

Density functional calculations on the loss of acetylene from the naphthalene radical cation

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Abstract

Ab initio (density functional) calculations on the loss of acetylene from the naphthalene radical cation produce possible reaction schemes similar to those for the corresponding dissociation of the benzene radical cation. The calculations did not succeed in showing that the barrier for dissociation to the benzocyclobutadiene fragment ion is lower than that for dissociation to the phenylacetylene cation as follows from experiment. Even calculations with much larger basis sets gave a total energy for the fragments which is about 5 kcal mol^{-1} too high. (Int J Mass Spectrom 214 (2002) 269–275) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dissociation of the naphthalene radical cation; Reaction schemes; Density functional calculations

1. Introduction

The mass spectra of polycyclic aromatic hydrocarbons have been the subject of a number of recent papers [1–8], both by experimental methods [1–5] and by ab initio calculations [6–8]. One of the major topics in these articles was the loss of the acetylene molecule from the naphthalene radical cation. On the basis of the calculated energies of the possible fragments it was concluded in [6,7] that the fragment ion formed has the benzocyclobutadiene structure and that other possibilities such as the phenylacetylene ion have (somewhat) higher dissociation limits. The conclusion that the fragment ion has the benzocyclobutadiene structure is in close agreement with the results from extensive experiments in [4] although the authors did not exclude some structures not consid-

ered before such as an acyclic structure obtained by a retro-[2 + 2]-cycloaddition of the benzocyclobutadiene ion.

In the present work, possible pathways for the formation of the phenylacetylene and benzocyclobutadiene fragment ions are studied by ab initio (density functional) calculations.

2. Methods

In order to keep the results comparable to those given in [7], the density functional calculations were done with Gaussian 98 [9] using the B3LYP functional with Dunning's cc-pVDZ (correlation consistent polarized double zeta) basis set [10]. Starting geometries for the transition states were obtained from calculations of possible reaction paths with either semi-empirical or ab initio methods using the

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4-31G basis set. In the latter case both Gaussian 98 [9] and GAMESS-UK [11] were used. Transition states were tested by a visualization of the vibration corresponding with the single imaginary frequency with VIBRAM [12].

3. Results

As mentioned in [7], the formation of phenylacetylene fragment ions from the naphthalene radical cation is only understandable when fragmentation is preceded by a large number of hydrogen shifts. Fig. 1 gives an overview of all structures that can be formed from the naphthalene radical cation by 1,2-hydrogen shifts. This figure clearly suggests that the only reasonable final intermediate in the fragmentation pathway is structure 5. This structure can be reached in many

different ways from the naphthalene radical cation 1. It should be noted, however, that there are two, essentially different, types of hydrogen shifts in Fig. 1. The horizontal arrows describe shifts of an sp^2 bonded hydrogen and the diagonal arrows of an sp^3 bonded hydrogen. As discussed previously [13], the barrier for this latter process is much lower than that for the first one. From these arguments we arrived at the scheme in Fig. 2 for the formation of the phenylacetylene fragment ion. The pathways shown in Fig. 2 are comparable to the pathways for the formation of the vinylacetylene fragment ion from the benzene radical cation as described in [14]. In a similar way, the formation of the benzocyclobutadiene radical cation will, very probably, be comparable to the formation of the cyclobutadiene fragment ion from the benzene radical cation via the Dewar benzene structure [14]. This leads to the reaction scheme shown in Fig. 3.

