# The Electronic Spectra of $\alpha,\omega$-Di-1- and $\alpha,\omega$-Di-2-naphthylpolyenes in Solution and in Solid State

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The electronic absorption spectra of $\alpha,\omega$-di-1- and $\alpha,\omega$-di-2-naphthylpolyenes have been studied in solution and in the crystalline state. Both polyenes have four distinct electronic band systems. The spectral properties indicate that the terminal naphthyl group reduces the symmetry of the short-chained polyene molecules whereas long naphthylpolyenes retain the usual conjugated polyene symmetry of $C_{2h}$. A plot of $\lambda^2_{max}$-$n$ gives a straight line and a nearly *all-trans* form seems to be retained by the polyene chain. Unlike that in some conjugated polyenes a good overlap between the first absorption band and the highest energy emission band is observed. This suggests that there is no low-lying forbidden state in these polyenes. Some of the absorption bands of naphthylpolyene crystal could be explained in terms of factor group split components. Two extra bands observed in $\alpha,\omega$-di-2-naphthylpolyenes seem to be related to naphthalene transitions.

Compared to the effort expanded in the spectral study of aromatic molecules little experimental works on the electronic spectrum of conjugated polyenes have been done. A systematic investigation of the electronic spectral properties of polyenes in different states has been undertaken in this laboratory. It has already been established[1—4] that in some linear polyenes with the general structure $R_1$-$(CH=CH)_n$-$R_2$, $R_1$ and $R_2$ being the end groups, there exists a low energy excited state ($^1A_g$) below the previously observed strongly allowed electronic state ($^1B_u$) and emission of polyenes originates from this state. The effect of the end groups on the electronic states of polyenes is well known.[5—8] In an earlier[9] paper it has been shown that in anthryl polyenes the lowest excited state is an allowed $^1B_u$ type. The terminal anthryl group interaction is such that $^1A_g$ is not lowered relative to $^1B_u$ in these polyenes. In order to study the effect of other end groups on the electronic excitation of polyacetylene chromophore, it was thought worthwhile to extend the investigation to other polyenes with terminal aromatic groups. Here we report the results of our investigation on the electronic spectra of a series of naphthylpolyenes in solution and also in the solid state.

## Experimental

Highly pure, synthetic $\alpha,\omega$-di-1- and di-2-naphthylpolyenes were obtained from Prof. Nakagawa of Osaka University as a gift. They were used without further purification. Solvent tetrahydrofuran (THF) and haxane used were spectrograde. The electronic absorption spectra were measured with Spektromom-202 spectrophotometer of Hungarian optical works at room temperature using a well-matched pair of 1-cm cells. The fluorescence spectra were measured using a high intensity UV mercury source and a Corning C.S 7-54 filter with right angle excitation. The spectra in the solid state were obtained by making a thin crystal on the quartz plate. Five $\alpha,\omega$-di-1-naphthylpolyenes ($I_n$) and six $\alpha,\omega$-di-2-naphthylpolyenes ($I_n'$) of type R-$(CH=CH)_n$-R where R stands for the naphthyl group and $n$=1—6, have been studied.

## Results

*Solution Spectra.* *$\alpha,\omega$-Di-1-naphthylpolyene($I_n$)*: The electronic absorption spectra of a series of $I_n$ are reproduced in Fig. 1. Results are summarized in Table 1. Solvent hexane has been used to get the high energy bands in the region 2000—2400 Å. The spectrum from 2400 Å to the visible region has been measured in solvent THF because of better solubility of the polyenes in this solvent and the THF itself has no absorption in this spectral region.

The solution spectra show four distinct band systems. The transition to the lowest excited singlet state of the polyene is observed in the region 3000—5000 Å and this is very intense. Its intensity increases linearly with the chain length. This band has been identified

