Frequencies and Normal Modes of Benz(a)anthracene. A MINDO/3-FORCES Treatment

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Quantum mechanical calculations, based on the MINDO/3-FORCES method, of the vibration frequencies and IR absorption intensities of benz(a)anthracene are reported and compared with calculated vibration frequencies of that molecule. For the first time a complete normal coordinate analysis for the molecule is reported. Interesting correlations between vibration motions of the same type but different symmetries are reported.

Key words: Benz(a)anthracene, Vibration Frequencies, MINDO/3-FORCES.

Introduction

Although there exist various theoretical and experimental studies of the geometry and electronic structure of benz(a)anthracene [1–5], all reported studies of its IR spectrum are of qualitative nature [6–10]. To elucidate the vibration modes of this molecule, we found it necessary to carry out a quantum mechanical study applying an appropriate semiempirical method which suits the size of the numerical problem. For this purpose we applied the MINDO/3-FORCES method [11], which had been applied formerly for the study of the vibration frequencies and IR absorption intensities of various other molecules [12].

The MINDO/3-FORCES method proved successful in all former treatments. It allowed a quantitative estimation of the partial participation of each atom in the vibration of each mode of a molecule. This could be accomplished through the numeric estimation of the so-called partial participation (APP) value [13]. Both the group theoretical character tables as well as the graphical pictures of the vibration modes, drawn through the DRAW.MOL routine [14], were applied for the correct assignment of the vibration frequencies.

Results and Discussion

The planar molecule benz(a)anthracene (C_s), with two symmetry operations (E, σ_h) should possess 84 modes of vibration; fifty-seven of them in-plane (57 A′) and twenty-seven out of plane (27 A′) vibrations. According to the character tables, all vibration modes should be active in the Raman and IR spectra. In order to evaluate the vibration frequencies, it was necessary to calculate the equilibrium geometry of the molecule. This was done applying the FORCES gradient method, such that the minimized geometry corresponds to energy gradients of the order of 10^{-5} au/au. The minimization was done considering all $3N$ atomic cartesian coordinates. The so calculated C–C and C–H bond lengths, Fig. 1, are listed in Table 1 and compared with other theoretically calculated values for the same molecule.

The calculated equilibrium geometry was applied then for the evaluation of the vibration frequencies, IR absorption intensities, and the atomic partial participation (APP) values, as well as Wilson's eigenvector coefficients which help to describe the vibration of the molecule [15]. These were used for the normal coordinate analysis of the vibration, of the molecule. The eigenvector coefficients were introduced then to the DRAW…MOL [14] routine in order to draw the graphical pictures of the atomic displacements for all modes of vibration, Figure 2.

To improve the calculated frequencies, they were multiplied with scaling factors, which had been determined for naphthalene and applied for anthracene and pyrene in [16]. The applied scaling factors in this work are

0.876 (CH str.); 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).

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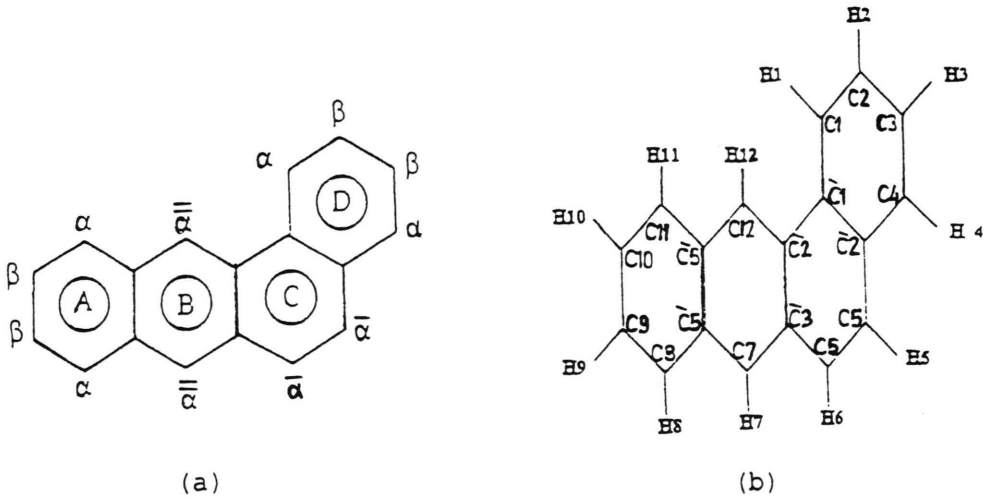

Fig. 1. Structure of the Benz(a)anthracene molecule. (a) Showing the different designations of the C and H atoms; (b) the numbering of the atoms according to the IUPAC convention.

