Frequencies and Normal Modes of Vibration of Benz[*a*]anthracene Radical Ions

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MINDO/3-FORCES calculations were carried out for the radical ions of benz[*a*]anthracene. Both ions exhibit C_s symmetry with C-C bond alternation in all four rings. The obtained equilibrium geometry was applied for the calculation of all $3N-6$ vibration frequencies of each ion, and for the analysis of their normal coordinates. The so calculated frequencies of the radical cation were close to the experimental frequencies and those of the ab initio calculations. They fall in the ranges

νCHstr. (3034 – 3087 cm^{-1}), νCCstr. (1237 – 1609 cm^{-1}), δCH (1142 – 1216 cm^{-1}).

Interesting correlations could be obtained for the frequencies of similar vibrations, e. g.

ν_{sym}CHstr. > ν_{asym}CHstr.

Exception is the frequency of vibration of CH_α in ring A for the radical cation and the same bond in ring D for the radical anion. The vibration frequencies for the CH bonds depend on the σ-electron densities of the corresponding carbon atoms, i. e.

νCH$^{\cdot+}$str. > νCHstr. > νCH$^{\cdot-}$str., where $\sigma-\rho_C^{+} > \sigma-\rho_C > \sigma-\rho_C^{-}$.

For the C-C stretching vibrations the relation

ν(C-C)*str.* > ν(C-C)$^{\cdot-}$str. > ν(C-C)$^{\cdot+}$str.

holds, with the exception of the C_β-C_β bond, for which the relation

ν(C-C)str. > ν(C-C)$^{\cdot+}$str. > ν(C-C)$^{\cdot-}$str.

is found. As for the in-plane and out of-plane deformations, the following general correlations

$\delta(\mathrm{CH}) > \delta(\mathrm{CH})^{\cdot-} > \delta(\mathrm{CH})^{\cdot+}$ and $\gamma(\mathrm{CC}) > \gamma(\mathrm{CC})^{\cdot-} > \gamma(\mathrm{CC})^{\cdot+}$.

Key words: Benz[*a*]anthracene; Vibrations; Ions.

1. Introduction

The chemistry of polyaromatic hydrocarbons (PAHs) is gaining increasing importance due to their carcinogenic properties and their presence in interstellar spaces [1]. They could become potential starting materials for petrochemical industries, being a significant component of the heavy fractions of earth oils [2]. For these reasons considerable efforts were made to study their chemical and physical properties [1], e. g. IR spectroscopic studies which were done for their radical cations too. Benz[*a*]anthracene, Fig. 1, is a prominent member of the PAH family, for which IR spectroscopic studies were done. Measurements were done for its radical cation in the isolated matrix [3], as well as ab initio theoretical studies [4]. However a complete normal coordinate analysis on the symmetry and the valence basis of all its $3N-6$ vibration modes is still missing.

In a former paper [5] we described MINDO/3-FORCES SCF-MO treatments for the evaluation of the vibration frequencies and IR absorption intensities of different organic molecules. The method yielded frequencies that were very close to the experimental and ab initio calculated frequencies. In addition to these results, it was possible to assign all the vibration modes both symmetrically and according to their valence nature. The valence assignment could be done considering the calculated atomic partial participation (APP) values [6] and the graphical pictures of all vibration modes as drawn applying the DRAW.MOL routine [7] (Figure 2).

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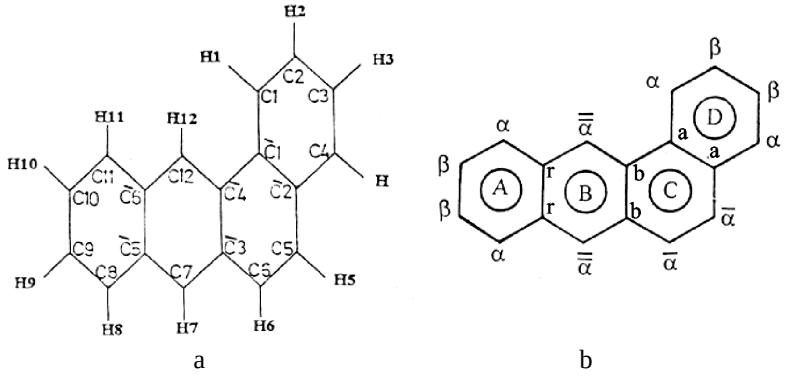

Fig. 1. Benz[*a*]anthracene molecule, (a) IUPAC and (b) nomenclature used in this text.

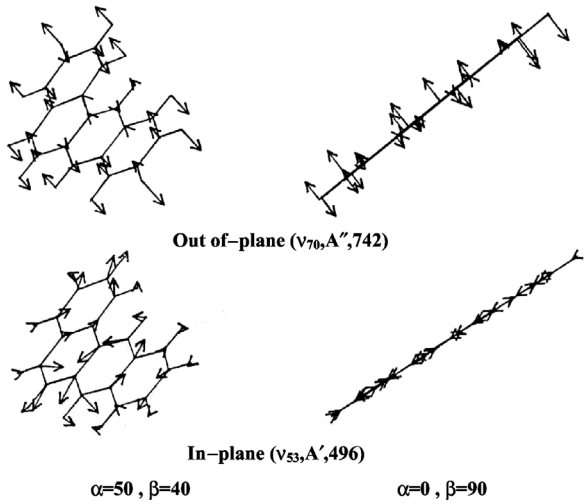

Fig. 2. DRAW.MOL plotted graphical pictures of two vibration modes of the benz[*a*]anthracene radical cation.

