Vibration Frequencies and Normal Coordinates of Benzo(c)phenanthrene

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MINDO/3-FORCES quantum mechanical calculations yielded non-planar (C_2) geometry of Benzo(c)phenanthrene. The result agrees with the majority of published results but disagrees with others in which a planar (C_{2v}) structure was accepted in order to simplify the analysis of certain spectroscopic data. Vibration frequencies and IR absorption intensities were calculated then, applying the non-planar (C_2) structure. A complete normal coordinate analysis for the molecule is reported. Inspection of these coordinates allowed the discovery of some useful comparative relations between them, which are reported in the paper.

Key words: Benzo(c)phenanthrene, Vibration Frequencies, MINDO/3-FORCES.

Introduction

The nonplanar geometry of Benzo(c)phenanthrene was established experimentally for its solid crystalline state [1] as well as theoretically applying the Hartree-Fock method [2, 3] and density functional theory (DFT) [4]. Applying the molecular force field calculation, Allinger et al. [5] came to similar results, estimating the angle of non-planarity as 24.9°. However in few cases reported in [6, 7] the planar structure (C_{2v}) was adopted in order to simplify the analysis of spectroscopic results. A study of the vibration spectrum for this molecule should be strongly dependent on its symmetry. However, besides few IR spectroscopic studies [6] with emphasis on the intensive bands, we could find no detailed vibration analysis for the molecule in the literature. For most of the vibration frequencies the results of the present study should be of a predictive nature then.

Normally the calculation of the vibration frequencies of a molecule should be done for its equilibrium geometry. Quantum mechanical methods are used nowadays for this purpose. Formerly we have used the MINDO/3-FORCES SCF-MO method [8], which proved successful in yielding molecular frequency values and normal coordinates. The resulting combination coefficients (L_i) of Wilson's secular equation [9], as well as the so called APP values [10] of the atoms in the molecule could be used for the assignment of the vibration modes. The L_i coefficients are usually supplied to a DRAW.MOL routine which draws graphically the picture of each vibration mode [11], enabling its correct assignment too.

Results and Discussion

As mentioned above, the treatment of the vibration problem for the molecule starts with the calculation of its equilibrium geometry, Figure 1.

Table 1 includes the calculated geometric values, which were obtained after reaching the minimal displacement forces, for all atoms accepted in this method, (10^{-5} au/au).

Of interest is the resulting non-planarity of the molecule. The dihedral angle for both halves of the molecule is 24°, in agreement with the results of Allinger et al. [5], Figure 2 shows a graphical picture of the non-planar molecule. The arrows at the atoms represent the displacement vectors for a vibration mode of the molecule. Such vectors are utilized for the identification of the vibration modes.

The non planar Benzo(c)phenanthrene shows a C_2 symmetry. According to the character table [14] its 84 modes of vibration are classified into the irreducible representation

$$\Gamma_{\text{vib}} = 42\,\text{A} + 42\,\text{B}.$$

All modes should be active both in IR and Raman spectra. Table 2 includes all calculated and scaled [15] vibration frequencies and their group theoretical and valence assignments.

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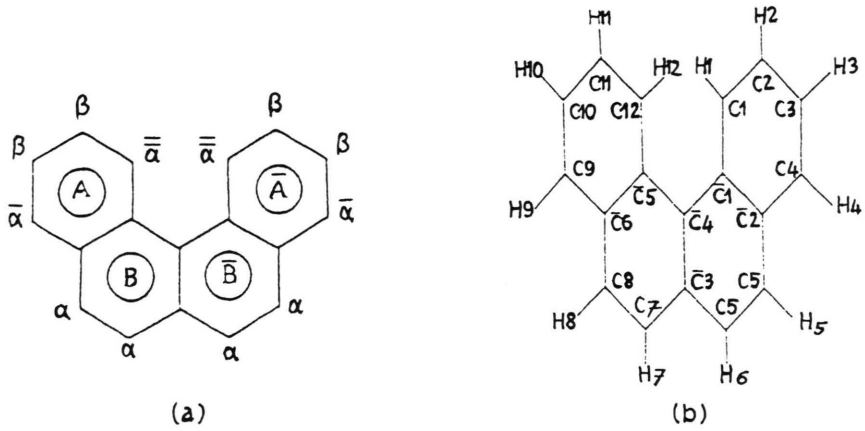

Fig. 1. Structure of the Benzo(c)phenanthrene molecule. (a) Showing the different designations of the C and H atoms; (b) the numbering of the atoms according to the IUPAC convention.

