Infrared Absorption Spectroscopic Studies of $\alpha,\omega$-Diphenylpolyenyl Anions with Odd Numbered Polyene Molecules

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Received March 29, 2001

Infrared absorption spectra of $\alpha,\omega$-diphenylpolyenyl anions $\text{Ph(CH)}_n\text{Ph}^-$ ($\text{DP}_n^-$, $n=7$, 9, and 13) in the tetrahydrofuran-$d_8$ solutions was measured in the range of 1700 and 1200 cm$^{-1}$. The infrared spectra obtained from anions ($\text{DP}_n$) showed considerable difference from their neutral species ($\text{DP}_n$); their intensities were enhanced at least two orders of magnitude stronger than their neutral species. The in-plane CH bending modes at 1464 and 1375 cm$^{-1}$ are correspondingly strengthened with the chain length increased, but the C=C stretching at 1541 cm$^{-1}$ is weakened and frequencies are not changed. We provide an IR evidence for the first time that the bond order or bond alternations of the anions (soliton) are different from those of radical anions (polaron) as well as neutral species.

Keywords: Soliton, $\alpha,\omega$-Diphenylpolyenyl aminos, Infrared spectroscopy.

Introduction

The structures and properties of conjugated polymers have been studied by various spectroscopic techniques. Infrared (IR) spectroscopy is increasingly being used as a powerful tool for studying conducting polymers, because it gives us knowledge on molecular structures of transient states as well as their dynamic properties. Various studies have been performed with the vibrational modes around a soliton in trans-polyacetylene (trans-PA), since three infrared absorption peaks of lightly doped-PA were observed at 1397, 1288, and 888 cm$^{-1}$. Su et al.$^1$ reported that the charged solitons which have charges but no spin act as the spinless charged carriers when the dopant content is below the critical value, 6 mol.%. Zannoni and Zerbi$^2$ have calculated the densities of the vibrational states of doped-PA using the force constant method, and Peluso et al.$^3$ have obtained the force constants using the cluster model by the MNDO method. Previous studies$^1$ showed that static charges and charge fluxes were the main factors to interpret the spectroscopic data of frequencies and intensities, and the calculations of inter-atomic distances and bond energies; they are also useful for the determination of intra-molecular$^4$ and inter-molecular$^5$ interactions. Mori et al.$^6$ suggested based on the MNDO method that the trends in wavenumbers are similar for positively and negatively charged solitons, and one of the wavenumbers is particularly sensitive to conjugation length. MO calculations by $ab$ initio method (6-31G) also indicate the dispersion of wavenumbers with conjugation lengths.$^7$ Nonetheless, infrared spectra of any charged species have not been reported in experimental method yet. More recent studies have been focused on the charge-storage mechanism in short polyenes and diphenylpolyenes,$^{8,9}$ which can be considered as oligomers of polyacetylene. Interest in the structural and spectral characteristics of the charged species (anions, radical anions and divalent ions) of conjugated compounds has been increasing from both the experimental and theoretical points of view. Studies on the charged species of oligo- and polyene compounds in particular are not only interesting in themselves but also important for understanding the electrical properties of doped PA.

In this paper, IR spectra with a model compounds of a negative soliton in trans-PA, $\alpha,\omega$-diphenylpolyenyl anions, $\text{Ph(CH)}_n\text{Ph}^-$ ($\text{DP}_n^-$, $n=7$, 9, and 13; see Figure 1), are reported. The molecular structures of $\text{DP}_n^-$ are schematically shown in Figure 1.

These compounds with odd numbers of carbons at the polyene parts have a negative charge, but no spin. Tolbert et al.$^{10}$ have been also reported the NMR and electronic absorption spectra of $\alpha,\omega$-diphenylpolyenyl anions, $\text{Ph(CH)}_n\text{Ph}^-$ (abbreviated as $\text{DP}_n^-$, $n=3$, 5, 7, 9, 13, and 17), as the good model compounds for the negative soliton in trans-PA. For the comparison, IR spectra of the radical anions, $\text{DP}_n^-$ ($n$ is 6, 8, and 10), as the model compounds for the negatively

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Molecular structures of $\alpha,\omega$-diphenylpolyenyl anions ($\text{DP}_n^-$): (a) $\text{DP}_7^-$, (b) $\text{DP}_9^-$, and (c) $\text{DP}_{13}^-$.}
\end{figure}

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charged polarons in trans-PA are also measured between 1700 and 1200 cm$^{-1}$.

Experimental Section

The $\alpha,\omega$-diphenylpolyenyl anions ($\text{DP}_n^-$, $n$=7, 9, and 13) and their neutral species ($\text{DP}_n$) were prepared using the previously reported methods. A $n$-butyllithium (Aldrich) was supplied as a 1.6 molar solution in $n$-hexane. This reducing agent is well known to produce the $\text{DP}_n^-$ anion solutions (THF-$d_6$) which are free of ion pairing. Solutions of $\text{DP}_n^-$ were prepared under high vacuum in Pyrex apparatus with specially designed CaF$_2$ infrared (IR) cell as shown in Figure 2.

