DOI: 10.1002/chem.200600913

On a Possible Growth Mechanism for Polycyclic Aromatic Hydrocarbon Dications: $C_7H_6^{2+}+C_2H_2$

Jana Roithová* and Detlef Schröder*[a]

Abstract: The mechanism of the bond-forming reaction between $C_7H_6^{2+}$ and C_2H_2 to yield C_9 entities has been investigated by density functional theory calculations with close comparison with experimental data. It is shown that the reaction produces the $C_9H_6^{2+}$ and $C_9H_7^{2+}$ dications with geometries most probably derived from the indene skeleton. In comparison, the formation of linear structures of dications is much more energy-demanding and therefore appears improbable.

Keywords: density functional calculations · dications · indene · polycyclic aromatic hydrocarbons · reaction mechanisms

Introduction

It has recently been shown that small- and medium-sized hydrocarbon dications (C_6–C_{14}) are able to react with acetylene to form higher hydrocarbon dications according to Equations (1) and (2).[1]

$$C_nH_m^{2+}+C_2H_2 \rightarrow [C_{n+2}H_{m+2}]^{2+} \rightarrow C_{n+2}H_m^{2+}+H_2 \quad (1)$$

$$C_nH_m^{2+}+C_2H_2 \rightarrow [C_{n+2}H_{m+2}]^{2+} \rightarrow C_{n+2}H_{m+1}^{2+}+H \quad (2)$$

The fact that molecular dications undergo bond-forming reactions with maintenance of the double charge in the products is already quite remarkable in itself. Although reactions of molecular dications have been extensively studied for more than two decades, most of the previously reported processes afford singly charged products.[2] The only exceptions are some hyperthermal reactions involving rare gases: it has been found that Ar^{2+} yields small amounts of ArN^{2+} and ArO^{2+} in its reactions with N_2 or O_2, respectively.[3,4] Argon can also act as a neutral reactant, as the reaction between CO^{2+} and Ar to produce the ArC^{2+} dication has been described.[5] In the thermal, bimolecular dication/neutral reactions of hydrocarbon dications discussed here, the formation of doubly charged products is made possible by disposal of the excess of internal energy contained in the reaction intermediate through losses of atomic or molecular hydrogen, rather than by the usually occurring Coulomb explosion of the intermediate into two singly charged products.[6,7] In fact, release of a neutral H_2 molecule appears to be a common—and energetically by far the most favored—dissociation pathway of hydrocarbon dications.[8–13]

Another interesting aspect of these reactions is to be found in the large amount of internal energy gained upon formation of the dication/neutral complexes. This energy is sufficient to surmount barriers associated with the formation of new bonds, so the reactions can proceed without the requirement of additional activation, which is consistent with their occurrence even at very low pressures (10^{-8} mbar). It has therefore been proposed that double ionization may serve as an energizing event to promote bimolecular reactions in media involving extremely low temperatures and pressures, such as in interstellar space, thereby providing a growth mechanism for the formation of larger hydrocarbon molecules under extreme conditions.[1] With regard to the mechanisms of these reactions, it is interesting to investigate whether the dications grow as linear chains or whether the reactions result in the formation of polycyclic hydrocarbons.

This study is devoted to the theoretical exploration of the possible mechanisms for the model reaction between the cycloheptatrienylidene dication $C_7H_6^{2+}$ and neutral acetylene, a reaction that has been studied in detail experimentally.[1] The $C_7H_6^{2+}$ dication was chosen because of its size, as it is large enough to permit an efficient coupling reaction with acetylene, while still allowing a detailed computational study of the possible reaction mechanisms to be performed. Our initial calculations suggested that the product dications $C_9H_6^{2+}$ and $C_9H_7^{2+}$ have structures derived from the indene

---

[a] Dr. J. Roithová, Dr. D. Schröder
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
16610 Praha (Czech Republic)
Fax: (+420) 220-183-583
E-mail: Jana.Roithova@uochb.cas.cz
Detlef.Schroeder@uochb.cas.cz

skeleton.[1] In support of this conjecture, the fragmentation of the indene dication as a function of internal energy has been studied by use of synchrotron radiation.[13] Here, all these available experimental data are used to sort out all possible reaction pathways in order to provide concise conclusions about the reaction mechanisms of the C–C coupling between $C_7H_6^{2+}$ and C_2H_2.

Computational Details

The calculations were performed by the B3LYP density functional method[14] in conjunction with the 6-311+G(2d,p) basis set as implemented in the Gaussian 03 suite.[15] Frequency analyses at the same level of theory were used for all optimized structures in order to assign them as genuine minima or transition structures on the potential energy surface (PES) as well as to calculate zero-point vibrational energies (ZPVEs). Transition structures were further characterized by intrinsic reaction coordinate (IRC) calculations.[16] The relative energies (E_{rel}s) of the structures given below refer to energies at 0 K and are anchored to E_{rel}($\mathbf{1}^{2+}$+C_2H_2) = 0.00 eV ($E_{0\,K}(\mathbf{1}^{2+})$ = −269.454068 hartree and $E_{0\,K}(C_2H_2)$ = −77.331214 Hartree). The minima are denoted by bold numbers together with the corresponding charge, while transition structures are denoted by the two numbers of the corresponding minima separated by a slash.

Comparative studies of theoretically derived and experimentally measured heats of formations of various molecules show that the absolute accuracy of the B3LYP calculations is usually better than ±0.2 eV.[17] However, for a single potential energy surface as described here, the errors would be expected to be systematic in nature, which should result in their partial cancellation when relative energetics are considered. Likewise, canceling of errors would be expected for ZPVEs. Furthermore, it is to be noted that the B3LYP method does not properly describe dispersion interactions,[18] which most probably gives rise to a slight underestimation of the stabilization energies of the van der Waals complexes discussed in the text.

