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Structures of the $C_8H_6^+$ Cation Formed upon Loss of Acetylene from Ionized Naphthalene

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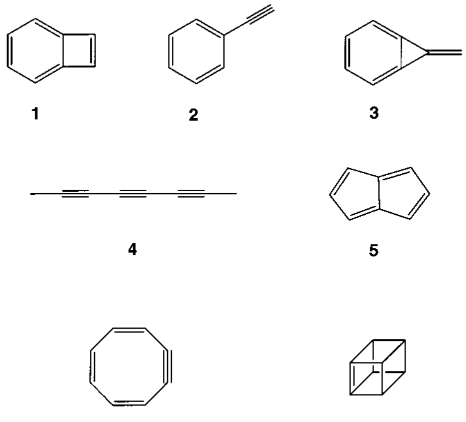
Ionized naphthalene undergoes unimolecular loss of acetylene in the gas phase, which leads to the formation of a $C_8H_6^+$ species of hitherto unknown structures. In order to possibly afford different isomers, $C_8H_6^+$ is generated using several precursors, i.e., naphthalene, azulene, 1-chlorobenzocyclobutene, benzocyclobuten-1-ol, 1,2-di(bromomethyl)benzene, phenylacetylene, 2,4,6-octatriyne, 2,7-dichloro-3,5-octadiyne, and 1,3,5,7-cyclooctatetraene. Mass-selected $C_8H_6^+$ ions are investigated by different mass spectrometric techniques, such as collisional activation (CA), neutralization reionization (NR), and charge reversal (CR). Charge reversal of cations to anions is most informative and yields structurally indicative fragmentations, which are much less pronounced with the other techniques. Comparison of the CR spectra of the $C_8H_6^+$ cations disputes the formation of ionized phenylacetylene and 2,4,6-octatriyne upon loss of acetylene from naphthalene ion. Further, formation of ionized cycloocta-1,3,5-triene-7-yne can be ruled out by comparison with the data obtained for the corresponding anionic species. While the experimental results are in accord with the formation of ionized benzocyclobutadiene upon loss of acetylene from naphthalene ion, other isomers which have not been considered previously may also represent likely candidates.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been assigned important environmental aspects due to their toxicity combined with their ubiquity as the combustion products of organic material in fuel-rich flames.[1] Further, PAHs and their ions are believed to be responsible for interstellar absorption bands in the infrared.[2,3] Thus, there is considerable interest in the formation and degradation of PAHs for fundamental reasons as well as analytical applications.

The mass spectrometry of PAHs has been studied for decades. Typically,[4] ionized PAHs show intense molecular ions along with little fragmentation due to their robust backbones in which carbon−carbon bond fission is often associated with a (partial) loss of aromaticity. Some effort has been made to distinguish isomeric PAHs by mass spectrometric means,[5] but this task is all but trivial. For example, the fragmentation patterns of the various isomers upon collisional activation are often almost identical, as are those of the daughter ions.[6] The similarity of the fragmention patterns has been regarded as an indication for the fact that most PAHs isomerize to common structures (or mixtures of isomers) upon ionization. Besides benzene ion as the parent system,[7,8] particular attention has been paid to ionized naphthalene, in which unimolecular loss of acetylene can be regarded as a prototype fission of PAH fragmentation.[5b,6,9,10] Even though this reaction has been studied quite extensively, the structure of the resulting cationic fragment $C_8H_6^+$ is still under debate. Ling et al.[11] have recently attempted to elucidate the nature of the $C_8H_6^+$ ion formed from ionized naphthalene and explicitly considered three different structures. Combination of theoretical calculations and experimental data implied that ionized benzocyclobutadiene $\mathbf{1}^+$ as well as phenylacetylene ion $\mathbf{2}^+$ are both plausible products on the basis of mere energetic considerations, while the formation of ionized 1-methylenebenzocyclopropene $\mathbf{3}^+$ has been ruled out (Chart 1). Formation of benzocyclobutadiene ion was preferred by these authors because $\mathbf{1}^+$ is by about 4 kcal/mol more stable than $\mathbf{2}^+$; however, this energy difference is smaller than the uncertainty of ±5 kcal/mol in the experimental threshold for acetylene loss from ionized naphthalene.[12] Further, Ling et al.[11] argued that formation of $\mathbf{1}^+$ from ionized naphthalene is kinetically favored because it does not require hydrogen migration prior to fragmentation, whereas $\mathbf{2}^+$ can only be formed after initial hydrogen transfer. The latter argument is somewhat flawed, however, since it is well established that complete H/D as well as $^{12}C/^{13}C$ equilibrations precede loss of acetylene from labeled naphthalene ions.[13]

CHART 1



Here, we report means to distinguish isomeric $C_8H_6^+$ ions by charge reversal (CR) of the cationic to anionic species, i.e., $^+CR^-$. The crucial difference between this and other methods, such as collisional activation (CA) or neutralization−reionization (NR), is the enhanced propensity to form structurally indicative fragments upon charge inversion of cations.[14] Because extensive rearrangements are likely to occur en route to the formation of $C_8H_6^+$, we consider not only $\mathbf{1}^+$ and $\mathbf{2}^+$, but include also some

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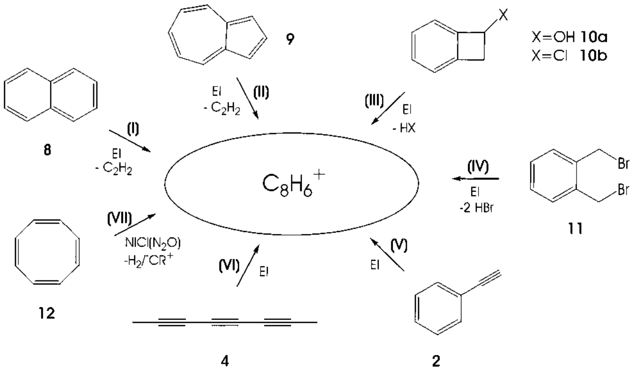


