# Energetics of the naphthalene/azulene monocation isomerization: density functional and coupled cluster calculations †‡

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The energetics of isomerization between the azulene and naphthalene radical cations have been investigated using the hybrid density functional method B3LYP with the cc-pVDZ basis sets. CCSD/cc-pVDZ energy calculations were also carried out for selected points along the reaction coordinate. The transition state barrier energies for isomerization are lower than the dissociation limit of $C_8H_6^{\bullet+}$ (benzocyclobutadiene$^{\bullet+}$) + $C_2H_2$ deduced earlier. A key intermediate is a hydrogen shifted naphthalene isomer analogous to the intermediate suggested in the Dewar–Becker isomerization mechanism for neutral azulene. The norcaradiene isomer of the Dewar–Becker mechanism was found to be a transition structure in the ionic system. Results of the present density functional theory (DFT) and coupled cluster calculations are discussed in the light of recent experimental evidence.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their cations have been proposed as carriers of the unidentified emission bands observed from the interstellar medium.[1,2] This has led to considerable work concerning the photoionization and photofragmentation of PAHs. One of the most interesting remaining open questions is to what extent do PAH cation radicals undergo isomerization to common intermediates below their dissociation thresholds. The mass spectral fragmentations of isomeric PAHs are extremely similar. One of the earliest electron impact studies of the azulene/naphthalene pair[3] has already suggested ionic intermediates common to both compounds. An early isotopic scrambling study[4] has suggested that azulene$^{\bullet+}$, **1**, only slowly isomerizes to the common intermediate formed from naphthalene$^{\bullet+}$, **2**, and azulene$^{\bullet+}$ but that the rearranged molecular ions of azulene have the same structure as those of naphthalene prior to the loss of $C_2H_2$. A more recent synchrotron photoionization and photofragmentation study of the azulene/naphthalene pair[5] came to a similar conclusion to that of the earlier electron ionization study,[3] namely that identical products are formed from the two isomers because of the constant difference between the fragment appearance energies (AEs) for naphthalene and azulene, which is equal to the difference in the heats of formation of the neutral parents. Several different ionization and activation methods were applied to larger PAH cations[6] and the conclusion was that rearrangement is favored because the ions have a high internal energy capacity as indicated by the abnormally large energies required for dissociation. Time resolved photoionization mass spectrometry was applied to naphthalene[7] and to the $C_{14}H_{10}$ isomers, phenanthrene and anthracene.[7,8] No clear cut conclusion was reached concerning whether fast isomerization of the anthracene/phenanthrene cation radical pair below their respective dissociation limits takes place. Microcanonical rate energy dependences, $k(E)$, deduced for H-loss and acetylene elimination, were plotted as a function of the absolute energy (*i.e.* relative to fourteen carbon atoms and five hydrogen molecules as the zero of the energy scale). The two sets of $k(E)$ curves, for anthracene and phenanthrene respectively, did not coalesce into one, as they should have in the case of a fast isomerization.[8] Furthermore, the H-loss reactions seem to lead to different products from anthracene and phenanthrene, on the basis of the ionic heats of formation deduced. On the other hand, acetylene elimination gives metastable peak shapes and kinetic energy releases which are nearly the same for the two compounds, demonstrating that dissociations probe the same regions of the potential energy hypersurface.[8] Density functional calculations[9] have also indicated that the two precursor molecules form the same (biphenylene$^{\bullet+}$) fragment ion upon acetylene elimination. Finally, there are two recent studies which led to seemingly contradictory results concerning the isomerization of the azulene/naphthalene pair.[10,11] In the first study, the naphthalene and azulene radical cations were formed by electron impact and subjected to visible and UV radiation from a xenon arc lamp.[10] While azulene was found to be photostable, naphthalene was completely photodissociated. This led to the conclusion[10] that a common intermediate structure as proposed by Jochims *et al.*[5] is not produced and led to the suggestion that mechanisms of ionization and energy deposition in naphthalene and azulene are not similar. However, the structures of the $C_8H_6^{\bullet+}$ cations formed upon acetylene loss from ionized naphthalene and azulene were found to be identical in the second study,[11] which used charge reversal from cations to anions, a method which was demonstrated to yield structurally indicative fragmentations.[11] The results were in accordance[11] with the previously suggested generation of ionized benzocyclobutadiene[9,12] from ionized naphthalene and did not support the access from ionized azulene to cyclic isomers, *e.g.* ionized pentalene, having other than six-membered rings.

