Electronic Absorption Spectra of Pyrene and Hydropyrenes

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Vibronic π-π^* transition bands of pyrene, 4,5-dihydropyrene (DHP), and 4,5,9,10-tetrahydropyrene (THP) were assigned by means of dichroism analysis using stretched poly(vinyl alcohol) films. The absorption spectra of the samples in the non-stretched films were divided into two component spectra polarized along the long (x) and short (z) axes of the molecular plane. For pyrene, in addition to the four conventionally-assigned band systems (^1L_b, ^1L_a, ^1B_b, and ^1B_a), some forbidden bands were found in the respective band regions. Most of the vibronic DHP and THP bands were also reasonably well assigned from comparisons with the calculated results for phenanthrene and biphenyl, respectively.

Three fundamental factors, the transition energy (wavelength), the transition moment (polarization), and the transition probability (intensity) must be considered in making assignments of electronic absorption spectra. Generally speaking, it is almost impossible to determine exactly all of these three factors for solution spectra, except in special cases where well-separated band systems are observed. Apparent bands observed in most cases are considered as consisting of more than two different kinds of transition bands. Accordingly, in order to precisely determine the three factors experimentally, we must separate or resolve the overlapped bands from one another, using methods such as photoselection techniques,[1] an external electric field,[2,3] a single or mixed crystal[4,5] and stretching of the polymer film.[6-8]

The stretching film method can be applied to various kinds of compounds and has the merit that the substrate of the film is transparent to the very short wavelengths of 220 nm for the poly(vinyl alcohol) [PVA] film, for example. If we choose planar molecules with proper symmetries, the π electronic spectra can be divided into components polarized parallel and perpendicular to a symmetry axis in the molecular plane.

The experience of the dichroism investigation tells us that the orientation direction of the sample molecule in the stretched PVA film depends mainly on molecular geometry. And it is expected that the three compounds, pyrene, 4,5-dihydro- and 4,5,9,10-tetrahydropyrene, in the stretched PVA films have the same orientation state since their skeletal structures are similar to one another (see Fig. 1).

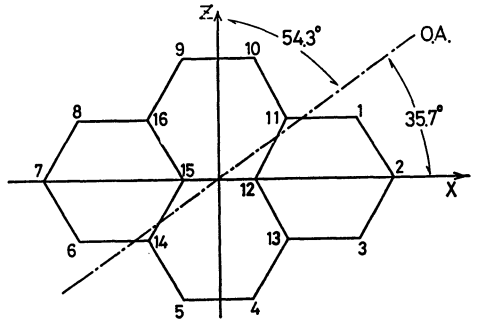

Fig. 1. Co-ordinates of the pyrene molecule. The orientation axis of the molecule in the streched PVA film is represented by O. A. which is determined by the orientation angle (54.3°) for the third band of pyrene [Fig. 2(a)].

The purpose of this paper is to make assignments of the π-π^* electronic spectra of pyrene, 4,5-dihydropyrene(abbreviation, DHP) and 4,5,9,10-tetrahydropyrene (THP). Pyrene shows well separated band systems and, therefore, its orientation direction is precisely determined by dichroism analysis with this orientation direction necessary in obtaining the divided spectra. On the other hand, the absorption spectra of DHP and THP do not show any isolated bands. Therefore, in order to divide these spectra into components, it is assumed here that the orientation direction determined for the pyrene molecule can be applied to the DHP and THP molecules.

Experimental

Commercially-available pyrene (ultra pure reagent, zone refined; Tokyo Kasei Kogyo Co., Ltd.) was used. The guaranteed reagents, 4,5-dihydropyrene (abbreviation:DHP) and 4,5,9,10-tetrahydropyrene (THP) were used with furtherpurification made at our request by the Tokyo Kasei Kogyo Co., Ltd.

Poly(vinyl alcohol) [PVA] having a mean polymerization of 1400 was obtained commercially (Koso Chemical Co., Ltd.) and used without further purification for making the PVA films.

Dichroism Analysis. The dichroic spectra were determined with a Shimadzu QV-50 Spectrophotometer equipped with a Glan-Thompson type calcite polarizer. Both the sample and reference films were stretched at 70—80 °C. The stretching ratio, R_s, was limited to 6.0 throughout the experiments.

