198 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 198—202 (1976) [Vol. 49, No. 1

The Electronic Spectra of *α,ω*-Di-1-anthrylpolyenes in Solution and in Solid State

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(Received January 6, 1975)

The electronic absorption spectra of a number of α,ω-Di-1-anthrylpolyenes have been studied in solution and in crystals. Three intense and two weak band systems have been observed. The plots of $\lambda^2 - n$ and $\varepsilon - n$ result in a good straight line in lower members. These results suggest that long anthrylpolyenes are not in *all-trans* form. Highest energy emission and lowest energy absorption bands show good overlap and identical solvent behavior. It has been concluded that in anthrylpolyenes the lowest excited state is an allowed ^1B_u type. The terminal anthryl-group interaction effect is such that ^1A_g is not lowered relative to ^1B_u in these polyenes. The absorption bands of anthrylpolyenes in the crystalline state could be explained in terms of factor group split components.

A systematic investigation of spectroscopic properties of conjugated polyenes in different states has been undertaken in this laboratory. It has already been established[1–4] in many linear polyenes with the general structure R_1–$(CH{=}CH)_n$–R_2 that there exists a low energy excited state below the strongly allowed electronic transition previously observed and that fluorescence of polyenes originates from this state. Here R_1 and R_2 are the end groups. The ground electronic state of these polyenes is ^1A_g and the excited states in increasing energy order are ^1B_u, ^1A_g, ^1A_g, ^1B_u according to the Pariser-Parr-Pople (PPP) method.[5] The ordering of the excited electronic states is altered when double-excited configuration interaction is included.[2] One of the two excited states (^1A_g) is significantly lowered in energy and the ordering of the excited electronic states changes to ^1A_g, ^1B_u, ^1A_g, ^1B_u in butadiene.[2] The high energy ^1B_u and ^1A_g state energies are altered less by inclusion of double-excited configuration, although in hexatriene and octatetraene the higher ^1B_u appears below the highest ^1A_g state.[2] The effect of the end groups on the electronic states of these molecules is well known.[6–9] The first intense transition $^1A_g \rightarrow {}^1B_u$ is at longer wavelength for the end group C_6H_5 than for the end group H or CH_3 when the polyene has the same number (n) of double bonds. In order to study the effect of the terminal groups on the electronic excitation of polyacetylene chromophore, it was thought worthwhile to extend the investigation to other polyenes terminated with aromatic groups. The present paper deals with the results of our investigation on the electronic absorption spectra of a number of anthrylpolyenes in solution and also in the solid state.

Experimental

Highly pure, synthetic α,ω-di-1-anthrylpolyene was obtained from Prof. Nakagawa, Osaka University, Japan as a gift. It was used without further purification. Solvent tetrahydrofuran (THF) used was of spectrograde quality. The electronic absorption spectra were measured at room temperature using a well-matched pair of 1-cm cells with a Spektromom-202 spectrophotometer of Hungarian Optical Works. The electronic spectra in the solid state were obtained in the same spectrophotometer by making a thin crystal film on the quartz plate by gently rubbing the polyene powder. The thickness of the film has been estimated from the absorption spectrum of the solid film. An absorption band unsplit in the crystalline state and its molar extinction coefficient in the solution spectrum have been taken to estimate the thickness. Six α,ω-di-1-anthrylpolyenes of type R–$(CH{=}CH)_n$–R, which is abbreviated as I_n, have been studied. Here R stands for the anthryl group and $n = 1$—6.