One way of deciding whether isomerization is fast on the

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† This paper is in memory of Bob Squires, a good friend and an excellent scientist.

‡ Tables of B3LYP/cc-pVDZ computed harmonic frequencies and infrared intensities of all the structures appearing in Table 2 are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/2383, otherwise available from BLDSC (SUPPL. NO. 57628, pp. 2) or the RSC library. See Instructions for Authors available *via* the RSC web page (http://www/rsc.org/authors).

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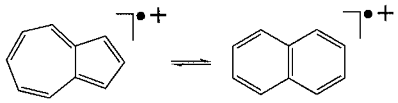
timescale of dissociation is to calculate by *ab initio* methods the isomerization barriers and compare them with dissociation limits calculated with the same level of theory. We have previously calculated,[9] at various levels of *ab initio* and density functional theory (DFT), the dissociation energies $D_0$ for acetylene loss from benzene, naphthalene and anthracene radical cations. In the present paper we present results of DFT calculations for the isomerization of the (azulene$^{\cdot+}$,**1**)/(naphthalene$^{\cdot+}$,**2**) radical ion pair, Scheme 1, including intermediates residing in potential energy minima and transition state structures. We made a special effort to search for the common intermediate suggested by previous research groups.[5,13]



**1** **2**

**Scheme 1**

## Computational details

### Isomerization mechanism

Three unimolecular mechanisms have been suggested for the thermal isomerization of neutral azulene to naphthalene.[14] Two of these mechanisms have been reviewed and discussed by Jochims *et al.*[5] as possibilities for the ionic rearrangement mechanism. The first of these is the Scott mechanism,[15] which involves the cleavage of the transannular bond in azulene (or naphthalene, in the case of the reverse reaction). The second is the Dewar–Becker mechanism[13,16] which involves a norcaradiene azulene valence tautomer intermediate and a carbene intermediate which is a hydrogen shifted naphthalene isomer. Jochims *et al.*[5] considered as possible intermediates for the ionic rearrangement (Scheme 1) and for the major dissociation reactions of the molecular radical cations, the ionic analogues of intermediates of both the Scott and the Dewar–Becker mechanisms. The hydrogen shifted naphthalene radical cation, **3**, was suggested as the precursor for H$^{\cdot}$, $C_2H_2$, $H_2$ and $C_4H_2$ eliminations from naphthalene and azulene, however no high level *ab initio* calculations were performed. MNDO calculations by Dewar and co-workers[13] have demonstrated the Scott mechanism to be a high-energy path for the neutral system. In the present paper we concentrate on DFT and coupled cluster calculations of the Dewar–Becker mechanism for the ionic system.

### Computational methods

Density functional calculations have been carried out using the GAUSSIAN94 package[17] running on a DEC Alpha TurboLaser 8400 at the Institute of Chemistry, on a Cray J90 with 32 CPUs at the Inter-University Computation Center, and on an SGI Origin 2000 at the Weizmann Institute of Science. The calculations employed the B3LYP (Becke three-parameter Lee–Yang–Parr) exchange-correlation functional[18,19] which combines the hybrid exchange functional of Becke[18] with the gradient-corrected correlation functional of Lee, Yang, and Parr.[19] The very good performance of B3LYP for geometries and harmonic frequencies has been noted before.[9]

Because of the size of the systems under consideration, only Dunning's cc-pVDZ (correlation consistent polarized valence double zeta[20]) basis set was considered, which is a [3s2p1d] contraction of a correlation-optimized (9s4p1d) primitive set. This set has also been employed in our previous study of the naphthalene radical cation dissociation threshold energy.[9] One of the major purposes of the present calculations is to compare isomerization barriers with dissociation thresholds at the same level of theory. The adequacy of the cc-pVDZ basis set for this type of study has been discussed before.[9]

Since correct reproduction of reaction barrier heights by B3LYP cannot necessarily be taken for granted,[21] we have in addition carried out single-point CCSD/cc-pVDZ (coupled cluster with all single and double substitutions[22]) calculations at the B3LYP/cc-pVDZ stationary points. Because of the low symmetry of some of the systems involved and the large number of electrons correlated, the inclusion of connected triple excitations by means of the CCSD(T) method[23] proved impossible with the available computational hardware, and we have not pursued this option further. Our previous work[9] suggests that the (T) contribution would not qualitatively affect the shape of the potential surface.

