

Infrared Absorption Spectroscopic Studies of α,ω -Diphenylpolyenyl Anions with Odd Numbered Polyene Molecules

Jin-Yeol Kim,^{*} Eung-Ryul Kim, Daewon Sohn, Akira Sakamoto,[†] and Mitsuo Tasumi[†]

Department of Chemistry, College of Natural Science, Hanyang Univ., Seoul 133-791, Korea

[†]Department of Chemistry, Faculty of Science, Saitama Univ., Urawa, Saitama 338, Japan

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Infrared absorption spectra of α,ω -diphenylpolyenyl anions $\text{Ph}(\text{CH})_n\text{Ph}^-$ (DP_n^- , $n=7, 9$, and 13) in the tetrahydrofuran- d_6 solutions was measured in the range of 1700 and 1200 cm^{-1} . The infrared spectra obtained from anions (DP_n^-) showed considerable difference from their neutral species (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, α,ω -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} .¹ Su *et al.*² 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 Zerbi³ have calculated the densities of the vibrational states of doped-PA using the force constant method, and Peluso *et al.*⁴ have obtained the force constants using the cluster model by the MNDO method. Previous studies⁵ 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-molecular⁶ and inter-molecular^{7,8} interactions. Mori *et al.*⁹ 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.¹⁰ 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,¹¹⁻¹³ which can be considered as oligomers of poly-

acetylene. 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, α,ω -diphenylpolyenyl anions, $\text{Ph}(\text{CH})_n\text{Ph}^-$ (DP_n^- , $n=7, 9$, and 13 ; see Figure 1), are reported. The molecular structures of 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.*¹¹ have been also reported the NMR and electronic absorption spectra of α,ω -diphenylpolyenyl anions, $\text{Ph}(\text{CH})_n\text{Ph}^-$ (abbreviated as 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, $\text{DP}_n^{\bullet-}$ (n is $6, 8$, and 10), as the model compounds for the negatively

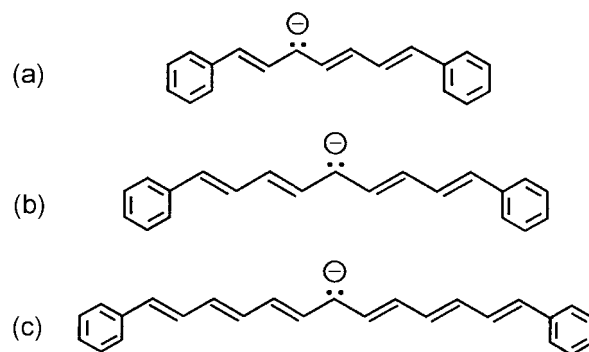


Figure 1. Molecular structures of α,ω -diphenylpolyenyl anions (DP_n^-): (a) DP_7^- , (b) DP_9^- , and (c) DP_{13}^- .

^{*}To whom correspondence should be addressed. e-mail; jinyeol@hanyang.ac.kr, jinyeol@unitel.co.kr

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

Experimental Section

The α,ω -diphenylpolyenyl anions (DP_n^- , $n=7, 9$, and 13) and their neutral species (DP_n) were prepared using the previously reported methods.^{11,14,15} A *n*-butyllithium (Aldrich) was supplied as a 1.6 molar solution in *n*-hexane. This reducing agent is well known to produce the DP_n^- anion solutions (THF- d_6) which are free of ion pairing.¹⁵ Solutions of 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 (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 (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 DP_n^- were carried out by contacting *n*-butyllithium (B in Figure 2) with 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 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. All-*trans*- DP_n ($n=6, 8$, and 10 ; even number) were purchased from the Tokyo Chemical Industry, Ltd. and Aldrich Chemical Co., respectively, and used without further purification. The radical anions ($\text{DP}_n^{\bullet-}$; $n=6, 8$, and 10) in each polyene were prepared by reducing the neutral polyene in

THF- d_6 solution in a tube B of sodium mirror.

Infrared absorption spectra were measured by a JEOL JIR 5500 FT-IR spectrophotometer with a MCT detector. The difference spectrum between DP_n^- in THF- d_6 solutions and pure THF- d_6 solvents are measured into the CaF_2 infrared cell between 1700 cm^{-1} and 1200 cm^{-1} regions. Hitachi U-3500 spectrophotometer was used for the electronic absorption spectra.