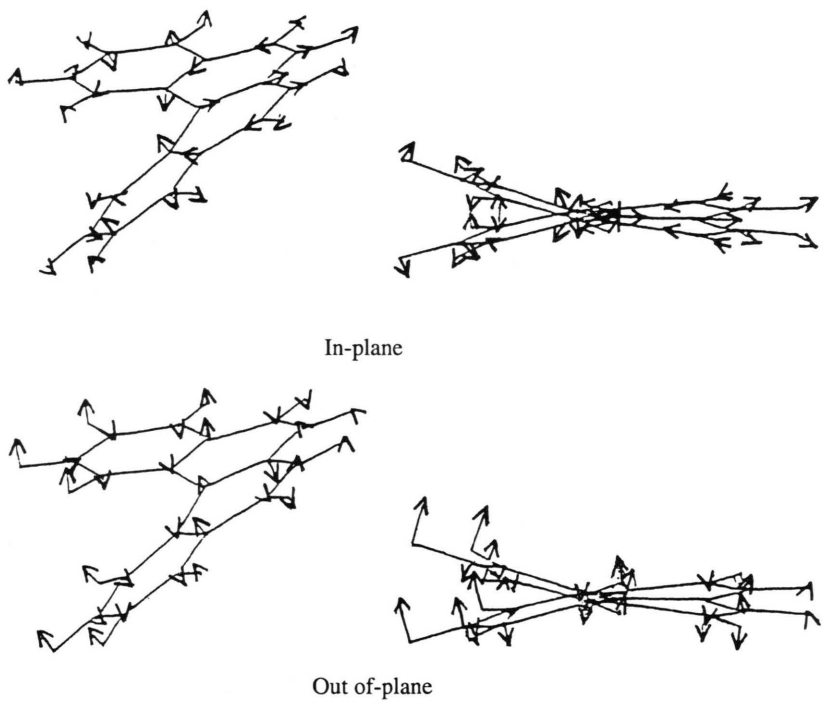

Fig. 2. DRAW.MOL graphical picture for two vibration modes of Benzo(c)phenanthrene, at different projection angles. The figure shows clearly the non-planarity of the molecule.

Comparison of the scaled calculated frequencies with the experimental values [6, 16] and those calculated with other methods [4] shows the obvious good agreement between the three sets of numbers. A study of the figures in Table 2 shows the following interesting results:

1) The twelve (CH str.) vibrations, $\nu_1 - \nu_6$ (A) and $\nu_{43} - \nu_{48}$ (B) with frequencies (3032–3067) cm^{-1} are localized at the relevant C–H bonds with two modes at only two CH bonds, ν_4 and ν_{46}. The order of these frequencies might be summarized in the scheme:

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

Table 1. Calculated equilibrium geometry for Benzo(c)phenanthrene together with some available experimental results.