Table 1. Geometry for Benz(a)anthracene molecule.

Bond length (Å)/ angle (deg.)	This work	Other work	
	calcd.	calcd. I [1]	calcd. II [4]
C_1-C_2	1.395	1.390	1.390
C_2-C_3	1.412	1.412	1.409
C_3-C_4	1.393	1.389	1.389
$C_4-\bar{C}_2$	1.431	1.412	1.411
$C_5-\bar{C}_2$	1.471	1.450	1.439
C_5-C_6	1.356	1.395	1.367
$C_6-\bar{C}_3$	1.472	1.451	1.439
$C_7-\bar{C}_3$	1.406	1.397	1.398
$C_7-\bar{C}_5$	1.431	1.417	1.411
$C_8-\bar{C}_5$	1.456	1.434	1.425
C_8-C_9	1.375	1.375	1.378
C_9-C_{10}	1.436	1.428	1.419
$C_{10}-C_{11}$	1.375	1.375	1.379
$C_{11}-\bar{C}_6$	1.456	1.434	1.425
$C_{12}-\bar{C}_6$	1.433	1.417	1.412
$C_{12}-\bar{C}_4$	1.408	1.396	1.396
$\bar{C}_1-\bar{C}_1$	1.434	1.415	1.410
$\bar{C}_1-\bar{C}_2$	1.456	1.409	1.412
$\bar{C}_1-\bar{C}_4$	1.502	1.455	1.455
$\bar{C}_3-\bar{C}_4$	1.478	1.427	1.426
$\bar{C}_5-\bar{C}_6$	1.463	1.421	1.424
C_1-H_1	1.107	–	–
C_2-H_2	1.105	–	–
C_3-H_3	1.105	–	–
C_4-H_4	1.107	–	–
C_5-H_5	1.107	–	–
C_6-H_6	1.107	–	–
C_7-H_7	1.109	–	–
C_8-H_8	1.107	–	–
C_9-H_9	1.105	–	–
$C_{10}-H_{10}$	1.105	–	–
$C_{11}-H_{11}$	1.107	–	–
$C_{12}-H_{12}$	1.109	–	–
$< \bar{C}_1\ C_1\ C_2$	123.367	–	–

Table 1. (Continued).