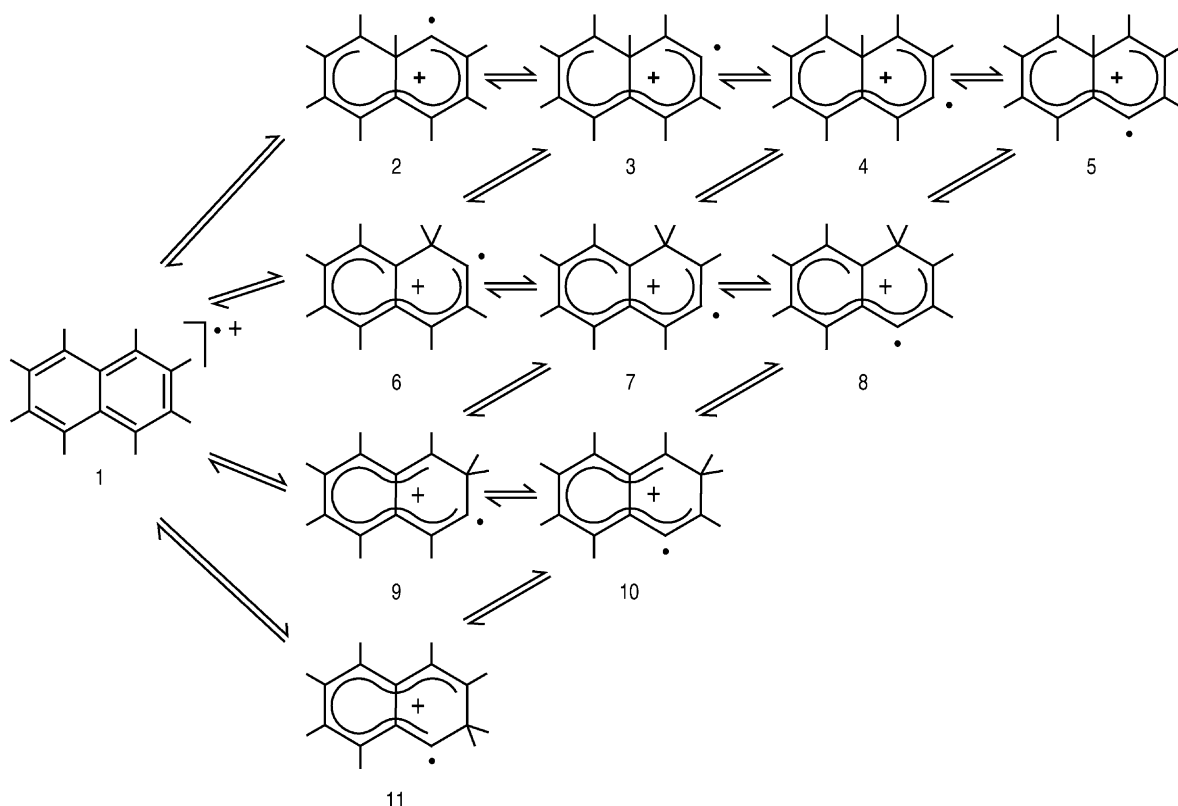


Fig. 1. Reaction scheme for hydrogen shifts in the naphthalene radical cation.

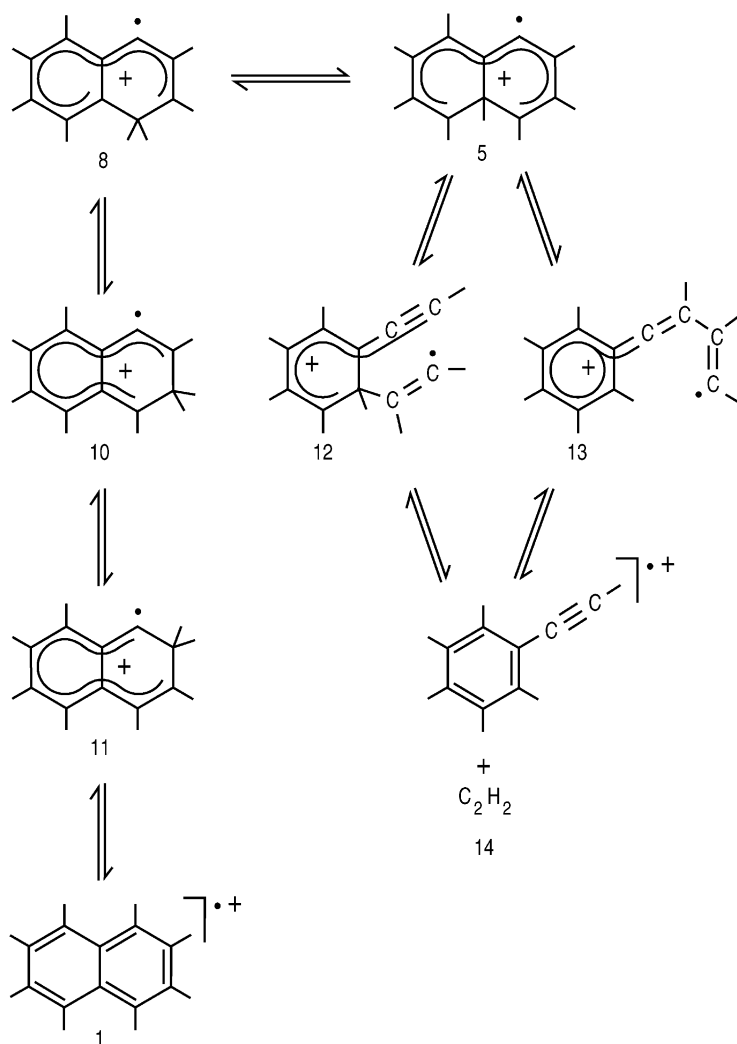


Fig. 2. Reaction scheme for the dissociation to the phenylacetylene ion.