Bond length (Å)/ angle (deg.)	This work	Other work	
	calcd.	[5] exptl. I	[3] exptl. II
C_1-C_2	1.368	1.382	1.378
$C_1-\bar{C}_1$	1.445	1.421	1.433
C_2-C_3	1.420	1.412	1.409
$C_3-\bar{C}_4$	1.384	1.384	1.374
$C_4-\bar{C}_2$	1.442	1.420	1.391
$C_5-\bar{C}_2$	1.456	1.437	1.443
C_5-C_6	1.364	1.366	1.342
$C_6-\bar{C}_3$	1.456	1.437	1.430
$\bar{C}_1-\bar{C}_1$	1.460	1.412	1.431
$\bar{C}_1-\bar{C}_4$	1.494	1.450	1.446
$\bar{C}_3-\bar{C}_4$	1.441	1.399	1.412
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	1.106	–	–
C_6-H_6	1.107	–	–
$< (C_1\,\bar{C}_1)\,(\bar{C}_1\,\bar{C}_4)\,(\bar{C}_4\,\bar{C}_5)$	24.000	24.900	–
$< C_2\,C_3\,\bar{C}_4$	118.685	–	–
$< \bar{C}_3\,C_4\,\bar{C}_2$	122.680	–	–
$< \bar{C}_2\,C_5\,C_6$	121.332	–	–
$< C_5\,C_6\,\bar{C}_3$	122.000	–	–
$< C_1\,\bar{C}_1\,\bar{C}_2$	114.834	–	–
$< \bar{C}_1\,\bar{C}_1\,\bar{C}_4$	125.450	–	–
$< \bar{C}_1\,\bar{C}_2\,C_4$	119.340	–	–
$< C_4\,\bar{C}_2\,C_5$	122.680	–	–
$< \bar{C}_4\,\bar{C}_3\,C_6$	120.000	–	–
$< C_6\,\bar{C}_3\,C_7$	120.663	–	–
$< \bar{C}_1\,\bar{C}_4\,\bar{C}_3$	117.387	–	–
$< \bar{C}_1\,\bar{C}_4\,\bar{C}_5$	125.450	–	–
$< H_1\,C_1\,\bar{C}_2$	116.743	–	–
$< H_1\,C_1\,\bar{C}_1$	119.340	–	–
$< H_2\,C_2\,C_3$	120.000	–	–
$< H_2\,C_2\,C_1$	120.663	–	–
$< H_3\,C_3\,C_2$	117.387	–	–
$< H_4\,C_4\,\bar{C}_3$	125.450	–	–
$< H_4\,C_4\,\bar{C}_2$	116.743	–	–
$< H_6\,C_6\,C_5$	119.340	–	–

2) The seventeen ring (C–C str.) vibrations, which are localized at the carbon atoms, might be classified as:

Eight C–C str. vibrations with frequencies (1487–1658) cm^{-1}; with the localization scheme

ν_2(A) ($C_\beta - C_\beta$) str.; ν_8(A) ($C_{\bar{\bar{\alpha}}} - C_\beta$) and ν_{49}(B) ($C_{\bar{\bar{\alpha}}} - C_\beta$) str.; ν_{50}(B) ($C_\alpha - C_\alpha$) str.; ν_9(A) and ν_{51}(B) ($C_\beta - C_\beta$) str.; ν_{56}(B) (rings A, B and $\bar{A}$, $\bar{B}$) str.; ν_{52}(B) and ν_{10}(A) (rings B, $\bar{B}$) $C_\alpha - C$, $C_\alpha - C$ and middle bonds.

Table 2. Calculated vibration frequencies and absorption intensities for Benzo(c)phenanthrene molecule.