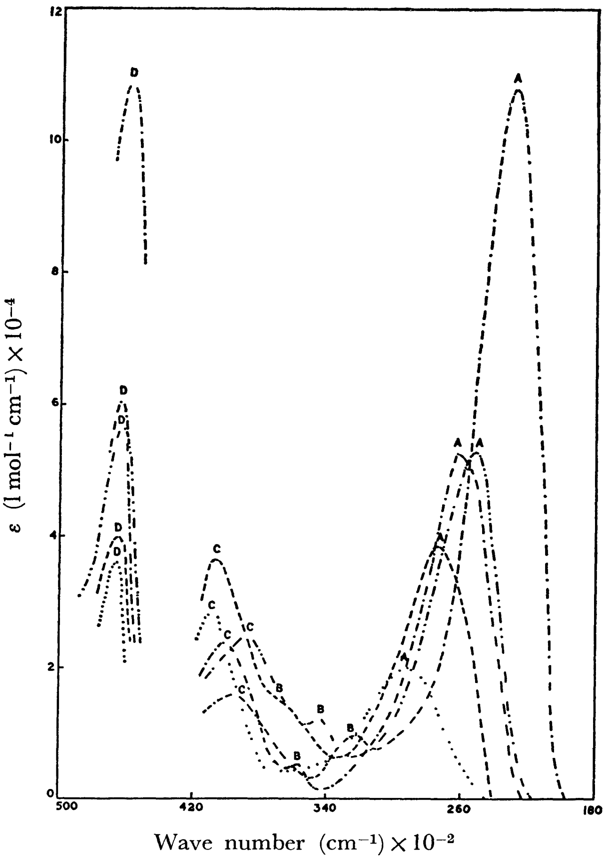

Fig. 1. ······: Solution spectrum of $I_1$, ----: Solution spectrum of $I_2$, -·-·-: Solution spectrum of $I_3$, -··-··-: Solution spectrum of $I_4$, ---·---: Solution spectrum $I_6$.

TABLE 1. ABSORPTION BANDS OF $\alpha,\omega$-DI-1-NAPHTHYLPOLYENES

| No. of double bonds ($n$) | Bands in solution[a)] | | Bands in crystalline state | |
|---|---|---|---|---|
| | Wave number (cm$^{-1}$) | Assignment | Wave number (cm$^{-1}$) | Assignment |
| 1 | 29200 ( s ) | $A(O_1)$ | 25600 | A |
| | 41000 (vs) | $C(O_3)$ | 40000 | C |
| | 46400 (vs) | $D(O_4)$ | 46300 | D |
| 2 | 27400 ( s ) | $A(O_1)$ | 26000 | A |
| | 37000 (vw) | $B(O_2)$ | | |
| | 40600 ( s ) | $C(O_3)$ | 39400 | C |
| | 46300 ( s ) | $D(O_4)$ | 45600 | D |
| 3 | 26200 ( s ) | $A(O_1)$ | 29600 | $A_1$ |
| | | | 23600 | $A_2$ |
| | 35700 (vw) | $B(O_2)$ | | |
| | 40000 (ms) | $C(O_3)$ | 39400 | C |
| | 46200 ( s ) | $D(O_4)$ | 45600 | D |
| 4 | 25000 (vs) | $A(O_1)$ | 29000 | $A_1$ |
| | | | 24000 | $A_2$ |
| | 34200 (w) | $B(O_2)$ | | |
| | 38800 (ms) | $C(O_3)$ | 38500 | C |
| | 46200 ( s ) | $D(O_4)$ | 45500 | D |
| 6 | 22800 (vs) | $A(O_1)$ | 23400 | $A_1$ |
| | | | 20000 | $A_2$ |
| | 32200 (w) | $B(O_2)$ | 27800 | B |
| | 39400 (w) | $C(O_3)$ | 35600 | C |
| | 45600 ( s ) | $D(O_4)$ | 47200 | $D_1$ |
| | | | 44000 | $D_2$ |

a) Values are for THF solution for the A—C bands and for hexane for the D band.
s: strong, w: weak, v: very, m: medium.

as A in the diagram. The band in the region 2600—3200 Å identified as B, is very weak. This band becomes more and more distinct as $n$ is increased in the polyene. An intense band C appears in the region 2400—2700 Å. Its intensity, in general, continues to decrease with the increase in polyene length. The highest energy band D is observed at about 2200 Å. This band is intense. It is observed that in long naphthylpolyenes two bands A, D are strong and B, C weak. The spectra of these polyenes in THF solution are in general agreement with that reported by Yasuhara *et al.*[10)]

The fluorescence spectra of $I_n$ have been studied in solvent hexane. The fluorescence bands of $I_2$ and $I_4$ are found to have band maxima at 22200 cm$^{-1}$ and 21800 cm$^{-1}$ respectively. The bands of $I_2$ and $I_4$ are shown in Fig. 2.