For technical reasons, the CCSD calculations were carried out using an unrestricted Hartree–Fock reference determinant, and unrestricted Kohn–Sham orbitals were used in the CCSD and B3LYP calculations. The CCSD energy was shown some time ago[24] to be intrinsically invariant to contamination by the next higher spin multiplicity, while it is well known[25] that open-shell systems exhibit much less spin contamination using B3LYP and other density functional methods than they would at the Hartree–Fock level.

## Results and discussion

The geometries calculated at the B3LYP/cc-pVDZ level are presented in Fig. 1 for the stable structures **1**, **2**, **3**, and **4** residing in potential energy minima, whose Hessian index is 0 indicating no negative eigenvalues of the Hessian. Structures **3** and **4** are hydrogen-shifted isomers of the naphthalene and azulene radical cations, respectively. Geometries calculated for transition structures **5**, **6**, **7**, and **8**, whose Hessian index is 1 indicating one negative eigenvalue, are presented in Fig. 2. We have considered two alternative reaction paths. These are shown in a very schematic fashion, without inclusion of double bonds or cation radical symbols (Scheme 2). In the first reaction path, the azulene radical cation, **1**, isomerizes first to a norcaradiene radical cation, **6**; the latter isomerizes to a hydrogen shifted naphthalene isomer, **3**, which isomerizes to naphthalene. This is the ionic equivalent of the Dewar–Becker mechanism.[13,16] In the second reaction path, azulene isomerizes first to a hydrogen shifted azulene structure, **4**, which isomerizes to a correspondingly hydrogen shifted norcaradiene isomer, **7**, followed by isomerization to naphthalene. We found that species **3** and **4** are genuine intermediates. They are separated from naphthalene, **2**, and azulene, **1**, by transition structures, **5** and **8**, respectively. On the other hand, the norcaradiene species, **6** and **7**, were found to be transition states on the ionic potential surface. Further details concerning dihedral angles of the structures are given in Table 1.

Absolute energies, zero point energies and relative energies calculated at the B3LYP/cc-pVDZ level for ions **1**–**8** are summarized in Table 2. The potential energy profile based on the B3LYP/cc-pVDZ relative energies is presented in Fig. 3. The energies are compared with the $C_8H_6^{\cdot+}$ (benzocyclobutadiene) + $C_2H_2$ dissociation limit calculated at the same level of theory.[9] All the intermediate structures and transition state barriers are lower in energy than the dissociation limit of 102.3 kcal mol$^{-1}$. At the CCSD/cc-pVDZ level the dissociation energy is lower by just 0.2 kcal mol$^{-1}$[9] but the transition state energy for ion **6** is lowered further by more than 4 kcal mol$^{-1}$ (see Table 2). We have calculated the two alternative reaction paths, the results for which are shown in Fig. 3. It is interesting to notice that the path corresponding to the Dewar–Becker mechanism requires less energy than the alternative path. In other words, azulene radical cations undergo first isomerization to the norcaradiene structure, **6**, by forming the extra carbon–carbon bond of the six-membered ring system, followed by formation of intermediate **3**, which is the hydrogen shifted naphthalene structure, rather than undergoing a hydrogen shift first to form intermediate **4**, followed by the norcaradiene