Results and Discussion

I. Solution Spectra. The electronic absorption

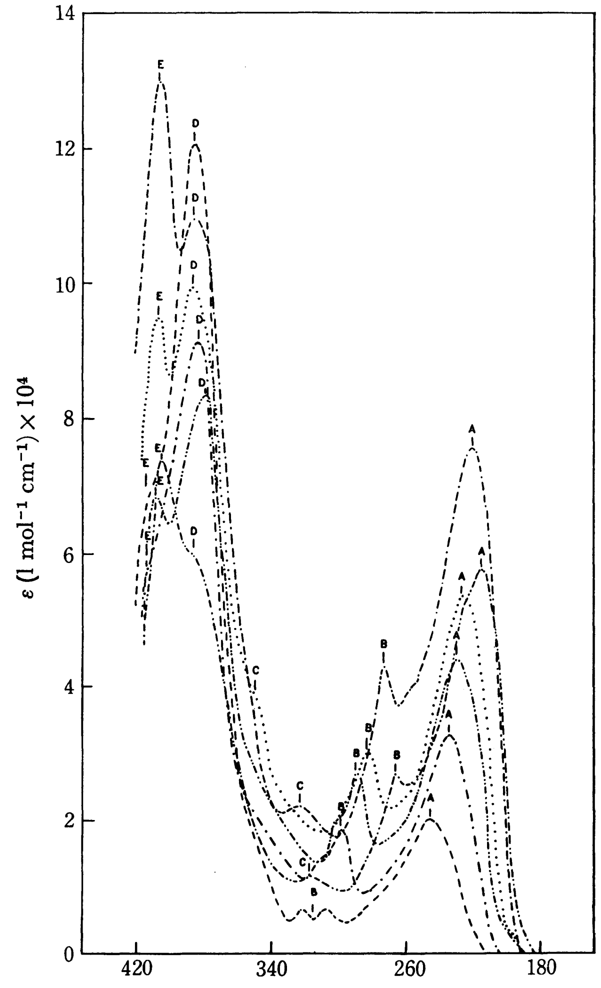

Fig. 1. Absorption spectra of anthrylpolyenes in THF solution.
---------: I_1, —·—·—: I_2, —··—: I_3, ······: I_4, ——·——: I_5, ——··——: I_6.

TABLE 1. ABSORPTION BANDS OF ANTHRYLPOLYENES

No. of double bonds (n)	Bands in solution (Solvent: THF)		Bands in crystalline state	
	Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
1	24630(s)	A(O$_1$)	22400	A
	30864(w)	B(O$_2$)		
	32258(w)	B(O$_2$+1400)		
	38610(vs)	D(O$_4$)	41322	D$_1$
			36496	D$_2$
	41493(vw)	E(O$_5$)		
2	23529(s)	A(O$_1$)	24630	A$_1$
			22624	A$_2$
	29940(s)	B(O$_2$)		
	31250(w)	B(O$_2$+1310)		
	38314(vs)	D(O$_4$)	43478	D$_1$
			37037	D$_2$
	41493(w)	E(O$_5$)	45455	E$_1$
			40322	E$_2$
3	23094(s)	A(O$_1$)	23200	A
	29069	B(O$_2$)		
	30120(w)	B(O$_2$+1061)		
	37878(vs)	D(O$_4$)	44052	D$_1$
			38167	D$_2$
	40983(s)	E(O$_5$)	44052	E$_1$
			38167	E$_2$
4	22727(vs)	A(O$_1$)	22800	A$_1$
			21100	A$_2$
	28328(s)	B(O$_2$)	26800	B
	34965(w)	C(O$_3$)	32400	C
	38610(s)	D(O$_4$)	44444	D$_1$
			36900	D$_2$
	40650(s)	E(O$_5$)	44444	E$_1$
			36900	E$_2$
5	22123(vs)	A(O$_1$)	21978	A$_1$
			20618	A$_2$
	27472(w)	B(O$_2$)	27000	B
	32258	C(O$_3$)	30800	C
	38610(s)	D(O$_4$)	41016	D$_1$
			34722	D$_2$
	40650(vs)	E(O$_5$)	44642	E$_1$
			35971	E$_2$
6	21739(vs)	A(O$_1$)	21459	A$_1$
			20000	A$_2$
	26737(w)	B(O$_2$)	26737	B
	31847(w)	C(O$_3$)	28900	C
	38610(vw)	D(O$_4$)	40983	D$_1$?
			34722	D$_2$?
	40650(vs)	E(O$_2$)	40983	E$_1$
			34722	E$_2$

s: strong, w: weak, v: very.