The optical density ratio, R_d, is defined as $D_{//}/D_{\perp}$, where $D_{//}$ and $D_{\perp}$ are optical densities measured with light polarized parallel and perpendicular to the stretched direction of the film, respectively. The R_d values are plotted in the figures showing the dichroic spectra.

From the dichroism analysis,[9] the orientation angle of any absorption band is defined as the angle between the transition moment and the orientation direction of the molecule, and it is obtained using the experimental values of R_s and R_d. The orientation angles thus obtained are indicated at the maxima and minima of the R_d curves of the dichroic spectra.

It is necessary to make a few remarks concerning the "orientation direction," which is a direction peculiar to molecular geometry. It is empirically known that, upon stretching, a sample molecule in the PVA substrate is longitudinally inclined in the stretched direction. In this case, the longitudinal direction does not, in general, coincide with the geometrically-defined long axis, say, the x-axis of the molecule (see Fig. 1).

It is a natural consequence of the inclination of the molecule, as mentioned above, that the absorption band having the

greater R_d value (or smaller orientation angle) must be polarized principally along the long (x) axis. Accordingly, if a planar molecule has at least one C_2-symmetry axis in the molecuar plane (xz-plane) and if one or more bands are found to be pure in the transition directions (x or z), we can divide the absorption spectrum (D) in the non-stretched PVA film into two component spectra (D_x, D_z) that are polarized parallel and perpendicular to the axis of symmetry.[9] In the present case, the relative errors in the absorbance of the component spectra were less than 10% and the oscillator strength of the relatively strong band was reproduced to within a relative error of 4—7%.

Calculation

The sample molecules, DHP and THP, have π-electron systems equivalent to those of phenanthrene and biphenyl, respectively. Therefore, for convenience, the latter were calculated instead of the former.

The MO calculations were carried out using the Pariser-Parr-Pople method.[10,11] The one-center repulsion integrals were evaluated in the Pariser-Parr approximation,[10] in which the ionization potential and the electron affinity were taken, respectively, as $I_p(C) = 11.16$ eV and $E_a(C) = 0.03$ eV for the carbon atom. The two-center repulsion integrals were evaluated using the Nishimoto-Mataga equation.[12] All the singly-excited configurations associated with the transitions between the occupied and vacant MO levels were included in the CI calculation.

The co-ordinates of the molecular framework of pyrene were taken as shown in Fig. 1. All the bond lengths and bond angles were assumed to be 1.395 Å and 120°, respectively. The framework of the π-electron system of DHP(4,5-dihydropyrene) was considered excluding the Nos. 4 and 5 carbon atoms in Fig. 1. Similarly, for THP(4,5,9,10-tetrahydropyrene), the Nos. 4, 5, 9, and 10 carbon atoms were excluded, and the C^{12}–C^{15} bond length (inter-ring distance) was assumed to be 1.48 Å. The x and z axes denote the long and short axes, respectively, in the molecular plane for the case of both the D_{2h} (pyrene and THP) and C_{2v} (DHP) point groups.

Results and Assignment

Dichroic Spectra. Figures 2(a)—(c) show the dichroic spectra and R_d curves of pyrene, DHP and THP, respectively.

The dichroic spectra of pyrene in Fig. 2(a) exhibits four well-separated absorption bands. The shape of the R_d curve clearly shows that these four bands are distinguished by transition directions; that is, the R_d values for the first (350—380 nm) and third (250—280 nm) bands are small, while those for the second (340 nm) and fourth (*ca.* 245 nm) are great. This indicates that the transition vectors of the former are in the same direction as the short axis of the molecule and the latter in that of the long axis. It is concluded, therefore, that the directions of the electronic transition moments of pyrene are z-, x-, z-,and x- polarized, in order of decreasing wavelength. Since the symmetry of the pyrene molecule is D_{2h}, the four corresponding excited

