Conformational interconversion in the monovalent ions of 1,2,3,6,7,8-hexahydropyrene II

by F. W. PIJPERS, M. R. ARICK, B. M. P. HENDRIKS and E. de BOER

Department of Physical Chemistry, University of Nijmegen, Nijmegen, The Netherlands

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The E.P.R. spectra of the monovalent positive and negative ions of 1,2,3,6,7,8-hexahydropyrene reveal an alternating line broadening, caused by the non-synchronized motion of the two aliphatic bridges in the molecule. When this motion is described by the modified Bloch equations, using a four-sites jump model, spectra are obtained which agree quite well with the experimental ones.

The potential barrier for the conformational interconversion can be calculated from the temperature dependence of the lifetime of each configuration and is found to be 10 · 0 ± 0 · 4 kcal mol$^{-1}$ for the radical anion and 3 · 5 ± 0 · 4 kcal mol$^{-1}$ for the radical cation. The inversion rate at 0°C equals 2 · 8 × 10$^6$ s$^{-1}$ for the anion and 4 · 2 × 10$^8$ s$^{-1}$ for the cation.

1. INTRODUCTION

In an earlier preliminary publication [1] (hereafter referred to as part I) one of us reported the linewidth alternation observed in the E.P.R. spectra of the monovalent ions of 1,2,3,6,7,8-hexahydropyrene (HHP) (figure 1). This phenomenon was attributed to a non-synchronized conformational isomerization of the ion radicals. Such an isomerization produces a rearrangement from a boat-like structure into a chair-like structure when one of the aliphatic chains in the molecule is displaced with respect to the other (see figure 2). The conclusion that the two chains move non-synchronized was drawn from the experimental intensity distribution of the resonance spectrum over the various spectral groups denoted by $M_{\beta CH_3} = \pm 4$, ± 2 and 0 (see figure 3, $M_{\beta CH_3}$ equals to the total $\pi$ component of the nuclear spin angular momenta of the methylene protons). These groups contain lines that are not affected by the broadening mechanism of the conformational rearrangement and

Figure 1. Structural formula of HHP.
Figure 2. Interconversion scheme for the four HHP configurations.

Figure 3. Experimental spectra of the negative ion of HHP at various temperatures in DME and with Na⁺ as counter ion together with the computer simulations of the right-hand sides of these spectra.
therefore remain sharp and well resolved in the temperature range from $-20^\circ C$ to $+20^\circ C$. Outside this temperature range the broadened parts of the spectrum become sharp too, and the intensity ratio of the non-broadened lines may be affected by partial overlap with the other lines. In the temperature range mentioned the intensity ratio of the three $M_{\beta CH_3}$ groups, measured with Na$^+$ as counter ion and 1,2-dimethoxyethane (DME) as solvent is $1 : 8 : 18$ which is expected for a non-synchronized motion. A synchronized motion would have produced an intensity ratio $1 : 16 : 36$. The use of other solvents and other counter ions influences the intensity ratio slightly [2], which has been attributed to ion pair formation and intramolecular cation transfer in a way similar to that reported for the pyracene anion radical [3].

We will show that the computer simulated spectra of HHP anion using the model for a non-synchronized motion agree extremely well with the spectra of the anion measured between $-30^\circ C$ and $+80^\circ C$ in various solvents and with different counter ions. The spectra of the cation measured between $-30^\circ C$ and $+25^\circ C$ can also be simulated remarkably well with this model. The simulated spectra enabled us to determine the thermodynamic constants for the molecular rearrangement.

2. Experimental

The HHP mononegative anion radical was prepared from commercial HHP by standard alkali metal reduction methods [4]. The alkali metals used were lithium, sodium and potassium and the solvents used were 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran (MTHF), tetrahydrofuran (THF) and liquid NH$_3$. The monopositive radical was prepared by dissolving HHP into concentrated sulphuric acid or in an SO$_2$/BF$_3$ mixture. The E.P.R. spectra were measured with a Varian V-4502 X-band E.P.R. spectrometer operating at 9500 MHz and using high-frequency modulation (100 kHz). Samples were kept at constant temperature with the aid of the Varian V-4540 variable temperature accessory. The temperatures were measured independently with a Cu-constantan thermocouple.