A weighed quantity of polyene ($\text{DP}_n$), 1.6 mol $n$-Butyllithium/$n$-hexane, and THF-$d_6$ solvents were put into the tube A, B, and D, respectively. C is the CaF$_2$ infrared cell (path length is 0.3 mm) with modified vacuum tight holder. This apparatus for the sampling of anions ($\text{DP}_n^-$) was completely sealed and connected with the high vacuum line. The $n$-hexane solution of $n$-butyllithium was removed under vacuum and replaced with the THF-$d_6$ solvents from tube D by the distillation method. The synthesis of $\text{DP}_n^-$ were carried out by contacting $n$-butyllithium (B in Figure 2) with $\text{DP}_n$ (A in Figure 2) and THF-$d_6$ solvents.

After the reaction (reduction), the sampling apparatus detached from the vacuum line (the position b in Figure 2) and the $\text{DP}_n^-$ solutions were introduced into the IR cell of part C. The concentration of sample in the THF-$d_6$ solution was $10^{-5}$-$10^{-4}$ mol/dm$^3$ range. The reduction reactions were identified from the change of electronic absorption spectra.

Results and Discussion

The reduction process can be identified by electronic absorption spectroscopy. The electronic absorption of $\text{DP}_n^-$ shows a strong single absorption band attributed to the $n$-$\pi^*$ electronic transition between the nonbonding orbital and the $\pi^*$ LUMO orbital. According to the MO energy level diagram, the non-bonding orbital which is occupied by two non-bonding electrons exists in the middle of the band gap. The maximum absorption band is shifted to a lower energy region with the increase of polyene chain length. These electronic absorption band characteristics of $\text{DP}_n^-$ in the THF-$d_6$ solution are similar with that in the DMSO solution. Our electronic absorption data are also consistent with the theoretical results using a continuum model, in which the soliton in PA is expected to have only one electronic absorption band at the mid-gap center. On the other hand, the radical anions of $\alpha,\omega$-diphenylpolyene and $\alpha,\omega$-dibutylpolyene are known to have two absorption bands caused by the $\pi$-$\pi^*$ transition ($1^2B_g \rightarrow 2^2A_u$ and $1^2B_g \rightarrow 1^2A_u$). In case of trans-PA, electronic transition to the soliton and transitions due to vibrations around a soliton are observed in the infrared spectrum. These are at 1397, 1288, and 888 cm$^{-1}$ for

Figure 2. Apparatus for obtaining anion samples for infrared spectra; A: $\text{DP}_n$ sample tube, B: $n$-Butyllithium tube or sodium mirror, C: CaF$_2$ infrared cell (path length is 0.3 mm) and holder, D: solvent tube.

Figure 3. Infrared spectra (1700-500 cm$^{-1}$) of $\alpha,\omega$-diphenylpolyene ($\text{DP}_n$, $n$ is even numbered carbon); (a) $\text{DP}_6$, (b) $\text{DP}_8$, and (c) $\text{DP}_{10}$, measured in KBr disk.
Table 1. Observed infrared frequencies of \( \alpha, \omega \)-diphenylpolyenes and its assignments (reference 18).

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \alpha, \omega )-Diphenylpolyene (DPn)</th>
<th>Ref. 18</th>
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<tbody>
<tr>
<td>( bu )</td>
<td>( v_1 ) 1593 1593 1612 1626 1627 ( \nu ) (C=C)</td>
<td></td>
</tr>
<tr>
<td>( v_2 )</td>
<td>1572 1562 – 1595 1586 ( \nu ) (C=C)</td>
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<tr>
<td>( v_3 )</td>
<td>1489 1487 1487 – – Phenyl group</td>
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<tr>
<td>( v_4 )</td>
<td>1446 1444 1446 1417 1422 ( \delta ) (CH)</td>
<td></td>
</tr>
<tr>
<td>( v_5 )</td>
<td>1331 – – 1320 1309 ( \delta ) (CH)</td>
<td></td>
</tr>
<tr>
<td>( v_6 )</td>
<td>1315 1309 1296 1279 1282 ( \delta ) (CH)</td>
<td></td>
</tr>
<tr>
<td>( v_7 )</td>
<td>1178 1178 1178 1153 1141 ( \nu ) (C-C)</td>
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</tr>
<tr>
<td>( v_8 )</td>
<td>1072 1072 1072 – – Phenyl group</td>
<td></td>
</tr>
<tr>
<td>( au )</td>
<td>( v_{10} ) 1005 1008 1009 1010 1020 ( \tau ) (C=C)</td>
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<tr>
<td>( v_{11} )</td>
<td>972 972 968 972 978 ( \gamma ) (CH)</td>
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<tr>
<td>( v_{12} )</td>
<td>930 947 – 945 947 ( \nu ) (C-C)</td>
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</tr>
<tr>
<td>( v_{13} )</td>
<td>912 912 912 912 912 ( \gamma ) (CH)</td>
<td></td>
</tr>
<tr>
<td>( v_{14} )</td>
<td>860 874 881 899 894 ( \gamma ) (CH)</td>
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</tr>
<tr>
<td>( v_{15} )</td>
<td>– 818 845 863 852 ( \gamma ) (CH)</td>
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</tr>
<tr>
<td>( v_{16} )</td>
<td>758 752 744 – – Phenyl group</td>
<td></td>
</tr>
<tr>
<td>( v_{17} )</td>
<td>694 692 690 ( \gamma ) (CH)</td>
<td></td>
</tr>
<tr>
<td>( v_{18} )</td>
<td>629 607 – 651 642 ( \gamma ) (CH)</td>
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</table>

Ref. 18: Observed and calculated vibrational frequencies of all-trans-1,3,5,7,9-decapentaene.

