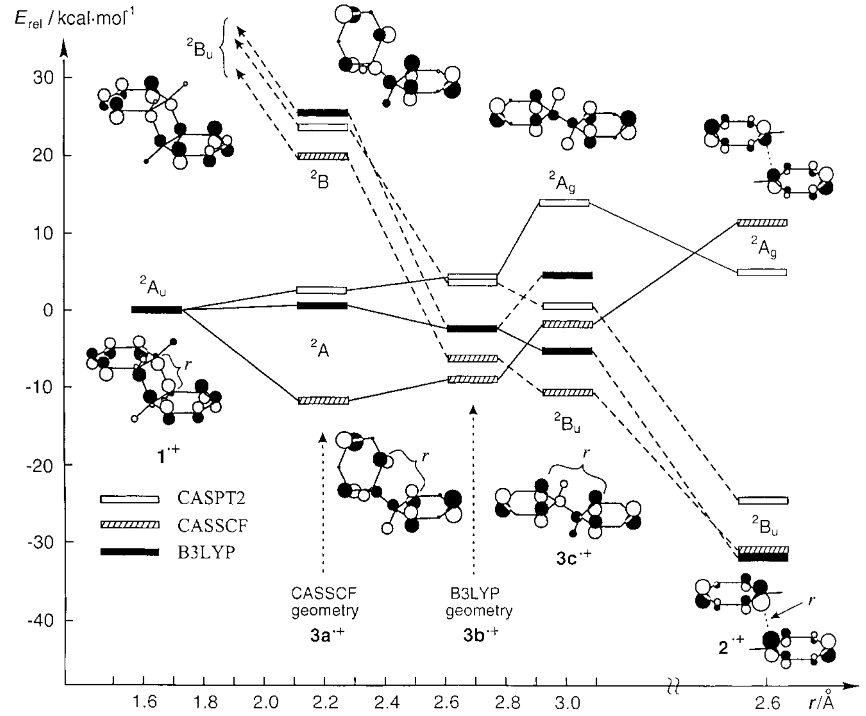

Figure 2. State-correlation diagram for the conversion of $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ via the bis-cyclohexadienyl radical cation $\mathbf{3}^{\cdot+}$. Each bar corresponds to a stationary point on the surface of the electronic ground state; note that the nature of the ground state changes between $\mathbf{3a}^{\cdot+}$ and $\mathbf{3c}^{\cdot+}$. Each electronic state is characterized by its singly occupied MO (SOMO). The SOMOs are shown as inserts which also indicate the meaning of the coordinate *r*.

Theoretical calculations: In an effort to shed further light on the key question of the kinetic stability of $\mathbf{1}^{\cdot+}$, we resorted to quantum chemical calculations of the potential-energy surfaces that connect $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ (Figures 2 and 3, and Table 3). In agreement with expectations from the nodal properties of the a_u HOMO of **1** (Figure 2, leftmost side), which contains a significant contribution from the cyclobutane C–C σ MOs, ionization leads to a noticeable lengthening of the bonds which connect the two cyclohexadiene moieties (from 1.58 to 1.65 Å), that is, ionization already takes $\mathbf{1}^{\cdot+}$ part of the way along the reaction coordinate to $\mathbf{2}^{\cdot+}$. Interestingly, optimization of the ^2A_u ground state $\mathbf{1}^{\cdot+}$ in its "native" C_{2h} symmetry by B3LYP leads to a saddle point, which is subject to spontaneous distortion along a coordinate of a_u symmetry. Following this coordinate leads to a C_2 minimum, which is 0.52 kcal mol^{-1} below the C_{2h} structure, where one of the above σ bonds has lengthened to 1.70 while the other has shortened to 1.60 Å. Note that this distortion must be the

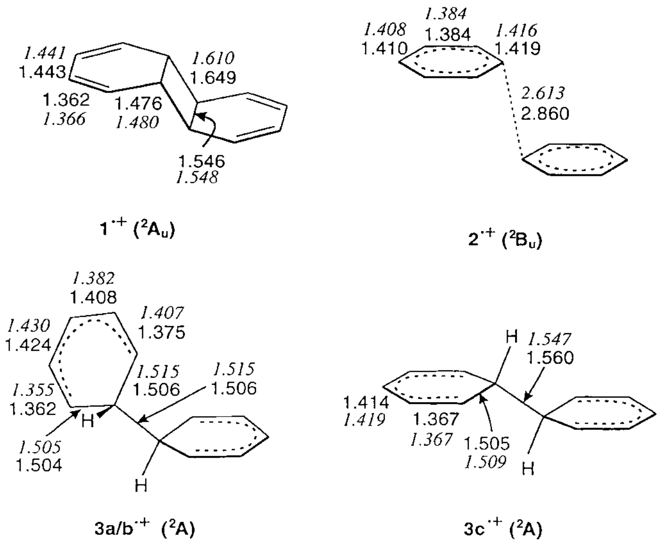

Figure 3. C–C bond lengths in $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, $\mathbf{3a}^{\bullet+}$, and $\mathbf{3b}^{\bullet+}$ (minima) as well as $\mathbf{3c}^{\bullet+}$ (transition structure for the tautomerization of **3a** and $\mathbf{3b}^{\bullet+}$) calculated at the B3LYP/6-31G* (normal font) and the (9,10) CASSCF levels (italics).

