Energetics of Acetylene Loss from $C_{14}H_{10}^{\bullet +}$ Cations: A Density Functional Calculation

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The energetics of acetylene loss from anthracene and phenanthrene radical cations and the relative stabilities of the six possible $C_{12}H_8^{\bullet +}$ fragments have been investigated using the hybrid density functional methods B3LYP and B3PW91. Isodesmic reactions involving the well-known fragmentation of the benzene radical cation were employed to derive the dissociation energies for the fragmentations of naphthalene, anthracene, and phenanthrene radical cations. CCSD(T) calculations were also carried out for the acetylene loss from benzene and naphthalene radical cations. The B3LYP and B3PW91 methods appear to bracket the CCSD(T) result. The result for the naphthalene radical cation agrees with the previous suggestion that the benzocyclobutadiene radical cation is the most plausible product of acetylene loss (*Chem. Phys.* **1995**, *191*, 165). Computational results for anthracene and phenanthrene will be discussed in the light of experimental data. Acetylene losses from anthracene and phenanthrene radical cations will be shown to form the same fragment, biphenylene$^{\bullet +}$, which indicates that the isomerization barrier between the two isomers is lower than the dissociation limits. Scaled B3LYP/cc-pVDZ vibrational frequencies for naphthalene, anthracene, and phenanthrene radical cations are compared with available experimental data. Frequencies at the same level of theory are provided for $C_4H_4^{\bullet +}$, $C_8H_6^{\bullet +}$, and $C_{12}H_8^{\bullet +}$ isomers as well as for the benzene radical cation and should facilitate further experimental work.

I. 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] Noncompact small linear PAHs like anthracene were mentioned as being responsible for the IR emission.[3] Considerable work has been performed, experimentally, using matrix isolation techniques,[4−12] and theoretically, through ab initio[13,14] and density functional calculations,[15] in order to get a better knowledge of the spectral properties of cationic PAHs.

Molecular photodissociation is the principal process competing with radiative relaxation of PAHs in the interstellar medium. Research on photostability of PAHs has been carried out recently[16−24] to understand the stability of PAHs and their photofragments under UV irradiation. The most common fragmentation is the loss of hydrogen atoms. However, acetylene loss appears to be very common in noncompact PAH cations like naphthalene, anthracene, and phenanthrene. In these PAHs, acetylene loss has an appearance energy comparable to that of the hydrogen loss.[16,17,24] The energetics of fragmentation of the benzene radical cation were thoroughly investigated.[25,26] The energetics and kinetics of fragmentation of PAHs have been studied recently by us using time-resolved photoionization mass spectrometry.[21−24] However, contrary to H loss, the acetylene loss reaction was not well investigated except for naphthalene.[21] The energetics and kinetics of acetylene loss from naphthalene were investigated jointly by time-resolved photoionization mass spectrometry and by time-resolved photodissociation.[27] Acetylene loss from phenanthrene was investigated in our group previously,[21] and acenaphthylene, the most stable isomer, was proposed to be the product. We have reinvestigated experimentally recently the acetylene loss channel from phenanthrene and studied the analogous reaction in anthracene as well, by using VUV photoionization mass spectrometry and electron ionization tandem mass spectrometry. Details of these studies will be published separately, including RRKM modeling of the data.[24] While the energetics of the reactions could be deduced from the experiments, product structures were hard to determine and the original conclusion[21] that acenaphthylene is the preferred structure for the product $C_{12}H_8^{\bullet +}$ from phenanthrene remained uncertain.

Isomeric PAHs exhibit almost identical fragmentation patterns since they can accommodate a large amount of internal energy before undergoing fragmentation, and isomerization processes are very likely to occur.[28] However, our recent study[22] of pyrene and fluoranthene indicated that the isomerization barrier is high and that the two isomers undergo separate dissociations without prior isomerization. A similar study on anthracene and phenanthrene is of interest.

The aim of this paper is to study computationally the energetics of the acetylene loss from the $C_{14}H_{10}^{\bullet +}$ isomers, anthracene and phenanthrene, and the different possible $C_{12}H_8^{\bullet +}$ isomeric products. It will be shown, through comparison with experiment, that acetylene loss from both anthracene and phenanthrene radical cations does not form the most stable isomer. However they form the same product, namely, the biphenylene radical cation, which indicates that the isomerization barrier is lower than the respective dissociation energies.

We have adopted for the computations the density functional theory (DFT), which has been widely applied in recent years to study the energetics of organometallic compounds.[29] These generally place higher demands on theoretical calculations than ordinary organic compounds. DFT has been recognized as a promising approach for large molecules due to its relatively low computational demands. Energetics of C−H bond cleavages for PAHs have been successfully investigated by DFT.[30]

II. Methods

All density functional calculations have been carried out using the Gaussian 94 package[31] running on a DEC Alpha TurboLaser 8400 at the Institute of Chemistry. All conventional ab initio

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calculations were carried out using MOLPRO 96[32] running on the same computational hardware.

Two variants of the three-parameter hybrid nonlocal exchange-correlation proposed by Becke[33] have been employed. In the first, commonly denoted B3LYP, nonlocal correlation is approximated by the Lee−Yang−Parr functional,[34] while in the second, commonly denoted B3PW91, the more recent (1991) nonlocal correlation functional of Perdew and Wang[35] is used instead. In a recent article,[36] it was noted that the performance of both methods is comparable for harmonic frequencies, except for highly polar compounds, where B3PW91 appears to be superior.[36] The very good performance of B3LYP for harmonic frequencies has been well-known for some time.[37−39]

For relative energies of different isomers, it has been noted previously[40] that both B3LYP and B3PW91 are fairly reliable, but that they tend to exhibit different biases.[41] It has therefore been suggested[41] that the average of B3LYP and B3PW91 isomerization energies might be a good estimate of the actual value within a given basis set.

The B3LYP and B3PW91 geometries were found to be all but identical in the present work.