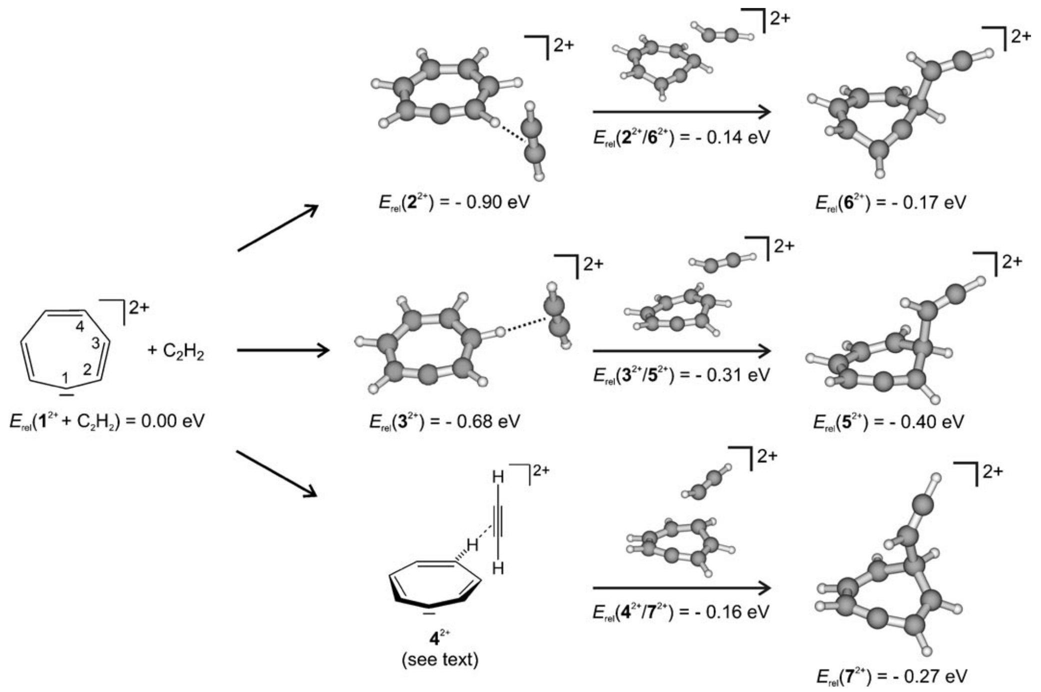
Results and Discussion

Theoretical results: As mentioned in the Introduction, the particular interest in the bond-forming reactions between hydrocarbon dications $C_nH_m^{2+}$ ($n > 5$) and acetylene stems from their reasonable efficiency at extremely low energies and pressures. Under these conditions, neutral hydrocarbons do not react with acetylene at all, while the corresponding singly charged $C_nH_m^{+}$ ions react only up to a size of five carbon atoms; further steps are kinetically hindered. In this respect, the advantage of dications stems from their high initial potential energy. The formation of a complex between a dication and the other reaction partner affords a relatively large amount of stabilization energy, which can be interpreted as energy gained from the delocalization of the charge over a larger number of atoms. If the complex formed in this way is isolated in vacuum, the energy is stored as internal energy of the system and can thus be used in subsequent steps to surmount the energy barriers for bond formations. To comply with the boundaries of the experimental studies—that is, a strictly bimolecular coupling reaction occurring without additional energizing events—the reaction must proceed with the initial energy of the reactant partners only. We note in passing that similar mechanisms may also apply for small singly charged ions, but that the energy gained from the complex formation with monocations is considerably smaller.

The coupling between $C_7H_6^{2+}$ and C_2H_2 may serve as a prototype for the reactions between hydrocarbon dications and acetylene.[1] The structure of $C_7H_6^{2+}$ has already been described by earlier density functional theory (DFT) calculations, which suggested that the most stable structure of $C_7H_6^{2+}$ corresponds to the cycloheptatrienylidene skeleton ($\mathbf{1}^{2+}$).[12] Furthermore, the singlet states lie lower in energy than the corresponding triplet states for all studied structures of $C_7H_6^{2+}$,[12] so it is assumed here that the $C_7H_6^{2+}$ reactant is in the ground singlet state, and accordingly only the singlet potential energy surface of the reaction has been investigated.

Formation of the initial ion/molecule complex between $C_7H_6^{2+}$ and acetylene involves a hydrogen bond between the electron-deficient $C_7H_6^{2+}$ and the π electrons of acetylene (Scheme 1). All hydrogen atoms in the $C_7H_6^{2+}$ dication can support this type of complexation. The most stable complex ($\mathbf{2}^{2+}$) is formed through the interaction of the hydrogen bonded to the carbon atom next to the carbene moiety. As far as the formation of a complex is concerned, it is usually assumed to be essentially a barrierless process, because the interaction between a dication and a neutral molecule can be described by the attractive potential of an ion/induced-dipole interaction. Thus, the formation of complex $\mathbf{2}^{2+}$, with a weak bond between acetylene and the hydrogen atom bonded to C2 of $\mathbf{1}^{2+}$, brings an energy of 0.90 eV with respect to the free reactants (E_{rel}($\mathbf{1}^{2+}$+C_2H_2) = 0.00 eV). The second complex ($\mathbf{3}^{2+}$, Scheme 1) has a weak bond between acetylene and the hydrogen atom bonded to C3 of $\mathbf{1}^{2+}$ and its formation provides an energy release of 0.68 eV (E_{rel}($\mathbf{3}^{2+}$) = −0.68 eV). The complex with a newly formed bond between C4 and acetylene ($\mathbf{4}^{2+}$) was not localized by the B3LYP method, but could be found at the MP2 level of theory.

As mentioned above, the relatively large stabilization in potential energy of these complexes is stored as their internal energy, which can be used in subsequent steps to surmount energy barriers for covalent coupling between the two reaction partners. The lowest-energy barrier for covalent C–C coupling corresponds to bond formation between C3 of $\mathbf{1}^{2+}$ and acetylene (E_{rel}($\mathbf{3}^{2+}$/$\mathbf{5}^{2+}$) = −0.31 eV). Formation of the C–C bonds starting from complexes $\mathbf{2}^{2+}$ and $\mathbf{4}^{2+}$ is energetically somewhat more demanding (E_{rel}($\mathbf{2}^{2+}$/$\mathbf{6}^{2+}$) = −0.14 eV and E_{rel}($\mathbf{4}^{2+}$/$\mathbf{7}^{2+}$) = −0.16 eV), but still achievable with the internal energy of the complexes. Nonetheless, to the first approximation the reaction rate is determined by the barrier height of the coupling step,[19] so we assume that, even though the complexes $\mathbf{2}^{2+}$ and $\mathbf{4}^{2+}$ might lie in deeper minima than the complex $\mathbf{3}^{2+}$, the coupling will proceed most efficiently via the complex $\mathbf{3}^{2+}$ towards the formation of the dication $\mathbf{5}^{2+}$ (Scheme 1). Moreover, the dication $\mathbf{5}^{2+}$ lies lower in energy (E_{rel}($\mathbf{5}^{2+}$) = −0.40 eV) than the competing dications $\mathbf{6}^{2+}$ (E_{rel}($\mathbf{6}^{2+}$) = −0.17 eV) and $\mathbf{7}^{2+}$ (E_{rel}($\mathbf{7}^{2+}$) =