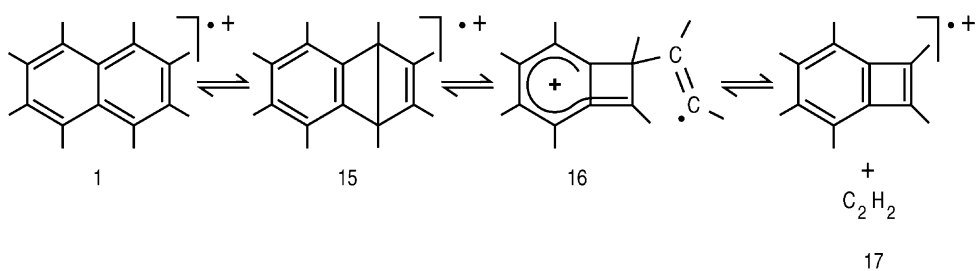


Fig. 3. Reaction scheme for the dissociation to the benzocyclobutadiene ion.

Table 1
DFT and ZPE energies of the different radical cation structures and transition states in Figs. 2 and 3 and relative energies (kcal mol⁻¹) corrected for the zero-point vibrational (ZPE) energy scaled with a factor of 0.985

	DFT	ZPE	ΔE
Acetylene (neutral)	-77.333227	0.026963	
Phenylacetylene	-308.106056	0.108566	
Benzocyclobutadiene	-308.111161	0.110374	
Open structure	-308.006574	0.103623	
Naphthalene 1	-385.631011	0.146871	0
Structure 5	-385.518602	0.143587	68.5
Structure 8	-385.552867	0.144737	47.7
Structure 10	-385.545262	0.144245	52.2
Structure 11	-385.548134	0.144651	50.6
Structure 12	-385.431242	0.138408	120.1
Structure 13	-385.474693	0.140002	93.8
Structure 14A (minimum)	-385.447285	0.136441	108.8
Structure 14B (minimum)	-385.444639	0.136114	110.3
Separated fragments ^a	-385.439283	0.135529	113.3
Structure 15	-385.498288	0.143251	81.2
Structure 16	-385.457745	0.140576	104.8
Structure 17 (minimum)	-385.450558	0.138104	107.8
Separated fragments ^a	-385.444388	0.137337	111.2
T _{1,11}	-385.534359	0.141488	63.6
T _{1,15}	-385.489568	0.141093	85.2
T _{5,8}	-385.510054	0.141493	72.6
T _{5,12}	-385.426959	0.137182	122.1
T _{5,13}	-385.450530	0.139113	108.5
T _{8,10}	-385.524609	0.141889	63.7
T _{10,11}	-385.515071	0.141546	69.5
T _{12,14}	-385.429422	0.136848	120.3
T _{13,14}	-385.447575	0.136715	108.8
T _{15,16}	-385.452271	0.140429	108.2
T _{16,17}	-385.435311	0.138075	117.4

^aCalculated from the fragment energies in the top of the table.

The calculated energies are summarized in Table 1. The resulting energy diagrams for the dissociation to the benzocyclobutadiene and the phenylacetylene radical cation fragments are shown in Figs. 4 and 5, respectively.

In addition to the structures in Figs. 4 and 5 we also did some calculations on the acyclic structure obtained by a retro-[2 + 2]-cycloaddition of the benzocyclobutadiene ion as suggested in [4]. Its energy, however, appeared to be about 60 kcal mol⁻¹ higher than that of the benzocyclobutadiene ion (compare Table 1). For this reason we paid no further attention to this structure.

4. Discussion

Because the calculations in the present work were done with the same method as used in [7], the energies of the fragments in Table 1 are identical to the values obtained in [7]. As already described in that article, the dissociation limit as obtained from the fragment energies is some 10 kcal mol⁻¹ higher than the experimental dissociation energy of 101.7 kcal mol⁻¹. A similar result was obtained for the loss of acetylene from the benzene radical cation. By combination of these results, via isodesmic reactions the authors could obtain a close agreement with the experiments. This approach, however, cannot be used in the present work where the fragmentation pathway and the transition states involved are considered. A difference of 10 kcal mol⁻¹ between calculated and observed dissociation energy of the benzene radical cation was also obtained in [14] from a very different approach: geometry optimization at the restricted open shell Hartree-Fock (ROHF) level followed by single-point multi-reference configuration interaction (MRCI) calculations. In [7], the authors ascribed the observed difference to basis set incompleteness. For this reason we have done single-point recalculations of the dissociation energy for the formation of the benzocyclobutadiene ion with the corresponding much larger triple-zeta (cc-pVTZ) and quadruple-zeta (cc-pVQZ) basis sets. The latter basis set includes f-functions on hydrogen and g-functions on carbon. As shown in Table 2, this does give an improvement but the calculated dissociation energy is still about 5 kcal mol⁻¹ too high with the difference between the cc-pVTZ and cc-pVQZ results being negligible. From this result one may conclude that the calculations are still not sufficiently accurate to obtain a close agreement with experiment.