The FT-IR spectra of DPn (n is 6, 8, and 10) in KBr disk between 500 and 1700 cm\(^{-1}\) are shown in Figure 3(a), (b), and (c), respectively. The tentative assignments of the bands observed from all-trans-DPn are listed in Table 1. In Table 1, the vibrational bands of DP6 (n is 6, 8, and 10) are in good agreement with the results of all-trans-1, 3, 5, 7, 9-decapentaene calculated at the MP2/6-31G level and its observed data. From this result, each infrared peak of DPn can be assigned. In the infrared spectrum of DPn (n is 7, 9, and 13) measured in THF-d\(_6\) solutions; (a) DP7 (0.8 \( \times \) \( 10^{-3} \)) mol/cm\(^3\), measured in CaF\(_2\) infrared cell, respectively. Solvent bands are subtracted.

As shown in Figure 3 and 4, the infrared spectra of anions (Figure 4) are quite different with its neutral species (Figure 3). Although detailed spectrum analysis of the observed anions is not possible at the present stage, the following points could be mentioned. In Figure 4, the peaks between 1502 and 1541 cm\(^{-1}\) are assigned to the C=C stretching mode, and the relative intensity decrease regularly with chain length (n) increases, but the wavenumbers are not changed. These peak positions are about 45-50 cm\(^{-1}\) lower than the corresponding band of its neutral states (\( v_1 \) and \( v_2 \) bands in Figure 3). According to the MNDO calculations on the anions of C\(_7\)H\(_7\) to C\(_{33}\)H\(_{35}\) reported by Mori et al.,\(^9\) infrared wavenumbers in this region were not particularly sensitive to the conjugation length, and its relative intensities. In doped polyacetylene,\(^1\) the C=C stretching band was not found in this region. The peaks between 1375 and 1465 cm\(^{-1}\) are assigned as the C-H bending mode, and their relative intensities are increased drastically with the chain length increase, but the wavenumbers are not changed. According to the calculation results by Mori et al.,\(^9\) the C-H bending modes for the cations of C\(_{13}\)H\(_{15}\), C\(_{17}\)H\(_{19}\) and C\(_{33}\)H\(_{35}\) have been reported at 1397, 1376 and 1358 cm\(^{-1}\), respectively. These bands are corresponding to the 1397 cm\(^{-1}\) band in the lightly iodine doped trans-PA.\(^1\) The frequency of this band depends upon the effect of electron-phonon interaction. Piaggio et al.\(^9\) reported that the infrared peak of 1397 cm\(^{-1}\) in doped PA shifts appreciably toward higher frequencies as the length of the conjugated sequences is shortened. The corresponding band in photo-induced PA have been also reported at 1369 cm\(^{-1}\).\(^2\) We indicate that the relative intensities of CH bending peaks are very sensitive with the change of chain lengths, but their wavenumbers are not. Especially, a peak at 1375 cm\(^{-1}\) is stronger than 1465 cm\(^{-1}\) as the polyene chain length (n) increases from 7 to 13. For the comparison, FT-IR
The corresponding peaks of the 1288 cm\(^{-1}\) associated with CH in-plane bending of benzene rings (end models) as well as its neutral species. The variance of spectrum between DP\(_n\) and DP\(_n^*\) indicates that the bond orders or bond alternations of the anions (soliton models) are weaker than those of the soliton models (DP\(_n\). The C=C stretching peak (1593-1531 cm\(^{-1}\)) have been shown a considerable difference with its neutral species (DP\(_n\)), and their IR intensities are enhanced at least two orders of magnitude stronger than its neutral species.

Anyway, as described above, the charge-induced IR bands of DP\(_n\) are clearly different from those of charge and spin-induced DP\(_n^*\). Tentative assignments for the observed bands have been discussed on the base of results obtained in the all-trans-1, 3, 5, 7, 9-decapentaene calculated at the MP2/6-31G level\(^{18}\) and the MNDO calculations on the anions of C\(_3\)H\(_2\) to C\(_3\)H\(_8\).\(^{9}\) However, for the more correct discussion about the differentia of structural and vibrational characteristics between anions (soliton) and radical anions (polaron) of DP\(_n\), the MO calculations of DP\(_n^*\) and DP\(_n^+\) at the high level are need, and more extensive studies for longer chain compounds are absolutely needed to clearly understand the self-localized charge domains in doped PA because Su\(^2\) and Kivelson\(^9\) have been actually proposed the soliton and polaron lattice structures in doped PA, respectively.

### References