Results and Discussion

The reduction process can be identified by electronic absorption spectroscopy. The electronic absorption of DP_n^- shows a strong single absorption band attributed to the $n\text{-}\pi^*$ electronic transition between the nonbonding orbital and the π^* 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 DP_n in the THF- d_6 solution are similar with that in the DMSO solution.¹¹ 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 α,ω -diphenylpolyene and α,ω -dibutylpolyene are known to have two absorption bands caused by the $\pi\text{-}\pi^*$ transition ($1^2\text{B}_g \rightarrow 2^2\text{A}_u$ and $1^2\text{B}_g \rightarrow 1^2\text{A}_u$). In case of *trans*-PA, electronic transition to the soliton and transitions due to vibrations around a soliton are observed in the infrared spectrum.^{1,16,17} These are at 1397, 1288, and 888 cm^{-1} for

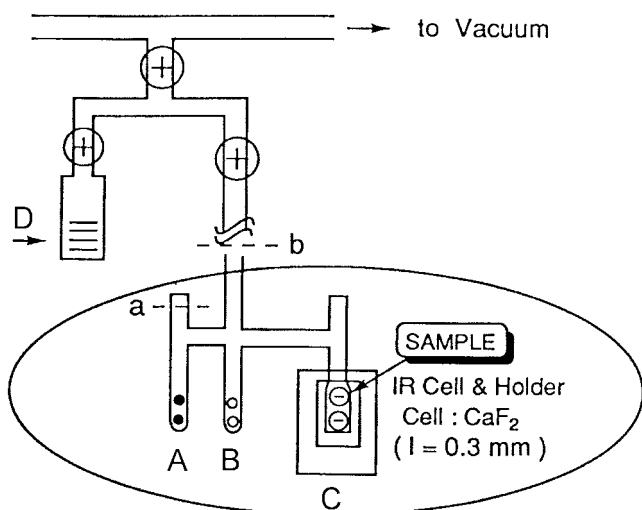


Figure 2. Apparatus for obtaining anion samples for infrared spectra; A: DP_n sample tube, B: *n*-Butyllithium tube or sodium mirror, C: CaF_2 infrared cell (path length is 0.3 mm) and holder, D: solvent tube.

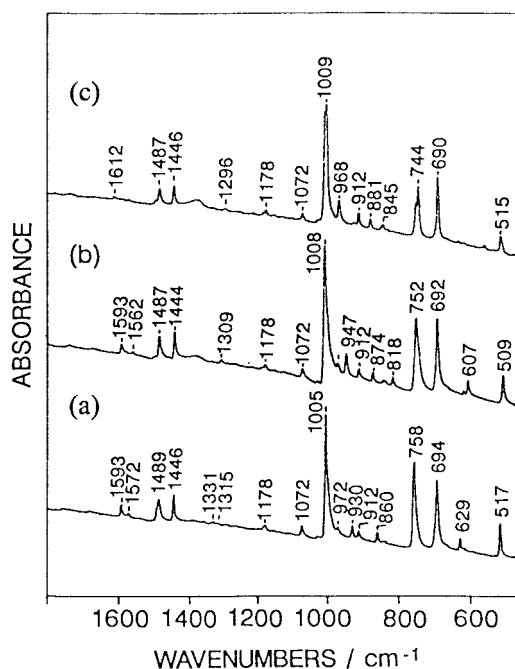


Figure 3. Infrared spectra (1700–500 cm^{-1}) of α,ω -diphenylpolyene (DP_n , n is even numbered carbon); (a) DP_6 , (b) DP_8 , and (c) DP_{10} , measured in KBr disk.