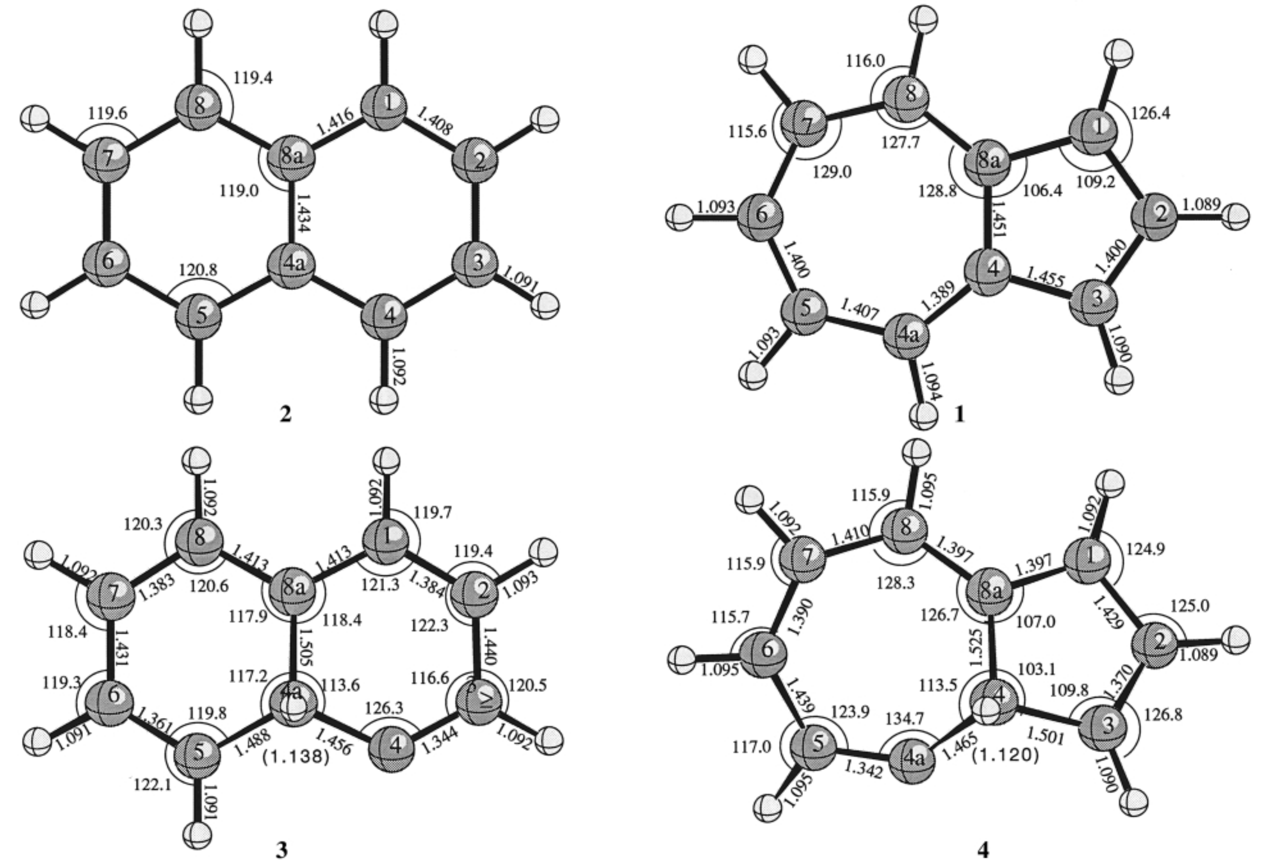


**Fig. 1** Structures of $C_{10}H_8^{\bullet +}$ isomers residing in potential energy minima. The numbering system used for the carbon atoms is conventional for naphthalene; the rest of the isomers are numbered in an internally consistent manner which views them as naphthalene isomers. **1**, azulene$^{\bullet +}$; **2**, naphthalene$^{\bullet +}$; **3**, hydrogen shifted naphthalene$^{\bullet +}$ (a shift of a hydrogen atom from carbon no. 4 to carbon no. 4a has taken place); **4**, hydrogen shifted azulene$^{\bullet +}$ (a shift of a hydrogen atom from carbon no. 4a to carbon no. 4 has taken place).