Table 1. MINDO/3-FORCES calculated geometric structures of benz[*a*]anthracene radical cation, radical anion and neutral molecule; lengths in Å, angles in deg.

Lengths	Cation	Neutral molecule [9]	Anion
C_1-C_2	1.394	1.395	1.392
C_2-C_3	1.423	1.412	1.423
C_3-C_4	1.383	1.393	1.382
C_4-C'_2	1.451	1.431	1.450
C_5-C'_2	1.434	1.471	1.433
C_5-C_6	1.393	1.356	1.390
C_6-C'_3	1.434	1.472	1.435
C_7-C'_3	1.435	1.406	1.432
C_7-C'_5	1.423	1.431	1.423
C_8-C'_5	1.447	1.456	1.447
C_8-C_9	1.392	1.375	1.391
C_9-C_{10}	1.417	1.436	1.415
C_{10}-C_{11}	1.401	1.375	1.399
C_{11}-C'_6	1.430	1.456	1.431
C_{12}-C'_6	1.450	1.433	1.448
C_{12}-C'_4	1.407	1.408	1.408
C_1-C'_1	1.433	1.434	1.435
C'_1-C'_2	1.476	1.456	1.476
C'_1-C'_4	1.492	1.502	1.493
C'_3-C'_4	1.486	1.478	1.488
C'_5-C'_6	1.477	1.463	1.478
C_1-H_1	1.106	1.107	1.111
C_2-H_2	1.104	1.105	1.107
C_3-H_3	1.103	1.105	1.109
C_4-H_4	1.105	1.107	1.110
C_5-H_5	1.106	1.107	1.110
C_6-H_6	1.106	1.107	1.110
C_7-H_7	1.109	1.109	1.110
C_8-H_8	1.106	1.107	1.109
C_9-H_9	1.103	1.105	1.110
C_{10}-H_{10}	1.104	1.105	1.108
C_{11}-H_{11}	1.105	1.107	1.110
C_{12}-H_{12}	1.109	1.109	1.110

2. Results and Discussion

Both radical ions of benz[*a*]anthracene are planar and of C_s symmetry, according to the MINDO/3-FORCES calculated geometric structures (Table 1). Both ions posses two irreducible representations, *E* and σ_h. Table 1 includes the MINDO/3-FORCES calculated geometry for the neutral molecule too.

The calculated geometric structures were applied for the calculation of the vibration frequencies and APP values for all vibration modes of the two radical ions. Table 2 shows the so obtained frequencies for the radical cation of benz[*a*]anthracene. The ordering of the modes follows the Herzberg convention [8]. Table 3 includes the calculated IR absorption intensities for each mode of the ion.

Generally the frequency values of the cation compare well with the experimental values of Allemendola and Hudgins [3] and the theoretical values of Langhoff [4]. The present treatment enables calculating and assigning all $3N - 6$ vibration modes at once. The knowledge of the valence form of each vibration,

Table 1 (continued).

Angles	Cation	Neutral molecule [9]	Anion
$\angle C_1C_2C_3$	120.600	120.000	119.300
$\angle C_2C_3C_4$	119.100	119.340	119.600
$\angle C_3C_4C'_2$	122.300	122.000	122.900
$\angle C'_2C_5C_6$	122.800	122.683	122.200
$\angle C_5C_6C'_3$	122.000	122.683	123.200
$\angle C'_3C_7C'_5$	124.900	124.750	124.750
$\angle C'_5C_8C_9$	121.900	122.000	122.000
$\angle C_8C_9C_{10}$	119.900	120.000	120.000
$\angle C_1C'_1C'_4$	124.700	124.050	124.050
$\angle C'_2C'_1C'_4$	119.000	119.340	119.340
$\angle C_4C'_2C_5$	122.900	122.683	122.683
$\angle C'_1C'_2C_5$	118.500	118.034	118.034
$\angle C_6C'_3C_7$	122.900	123.367	123.367
$\angle C_7C'_3C'_4$	118.600	118.683	118.683
$\angle C'_3C'_4C_{12}$	116.000	116.104	116.104
$\angle C'_1C'_4C_{12}$	124.900	124.750	124.750
$\angle C_7C'_5C'_8$	125.200	125.450	125.700
$\angle C_8C'_5C'_6$	117.900	118.034	117.000
$\angle C'_5C'_6C_{11}$	117.900	117.387	117.900
$\angle C_{11}C'_6C_{12}$	124.700	124.750	125.000
$\angle C'_6C_{12}C'_4$	126.100	125.450	126.100
$\angle H_1C_1C_2$	117.900	117.400	116.400
$\angle H_2C_2C_3$	119.700	120.000	119.800
$\angle H_3C_3C_4$	120.900	120.664	120.800
$\angle H_4C_4C'_2$	117.700	118.685	118.300
$\angle H_5C_5C_6$	118.400	120.000	119.200
$\angle H_6C_6C'_3$	118.900	122.683	118.500
$\angle H_7C_7C'_5$	117.900	117.400	117.500
$\angle H_8C_8C_9$	119.800	120.000	118.800
$\angle H_9C_9C_{10}$	119.900	118.680	119.400
$\angle H_{10}C_{10}C_{11}$	119.700	120.664	120.600
$\angle H_{11}C_{11}C_{10}$	119.200	120.000	118.200
$\angle H_{11}C_{11}C'_6$	118.900	118.034	119.000
$\angle H_{12}C_{12}C'_4$	118.700	118.685	118.800