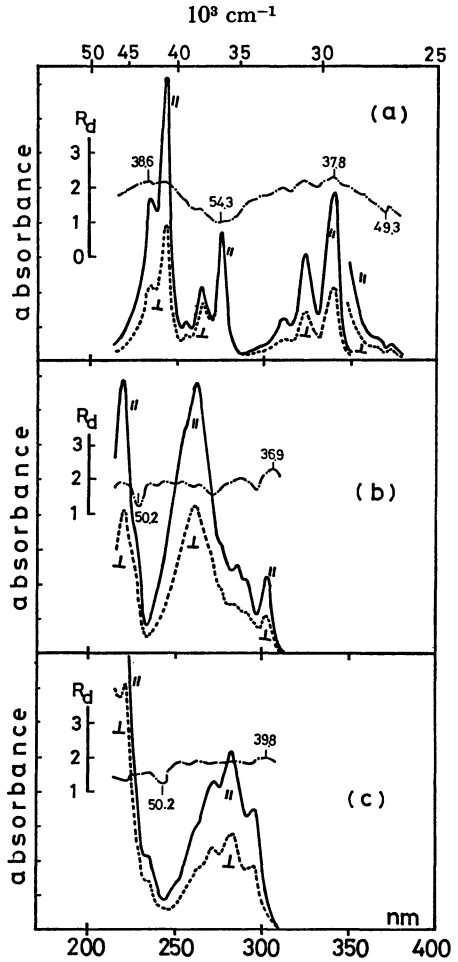

Fig. 2. Dichroic spectra and R_d curves for (a) pyrene, (b) DHP (4,5-dihydropyrene) and (c) THP (4,5,9,10-tetrahydropyrene). $R_s = 6.0$. The numerals at the maxima and minima of R_d curves indicate the orientation angle (in degree) of the polarizations at those wavelengths.

states are assigned to B_{2u}, B_{1u}, B_{2u} and B_{1u}, respectively. According to the Platt notation, these are L_b, L_a, and B_b and B_a, respectively (see Fig. 3). In Figs. 2(b) and (c), no remarkable variations of the R_d curves similar to those in Fig. 1(a) are found. Only for a couple of bands, however, are the polarizations distinguishable by the relative R_d values; for example, for DHP (C_{2v}) in Fig. 2(b), the R_d value at 305 nm is the greatest and that at 228 nm (shoulder) the smallest in the region observed. This suggests that the 305-nm band and the shoulder consist mainly of bands with long- and short-axis transitions, respectively. Indeed, the sum (87.1°) of the orientation angles of these bands becomes nearly 90°. Thus, we can conclude that the 305-and 230-nm bands are polarized along the molecular long (x, B_2) and short (z, A_1) axes, respectively. It must be noted here that in the DHP spectra in Fig. 2(b), the 305-nm band is not first but is second. The first band at 343 nm, which corresponds to the ^1L_b of phenanthrene at the longest wavelength, could not be determined in the present work owing to experimental difficulties.

For the THP(D_{2h}) spectra in Fig. 2(c), polarizations of at least two absorption bands were also observed;

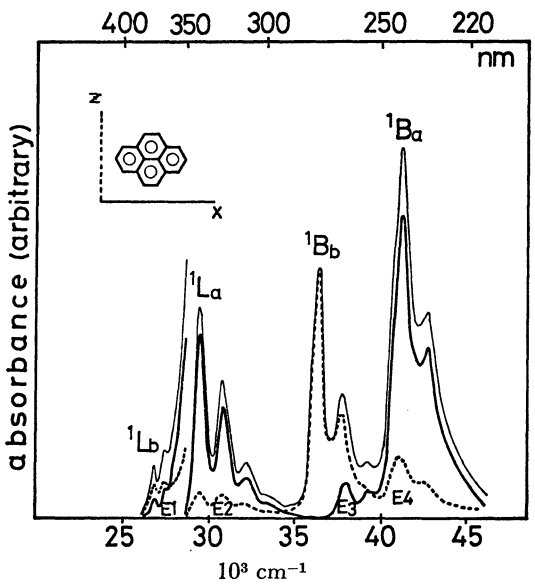

Fig. 3. Divided spectra of pyrene. The fine line means the absorption spectrum (D) of pyrene in the non-stretched PVA film. The conventional assignment is indicated by ^1L_b, ^1L_a, ^1B_b and ^1B_a. The solid line is the x-component spectrum (D_x) and the dotted line the z-component (D_z). Extra band systems are temporarily marked with E_1 to E_4.