*$\alpha,\omega$-Di-2-naphthylpolyene ($I_n'$)*: The electronic absorption spectra of $I_n$ are presented in Fig. 3. For clarity the spectra of $I'_{1-3}$ and $I'_{4-6}$ are shown separately in the diagram. Results are given in Table 2. The spectrum, in general, consists of four band systems. One more high energy band is observed in higher members $I_4'$, $I_5'$ and $I_6'$ and an extra low energy weak band is observed only in the lowest member $I_1$ of the polyene. Here too the high energy bands are measured in hexane and the rest part of the spectrum, in THF.

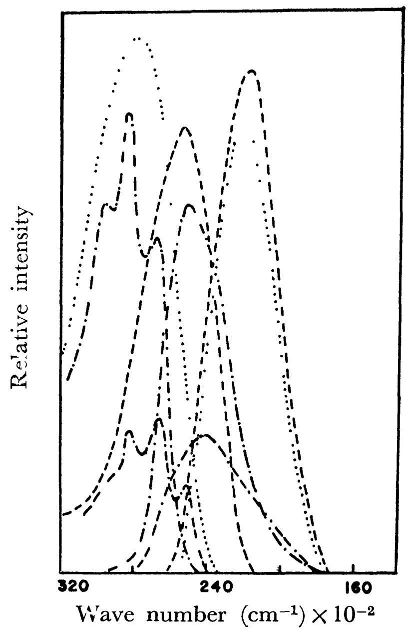

Fig. 2. ······: First absorption band and fluorescence band of $I_2$, ----: First absorption band and fluorescence band of $I_4$, –·–·–: First absorption band and fluorescence band of $I_2'$, –··–··–: First absorption band and fluorescence band of $I_3'$.

The first allowed singlet–singlet transition appears in the region 3000—5000 Å with sharp vibrational structure. The vibrational spacing is about 1400 cm$^{-1}$. This band system is very intense. The band in this region has been identified as A in the diagram. In the region 2400—3400 Å, there are two bands B and C in each of $I_n'$. This is clearly observed in $I_2'$. Here the band B is in the region 2700—3100 Å and the band C, in the region 2400—2700 Å. The bands B and C become weaker relative to other bands with increasing $n$. The band D is found to be in the region 2000—2600 Å. The band E in the region 2000—2300 Å appears only in $I_4'$, $I_5'$ and $I_6'$ whereas in $I_1'$ a very weak band is observed at about 3590 Å. The spectra of these polyenes in THF solution are similar to that reported by Yasuhara *et al.*[10)]

In THF the second band (B) is much weaker than the first band A. In hexane, however, appreciable intensity enhancement of B band compared to A band is observed in $I_1'$, $I_2'$ and $I_4'$, particularly in the first member.

The fluorescence spectra of $I_n'$ have been studied in solution. The fluorescence band maxima of $I_1'$ in THF is observed at 25000 cm$^{-1}$. Polyenes $I_2'$ and $I_3'$ (Fig. 2) are found to have fluorescence maxima at 24900 cm$^{-1}$ and 24000 cm$^{-1}$ respectively in hexane.

*Solid Film Spectra.* The crystal spectra of $I_n$ are broad and the spectral data are summarized in Table 1. The spectra of $I_1$ and $I_2$ in the solid state are very broad and retain identity with the spectra in solution. The band B in solution of $I_{2-4}$ is absent in crystals. The crystal spectrum of $I_6$ is shown in Fig. 4. For brevity crystal spectra of $I_3$ and $I_4$ are not presented, the data, however, have been shown in Table 1.