Table 3. Relative energies [kcal mol^{-1}] of different $C_{12}H_{12}^{\bullet+}$ structures.[a]

		B3LYP[b]	(9/10)CASSCF[c]	CASPT2[c, d]
$\mathbf{1}^{\bullet+}$	^2A_u	(0)[e]	(0)[f]	(0)[g]
	^2B_u	70.3	74.6	54.6
$\mathbf{2}^{\bullet+}$	^2A_g	−31.9	11.5	5.2
	^2B_u	−31.9	−30.9	−24.4
$\mathbf{3a}^{\bullet+}$	^2A	0.7	−11.5	2.7
	^2B	25.7	19.9	21.4
$\mathbf{3b}^{\bullet+}$	^2A	−2.2	−8.8	4.5
	^2B	−2.2	−6.1	3.8
$\mathbf{3c}^{\bullet+}$	^2A_u	4.8	−1.7	12.6
	^2B_u	−5.1	−10.5	0.7

[a] See Figure 2. All geometries were obtained from (9,10)CASSCF calculations except for $\mathbf{3b}^{\bullet+}$, which is the B3LYP geometry of $\mathbf{3}^{\bullet+}$ in C_2 symmetry. [b] Calculated with a 6-31G* basis set. [c] Calculated with a DZ ANO basis set. [d] Based on the (9,10)CASSCF wavefunction. [e] Total energy: −464.151388 Hartrees. [f] Total energy: −461.189058 Hartrees. [g] Total energy: −462.594760 Hartrees.

result of vibronic interaction with an excited state of A_g symmetry.

At the CASSCF(9,10) level, the C_{2h} structure of $\mathbf{1}^{\bullet+}$ is subject to a symmetry-breaking effect, because even the slightest distortion to C_2 symmetry leads to a drop of the energy by more than 0.5 eV. Reoptimization of this structure leads to complete cleavage of one of the C–C σ bonds which link the two cyclohexadiene moieties, namely to a species which is best described as a bis-cyclohexadienyl radical cation, $\mathbf{3a}^{\bullet+}$.[24] A similar structure is also found on the B3LYP surface where it can be identified as a potential-energy minimum of C_2 symmetry (structure **3b**). The two geometries look very similar except for the distance of the formerly bonded C atoms, which is ≈0.5 Å longer at the B3LYP level. In view of the correlation with the product, $\mathbf{2}^{\bullet+}$ (see below), we also optimized $\mathbf{3}^{\bullet+}$ in C_{2h} symmetry ($\mathbf{3c}^{\bullet+}$), where it corresponds to a saddle point for the interconversion of two identical C_2 structures by B3LYP (the geometry is very similar with that found with CASSCF).

So far, the electronic states of the different species (i.e., their SOMOs) were always symmetric with regard to the twofold axis that is present throughout, namely ^2A in C_2 (^2A_u in $\mathbf{1}^{\bullet+}$, ^2A_g in $\mathbf{3c}^{\bullet+}$, both in C_{2h}). However, this is no longer the ground-state symmetry for $\mathbf{3c}^{\bullet+}$ as a ^2B_u state lies at lower energy. Thus, a state crossing had apparently taken place on the way from $\mathbf{1}^{\bullet+}$ to $\mathbf{3c}^{\bullet+}$. Reoptimization of the geometry of this ^2B_u state of $\mathbf{3c}^{\bullet+}$ by B3LYP led to spontaneous decay to the ionized benzene dimer $\mathbf{2}^{\bullet+}$ (cf. right-hand side of Figure 2) in which the benzene rings are separated by 2.86 Å.

Indeed, frequency calculations showed that the ^2B_u state thus obtained represents the equilibrium structure of the ground state of this complex ($\mathbf{2a}^{\bullet+}$). According to the B3LYP calculations, $\mathbf{2a}^{\bullet+}$ is bonded by 20.2 kcal mol^{-1} relative to free benzene and its radical cation. Addition of the thermal corrections from frequency calculations leads to $\Delta H_{298} =$ 18.2 kcal mol^{-1}. This value can be compared with the experimentally determined gas-phase binding enthalpy of 20.6 ± 1.0 kcal mol^{-1} for $\mathbf{2}^{\bullet+}$ at this temperature.[8] Thus, B3LYP seems to perform quite well, and the slight underestimation of the binding energy is within the expected error margins of this approach for a molecular ensemble of this size.