Symmetry and description Intensiv	Frequency cm^{-1}				
	This work scaled	[4] calcd.	[16] expt.	[6] expt.	absorb.Ai this work km/mol
A					
ν_1 CH_β str. (out, out) (out, out)	3067	3064	–	–	58.53
ν_2 CH_β str. (in, out) (in, out)	3055	3056	3058	–	48.03
ν_3 CH_α str. (out, out) (out, out)	3050	–	–	–	146.3
ν_4 $CH_{\alpha,\alpha}$ str. (in, in) (in, in)	3040	3046	3042	–	1.23
ν_5 CH_α str. (in, out) (in, out)	3036	3036	–	3038	12.83
ν_6 CH_α str. (out, out)	3034	–	–	3013	4.80
ν_7 ring $(CC)_{(\alpha-\alpha)}$ str.	1658	–	–	–	0.16
ν_8 ring (A, $\bar{A}$) $(CC)_{(\alpha-\beta)}$ str.	1643	–	–	–	0.04
ν_9 ring (A, $\bar{A}$, middle bond) (CC str.)	1549	–	–	–	0.01
ν_{10} ring (B, $\bar{B}$) (CC str.)	1491	1494	1496	1496	0.00
ν_{11} ring (A, $\bar{A}$) (CC str.)	1470	–	–	–	0.02
ν_{12} ring (B, $\bar{B}$, middle bond) (CC str.)	1407	1418	–	1417	0.21
ν_{13} ring (CCC str.)	1398	–	–	–	0.01
ν_{14} ring (CC str.) + δCH_α	1368	–	–	–	0.00
ν_{15} ring (CCC str.) + δCH	1295	–	–	–	0.39
ν_{16} δCH_α	1267	–	–	–	0.56
ν_{17} $\delta CH_{\bar{\alpha},\bar{\bar{\alpha}},\alpha}$	1251	1237	–	1229	0.24
ν_{18} $\delta CH_{\alpha,\beta}$	1188	–	–	–	0.03
ν_{19} $\delta CH_{\bar{\alpha},\bar{\bar{\alpha}}}$	1171	–	–	–	2.06
ν_{20} δCH_α	1165	–	–	–	0.49
ν_{21} $\delta CH_{\beta,\alpha}$ + ring (CCC str.)	1069	–	–		1.43
ν_{22} ring (δCCC) + δCH_α	1038	–	1030	1030	1.19
ν_{23} γCH_β	969	–	–	–	0.00
ν_{24} γCH_α	963	–	–		0.02
ν_{25} $\gamma CH_{\alpha,\bar{\alpha},\beta}$	951	951	–		0.00
ν_{26} $\gamma CH_{\bar{\alpha},\bar{\bar{\alpha}},\beta}$	916	–	–	–	0.15
ν_{27} ring (δCCC)	819	–	–	–	0.24
ν_{28} γCH_α	860	–	863	863	0.03
ν_{29} $\gamma CH_{\beta,\bar{\alpha}}$	800	839	832	795	0.04
ν_{30} ring (δCCC)	753	758	750	–	0.03
ν_{31} γCCC	762	–	–	744	40.28
ν_{32} ring (δCCC)	692	–	–	–	0.00
ν_{33} ring (δCCC)	564	–	–	–	0.02
ν_{34} γCCC	544	–	–	–	0.00
ν_{35} ring (δCCC)	532	–	–	–	0.02
ν_{36} ring (δCCC)	490	–	469	–	0.03
ν_{37} γCCC + γCH	426	–	431	–	0.00
ν_{38} γCCC	392	–	–	–	0.05
ν_{39} γCCC + γCH	274	–	–	–	0.00
ν_{40} γCCC + γCH	195	–	–	–	0.01
ν_{41} γCCC + γCH	127	–	–	–	0.01
ν_{42} γCCC + γCH	72	–	–	–	0.00
B					
ν_{43} CH_β str. (in, in) (out, out)	3066	3064	–		97.37
ν_{44} CH_β str. (in, out) (out, in)	3055	3056	–	–	75.78
ν_{45} CH_α str. (in, in) (out, out)	3048	3046	3042	–	45.44
ν_{46} $CH_{\bar{\alpha}}$ (in, out)	3038			3038	10.20
ν_{47} CH_α str. (in, out) (out, in)	3033	–	–	–	0.26
ν_{48} $CH_{\bar{\bar{\alpha}}}$ str. (in, out)	3032	–	–	3013	57.75
ν_{49} ring (A, $\bar{A}$) (CC str.)$_{(\beta,\alpha)}$	1643	–	–	–	0.07
ν_{50} ring (CC str.)	1625	–	1600	–	0.25
ν_{51} ring (CC str.)	1534	–	1519	–	0.27
ν_{52} ring (CCC str.)	1487	1494	1495	1496	0.83
53 ring (B, $\bar{B}$) (CCC str.)	1473	–	–	–	0.02
ν_{54} ring (A, $\bar{A}$) (CCC str.)	1422	1418	1419	1417	0.08
ν_{55} ring (B, $\bar{B}$) (CCC str.)	1360	–	1363	–	0.02
ν_{56} ring (CCC str.)	1320	–	–	–	0.09
ν_{57} $\delta CH_{\bar{\alpha},\bar{\bar{\alpha}},\alpha}$	1250	–	–	–	2.04

Table 2. (Continued).