Using the B3LYP reference geometries, relative energies of $C_4H_4^{\bullet+}$ and $C_8H_6^{\bullet+}$ isomers were then obtained from single-point CCSD(T)[42,43] calculations, where CCSD(T) stands for the coupled cluster with single and double substitutions (CCSD) method[44] augmented with a quasiperturbative estimate[42] of connected triple excitations. For all the systems considered here, the τ_1 diagnostic,[45] which is a measure for the importance of nondynamical correlation effects, is sufficiently small that the CCSD(T) relative energies should be very close to the full CI ones.

Because of the size of the systems under consideration, only Dunning's cc-pVDZ (correlation consistent polarized valence double zeta[46]) basis set was considered, which is a [3s2p1d] contraction of a correlation-optimized (9s4p1d) primitive set. In a recent systematic study of basis set convergence for geometries and harmonic frequencies at the B3LYP level,[39] it was found that enlarging the basis set to cc-pVTZ (i.e. correlation consistent polarized valence triple zeta), a basis set of [4s3p2d1f] quality[46] leads to somewhat improved geometries but no significant improvement in harmonic frequencies. Moreover, it was found earlier[47] that isomeric energy differences for such notoriously problematic molecules as carbon clusters only differ by a few kcal/mol from those obtained with much larger basis sets.

III. Results and Discussion

A. Geometry and Frequencies. To evaluate the reliability of the DFT calculation, the acetylene loss from benzene and naphthalene radical cations was also investigated, since these systems are sufficiently small to permit a coupled cluster treatment for comparison. The structures of all relevant fragment radical cations, as well as the benzene and naphthalene radical cations, are given in Figure 1. Two $C_4H_4^{\bullet+}$ isomers, methylenecyclopropene and vinylacetylene, are considered here. The cyclic structure belongs to the C_{2v} point group, and the open chain one belongs to C_s symmetry. The product of the benzene radical cation fragmentation at threshold is the more stable cyclic structure.[26] Three possible structures of $C_8H_6^{\bullet+}$ isomers, formed by acetylene elimination from the naphthalene radical cation, are phenylacetylene (**I**), benzocyclobutadiene (**II**), and benzocyclopropenemethylene (**III**). They all belong to the C_{2v} point group. Only structure **II** can be formed from C−C cleavages without H migration; the other two correspond to the elimination of $HC\equiv CH$, followed by H migration. Six plausible $C_{12}H_8^{\bullet+}$ isomer structures, which might be formed from the acetylene loss from $C_{14}H_{10}^{\bullet+}$, are shown in Figure 2, together with the anthracene and phenanthrene radical cations. They are acenaphthylene (**A**), biphenylene (**B**), 1-naphthylacetylene (**C**), 2-naphthylacetylene (**D**), 2,3-naphthocyclobutadiene (**E**), and 1,2-naphthocyclobutadiene (**F**). Acenaphthylene cannot be formed directly from anthracene and phenanthrene, while biphenylene can be obtained directly through elimination of $HC\equiv CH$ from positions 9 and 10 of phenanthrene. (It could then be formed indirectly from anthracene upon isomerization of the latter to phenanthrene.) Structures **C** and **D** are the analogues of structure **I**, phenylacetylene, while structures **E** and **F** are the analogues of benzocyclobutadiene (**II**). Formation of structures **C** and **D** requires H migration subsequent to fragmentation, while **E** and **F** do not. Only CC bond distances are given in the figures. The calculated vibrational frequencies (unscaled) as well as the infrared (IR) intensities for the IR active bands of the $C_6H_6^{\bullet+}$, $C_{10}H_8^{\bullet+}$, $C_{14}H_{10}^{\bullet+}$, $C_4H_4^{\bullet+}$, $C_8H_6^{\bullet+}$, and $C_{12}H_8^{\bullet+}$ isomers considered in this work are available as Supporting Information to the paper. The calculated IR frequencies for naphthalene, anthracene, and phenanthrene radical cations will be compared with the available experimental data in this work, and the calculated data for other species should facilitate further experimental work.

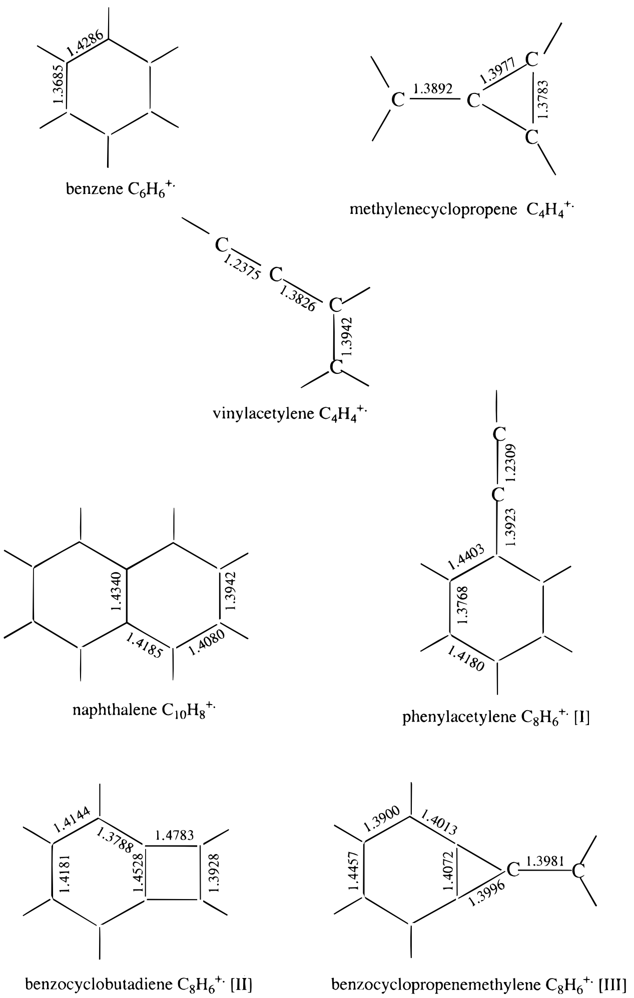

Figure 1. Structures of $C_6H_6^{\bullet+}$ and $C_{10}H_8^{\bullet+}$, as well as $C_4H_4^{\bullet+}$ isomers and $C_8H_6^{\bullet+}$ isomers considered in this study.