Table 1. Observed infrared frequencies of α,ω -diphenylpolyenes and its assignments ("reference 18)

Mode	α,ω -Diphenylpolyene (DPn)				Ref. 18		
	DP6	DP8	DP10	Obs.	Cal.	Assignment	
<i>bu</i>	ν_1	1593	1593	1612	1626	1627	ν (C=C)
	ν_2	1572	1562	—	1595	1586	ν (C=C)
	ν_3	1489	1487	1487	—	—	Phenyl group
	ν_4	1446	1444	1446	1417	1422	δ (CH)
	ν_5	1331	—	—	1320	1309	δ (CH)
	ν_6	1315	1309	1296	1279	1282	δ (CH)
	ν_7	1178	1178	1178	1153	1141	ν (C-C)
	ν_8	1072	1072	1072	—	—	Phenyl group
<i>au</i>	ν_9	1005	1008	1009	1010	1020	τ (C=C)
	ν_{10}	972	972	968	972	978	γ (CH)
<i>bu</i>	ν_{11}	930	947	—	945	947	ν (C-C)
<i>au</i>	ν_{12}	912	912	912	918	922	γ (CH)
	ν_{13}	860	874	881	899	894	γ (CH)
	ν_{14}	—	818	845	863	852	γ (CH)
	ν_{15}	758	752	744	—	—	Phenyl group
	ν_{16}	694	692	690	—	—	Phenyl group
	ν_{17}	629	607	—	651	642	γ (CH)
	ν_{18}	517	509	515	-	-	γ (CH)

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

(CH)_n, and at 1140 and 790 cm⁻¹ for (CD)_n with lightly iodine doped *trans*-PA.¹

The FT-IR spectra of DP_n (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*-DP_n are listed in Table 1. In Table 1, the vibrational bands of DP_n (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.¹⁸ From this result, each infrared peak of DP_n can be assigned. In the infrared spectrum of DP_n (n is 7, 9, and 13; Figure 3), the most intensive band is observed at the 1005-1009 cm⁻¹ range (ν_9). This band is assigned to the out-of plane CH deformation or C=C wagging. Another C=C stretches bands are also observed between 1562 and 1612 cm⁻¹ (ν_1 and ν_2), although its intensities are very weak. The weak infrared band at 1178 cm⁻¹ mainly consists of the C-C stretches and the in-plane CH bends (ν_7). The 930(DP₆) and 947(DP₈) cm⁻¹ (ν_{11}) are the C-C stretches bands. The bands between 1446 and 1296 cm⁻¹ (ν_4 , ν_4 and ν_6) can be assigned to the in-plane CH bending, and bands between 912 and 515 cm⁻¹ (ν_{12} , ν_{13} , ν_{14} , ν_{17} and ν_{18}) to the out-of plane CH bending, respectively. In particular, the ν_3 , ν_8 , ν_{15} and ν_{16} bands are induced from phenyl groups.

The FT-IR spectra of DP_n⁻ (n is 7, 9, and 13) measured between 1700 and 1200 cm⁻¹ are shown in Figure 4(a), (b), and (c), respectively.

As show 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

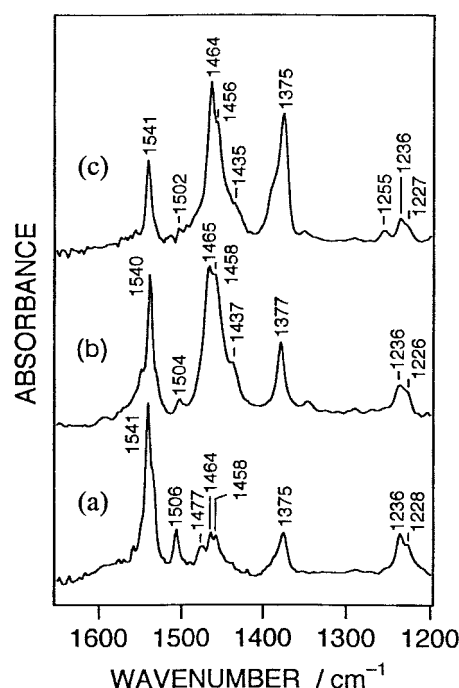


Figure 4. Infrared spectra (1700-1200 cm⁻¹) of α,ω -diphenylpolyenyl anions (DP_n⁻) in THF-d₆ solutions; (a) DP₇⁻ (0.8×10^{-4}), (b) DP₉⁻ (0.1×10^{-4}), and (c) DP₁₃⁻ (0.02×10^{-4} mol/cm³), measured in CaF₂ infrared cell, respectively. Solvent bands are subtracted.