Figure 1. Methods I−VII used to generate $C_8H_6^+$ ions from different precursors. Note that method (VII) also provides an access to $C_8H_6^-$ anion.

additional precursors which may provide acyclic $C_8H_6^+$ ions, e.g. **4**$^+$, or cyclic ones having other than six-membered rings, e.g. **5**$^+$ and **6**$^+$. Ions with three-dimensional structures such as **7**$^+$ are also conceivable,[15,16] but far beyond the scope of this study.[17]

Experimental Section

The 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.[18] All spectra were accumulated (5−50 scans) and on-line processed with the AMD/Intectra data system. The ions of interest were generated by electron ionization (EI, 70 eV) or negative ion chemical ionization (NICI) of appropriate precursors (Figure 1). After acceleration to 8 keV, the ions of interest were mass-selected using B(1)/E(1) at a resolution of $m/\Delta m \geq 4000$, which was sufficient to resolve isobaric species, and ion structures were probed by various MS/MS experiments.[18,19] Unimolecular dissociations of metastable ions (MI) in the field-free region preceding B(2) were monitored by scanning this sector. For collisional activation (CA) helium was used as a target gas (80% transmission, T) in the field-free region preceding B(2), and the fragment ions were monitored by scanning B(2). Charge-stripping (CS) experiments were performed in a similar manner in that the B(1)/E(1) mass-selected monocations were collided with oxygen (80% T) in the field-free region preceding B(2) in order to generate dicationic species. For neutralization−reionization of cations via neutrals to cations again ($^+NR^+$) two collision cells in the field-free region preceding B(2) were used. For neutralization, the cations were collided with xenon (80% T) in the first collision cell. Then, the remaining cations were deflected by an electric potential, the beam of neutral molecules was subsequently reionized with oxygen (80% T) in the second collision cell, and the mass spectra of the resulting cations were recorded by scanning B(2). 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). Charge reversal of B(1)/E(1) mass-selected anions ($^-CR^+$) also applied oxygen (80% T) as a collision gas. Collisional activation of the charged-reversed ions ($^-CR^+$/CA) commenced with mass selection of the $C_8H_6^-$ precursors using B(1)/E(1) followed by charge inversion (O_2, 80% T) in the field-free region preceding B(2), selection of the $C_8H_6^+$ cation formed using B(2), and CA (He, 80% T) in the next field-free region while scanning the fragments using E(2). For comparison, also CA spectra of source-generated $C_8H_6^+$ were recorded with E(2).

All experiments involving ionization to anions, i.e., $^+CR^-$ and $^-NR^-$, were performed using only B(1) for mass selection, and the resulting anions were recorded by scanning E(1). This method was chosen in order to achieve maximal sensitivity considering the low efficiencies of the $^+CR^-$ and $^-NR^-$ processes.[14,20] Mass selection using only B(1) appeared to be no major drawback in the present case, because neither isobaric interferences nor artifacts were obvious.[21] Charge reversal of cations ($^+CR^-$) was achieved by colliding the ions with xenon (60% T) in the field-free region preceding E(1), and the resulting anions were monitored by scanning E(1). Finally, $^-NR^-$ was performed with B(1) selected anions using the collision gas combination O_2/Xe (80% T, each).

All precursors were used to generate $C_8H_6^+$ ions. Except **4**, limited volatilities resulted in considerable memory effects in the inlet systems of the mass spectrometer. Therefore, only a single precursor was examined per day. This procedure goes in hand with differences in the focusing conditions due to day-to-day variations. We attempted to use as uniform focusing conditions as possible; however, direct comparison of the precursors under identical conditions was impossible due to memory effects. Based on the reproducibility of the spectra in independent experiments, the average experimental error of the fragment ion intensities is estimated as ±20% unless stated otherwise.

Naphthalene (**8**), azulene (**9**), 1,2-di(bromomethyl)benzene (**11**), phenylacetylene (**2**), and cyclooctatetraene (**12**) were commercially available and used as purchased. Benzocyclobuten-1-ol (**10a**) and 1-chlorobenzocyclobutene (**10b**) were synthesized via the following sequence:[22] Anthranilic acid was treated with isoamyl nitrite in neat vinyl acetate to give 1-acetoxybenzocyclobutene. Subsequent hydrolysis with aqueous sodium carbonate affords **10a**, which was further transformed to yield **10b** upon treatment with phosphorus pentachloride. 2,7-Dichloro-3,5-octadiyne and 2,4,6-octatriyne (**4**) were synthesized via a route starting with the Glaser coupling of two equivalents of but-3-yne-2-ol to 3,5-octadiyne-2,7-diol.[23] The latter gives 2,7-dichloro-3,5-octadiyne upon reaction with thionyl chloride, and subsequent treatment with sodium amide in liquid ammonia affords **4**.[24]

Results

In view of the vast complexity which would arise from a more complete consideration of C_8H_6 structures,[17] let us first outline the strategy behind the choice of the precursors shown in Figure 1. Loss of acetylene from ionized naphthalene (method I) gives rise to the ion of interest. Earlier labeling experiments[25] suggest that dissociative ionization of azulene (method II) could provide an access to cyclic isomers having other than six-membered rings, e.g. ionized pentalene **5**$^+$. Dissociative ionization of benzocyclobutene derivatives (method III) may yield benzocyclobutadiene ion, **1**$^+$, in a straigthforward manner. We note in passing that the spectra obtained with the hydroxy (**10a**) and chloro derivatives (**10b**) were identical within experimental error, and here we refer to the latter which gave better yields of $C_8H_6^+$. A similar skeleton may be formed by dissociative ionization of 1,2-di(bromomethyl)benzene, **11**; yet the $C_8H_6^+$ ion formed via method IV may not have an intact four-membered ring. Next, ionization of phenylacetylene (V) is assumed[26] to afford an intact molecular ion, **2**$^+$. 2,4,6-Octatriyne **4** is considered as a representative for acyclic isomers, which may possibly form the corresponding molecular ions upon ionization (method VI). We note in passing that the spectra of the $C_8H_6^+$ species made by dissociative ionization of 2,7-

dichloroocta-3,5-diyne (not shown) differ from those obtained in method VI and are instead almost identical to the results with methods I and II; this suggests that the chloro derivative collapses to the same isomer(s) as naphthalene upon dissociative ionization.[27] Finally, chemical ionization of cyclooctatetraene **12** in the negative ion mode (method VII, see below) is considered as a precursor for C_8H_6 having a cyclooctane skeleton, for example $\mathbf{6}^+$. At this point, it should be stressed that we do not assume that the ion structures will directly reflect the precursor connectivities; quite to the contrary, we consider that the outcome of each method in terms of $C_8H_6^+$ structure will be per se unknown. The mass-selected ions were then investigated using several mass spectrometric variants aimed at distinguishing between different structural motifs.