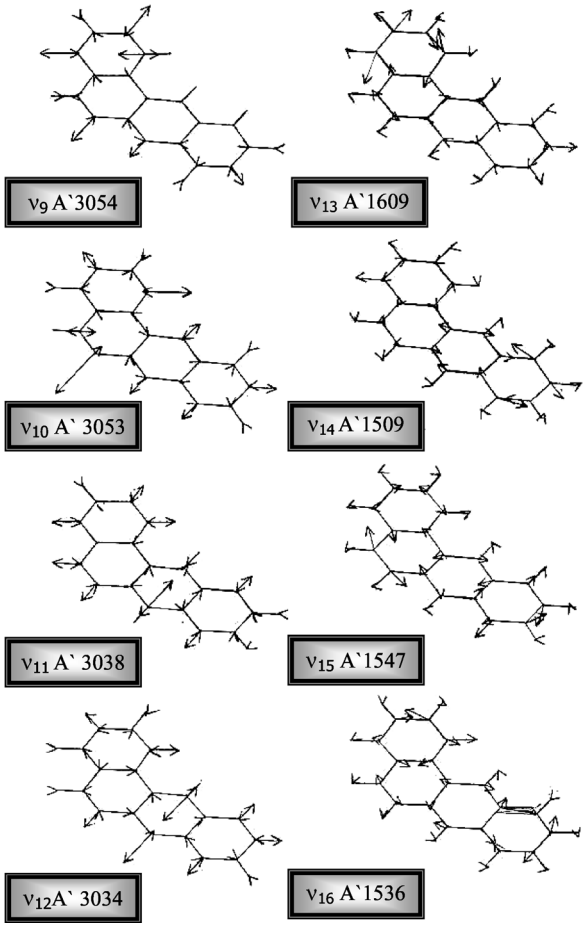

Fig. 3. Graphical pictures of some vibration modes of the benz[*a*]anthracene radical cation as drawn through the DRAW.MOL routine.

as provided by the APP values and DRAW.MOL pictures, Fig. 3 allows a correlative comparison of the modes and consequently the force constants and bond strengths within the molecule.

As for the benz[*a*]anthracene anion no experimental IR data are known in the literature. However, since such an anion can be formed as intermediate in chemical reactions, it is interesting to study its vibrations theoretically. For this reason we carried out a similar treatment for the molecule's anion as was done for its cation. Table 4 includes the calculated vibration frequencies and IR absorption intensities for the benz[*a*]anthracene anion.

2.1. The C-H Stretching Vibrations

For each ion and neutral molecule 57 C-H stretching modes are calculated. Inspection of their frequencies reveals that for both ions the following relation holds:

$$\nu_{sym}\text{CHstr.} > \nu_{asym}\text{CHstr.}$$

Exceptions are for the cation:

$$\nu_{asym}\text{CH}_\alpha\text{str.(ring D)} > \nu_{sym}\text{CH}_\alpha\text{str. (ring D)},$$

and for the anion:

$$\nu_{asym}\text{CH}_\alpha\text{str. (ring A)} > \nu_{sym}\text{CH}_\alpha\text{str. (ring A)}.$$

The νCHstr. frequency increases on going from the radical cation to the neutral and the radical anion:

$$\nu\text{CH}^{\cdot+}\text{str.} > \nu\text{CHstr.} > \nu\text{CHstr.}^{\cdot-}$$

As explained in [10] the introduction of a positive charge to the molecule causes an increase, that of a negative charge a decrease in the σ-electron density of the carbon atoms of the PAH molecules. In fact, the

Table 2. Calculated vibration frequencies and IR absorption intensities of the benz[*a*]anthracene radical cation.

