Vibration Frequencies and Normal Coordinates of Benzo(c)phenanthrene

Rehab M. Kubba and Muthana Shanshal

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

Reprint requests to Prof. M. S.; Fax: 009 641-7763 592

Z. Naturforsch. 56a, 499–504 (2001); received September 8, 2000

MINDO/3-FORCES quantum mechanical calculations yielded non-planar (C2) geometry of Benzo(c)phenanthrene. The result agrees with the majority of published results but disagrees with others in which a planar (C2v) structure was adopted in order to simplify the analysis of certain spectroscopic data. Vibration frequencies and IR absorption intensities were calculated then, applying the non-planar (C2) 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, MINDO3-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 (C2v) 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, ) 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, 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 C2 symmetry. According to the character table [14] its 84 modes of vibration are classified into the irreducible representation

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

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.
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, \( \nu_4 \) and \( \nu_{46} \). The order of these frequencies might be summarized in the scheme:

\[
\nu_{\text{sym}}(\text{CH str.})_{\beta} > \nu_{\text{asym}}(\text{CH str.})_{\beta} > \\
\nu_{\text{sym}}(\text{CH str.})_{\alpha} > \nu_{\text{asym}}(\text{CH str.})_{\alpha} > \\
\nu_{\text{sym}}(\text{CH str.})_{\bar{\alpha}} > \nu_{\text{asym}}(\text{CH str.})_{\bar{\alpha}} > \\
\nu_{\text{sym}}(\text{CH str.})_{\bar{\beta}} > \nu_{\text{asym}}(\text{CH str.})_{\bar{\beta}}.
\]
Table 1. Calculated equilibrium geometry for Benzo(c)phenanthrene together with some available experimental results.

<table>
<thead>
<tr>
<th>Bond length (Å) / angle (deg.)</th>
<th>This work</th>
<th>Other work</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁-C₆</td>
<td>1.368</td>
<td>1.382</td>
</tr>
<tr>
<td>C₁-C₇</td>
<td>1.445</td>
<td>1.421</td>
</tr>
<tr>
<td>C₂-C₇</td>
<td>1.420</td>
<td>1.412</td>
</tr>
<tr>
<td>C₃-C₇</td>
<td>1.384</td>
<td>1.384</td>
</tr>
<tr>
<td>C₄-C₇</td>
<td>1.442</td>
<td>1.420</td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>1.456</td>
<td>1.437</td>
</tr>
<tr>
<td>C₆-C₇</td>
<td>1.364</td>
<td>1.366</td>
</tr>
<tr>
<td>C₇-C₈</td>
<td>1.456</td>
<td>1.437</td>
</tr>
<tr>
<td>C₈-C₉</td>
<td>1.460</td>
<td>1.412</td>
</tr>
<tr>
<td>C₉-C₁₀</td>
<td>1.494</td>
<td>1.450</td>
</tr>
<tr>
<td>C₁₀-C₁₁</td>
<td>1.441</td>
<td>1.399</td>
</tr>
<tr>
<td>C₁₁-C₁₂</td>
<td>1.107</td>
<td>-</td>
</tr>
<tr>
<td>C₁₂-C₁₃</td>
<td>1.105</td>
<td>-</td>
</tr>
<tr>
<td>C₁₃-C₁₄</td>
<td>1.105</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄-C₁₅</td>
<td>1.106</td>
<td>-</td>
</tr>
<tr>
<td>C₁₅-C₁₆</td>
<td>1.107</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆-C₁₇</td>
<td>24.000</td>
<td>24.900</td>
</tr>
<tr>
<td>C₁₇-C₁₈</td>
<td>118.685</td>
<td>-</td>
</tr>
<tr>
<td>C₁₈-C₁₉</td>
<td>122.680</td>
<td>-</td>
</tr>
<tr>
<td>C₁₉-C₁₀</td>
<td>121.332</td>
<td>-</td>
</tr>
<tr>
<td>C₁₀-C₁₁</td>
<td>122.000</td>
<td>-</td>
</tr>
<tr>
<td>C₁₁-C₁₂</td>
<td>114.834</td>
<td>-</td>
</tr>
<tr>
<td>C₁₂-C₁₃</td>
<td>125.450</td>
<td>-</td>
</tr>
<tr>
<td>C₁₃-C₁₄</td>
<td>119.340</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄-C₁₅</td>
<td>122.680</td>
<td>-</td>
</tr>
<tr>
<td>C₁₅-C₁₆</td>
<td>120.000</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆-C₁₇</td>
<td>120.663</td>
<td>-</td>
</tr>
<tr>
<td>C₁₇-C₁₈</td>
<td>117.387</td>
<td>-</td>
</tr>
<tr>
<td>C₁₈-C₁₉</td>
<td>125.450</td>
<td>-</td>
</tr>
<tr>
<td>C₁₉-C₁₀</td>
<td>116.743</td>
<td>-</td>
</tr>
<tr>
<td>C₁₀-C₁₁</td>
<td>119.340</td>
<td>-</td>
</tr>
<tr>
<td>C₁₁-C₁₂</td>
<td>120.000</td>
<td>-</td>
</tr>
<tr>
<td>C₁₂-C₁₃</td>
<td>120.663</td>
<td>-</td>
</tr>
<tr>
<td>C₁₃-C₁₄</td>
<td>117.387</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄-C₁₅</td>
<td>125.450</td>
<td>-</td>
</tr>
<tr>
<td>C₁₅-C₁₆</td>
<td>116.743</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆-C₁₇</td>
<td>119.340</td>
<td>-</td>
</tr>
</tbody>
</table>

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

\[ \nu_2(A) \text{ (C}_\beta - \text{C}_\beta \text{ str.); } \nu_8(A) \text{ (C}_\beta - \text{C}_\beta \text{ str.) and} \]

\[ \nu_{40}(B) \text{ (C}_\beta - \text{C}_\beta \text{ str.); } \nu_{50}(B) \text{ (C}_\alpha - \text{C}_\alpha \text{ str.);} \]

\[ \nu_6(A) \text{ and } \nu_{51}(B) \text{ (C}_\beta - \text{C}_\beta \text{ str.);} \]

\[ \nu_{56}(B) \text{ (rings A, B and A, B str.); } \nu_{52}(B) \text{ and} \]

\[ \nu_{50}(A) \text{ (rings B, B) } \text{C}_\alpha - \text{C}, \text{C}_\alpha - \text{C} \]

and middle bonds.
Table 2. (Continued).

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

The authors thank Doz. Dr. W. Schmidt, Inst. Für PAH Forschung, Greiffenberg, Germany, for providing them with unpublished experimental results.
Fig. 3. The graphical pictures of some vibration modes as drawn through DRAW.MOL routine.
Fig. 3. (Continued).