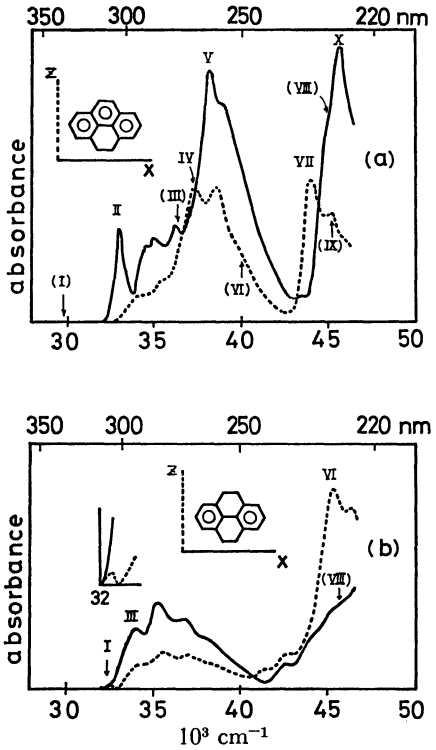

Fig. 4. Divided spectra of (a) DHP (4,5-dihydropyrene) and (b) THP (4,5,9,10-tetrahydropyrene). The solid lines are the x-component spectra (D_x) and the dotted lines the z-components (D_z). Roman numerals are the transition numbers calculated for (a) phenanthrene and (b) biphenyl.

main absorption at 300 nm being due to the long-axis transition (x, B_{1u}) and that at 240 nm to the short-axis transition (z, B_{2u}).

Divided Spectra. In order to make more precise assignments of the electronic bands, especially for DHP and THP, the absorption curves in the non-stretched PVA films were divided into two component spectra (D_x and D_z).[9] To divide the spectra, it was necessary to determine a standard direction relative to the geometry of the molecule. A standard direction, namely, in general, an orientation direction, can be determined for a symmetrical molecule provided that at least two electronic bands with polarizations orthogonal to each other can be observed separately. Fortunately, the pyrene molecule satisfies such a condition.

It has already been mentioned that the second and third bands of pyrene [Fig. 2(a)] are due to the electronic transitions along the x (long) and z (short) axes of the molecule, respectively, and that the sum of the orientation angles for the second (37.8°) and third (54.3°) bands becomes 92.1°. This value is somewhat greater than 90°. This fact indicates that the degree of mixing of the z-polarized absorption in the x band (second) is greater than that of the x-polarized absorption in the z band (third band). Considering that the absolute deviation from 90° is small, let us assume here that the transition direction at 276 nm, for the third band, is exactly in accord with the transition direction of the z axis of the pyrene molecule. Then, the orientation direction of the molecule relative to the coordinates is determined as shown in Fig. 1, that is, the orientation axis (O.A.) is 35.7° with respect to the x axis.

The skeletal structure of the other molecules are very similar to that of the pyrene molecule. It was assumed, therefore, that the other molecules have the same orientation direction as pyrene. Thus, by taking the standard angles of other sample molecules to be 35.7°, the component spectra are obtained from the spectra of the non-stretched sample film.

The divided spectrum of pyrene is shown in Fig. 3, and those of DHP and THP in Fig. 4. It is seen that every band is more or less composed of overlapping of the x and z bands. For this reason, it is expected that some additional absorptions will be found from a comparison with the calculated results. These extra absorption bands may be explained in terms of vibronic interactions or intensity borrowing, neglecting the so-called hot absorptions.

Assignments for Pyrene Spectrum. The results of an MO calculation for pyrene, which is shown in Table 1, indicate four symmetry-allowed transitions below 46×10^3 cm^{-1}, which is the limit of the spectral region observed. These allowed transitions may correspond to the divided component bands shown in Fig. 3, as follows.

The peak at 26.8×10^3 cm^{-1} is considered to be the 0-0 transition of the very weak first band system. Since the intensity at the peak is stronger for the z component than for the x component, the former is regarded as the first band. Therefore, the I transition calculated as $B_{2u}\leftarrow A_g$ for pyrene must be compared with the first band which is z-polarized. The other three allowed transitions, II, V, and IX, correspond to the three strong band systems in Fig. 3, respectively. The II

TABLE 1. CALCULATED AND EXPERIMENTAL RESULTS FOR PYRENE (D_{2h})