The calculated IR frequencies and intensities for the naphthalene radical cation are compared with the experimental data[4,10] in Table 1, as well as with the calculated B3LYP/4-31G data of Langhoff[15] scaled by his proposed factor of 0.958.[15] The present calculated frequencies were scaled by a uniform

TABLE 1: Comparison of the Infrared Frequencies (cm^{-1}) and Intensties (km/mol) for the Naphthalene Radical Cation

	B3LYP/cc-pVDZ		expt[a]		B3LYP/4-31G[f]	
irrep	freq[d]	int[e]	SRPEPV[b]	HSA[c]	freq	int
b_{3u}	420	19.9(0.09)			422.2	23.9(0.12)
b_{2u}	590	8.3(0.04)				
b_{3u}	762	78.3(0.36)		758.7(0.27)	766.8	115.3(0.60)
b_{2u}	1015	11.1(0.05)	1016(0.26)	1016(−)	1007.7	21.5(0.11)
			1023(0.06)	1023.2(0.05)		
b_{1u}	1092	3.5(0.02)			1102.7	7.2(0.04)
b_{2u}	1154	10.2(0.05)			1181.8	50.3(0.26)
b_{2u}	1201	215.6(1.00)	1218(1.00)	1218.0(1.00)	1218	193.2(1.00)
				1214.9(0.20)		
b_{1u}	1262	10.7(0.05)			1283.8	8.9(0.05)
b_{1u}	1386	27(0.13)				
b_{2u}	1396	23.2(0.11)	1401(0.04)	1400.9(0.04)	1375.4	20.1(0.10)
b_{1u}					1410.8	16.2(0.08)
b_{1u}	1516	82.2(0.38)	1519(0.08)	1518.8(0.10)	1501.4	97.8(0.51)
b_{2u}	1531	30.2(0.14)	1525(0.16)	1525.7(0.29)	1523.8	17.5(0.09)

[a] Frequencies are given first followed by relative intensities in parentheses. [b] Matrix isolation, Szczepanski et al.[4] [c] Matrix isolation, Hudgins et al.[10] [d] The frequencies are scaled by 0.976. [e] Absolute values given first with relative intensities given in parentheses. [f] Langhoff.[15]

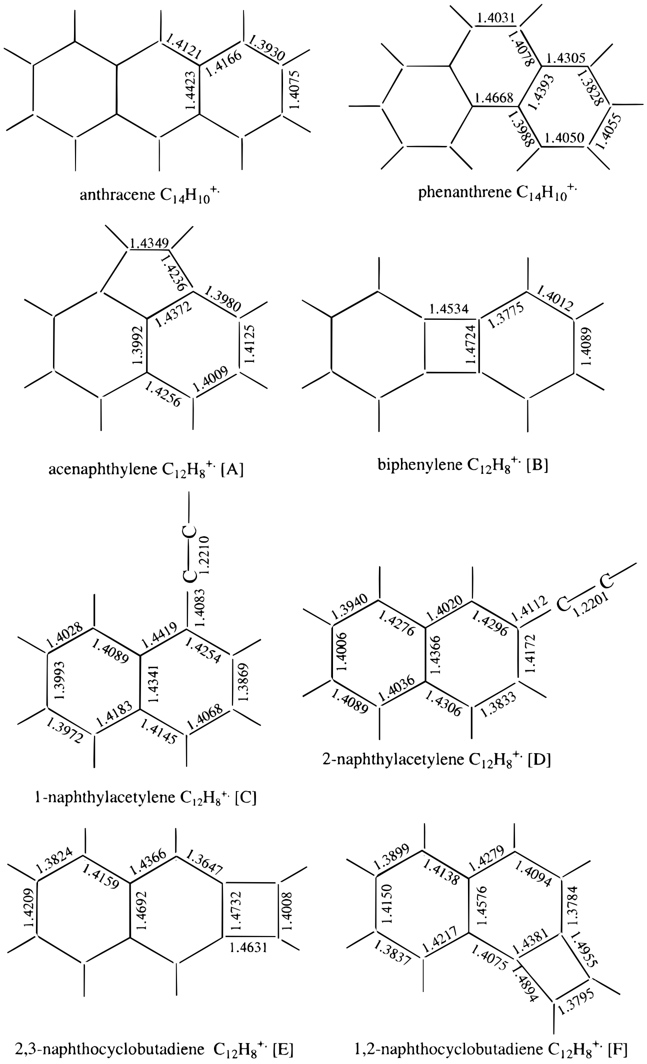

Figure 2. Structures of $C_{14}H_{10}^{\bullet+}$ isomers and $C_{12}H_8^{\bullet+}$ isomers considered in this study.

factor of 0.976 except for the CH stretches, which were scaled by 0.96. These factors are based on the ν(obsd)/ω(calcd) at B3LYP/cc-pVDZ level for neutral benzene, naphthalene, anthracene, and phenanthrene[48] and were recently shown to yield very good results for the coronene and corannulene systems.[49] Only relative intensities are given for the experimental work, because the experimental estimates of the absolute intensities vary greatly. The relative intensties are in reasonable agreement with the present theoretical values. The strongest bands at 1215/1218 cm^{-1} observed experimentally correlate with the strongest calculated band at 1201 cm^{-1}. The band at 1214.9 cm^{-1} is probably due to a matrix site of the 1218 cm^{-1} band. The strong out-of-plane CH bend mode (b_{3u}) compares well with the band at 758.7 cm^{-1} observed by Hudgins et al.[10] The calculated band at 1015 cm^{-1} fits well with the observed band at 1016 cm^{-1}, of which 1023 cm^{-1} is probably a matrix site. The differences between the scaled calculated values and the experimental band positions are less than 10 cm^{-1} in the majority of cases and less than 20 cm^{-1} in worst cases. This confirms the validity of the scaling procedure. The fact that the scaled B3LYP/4-31G data of Langhoff[15] are generally comparable with the present scaled B3LYP/cc-pVDZ results would seem to indicate that the correlation effects on the vibrational frequencies of these molecules are dominated by radial correlation effects since the 4-31G basis set, which does not include any polarization functions, by construction cannot accommodate angular correlation. On the other hand, the fact that the DFT basis set limit for the Be atom can be reached without any p, d, f, ... functions strongly suggests that basis set convergence behavior for DFT is qualitatively different from that for correlated ab initio calculations. (We thank a referee for pointing this out.) The present assignment differs in a number of instances from that proposed by Langhoff.[15]