Bond length (Å)/ angle (deg.)	This work	Other work	
	calcd.	calcd. I [1]	calcd. II [4]
$< C_1\ C_2\ C_3$	120.000	–	–
$< C_2\ C_3\ \bar{C}_4$	119.340	–	–
$< \bar{C}_3\ C_4\ \bar{C}_2$	122.000	–	–
$< \bar{C}_2\ C_5\ C_6$	122.683	–	–
$< \bar{C}_5\ C_6\ \bar{C}_3$	122.683	–	–
$< \bar{C}_3\ C_7\ \bar{C}_5$	124.750	–	–
$< \bar{C}_5\ C_8\ C_9$	122.000	–	–
$< C_8\ C_9\ C_{10}$	120.000	–	–
$< \bar{C}_1\ \bar{C}_1\ \bar{C}_4$	124.050	–	–
$< \bar{C}_2\ \bar{C}_1\ \bar{C}_4$	119.340	–	–
$< \bar{C}_4\ \bar{C}_2\ C_5$	122.683	–	–
$< \bar{C}_1\ \bar{C}_2\ C_5$	118.034	–	–
$< C_6\ \bar{C}_3\ \bar{C}_7$	123.367	–	–
$< \bar{C}_7\ \bar{C}_3\ \bar{C}_4$	118.683	–	–
$< \bar{C}_3\ \bar{C}_4\ C_{12}$	116.104	–	–
$< \bar{C}_1\ \bar{C}_4\ \bar{C}_{12}$	124.750	–	–
$< C_7\ \bar{C}_5\ \bar{C}_8$	125.450	–	–
$< \bar{C}_8\ \bar{C}_5\ \bar{C}_6$	118.034	–	–
$< \bar{C}_5\ \bar{C}_6\ C_{12}$	117.387	–	–
$< \bar{C}_{11}\ \bar{C}_6\ \bar{C}_{12}$	124.750	–	–
$< \bar{C}_6\ C_{12}\ \bar{C}_4$	125.450	–	–
$< H_1\ C_1\ C_2$	117.400	–	–
$< H_2\ C_2\ C_3$	120.000	–	–
$< H_3\ C_3\ \bar{C}_4$	120.664	–	–
$< H_4\ C_4\ \bar{C}_2$	118.685	–	–
$< H_5\ C_5\ \bar{C}_6$	120.000	–	–
$< H_6\ C_6\ \bar{C}_3$	122.683	–	–
$< H_7\ C_7\ \bar{C}_5$	117.400	–	–
$< H_8\ C_8\ C_9$	120.000	–	–
$< H_9\ C_9\ C_{10}$	118.680	–	–
$< H_{10}\ C_{10}\ C_{11}$	120.664	–	–
$< H_{11}\ C_{11}\ \bar{C}_{10}$	120.000	–	–
$< H_{11}\ C_{11}\ \bar{C}_6$	118.034	–	–
$< H_{12}\ C_{12}\ \bar{C}_4$	118.685	–	–

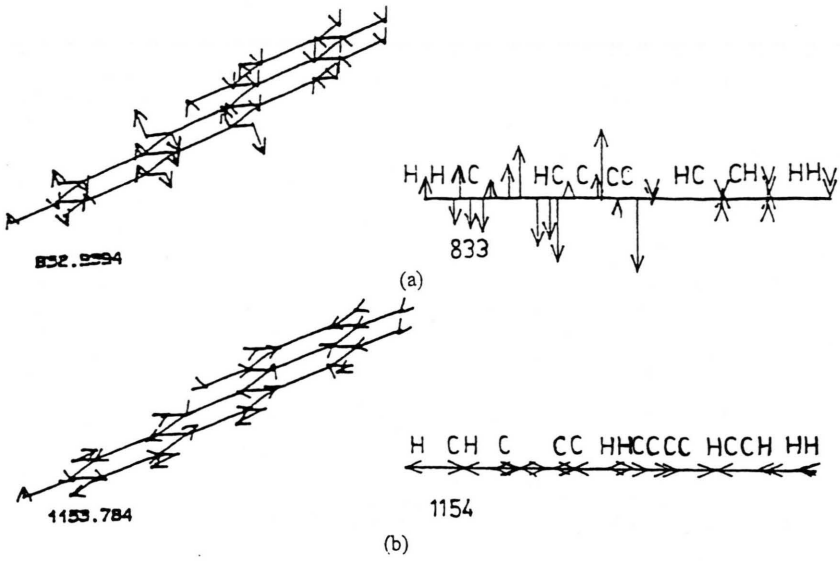

Fig. 2. Graphical representation of two modes of vibration of Benz(a)anthracene. (a) In plane; (b) out of plane as drawn applying the DRAW.MOL routine.

Special scalings factors were used for vibration modes with overlaps of different types of motion; 1.00 (ring (CC) str. + δCH); 1.00 (δCH + ring (CCC) str.); 1.00 (ring δCCC + δCH); 1.06 (ring (CCC) str. + δCH); 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH + γCC).

Table 2 shows the final calculated frequencies and IR absorption intensities for all eighty-four vibration modes of benz(a)anthracene, their group theoretical and valence chemical assignments. Some of the frequencies are compared with other calculated frequencies using density functional theory (DFT) [17].