Transition No.	Transition energy		Oscillator strength f		Polarization		Symmetry
	Calcd 10^3 cm^{-1} (nm)	Obsd 10^3 cm^{-1} (nm)	Calcd[a]	Obsd[b]	Calcd	Obsd	
I	27.05 (370)	26.8 (373)	0.005	0.0014	z	z	B_{2u}
II	28.00 (357)	29.4 (340)	0.764	0.326	x	x	B_{1u}
III	34.24 (292)		forb.				B_{3g}
IV	34.51 (290)		forb.				B_{3g}
V	38.17 (262)	36.4 (275)	0.954	0.418	z	z	B_{2u}
VI	38.58 (259)	[37.9]	forb.		[$\times b_{1u}$]	x	A_g
VII	39.79 (251)		forb.				B_{3g}
VIII	42.76 (234)	[41.0]	forb.		[$\times b_{2u}$]	z	A_g
IX	43.57 (230)	41.2 (243)	1.468	0.750	x	x	B_{1u}
X	43.64 (229)		forb.				A_g
XI	47.91 (209)		0.004		z		B_{2u}
XII	48.60 (206)		forb.				A_g

a) Calculated using the dipole-length method with off-diagonal (adjacent) terms included in the calculation of the oscillator strength. R. S. Mulliken, *J. Chem. Phys.*, **7**, 14 (1939). b) Determined using $f=4.32\times10^{-9}\int\varepsilon d\sigma$, assuming that the molar extinction coefficient ε at the band maximum in the non-stretched PVA film is equivalent to that of the corresponding band in an ethanol solution.

transition ($B_{1u}\leftarrow A_g$) corresponds to the second band system starting at 29.4×10^3 cm^{-1}, which is x-polarized and reveals a progression of five vibrational bands reaching as far as 35×10^3 cm^{-1}. The V transition ($B_{2u}\leftarrow A_g$) corresponds to the third band system which is z-polarized and has its 0-0 peak at 36.4×10^3 cm^{-1}. Finally, the IX transition corresponds to the fourth band with x-polarization, which has its 0-0 peak at 41.2 $\times10^3$ cm^{-1}. The bands thus assigned are designated in the Platt notation as ^1L_b, ^1L_a, ^1B_b, and ^1B_a, respectively, as shown in Fig. 3.

For the oscillator strengths, a very good correlation is observed between the calculated and observed results; the calculated values are nearly twice as large as the corresponding observed values.

According to the above correspondence between the band systems and the calculated transitions, the other four absorption bands remain as extra bands which are temporarily designated as E_1 to E_4, as is shown in Fig. 3. In order to discuss the extra absorption bands, it will be necessary to determine some basis for making assignments. Fortunately, it was found that the calculated and experimental transition energies (in wavenumbers) correspond well to each other. That is to say, when the calculated (abscissa) and experimental wavenumbers (ordinate) are plotted on a graph, a straight line is obtained as shown in Fig. 5, in which the wavenumbers at the 0-0 peaks are taken from the experimental values and the white circles represent the allowed transitions. The fact that almost all the white circles lie on a straight line shows that the semi-empirical calculations employed here lead to quite reliable results for making assignments. Accordingly, utilizing this linear relation as a basis, the extra absorption bands are assigned.

First of all, from the point of view of the linearity between the calculated and experimental results, only the experimental value for ^1L_a is unexpected. If we

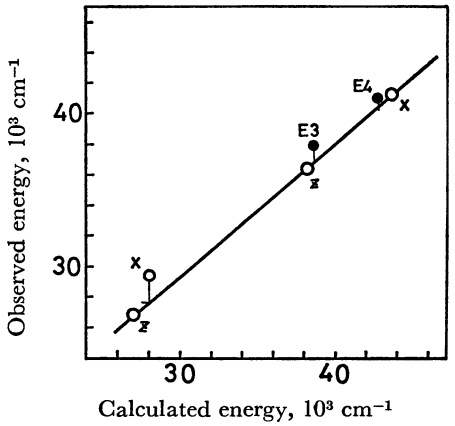

Fig. 5. Correlation between the observed (ordinate) and calculated wave numbers (abscissa) of pyrene. White circles represent the 0-0 peaks of band systems and the corresponding transitions calculated, where x and z mean the polarizations along the long and short axes of the molecule, respectively.

take the linearity seriously, the peak at 29.4×10^3 cm^{-1} may not be a 0-0 but a 1-0 transition. In this case, if we regard the shoulder of the x component band at 27.8×10^3 cm^{-1} in Fig. 3 to be the 0-0 peak of ^1L_a, linearity for all the allowed transitions, including ^1L_a, is nearly satisfied.