Symmetry and description Intensiv	Frequency cm^{-1}				
	This work scaled	[4] calcd.	[16] expt.	[6] expt.	absorb.Ai this work km/mol
$\nu\nu_{58}$ δCH	1237	1237	1238	1229	1.66
ν_{59} ring (δCCC) + $\delta CH_{\bar{\alpha},\bar{\bar{\alpha}}}$	1206	–	–	–	2.00
ν_{60} $\delta CH_{\alpha,\bar{\alpha}}$	1182	–	–	–	0.34
ν_{61} $\delta CH_{\beta,\bar{\bar{\alpha}}}$	1167	–	–	–	1.85
ν_{62} δCH_{β}	1163	–	–	–	0.91
ν_{63} $\delta CH_{\bar{\alpha},\alpha}$	1156	–	1113	–	4.24
ν_{64} ring (δCCC)	1007	–	1030	1030	0.28
ν_{65} $\gamma CH_{\beta,\bar{\alpha},\alpha}$	968	–	978	–	0.02
ν_{66} γCH_{α}	965	–	–	–	0.03
ν_{67} $\gamma CH_{\beta,\alpha,\alpha}$	950	–	945	–	0.06
ν_{68} $\gamma CH_{\bar{\alpha},\bar{\bar{\alpha}}}$	912	–	–	–	0.65
ν_{69} γCH_{α} sym. + γCC (puck.)	895	–	–	–	0.86
ν_{70} ring (δCCC)	861	872	867	864	1.13
ν_{71} γCCC (puck.) + γCH	842	839	831	–	0.34
ν_{72} $\gamma CH_{\bar{\bar{\alpha}},\beta}$	790	758	759	795	0.90
ν_{73} ring (δCCC)	741	750	745	744	1.39
ν_{74} γCC (puck.) + γCH	678	674	668	–	1.13
ν_{75} ring (δCCC)	616	–	615	–	1.20
ν_{76} γCCC (puck.) + γCH	619	628	–	–	0.10
ν_{77} ring (δCCC)	533	578	543	–	0.23
ν_{78} γCCC (puck.) + γCH	526	509	504	–	0.05
ν_{79} ring (δCCC)	443		649	–	0.14
ν_{80} γCCC (puck.) + γCH	432	–	431	–	0.02
ν_{81} ring (δCCC)	330			–	0.11
ν_{82} γCCC (puck.) + γCH	264	–	–	–	0.04
ν_{83} γCC (puck.) + γCH	179	–	–	–	0.04
ν_{84} γCC (puck.) + γCH	75	–	–	–	0.01

Scaling factors: 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).
Special scaling 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).
The designation (in, in) (in, in) indicates that the four hydrogen atoms in two rings vibrate in the same phase; (out, out) (in, in): two hydrogen atoms at one ring vibrate in phase and the other two in the other ring vibrate with different phase; (out, in): two hydrogen atoms vibrate with different phases, middle bond: bond between tow rings.

Their frequency order of magnitudes is found to be

$$\nu_{sym}(C_\alpha - C_\alpha)\,\text{str.} > \nu_{sym}(C_{\bar{\alpha}} - C_\beta;\ C_{\bar{\bar{\alpha}}} - C_\beta)\,\text{str.} > \nu_{asym}(C_{\bar{\alpha}} - C_\beta;\ C_{\bar{\bar{\alpha}}} - C_\beta)\,\text{str.} > \nu_{asym}(C_\alpha - C_\alpha)\,\text{str.} > \nu_{sym}(C_\beta - C_\beta)\,\text{str.} > \nu_{asym}(C_\beta - C_\beta)\,\text{str.} > \nu_{asym}(C_\alpha - C)\,\text{str.} > \nu_{sym}(C_\alpha - C)\,\text{str.}$$

Ten (CCC str.) vibrations with frequencies (1320–1473) cm^{-1}. The highest frequency among them belongs to the ν_{51}(B) mode, and the lowest to ν_{13}(A).

Two (C–C str.) vibrations mixed with δCH motion; these are ν_{14}(A) and ν_{15}(A).

Generally the IR absorption intensities of these vibrations are low: (0.0–0.83) km/mol.