spectra of di-1-anthrylpolyene in THF are shown in Fig. 1. Results are summarized in Table 1. The electronic absorption spectrum seems to be composed of three distinct intense electronic band systems. Two more bands are also observed for higher members. The first band system observed in the region 4000—5000 Å is very intense and structureless: its intensity increases with the increase of the number of double bonds. This band is designated as A in the diagram. The band system in the region 3200—3800 Å designated as B is of moderate intensity and shows some structures in the spectra of lower polyenes. The vibronic band represents the upper state fundamental frequency of about 1400 cm^{-1} in I$_1$, 1310 cm^{-1} in I$_2$ and 1061 cm^{-1} in I$_3$. The band system in the high energy region (2500 Å) is also very intense in all the polyenes. This system consists of two bands with a separation of about 200 cm^{-1} between them. These two bands (D and E) seem to belong to two different systems. Finally a weak broad band (C) in the region 2900 Å is observed in the higher members of the group. These results are in complete agreement with that reported by Takeuchi *et al.*[10]

As can be seem from Fig. 1 and Table 1, the longest wavelength maxima and second-longest wavelength maxima both undergo redshift with the increase in length of polyene chain. For linear polyenes, it has generally been accepted[11] that for the longest wavelength band

$$\lambda^2_{\max} = A + Bn$$

where n is the number of conjugated double bonds, A and B are constants. This relation has been seen to hold well also for phenylpolyenes, diphenylpolyenes and triphenylpolyenes.[9] We have attempted such a plot for these anthrylpolyenes. For the longest wavelength band a reasonably good straight line is obtained for the lower polyenes only. Owing to broadness of the band, exact estimation of $\lambda_{\max}$ is, however, difficult. For the second band the plot of $\lambda^2{}_{\max}$ against n-values results in a straight line. These plots are shown in Fig. 2. Shift of other bands with the increase of n is negligible.

For long polyenes the transition moment for the first $^1A_g \rightarrow {}^1B_u$ transition is along the long axis of the molecule and is proportional to the length of the molecule.[12] Molecular orbital theory predicts the same.[12] The

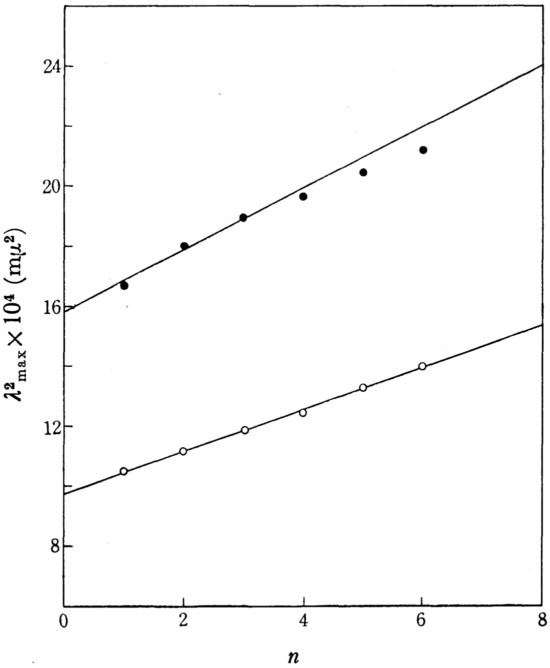

Fig. 2. Plot of $\lambda^2{}_{\max}$ against n.
—●—: Longest wavelength maxima,
—○—: Second-longest-wavelength maxima.

Table 2. Observed oscillator strength of absorption bands of anthrylpolyenes in solution

No. of double bonds n	Oscillator strength for bands A	B	D	E
1	0.377	0.036	2.50	0.01
2	0.634	0.101	1.96	0.01
3	0.883	0.151	1.84	0.30
4	1.220	0.172	1.60	1.30
5	1.690	0.211	1.34	2.48
6	1.225	0.103	0.304	1.47