Now, utilizing the linear relation, the extra bands are assigned as follows. According to Fig. 3, the E_1 band, which is x-polarized and has fine structure, starts at about 26.8×10^3 cm^{-1}, but, strictly speaking, this is slightly lower than 26.8×10^3 cm^{-1}. It is clear from Table 1 that no excited state relevant to E_1 exists. Therefore, the E_1 band may be induced by intensity borrowing from the second (^1L_a, x) band. The E_2 band, which is z-polarized, has its first peak at 29.5×10^{-3} cm^{-1}. In Table 1, no transition corresponding to

Table 2. Comparison of calculated results for phenanthrene and experimental results for DHP (C_{2v})

Transition No.	Transition energy: Calcd 10^3 cm^{-1} (nm)	Transition energy: Obsd 10^3 cm^{-1} (nm)	Oscillator strength: Calcd[a]	Oscillator strength: Obsd[b]	Polarization: Calcd	Polarization: Obsd	Symmetry
I	29.00 (345)	[29.2] [343][c]	0.001	—	z		A_1
II	32.96 (303)	33.1 (302)	0.372	0.149	x	x	B_2
III	37.40 (267)		0.002		x		B_2
IV	39.85 (251)	37.3 (268)	0.526	0.279	z	z	A_1
V	39.87 (251)	38.2 (262)	1.440	0.396	x	x	B_2
VI	41.81 (239)		3.0×10^{-5}		z		A_1
VII	45.25 (221)	44.0 (227)	0.348	0.167	z	z	A_1
VIII	46.94 (213)		7.0×10^{-5}		x		B_2
IX	47.80 (209)		2.4×10^{-4}		z		A_1
X	48.85 (205)	45.7 (219)	0.086	0.317	x	x	B_2
XI	49.56 (202)		0.464		x		B_2

a), b) See footnote in Table 1. c) See Ref. 18.

29.5×10^3 cm^{-1} is found, because, according to the linear relation of Fig. 5, the calculated energy corresponding to the E_2 band must be less than 30.0×10^3 cm^{-1}. Therfore, the E_2 band may also be attributed to an intensity-borrowing absorption from the $^1B_b(z)$ band.

The E_3 band of which the first peak occurs at 37.9×10^3 cm^{-1} is polarized in the x direction. According to the linear relation of Fig. 5, the calculated transition energy corresponding to 37.9×10^3 cm^{-1} is 39.8×10^3 cm^{-1}. If the E_3 band is electronically forbidden, E_3 must vibronically be allowed. Then the calculated energy should be less than 39.8×10^3 cm^{-1}, at least by one vibrational quantum number. The only relevant transition in Table 1 is the VI transition, which has A_g symmetry. Consequently, the vibration to be coupled with the A_g electronically excited state must have a mode of b_{1u} symmetry. The vibrational energy of b_{1u} for the present case is estimated to be about 1×10^3 cm^{-1} from the linear relation of Fig. 5.

Similarly, it is considered that the E_4 band, which has its first peak at 41.0×10^3 cm^{-1}, is a vibronically-induced transition of VIII (A_g) resulting from the coupling of a b_{2u}-type vibration because of the z-polarized absorption. From the linear relation of Fig. 5, the coupled vibrational energy is estimated to be about 0.6×10^3 cm^{-1}.

Assignment of DHP and THP Spectra. The DHP and THP component spectra are shown in Figs. 4(a) and (b), respectively. In Fig. 4(a), the first band, which is observed at 343 nm (29.15×10^3 cm^{-1}) in an ethanol solution, is not shown here as explained above. Therefore, the first peak at 33.1×10^3 cm^{-1} is the 0-0 peak of the second band which is evidently x-polarized. Generally speaking, when both the x and z component spectra are complicated, the band shape can not be easily determined. For this reason, let us first examine only the prominent band peaks and compare them with the calculated results for phenanthrene. The prominent band peaks are found at 33.1 (x), 37.3 (z), 38.2 (x), 44.0 (z), and 45.7×10^3 cm^{-1} (x).

On the other hand, the calculated results for phenanthrene (C_{2v}) are shown in Table 2: The transitions with oscillator strengths stronger than 0.01 are the II (B_2), IV (A_1), V (B_2), VII (A_1) and X (B_2) transitions. These transitions and the above-mentioned band peaks are compared in Table 2. The calculated and experimental polarizations are in complete agreement. Furthermore, the correspondence between the transition energies, as well as the intensities, is fairly good.

