Polarized Absorption Spectra of Indole and Benzimidazole

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The polarization spectra of indole, 3-indolebutyric acid, and benzimidazole have been measured and analyzed by means of MO theory taking Σ-Π interaction into consideration. Induced transition moment due to Σ-Π interaction can be assigned to each σ-bond (both direction and magnitude) pictorially. The effect of hetero atom on the electronic absorption spectra can be interpreted reasonably. Agreement between experimental and calculated results is satisfactory.

In previous papers[1,2] the effects of Σ-Π interaction on π-π* transition energy and on the transition moment in a conjugated system were formulated with use of the partitioning technique,[3] Σ-Π interaction being shown to have an important effect upon the excited singlet states. The effect can be neglected for the triplet states, since it arises from the exchange interaction between σ- and π-electrons. The calculated oscillator strength was reduced to almost one-half of the reference one evaluated by the conventional π-electron approximation (P-P-P method). The MO-CI method based on the π-electron approximation usually gives too large transition moments.

Our aim is to elucidate the effect of substituent or hetero atoms in a large conjugated system on the direction and magnitude of the transition moment in view of Σ-Π interaction. The transition moment of π-π* transition is important in weak intermolecular interaction, exciton interaction in the solid state or in enzyme systems, and in optical properties of molecules, such as optical activity, CD and MCD spectra.

A photoabsorbed tryptophan in an enzyme which has indole residue as its functional group interacts with a distant tryptophan in the same enzyme. The origin of such long distance interaction (*ca.* $R=30$ Å) is thought to be an exciton interaction. Comprehensive studies[4-6] have been made on electronic spectra of indole which is an active part of tryptophan.

We have determined the direction of transition moment of indole, 3-indolebutyric acid, and benzimidazole and compared the result with that of MO-CI calculation taking Σ-Π interaction into consideration. By our method the induced transition moment caused by Σ-Π interaction can be decomposed into individual σ-bonds which are mostly localized. The decomposition of the induced moment will help to clarify the general feature of Σ-Π interaction in a molecule.

Experimental

Materials. Indole, 3-indolebutyric acid, and benzimidazole (guaranteed, Tokyo Kasei Co., Ltd.) were purified by repeated recrystalization from ethanol or a mixed ethanol–water solution. PVA (polyvinyl alcohol) powder (Koso Chemical Co., Ltd., average polymerization degree 1400) was used for preparation of the film. Preparation of the PVA film and details of dichroism were reported.[7]

Measurement. Dichroic spectra of indole and 3-indolebutyric acid in the stretched PVA films were measured with a Simadzu QV-50 spectrophotometer equipped with a Glan-Thompson polarizer available for the region over 220 nm. The dichroic spectra of benzimidazole, whose maximum corresponding to the intense band at 220 nm of indole is at 205 nm, were measured with a Simadzu UV-200S automatic recording spectrophotometer available for the region over 190 nm.

In the dichroism analysis, the stretched ratio Rs indicates the degree of deformation of the PVA structure, the dichroic ratio Rd the ratio of optical densities $(D_{\parallel}/D_{\perp})$ at a given wavelength, and $D_{\parallel}$ and $D_{\perp}$ are the densities for the incident polarized light the electric vector of which is parallel and perpendicular, respectively, to the stretching direction of the film.

Rd can be expressed as a function of Rs and a parameter r, which is defined as the ratio of two components (μ_a and μ_b) of a transition moment of an electronic transition. μ_a and μ_b are the components parallel and perpendicular, respectively, to an orientation axis (OA) peculiar to the molecule.[7] The angle of the transition moment against OA, which will be referred to as the orientation angle, can be obtained using the Rd and Rs values. The apparent orientation angles for the bands are indicated along the Rd curve in Figs. 1 and 2.