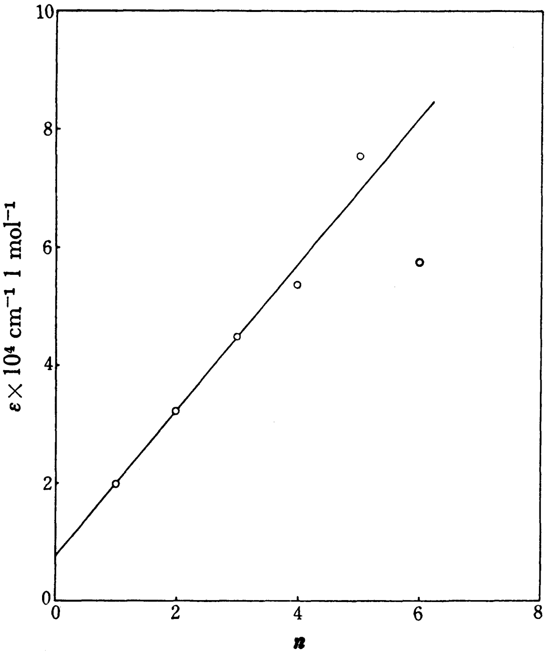

Fig. 3. Plot of ε against n for the longest wavelength maxima.

experimentally obtained oscillator strength values, as presented in Table 2, agree satisfactorily with the prediction. A plot of ε, molar extinction coefficient, *vs*. n, the number of double bonds, gives a good straight line for the first three polyenes. This linear plot (shown in Fig. 3) is also taken as a proof[9)] of *all-trans* configuration of the polyene. That I_4—I_6 do not fall in the straight line proves that the higher anthrylpolyenes are not purely *trans*. Both in λ^2–n and ε–n plots, I_6 deviates significantly from the straight line and the molecule is definitely not in *trans* form. Small deviation is also observed in I_4 and I_5 and these two polyenes also do not seem to be in purely *all-trans* form. The high energy symmetry allowed band $^1A_g \rightarrow {}^1B_u$ (^1D in Platt's notation) is intense in *all-trans* polyenes. It has, however, generally been observed that the low energy $^1A_g \rightarrow {}^1B_u$ (^1B in Platt's notation) is more intense than the high energy $^1A_g \rightarrow {}^1B_u$ transition. In *all-trans* lycopene[13)] the molar extinction coefficient have values 186×10^3 and 52×10^3 respectively for the two transitions. As can be seen from Table 2, in anthrylpolyenes the low energy allowed transition is less intense than the high energy allowed transition. This possibly is due to intensity "stealing" from the adjacent intense band E on the high energy side. Of the two bands D and E the lower energy one at about 2620 Å is intense in lower polyenes. As the number of double bonds increases, this band becomes weaker whereas the other at higher energy at about 2430 Å gains in intensity. This high energy band possibly arises from the interaction between ^1B_u state of *all-trans* polyene and the $^1B_{3u}$ state of the anthryl group.

The plots of λ^2 against n, ε against n and the enhancement in intensity of 2430 Å band in I_5 and I_6 perhaps indicates that the long polyenes are not in *all-trans* form. The long polyene chromophore with the large anthryl terminal group may bend the $(CH{=}CH)_n$ chain. In such *cis* form, the transition moment of the $^1A_{1g} \rightarrow {}^1B_{3u}$ transition along the long axis of the anthracene molecule makes a smaller angle with the direction of the transition moment of $^1A_g \rightarrow {}^1B_u$ of the polyene chromophore and the intensity of 2430 Å band may be enhanced in higher members. This *cis* configuration of long anthrylpolyenes is further supported by increased intensity of the *cis* peak at 3640 Å and 3740 Å at I_5 and I_6 respectively and also by the appearance of another symmetry forbidden band (as evidenced from its low intensity) at about 3100 Å and 3140 Å in I_5 and I_6 respectively.

II. Solvent Behavior. In some linear conjugated polyenes there exists a low-lying π-electronic state, transition to which is normally forbidden in *all-trans* form. Emission is observed from this low-lying state and as a result no overlap is usually observed between the intense lowest energy absorption band and the emission band of this *trans* polyene.[14)] In the anthrylpolyenes we have observed two weak bands around 3500 Å (B) and 3000 Å (C). These are of forbidden nature and possibly belong to the ^1A_g states of polyene. In addition, three allowed type strong bands A, D, and E have been observed. A and D most likely are transitions to the ^1B_u state of polyene. The E band seems to be related to the $^1B_{3u}$ band of anthracene nucleus. It, therefore, appears that in these polyenes the first excited ^1A_g state is not below the ^1B_u state of polyene. Significant overlap has been observed between the absorption and emission bands in I_1. Solvent effect is a good clue as to the identity of the absorbing and emitting states. The major contribution to the solvent shift of the strong transition can be written in the form[3,15)]