Symmetry and description	Frequency in cm^{-1} This work Scaled	Others Calcd. [4]	Others Exptl. [3]
A′			
ν_1 CH_β str.	3087	3104	—
ν_2 CH_β str.	3086	—	—
ν_3 CH_β str.	3076	—	—
ν_4 CH_β str.	3074	—	—
ν_5 $CH_{\alpha'}$ str.	3065	—	—
ν_6 CH_α str.	3062	—	—
ν_7 CH_α str.	3061	—	—
ν_8 CH_α str.	3059	—	—
ν_9 CH_α str.	3054	—	—
ν_{10} $CH_{\alpha'}$ str.	3053	—	—
ν_{11} $CH_{\alpha''}$ str.	3038	—	—
ν_{12} $CH_{\alpha''}$ str.	3034	—	—
ν_{13} (C_β-C_α)str.	1609	—	—
ν_{14} C_β-C_α)str.	1579	1588	1578
ν_{15} ($C_{\alpha'}$-$C_{\alpha'}$)str. + (C_β-C_β)str. + (C_r-C_r)str.	1547	1557	—
ν_{16} (C_β-C_β)str. + (C_r-C_α)str.	1536	1535	1540
ν_{17} ($C_{\alpha'}$-$C_{\alpha'}$)str. + (C_a-C_b)str.	1515	1523	1528
ν_{18} (C_a-$C_{\alpha'}$)str. + (C_b-$C_{\alpha'}$)str.	1506	1499	—
ν_{19} (C_r-$C_{\alpha''}$)str. + (C_b-$C_{\alpha''}$)str.	1466	1472	1477
ν_{20} (C_b-$C_{\alpha''}$)str. + (C_r-$C_{\alpha''}$)str.	1429	—	1406
ν_{21} ($C_{\alpha'}$-$C_{\alpha'}$)str.	1400	—	1392
ν_{22} (C_a-C_a)str.	1360	1373	1376
ν_{23} ring(CC)str.	1339	—	1351
ν_{24} (C_β-C_α)str. + ($C_{\alpha''}$-C_r)str.	1334	1335	1333
ν_{25} (C_r-C_r)str. + (C_b-$C_{\alpha''}$)str.	1319	1300	—
ν_{26} (C_b-C_b)str. + (C_a-$C_{\alpha'}$)str. + (C_r-$C_{\alpha''}$)str.	1297	1287	—
ν_{27} ring(CC)str. (ring A & B)	1245	1243	—
ν_{28} ring(CCC)str.	1239	—	—
ν_{29} ring(CCC)str.	1237	—	1231
ν_{30} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + (C_β-C_β) & (C_α-C_α)str.	1216	1233	1226
ν_{31} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + (C_α-C_a)str.	1204	—	1209
ν_{32} $\delta CH_{\alpha''}$ + δCH_α + ring(δCCC)	1195	1188	1182
ν_{33} δCH_α + ring(δCCC)	1174	—	—
ν_{34} δCH_α + $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + ring(CCC)str.	1166		—
ν_{35} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + δCH_α + ring(δCCC)	1129	—	—
ν_{36} $\delta CH_{\alpha'}$ + δCH_β + δCH_α	1177	—	—
ν_{37} δCH_β + δCH_α	1164	—	—
ν_{38} δCH_β + δCH_α	1161	—	—
ν_{39} δCH_α + δCH_β + ring(δCCC)	1092	1098	1102
ν_{40} δCH_β + δCH_α	1156	1153	—
ν_{41} δCH_β + δCH_α	1150	—	—
ν_{42} δCH_β + $\delta CH_{\alpha'}$ + δCH_α	1142	—	—
ν_{43} ring(δCCC)+ $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$	1010	—	—
ν_{44} ring(δCCC)+ δCH_α & $\delta CH_{\alpha''}$	883	—	—
ν_{45} ring($\delta C_\alpha C_\beta C_\beta$)	860	—	—
ν_{46} ring($\delta C_\alpha C_\beta C_\beta$)	851	—	—
ν_{47} ring(δCCC)	832	—	—
ν_{48} ring(δCCC)	738	—	—
ν_{49} ring(δCCC)	654	—	—
ν_{50} ring(δCCC)	611	—	—
ν_{51} ring(δCCC)	577	—	—
ν_{52} ring(δCCC)	527	522	—
ν_{53} ring(δCCC)	496	—	—
ν_{54} ring(δCCC)	454	—	—
ν_{55} ring(δCCC)	371	—	—
ν_{56} ring(δCCC)	310	—	—
ν_{57} ring(δCCC)	166	—	—
Out of-plane			
A″			
ν_{58} γCH_β + γCH_α	984	—	
ν_{59} γCH_β + γCH_α	981	—	—
ν_{60} $\gamma CH_{\alpha'}$ + γCH_β	980	—	—
ν_{61} γCH_β + γCH_α	974	—	—
ν_{62} γCH_α + γCH_β	963	—	—
ν_{63} γCH_α + $\gamma CH_{\alpha''}$	950	—	—
ν_{64} $\gamma CH_{\alpha''}$	941	—	—
ν_{65} γCH_α + γCH_β	921	—	—
ν_{66} $\gamma CH_{\alpha''}$ + γCH_α	907	909	911
ν_{67} $\gamma CH_{\alpha'}$ + $\gamma CH_{\alpha''}$	867	—	—
ν_{68} γ(C_a-C_a) + γ(C_b-C_b) + γCH_α	815	827	—
ν_{69} γCH_β + γCH_α	798	756	—
ν_{70} γCH_β + γCH_α	791	—	—
ν_{71} γ(C_r-C_r) + $\gamma CH_{\alpha''}$ + γCH_α	757	769	—
ν_{72} γ(C_b-C_b) + γ(C_a-C_a)	649	—	—
ν_{73} γ(C_a-C_a) + γ(C_b-C_b) + γCH_α	548	—	—
ν_{74} γ(C_β-C_β) + γCH_β	518	—	—
ν_{75} γ(C_β-C_β) + γCH_β	506	—	—
ν_{76} γ(C_r-C_r) + γCH_α + $\gamma CH_{\alpha''}$	483	—	—
ν_{77} ring(γCCC)+ γCH_α	431	439	—
ν_{78} ring(γCCC)+ $\gamma CH_{\alpha''}$	382	—	—
ν_{79} γ($C_{\alpha''}$-$C_{\alpha''}$)	264	—	—
ν_{80} γ($C_{\alpha''}$-C_b)	249	—	—
ν_{81} ring(γCCC)	180	—	—
ν_{82} ring(γCCC)	136	—	—
ν_{83} γ(C_α-C_β) + γ($C_{\alpha''}$-C_b) & γ(C_β-C_β)	60	—	—
ν_{84} γ(C_α-C_α)+ γ(C_α-C_β)	58	—	—