Table 2 compares the calculated frequencies for the anthracene radical cation and experimental data.[5,12] Our calculated relative intensities generally agree well with the experimental values, as well as with the values of Langhoff.[15] The band at 1034 cm^{-1} observed by Szczepanski et al.[5] was not observed by Hudgins and Allamandola.[12] This corresponds to a very weak band at 1027 cm^{-1} in our calculation. The strongest band at 1341 cm^{-1} corresponds to our predicted one at 1361 cm^{-1}. The differences between the experimental values and our scaled calculated values are generally less than 10 cm^{-1}, and about 20 cm^{-1} in some worse cases. Our calculation shows better prediction than those of Langhoff on the relative intensities of two experimental bands at 1188 and 1418 cm^{-1} and the strongest bands at 1341 $cm^{-1\cdot}$ This is not surprising given the importance of polarization functions for electrical properties. As mentioned before,[15] multiple peaks in the vicinity of the strong bands observed by Hudgins and Allamandola[12] are probably due to mutiple sites in the matrix or overtone/combination peaks.

The experimental frequencies and our calculated values for the phenanthrene radical cation are compared in Table 3. The

TABLE 2: Comparison of the Infrared Frequencies (cm^{-1}) and Intensties (km/mol) for the Anthracene Radical Cation

	B3LYP/cc-pVDZ		expt[a]		B3LYP/4-31G[f]	
irrep	freq[d]	int[e]	SVTPE[b]	HA[c]	freq	int
b_{3u}	438	27.2(0.10)	432(0.07)		438	31.2(0.09)
b_{3u}	752	68.4(0.25)		748.3(0.26)	753.3	95.6(0.27)
b_{2u}	814	2.5(0.01)			806.4	5.1(0.01)
b_{3u}	917	20.9(0.08)	912(0.15)	912.0(0.09)	912.6	38.3(0.11)
b_{3u}	982	4.7(0.02)			984.9	8.8(0.02)
b_{2u}	1027	3.6(0.01)	1034(0.20)		1023.4	6.0(0.02)
b_{2u}	1151	0.04(<0.01)			1181.9	11.4(0.03)
b_{2u}	1174	156.1(0.58)	1188(0.98)	1188.6(0.70)	1195.9	140.0(0.39)
				1181.3(0.01)		
b_{1u}	1266	12.1(0.04)		1290.4(0.06)	1279.1	22.7(0.06)
b_{1u}	1285	16.4(0.06)	1291(0.07)	1314.6(0.06)		
b_{2u}	1361	267.4(1.00)	1341(1.00)	1341.0(1.00)	1339.6	357.4(1.00)
				1352.6(0.31)		
				1364.4(0.04)		
b_{2u}	1410	196.8(0.73)	1418(0.97)	1418.4(0.86)	1393.1	131.9(0.37)
			1410(0.09)	1406.1(0.02)		
				1409.5(0.11)		
b_{2u}	1440	48.7(0.18)		1430.2(0.01)	1458.8	57.6(0.16)
b_{1u}	1444	21(0.08)	1457(0.05)	1456.6(0.07)	1454.9	21.6(0.06)
b_{2u}	1537	91.8(0.34)	1540(0.04)	1539.9(0.15)	1523.3	75.3(0.21)
b_{1u}	1584	54.5(0.20)		1586.4(0.14)	1564.5	62.2(0.17)

[a] Frequencies are given first followed by relative intensities in parentheses. [b] Matrix isolation, Szczepanski et al.[5] [c] Matrix isolation, Hudgins et al.[12] [d] The frequencies are scaled by 0.976. [e] Absolute values given first with relative intensities given in parentheses. [f] Langhoff.[15]

TABLE 3: Comparison of the Infrared Frequencies (cm^{-1}) and Intensties (km/mol) for the Phenanthrene Radical Cation

	B3LYP/cc-pVDZ			B3LYP/4-31G[d]	
irrep	freq[b]	int[c]	expt[a]	freq	int
b_1	212	6.3(0.02)			
b_1	406	9.3(0.04)		406.8	10.0(0.05)
b_2	581	45.3(0.20)	582.0(0.22)	597.2	46.4(0.25)
b_1	703	34.5(0.15)	694.5(0.09)	693.2	38.6(0.21)
b_1	760	34.3(0.15)	756.2(0.07)	758.9	57.3(0.31)
b_1	840	31.4(0.13)	836.0(0.06)	839	53.6(0.29)
b_2	855	5.9(0.02)			
b_1	885	5.0(0.02)			
b_2	978	21.9(0.09)		986.4	31.3(0.17)
b_1	1033	5.4(0.02)			
b_1	1120	3.2(0.01)		1138.9	10.3(0.06)
b_2	1132	141.5(0.62)		1154.2	160.5(0.86)
a_1	1207	9.9(0.04)		1218.2	16.1(0.09)
b_2	1213	54.1(0.24)		1230.5	44.8(0.24)
			1258.7(0.04)		
a_1	1249	40.9(0.18)	1267.0(0.14)	1263	30.1(0.16)
			1227.5/1282.5(0.84)		
b_2	1272	1.5(<0.01)	1299.0(0.09)	1291.7	61.3(0.33)
b_2	1316	228.2(1.00)		1309.6	186.4(1.00)
b_2	1415	14.2(0.06)			
b_2	1424	74.9(0.33)		1419.7	80.8(0.43)
b_2	1505	5.84(0.02)		1496.2	15.8(0.08)
a_1	1515	6.97(0.03)	1513.0(0.04)	1513.1	10.8(0.06)
b_2	1521	16.4(0.07)			
a_1	1550	108.9(0.47)	1551.0(0.06)	1532.7	112.7(0.60)
			1558.2(0.02)		
b_2	1570	213.3(0.93)	1565.0(1.00)	1549.8	184.0(0.99)
a_1	1607	19.8(0.09)		1583.1	23.1(0.13)

