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

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 mole^{-1} for the radical anion and 3.5 ± 0.4 kcal mole^{-1} for the radical cation. The inversion rate at 0°C equals 2.8×10^6 s^{-1} for the anion and 4.2×10^6 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 $M_{\beta CH_2} = \pm 4, \pm 2$ and 0 (see figure 3, $M_{\beta CH_2}$ equals to the total z 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
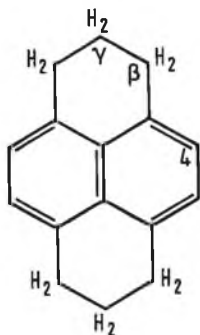

Figure 1. Structural formula of HHP.
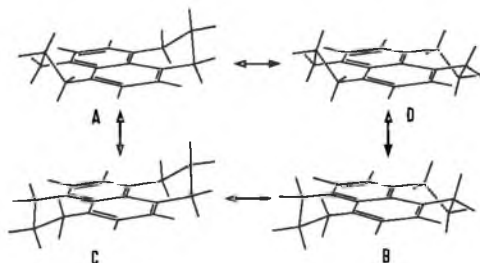
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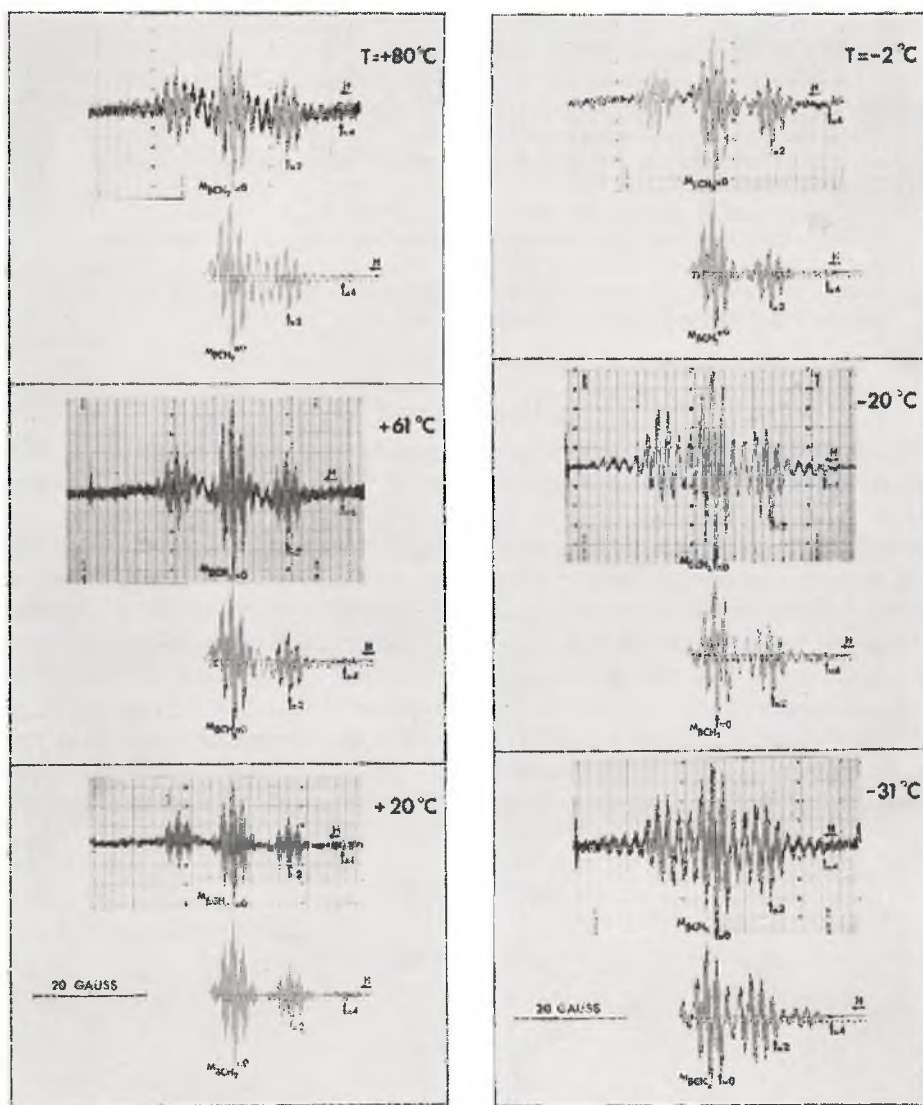Figure 2.   Interconversion scheme for the four HHP configurations.