In order to observe the correlation between the calculated and experimental transition energies for DHP, the wavenumbers were plotted in the same way

Table 3. Comparison of calculated results for biphenyl and experimental results for THP

Transition No.	Transition energy: Calcd 10^3 cm^{-1} (nm)	Transition energy: Obsd 10^3 cm^{-1} (nm)	Oscillator strength: Calcd[a]	Oscillator strength: Obsd[b]	polarization: Calcd	polarization: Obsd	Symmetry
I	34.63 (289)	32.6 (307)	3.1×10^{-4}	4.4×10^{-4}	z	z	B_{2u}
II	35.09 (285)		forb.				B_{3g}
III	36.40 (275)	33.9 (295)	0.847	0.24	x	x	B_{1u}
IV	46.50 (215)		forb.				B_{3g}
V	47.82 (209)		forb.				A_g
VI	48.85 (205)	45.3 (221)	0.887	0.53	z	z	B_{2u}
VII	48.87 (205)		forb.				A_g
VIII	49.66 (201)	[46] [217]	1.083		x	x	B_{1u}

a), b) See footnote in Table 1.

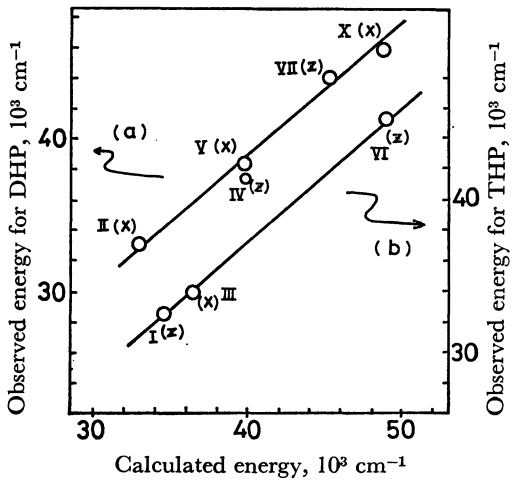

Fig. 6. Correlation between the observed (ordinate) and calculated wave numbers (abscissa) of (a) DHP (4,5-dihydropyrene) and (b) THP (4,5,9,10-tetrahydropyrene), where the calculated values are taken for (a) phenanthrene and (b) biphenyl. Roman numerals represent the transition numbers calculated.

as in the case of pyrene. In this case, however, on the abscissa are plotted the calculated wavenumbers for phenanthrene instead of DHP. The result is illustrated in Fig. 6(a), in which the Roman numerals represent the calculated transition numbers. The linearity is not as good as that shown in Fig. 5 for pyrene. This may be interpreted as resulting from the fact that the calculation for phenanthrene is used instead of that of DHP itself, with the result that the effect of the methylene groups at the 4 and 5 positions of DHP was neglected (see Fig. 1). At any rate, let us use the straight line shown in Fig. 6(a) as a basis for discussing the DHP spectrum.

According to Table 2, transition III (37.4×10^3 cm^{-1}) is of weak intensity and x (B_2) polarization. The linear relation in Fig. 6(a) indicates that the calculated value of 37.4×10^3 cm^{-1} corresponds to the experimental value of 36.3×10^3 cm^{-1} on the x-component curve of Fig. 4(a). For this reason, the peak may be attributed to transition III. The z-polarized band in Fig. 4(a), which extends from 32×10^3 cm^{-1} to about 36×10^3 cm^{-1}, could not be assigned, since no relevant transition is listed in Table 2. Other calculated transitions, transitions VI (41.8×10^3 cm^{-1}, A_1), VIII (46.9×10^3 cm^{-1}, B_2), and IX (47.8×10^3 cm^{-1}, A_1), which are of very weak intensity, correspond respectively to the experimental wavenumbers of 40.2×10^3 cm^{-1} (z), 44.8×10^3 cm^{-1} (x) and 45.4×10^3 cm^{-1} (z). They may appear as shoulders at the corresponding positions which are indicated respectively by the Roman numerals in parenthesis in Fig. 4(a), VI, VIII, IX.