This inaccuracy is also more or less reflected in the energy diagrams in Figs. 4 and 5 where the calculated barrier for the dissociation towards the phenylacetylene fragment ion is shown to be 4 kcal mol⁻¹ lower than that to the benzocyclobutadiene ion. This result is in contrast with the conclusions from the experiments in [4] which show that the ion fragment should have the benzocyclobutadiene structure. This latter result is

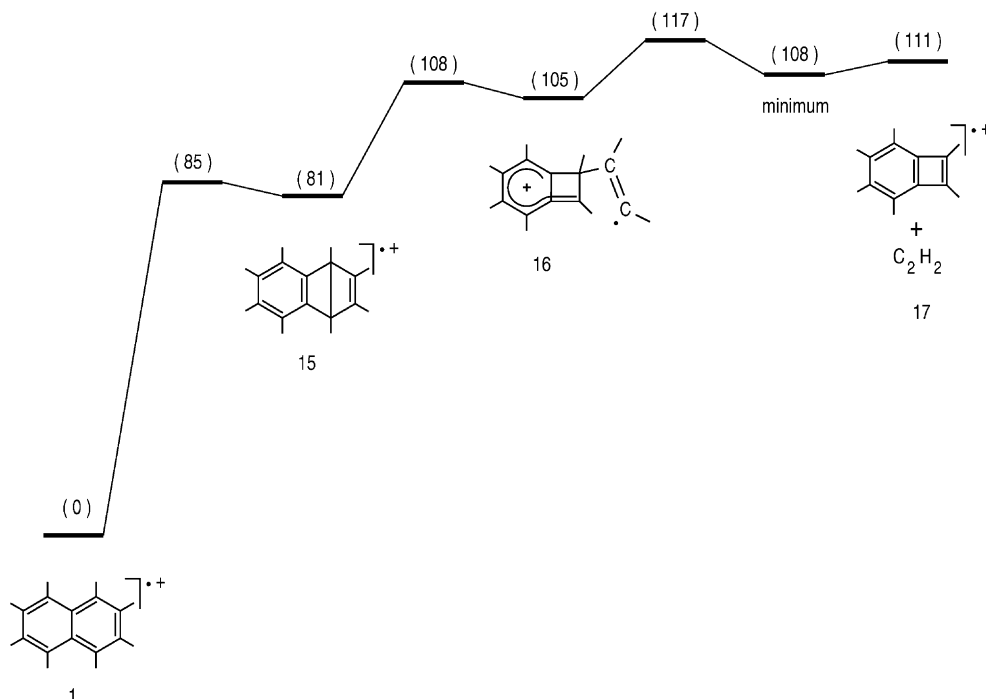


Fig. 4. Energy diagram for the dissociation to the benzocyclobutadiene ion.

in agreement with the energies of the fragments calculated in the present and in previous work [6,7]. An additional single-point cc-pVTZ calculation lowers the relative energy of the transition state by 2 kcal mol⁻¹ but this is insufficient to explain the difference with the total energy of the fragments (compare Table 2). Because the position of the acetylene fragment in the transition state is very flexible, we have also tried to find a transition state of lower energy by variation of its position. The results of this search were negative.

For this reason we have repeated the previous ROHF/MRCI calculations on the dissociation of the benzene radical cation to the cyclobutadiene ion [14] with the method used in the present work just to see if there were some, maybe significant, differences with the present approach. A comparison of the new with the older relative values is shown in Table 3.