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 $-20°C$ to $+20°C$. 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 $M_{\beta CH_2}$ 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 $-30°C$ and $+80°C$ in various solvents and with different counter ions. The spectra of the cation measured between $-30°C$ and $+25°C$ 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 β protons and two sets of two γ 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 $+80°C$ some broad lines are measured between $M_{\beta CH_2} = 0$ and $M_{\beta CH_2} = \pm 2$. 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 $+61°C$) and finally disappear at about $+20°C$ (the amplitude of the field modulation is kept constant). At still lower temperatures these lines sharpen again and are

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	HHP anion†	HHP cation‡
a_4 (aromatic)	1·68 gauss	1·90 gauss
a_β (equatorial)	2·02 gauss	3·78 gauss
$a_{\beta'}$ (axial)	8·03 gauss	14·60 gauss
a_γ (equatorial)	0·36 gauss ⎫ $T < -45°C$	
$a_{\gamma'}$ (axial)	0·50 gauss ⎭	
a_γ	0·41 gauss $T > -31°C$	0·40 gauss
Derivative linewidth	0·200 gauss	0·100 gauss

† See [1, 7].
‡ See [1].

Table 1.   Values of the parameters used in the computer simulation of the spectra of the monovalent ions of HHP.

split into two groups of lines symmetrically positioned around an averaged magnetic field strength $\bar{H}$.   The results of sharpening and repositioning of the broadened parts is demonstrated in figure 3 in the experimental spectra at $-2°C$, $-20°C$ and at $-31°C$.

The above series of spectra have been simulated by application of a model describing the exchange between four equally populated sites (see figure 2).   The mathematical formulation of this model, derived from the modified Bloch equations, has been given by Carrington [5] and has been applied by Bolton *et al.* [6] to describe the rotational isomerism in the naphthazarin semiquinone cation. Interconversion of configuration A into B and C into D—synchronized jumps—are ruled out because of the experimentally found intensity distribution of the unbroadened peaks in the spectra (cf. I).   The theoretical spectra based on this four-jump model are represented in figure 3, together with the experimental spectra measured in DME with Na^+ as counter ion.   The simulation required three independent parameters only, viz. $T_{2,0}^{-1}$ the linewidth in the absence of exchange, the lifetime τ of a particular conformation and the positions of the hyperfine lines at conditions of very slow exchange ($\tau \to \infty$).   The latter can be derived from the hyperfine splitting constants listed in table 1, thereby it was assumed that the γ protons could be considered as equivalent.   The linewidth $T_{2,0}^{-1}$ was chosen such that the line pattern of the group $M_{\beta CH_2} = 0$ is matched to that in the experimental spectrum; this group was selected because it is not affected by the line broadening mechanism and depends critically on this linewidth.   By adaptation of τ the experimental spectra measured between $-30°C$ and $+80°C$ could be simulated quite well (see figure 3).

It is noted that the E.P.R. spectra measured in NH_3 are identical to those measured in DME, THF or MTHF, irrespective of the alkali metal used for the reduction.   Thus the interconversion rate is independent of counter ion and solvent and therefore can be considered as an inherent property of the free anion.

3.2. *The low temperature spectra of the monoanion of HHP*

At temperatures lower than $-30°C$ the γ protons cannot be taken as equivalent as was first noted by Claridge and Peake [7].   These spectra should be simulated by a model that takes into account both the movements of the β and the γ protons. Since no extra information is obtained from the τ values of the spectra showing

effects due to the movement of the γ protons, we did not endeavour to simulate them. At $-75°C$ 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 CH_2 groups can be considered as frozen out.