Table 2. Absorption bands of $\alpha,\omega$-di-2-naphthylpolyenes

| No. of double bonds ($n$) | Bands in solution[a] | | Bands in crystalline state | |
|---|---|---|---|---|
| | Wave number (cm$^{-1}$) | Assignment | Wave number (cm$^{-1}$) | Assignment |
| 1 | 27800 (vw) | N (related to $^1A_g \rightarrow {}^1B_{3u}$ band of naphthalene) | 26400 | New band system |
| | 28700 (vw) | A ($O_1$) | 28400 | A ($O_1$) |
| | 30000 ( s ) | A ($O_1+1300$) | 29800 | A ($O_1+1400$) |
| | 31300 (vw) | A ($O_1+2\times1300$) | 31200 | A ($O_1+2\times1400$) |
| | 34800 (w) | B ($O_2$) | 34600 | B |
| | 36200 ( s ) | B ($O_2+1400$) | | |
| | 37400 (vw) | C ($O_3$) | | |
| | 38600 (w) | C ($O_3+1200$) | | |
| | 48400 ( s ) | D ($O_4$) | | |
| 2 | — | — | 24600 | New band system |
| | 26400 (w) | A ($O_1$) | 26300 | A ($O_1$) |
| | 27800 (vs) | A ($O_1+1400$) | 27700 | A ($O_1+1400$) |
| | 29300 (w) | A ($O_1+2\times1400$) | 29200 | A ($O_1+2\times1400$) |
| | 30600 (vw) | A ($O_1+3\times1400$) | 30500 | A ($O_1+3\times1400$) |
| | 32600 (w) | B ($O_2$) | 32600 | B ($O_2$) |
| | 33900 (ms) | B ($O_2+1300$) | 33900 | B ($O_2+1300$) |
| | 35200 (w) | B ($O_2+2\times1300$) | 35200 | B ($O_2+2\times1300$) |
| | 38100 (w) | C ($O_3$) | 37900 | C ($O_3$) |
| | 39300 (w) | C ($O_3+1200$) | | |
| | 46800 ( s ) | D ($O_4$) | 47900 | D$_1$ |
| 3 | — | — | 22900 | New band system |
| | 24700 (w) | A ($O_1$) | 24900 | A ($O_1$) |
| | 26200 ( s ) | A ($O_1+1500$) | 26400 | A ($O_1+1500$) |
| | 27700 (w) | A ($O_1+2\times1500$) | 27900 | A ($O_1+2\times1500$) |
| | 29200 (vw) | A ($O_1+3\times1500$) | 29200 | A ($O_1+3\times1500$) |
| | 31600 (w) | B ($O_2$) | 31500 | B ($O_2$) |
| | 33000 (w) | B ($O_2+1400$) | 33000 | B ($O_2+1500$) |
| | 35400 (ms) | C ($O_3$) | 35300 | C |
| | 45500 (ms) | D ($O_4$) | 47500 | D$_1$ |
| | | | 45000 | D$_2$ |
| 4 | — | — | 21700 | New band system |
| | 23400 ( s ) | A ($O_1$) | 23600 | A ($O_1$) |
| | 24800 (vs) | A ($O_1+1400$) | 25000 | A ($O_1+1400$) |
| | 26200 ( s ) | A ($O_1+2\times1400$) | 26400 | A ($O_1+2\times1400$) |
| | 27600 (vw) | A ($O_1+3\times1400$) | | |
| | 30800 (vw) | B ($O_2$) | 33000 | B |
| | 32200 (vw) | B ($O_2+1400$) | | |
| | 33600 (vw) | B ($O_2+2\times1400$) | | |
| | 35600 (w) | C ($O_3$) | 35000 | C |
| | 43600 (ms) | D ($O_4$) | 43000 | D |
| | 48000 (ms) | E ($O_5$) | 48000 | E |
| 5 | — | — | 21000 | New band system |
| | 22300 ( s ) | A ($O_1$) | 22800 | A ($O_1$) |
| | 23700 (vs) | A ($O_1+1400$) | 24200 | A ($O_1+1400$) |
| | 25100 ( s ) | A ($O_1+2\times1400$) | 25600 | A ($O_1+2\times1400$) |
| | 26500 (vw) | A ($O_1+3\times1400$) | | |
| | 29900 (vw) | B ($O_2$) | | |
| | 30800 (w) | B ($O_2+1000$) | | |
| | 31900 (vw) | B ($O_2+2\times1000$) | | |
| | 33800 (vw) | C ($O_3$) | | |
| | 40400 (ms) | D ($O_4$) | 40000 | D |
| | 47400 (ms) | E ($O_5$) | 44000 | E |
| 6 | — | — | 19600 | New band system |
| | 21200 ( s ) | A ($O_1$) | 21600 | A ($O_1$) |
| | 22800 ( s ) | A ($O_1+1600$) | 23200 | A ($O_1+1600$) |
| | 24400 (vs) | A ($O_1+2\times1600$) | 24800 | A ($O_1+2\times1600$) |
| | 26000 ( s ) | A ($O_1+3\times1600$) | 26400 | A ($O_1+3\times1600$) |
| | 27600 (vw) | A ($O_1+4\times1600$) | | |