Scaling factors: 0.876 (CHstr.); 0.96 (ring (CC)str.); 1.00 (ring (CCC)str.); 1.06 (δCH); 1.08 (ring(δCCC); 1.11 (γCH); 1.11 (γCCC); 1.03 (γCC). Special scaling factors were used for vibration modes with overlaps of different types of motion; 1.06 [ring (CCC)str. + δCH]; 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH+ γCC).

calculation of the σ-electron densities at the carbon atoms ($\rho_{2s} + \rho_{2p_x} + \rho_{2p_y}$) yields the following correlation for all atoms:

$$\sigma - \rho_C^+ > \sigma - \rho_C > \sigma - \rho_C^- .$$

Figure 4 shows the correlation curve between the C-H stretching frequencies and the calculated σ-electron densities for the corresponding carbon atoms.

2.2. The C-C Stretching Vibrations

Totally seventeen such vibration modes (Nc-1) were calculated. For these bonds also different vibration frequencies and consequently force constants may be detected. The order of magnitudes of the C-C vibration frequencies follows the relation

$$\underset{\text{ring D}}{\nu_{asym}(C_\beta - C_\alpha)str.} > \underset{\text{ring A}}{\nu_{asym}(C_\beta - C_\alpha)str.},$$

and for the rings:

Ring D:

$$\nu_{asym}(C_\beta - C_\alpha)\text{str.} > \nu_{sym}(C_\beta - C_\beta)\text{str.} > \nu_{sym}(C_a - C_a)\text{str.}$$

Table 3. Calculated IR absorption intensities of the benz[*a*]anthracene radical cation.