The following section is organized such that we subsequently describe the results obtained in the different mass-spectrometric experiments, rather than discussing the precursors separately. As a consequence of this ordering, the characterization of the $C_8H_6^-$ anion formed by chemical ionization of cyclooctatetraene with N_2O (method VII) forms a separate section. Unless stated otherwise, let us further neglect the actual hydrogen content of the product ions and for the sake of simplicity only consider fragmentations of the carbon backbone, i.e., C_8H_n, C_7H_n, C_6H_n, etc. ($n = 0-6$).

MI, CA, and CS Mass Spectra. Although the metastable ion (MI) and collisional activation spectra of the $C_8H_6^+$ ions made via methods I−VI display some differences, none of these can be considered to be structurally diagnostic. Thus, the fragmentation patterns are qualitatively similar and only differ as far as intensity variations of certain fragment groups are concerned. Acetylene losses predominate the MI spectra of all $C_8H_6^+$ species (not shown), and also the CA spectra are quite similar (Figure 2). A minor difference occurs in Figure 2f in which the group of $C_7H_n^+$ fragments is slightly more pronounced compared to the other spectra. This observation can be regarded as a remnant of the presence of a methyl group in the precursor triyne. Nevertheless, these variations are moderate and far from being conclusive as far as ion structures are concerned. The most prominent difference is the less pronounced C_2H_2 loss to yield $C_6H_4^+$ in Figure 2d compared to the other spectra. Loss of acetylene is, however, also a unimolecular process for energized $C_8H_6^+$ and variation of its abundance may therefore be ascribed to different internal energies in the ions formed.[14,28] In particular, none of these decomposition processes can be considered as being conclusive in terms of the connectivity of the carbon skeleton. As far as the ion of interest formed upon dissociative ionization of naphthalene is concerned, also the otherwise powerful application of labeling techniques cannot be expected to provide valuable insight because isotopic scrambling in ionized naphthalene is well documented.[13]

In addition, charge stripping (CS) experiments were performed, because this method has previously been applied successfully for the distinction of isomeric hydrocarbon ions.[5a,29] For the $C_8H_6^+$ ions under study, the $C_8H_n^{2+}$ dications signals were minor, however, and also interfered by monocation signals due to $C_4H_n^+$ fragments. Although the dication intensities in the CS spectra (not shown) differed among methods I−VI, no valuable information could be extracted with regard to ion structures.

NR Mass Spectra. The neutralization−reionization ($^+NR^+$) spectra of the $C_8H_6^+$ cations obtained with methods I−VI reveal some distinct differences (Figure 3), which are most pronounced for the intensities of the recovery signals. The fact that the survivor-ion yields depend on the precursors used indicates that at least some of the $C_8H_6^+$ ions made via methods I−VI exhibit structurally distinct features and are not fully equilibrated to the same isomer(s).

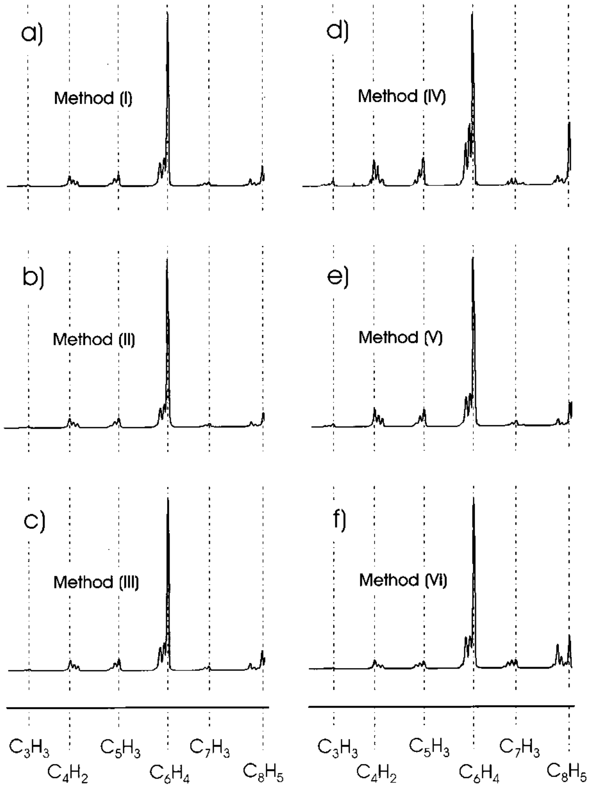


Figure 2. Collisional activation (CA, He, 80% T) mass spectra of B(1)/E(1) mass-selected $C_8H_6^+$ generated by ionization of (a) naphthalene (method I), (b) azulene (method II), (c) 1-chlorobenzocyclobutene (method III), (d) 1,2-di(bromomethyl)benzene (method IV), (e) phenylacetylene (method V), and (f) 2,4,6-octatriyne (method VI).