The present study represents the first quantum mechanical treatment for the vibration problem of benz(a)anthracene. It allows the assignment of twenty two frequencies, appearing in its measured IR spectrum, to their corresponding vibration modes, and the preestimation of the other sixty two frequencies. The predicted frequencies are suitable for future experimental investigations. Comparing the frequencies of the different modes with each other provides some interesting correlations among them, Figure 3.

In Plane Vibration Modes

C-H str. Modes

These are twelve in number ($\nu_1 - \nu_{12}$), the atomic motion of each of them is localized at two C–H bonds only. The four highest frequencies among them belong to the vibration of the $(C–H)_\beta$ bond at the A ring (ν_2), the asymmetric $(C–H\ str.)_\beta$ at the A ring (ν_3) and the asymmetric $(C–H\ str.)_\beta$ at the D ring (ν_4). They are followed by the three symmetric str. vibrations of the H_α and $H_{\alpha'}$ atoms localized at the C, A and D rings ($\nu_5 - \nu_7$); then by three asymmetric α and $\bar{\bar{\alpha}}$ C–H str. vibrations at the rings A, D, C; then by two $(C–H)_{\bar{\bar{\alpha}}}$ vibrations (sym. and asym.). The correlations among these frequencies are summarized as follows:

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

$$\underset{\text{ring D}}{\nu_{asym}(CH\ str.)_\beta} > \underset{\text{ring C}}{\nu_{sym}(CH\ str.)_{\bar{\alpha}}} > \underset{\text{ring A}}{\nu_{sym}(CH\ str.)_\alpha} >$$

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

$$\underset{\text{ring C}}{\nu_{asym}(CH\ str.)_{\bar{\alpha}}} > \underset{\text{ring B}}{\nu_{sym}(CH\ str.)_{\bar{\bar{\alpha}}}} > \underset{\text{ring B}}{\nu_{asym}(CH\ str.)_{\bar{\bar{\alpha}}}} .$$

High IR absorption intensities are calculated for these modes of vibration (0.23–1.46) km/mol.

C–C str. Modes

These are seventeen in number (Nc–1), among which are six C–C str. vibrations, each of which is localized at one ring only. For these vibrations the assumed general relation $\nu_{sym} > \nu_{asym}$ holds. The highest frequency among them (ν_{13}) corresponds to the $C_{\bar{\alpha}} - C_{\bar{\alpha}}$ vibration

Table 2. Vibration frequencies and absorption intensities for Benz(a)anthracene molecule.