TABLE 2. Continued.

| No. of double bonds ($n$) | Bands in solution[a)] |  | Bands in crystalline state |  |
|---|---|---|---|---|
|  | Wave number ($cm^{-1}$) | Assignment | Wave number ($cm^{-1}$) | Assignment |
| 6 | 29200 (vw) | A ($O_1+5\times1600$) |  |  |
|  | 31600 (vw) | B ($O_2$) |  |  |
|  | 33000 (vw) | B ($O_2+1400$) |  |  |
|  | 35600 (w) | C ($O_3$) | 35000 | C |
|  | 40600 (ms) | D ($O_4$) | 39000 | D |
|  | 45400 (s) | E ($O_5$) | 44800 | E |

a) Values are for THF solution for the A—C bands, and for hexane solution for the D—E bands.
s: strong, w: weak, v: very, m: medium.

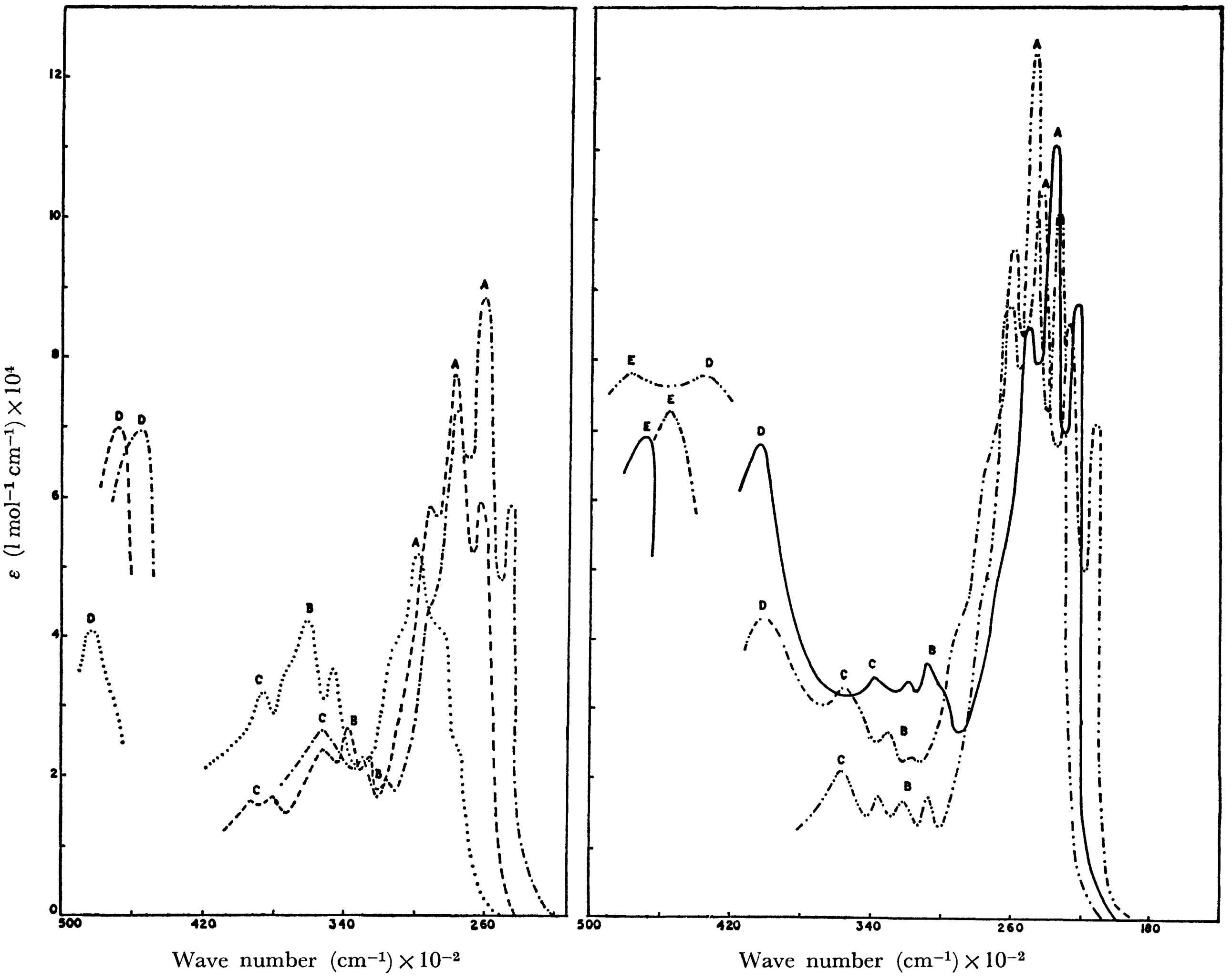

Fig. 3. ······: Solution spectrum of $I_1'$, ----: Solution spectrum of $I_2'$, -·-·-: Solution spectrum of $I_3'$, -·-·-·-: Solution spectrum of $I_4'$, ——: Solution spectrum of $I_5'$, --·--; Solution spectrum of $I_6'$.