CASSCF(9,10) reoptimization of $\mathbf{2a}^{\bullet+}$ resulted in a shortening of the bond that connects the benzene moieties in the complex cation from the B3LYP value of 2.86 to 2.61 Å. An indication that the CASSCF structure is probably closer to reality is provided by CASPT2 calculations. Firstly, the CASPT2 energy drops by 1.6 kcal mol^{-1} on going from the B3LYP to the CASSCF structure. Secondly, the $^2B_u \rightarrow {}^2A_g$ excitation, which is responsible for the observed strong 900 nm charge resonance band of $\mathbf{2}^{\bullet+}$ (Figure 1), is predicted by CASPT2 in much better agreement with experiment for the CASSCF structure (966 nm) than for the B3LYP structure (1370 nm).[46]

In Figure 2, we present full correlation diagrams for the A and B states that are involved in the dissociation of $\mathbf{1}^{\bullet+}$. This allows us to return to the central question, namely, the mechanism and energetics of the [2+2] retrocyclization. As mentioned above, one of the C–C bonds that links the two cyclohexadiene moieties in $\mathbf{1}^{\bullet+}$ undergoes spontaneous cleavage at the CASSCF(9,10) level. On the B3LYP surface, where $\mathbf{1}^{\bullet+}$ represents a true minimum (albeit slightly distorted to C_2), we were able to find a transition structure for the conversion to $\mathbf{3}^{\bullet+}$, 1.7 kcal mol^{-1} above $\mathbf{1}^{\bullet+}$ (0.9 kcal mol^{-1} after accounting for the difference in zero-point energies). In contrast, at the CASPT2 level, for which geometry optimizations are unfortunately impossible, the process is endothermic by ≈5 kcal mol^{-1}.

More importantly, however, the A and B states are nearly degenerate at the B3LYP equilibrium geometry of $\mathbf{3}^{\bullet+}$ (i.e., structure **3b**), both at the B3LYP and at the CASPT2 level (at CASSCF they are still separated by 2.7 kcal mol^{-1}). This indicates that **3b** is very close to a *conical intersection* between these two states (although not necessarily the lowest point of conical intersection). In reality, the system will seek and find a way around this non-stationary point by distorting to C_1 symmetry. Unfortunately, $\mathbf{3}^{\bullet+}$ is too big to allow a mapping of this pathway by any reliable method of computation. However, the energy of the conical intersection certainly presents an upper limit for the highest point that has to be crossed on the way from the reactant to the ground-state surface of the product. Accordingly, both methods predict that the activation barrier associated with the retrocyclization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ is almost negligible, especially under conditions where excess energy cannot be readily dissipated.[47] At the CASPT2 level, the conical intersection lies $\approx 4\,\mathrm{kcal\,mol^{-1}}$ above $\mathbf{1}^{\bullet+}$, and hence this number represents an upper limit for the activation energy of ring cleavage at the highest level of theory that we were able to apply to this molecule. This is in agreement with our observations in low-temperature matrix experiments.

Conclusions

Mass spectrometry reveals that intact dibenzene (**1**) can be introduced into the instruments by means of standard inlet systems. While the electron ionization spectrum of **1** is dominated by ionized benzene on account of the facile [2+2] retrocyclization, the existence of a $C_{12}H_{12}^{\bullet+}$ molecular ion that has a lifetime of at least several microseconds is demonstrated. Moreover, unimolecular and collision-induced fragmentations of the long-lived $C_{12}H_{12}^{\bullet+}$ ion do not afford losses of neutral benzene as the major reaction pathway, as expected for retrocyclization. These results seem to conflict with the suggestion that retrocyclization of **1** should prevail upon ionization because of the dramatic acceleration of this process upon electron transfer in solution.[5] The matrix experiments as well as ab initio theory indicate, however, that the genuine radical cation $\mathbf{1}^{\bullet+}$ is unlikely to persist for any length of time, although an educated guess of the lifetime at low temperatures cannot presently be made. A possible explanation of these discrepancies may be because of the enormous sensitivity of the mass spectrometric approach used, which can sample minor fractions of either intact and/or rearranged $C_{12}H_{12}^{\bullet+}$ which escaped experimental detection in the condensed phase.

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[24] Strictly speaking, all $C_{12}H_{12}^{\bullet+}$ radical cations considered here are ionized dimers of benzene. As far as the nomenclature in Scheme 1 is concerned, we designate the intact dibenzene ion as $\mathbf{1}^{\bullet+}$ (intact cyclobutane unit), the well-known dimer of ionized benzene as $\mathbf{2}^{\bullet+}$ (no cyclobutane unit), and the bis-cyclohexadienyl-type structures as $\mathbf{3}^{\bullet+}$ (one C−C bond of the cyclobutane still intact).

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[46] It should be added that the $^2B_u \rightarrow {}^2A_g$ transition is not the lowest one. However, the lower-lying excitations to ^2A_u and ^2B_g states have vanishingly small oscillator strengths.

[47] At the CASSCF level, $\mathbf{3}^{\bullet+}$ appears to lie in a potential well of $\approx 4\,\text{kcal mol}^{-1}$ depth which would open the possibility for the stabilization of this species at low temperature. However, we have no indication that this occurs in our cryogenic experiments.

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