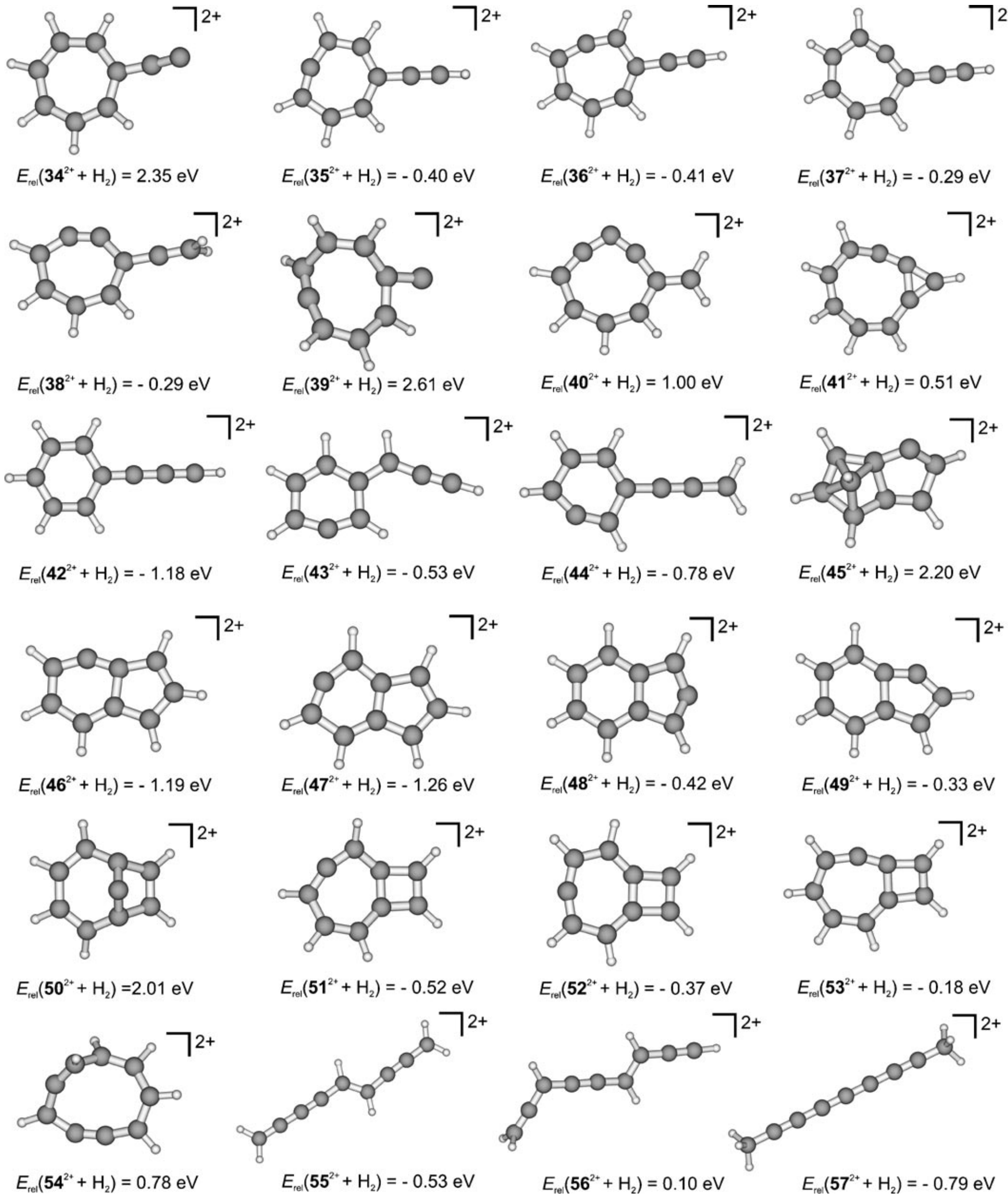


Scheme 1.

-0.27 eV). We note in passing that an isomer, in which the acetylene part would be bonded to the carbene carbon of $\mathbf{1}^{2+}$, could not be localized. Instead, a rearrangement involving a hydrogen atom of acetylene occurs during the optimization of the geometry, affording the dication $\mathbf{10}^{2+}$ (see below).

The experimental findings reveal that all newly formed hydrocarbon dications lose atomic and molecular hydrogen at the end of the coupling sequence.[1] If a 1,2-elimination of H_2 is allowed (after some conformational changes), then elimination of H_2 could afford the dications $\mathbf{35}^{2+}$–$\mathbf{37}^{2+}$, with relative energies well below the level of the entrance channel (Scheme 2). In comparison, the most stable structure of a dication derived from $\mathbf{5}^{2+}$ by elimination of a hydrogen atom corresponds to $\mathbf{58}^{2+}$, which lies well above the energy of the initial reactants ($E_{\mathrm{rel}}(\mathbf{58}^{2+}$+H) = 2.81 eV, Scheme 3). The internal energy of the dication $\mathbf{5}^{2+}$ is thus not large enough to complete the coupling sequence shown in Equation (2) and so it is expected that rearrangements to more stable isomers of $C_9H_8^{2+}$ take place prior to elimination of H or H_2.