3) Twelve δCH deformation vibrations, which are mainly localized at the hydrogen atoms with frequencies ranging within (790–969) cm^{-1}, show the following sequence magnitudes:

$$\underset{\nu_{16}}{\nu_{sym}(\delta CH)_{\bar{\bar{\alpha}}}} > \underset{\nu_{58}}{\nu_{asym}(\delta CH)_\alpha} > \underset{\nu_{18}}{\nu_{sym}(\delta CH)_\alpha} > \underset{\nu_{17}}{\nu_{sym}(\delta CH)_{\bar{\alpha}}} > \underset{\nu_{61}\ \text{(two bonds)}}{\nu_{asym}(\delta CH)_\beta} > \underset{\nu_{20}\ \text{(four bonds)}}{\nu_{sym}(\delta CH)_\beta} > \underset{\nu_{62}\ \text{(two bonds)}}{\nu_{asym}(\delta CH)_\beta} > \underset{\nu_{63}}{\nu_{asym}(\delta CH)_\alpha}.$$

Their calculated IR absorption intensities range within (2.06–2.04) km/mol.,

4) Eleven ring (δCCC) deformation vibrations with frequencies within (1007–1330) cm^{-1}. The highest frequency belong to ν_{64}(B). In ν_{27}(A) a clock-anticlockwise motion of the C–C and C–H bonds is notices.

5) Ten γCH out of plane vibrations within (800–969) cm^{-1}. They are ordered according to their frequencies as

$$\underset{\nu_{30}}{\nu_{asym}(\gamma CH)_\beta} > \underset{\nu_{71}}{\nu_{sym}(\gamma CH)_\beta} > \underset{\nu_{72}}{\nu_{sym}(\gamma CH)_\alpha} > \underset{\nu_{31}}{\nu_{asym}(\gamma CH)_\alpha} > \underset{\nu_{32}}{\nu_{sym}(\gamma CH)_{\beta,\alpha}} > \underset{\nu_{33}}{\nu_{asym}(\gamma CH)_{\bar{\alpha}}} > \underset{\nu_{74}}{\nu_{sym}(\gamma CH)_{\bar{\alpha},\alpha}}.$$

Their IR absorption intensities range from (0.00–0.90) km/mol.,

6) Fifteen (γCC) and (γCCC) out of plane vibrations with the low frequencies (75–842) cm^{-1}. In most of these vibrations, the C–H bonds are displaced in the opposite direction of the corresponding carbon atoms. Their calculated IR absorption intensities are (0.0–40.28) km/mol.