Symmetry and description	Intensity in Km/mol This work	Calcd. [4]
In-plane		
A′		
ν_1 CH_β str.	28.14	12.1
ν_2 CH_β str.	34.38	—
ν_3 CH_β str.	22.02	—
ν_4 CH_β str.	20.80	—
ν_5 $CH_{\alpha'}$ str.	35.67	—
ν_6 CH_α str.	0.11	—
ν_7 CH_α str.	7.60	—
ν_8 CH_α str.	19.84	—
ν_9 CH_α str.	7.36	—
ν_{10} $CH_{\alpha'}$ str.	6.36	—
ν_{11} $CH_{\alpha''}$ str.	8.21	—
ν_{12} $CH_{\alpha''}$ str.	25.39	—
ν_{13} (C_β-C_α)str.	71.33	—
ν_{14} (C_β-C_α)str.	27.61	69.8
ν_{15} ($C_{\alpha'}$-$C_{\alpha'}$)str. + (C_β-C_β)str. + (C_r-C_r)str.	15.55	76.6
ν_{16} (C_β-C_β)str. + (C_r-C_α)str.	128.02	—
ν_{17} ($C_{\alpha'}$-$C_{\alpha'}$)str. + (C_a-C_b)str.	248.90	145.5
ν_{18} (C_a-$C_{\alpha'}$)str. + (C_b-$C_{\alpha'}$)str.	25.03	29.3
ν_{19} (C_r-$C_{\alpha''}$)str. + (C_b-$C_{\alpha''}$)str.	117.79	122.1
ν_{20} (C_b-$C_{\alpha''}$)str. + (C_r-$C_{\alpha''}$)str.	36.82	—
ν_{21} ($C_{\alpha'}$-$C_{\alpha'}$)str.	64.54	142.1
ν_{22} (C_a-C_a)str.	7.28	—
ν_{23} ring(CCC)str.	24.20	—
ν_{24} (C_β-C_α)str. + ($C_{\alpha''}$-C_r)str.	49.89	620.5
ν_{25} (C_r-C_r)str. + (C_b-$C_{\alpha''}$)str.	53.76	—
ν_{26} (C_b-C_b)str. + (C_a-$C_{\alpha'}$)str. + ($C_r C_{\alpha''}$)str.	473.78	—
ν_{27} ring(CC)str.	60.56	46.6
ν_{28} ring(CC)str. (ring A + B)	13.93	46.8
ν_{29} ring(CCC)str.	10.49	70.1
ν_{30} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + (C_β-C_β) & ($C_\alpha C_\alpha$)str.	329.67	177.8
ν_{31} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + (C_α-Ca)str.	8.19	—
ν_{32} $\delta CH_{\alpha''}$ + δCH_α + ring(δCCC)	71.96	20.6
ν_{33} δCH_α + ring(δCCC)	50.46	—
ν_{34} δCH_α + $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$	0.56	—
ν_{35} $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$ + δCH_α + ring(δCCC)	29.56	—
ν_{36} $\delta CH_{\alpha'}$ + δCH_β + δCH_α	0.12	—
ν_{37} δCH_β + δCH_α	20.15	—
ν_{38} δCH_β + δCH_α	1.84	41.2
ν_{39} δCH_α + δCH_β + ring(δCCC)	0.68	41.2
ν_{40} δCH_β + δCH_α	7.68	—
ν_{41} δCH_β + δCH_α	4.83	—
ν_{42} δCH_β + $\delta CH_{\alpha'}$ + δCH_α	6.02	—
ν_{43} ring(δCCC) + $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$	2.96	—
ν_{44} ring(δCCC) + δCH_α & $\delta CH_{\alpha''}$	11.09	—
ν_{45} ring($\delta C_\alpha C_\beta C_\beta$)	5.05	—
ν_{46} ring($\delta C_\alpha C_\beta C_\beta$)	0.06	—
ν_{47} ring(δCCC)	0.81	—
ν_{48} ring(δCCC)	0.08	—
ν_{49} ring(δCCC)	0.16	—
ν_{50} ring(δCCC)	0.13	—
ν_{51} ring(δCCC)	0.69	—
ν_{52} ring(δCCC)	15.95	31.7
ν_{53} ring(δCCC)	0.51	—
ν_{54} ring(δCCC)	0.04	—
ν_{55} ring(δCCC)	0.19	—
ν_{56} ring(δCCC)	1.17	—
ν_{57} ring(δCCC)	0.23	—
Out of-plane		
A″		
ν_{58} γCH_β + γCH_α	0.06	—
ν_{59} γCH_β + γCH_α	0.47	—
ν_{60} $\gamma CH_{\alpha'}$ + γCH_β	0.16	—
ν_{61} γCH_β + γCH_α	0.14	—
ν_{62} γCH_α + γCH_β	0.00	—
ν_{63} γCH_α + $\gamma CH_{\alpha''}$ + ring(γCCC)	0.03	—
ν_{64} $\gamma CH_{\alpha''}$	0.31	—
ν_{65} γCH_α + γCH_β	0.10	—
ν_{66} $\gamma CH_{\alpha''}$ + γCH_α	0.47	40.9
ν_{67} $\gamma CH_{\alpha'}$ + $\gamma CH_{\alpha''}$	1.19	—
ν_{68} γ(C_a-C_a) + γ(C_b-C_b) + γCH_α	1.74	26.5
ν_{69} γCH_β + γCH_α	4.26	60.5
ν_{70} γCH_β + γCH_α	0.11	—
ν_{71} γ(C_r-C_r) + $\gamma CH_{\alpha''}$ + γCH_α	0.47	25.6
ν_{72} γ(C_b-C_b) + γ(C_a-C_a)	0.29	—
ν_{73} γ(C_a-C_a) + γ(C_b-C_b) + γCH_α	0.32	—
ν_{74} γ(C_β-C_β) + γCH_β	0.13	—
ν_{75} γ(C_β-C_β) + γCH_β	0.10	—
ν_{76} γ(C_r-C_r) + γCH_α + $\gamma CH_{\alpha''}$	1.65	—
ν_{77} ring(γCCC)+ γCH_α	0.34	13.1
ν_{78} ring(γCCC)+ $\gamma CH_{\alpha''}$	0.59	—
ν_{79} γ($C_{\alpha''}$-$C_{\alpha''}$)	0.09	—
ν_{80} γ($C_{\alpha''}$-C_b)	0.20	—
ν_{81} ring(γCCC)	0.27	—
ν_{82} ring(γCCC)	0.12	—
ν_{83} γ(C_α-C_β) + γ($C_{\alpha''}$-C_b) & γ(C_β-C_β)	0.12	—
ν_{84} γ(C_α-C_α) + γ(C_α-C_β)	0.09	—

Ring C:

$$\nu_{sym}(\mathrm{C}_{\alpha'}-\mathrm{C}_{\alpha'})\mathrm{str.} > \nu_{sym}(\mathrm{C}_{\alpha'}-\mathrm{C_a})\mathrm{str.} > \nu_{sym}(\mathrm{C}_{\alpha'}-\mathrm{C}_{\alpha'})\mathrm{str.} > \nu_{sym}(\mathrm{C_a}-\mathrm{C_a})\mathrm{str.} > \nu_{sym}(\mathrm{C_b}-\mathrm{C_b})\mathrm{str.},$$

Ring B:

$$\nu_{sym}(\mathrm{C}_{\alpha''}-\mathrm{C_r})\mathrm{str.} > \nu_{sym}(\mathrm{C}_{\alpha''}-\mathrm{C_b})\mathrm{str.} > \nu_{sym}(\mathrm{C_r}-\mathrm{C_r})\mathrm{str.} > \nu_{sym}(\mathrm{C_b}-\mathrm{C_b})\mathrm{str.},$$

Ring A:

$$\nu_{asym}(\mathrm{C}_\beta-\mathrm{C}_\alpha)\mathrm{str.} > \nu_{sym}(\mathrm{C}_\beta-\mathrm{C}_\beta)\mathrm{str.} > \nu_{sym}(\mathrm{C_r}-\mathrm{C_r})\mathrm{str.}.$$