Symmetry and description	Frequency cm^{-1}		Intensiv	
	This work scaled	other [17] calcd.	Integ. Γ_I cm^2/mol	absorb. A_I km/mol
In-plane				
A				
ν_1 CH_β str. (in, in) (ring D)	3066	3075	1145.06	40.08
ν_2 CH_β str. (out, out) (ring A)	3065	3064	4195.59	146.80
ν_3 $CH_{(\beta,\alpha)}$ str. (out, in) (ring A)	3054	3055	2725.59	95.05
ν_4 $CH_{(\beta,\alpha)}$ str. (out, in) (ring D)	3053	–	240.24	43.23
ν_5 CH_α str. (out, out) (ring C)	3047	3046	3006.25	104.58
ν_6 CH_α str. (out, out) (ring A)	3041	3043	6.69	0.23
ν_7 CH_α str. (out, in) (ring D)	3039	3039	42.88	1.49
ν_8 $CH_{(\alpha,\beta)}$ str. (out, in) (ring A)	3036	–	996.23	34.53
ν_9 $CH_{(\alpha,\beta)}$ str. (out, in) (ring D)	3034	–	782.12	27.09
ν_{10} CH_α str. (out, in) (ring C)	3031	–	100.10	3.46
ν_{11} CH_α str. (out, out) (ring B)	3023	–	320.28	11.05
ν_{12} CH_α str. (out, in) (ring B)	3017	–	1190.02	40.99
ν_{13} ring $(CC)_{(\bar{\alpha}-\bar{\alpha})}$ str.	1679	–	8.88	0.16
ν_{14} ring (A) $(CC)_{(\alpha-\beta)}$ str.	1661	–	8.60	0.15
ν_{15} ring (D) $(CC)_{(\alpha-\beta)}$ str.	1633	–	2.56	0.04
ν_{16} ring (B) (CC) str.	1626	1618	5.16	0.09
ν_{17} ring (A) (CC) str.	1568	–	3.97	0.06
ν_{18} ring (D) (CC) str.	1557	–	14.13	0.23
ν_{19} ring (B, C) (CCC) str.	1546	–	38.30	0.59
ν_{20} ring (B) (CCC) str.	1543	–	5.63	0.09
ν_{21} rings (A, B, C, D) (CCC) str.	1508	1496	17.89	0.27
ν_{22} rings (A, B, C, D) (CCC) str.	1474	1479	8.04	0.12
ν_{23} ring (A) (CCC) str.	1456	1457	34.15	0.50
ν_{24} rings (C) (CCC) str.	1426	–	3.99	0.60
ν_{25} rings (B, C, D) (CCC) str.	1380	–	16.89	0.23
ν_{26} rings (A, B, C, D) (CCC) str.	1372	–	17.47	0.24
ν_{27} ring (CCC) str. + δCH_β	1363	–	33.19	0.43
ν_{28} $\delta CH_{\bar{\alpha},\bar{\alpha}}$ + ring (CCC) str.	1336	1338	73.80	0.93
ν_{29} ring (CCC) str. + δCH_α	1308	–	37.72	0.47
ν_{30} rings (B, D) (CCC) str. alternate str. + $\delta CH_{\bar{\alpha},\bar{\alpha}}$	1292	–	3.15	0.04
ν_{31} $\delta CH_{\bar{\alpha},\alpha}$ (ring B + A)	1275	–	27.94	0.34
ν_{32} δCH_α (ring D)	1254	–	11.82	0.14
ν_{33} $\delta CH_{\alpha,\bar{\alpha},\bar{\alpha}}$ (ring A, B + C)	1237	–	439.07	5.12
ν_{34} $\delta CH_{\bar{\alpha},\alpha}$ (ring B + A)	1223	–	122.68	1.42
ν_{35} $\delta CH_{(\alpha,\beta)}$ (ring D)	1198	–	88.69	1.00
ν_{36} $\delta CH_{\alpha,\bar{\alpha}}$ (ring D + C)	1173	–	207.57	2.30
ν_{37} $\delta CH_{(\beta,\alpha)}$ (ring A), $_\beta$ (ring D)	1166	–	93.19	1.03