The absorption spectra of $I_n'$ in the crystalline state are shown in Fig. 5. The bands in the solid state are broad and shift little towards red or blue from their position in solution. The long wavelength band A appears with subbands. The vibrational spacing is about 1400—1600 $cm^{-1}$. The spacing between the longest wavelength subband and the next is found to be about 2000 $cm^{-1}$.

## Discussion

*Solution Spectra.* All-*trans* conjugated polyenes belong to $C_{2h}$ point group. 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.[11)] As

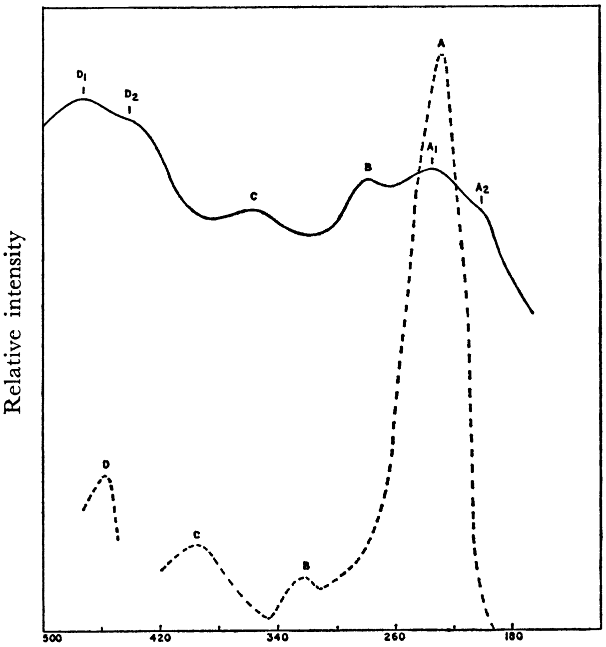

Fig. 4. —— Solid film spectrum of $I_6$, ----: Solution spectrum of $I_6$.

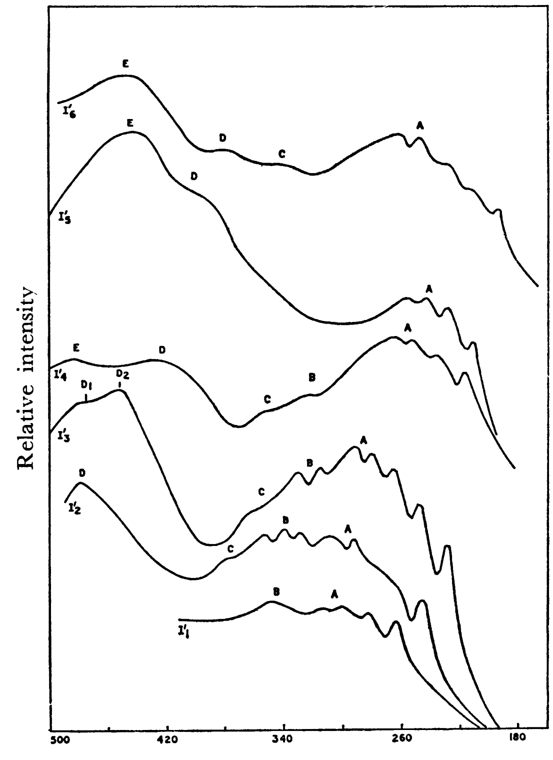

Fig. 5. Solid film spectra of $I'_{1-6}$.