Specifically, spectra a and b of Figure 3, are quite similar, suggesting that dissociative ionization of naphthalene and azulene gives rise to the same $C_8H_6^+$ species.[30] The minor differences between spectra a and b of Figure 3 with respect to the relative intensities of the $C_mH_n^+$ fragment groups are attributed to slightly different focusing conditions under which the actual spectra shown were obtained (see Experimental Section). Compared to Figure 3, a and b, the recovery signals decrease to about a half in Figure 3, c and d, but are roughly twice as abundant in Figure 3, e and f. For example, the ratios $C_8H_6^+/C_6H_2^+$ change from ca. 1.3 in Figure 3a and b, to ca. 0.8 in Figure 3c and d, and rise to 2.2 and 3.2 in Figure 3e and f. Variations in the fragmentation patterns are minor, however, among Figure 3a−f. The most pronounced differences occur with Figure 3f in which the characteristic $C_7H_n^+$ fragments are much more intense, e.g. the $C_7H_n^+/C_4H_n^+$ ratio is ca. 2 in Figure 3f, while it amounts to 0.1−0.2 in Figure 3a−e. In analogy to the interpretation of the CA spectra, the enhanced intensity of $C_7H_n^+$ fragments in Figure 3f can again be regarded as a reminiscence of the presence of a methyl group in the neutral triyne **4** used as a precursor. This observation indicates that at least to some extent ionization of 2,4,6-octatriyne (**4**) may form a long-lived, intact molecular ion (see below). Except Figure 3f, however, the obvious differences of the recovery-ion yields in the $^+NR^+$ spectra cannot be used to deduce any particular ion structures because the fragmentation patterns are far from being characteristic. For example, a characteristic fragment of the phenylacetylene ion $\mathbf{2}^+$ would be the phenyl cation, but the yield of $C_6H_5^+$ is low in Figure 3e. This behavior could in turn

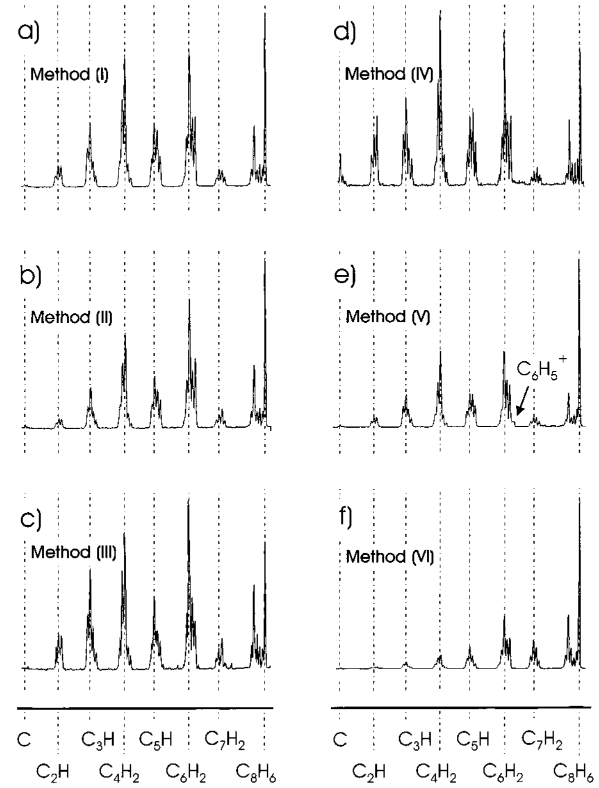


Figure 3. Neutralization reionization ($^+NR^+$, Xe/O_2, 80% T each) mass spectra of B(1)/E(1) mass-selected $C_8H_6^+$ generated by ionization of (a) naphthalene (method I), (b) azulene (method II), (c) 1-chlorobenzocyclobutene (method III), (d) 1,2-di(bromomethyl)benzene (method IV), (e) phenylacetylene (method V), and (f) 2,4,6-octatriyne (method VI).

be expected from the similarity of the CA spectra, because the $^+NR^+$ experiments preferentially involve fragmentations at the cationic stage,[20] and the latter do not allow to distinguish $C_8H_6^+$ ions.

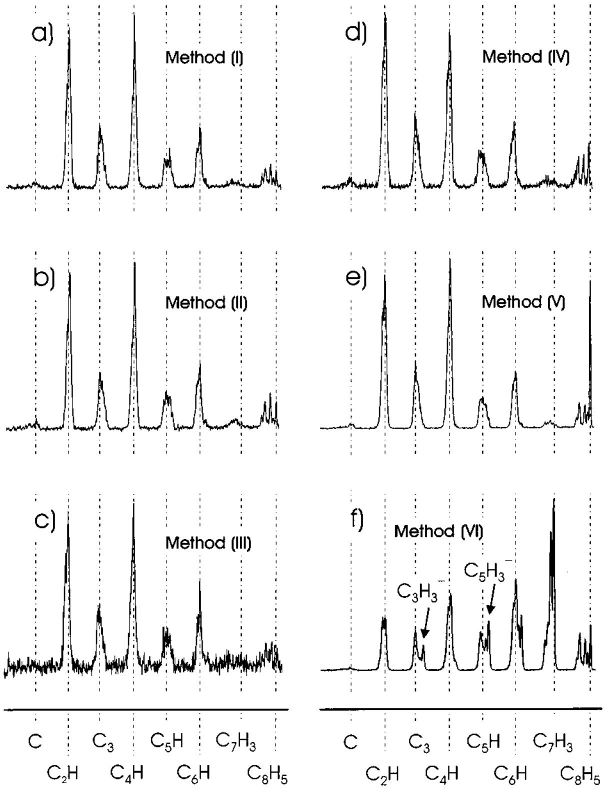


Figure 4. Charge reversal ($^+CR^-$, Xe, 60% T) mass spectra of B(1) mass-selected $C_8H_6^+$ generated by ionization of (a) naphthalene (method I), (b) azulene (method II), (c) 1-chlorobenzocyclobutene (method III), (d) 1,2-di(bromomethyl)benzene (method IV), (e) phenylacetylene (method V), and (f) 2,4,6-octatriyne (method VI). The reduced resolution in Figure 4 compared to the CA and NR spectra in Figures 2 and 3 is due to use of B(1) only for parent-ion selection (see Experimental Section).