[a] Matrix isolation, Hudgins et al.[11] Frequencies are given first followed by relative intensities in parentheses. [b] The frequencies are scaled by 0.976. [c] Absolute values given first with relative intensities given in parentheses. [d] Langhoff.[15]

strongest band at 1565 cm^{-1} corresponds to the calculated one at 1570 cm^{-1}. However relatively strong bands obtained theoretically at 1132, 1213, 1316, and 1424 cm^{-1} were not observed in the experiment. This agrees with the previous calculation.[15] The lack of these cation bands was explained by Langhoff by the screening of neutral bands.[15]

B. Relative Stability. The calculated total energies for relevant species in their ground states and zero-point vibrational energies (ZPVEs) at the B3LYP/cc-pVDZ level are summarized in Table 4. We also carried out CCSD(T) calculations on the fragmentation products of benzene and naphthalene radical cations to assess the reliability of the B3LYP and B3PW91 methods for our problem. Table 5 gives the relative energies for $C_4H_4^{\bullet+}$ isomers. The ZPVE corrections were made from B3LYP/cc-pVDZ frequencies throughout. It can been seen that, compared with the CCSD(T) result, B3LYP is lower and B3PW91 is higher. Both are close to CCSD(T). However, interestingly, the average value of B3LYP and B3PW91 (9.6 kcal/mol) is in excellent agreement with CCSD(T) (9.3 kcal/mol). The contribution of connected triple excitations is not overly important, as the CCSD relative energy is also close to CCSD(T). However, electron correlation is very important here: the energy difference between the two structures decreases by about 50% upon introducing electron correlation. The relative energy from the literature agrees with the present calculation, but the heats of formation of both isomers quoted in ref 50 are too high, as will be shown later.

The relative energies of $C_8H_6^{\bullet+}$ isomers are given in Table 6. Firstly, the benzocyclobutadiene (**II**) is shown to be the most stable structure, although the phenylacetylene structure (**I**) was often proposed to be the structure in experimental studies.[21] Structure (**II**) was also found to be the most stable isomer in a previous ab initio study.[20] As can been seen again in Table 6, B3LYP is lower and B3PW91 is higher compared with the CCSD(T) value for **I** vs **II**. However, the average of both B3LYP and B3PW91 (4.4 kcal/mol) is in excellent agreement with CCSD(T) (4.1 kcal/mol). This parallels the observation previously made for the isomers of C_{20} and C_{24}.[40,41] Electron correlation hardly affects the relative energy for **I** vs **II**. It is important however for **III** vs **II** since the relative energy increases by about 50% upon going from SCF to CCSD(T). Connected triple excitations are found to be relatively unimportant for **I** vs **II**, but more important for **III** vs **II**. A recent CIPSI/6-31G* calculation[20] is in fairly good agreement with present work. It seems that the relative stability of the isomers in ref 50 is not correct.

We conclude at this point that B3LYP and B3PW91 should be sufficiently accurate for our purpose and that the average

TABLE 4: Summary of Absolute Energies (hartrees) and Zero-Point Vibrational Energies (kcal/mol)

species[a]	B3LYP/cc-pVDZ	ZPVE[b]	B3PW91/cc-pVDZ	CCSD(T)/cc-pVDZ	CCSD/cc-pVDZ	SCF/cc-pVDZ
acetylene	−77.333 226	16.92	−77.298 683	−77.110 132	−77.098 900	−76.825 206
methylenecyclopropene ($^2B_1$)	−154.421 230	37.63	−154.365 549	−153.968 890	−153.949 383	−153.447 016
vinylacetylene ($^2A''$)	−154.409 650	37.58	−154.343 455	−153.953 964	−153.931 492	−153.412 972
benzene ($^2B_{2g}$)	−231.931 955	61.16	−231.841 883	−231.253 043	−231.218 157	−230.424 735
benzene ($^2B_{1g}$)	−231.931 796		−231.841 630	−231.253 138	−231.217 834	−230.423 519
phenylacetylene ($^2B_1$) (**I**)	−308.106 055	68.11	−307.981 841	−307.208 078	−307.157 564	−306.112 644
benzocyclobutadiene ($^2B_1$) (**II**)	−308.111 185	69.26	−307.994 475	−307.216 489	−307.165 136	−306.119 764
benzocyclopropenemethylene ($^2B_1$) (**III**)	−308.077 482	68.03	−307.960 940	−307.180 190	−306.095 929	−307.131 402
naphthalene (^2A_u)	−385.631 009	92.15	−385.483 184	−384.507 417	−384.442 653	−383.120 915
acenaphthylene ($^2B_1$) (**A**)	−461.836 716	99.48	−461.662 579			
biphenylene ($^2B_{2g}$) (**B**)	−461.796 376	99.43	−461.622 396			
1-naphthylacetylene ($^2A''$) (**C**)	−461.787 870	97.92	−461.606 321			
2-naphthylacetylene ($^2A''$) (**D**)	−461.785 377	97.75	−461.603 609			
2,3-naphthocyclobutadiene ($^2B_1$) (**E**)	−461.780 565	98.55	−461.606 245			
1,2-naphthocyclobutadiene ($^2A''$) (**F**)	−461.780 977	98.75	−461.606 866			
anthracene ($^2B_{2g}$)	−539.306 573	121.87	−539.101 401			
phenanthrene ($^2B_1$)	−539.296 310	121.65	−539.091 044			

[a] All species are radical cations except acetylene. [b] ZPVEs are calculated at the B3LYP/cc-pVDZ level.