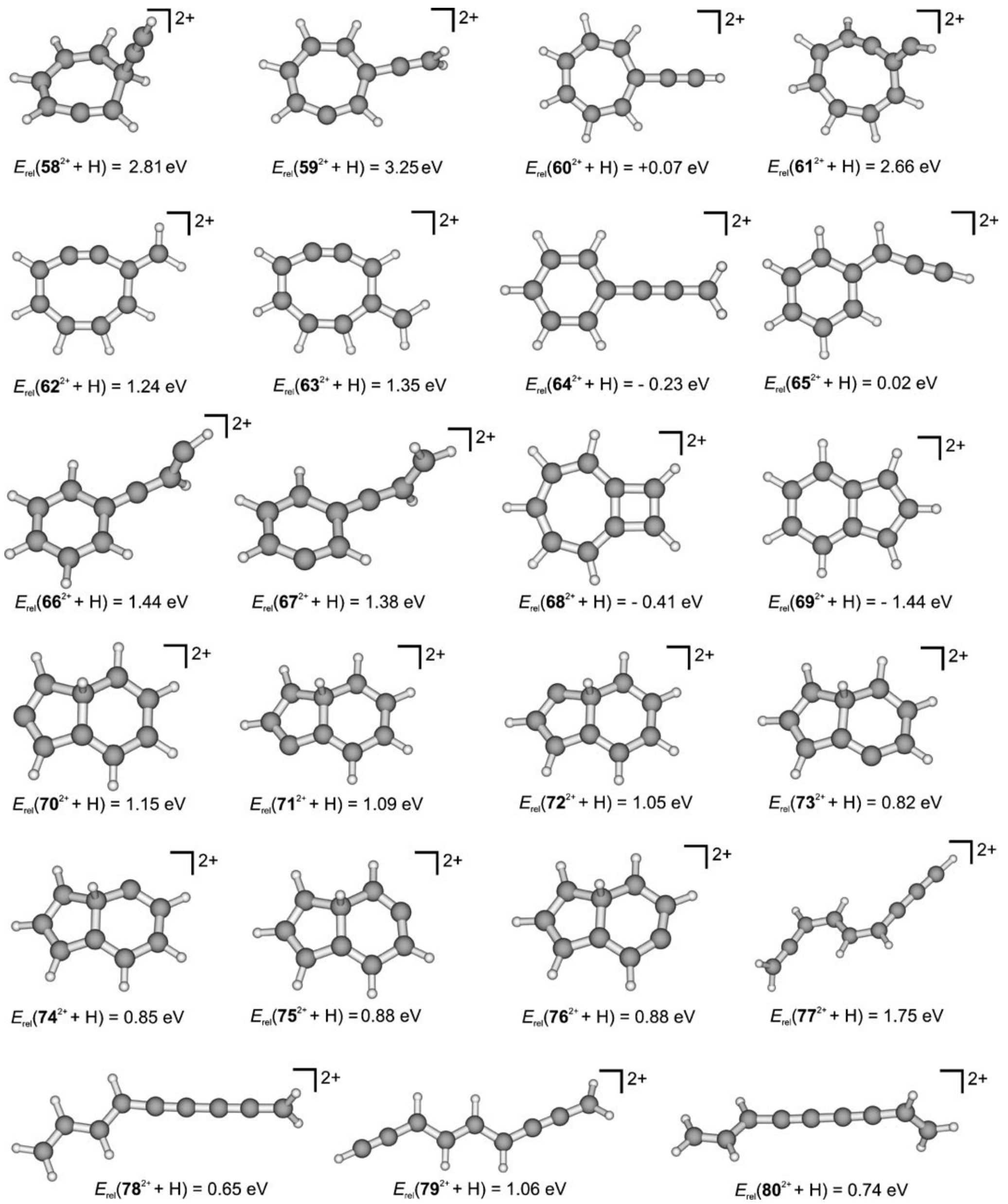
Subsequent rearrangements may involve either only hydrogen atoms or the whole skeleton of $C_9H_8^{2+}$. The most stable $C_9H_8^{2+}$ dication derived from the initially formed coupling product $\mathbf{5}^{2+}$ solely by simple rearrangements of hydrogen atoms corresponds to the isomer $\mathbf{10}^{2+}$ ($E_{\mathrm{rel}}(\mathbf{10}^{2+}) = -3.91$ eV, Scheme 4). Several pathways leading to $\mathbf{10}^{2+}$ can be suggested. The first step may involve migration of a hydrogen atom either from the acetylenic unit (i) or from the seven-membered ring (ii and iii). Hydrogen rearrangement within the side chain of $\mathbf{5}^{2+}$ towards its terminus produces a more stable isomer $\mathbf{8}^{2+}$ ($E_{\mathrm{rel}}(\mathbf{8}^{2+}) = -0.87$ eV). The internal energy of the system is sufficient to surmount the energy barrier associated with this rearrangement ($E_{\mathrm{rel}}(\mathbf{5}^{2+}/\mathbf{8}^{2+}) = -0.33$ eV). In the remaining reaction sequence, the hydrogen atom bonded to the sp^3 carbon of the ring must migrate to the carbene carbon atom. The migration of the hydrogen atom bonded to the sp^3 carbon to the next carbon in the ring is associated with an energy barrier larger than the internal energy available in the system ($E_{\mathrm{rel}}(\mathbf{8}^{2+}/\mathbf{9}^{2+}) = 0.27$ eV), so this pathway is disfavored on energetic grounds. The alternative path from $\mathbf{8}^{2+}$ to $\mathbf{10}^{2+}$ proceeds through the migration of the hydrogen atom from the carbon atom next to the sp^3 carbon to the carbene carbon atom to form isomer $\mathbf{11}^{2+}$. Although several transition structures leading to $\mathbf{11}^{2+}$ can be localized and characterized by vibrational analysis and the associated intrinsic reaction coordinate (IRC), the minimum corresponding to $\mathbf{11}^{2+}$ could not be optimized as the optimization of the geometry of $\mathbf{11}^{2+}$ always resulted in a rearrangement to a more stable isomer $\mathbf{14}^{2+}$, with an eight-membered ring (see below); it is therefore believed that the isomer $\mathbf{11}^{2+}$ lies in a very shallow minimum on the potential energy surface (PES). The energy given in Scheme 4 ($E_{\mathrm{rel}}(\mathbf{11}^{2+}) = -0.45$ eV) corresponds to the product structure obtained from IRC calculations. A transition structure for a mutual rearrangement of isomers $\mathbf{8}^{2+}$ and $\mathbf{11}^{2+}$ was also not localized, due to the same difficulties as encountered during optimization of $\mathbf{11}^{2+}$. The last step, in which the hydrogen from the sp^3 carbon atom of $\mathbf{11}^{2+}$ migrates to the carbene carbon, requires an amount of energy right at the border of available internal energy ($E_{\mathrm{rel}}(\mathbf{11}^{2+}/\mathbf{10}^{2+}) = 0.01$ eV).



Scheme 2. Possible structures of $C_9H_6^{2+}$ dications formed upon loss of molecular hydrogen from the reaction intermediates $C_9H_8^{2+}$.

Alternative pathways towards the isomer $\mathbf{10}^{2+}$ first involve migration of a hydrogen atom from the ring of the dication $\mathbf{5}^{2+}$. In principle, the rearrangement might take place either through migration of the hydrogen atom bonded to the sp^3 carbon atom (ii) or through that bonded to a carbon atom next to the sp^3 carbon atom (iii). The first possibility is associated with an energy barrier—$E_{\mathrm{rel}}(\mathbf{5}^{2+}/\mathbf{12}^{2+}) = 0.71$ eV—well above the entrance channel and therefore can be excluded as a possible mechanism leading to $\mathbf{10}^{2+}$. We note in passing that no transition structure for the hydrogen migration around the ring in the opposite direction was localized, because a concomitant rearrangement of a hydrogen atom of the CH−CH chain always occurred during the optimization, finally resulting in the isomer $\mathbf{9}^{2+}$. The second possibility gives the isomer $\mathbf{6}^{2+}$ ($E_{\mathrm{rel}}(\mathbf{6}^{2+}) = -0.17$ eV) and, similarly to the first scenario, the associated energy barrier is well above the available internal energy ($E_{\mathrm{rel}}(\mathbf{5}^{2+}/\mathbf{6}^{2+}) = 1.19$ eV).

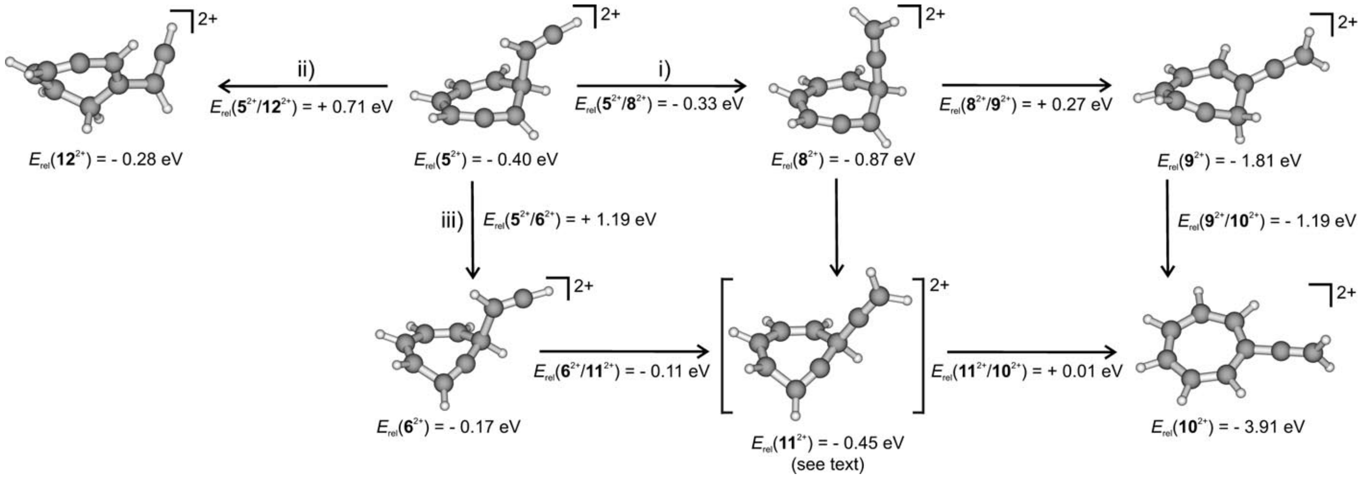
In summary, it can be concluded that an energetically possible series of hydrogen rearrangements leading from the initially formed dication $\mathbf{5}^{2+}$ to the more stable isomer $\mathbf{10}^{2+}$ starts with a migration of a hydrogen atom within the attached C_2-side chain. The experimental results further reveal that the final species resulting from the $C_7H_6^{2+}/C_2H_2$ coupling lose a hydrogen atom as well as molecular hydrogen. Therefore, several feasible products of these fragmentations are shown in Schemes 2 and 3. Although several isomers of $C_9H_6^{2+}$ closely linked to $\mathbf{10}^{2+}$ have relative energy below zero ($\mathbf{35}^{2+}$–$\mathbf{38}^{2+}$, Scheme 2), their formation would require further hydrogen atom migrations prior to the dehy-