ν_{38} δCH_β (rings D + A)	1165	–	178.99	1.97
ν_{39} $\delta CH_{\beta,\alpha}$ (ring A) + ring (CC) str.	1162	–	103.21	1.13
ν_{40} $\delta CH_{\alpha,\beta}$ (ring A) + ring (CC) str.	1154	–	536.72	5.85
ν_{41} $\delta CH_{\beta,\bar{\alpha}}$+ring (D,B) (CC) str.	1146	–	212.48	2.30
ν_{42} δCH + ring (CC) str.	1073	1049	2.73	0.03
ν_{43} ring (δCCC) + δCH	1002	–	33.47	0.34
ν_{44} ring (δCCC)	958	–	2.12	0.02
ν_{45} ring (δCCC)	863	–	15.31	0.12
ν_{46} ring (δCCC)	855	–	12.31	0.10
ν_{47} ring (δCCC)	834	–	16.26	0.13
ν_{48} ring (δCCC)	740	–	81.38	0.56
ν_{49} ring (δCCC)	658	–	172.26	1.05
ν_{50} ring (δCCC)	619	–	42.49	0.24
ν_{51} ring (δCCC)	581	–	70.55	0.38
ν_{52} ring (δCCC)	536	–	21.40	0.11
ν_{53} ring (δCCC) (clock. bend. ring B)	500	–	0.70	0.00
ν_{54} ring (δCCC) (anti clock bend. ring B)	461	–	8.67	0.04
ν_{55} ring (δCCC)	374	–	5.15	0.02
ν_{56} ring (δCCC)	315	–	41.13	0.12
ν_{57} ring (δCCC) (clock. anti clock ring (A + D) bend)	167	–	20.34	0.03
Out of plane				
A				
ν_{58} γCH_β (ring A) asy.	970	–	0.08	0.00
ν_{59} γCH_β (ring D) asy.	969	–	0.00	0.00
ν_{60} $\gamma CH_{\bar{\alpha}}$	968	–	0.50	0.00
ν_{61} $\gamma CH_{\alpha,\beta}$ (ring A) sym.	958	–	11.34	0.10
ν_{62} $\gamma CH_{\alpha,\beta}$ (ring D)	952	956	2.00	0.02
ν_{63} $\gamma CH_{\bar{\alpha}}$	929	943	4.70	0.28
ν_{64} γCH_α asy. (ring D)	919	–	34.39	0.01
ν_{65} $\gamma CH_{\alpha,\bar{\alpha}}$ (ring A + B) asy.	912	–	0.69	0.01
ν_{66} $\gamma CH_{\bar{\alpha}}$ sym.	904	904	131.20	0.12
ν_{67} $\gamma CH_{\bar{\alpha}}$ sym.	872	–	35.11	0.28
ν_{68} γCC (puck.) (ring C) + γCH	825	–	55.81	0.41
ν_{69} $\gamma CH_{\beta,\alpha}$ (ring D) sym.	801	803	128.98	0.43
ν_{70} $\gamma CH_{\beta,\alpha}$ (ring A) sym.	791	779	19.58	0.14
ν_{71} γCC (puck.) middle bond (A + B)	715	–	0.25	0.00
ν_{72} γCC (puck.)(ring C) + γCH	690	688	8.33	1.05
ν_{73} γCC (puck.)(ring C) + γCH	581	580	13.94	0.07
ν_{74} γCC (puck.)(ring A+D) + γCH	547	539	0.53	0.00
ν_{75} γCC (puck.)(ring A+D) + γCH	524	–	2.32	0.01
ν_{76} γCC (puck.)$_{\text{middle bond (A+B)}}$ + γCH	509	–	8.85	0.02
ν_{77} γCC (puck.)(ring A+D) + γCH	433	469	0.24	0.00
ν_{78} γCC (puck.)(ring B+C) + γCH	384	–	1.23	0.00
ν_{79} γCC (puck.) + γCH	290	–	2.38	0.01
ν_{80} γCC (puck.) + γCH	273	–	4.28	0.01
ν_{81} γCC (puck.)	186	–	6.90	0.01
ν_{82} γCC (puck.)	143	–	9.42	0.00
ν_{83} γCC (puck.) (ring A, B+D)	64	–	1.50	0.00
ν_{84} γCC (puck.) (ring A, B+D)	60	–	18.87	0.01