It will be clear that, in this case, the difference between the two approaches is negligible and that the energy of the final transition state is lower than the energy of the fragments, both in the present DFT and

Table 2

Single-point energies with different basis sets for the acetylene molecule and the benzocyclobutadiene and naphthalene radical cations and the resulting dissociation energy (kcal mol⁻¹) corrected for the ZPE at the cc-pVDZ level from Table 1

	cc-pVDZ	cc-pVTZ	cc-pVQZ
Acetylene (neutral)	-77.333227	-77.363014	-77.368751
Benzocyclobutadiene	-308.111187	-308.194542	-308.215521
Naphthalene	-385.631011	-385.736369	-385.762802
E_{diss}	111.1	106.2	106.0

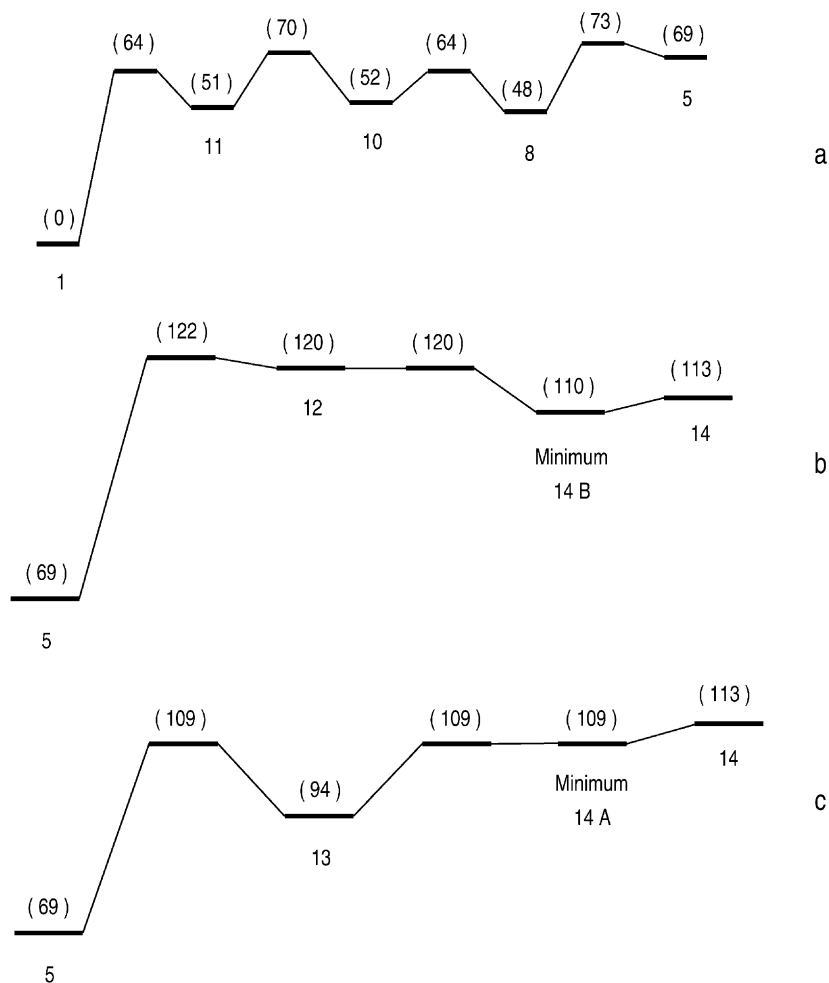


Fig. 5. Energy diagram for the dissociation to the phenylacetylene ion.

Table 3

Comparison of the present DFT values for the final steps in the dissociation of the benzene radical cation to the cyclobutadiene fragment ion with the ROHF/MRCI values in [14]^a

	DFT	ROHF/MRCI
Ring-opened Dewar benzene ion	90	88
Final transition state	106	110
Minimum	106	108
Fragments at 10 Å	115	114
Separated fragments	113	

^aAll values are in kcal mol⁻¹ relative to the benzene radical cation.

the previous ROHF/MRCI calculations. The main difference between the two results is in the shortest C–C distance between the leaving acetylene molecule and the cyclobutadiene ionic fragment: 1.93 Å in the transition state from the previous ROHF/MRCI approach and 2.20 Å in the present DFT calculation.

The geometry of the final transition state T_{16,17} in Table 1 and Fig. 4 is very similar to that of the final transition state in the benzene dissociation; in this case the shortest C–C distance is 2.02 Å. From this result we conclude that there is no essential difference

between the dissociation of the benzene radical cation to the cyclobutadiene ion and the present dissociation of the naphthalene radical cation to the benzocyclobutadiene ionic fragment. This implies that we do not have an explanation why the energy of $T_{16,17}$ is higher than the energy of the fragments and why, in contrast with the experimental conclusions, it is higher than the barrier in the dissociation to the phenylacetylene fragment ion. Our conclusion from all results together thus can only be that the present calculations are not sufficiently accurate to obtain a clear agreement with the experiments. Given the fact that even the calculations with much larger basis sets in Table 2 give a total energy for the fragments which is some 5 kcal mol^{-1} too high we furthermore conclude that it will be very difficult and time-consuming to get a better agreement with the experiments.

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