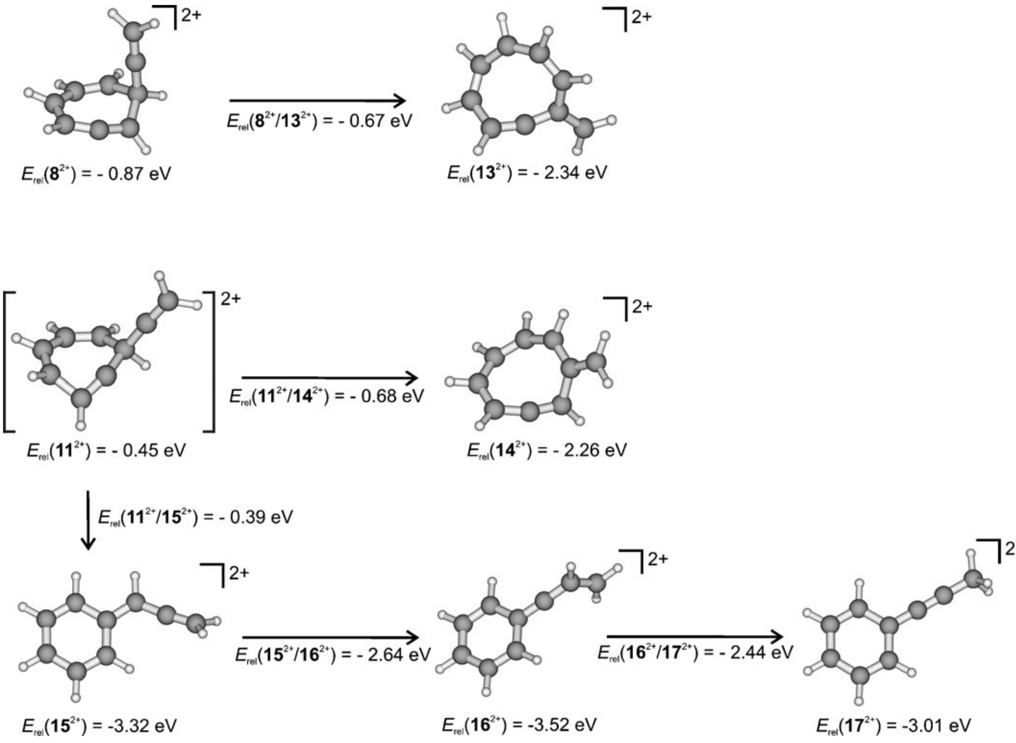
Scheme 3. Possible structures of $C_9H_7^{2+}$ dications formed upon loss of atomic hydrogen from the reaction intermediates $C_9H_8^{2+}$.

drogenation step. Such rearrangements would certainly again produce $C_9H_8^{2+}$ isomers lying relatively high in energy. As to the loss of hydrogen atom from **10**$^{2+}$, the most stable isomer of $C_9H_7^{2+}$ with a structure derived from **10**$^{2+}$ corresponds to the dication **60**$^{2+}$. Its relative energy is above the entrance channel (E_{rel}(**60**$^{2+}$+ H) = +0.07 eV), so although isomer **10**$^{2+}$ cannot be excluded as a possible intermediate in Equations (1) and (2), it appears rather improbable as a final precursor for the loss of atomic or molecular hydrogen.

Besides the migrations of hydrogen atoms, skeletal rearrangements can also produce more stable isomers of $C_9H_8^{2+}$. Simple skeletal rearrangements involve ring expansions and ring-contractions (Scheme 5). Several mechanisms for ring expansions have been found; one of them is mentioned above in that the dication **11**$^{2+}$ undergoes an immediate rearrangement to isomer **14**$^{2+}$ with an eight-membered ring (E_{rel}(**14**$^{2+}$) = −2.26 eV). More isomers derived from **14**$^{2+}$ by hydrogen rearrangements were localized (e.g., **13**$^{2+}$ with E_{rel}(**13**$^{2+}$) = −2.34 eV)). Nevertheless, the relative energies of all these structures are around −2.3 eV, which is an insufficient amount of internal energy for the subsequent loss of atomic or molecular hydrogen. Loss of atomic hydrogen from this class of $C_9H_8^{2+}$ dications gives structurally related $C_9H_7^{2+}$ dications with eight-membered rings and relative energies at least 1 eV above the entrance channel (**61**$^{2+}$–**63**$^{2+}$, Scheme 3). The formation of the most stable product of dehydrogenation with an eight-membered ring, **41**$^{2+}$, requires



Scheme 4.



Scheme 5.

+0.51 eV (Scheme 2). It can thus be concluded that $C_9H_8^{2+}$ isomers with eight-membered rings may be involved as intermediates in Equations (1) and (2), but cannot serve as precursors for the eliminations of either atomic or molecular hydrogen.

Ring-contraction of the initially formed $C_9H_8^{2+}$ dication produces structures with six-membered rings. The least energy-demanding pathway starts with the dication $\mathbf{11}^{2+}$. The internal energy of this isomer is large enough to surmount the energy barrier associated with the ring-contraction ($E_{rel}(\mathbf{11}^{2+}/\mathbf{15}^{2+}) = -0.39$ eV) and the resulting dication $\mathbf{15}^{2+}$ lies considerably lower in energy ($E_{rel}(\mathbf{15}^{2+}) = -3.32$ eV). In contrast with the dication isomers with seven- and eight-membered rings, the structures with six-membered rings can provide hydrogen-depleted dications within the internal energy range available to the reactant system [$E_{rel}(\mathbf{64}^{2+}+H) = -0.23$ eV and $E_{rel}(\mathbf{42}^{2+}+H_2) = -1.18$ eV]. Rearrangements to the favorable precursors for atomic and molecular hydrogen loss $\mathbf{16}^{2+}$ and $\mathbf{17}^{2+}$ are also subject to only very small energy barriers with respect to the internal energy stored in the dications (Scheme 5), so dications with the structures derived from C_3-substituted benzene might be among products of Equations (1) and (2).