CR Mass Spectra. Clearly, a successful structural discrimination of possible $C_8H_6^+$ isomers must apply a fragmentation scheme which does not involve cations. A promising perspective in this respect are $^+CR^-$ experiments,[14,20] in which the cations are converted to anionic species by two electron transfers (ETs), occurring either stepwise (two single-ET) or in a direct manner (one double-ET).[31] Charge inversion of cations is quite a demanding experiment because it requires the interconversion of cations to anions which often bear rather different geometries and stabilities. Furthermore, electron attachment to a fast neutral in a high-energy collision is always quite endothermic. Accordingly, electron detachment is likely to occur, and only fragments having considerably positive electron affinities (EAs) are detected in most cases.[32] Another, major disadvantage of $^+CR^-$ is that the effective charge-reversal yields are rather low and require maximum sensitivity;[20,31] therefore, intensity variations by less than a factor of 2 are considered insignificant in the present study. On the other hand, precisely these conditions may permit structural discrimination via direct bond cleavages revealing the connectivity of the precursor cations.[14] Thus, if a certain fragment having a significant EA can be formed from the precursor structure by a single bond rupture, it is likely to be observed in the corresponding $^+CR^-$ experiment. Otherwise, nonspecific, multistep fragmentations prevail, which are not at all structurally diagnostic. For hydrocarbons[14b,31a,33] these circumstances lead preferentially to formation of hydrogen-depleted carbon oligomers such as C_m^- and C_mH^- (here, $m = 2-8$) which are known to have sizable EAs;[34] note that for $m = 5$ also some $C_5H_2^-$ is observed, suggesting a particular stability of anions having this composition.[35]

Despite appreciable electron affinities of some PAHs,[36] none of the $^+CR^-$ spectra exhibits a recovery signal due to the $C_8H_6^-$ anion (Figure 4); also at highest sensitivity using single-ion monitoring, no significant recovery signals were found. In addition to the nonspecific, hydrogen-depleted $C_mH_n^-$ fragments ($m = 2-8$, $n = 0$, 1), all spectra show $C_8H_3^-$ and $C_8H_5^-$ signals, though in considerably different amounts. Based on the fragmentation patterns, the $^+CR^-$ spectra can be categorized as follows. In Figure 4a−d, the $C_2H_n^-$ and $C_4H_n^-$ fragments ($n = 0$, 1) predominate; in addition, a triplet of C_8H^-, $C_8H_3^-$, and $C_8H_5^-$ ions in comparable amounts is observed in the parent-ion region. In these spectra, the intensity variations of the fragment ions are minor and within experimental error. Figure 4e shows a similar fragmentation pattern, except a characteristically large yield of $C_8H_5^-$. This is precisely the anionic fragment expected for $^+CR^-$ of ionized phenylacetylene, **2**$^+$, i.e., the acetylide ion $C_6H_5C{\equiv}C^-$. Figure 4f is entirely different from the other $^+CR^-$ spectra and exhibits a pronounced $C_7H_3^-$ fragment, which can directly be attributed to the loss of a methyl radical from structure **4** to afford the corresponding acetylide, i.e., $H_3C-C{\equiv}C-C{\equiv}C-C{\equiv}C^-$. In addition, some other hydrogen-rich anions are observed in Figure 4f, e.g. the complementary fragments $C_5H_3^-$ and $C_3H_3^-$, which can be assigned to cleavage of the C(3)−C(4) bond in **4**, i.e., $H_3C-C{\equiv}C-C{\equiv}C^-$ and $H_3C-C{\equiv}C^-$, respectively. These observations can be considered as direct evidence for the preservation of the octatriyne skeleton. Hence, we conclude that, at least in part, **2**

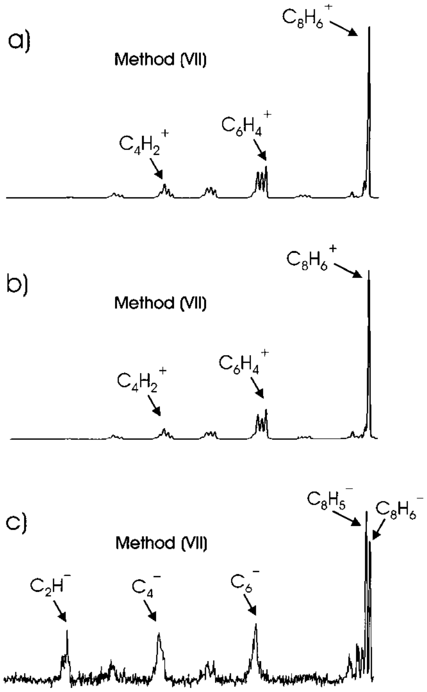


Figure 5. (a) Charge reversal ($^{-}$CR^{+}, O_2, 80% T) and (b) neutralization reionization ($^{-}$NR^{+}, O_2/O_2, 80% T each) mass spectra of B(1)/E(1) mass-selected $C_8H_6^-$ generated by chemical ionization of 1,3,5,7-cyclooctatetraene with N_2O as reagent gas (method VII). (c) Neutralization reionization ($^{-}$NR^{-}, O_2/Xe, 80% T each) mass spectrum of B(1) mass-selected $C_8H_6^-$. The reduced resolution in Figure 5c is due to use of B(1) only for parent-ion selection (see Experimental Section).

as well as **4** have retained their structures upon ionization to the corresponding cations, a conclusion which could not have been deduced from the MI, CA, CS, and NR mass spectra discussed above.