TABLE 5: Relative Energies (kcal/mol) of $C_4H_4^{\bullet+}$ Isomers

species	methylenecyclopropene ($^2B_1$)	vinylacetylene ($^2A''$)
B3LYP/cc-pVDZ	0.0	7.2
B3PW91/cc-pVDZ	0.0	11.9
average	0.0	9.6
CCSD(T)/cc-pVDZ	0.0	9.3
CCSD/cc-pVDZ	0.0	11.2
SCF/cc-pVDZ	0.0	21.3
experiment[a]	0.0	(5.0)

[a] Lias et al.[50]

TABLE 6: Relative Energies (kcal/mol) of $C_8H_6^{\bullet+}$ Isomers

species	phenylacetylene ($^2B_1$) (**I**)	benzocyclobutadiene ($^2B_1$) (**II**)	benzocyclopropenemethylene ($^2B_1$) (**III**)
B3LYP/cc-pVDZ	2.1	0.0	19.9
B3PW91/cc-pVDZ	6.8	0.0	19.8
average	4.4	0.0	19.9
CCSD(T)/cc-pVDZ	4.1	0.0	21.5
CCSD/cc-pVDZ	3.6	0.0	19.9
SCF/cc-pVDZ	3.3	0.0	13.7
ROHF/6-311G**[a]	1.7	0.0	12.2
CIPSI/6-31G*[a]	3.7	0.0	20.3
experiment[b]	0.0	(15)	

[a] Granucci et al.[20] [b] Lias et al.[50]

TABLE 7: Relative Energies (kcal/mol) of $C_{12}H_8^{\bullet+}$ Isomers

species	B3LYP/cc-pVDZ	B3PW91/cc-pVDZ	av	expt[a]
A, acenaphthylene ($^2B_1$)	0.0	0.0	0.0	0.0
B, biphenylene ($^2B_{2g}$)	25.3	25.2	25.2	27
C, 1-naphthylacetylene ($^2A''$)	29.1	33.7	31.4	(27)
D, 2-naphthylacetylene ($^2A''$)	30.5	35.3	32.9	(27)
E, 2,3-naphthocyclobutadiene ($^2B_1$)	34.3	34.4	34.4	
F, 1,2-naphthocyclobutadiene ($^2A''$)	34.2	34.2	34.2	

[a] Lias et al.[50]

TABLE 8: Calculated Dissociation Energies D_0 (kcal/mol) for Benzene Radical Cation Acetylene Loss: $C_6H_6^{\bullet+} \Rightarrow C_4H_4^{\bullet+} + C_2H_2$

product	methylenecyclopropene ($^2B_1$)		vinylacetylene ($^2A''$)
	D_0	deviation[c]	
B3LYP/cc-pVDZ	104.8	8.8	112.0
B3PW91/cc-pVDZ	106.8	10.8	118.7
average	105.8	9.8	115.3
CCSD(T)/cc-pVDZ	102.6	6.7	111.9
CCSD/cc-pVDZ	100.0	4.1	111.2
SCF/cc-pVDZ	89.1	−6.8	110.4
experiment[a]	96[b]		

[a] Kühlewind et al.[25] [b] The error limit was not given in ref 25, but it is estimated to be about 3 kcal/mol. [c] The deviation is the difference between the calculated dissociation energy and the experimental value.

value of both B3LYP and B3PW91 should give a good estimate of the CCSD(T) value.

The relative energies of $C_{12}H_8^{\bullet+}$ isomers are given in Table 7. B3LYP and B3PW91 yield almost the same relative energies except for **C** and **D**, where the difference is about 5 kcal/mol. We propose the average of both calculations as the best estimate. Acenaphthylene (**A**) is the most stable structure, with a ring skeleton reminiscent of the adjacent 6−5 rings in fullerenes. The next stable one is biphenylene (**B**), while structures **C**, **D**, **E**, and **F** are nearly isoenergetic. The calculated difference **B** vs **A** of 25.2 kcal/mol is in very good agreement with the experimental value of 27 kcal/mol, while the **C**−**A** and **D**−**A** differences are larger than the corresponding experimental values.[50] No experimental values are available for **E** and **F**.

C. Dissociation Energies. It was shown in a recent paper[30] that gradient-corrected DFT reproduces the experimental C−H bond energies of neutral PAHs very well. We tested the B3LYP and B3PW91 functionals for the direct calculation of the acetylene loss energies of the benzene and naphthalene radical cations, where the experimental values are well established.[25,27] The calculated results for the benzene radical cation fragmentation (1) are compared with the experimental value[25] in Table 8. Both experimental and calculated values are at 0 K. The experimental error limit was not given in ref 25; we conservatively estimate it to be 3 kcal/mol.

$$C_6H_6^{\bullet+} \Rightarrow C_4H_4^{\bullet+} + C_2H_2 \tag{1}$$

It can be seen that the calculated value is higher than the experimental one. The average value of B3LYP and B3PW91 is about 10 kcal/mol higher than the experimental value, provided that experimentally the product is methylenecyclopropene, and 2 kcal/mol higher than the CCSD(T) value. (The difference between the latter and experiment will be mostly due to basis set incompleteness.) The comparison of the various results for acetylene loss from the naphthalene radical cation (2) is summarized in Table 9.

$$C_{10}H_8^{\bullet+} \Rightarrow C_8H_6^{\bullet+} + C_2H_2 \tag{2}$$

Again the average value of both methods is about 10 kcal/mol higher than the experimetal value if the assumed structure is

TABLE 9: Calculated Dissociation Energies D_0 (kcal/mol) for Naphthalene Radical Cation Acetylene Loss: $C_{10}H_8^{\bullet+} \Rightarrow C_8H_6^{\bullet+} + C_2H_2$

product	phenylacetylene ($^2B_1$) (**I**)		benzocyclobutadiene ($^2B_1$) (**II**)		benzocyclopropenemethylene ($^2B_1$) (**III**)	
	D_0	deviation	D_0	deviation	D_0	deviation
B3LYP/cc-pVDZ	113.2	11.5	111.1	9.4	131.0	29.3
B3PW91/cc-pVDZ	120.0	18.3	113.2	11.5	133.1	31.4
average	116.6	14.9	112.2	10.5	132.0	30.3
CCSD(T)/cc-pVDZ	111.6	9.9	107.5	5.8	129.0	27.3
CCSD/cc-pVDZ	109.7	8.0	106.1	4.4	126.1	26.7
SCF/cc-pVDZ	107.8	6.1	104.4	2.7	118.2	16.5
experiment[a]			101.7 ± 5			

[a] Ho et al.[27] [b] The deviation is the difference between the calculated dissociation energy and the experimental value.