δ: deformation in-plane; γ: out of plane.

of the C ring; the lowest belongs to the C–C str. vibration of the D ring. The modes include nine different ring CCC str. vibrations, delocalized at different C–C bonds and in some cases mixed with δCH motion. The comparison of their vibration frequencies are summarized as follows:

$$\underset{\text{ring C}}{\nu_{sym}(CC\ str.)_{\bar{\alpha}-\bar{\alpha}}} > \underset{\text{ring A}}{\nu_{sym}(CC\ str.)_{\alpha-\beta}} >$$

$$\underset{\text{ring D}}{\nu_{sym}(CC\ str.)_{\alpha-\beta}} > \underset{\text{ring B}}{\nu_{sym}(CC\ str.)_{\bar{\alpha}}} >$$

$$\underset{\text{ring A}}{\nu_{sym}(CC\ str.)_{\beta-\beta}} > \underset{\text{ring D}}{\nu_{sym}(CC\ str.)_{\beta-\beta}}.$$

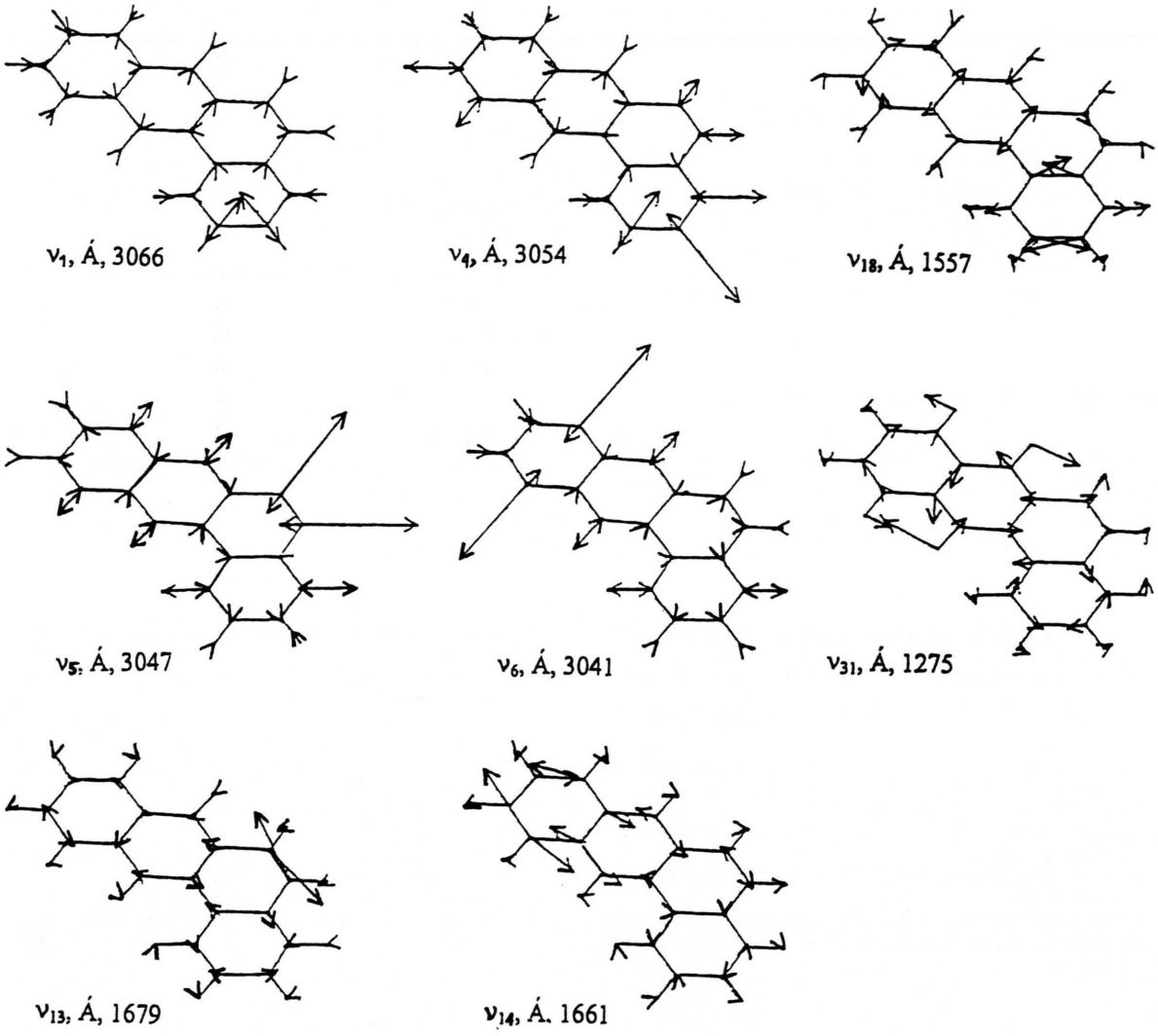

Fig. 3. Graphical pictures of some vibration modes as drawn through the DRAW.MOL routine.

Small values for the IR absorption intensities are calculated for these modes (0.04–0.59) km/mol.