$$\bar{\nu} - \bar{\nu}_{\text{gas}} = K f_{\text{eg}} \frac{n^2-1}{n^2+2}$$

where $\bar{\nu}$ is the transition energy in cm^{-1}, K is a parameter which is constant for a given molecule, f_{eg} is the oscillator strength for a particular transition of the molecule, n is the solvent refractive index and $(n^2-1)/(n^2+2)$ is the solvent polarizability. A plot of $\bar{\nu}$ for the first absorption and the emission bands of I_1 *versus* $(n^2-1)/(n^2+2)$ is shown in Fig. 4. The slopes of the lines are the same indicating similar value for the absorption and emission oscillator strengths. This result is different from that usually observed[1,16)] in linear conjugated polyenes where ^1A_g state has been established to be the lowest excited electronic state. State ordering may as well be different for polyenes with different substituents. We conclude that in α,ω-di-1-anthrylpolyenes the lowest excited state is an allowed ^1B_u type. The terminal anthryl group

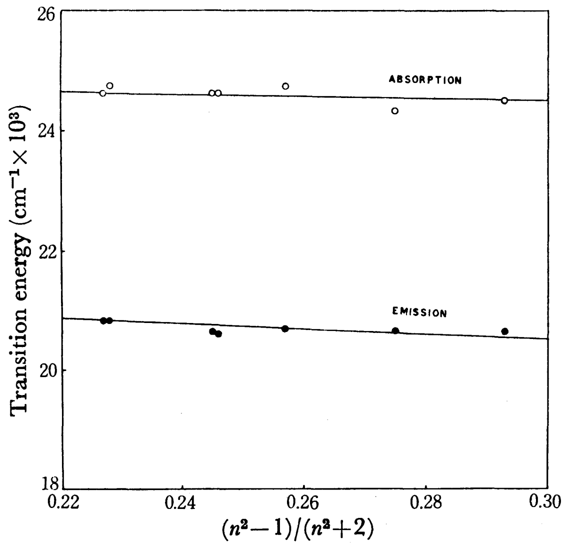

Fig. 4. The positions of the highest energy emission band and lowest energy strong absorption band of I_1 as a function of $(n^2-1)/(n^2+2)$.

interaction effect is such that the electronic state of the acetylene chromophore is lowered in energy with ^1A_g as the ground state and with ^1B_u, ^1A_g, ^1A_g, ^1B_u as the excited states in increasing energy order, the same as when only single-excitation configuration interaction is considered in PPP calculation.

III. Solid Film Spectra. The electronic absorption spectra of anthrylpolyenes in crystalline state are shown in Fig. 5. The bands are broad and there is overlapping between bands. The ordinate shows the intensity of a band relative to others in the same spectrum.