C_8H_6 from Cyclooctatetraene. Inspired by recent spectroscopic studies of the cycloocta-1,3,5-trien-7-yne anion,[37] we also examined the $C_8H_6^-$ ion which is accessible by chemical ionization of cyclooctatetraene with N_2O in the negative ion mode. In order to probe whether structure **6**$^-$ can be inferred from electron-transfer experiments in high-energy collisions, the so-formed $C_8H_6^-$ was subjected to $^{-}$CR^{+}, $^{-}$NR^{+}, $^{-}$NR^{-}, and $^{-}$CR^{+}/CA experiments. The $^{-}$CR^{+}, $^{-}$NR^{+}, and $^{-}$NR^{-} mass spectra are characterized by pronounced recovery signals (Figure 5). This result confirms the stability of neutral cycloocta-1,3,5-trien-7-yne already demonstrated by Kato et al.[37a] The $^{-}$CR^{+} and $^{-}$NR^{+} spectra obtained via method VII are almost identical, except for a slightly enhanced survivor-ion yield in the latter. In terms of the recently developed NIDD scheme (NIDD = neutral and ion decomposition difference)[31,38] for a quantitative comparison of CR and NR spectra, this similarity indicates that neutral **6** is stable toward fragmentation as well as unimolecular rearrangements when formed by electron detachment of **6**$^-$. The slight increase of the recovery signal in Figure 5b compared to Figure 5a can be attributed to poor Franck−Condon overlap between the anionic and the cationic species due to geometry differences, such that stepwise ET (e.g. NR) is likely to yield less fragmentation than direct transfer of two electrons in CR.[31,38] The existence of neutral C_8H_6 can further be inferred from the survivor ion observed in the $^{-}$NR^{-} spectrum (Figure 5c) which demonstrates that the neutral counterpart remains intact during the passage from the first to the second collision cell in the NR experiment (time scale ca. 1 μs). In conjunction with the complete absence of recovery signals in the $^{+}$CR^{-} experiments described above for methods I−VI, this finding implies that the $C_8H_6^-$ signal in Figure 5c is due to the reionization of genuine neutral **6**. In turn, we (indirectly) conclude that the eight-membered carbocycle **6** does not contribute to the structural manifold of the $C_8H_6^+$ cations made via methods I−VI because otherwise recovery signals were expected. Interestingly, structural insight can again only be gained from the analysis of the $^{-}$NR^{-} experiment, while the $^{-}$CR^{+} and $^{-}$NR^{+} spectra on their own are not informative in this respect because the fragmentations at the cationic stage are nonspecific and qualitiatively resemble those observed in the CA spectra with methods I−VI as described above.[39] In fact, the $^{-}$CR^{+}/CA spectrum of $C_8H_6^+$ obtained by charge inversion of $C_8H_6^-$ as well as the CA, $^{+}$NR^{+}, and $^{+}$CR^{-} spectra of the $C_8H_6^+$ ion generated by dissociative ionization of cyclooctatetraene in the positive ion mode (all not shown) are between those obtained with methods I and III. Therefore, we conclude that structure **6** is stable at the anionic as well as the neutral stage, but it collapses to other isomers as a cation.

Discussion

Considering the results presented above, it can be concluded that despite its poor sensitivity $^{+}$CR^{-} is the superior method for a structural characterization of the $C_8H_6^+$ isomers under study. Specifically, $^{+}$CR^{-} give rise to some structurally indicative fragmentations for the different hydrocarbon isomers, while the MI, CA, CS, and NR experiments are much less diagnostic. Therefore, the title problem of the unknown $C_8H_6^+$ structures formed upon dissociative ionization of naphthalene can be tackled by comparing the $^{+}$CR^{-} spectra along with some complementary information derived from the NR experiments.

In the analysis with regard to the structures of the $C_8H_6^+$ species formed from naphthalene, two aspects need to be considered: (i) the comparative analysis of the fragmentation patterns observed experimentally, and (ii) some more general energetic considerations which arise from the threshold for loss of acetylene from naphthalene ion.

The CA spectra of the $C_8H_6^+$ ions made via methods I−VII hardly exhibit any differences and do not allow any structural assignment. This failure is due to both, the large energy demands of conceivable fragmentations and possible effects of the ions' internal energies.[7,28] As far as the $^{+}$NR^{+} spectra are concerned, four different patterns occur. Among methods I−V, naphthalene and azulene (methods I and II) form one group which differs from methods III and IV as well as V based on the intensities of the recovery signals (see below). The spectrum obtained with method VI is further distinguished by the more intense $C_7H_n^+$ fragments. Again, the $^{+}$NR^{+} yields may depend on the actual internal energy contents of the ions under study, but this effect is diminished as compared to the CA experiments. For example, the obvious difference of the CA mass spectra c and d in Figure 2 is ascribed above to internal energy effects, yet the corresponding $^{+}$NR^{+} spectra (Figure 3c and d) obtained with the same precursors are much more similar.[40] In other words, the Franck−Condon effects in vertical neutralization and reionization[20a,41] are more important than the actual internal energy content in the precursor ions. In the context of the present analysis let us therefore assume that methods III and IV give rise to the same manifold of $C_8H_6^+$ ions.

The $^{+}$CR^{-} spectra are more or less identical for methods I−IV, while those obtained with methods V and VI are clearly distinguished. Most significantly, the different patterns observed in Figure 4, e and f, can directly be related to the underlying precursor structures, i.e., an intense $C_6H_5C{\equiv}C^-$ fragment from **2**$^+$ and a pronounced $H_3C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C^-$ anion due to dissociative charge inversion of **4**$^+$. Therefore, we conclude quite safely that at least parts of **2** and **4** retain their connectivity and form the corresponding molecular cations upon electron ionization. This conjecture also accounts for the different survivor-ion yields in the $^+NR^+$ spectra with these precursors. If we now assume that methods III and IV give rise to genuine **1**$^+$, the difference of the $^+NR^+$ spectra between methods I–IV suggest that at least one additional structure different from **1**$^+$ must contribute to the $C_8H_6^+$ species generated from ionized naphthalene. Internal energy may also play a role, but as discussed above the close similarities between the Figure 3a and b, versus Figure 3c and d, respectively, disfavor this option. Next, comparison of the $^+CR^-$ data disputes structures **2** and **4** as probable candidates for this additional component (see below). The $^-CR^+$, $^-NR^+$, and $^-NR^-$ data obtained with method VII further discount involvement of structure **6** for the naphthalene case because any significant contribution of structure **6** to the $C_8H_6^+$ species is expected to give rise to a detectable recovery signal upon $^+CR^-$, which is not observed experimentally.