Scheme 6 shows the complex rearrangements of the $C_9H_8^{2+}$ dications to bicyclic structures. Simple ring-closure starting from the dication $\mathbf{6}^{2+}$ with a seven-membered ring gives the dication $\mathbf{18}^{2+}$ with seven- and four-membered rings. The transition structure associated with this rearrangement lies above the entrance channel ($E_{rel}(\mathbf{6}^{2+}/\mathbf{18}^{2+})$ = 0.20 eV), and its participation in the title reaction is therefore considered unlikely. The other mechanism for the rearrangement to a bicyclic structure involves the initially formed isomer $\mathbf{5}^{2+}$, in which the terminal carbon atom of the C_2H_2 chain attacks the carbene carbon atom of the ring. The complex rearrangement ($E_{rel}(\mathbf{5}^{2+}/\mathbf{19}^{2+})$ = −0.06 eV) then produces a bicyclic dication with an indene skeleton ($E_{rel}(\mathbf{19}^{2+})$ = −4.10 eV). The $C_9H_8^{2+}$ dications with structures derived from indene are the most stable ones found and their mutual rearrangements are associated with only small energy barriers (Scheme 6). As the rearrangement of $\mathbf{5}^{2+}$ to $\mathbf{19}^{2+}$ appears to be a key step of the $C_7H_6^{2+}+C_2H_2$ coupling, it is depicted in detail in Figure 1 as a function of the associated intrinsic reaction coordinate. It is worth noting that the geometry of the $C_9H_8^{2+}$ along the reaction coordinate resembles an often favored geometrical arrangement of dications, in the form of a CH cation bonded to the π electron system of the remaining part of the dication. Such a "pyramidal" skeleton, involving a C_5H_5 ring with a CH group at the apex, represents, for example, the most stable isomer of benzene dication.[20]

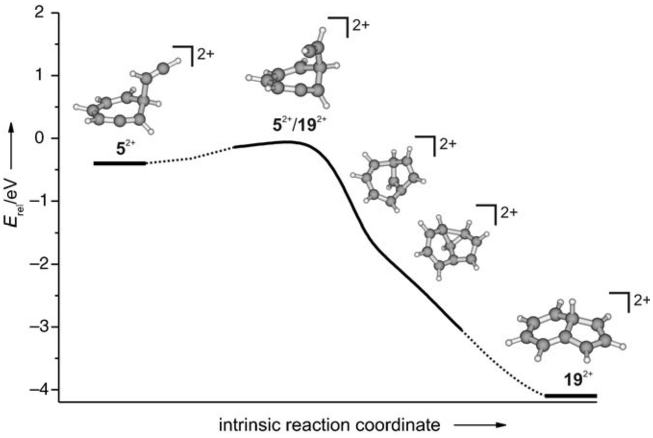
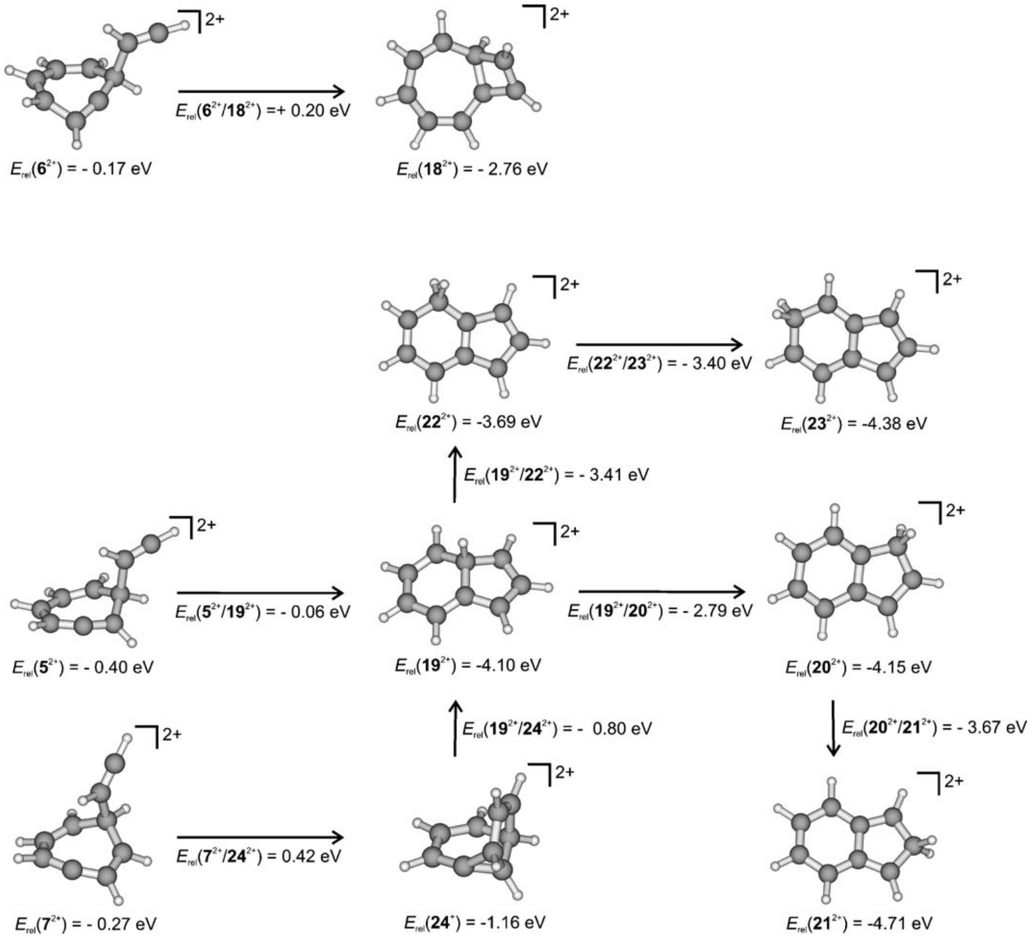


Figure 1. Energy profile along the IRC for the rearrangement of $\mathbf{5}^{2+}$ to $\mathbf{19}^{2+}$ (B3LYP/6-311+G(2d,p)). The IRC calculations only covered the range given as a full line; the dotted connections to the related minima are tentative.



Scheme 6.