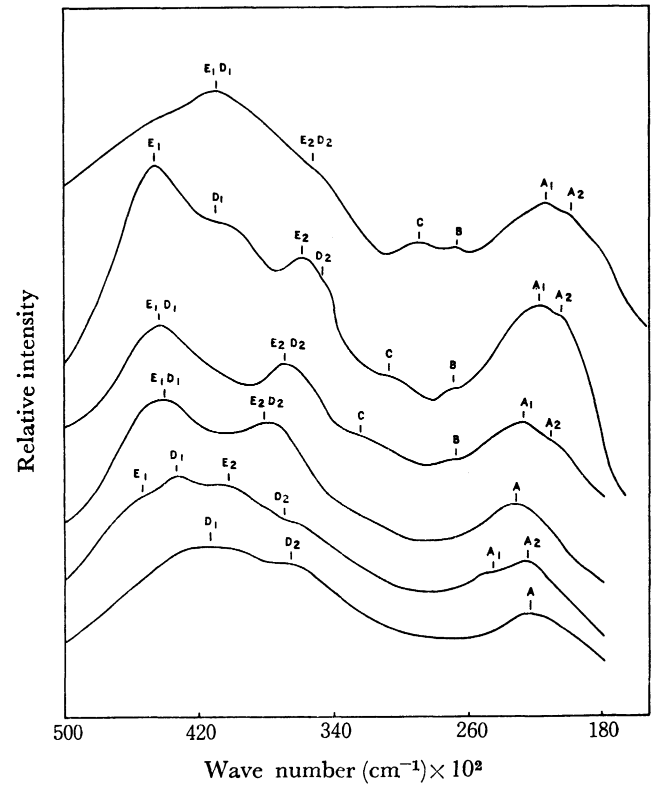

Fig. 5. Absorption spectra of di-1-anthrylpolyenes (I_n) in the solid state. The curves (n=1—6) have been displaced upward successively on the ordinate axis from the curve immediately below for clarity.

The band B in the region 3200—3800 Å, which is of moderate intensity in solution, seems to be absent in the lower member in the crystalline state. In the higher members, this band appears with moderate intensity. Further, the other weak band at about 3140 Å appears with moderate intensity in higher polyene crystal spectra but is absent in lower polyenes. These observations indicate that in the crystalline state also lower anthrylpolyenes remain in *all-trans* form but the higher members are in *cis* form: this is likely in view of the longer chain between the two anthryl terminal groups.

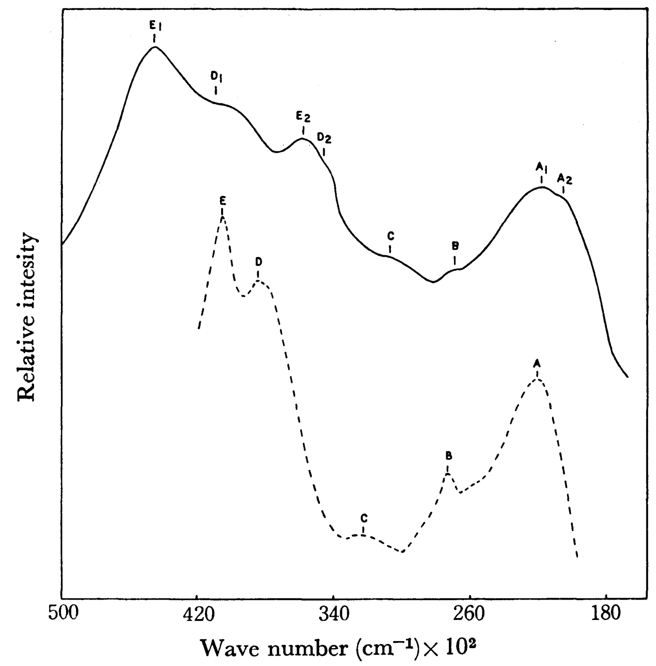

Fig. 6. Absorption spectrum of I_5.
---: Spectrum in THF solution, —: Solid film spectrum.

The crystal spectra differ from the spectra of free molecules in that in the solid state there are more number of bands than in solution and these bands are on both high and low energy sides of the intense solution bands. Some of these bands seem to be the factor group split components of the intense free molecular bands. This is better observed in the solid film spectrum of I_5 which shows structures and better resolution (Fig. 6). Solid state bands A_1 and A_2 on high and low energy sides of solution band A respectively seem to be the split components of A. Identification of weak B and C solution bands in solid film is obvious and no additional structure is observed in this region. In the region of solution bands D and E there are four distinct resolved bands in the crystal spectra. From the structures of the bands it seems that the band D is split into D_1 and D_2 and E is split into E_1 and E_2 in the solid state. Assignments of the bands in the crystal spectra of other anthrylpolyenes are less straightforward. We have, however, attempted a tentative identification of these bands in terms of solution band in other anthrylpolyenes (Fig. 5). The assignment of the factor group split components in Table 1 is only tentative and numerical values of splitting are of no significance. Study of single crystal polarized spectra at liquid N_2 or liquid He temperature is required for any inequivocal identification of factor group split components.

The authors are thankful to Prof. Nakagawa for his generous gift of anthrylpolyenes. One of the authors (K.G.M.) expressess his thanks to the University Grants Commission, India for a fellowship.

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