3. Results and Discussion

3.1. The spectra of the monoanion of HHP

The hyperfine splitting pattern in the E.P.R. spectrum of the monovalent ions of HHP arises from the interaction of the unpaired electron with five sets of equivalent protons, viz. the four aromatic protons, two sets of four $\beta$ protons and two sets of two $\gamma$ protons, axial ones and equatorial ones which mutually interconvert. The magnitude of the coupling constants is given in table 1. In figure 3 representative spectra demonstrate the drastic changes of the HHP anion spectrum with temperature, caused by the motion of the two aliphatic bridges in the molecule. Similar spectra were obtained for the monopositive ion of HHP.

Figure 3 shows that at $+80^\circ C$ some broad lines are measured between $M_{\beta CH_3}=0$ and $M_{\beta CH_3}=\pm 2$. These lines represent some of the exchange narrowed parts of the spectrum in the limit of rapid exchange. Upon lowering of the temperature these parts of the spectrum broaden and become less intense (see spectrum at $+61^\circ C$) and finally disappear at about $+20^\circ C$ (the amplitude of the field modulation is kept constant). At still lower temperatures these lines sharpen again and are
Table 1. Values of the parameters used in the computer simulation of the spectra of the monovalent ions of HHP.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HHP anion†</th>
<th>HHP cation‡</th>
</tr>
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<tbody>
<tr>
<td>$a_4$ (aromatic)</td>
<td>1·68 gauss</td>
<td>1·90 gauss</td>
</tr>
<tr>
<td>$a_\beta$ (equatorial)</td>
<td>2·02 gauss</td>
<td>3·78 gauss</td>
</tr>
<tr>
<td>$a_\alpha$ (axial)</td>
<td>8·03 gauss</td>
<td>14·60 gauss</td>
</tr>
<tr>
<td>$a_\gamma$ (equatorial)</td>
<td>0·36 gauss</td>
<td></td>
</tr>
<tr>
<td>$a_\gamma'$ (axial)</td>
<td>0·50 gauss</td>
<td></td>
</tr>
<tr>
<td>Derivative linewidth</td>
<td>0·20 gauss</td>
<td>0·100 gauss</td>
</tr>
</tbody>
</table>

† See [1, 7].
‡ See [1].
effects due to the movement of the \( \gamma \) protons, we did not endeavour to simulate them. At \(-75^\circ\text{C}\) the experimental spectrum could be matched completely with the hyperfine splitting constants in table 1. This means that on an E.P.R. time scale, at this temperature, the movement of the \( \text{CH}_2 \) groups can be considered as frozen out.

3.3. The spectra of the monocation of HHP

The E.P.R. spectra between \(-89^\circ\text{C}\) and \(+25^\circ\text{C}\) could be simulated in the same way as the spectra for the negative ion. For the simulation we used the hyperfine splitting constants listed in table 1. The spectra in the temperature range from \(-30^\circ\text{C}\) to \(+25^\circ\text{C}\) could be simulated quite well by utilizing the same set of coupling constants for the boat and the chair form (see table 1 and part I) and by taking the \( \gamma \) protons as equivalent. Spectra measured at lower temperatures exhibited second-order hyperfine structure, which cannot be produced by our programme, which only accounts for the diagonal part of the hyperfine interaction. Apart from this the theoretical spectra simulated as indicated above agreed well with the experimental ones. In \( \text{SO}_2/\text{BF}_3 \) mixtures spectra could be measured up to \(-20^\circ\text{C}\). The best spectra were obtained by taking the concentration of HHP equal to \(10^{-3}\) M and the \( \text{BF}_3 \) concentration equal to \(10^{-1}\) M. At temperatures where spectra could be measured in \( \text{SO}_2/\text{BF}_3 \) as well as in \( \text{H}_2\text{SO}_4 \), the spectra could be simulated with the same \( \tau \) values. Hence the interconversion rate does not depend on the solvent used.