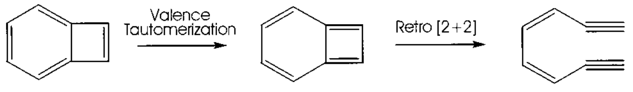
As mentioned above, some additional structural implications can be derived from mere energetic considerations. Thus, the threshold for acetylene loss from ionized naphthalene has been determined as 101.7 ± 5 kcal/mol.[12] Combined with the heats of formation ($\Delta_fH°$) of naphthalene ion (223.6 kcal/mol)[36] and acetylene (54.5 kcal/mol),[36] we arrive at an upper limit of $\Delta_fH° \leq 270.8 \pm 5.3$ kcal/mol for the $C_8H_6^+$ species formed. The mere magnitude of this value excludes high-energy isomers such as some acyclic polyynes and cumulenes. For example, literature data[36] can be used to estimate the heat of formation of neutral 2,4,6-octatriyne as $\Delta_fH°$(**4**) ≈ 140 kcal/mol via isodesmic reactions.[42] Together with IE(**4**) = 8.6 eV,[43] we arrive at $\Delta_fH°$(**4**$^+$) ≈ 338 kcal/mol, which is much above the upper bound defined by the threshold measurement. In addition to the putatively prohibitive energy requirements for the barriers involved en route to the substantial rearrangement from the naphthalene structure to that of an acyclic triyne, generation of **4**$^+$ at threshold for loss of acetylene from naphthalene ion can thus be ruled out on mere thermochemical grounds. Similar conclusions are implied for several other polynes as well as cumulenes (see below).

With respect to the problem posed by the studies of Lifshitz and co-workers,[11,12] i.e., the distinction between structures **1** and **2**, our experimental results clearly disfavor the latter isomer as a major component. An important question is, however, whether **2**$^+$ contributes to the $C_8H_6^+$ ions generated from naphthalene as a minor component. This aspect is particularly important because our methods do not ionize at threshold and may thus sample an ensemble of structures rather than a single isomer. Strictly speaking, a quantitative analysis of NR and CR spectra is impossible as long as one cannot guarantee that a certain method gives a "pure" ion beam consisting of a single structure (or a well-defined mixture of isomers). Moreover, the NR and CR efficiencies may tremendously differ for the various structures.[20] For a semiquantitative analysis of this aspect, let us compare spectra a and e of Figure 4 once more by considering two extreme cases. First, we assume that the ion beam formed from phenylacetylene via method V is virtually "pure" **2**$^+$ and that **2**$^+$ is the only source of the $C_8H_5^-$ fragment. Accordingly, a superposition of spectra a and e implies that no more than about 10% of the $C_8H_6^+$ ions formed from naphthalene via method I can correspond to **2**$^+$. For the other extreme, let us assume that only a very small fraction (<1%) of **2**$^+$ remains intact when generated via method V, and that dissociative charge inversion to $C_6H_5C{\equiv}C^-$ occurs with a very large efficiency compared to other isomers. Consequently, the contribution of **2**$^+$ to the $C_8H_6^+$ ions formed from naphthalene must even be much lower in this case. Given the reasonable assumption that the mechanism for expulsion of C_2H_2 from ionized naphthalene obeys a regular energy behavior, i.e., formation of a certain isomer at threshold and possible involvement of other species at higher energies, we can therefore quite safely conclude that **2**$^+$ does not contribute to the $C_8H_6^+$ ions formed at threshold from ionized naphthalene. In other words, if the contribution of **2**$^+$ to the ion beam made via method I is below 10%, then it is expected to be even lower than that if ionization occurs close to the appearance energy of $C_8H_6^+$ from naphthalene. This conclusion does certainly not prove, but coincides with, the prediction of Ling et al.[11] that only **1**$^+$ is formed upon unimolecular dissociation of naphthalene ion.

It is interesting to note that this kind of rough quantification of the $^+CR^-$ mass spectra does not work always because the $^+CR^-$ efficiencies may differ tremendously. In fact, the contribution of intact **2**$^+$ to the ion beam formed in method V may vary between 100% and almost zero. This is because Figure 4a–d does not display any signals which are not observed in Figure 4e. Given the possibility of extremely large differences in the $^+CR^-$ efficiencies, even a minuscule amount of **2**$^+$ may therefore account for the spectrum shown in Figure 4e. Similarly, method VI could generate an ion beam which may either be pure **4**$^+$ or almost entirely consist of other isomers. On the other hand, the same type of analysis applied above implies that the contribution of **4**$^+$ to the ions formed via methods I–V is less than 1%, because the characteristic $C_7H_3^-$ signal of Figure 4f vanishes in the noise in Figure 4a–e. From a more general point of view, the $^+CR^-$ experiments can be described as follows: Irrespective of the actual structure, every $C_8H_6^+$ ion gives rise to a nonspecific "background" of hydrogen-depleted $C_mH_n^-$ signals ($m = 2–8$, $n = 0, 1$). Only if some direct, and preferentially energetically low-lying, bond cleavages give rise to fragments having considerable EAs, certain fragments peak out of the background. Given the reasonable assumption that the $^+CR^-$ efficiencies largely differ in direct versus multistep, nonspecific fragmentations, charge reversal is therefore a rather sensitive method for the characterization of isomeric mixtures but cannot be applied in every case. Further, the overall sensitivity of the $^+CR^-$ process is not satisfactory due to the low efficiency of double ET from the target to the projectile in keV collisions. Although far from being trivial, the latter aspect is by and large technical, and substantial improvements may be achieved by variation of the experimental conditions.[44]