TABLE 10: Calculated Energy Changes ΔE (kcal/mol) for Isodesmic Reactions $C_{10}H_8^{\bullet+} + C_4H_4^{\bullet+} \Leftrightarrow C_8H_6^{\bullet+} + C_6H_6^{\bullet+}$ and the Dissociation Energy D_0 for Acetylene Loss from Naphthalene, $C_{10}H_8^{\bullet+} \Rightarrow C_8H_6^{\bullet+} + C_2H_2$

product	phenylacetylene ($^2B_1$) (**I**)		benzocyclobutadiene ($^2B_1$) (**II**)		benzocyclopropenemethylene ($^2B_1$) (**III**)	
	ΔE	D_0	ΔE	D_0	ΔE	D_0
B3LYP/cc-pVDZ	8.4	104.4	6.3	102.3	26.3	122.2
B3PW91/cc-pVDZ	13.3	109.2	6.5	102.4	26.3	122.2
average	10.8	106.8	6.4	102.4	26.3	122.2
CCSD(T)/cc-pVDZ	9.0	105.0	4.9	100.8	26.4	122.4
CCSD/cc-pVDZ	9.7	105.7	6.1	102.1	26.1	122.0
SCF/cc-pVDZ	18.7	114.6	15.3	111.3	29.1	125.0
experiment[a,b]			5.5	101.7 ± 5		

[a] Kühlewind et al.[25] [b] Ho et al.[27]

TABLE 11: Calculated Energy Changes ΔE (kcal/mol) for Isodesmic Reactions $C_{14}H_{10}^{\bullet+} + C_4H_4^{\bullet+} \Leftrightarrow C_{12}H_8^{\bullet+} + C_6H_6^{\bullet+}$ and the Dissociation Energy D_0 for Acetylene Loss from Anthracene, $C_{14}H_{10}^{\bullet+} \Rightarrow C_{12}H_8^{\bullet+} + C_2H_2$

	B3LYP/cc-pVDZ		B3PW91/cc-pVDZ		average	
product	ΔE	D_0	ΔE	D_0	ΔE	D_0
A, acenaphthylene ($^2B_1$)	−24.5	71.4	−24.3	71.7	−24.4	71.5
B, biphenylene ($^2B_{2g}$)	0.8	96.7	0.9	96.8	0.8	96.8
C, 1-naphthylacetylene ($^2A''$)	4.6	100.5	9.5	105.4	7.0	103.0
D, 2-naphthylacetylene ($^2A''$)	6.0	101.9	11.0	106.9	8.5	104.4
E, 2,3-naphthocyclobutadiene ($^2B_1$)	9.8	105.7	10.1	106.1	10.0	105.9
F, 1,2-naphthocyclobutadiene ($^2A''$)	9.7	105.7	9.9	105.9	9.8	105.8
experiment[a,b]					0.8	≤97 ± 3

[a] Kühlewind et al.[25] [b] Ling et al.[24]

benzocyclobutadiene. Obviously basis set incompleteness will again account for the lion's share of this difference, since the DFT and CCSD(T) values within the same basis set were seen to agree well for eq 1, and it is well-known (e.g. ref 51 and references therein) that dissociation energies for high bond orders exhibit much slower basis set convergence than those for low bond orders, thus causing substantial basis set dependence for the reaction energy of reactions involving changes of bond order.

While clearly the cc-pVDZ basis set is inadequate for computing the energy change directly for acetylene loss from anthracene or phenanthrene radical cations (3),

$$C_{14}H_{10}^{\bullet+} \Rightarrow C_{12}H_8^{\bullet+} + C_2H_2 \qquad (3)$$

we may instead consider the isodesmic reaction 4, calculate the energy change, and obtain the desired quantity for reaction 3 from a thermochemical cycle involving the experimentally well-known reaction energy of (1), which is 4.16 eV.[25]

$$C_{14}H_{10}^{\bullet+} + C_4H_4^{\bullet+} \Leftrightarrow C_{12}H_8^{\bullet+} + C_6H_6^{\bullet+} \qquad (4)$$

First we test our approach for the following isodesmic reaction, reactions 5, where the experimental value is available.

$$C_{10}H_8^{\bullet+} + C_4H_4^{\bullet+} \Leftrightarrow C_6H_6^{\bullet+} + C_6H_6^{\bullet+} \qquad (5)$$

The result is given in Table 10. As can been seen from the table, all levels of theory agree well with each other, except SCF. The experimental energy change for reaction 5 is from the energy difference between reactions 1 and 2. The calculated D_0 for the most stable structure (**II**) is in excellent agreement with experimental results. However the D_0 for structure **I** is still within the experimental error limits. Kinetically, formation of structure **II** is more favorable than structure **I**, since H migration is needed in the formation of **I**. Structure **II** is thus the most plausible product of the fragmentation from naphthalene. This agrees with the suggestion made previously in ref 20.

The calculated energy changes for reaction 4 and the derived dissociation energy for reaction 3 are given in Table 11, where $C_{14}H_{10}^{\bullet+}$ is anthracene. We see first that B3LYP and B3PW91 yield very similar numbers. The experimental activation energy for reaction 3 was determined to be 104 ± 3 kcal/mol. Since the minimum kinetic energy release is 7 kcal/mol for acetylene loss from the anthracene radical cation,[24] the thermochemical energy change for reaction 3 should be ≤97 ± 3 kcal/mol. The energy change for the isodesmic reaction 4 is 0.8 kcal/mol. The difference between the calculated fragmentation energy giving **A**, 71.5 kcal/mol, is well outside any plausible error margin, which indicates that the observed fragmentation product is not the thermodynamically most stable one, **A**. It can rather be seen immediately that the product is the biphenylene structure, **B**.