As for the middle bonds, the following relation applies:

$$\nu_{sym}(\mathrm{C_a}-\mathrm{C_a})\mathrm{str.} > \nu_{sym}(\mathrm{C_r}-\mathrm{C_r})\mathrm{str.} > \nu_{sym}(\mathrm{C_b}-\mathrm{C_b})\mathrm{str.}.$$

Comparing the frequencies of the C-C bonds of the three differently charged species one finds the general relation

$$\nu(\mathrm{C\text{-}C})\mathrm{str.} > \nu(\mathrm{C\text{-}C})^{\cdot-}\mathrm{str.} > \nu(\mathrm{C\text{-}C})^{\cdot+}\mathrm{str.}$$

with the exception of the C_β-C_β bond, for which the radical cation shows a higher frequency than the radical anion, i. e.

$$\nu(\mathrm{C\text{-}C})\mathrm{str.} > \nu(\mathrm{C\text{-}C})^{\cdot+}\mathrm{str.} > \nu(\mathrm{C\text{-}C})^{\cdot-}\mathrm{str.}.$$

Table 4. Calculated vibration frequencies and IR absorption intensities of benz[*a*]anthracene radical anion.

Symmetry and description	Frequency in cm^{-1} Scaled	Intensity in Km/mol Calcd.
A′		
ν_{27} ring(CCC)str. + δCH_{β}	1385	75.76
ν_{28} ring(CCC)str. + $\delta CH_{\alpha'}$ & $\delta CH_{\alpha''}$	1368	6.17
ν_{29} ring(CCC)str.	1238	1.70
ν_{30} $\delta CH_{\alpha'}$ + ring(C-C)str.	1214	86.97
ν_{31} $\delta CH_{\alpha''}$ + δCH_{α}	1284	13.62
ν_{32} $\delta CH_{\alpha''}$ + δCH_{α} + ring(C-C)str.	1189	11.64
ν_{33} δCH_{α} + $\delta CH_{\alpha'}$ & $\delta CH_{\alpha''}$ + ring(δCCC)	1181	10.04
ν_{34} δCH_{α} + $\delta CH_{\alpha''}$ + ring(δCCC)	1171	43.25
ν_{35} $\delta CH_{\alpha'}$ + δCH_{β}	1185	0.63
ν_{36} δCH_{α} + δCH_{β}	1177	1.58
ν_{37} δCH_{β} + δCH_{α}	1117	7.03
ν_{38} δCH_{α} + δCH_{β} + ring(δCCC)	1100	0.76
ν_{39} δCH_{β}	1165	6.76
ν_{40} δCH_{β} + δCH_{α}	1160	3.42
ν_{41} δCH_{β} + $\delta CH_{\alpha'}$ + ring(δCCC)	1086	54.63
ν_{42} ring(C-C)str. + $\delta CH_{\alpha'}$ + $\delta CH_{\alpha''}$	1066	173.16
ν_{43} ring(δCCC) + $\delta CH_{\alpha''}$ + $\delta CH_{\alpha'}$	1014	9.42
ν_{44} ring(δCCC) + $\delta CH_{\alpha''}$	888	29.51
ν_{45} ring($\delta C_{\alpha}C_{\beta}C_{\beta}$)	863	3.18
ν_{46} ring($\delta C_{\alpha}C_{\beta}C_{\beta}$)	845	0.09
ν_{47} ring(δCCC)	833	10.90
ν_{48} ring(δCCC)	736	1.95
ν_{49} ring(δCCC)	660	6.41
ν_{50} ring(δCCC)	617	0.05
ν_{51} ring(δCCC)	583	1.44
ν_{52} ring(δCCC)	535	0.04
ν_{53} ring(δCCC)	502	2.97
ν_{54} ring(δCCC)	461	0.46
ν_{55} ring(δCCC)	376	0.23
ν_{56} ring(δCCC)	314	0.57
ν_{57} ring(δCCC)	168	0.34