Figure 4. Arrhenius diagram of the rate constant for the interconversion process in the monovalent ions of HHP. □ refers to the positive ion in \( \text{SO}_2/\text{BF}_3 \). ■ refers to the positive ion in \( \text{H}_2\text{SO}_4 \). ● refers to the negative ion. ○ refers to the spectrum, measured at \(-75^\circ\text{C}\) (see text).
3.4. Thermodynamic constants

Figure 4 shows the Arrhenius plots for both ions. A striking difference is observed between the slopes of the straight lines, pointing to a quite different activation energy for the interconversion process occurring in the two ions. In table 2 the thermodynamic constants are listed. The activation energy of 10·0 kcal mole\(^{-1}\) for the anion of HHP compares favourably with the activation energies observed for chair-boat interconversions of non-charged cyclic molecules, e.g. for cyclohexane an activation energy of 10·0 kcal mole\(^{-1}\) has been found [8]. It is surprising that the activation energy for the positive ion is so much smaller, only 3·5 kcal mole\(^{-1}\). As stated before no influence of solvent is observed: the measurements in H\(_2\)SO\(_4\) yield \(r\) values that produce the same straight line as those measured for the ion dissolved in SO\(_2\)/BF\(_3\).

<table>
<thead>
<tr>
<th></th>
<th>HHP anion</th>
<th>HHP cation</th>
</tr>
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<tbody>
<tr>
<td>(E_{act}) (kcal mole(^{-1}))</td>
<td>+10·0±0·4</td>
<td>+3·5±0·4</td>
</tr>
<tr>
<td>(k^{273}) (s(^{-1}))</td>
<td>2·8×10(^{14})±5 per cent</td>
<td>4·2×10(^{14})±5 per cent</td>
</tr>
<tr>
<td>(k_0) (s(^{-1}))</td>
<td>2·5×10(^{14})±5 per cent</td>
<td>2·0×10(^{14})±5 per cent</td>
</tr>
<tr>
<td>(\Delta H^*) (273 K, kcal mole(^{-1}))</td>
<td>+9·5±0·4</td>
<td>+2·8±0·4</td>
</tr>
<tr>
<td>(\Delta S^*) (273 K, e.u.)</td>
<td>+5·2±0·1</td>
<td>−18·0±0·4</td>
</tr>
<tr>
<td>(\Delta G^*) (273 K, kcal mole(^{-1}))</td>
<td>+8·1±0·5</td>
<td>+7·7±0·5</td>
</tr>
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</table>

Table 2. Thermodynamic constants of the interconversion process for the monovalent ions of HHP.

At 0°C the reaction rate constant of the positive ion is 50 per cent higher than that of the negative ion. The activation energy combined with the reaction rate constant yields the \(k_0\) values via the relation \(k_T=k_0\exp(-E_{act}/RT)\).

The thermodynamic constants for the activated complex \(\Delta G^*, \Delta H^*\) and \(\Delta S^*\) result from application of the Eyring equation with a path degeneracy factor of 1. The difference in \(\Delta H^*\) values found for the monopositive and mononegative ions of HHP reflects the difference in activation energy. A highly negative entropy of activation generally indicates that there is a higher degree of order in the activated complex than in the reactants. For the positive ion the higher degree of order of the activated complex must be caused by a better solvation. For the negative ion the activation entropy is low and positive thus indicating that the solvation of the activated complex is slightly lower than that of the compound in the initial state. The effect of \(\Delta H^*\) and \(\Delta S^*\) cancel each other partially which results in about the same value of \(\Delta G^*\) for both HHP ions.

It should be very interesting to see whether the positive and negative ions of other similar molecules reveal the same behaviour of the activation energy.

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REFERENCES
E.P.R. spectra of the ions of 1,2,3,6,7,8-hexahydropyrene