3.3. *The spectra of the monocation of HHP*

The E.P.R. spectra between $-89°C$ and $+25°C$ 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 $-30°C$ to $+25°C$ 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 γ 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 SO_2/BF_3 mixtures spectra could be measured up to $-20°C$. The best spectra were obtained by taking the concentration of HHP equal to 10^{-3} M and the BF_3 concentration equal to 10^{-1} M. At temperatures where spectra could be measured in SO_2/BF_3 as well as in H_2SO_4, the spectra could be simulated with the same τ values. Hence the interconversion rate does not depend on the solvent used.
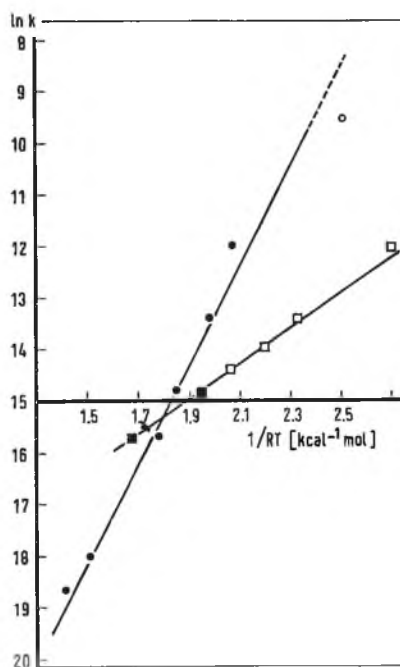

Figure 4. Arrhenius diagram of the rate constant for the interconversion process in the monovalent ions of HHP. □ refers to the positive ion in SO_2/BF_3. ■ refers to the positive ion in H_2SO_4. ● refers to the negative ion. ○ refers to the spectrum, measured at $-75°C$ (see text).

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 $10 \cdot 0$ 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 $10 \cdot 0$ kcal mole^{-1} has been found [8]. It is surprising that the activation energy for the positive ion is so much smaller, only $3 \cdot 5$ kcal mole^{-1}. As stated before no influence of solvent is observed: the measurements in H_2SO_4 yield τ values that produce the same straight line as those measured for the ion dissolved in SO_2/BF_3.

	HHP anion	HHP cation
E_{act} (kcal mole^{-1})	$+10 \cdot 0 \pm 0 \cdot 4$	$+3 \cdot 5 \pm 0 \cdot 4$
k^{273} (s^{-1})	$2 \cdot 8 \times 10^6 \pm 5$ per cent	$4 \cdot 2 \times 10^6 \pm 5$ per cent
k_0 (s^{-1})	$2 \cdot 5 \times 10^{14} \pm 5$ per cent	$2 \cdot 0 \times 10^9 \pm 5$ per cent
$\Delta H^{\neq}$ (273 K, kcal mole^{-1})	$+9 \cdot 5 \pm 0 \cdot 4$	$+2 \cdot 8 \pm 0 \cdot 4$
$\Delta S^{\neq}$ (273 K, e.u.)	$+5 \cdot 2 \pm 0 \cdot 1$	$-18 \cdot 0 \pm 0 \cdot 4$
$\Delta G^{\neq}$ (273 K, kcal mole^{-1})	$+8 \cdot 1 \pm 0 \cdot 5$	$+7 \cdot 7 \pm 0 \cdot 5$

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 $k_T = k_0 \exp(-E_{\text{act}}/RT)$.

The thermodynamic constants for the activated complex $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ result from application of the Eyring equation with a path degeneracy factor of 1. The difference in $\Delta H^{\neq}$ 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 $\Delta H^{\neq}$ and $\Delta S^{\neq}$ cancel each other partially which results in about the same value of $\Delta G^{\neq}$ 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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