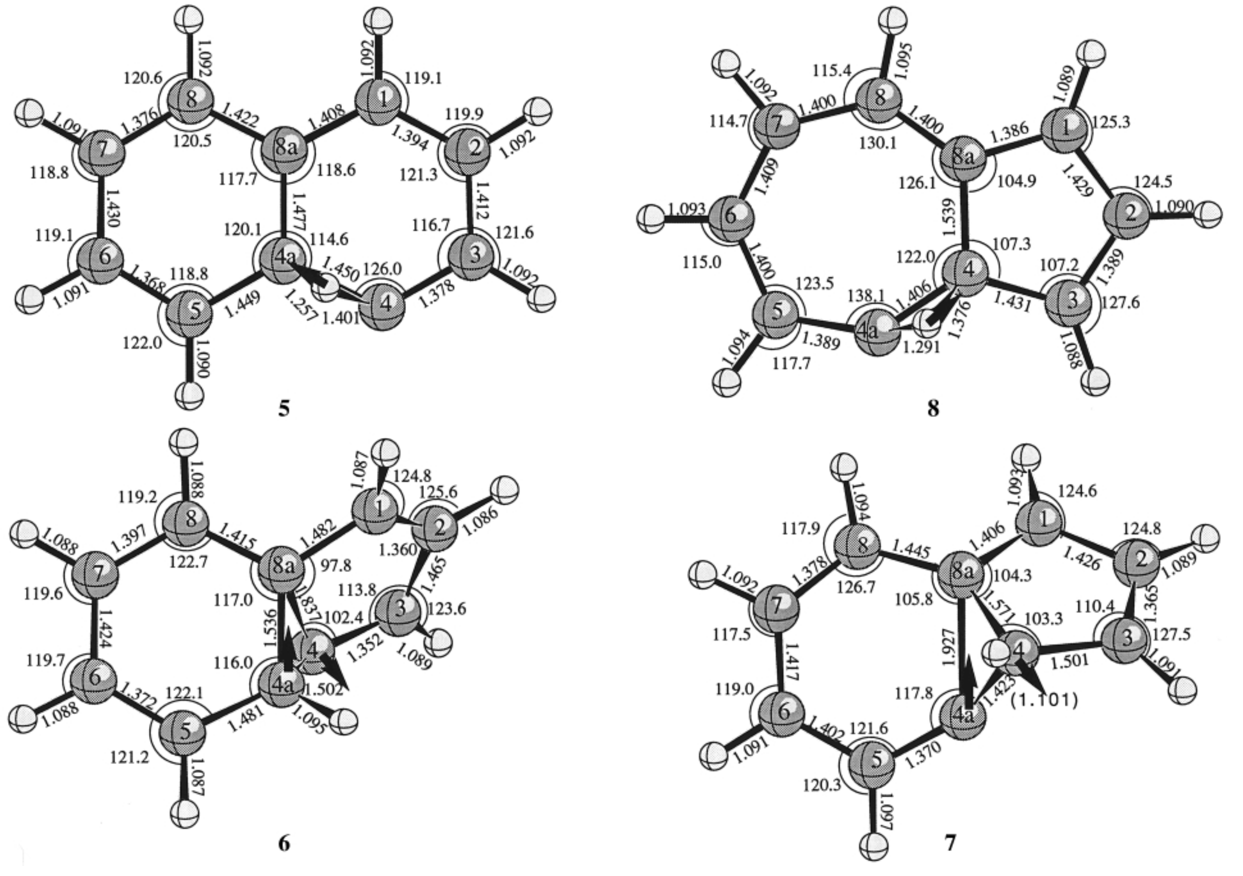


**Fig. 2** Structures of $C_{10}H_8^{\bullet +}$ isomers which are transition states along the isomerization paths between azulene$^{\bullet +}$ and naphthalene$^{\bullet +}$.

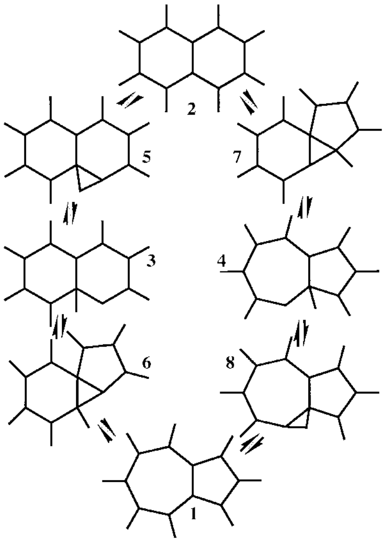
**Table 1** Selected dihedral angles (°) for ions **1** to **8** (Figs. 1 and 2)