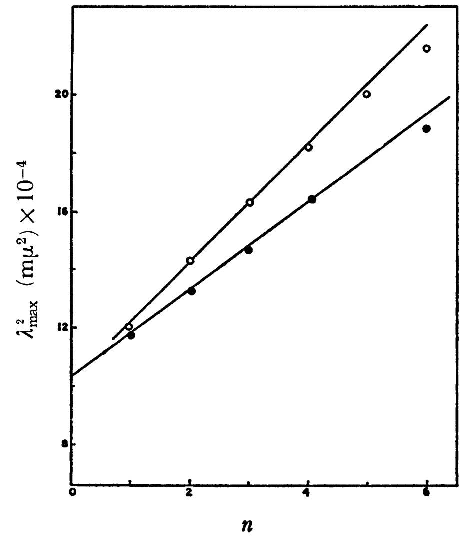

Fig. 6. -●-●-: Plot of $\lambda^2_{\max} - n$ of $I_n$, -O-O-: Plot of $\lambda^2_{\max} - n$ of $I_n'$.

a result the transitions $^1A_g \to {}^1B_u$, $^1A_g \to {}^1B_u$ are generally observed and are strongly allowed. Two $^1A_g \to {}^1A_g$ transitions are forbidden. From the band-intensity of $I_n$ amd $I_n'$ it is observed that in the higher members two transitions are strongly allowed and the other two transitions, weakly allowed. As the chain length of the polyene decreases the weakly allowed bands become equally intense with the allowed ones. The strong allowedness of the weak bands seems to be due to reduction in symmetry of the molecule by the presence of the terminal naphthyl group. When the polyene chain is short, the naphthyl group possibly destroys the center of symmetry and the lower members of the naphthylpolyene seem to have lower symmetry than $C_{2h}$. As a result one gets B and C bands as allowed in lower members of both $I_n$ and $I_n'$.

In our spectra of $I_n$ the bands in the region 3000—5000 Å (A), 2600—3200 Å (B), 2400—2700 Å (C) and 2160—2200 Å (D) possibly belong to the transitions $^1A_g \to {}^1B_u$, $^1A_g \to {}^1A_g$, $^1A_g \to {}^1A_g$ and $^1A_g \to {}^1B_u$ respectively of $C_{2h}$ symmetry (true for higher members).

In the spectra of $I_n'$, similarly, the bands in the region 3000—5000 Å (A), 2700—3400 Å (B), 2400—2900 Å (C) and 2000—2600 Å (D) seem to belong to transitions $^1A_g \to {}^1B_u$, $^1A_g \to {}^1A_g$, $^1A_g \to {}^1A_g$, and $^1A_g \to {}^1B_u$ respectively. The band E in the region 2000—2300 Å of $I_4'$, $I_5'$ and $I_6'$ is possibly related to the $^1A_g \to {}^1B_{3u}$ ($^1B_b$ in Platt's notation) transition of naphthalene and arises from the interaction between the $^1B_u$ state of the polyene chromophore and the $^1B_{3u}$ state of naphthalene. The long wavelength band at about 3590 Å of $I_1'$ is structurally different from the lowest transition $^1A_g \to {}^1B_u$ of the polyene chromophore and may be related to the $^1A_g \to {}^1B_{3u}$ ($^1L_b$ band in Platt's notation) of naphthalene group. In the higher members $I'_{2-6}$ of the naphthylpolyene the band related to the lowest $^1A_g \to {}^1B_{3u}$ transition of naphthalene molecule may be hidden under the intense $^1A_g \to {}^1B_u$ band of the polyene chromophore.