δCH Modes

Twelve such modes are calculated, seven of which show motions completely localized at the H atoms. The highest frequency belongs to the ν_{31} of the $(C\text{–}H)_{\bar{\alpha}}$ bonds at the C ring, followed by two modes in which one H participate. Then other modes follow belonging to the C–H vibrations at the rings A, B and C. The sequence of these vibration frequencies is as follows:

$$\underset{\text{ring C}}{\nu_{\text{asym}}(\delta\text{CH})_{\bar{\alpha}}} > \underset{\text{ring B}}{\nu_{\text{asym}}(\delta\text{CH})_{\bar{\bar{\alpha}}}} > \underset{\text{ring D}}{\nu_{\text{asym}}(\delta\text{CH})_{\alpha}} >$$

$$\underset{\text{ring A, B, C}}{\nu_{\text{asym}}(\delta\text{CH})_{\alpha,\bar{\bar{\alpha}}\,\bar{\alpha}}} > \underset{\text{ring A + B}}{\nu_{\text{sym}}(\delta\text{CH})_{\alpha,\bar{\bar{\alpha}}}} >$$

$$\underset{\text{ring B, C + D}}{\nu_{\text{asym}}(\delta\text{CH})_{\alpha,\,\bar{\bar{\alpha}}\,,\bar{\alpha}\beta}} > \underset{\text{ring D + C}}{\nu_{\text{asym}}(\delta\text{CH})_{\alpha,\bar{\alpha}}} >$$

$$\underset{\text{ring D}}{\nu_{\text{sym}}(\delta\text{CH})_{\alpha}} > \underset{\text{ring B}}{\nu(\delta\text{CH})_{\bar{\bar{\alpha}}}} > \underset{\text{ring D}}{\nu_{\text{sym}}(\delta\text{CH})_{\alpha}} >$$

$$\underset{\text{ring A + D}}{\nu_{\text{sym}}(\delta\text{CH})_{\beta}} > \underset{\text{ring A}}{\nu_{\text{asym}}(\delta\text{CH})_{\beta}} > \underset{\text{ring D}}{\nu_{\text{asym}}(\delta\text{CH})_{\beta}}\,.$$

Intermediate IR absorption intensities are calculated for these modes (0.14–5.12) km/mol.

δCCC Deformation Modes

These are fifteen modes, all of which show small IR absorption intensities (0.0–1.05) km/mol. The sequence of these frequencies is as follows:

$$\underset{\text{ring A + B}}{\text{Ring }(\delta\text{CCC})} > \underset{\text{ring B, C + D}}{\text{Ring }(\delta\text{CCC})} > \underset{\text{ring A, B, C + D}}{\text{Ring }(\delta\text{CCC})}.$$

Out of Plane Deformation Modules

Twenty seven such modes are calculated, twelve CH with small intensity values (0.0–1.07) km/mol and fifteen ring (Nc–3) modes, the intensities of which are also small (0.0–0.07) km/mol. A comparison of their vibration frequencies is summarized in the relation

γCH Modes:

$$\underset{\text{ring A}}{\nu_{\text{asym}}(\gamma\text{CH})_\beta} > \underset{\text{ring D}}{\nu_{\text{asym}}(\gamma\text{CH})_\beta} > \underset{\text{ring C}}{\nu_{\text{asym}}(\gamma\text{CH})_\alpha} >$$

$$\underset{\text{ring A}}{\nu_{\text{sym}}(\gamma\text{CH})_{\alpha,\beta}} > \underset{\text{ring C}}{\nu_{\text{sym}}(\gamma\text{CH})_{\alpha,\beta}} > \underset{\text{ring B}}{\nu_{\text{asym}}(\gamma\text{CH})_\alpha} >$$

$$\underset{\text{ring D}}{\nu_{\text{asym}}(\gamma\text{CH})_\alpha} > \underset{\text{ring A}}{\nu_{\text{asym}}(\gamma\text{CH})_{\alpha,\alpha}} > \underset{\text{ring B}}{\nu_{\text{sym}}(\gamma\text{CH})_\alpha} >$$

$$\underset{\text{ring C}}{\nu_{\text{sym}}(\gamma\text{CH})_\alpha}.$$

γring Modes:

$$\underset{\text{middle bonds between B+C, C+D}}{\gamma\text{ring(CC)}} > \underset{\text{middle bond between ring A+B}}{\gamma\text{ring(CC)}} > \underset{\text{ring B, C+D}}{\gamma\text{ring(CC)}} > \underset{\text{ring A, B, C+D}}{\gamma\text{ring(CC)}}$$

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