Symmetry and description	Frequency in cm^{-1} Scaled	Intensity in Km/mol Calcd.
Out of-plane		
A″		
ν_{58} γCH_{β} + γCH_{α}	955	0.51
ν_{59} γCH_{β} + γCH_{α}	946	0.77
ν_{60} γCH_{α} + γCH_{β}	943	0.54
ν_{61} γCH_{α} + γCH_{β}	909	0.23
ν_{62} $\gamma CH_{\alpha'}$	897	0.05
ν_{63} γCH_{α} + γCH_{β}	871	0.04
ν_{64} γCH_{α} + γCH_{β}	848	0.50
ν_{65} $\gamma CH_{\alpha''}$ + $\gamma(C_a\text{-}C_b)$	773	1.85
ν_{66} $\gamma CH_{\alpha'}$ + γCH_{β} + ring(γCCC)	753	4.45
ν_{67} $\gamma(C_a\text{-}C_b)$ + $\gamma CH_{\alpha''}$	800	0.03
ν_{68} $\gamma CH_{\alpha''}$ + γCH_{β} + γCH_{α}	791	1.58
ν_{69} γCH_{β} + $\gamma(C_b\text{-}C_b)$	721	0.09
ν_{70} $\gamma CH_{\alpha''}$ + γCH_{α} & γCH_{β}	767	0.91
ν_{71} $\gamma(C_r\text{-}C_r)$ + $\gamma CH_{\alpha''}$	758	0.41
ν_{72} $\gamma(C_a\text{-}C_a)$ + $\gamma(C_b\text{-}C_b)$ + $\gamma CH_{\alpha'}$	697	0.15
ν_{73} $\gamma(C_a\text{-}C_a)$ + $\gamma(C_b\text{-}C_b)$ + γCH_{α}	554	0.01
ν_{74} $\gamma(C_{\beta}\text{-}C_{\beta})$	498	0.35
ν_{75} $\gamma(C_{\beta}\text{-}C_{\beta})$ + γCH_{β}	524	0.00
ν_{76} $\gamma(C_r\text{-}C_r)$ + γCH_{α}	500	1.11
ν_{77} ring(γCCC) + γCH_{α}	436	0.06
ν_{78} $\gamma(C_{\alpha'}\text{-}C_{\alpha'})$ + $\gamma(C_{\alpha''}\text{-}C_b)$	351	0.76
ν_{79} ring(γCCC)	299	0.02
ν_{80} $\gamma(C_{\alpha''}\text{-}C_{\alpha''})$	245	0.06
ν_{81} ring(γCCC)	188	0.11
ν_{82} ring(γCCC)	143	0.01
ν_{83} ring(γCCC)	70	0.05
ν_{84} ring(γCCC)	64	0.00

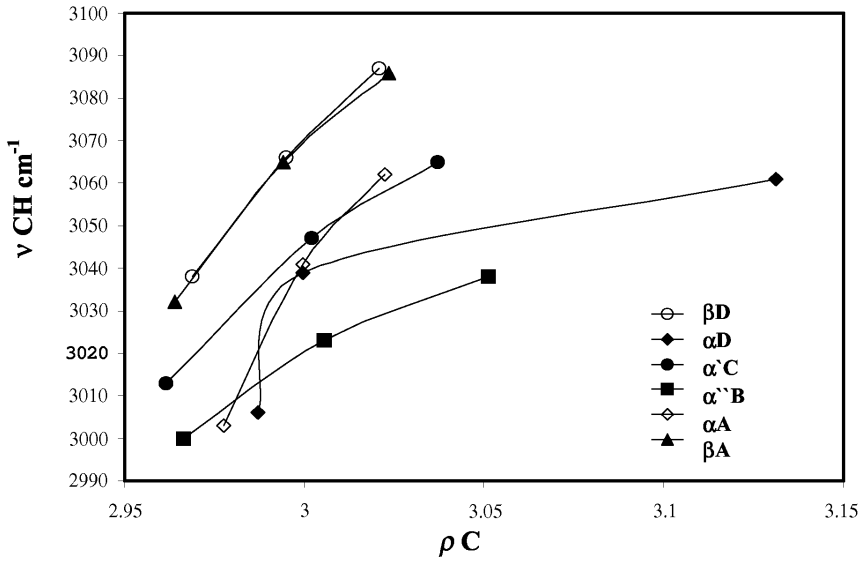

Fig. 4. Graphical correlation of the calculated σ-ρ_C at different carbon atoms with the corresponding C-H vibration frequencies ν for each carbon atom in benz[*a*]anthracene radical ions and the neutral molecule.

2.3. The In-plane δCH Vibration

Similarly, different frequencies are calculated for the δCH deformation vibrations of the different CH bonds. As for the radical cation twelve such vibrations were detected ($\nu = 1032-1236\ \mathrm{cm}^{-1}$), and in general the symmetric modes have higher frequencies than the asymmetric ones. The frequencies values decrease on going from the neutral molecules to the radical cation, through the radical anion.

$$\delta(\mathrm{CH}) > \delta(\mathrm{CH})^{\cdot -} > \delta(\mathrm{CH})^{\cdot +}.$$

2.4. The out of-plane γCH Vibration

On their turn these vibrations show different frequencies for the different valence positions. For the γCH vibration, the frequency of the radical cation is higher than that of the neutral molecule, which is higher than that of the radical anion. Exception is $\gamma\mathrm{CH}_{\alpha'}$ of the ring C. For the γCC vibration the highest frequency belongs to the neutral molecule followed by the radical anion and then the radical cation; i. e.

$$\gamma(\mathrm{CC}) > \gamma(\mathrm{CC})^{\cdot -} > \gamma(\mathrm{CC})^{\cdot +}.$$

3. Conclusion

It was possible, on applying the MINDO/3-FORCES method, to calculate the different vibration frequencies of all $3N-6$ vibration modes of the PAH benz[*a*]anthracene and its radical ions. Minor deviations of the calculated frequencies for the cation from the available experimental and theoretical ab initio values are detected. Both valence and symmetry assignments of the frequencies allow useful comparison between modes of the same valence nature for the three species. Comparing the frequencies for the different charged species some general and interesting correlations between these and the charge of the molecule are found. The results are expected to be of major importance in discussing the bond strengths and reactivity of the species at different sites of the molecule.

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