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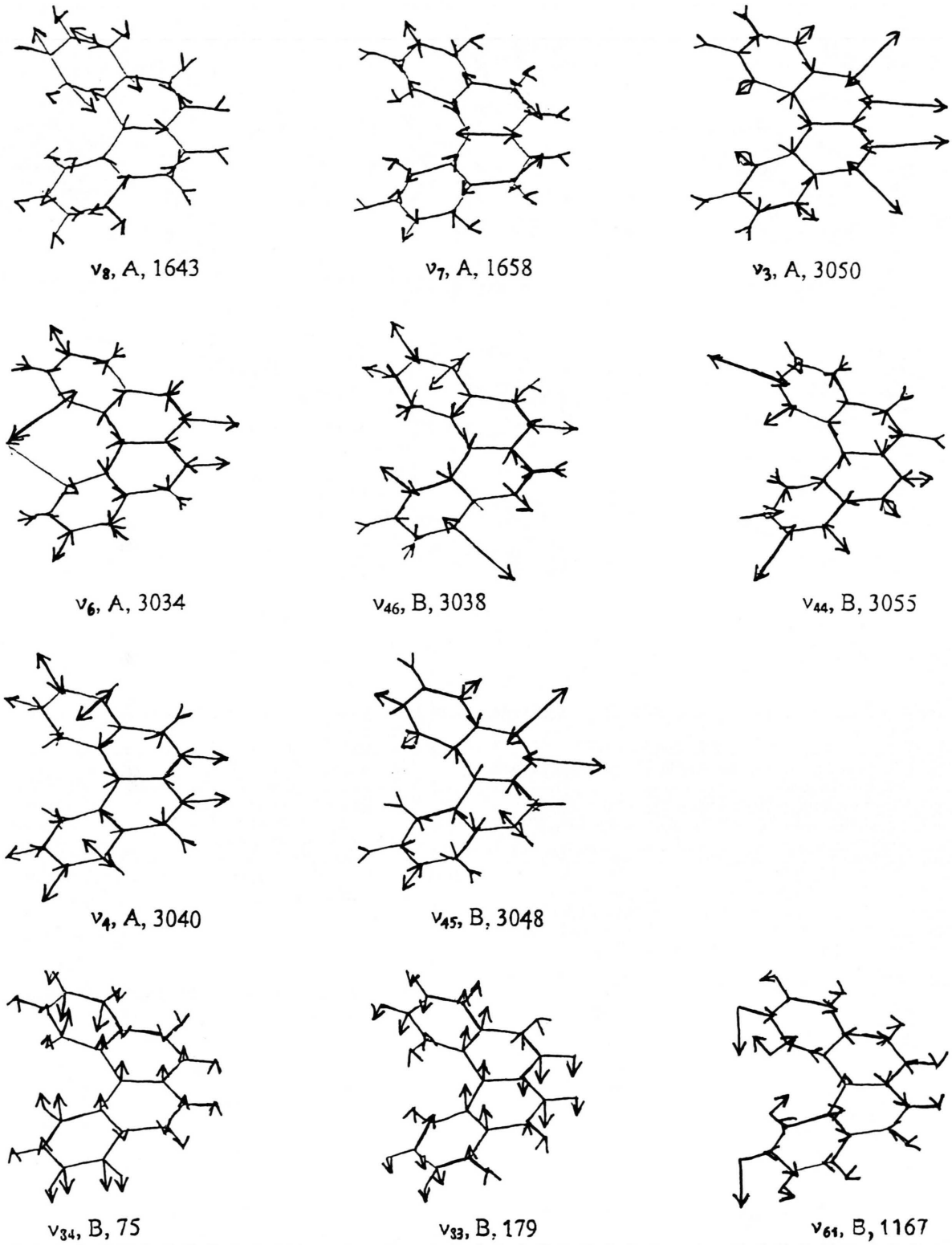
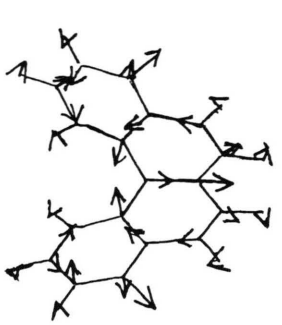
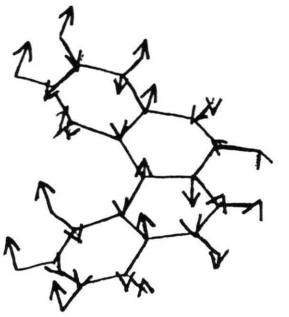


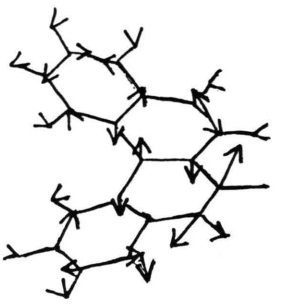
Fig. 3. The graphical pictures of some vibration modes as drawn through DRAW.MOL routine.



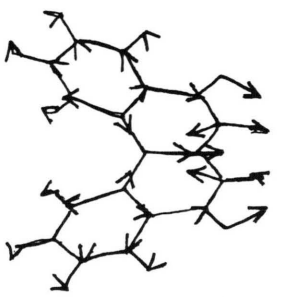
ν_{35}, A, 532



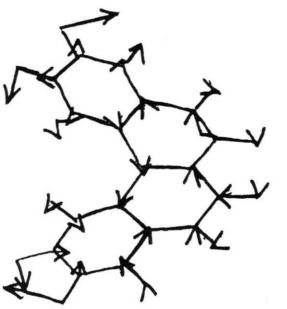
ν_{72}, B, 790



ν_{50}, B, 1625



ν_{22}, A, 1038



ν_{62}, B, 1163

Fig. 3. (Continued).

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