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 (ν_1 and ν_2 bands in Figure 3). According to the MNDO calculations on the anions of C₅H₇ to C₃₃H₃₅ 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 CH 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 CH bending modes for the cations of C₁₃H₁₅, C₁₇H₁₉ and C₃₃H₃₅ 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.*¹⁹ 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⁻¹.²⁰ 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

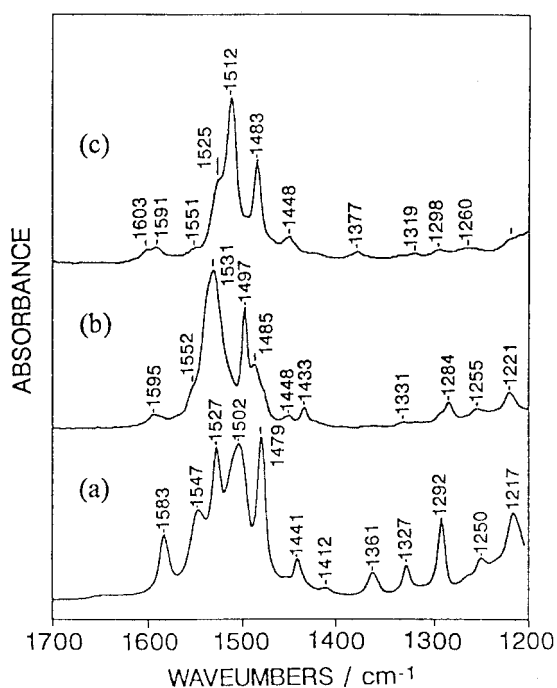


Figure 5. Infrared spectra (1700-1200 cm^{-1}) of radical anions of α,ω -diphenylpolyene ($\text{DP}_n^{\bullet-}$) in THF-d_6 solutions; (a) $\text{DP}_6^{\bullet-}$ (0.5×10^{-4}), (b) $\text{DP}_8^{\bullet-}$ (0.4×10^{-4}), and (c) $\text{DP}_{10}^{\bullet-}$ (0.2×10^{-4} mol/ cm^3), measured in CaF_2 infrared cell, respectively. Solvent bands are subtracted.

spectra of the radical anions of DP_n ($\text{DP}_n^{\bullet-}$; n is 6, 8, and 10) as the model compounds of a negatively polaron in *trans*-PA measured between 1700 and 1200 cm^{-1} are also shown in Figure 5(a), (b), and (c), respectively.

The IR spectra of the polaron models ($\text{DP}_n^{\bullet-}$) are quite different with those of the soliton models (DP_n^-). But, the CH bending modes of $\text{DP}_n^{\bullet-}$ observed between 1433 and 1552 cm^{-1} are 50-80 cm^{-1} higher frequency regions than corresponding bands of DP_n^- . We could not find the corresponding band at around 1397 cm^{-1} on the doped *trans*-PA. The C=C stretching peak (1593-1531 cm^{-1}) are weaker than those of the soliton models (DP_n^-). The variance of spectrum between DP_n^- and $\text{DP}_n^{\bullet-}$ indicates that the bond orders or bond alternations of the anions (soliton models) are somewhat different from those of radical anions (polaron models) as well as its neutral species.

In Figure 4, the bands of 1226 and 1236 cm^{-1} may be associated with CH in-plane bending of benzene rings (end groups) with charge. The corresponding peaks of the 1288 cm^{-1} (C-C stretching) and 888 cm^{-1} (C=C stretching) in doped PA could not be clearly observed because a limit of the CaF_2 IR cell and solvent system used in this experiment. The infrared spectra obtained from anions (DP_n^-) or radical anions ($\text{DP}_n^{\bullet-}$) 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 level¹⁸ and the MNDO calculations on the anions of C_5H_7 to $\text{C}_{33}\text{H}_{35}$.⁹ However, for the more correct discussion about the different structural and vibrational characteristics between anions (soliton) and radical anions (polaron) of DP_n , the MO calculations of DP_n and $\text{DP}_n^{\bullet-}$ 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 Su² and Kivelson⁹ have been actually proposed the soliton and polaron lattice structures in doped PA, respectively.

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