Figure 4(b) illustrates the component spectra of THP (D_{2h}). Table 3 shows that the calculation for biphenyl (D_{2h}) produces four allowed transitions. Transition I (z, B_{2u}) is of very weak intensity and the other three transitions, transitions III (x, B_{1u}), VI (z, B_{2u}) and VIII (x, B_{1u}) are strong. Accordingly, the first three transitions can easily be assigned as indicated in Fig. 4(b) by the Roman numerals. Again, a linearity similar to the case of DHP is found [Fig. 6(b)]. Using the linear relation in Fig. 6(b), the experimental wavenumber corresponding to the fourth allowed transition, transition VIII (49.66×10^3 cm^{-1}), becomes 45.7×10^3 cm^{-1}. However, no prominent band peak appears although a very slight shoulder appears, as indicated by VIII in Fig. 4(b).

Figure 4(b) shows that an additional z absorption, the first peak of which is at 33.9×10^3 cm^{-1}, occurs together with the x band indicated by III. This z absorption can be interpreted in two ways. One possible interpretation is that the band is vibronically induced by the coupling of transition II (35.09×10^3 cm^{-1}, B_{3g}) with a b_{1u} type vibration. In this case, the experimental band origin must be located at 33.7×10^3 cm^{-1} as estimated from the linear relation in Fig. 6(b). The other interpretation is to consider the additional z absorption as a progression of the first z band starting at 32.6×10^3 cm^{-1}, which is assigned to the very weak allowed transition I.

Discussion

The first four allowed π-π^* transitions of pyrene have been established theoretically to have z-, x-, z-, and x-polarizations.[13-15] Experimental studies on the polarization of pyrene have been carried out for the crystalline state[16] using the photoselection method[17] and the stretched polyethylene sheet technique.[8] These experimental results agree quite well with one another and also with the theoretical values. Thulstrup, Michl and Eggers[8] have obtained a reduced spectrum of pyrene from a dichroic spectrum in a stretched polyethylene sheet. Their reduced spectrum for pyrene is very similar as a whole to the separated spectra shown in Fig. 3. However, the weak first band and some of the extra bands are not found in their reduced spectra.

A few spectroscopic studies have been carried out on DHP[18] and THP.[19] On the other hand, many descriptions[20-30] have been given for phenanthrene and biphenyl, which are iso-electronic with DHP and THP, with respect to the π-electron systems, respectively. For instance, according to Zimmermann and Joop[28] and other workers,[30] the third and fourth transition bands of phenanthrene occur close together, but with different polarization directions. Regarding the polarization directions, however, most of the experimental studies reported were only qualitative and were not effective in analyzing overlapping bands, such as the third band of phenanthrene, without aid of theoretical calculations, while the component spectra presented here give quantitative information.

The separated spectra of DHP shown in Fig. 4(a) are in agreement with the case of phenanthrene.[7,8] But in Fig. 4(a), the z-polarized absorption in the 32—36 $\times10^3$ cm^{-1} region, which should be distinguishable from the third band (transition IV, z), could not be clearly assigned. Even in phenanthrene itself, this third (z-polarized) band shows anomalous width in the component spectra. Thulstrup *et al.*[8] have considered this band to be the result of vibronic coupling.

For THP, as is shown in Fig. 4(b), a very weak hidden band at 33.9×10^3 cm^{-1} is revealed as a z-polarized band.

The presence of such an extraordinarily weak absorption in the case of biphenyl has been confirmed by Berlman *et al.*[23] from an investigation of the fluorescence lifetimes of biphenyls. However, there are some ambiguities in the number of allowed transitions in the first band region of biphenyl.[26] On the other hand, the results of the present work for THP show that there are an extremely weak (hidden) z band, a relatively strong x band and an additional intensity-borrowing or vibronically-induced z band in the first-band region, though THP has a structured band shape and a considerable red shift relative to biphenyl. The oscillator strength for the very weak first band of THP was determined from the component spectra, even though the estimated value may contain a large error because of the extreme weakness of the intensity.

There are few experimental studies on the oscillator strengths. Furthermore, in most cases, the conventional value has been determined from a band which is composed of overlapping bands of different polarizations. In order to make a more precise comparison with theory, the experimental values should be determined using the component spectra. The experimental oscillator strengths in Tables 1—3 are determined from the component spectra. The values calculated using the dipole length method are about twice as large as the experimental results. In the calculations of the oscillator strengths, it should be noted that, when only diagonal matrix elements are considered, the oscillator strengths for the allowed L_b bands become zero, while those including the off-diagonal elements give non-zero values in agreement with the experimental results. It must be emphasized, therefore, that the off-diagonal elements of the transition density matrix become very important in the calculation of the allowed L_b band, especially when using the dipole-length method.

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