What remains to be clarified is the difference between the $^+NR^+$ spectra obtained with methods I and II compared to III and IV. Apparently, dissociative ionization of naphthalene and azulene (methods I and II) gives rise to the same $C_8H_6^+$ structure(s),[30] while the precursors used in methods III and IV give rise to a different manifold. For the time being, our experiments cannot provide definitive answers in this respect. Notwithstanding, we can offer some speculations which may serve as guidelines for further research. At first, acyclic species such as **4**$^+$ can be excluded due to the experimental results as well as some simple energetic criteria. Similarly, involvement of structures **2** and **6** appears improbable in view of the data obtained with methods V and VII. The absence of hydrogen-rich fragments in the $^+CR^-$ spectrum with method I further suggests that the hydrogen atoms are more or less equally distributed over the carbon backbone. Many other putative $C_8H_6^+$ isomers do probably not fulfill the energetic requirements defined by the threshold for loss of acetylene from ionized

SCHEME 1



1 **13**

naphthalene (see above). Moreover, the difference between methods I and II versus III and IV may entirely be due to the fact that we do not apply threshold ionization. Notwithstanding, as the ensemble of conceivable C_8H_6 structures is enormous,[17] further experimental and in particular theoretical studies are indicated to explore the potential-energy surface of this interesting hydrocarbon ion in more detail.

Finally, it is worthwhile to pay attention to one particular aspect of the $C_8H_6^+$ manifold. As stated above, several acyclic $C_8H_6^+$ are unlikely to be formed from naphthalene ion at threshold for acetylene loss. The fully conjugated octa-3,5-diene-1,7-diyne (**13**),[45] however, represents a plausible structure for $C_8H_6^+$, not only because of its low IE (7.8 eV)[46] but in particular if one considers the close generic similarity to the naphthalene skeleton. Thus, a sequence starting with valence tautomerization and followed by a retro-[2+2]-cycloaddition (Scheme 1) provides an attractive route for an interconnection between the bicyclic structure **1** and the open-chain isomer **13** (either neutral or charged).

In this respect, the charge reversal approach highlighted above fails and indeed cannot provide any further structural insight because structures **1** and **13** bear the same connectivities of C and H atoms. For example, on the basis of the arguments outlined above, a characteristic fragment of $\mathbf{13}^+$ in a $^+CR^-$ experiment would be the acetylide ion $HC{\equiv}C{-}CH{=}CH{-}CH{=}CH{-}C{\equiv}C^-$. This corresponds, however, to the $C_8H_5^-$ species which is observed in all the $^+CR^-$ spectra obtained with methods I−VI. While the pronounced $C_8H_5^-$ fragment in Figure 4e is considered as direct evidence for $\mathbf{2}^+$, the corresponding signal in Figure 4a therefore provides neither positive nor negative evidence, but is simply inconclusive. In contrast to $\mathbf{4}^+$ (see above), other characteristically hydrogen-rich fragments are further not expected to be formed from either $\mathbf{1}^+$ or $\mathbf{13}^+$ because the hydrogen atoms are almost equally distributed across the carbon backbone; the same arguments equally well apply for most other cyclic structures, e.g. **5** and **7**. On the basis of the few known thermochemical data of C_8H_6 compounds,[36] the acyclic structure $\mathbf{13}^+$ in fact appears as quite an attractive candidate for the $C_8H_6^+$ ion formed upon dissociative ionization of naphthalene. Thus, the Lias compendium[36] gives $\Delta_fH°(\mathbf{13}^+) = 278$ kcal/mol compared to $\Delta_fH°(\mathbf{2}^+) = 276$ kcal/mol and $\Delta_fH°(\mathbf{1}^+) \leq 291$ kcal/mol; on the basis of the theoretical data given by Ling et al.[11] $\Delta_fH°(\mathbf{1}^+) \approx 272$ kcal/mol appears more adequate. All values roughly fit with $\Delta_fH°(C_8H_6^+) \leq 270.8 \pm 5$ kcal/mol derived from the threshold measurements. Considering the experimental uncertainties,[47] $\mathbf{13}^+$ thus may indeed also fulfill the energetic requirements for acetylene loss from naphthalene ion.[48] Moreover, facile decyclization of fused cyclobutane derivatives upon ionization is known from related examples[49] and also likely to be favored on entropic grounds.[50] Besides other (poly)cyclic $C_8H_6^+$ isomers, the acyclic species $\mathbf{13}^+$ may therefore also be regarded as a hitherto overlooked, but plausible product of the dissociative ionization of naphthalene.

Conclusions

A combination of different mass-spectrometric experiments indicates that loss of acetylene upon dissociative ionization of naphthalene does not lead to phenylacetylene ion, $\mathbf{2}^+$, as a major contribution. Formation of several acyclic $C_8H_6^+$ species can also be ruled out based on the experimental findings as well as complementary energetic considerations. Further, the experimental data disfavor formation of a $C_8H_6^+$ species having an eight-membered ring. These results are in accordance with the previously suggested generation of ionized benzocyclobutadiene, $\mathbf{1}^+$, upon loss of acetylene from naphthalene ion.[11] However, some acyclic conjugated enynes such as $\mathbf{13}^+$ as well as more elusive structures, e.g. **5** or **7**, are conceivable and demand further consideration of the rich C_8H_6 manifold by experimental and in particular theoretical means. Considering the rapid progress of theoretical methods, it is indeed indicated that theoreticians proceed with the next step,[51] because a more comprehensive treatment even only including the local minima would very much assist and guide further research on this topic. For example, the somewhat ambiguous data[48] for the heats of formation of the neutral polyynes **4** and **13** may easily be revisited by modern theoretical studies, while experimental determinations of $\Delta_fH°$ are a profound challenge for sensitive substances such as **4** and **13**.

In a more general sense, the present results demonstrate that charge inversion of cations, although quite inefficient, is a complementary and particularly valuable tool for the structural characterization of hydrocarbon cations.[14b,33] The low sensitivity of $^+CR^-$ is possibly prohibitive for analytical applications of this method, but in terms of structural insight it appears to be a versatile, though not ideal, alternative to determine ion structures when other techniques fail. Hopefully, further developments may lead to more efficient methods for electron attachment to fast moving neutrals in order to extend the perspectives of $^+CR^-$, $^+NR^-$, and $^-NR^-$ methods.

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