| Dihedral angle | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| C8–C8a–C4a–C5 | 0.0 | 0.0 | 14.1 | 3.8 | 3.0 | −10.4 | 1.3 | −0.7 |
| C8a–C4a–C5–C6 | 0.0 | 0.0 | −11.8 | −15.3 | −1.9 | 10.9 | −3.1 | 2.6 |
| C7–C8–C8a–C4a | 0.0 | 0.0 | −8.8 | 11.2 | −2.2 | 3.8 | 3.6 | −1.3 |
| C1–C8a–C4a–C5 | 180.0 | 180.0 | −166.3 | −155.5 | −176.0 | 172.6 | −146.3 | −175.7 |
| C5–C4a–C4–C8a | 0.0 | 180.0 | 150.9 | −43.5 | 172.3 | 111.5 | −91.8 | 1.8 |
| C1–C8a–C4–C4a | 180.0 | 180.0 | 167.9 | −138.7 | 177.1 | 125.6 | −117.6 | −177.6 |
| C1–C8a–C4–C3 | 0.0 | 0.0 | −2.0 | −4.9 | 0.4 | −5.6 | −5.4 | 0.8 |
| C2–C3–C4–C8a | 0.0 | 0.0 | 1.7 | 4.6 | −0.5 | 2.4 | 4.3 | −0.7 |
| C1–C8a–C4a–C4 | 0.0 | 0.0 | −13.7 | 54.6 | −3.3 | −72.8 | 81.5 | 3.1 |
| C8a–C4a–C4–C3 | 180.0 | 0.0 | 12.6 | −124.3 | 4.5 | 74.1 | −100.3 | −178.0 |
| H8–C8–C7–C6 | 180.0 | 180.0 | 177.2 | 160.7 | 179.5 | −174.6 | 166.7 | −179.9 |
| H7–C7–C6–C5 | 180.0 | 180.0 | −179.4 | 173.9 | −179.3 | 180.0 | 178.6 | −179.1 |
| H6–C6–C7–C8 | 180.0 | 180.0 | −177.2 | −171.4 | −178.7 | 174.5 | −172.2 | 178.9 |
| H5–C5–C6–C7 | 180.0 | 180.0 | 178.5 | −164.7 | 179.6 | 177.3 | −176.6 | 175.8 |
| H1–C1–C2–C3 | 180.0 | 180.0 | −177.6 | 177.3 | −179.2 | 179.1 | 176.3 | 178.3 |
| H2–C2–C3–C4 | 180.0 | 180.0 | 179.8 | 177.0 | −179.4 | 179.0 | −179.0 | 178.5 |
| H3–C3–C2–C1 | 180.0 | 180.0 | 177.6 | −179.4 | 179.0 | 184.5 | 174.2 | 180.0 |
| H4–C4–C4a–C8a | 180.0 | 180.0 | 104.7 | 118.7 | 96.6 | 113.4 | 114.8 | 102.1 |

**Table 2** Summary of absolute energies (hartree), zero-point vibrational energies (kcal mol$^{-1}$) and relative energies, $\Delta E$ (kcal mol$^{-1}$). The cc-pVDZ basis set was used throughout

| Ion | *E*(B3LYP) | ZPVE[a] | *E*(CCSD) | Δ*E*(B3LYP) | Δ*E*(CCDD) |
|---|---|---|---|---|---|
| **1** | −385.60145 | 90.33 | −384.41464 | 18.1 | 17.8 |
| **2** | −385.63101 | 90.77 | −384.44367 | 0 | 0 |
| **3** | −385.51953 | 88.93 | −384.33466 | 68.1 | 66.6 |
| **4** | −385.50311 | 88.84 | | 78.3 | |
| **5** | −385.50865 | 87.25 | −384.32336 | 73.3 | 72.0 |
| **6** | −385.47693 | 87.45 | −384.29605 | 93.4 | 89.3 |
| **7** | −385.48191 | 87.15 | | 89.9 | |
| **8** | −385.46524 | 85.78 | | 99.0 | |

[a] B3LYP/cc-pVDZ values scaled by 0.985.