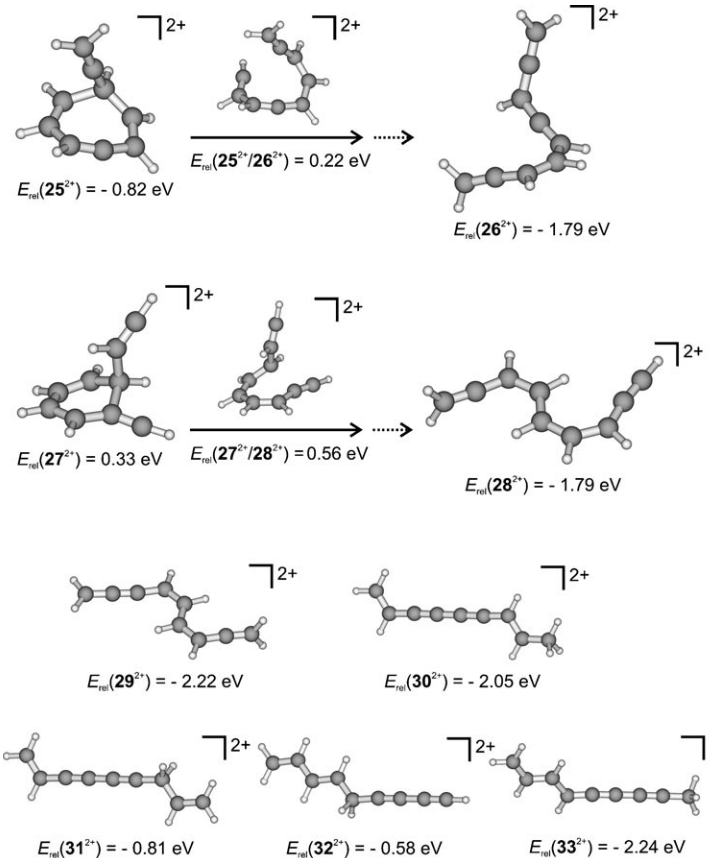
The energy demands for losses either of hydrogen atom or of molecular hydrogen from $C_9H_8^{2+}$ dications with indene skeletons are well below the internal energy available to the system. The most stable isomer formed upon H atom loss corresponds to the dication $\mathbf{69}^{2+}$ ($E_{rel}(\mathbf{69}^{2+})$ = −1.44 eV). In fact all other isomers of $C_9H_7^{2+}$ with indene skeletons ($\mathbf{70}^{2+}$–$\mathbf{76}^{2+}$, Scheme 3) lie considerably higher in energy (E_{rel} = 0.8–1.2 eV), and can therefore be excluded as products of hydrogen atom loss. On the other hand, the internal energy contents of all isomers of $C_9H_8^{2+}$ with the indene skeleton ($\mathbf{19}^{2+}$–$\mathbf{23}^{2+}$) are sufficient for the elimination of molecular H_2 to afford dehydrogenated dications $\mathbf{46}^{2+}$–$\mathbf{49}^{2+}$ (Scheme 2), the most stable product among them being dication $\mathbf{47}^{2+}$ ($E_{rel}(\mathbf{47}^{2+}+H_2)$ = −1.26 eV). The difference in the number of conceivable pathways has an important consequence with regard to the mechanistic analysis of the theoretical results. If it is assumed that C−C coupling between $C_7H_6^{2+}$ and acetylene produces a dication with an indene skeleton, the ease of hydrogen rearrangements implies a rapid equilibration of all structures. While all of them can lose H_2, only a single one can expel atomic hydrogen. As a consequence, even though $C_9H_8^{2+} \rightarrow \mathbf{69}^{2+}+H$ is the lowest-lying pathway of all considered fragmentation mechanisms, the loss of molecular hydrogen is favored on a statistical basis, which is consistent with the fact that a greater abundance of $C_9H_6^{2+}$ than of $C_9H_7^{2+}$ was observed in the experiment. Product dications with structures derived from the indene skeleton are also accessible by cyclization of the dication $\mathbf{7}^{2+}$. However, the energy barrier for the cyclization step ($E_{rel}(\mathbf{7}^{2+}/\mathbf{24}^{2+})$ = 0.42 eV) is larger than that found for the more stable isomer $\mathbf{5}^{2+}$ (Scheme 6).

Finally the possibility of ring-opening and formation of dications with linear structures is addressed. Cleavage of a C−C bond is an energy-demanding reaction step, and no transition structures for any direct opening of the rings in the initially formed dications $\mathbf{5}^{2+}$–$\mathbf{7}^{2+}$ were found. Most probably, a sequence of hydrogen atom and skeletal rearrangements is required before a structure suitable for C−C bond cleavage to occur is achieved. For illustration, two of the ring-opening mechanisms are shown, together with several other optimized linear structures of dications $C_9H_8^{2+}$, in Scheme 7. The energy barriers associated with C−C bond cleavages in dications are large and, moreover, the isomers with open structures lie higher in energy than the isomers with cyclic or bicyclic structures.

As in the cases of the dications with cyclic structures, the feasibility of hydrogen atom loss should be considered the decisive criterion for comparison with experimental observations. Whereas loss of molecular hydrogen is often allowed within the available internal energy of the system (Scheme 2), the loss of a hydrogen atom is much more energetically demanding (Scheme 3). As the experimental results clearly show that the $C_9H_8^{2+}$ dications formed in the reaction between $C_7H_6^{2+}$ and acetylene readily lose both H and H_2, feasibility of H elimination from $C_9H_8^{2+}$ is one of the basic criteria for examination of the probability of the formation of a particular isomer. In fact, none of the $C_9H_7^{2+}$ dications with an open structure ($\mathbf{77}^{2+}$–$\mathbf{80}^{2+}$, Scheme 3) has a relative energy [$E_{rel}(C_9H_7^{2+}$+H)] below zero, and so it can be concluded that the reaction mechanisms including a ring-opening step are much more energy-demanding than the mechanisms resulting in cyclic and especially bicyclic structures. Moreover, the dications with open chains do not have enough internal energy to undergo elimination of atomic hydrogen. Hence, mechanisms producing dications with linear chains are considered to be less probable than those affording dications with (poly)cyclic structures.

In summary, two possible general pathways for Equations (1) and (2) are proposed on the basis of DFT calculations. Either the initial coupling of $C_7H_6^{2+}$ and C_2H_2 is followed by contraction of the seven-membered ring, which produces isomers of C_3-substituted benzene, or the initially formed coupling product undergoes a cyclization step to form the dications $C_9H_8^{2+}$ with geometries based on the indene skeleton.

Comparison with experimental results: The computed data can be compared with the experimental results obtained for the reaction between $C_7H_6^{2+}$ and C_2H_2,[1] as well as with a recent study of the double ionization of indene and its subsequent fragmentations based on photoionization measurements.[13] Thus, the experimentally determined energy thresholds for losses of H and H_2 from $C_9H_8^{2+}$ generated



Scheme 7.

from indene were determined as $E_{thres}(C_9H_7^{2+}) = 3.96 \pm 0.10$ eV and $E_{thres}(C_9H_6^{2+}) = 3.9 \pm 0.2$ eV, respectively.[13] In comparison, the endothermicities of H and H_2 losses are calculated as 2.71 eV and 2.89 eV (formation of $\mathbf{69}^{2+}$+H and $\mathbf{47}^{2+}$+H_2, respectively, from $\mathbf{20}^{2+}$). Accordingly, a level of about 1 eV of internal energy above the thermodynamic threshold is necessary for the fragmentations to occur in the time window of the experiment. Even though the threshold measurements[13] and the reactivity studies[1] were performed with different instruments, both of them are based on quadrupole–octopole–quadrupole configurations and roughly similar time windows can therefore be assumed. In the photoionization experiments, however, the threshold energies were determined by scanning of the first quadrupole, whereas the reactivity studies were performed in the octopole cell and then monitored by means of the second quadrupole. With allowance for the different timescales of the instrumentation sets used, a roughly twofold lifetime can be estimated for the studied ions in the reactivity experiment, in comparison with the threshold measurements. Accordingly, somewhat less excess energy is required for the H and H_2 losses to be monitored in the reactivity study than in the photoionization experiments.