As is evident from Figs. 1 and 3 and Tables 1 and 2, the longest wavelength maxima undergo red shift with increasing $n$. For conjugated polyenes it has generally been accepted[12] and $\lambda^2_{\max}$ is proportional to $n$, the number of conjugated double bonds. We have made such a plot of $\lambda^2_{\max}$ against $n$ for both $I_n$ and $I_n'$ and the plot as shown in Fig. 6 is a straight line for the four lower members. $I_6$ and $I'_{5-6}$ are not quite in the straight line. Further weakly allowed

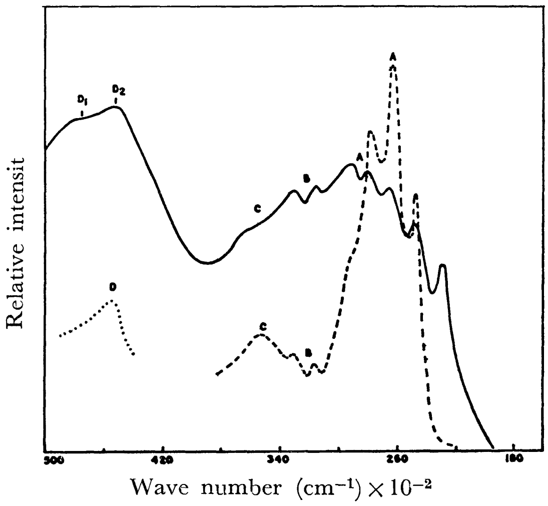

Fig. 7. —— Solid film spectrum of $I_3'$, ----: Solution spectrum of $I_3'$.

transitions appear in the higher members. This suggests some deviations of the polyene chain from *all-trans* form in higher naphthylpolyenes.

In some conjugated polyenes there exists a low-lying forbidden $\pi$-electronic state.[1,4] Fluorescence originates from this state. In naphthylpolyenes four transitions have been observed. No forbidden transition is, therefore, expected. Our fluorescence and absorption spectra of naphthylpolyene $I_n$ and $I_n'$ show that there is a good overlap between the low energy absorption and highest energy emission bands (Fig. 7). We, therefore, conclude that in naphthylpolyenes there is no such low-lying forbidden state as is observed in some other polyenes.[1,4]

*Solid Film Spectra.* The crystal spectra of $I_n$ differ somewhat from the spectra of free molecules. Identification of solution C and D bands of $I_3$ and $I_4$ in the solid state is obvious and no additional band is observed in this region. Both $I_3$ and $I_4$ in the solid state have two bands, one intense on the higher energy side and the other broad on the low-energy side of the solution band A. It seems that the band A is split into components $A_1$ and $A_2$ in the crystalline state. Free molecular bands B and C of $I_6$ as shown in Fig. 4 undergo red shift in the solid state. In $I_6$ in the region of each of the solution bands A and D there are two bands in the spectra of crystal. From these structures of the bands it seems that the band A is split into $A_1$ and $A_2$ and D into $D_1$ and $D_2$ in the solid state. In solid state the absorption bands of all these polyenes are broad and 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 unequivocal identification of factor group split components.

The solid film spectra of $I_n'$, in general, are very similar to the solution spectra. The bands D of $I_2'$ and $I_3'$ in solution seem to show some factor group splitting. In $I_2'$ the band D is blue shifted in the solid state and this may be one of the factor group split components, $D_1$. As is obvious from the spectrum in Fig. 7 the band D of $I_3'$ in the free molecular state has two bands on its high and low energy side in the crystalline state. Two bands are possibly the split components $D_1$ and $D_2$ of solution band D. No factor group splitting is observed in other members of $I_n'$. As has already been pointed out, assignment of these factor group split components is only tentative.

In the intense lowest energy band of each crystal spectrum of $I_n'$ it is observed that the vibrational spacing between the subbands of A is 1400—1600 cm$^{-1}$ in agreement with those observed in solution. The spacing between the longest wavelength maxima and the next, however, is about 2000 cm$^{-1}$. Thus it seems that this longest wavelength band is a new band system and appears in each of $I_n'$ in the crystalline state. This band is possibly related to the $^1A_g \rightarrow {}^1B_{3u}$ band ($^1L_b$ band in Platt's notation) of naphthalene molecule. In solution this band is found only in $I_1'$. In the solid state this band is separated out from the intense $^1A_g \rightarrow {}^1B_u$ band of the polyene chromophore in other $I_n'$ polyenes.

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