Scheme 2

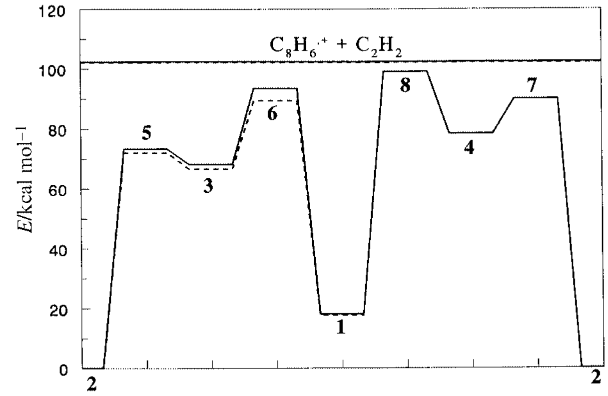


**Fig. 3** Potential energy profile at the B3LYP/cc-pVDZ level (continuous lines) and CCSD/cc-pVDZ level (dashed lines) for the azulene$^{\bullet+}$: **1**, naphthalene$^{\bullet+}$; **2**, isomerization *via* two alternative reactions paths. The structures of ions **1**–**8** are given in Figs. 1 and 2. The path leading from **1** to **2** *via* **6**, **3** and **5** is the ionic equivalent of the Dewar–Becker mechanism (see text and Table 2).

structure **7**. By the same token, naphthalene isomerizes to azulene by a hydrogen shift intermediate **3**, followed by the norcaradiene transition state **6**. We note that the computed B3LYP and CCSD energy profiles (Fig. 3) are not only close together but are also largely parallel. It appears to be very unlikely that more extensive calculations would reverse the order of the barrier heights for the two possible channels.

The hydrogen shifted naphthalene ion, intermediate **3**, is observed to play a central role as predicted.[5,13] Whether it is instrumental in producing all the major fragment ions from naphthalene as has been suggested by Jochims *et al.*[5] remains an open question. As noted earlier, the product ion formed with acetylene is benzocyclobutadiene$^{\bullet+}$[9,11] and not phenylacetylene$^{\bullet+}$ as had been proposed earlier.[5] It is not at all clear that intermediate **3** is advantageous for benzocyclobutadiene$^{\bullet+}$ formation. Whether the isomerizations are fast on the timescale of the dissociation threshold is also an open question. This question can possibly be solved by doing Rice–Ramsperger–Kassel–Marcus (RRKM) calculations of the microcanonical isomerization rate coefficients at the appropriate energies on the potential surfaces deduced here, using the properly scaled *ab initio* frequencies of the reactants and transition structures. (In order to facilitate such a study, our computed B3LYP/cc-pVDZ harmonic frequencies for all structures discussed in the present paper are available as supplementary material.[‡][26]) It would seem that the norcaradiene transition state **6** is rate determining. Acetylene elimination from naphthalene$^{\bullet+}$ can circumvent passage over the barrier of transition structure **6**, while that from azulene$^{\bullet+}$ cannot. This could be the reason for the seemingly conflicting results of references 10 and 11. What the DFT and CCSD calculations indicate is that, in agreement with Stolze and Budzikiewicz,[4] azulene$^{\bullet+}$, only slowly isomerizes to the common intermediate formed from **1** and **2**, but that the rearranged molecular ions of azulene have the same structure as those of naphthalene prior to the loss of $C_2H_2$. Finally, isomerization of the anthracene$^{\bullet+}$/phenanthrene$^{\bullet+}$ pair can take place *via* a similar mechanism to the one calculated here, namely anthracene isomerizes *via* a hydrogen shifted intermediate, to a norcaradiene transition state followed by a benzazulene intermediate which isomerizes back along similar intermediates to phenanthrene. Since the norcaradiene barrier is very close to the dissociation limit in the present calculation, increasing the number of degrees of freedom to the anthracene system might make the isomerization, which goes *via* tight transition states, even slower relative to the dissociation in the larger system.

## Conclusions

Naphthalene$^{\bullet+}$ isomerizes to azulene$^{\bullet+}$ *via* the Dewar–Becker mechanism at energies which are lower than its dissociation limit for acetylene elimination. The hydrogen shifted isomer, **3**, is a proper intermediate while the norcaradiene isomer, **6**, is a transition structure. Further *ab initio* and DFT calculations would be required for the following: a. deciding whether intermediate **3** is instrumental in the acetylene elimination; b. deciding whether a similar isomerization mechanism is important for the anthracene$^{\bullet+}$/phenanthrene$^{\bullet+}$ pair. RRKM calculations of rate energy dependences, $k(E)$ are required to ascertain the degree to which isomerization is fast at energies near or above the dissociation threshold.

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