Furthermore, the threshold measurements have shown that the amount of H elimination decreases relative to H_2 elimination with decreasing internal energy of the $C_9H_8^{2+}$ parent ion.[13] The H/H_2 ratio amounts to 45%:55% for an internal energy (E_{int}) 2.2 eV above the threshold energy ($E_{int} = E_{thres}$+2.2 eV; E_{thres} is taken as 3.9 eV). When the internal energy drops to $E_{int} = E_{thres}$+1.5 eV the ratio of H elimination decreases to 43%, while for $E_{int} = E_{thres}$+0.8 eV the H elimination represents only 40%.[13] The experimental results for the reaction between $C_7H_6^{2+}$ and C_2H_2 reveal that the coupling sequence ends with losses of atomic and molecular hydrogen in a roughly 33:67 ratio.[1] If it is assumed that the final coupling intermediate corresponds to the indene dication, only a very small excess of the internal energy above the reported thresholds is expected, and this scenario is perfectly consistent with the theoretical results obtained here. The $C_9H_8^{2+}$ isomers with structures derived from the indene skeleton thus have relative energies in the range $E_{rel} = -4.1$ to -4.7 eV with respect to the entrance channel (Scheme 6), which represents the amount of internal energy available for the subsequent loss of H or H_2, meaning that only a small amount of excess internal energy above the reported threshold energy $E_{thres} = 3.9$ eV is available. Accordingly, it can be predicted that less than 40% of the $C_9H_8^{2+}$ intermediate containing the indene structure in Equations (1) and (2) will lose atomic H and more than 60% will lose molecular hydrogen. This conclusion is in very good agreement with the values found in the reactivity study.

So far, no similar studies of the double-ionization thresholds for phenylallene or phenylpropyne (precursors of the dications $\mathbf{15}^{2+}$ and $\mathbf{17}^{2+}$, respectively) exist. For the time being, the fragmentation behavior can therefore only be estimated on the basis of comparison with the results obtained for indene. Analogously, it can be expected that a certain excess of internal energy will be necessary for the eliminations to occur in the timescale of the experiment. Calculations suggest that the loss of H_2 either from $\mathbf{15}^{2+}$ or from $\mathbf{17}^{2+}$ produces the dication $\mathbf{42}^{2+}$ with $E_{rel}(\mathbf{42}^{2+}+H_2) = -1.18$ eV, which means that there is more than 1 eV of excess internal energy for this fragmentation to occur. The products of the loss of hydrogen atom are formed with a larger relative energy [$E_{rel}(\mathbf{64}^{2+}+H) = -0.23$ eV], so this fragmentation channel would be expected to be kinetically disfavored in the reactivity study. Reviewing these arguments, we can accordingly conclude that if the reaction between $C_7H_6^{2+}$ and C_2H_2 were to produce derivatives of benzene such as $\mathbf{15}^{2+}$, $\mathbf{16}^{2+}$, and $\mathbf{17}^{2+}$, reaction (1) should be strongly preferred over reaction (2).

In summary, comparison of theoretical results with experimental findings suggests that a substantial amount of the $C_9H_8^{2+}$ product formed in the ion/molecule reaction between $C_7H_6^{2+}$ and C_2H_2 has a structure based on the indene skeleton. Additional channels are most likely to afford $C_9H_8^{2+}$ dications with structures derived from benzene with a C_3 side chain. These products preferably eliminate molecular hydrogen, which might be another factor contributing to a large ratio of H_2/H elimination found experimentally.

Conclusion

The mechanisms involved in the reaction between $C_7H_6^{2+}$ and C_2H_2 were studied by DFT calculations with close comparison to experimental results. The initial step involves the formation of a hydrogen-bonded complex between $C_7H_6^{2+}$ dication and acetylene, mediated by a hydrogen atom of the dication and the π electrons of acetylene. This initial complexation affords enough internal energy to surmount the subsequent barriers associated with the formation of a new, covalent C−C bond. In addition, a large number of mechanisms for subsequent rearrangements to more stable isomers of the product $C_9H_8^{2+}$ dications were pursued in detail: i) hydrogen-atom migrations, ii) ring-contractions, iii) ring-expansion, iv) formation of isomers with bicyclic structures, and v) formation of dications with open chains. Among this plethora of possible routes, the formation of $C_9H_8^{2+}$ with a structure derived from the indene skeleton appears the most probable one. Firstly, these dications are the most stable ones found and, secondly, they would be formed with enough internal energy to complete the coupling sequence by elimination of both atomic and molecular hydrogen according to Equations (1) and (2). Another conceivable channel could result in the formation of $C_9H_8^{2+}$ species with structures based on C_3-substituted benzenes. However, fragmentations of these dications would be expected to result in preferential loss of H_2. This theoretical study hence reveals that the reactions between doubly ionized arenes and acetylene do indeed provide a route for the generation of polycyclic hydrocarbons. However, the growth mechanism is rather complex and many different types of reaction intermediates are conceivable. In addition to mere mass spectrometric evidence, further spectroscopic characterization of gaseous $C_mH_n^{2+}$ dications would therefore be desirable.

Acknowledgements

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (No. KJB4040302).

[1] J. Roithová, D. Schröder, *J. Am. Chem. Soc.* **2006**, *128*, 4208.
[2] S. D. Price, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1717.
[3] P. Tosi, R. Correale, W. Y. Lu, S. Falcinelli, D. Bassi, *Phys. Rev. Lett.* **1999**, *82*, 450.
[4] D. Ascenzi, P. Franceschi, P. Tosi, D. Bassi, M. Kaczorowska, J. N. Harvey, *J. Chem. Phys.* **2003**, *118*, 2159.
[5] W. Y. Lu, P. Tosi, D. Bassi, *J. Chem. Phys.* **2000**, *112*, 4648.
[6] D. Mathur, *Phys. Rep.* **1993**, *225*, 193.
[7] D. Schröder, H. Schwarz, *J. Phys. Chem. A* **1999**, *103*, 7385.
[8] P. G. Sim, W. D. Jamieson, R. K. Boyd, *Org. Mass Spectrom.* **1989**, *24*, 327.
[9] H. Perreault, L. Ramaley, F. M. Benoit, P. G. Sim, R. K. Boyd, *J. Phys. Chem.* **1991**, *95*, 4989.
[10] S. Leach, J. H. D. Eland, S. D. Price, *J. Phys. Chem.* **1989**, *93*, 7583.
[11] J. Roithová, D. Schröder, R. Berger, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 1650.
[12] J. Roithová, D. Schröder, P. Gruene, T. Weiske, H. Schwarz, *J. Phys. Chem. A* **2006**, *110*, 2970.
[13] J. Roithová, J. Žabka, D. Ascenzi, P. Franceschi, C. L. Ricketts, D. Schröder, *Chem. Phys. Lett.* **2006**, *423*, 254.
[14] a) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200; d) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[15] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[16] a) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154; b) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.
[17] C. W. Bauschlicher, Jr., A. Ricca, H. Partridge, S. R. Langhoff in *Recent Advances in Density Functional Methods*, Part II (Ed.: D. P. Chong), World Scientific Publishing Company, Singapore, **1997**, p. 165.
[18] A. K. Rappé, E. R. Bernstein *J. Phys. Chem. A* **2000**, *104*, 6117.
[19] The reaction rate can be further influenced by dynamic effects. See also: K. F. Donchi, P. J. Derrick, in *Comprehensive Chemical Kinetics, Vol. 24* (Eds.: C. H. Bamford, C. F. H. Tipper), **1983**, p. 53.
[20] K. Krogh-Jespersen, *J. Am. Chem. Soc.* **1991**, *113*, 417.

Received: June 27, 2006