TABLE 12: Calculated Energy Changes Δ*E* (kcal/mol) for Isodesmic Reactions $C_{14}H_{10}^{\bullet+} + C_4H_4^{\bullet+} \leftrightarrow C_{12}H_8^{\bullet+} + C_6H_6^{\bullet+}$ and the Dissociation Energy D_0 for Acetylene Loss from Phenanthrene, $C_{14}H_{10}^{\bullet+} \Rightarrow C_{12}H_8^{\bullet+} + C_2H_2$

	B3LYP/cc-pVDZ		B3PW91/cc-pVDZ		average	
product	Δ*E*	D_0	Δ*E*	D_0	Δ*E*	D_0
A, acenaphthylene ($^2B_1$)	−30.7	65.2	−30.6	65.4	−30.6	65.3
B, biphenylene ($^2B_{2g}$)	−5.5	90.5	−5.4	90.5	−5.4	90.5
C, 1-naphthylacetylene ($^2A''$)	−1.6	94.3	3.2	99.1	0.8	96.7
D, 2-naphthylacetylene ($^2A''$)	−0.2	95.7	4.7	100.7	2.2	98.2
E, 2,3-naphthocyclobutadiene ($^2B_1$)	3.6	99.5	3.9	99.8	3.7	99.7
F, 1,2-naphthocyclobutadiene ($^2A''$)	3.5	99.5	3.7	99.6	3.6	99.5
experiment[a]					−10.4	≤85.5 ± 3

[a] Kühlewind et al.[25] [b] Ling et al.[24]

TABLE 13: Thermochemical Data[a]

		ΔH_f°(neutral), kcal/mol		ΔH_f°(ion), kcal/mol	
species	IE, eV	0 K	298 K	0 K	298 K
$C_{14}H_{10}$					
anthracene[b]	7.40 ± 0.02	62.0	55.44	232.6	227
phenanthrene[c]	7.86 ± 0.01	56.4	49 ± 0.2	237.7	230.3
$C_{12}H_8$					
acenaphthylene	(8.22 ± 0.04)		62 ± 0.2	249.5[d]	(252)
biphenylene	7.56 ± 0.02		104 ± 3	274.7[d]	279
1-naphthylacetylene	(8.03)		93	280.9[d]	(279)
2-naphthylacetylene	(8.11)		93	282.4[d]	(280)
2,3-naphthocyclobutadiene				283.9[d]	
1,2-naphthocyclobutadiene				283.7[d]	
$C_{10}H_8$					
naphthalene[c]	8.14	41.4	35.9 ± 0.3	229.2	223.6
C_8H_6					
phenylacetylene	8.81 ± 0.04		73 ± 0.5	280.0[d]	276
benzocyclobutadiene	(≤7.5)		118	275.9[d]	(≤291)
C_6H_6					
benzene	9.2459 ± 0.0002	24.0 ± 0.2	19.8 ± 0.1	237.2	233.2
C_4H_4					
methylenecyclopropene	8.15		101	278.4[d]	(289)
vinylacetylene	9.58 ± 0.02		73	287.7[d]	(294)
C_2H_2					
acetylene	11.400 ± 0.002	54.7	54.5 ± 0.25	317.5	317.4

[a] All values are taken from Lias et al.[50] unless indicated otherwise. [b] Ling et al.[24] [c] Gotkis et al.[21] [d] Present work. The error limit is estimated to be 5 kcal/mol.

Table 12 gives the result for phenanthrene radical cation fragmentation. The calculated isomerization energy is 6.2 kcal/mol, while experimentally the anthracene radical cation is 5.1 ± 1.2 kcal/mol more stable than phenanthrene (see Table 13). This indicates the reliability of the level of theory used in the present work. The experimental dissociation energy of phenanthrene radical cation is ≤85.5 ± 3 kcal/mol.[24] This is much higher than the 65.3 kcal/mol predicted theoretically for acenaphthylene formation, which is the most stable isomer. The most plausible structure is biphenylene, for which the calculated dissociation energy is 90.5 kcal/mol. Kinetically the formation of biphenylene is a favorable process since it is a direct HC≡CH elimination from the original 9,10 positions of phenanthrene concomitant with the four-membered-ring closure. Thus both anthracene and phenanthrene yield the same product, **B**. This means that the anthracene radical cation isomerizes to phenanthrene, and the isomerization barrier is lower than the dissociation energy of 104 ± 3 kcal/mol.

D. Evaluation of Thermochemical Data. The heats of formation for most of the product isomers mentioned in this work were not well established (see Table 13). The present calculations allow us to evaluate some of the values. First the most stable $C_4H_4^{\bullet+}$ isomer, methylenecyclopropene, is formed in the fragmentation of the benzene radical cation.[26] From the experimental ΔH_f° values of $C_6H_6^{\bullet+}$ and C_2H_2 and the D_0 of 4.16 ± 0.15 eV,[25] the heat of formation of this cyclic $C_4H_4^{\bullet+}$ isomer should be 278.4 ± 4 kcal/mol. This is about 10 kcal/mol lower that the estimated value (289 kcal/mol) in ref 50 and suggests that the latter (which does not take ref 25 into account) should be revised. The open chain isomer vinylacetylene should have a heat of formation of about 287.7 ± 4 kcal/mol, since it is calculated to be 9.3 kcal/mol higher than the cyclic isomer at the CCSD(T) level. The heat of formation for the benzocyclobutadiene radical cation was calculated to be 275.9 kcal/mol from the experimental dissociation energy of the naphthalene radical cation in a similar way as for methylenecyclopropene, provided it is the product. The phenylacetylene radical cation is calculated to be 4.1 kcal/mol higher at the CCSD(T) level, so the heat of formation for phenylacetylene radical cation should be 280.0 kcal/mol.

Turning to the $C_{12}H_8^{\bullet+}$ isomers, the heat of formation for biphenylene can be calculated from reaction 4 since the values for all the other three reagents are known. This leads to a value of 274.7 kcal/mol. Using the relative energies from the average of B3LYP and B3PW91, we can calculate approximate heats of formation for other isomers. They are listed in Table 13.

Conclusion

The hybrid density functional methods, B3LYP and B3PW91, were tested for calculation of energetics of the acetylene loss from the naphthalene radical cation, together with the CCSD(T) method. The benzocyclobutadiene radical cation is about 4 kcal/mol more stable than the phenylacetylene radical cation, and it was shown to be the most plausible product of the naphthalene radical cation fragmentation. The acetylene loss from anthracene and phenanthrene radical cations doesn't form the most stable isomer, acenaphthylene, when comparing the present calculation and our recent experimental work.[24] Instead they form the same product, biphenylene, which indicates that the isomerization barrier is lower than the dissociation energy.

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Supporting Information Available: B3LYP/cc-pVDZ harmonic frequencies and IR intensities (3 pages). Ordering information is given on any current masthead page.

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