Theoretical

A report was given on an improvement of the P-P-P method considering Σ-Π interaction, which was
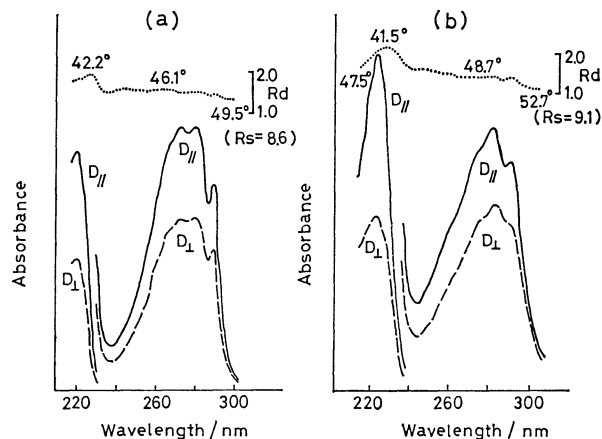

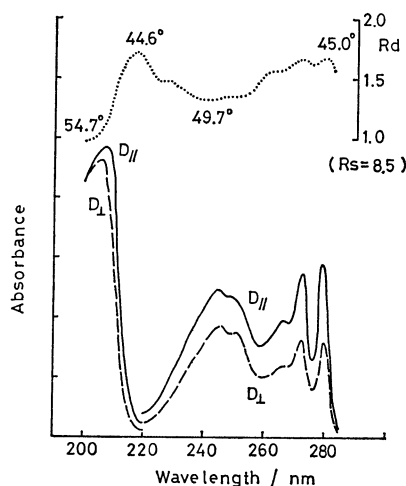Fig. 1. Dichroic spectra of (a) indole and (b) 3-indole-butyric acid in the stretched PVA film.

Fig. 2. Dichroic spectra of benzimidazole in the stretched PVA film.

found to be satisfactory for the calculation of electronic spectra of conjugated systems, particularly for the calculation of transition moments.[1]

A physical picture is given of the effect of Σ-Π interaction on the transition moment. The transition moment, $\tilde{m}$, can be expressed by

$$\tilde{m} = m_0 + \Delta m \tag{1}$$

$$\Delta m = \frac{1}{\sqrt{2}\,\varepsilon} \sum_{i\alpha} \sum_{\mu} C_{i\alpha} d_{i\mu} d_{\alpha\mu} \sum_{AB} r_A B_{AB} \gamma_{B\mu}, \tag{2}$$

where m_0 is the transition moment obtained by the conventional P-P-P calculation, Δm the correction term due to the Σ-Π interaction, and ε the energy parameter. In Eq. 2, $C_{i\alpha}$ is the variation parameter associated with the configuration, $|_i^\alpha\!>$, and $d_{i\mu}$ the μ-th AO coefficient of the i-th MO. Δm can be decomposed into the individual A–B σ-bond polarization, Δm_{AB}, as follows.

$$\Delta m = \sum_{A>B} \Delta m_{AB}$$

$$\Delta m_{AB} = (r_A - r_B) B_{AB}(X_B - X_A), \tag{3}$$

where

$$X_B = \frac{1}{\sqrt{2}\,\varepsilon} \sum_{i\alpha} C_{i\alpha} d_{i\mu} d_{\alpha\mu} \gamma_{B\mu} \tag{4}$$

and r_A is the position vector of the atom A. Equation 4 can be rewritten as

$$X_B = \frac{1}{\sqrt{2}\,\varepsilon} \sum_{\mu} Y_\mu \gamma_{B\mu}, \tag{5}$$

where Y_μ is defined by

$$Y_\mu = \sum_{i\alpha} C_{i\alpha} d_{i\mu} d_{\alpha\mu}, \tag{6}$$

Y_μ represents the component of the transition density (CTD) at μ-th atom. When π-π^* transition takes place, Y_μ is produced at μ-th atom, creating an induced charge, X_B, on the atom B. In Eq. 3, the vector $(r_A - r_B)$ indicates the A-B σ-bond given by the structural formula. $(X_B - X_A)$ gives the difference between the induced charge of atom A and that of atom B. B_{AB} plays the role of projection operator whether a σ-bond exists or not between the atoms

A and B.

MO-CI calculations have been carried out for indole, 3-methylindole and benzimidazole. As regards their geometry, it is assumed that all molecules consist of regular hexagons and pentagons, in which each C–C and C–N bond length is 1.40 Å. Values for the valence-state ionization potentials, I, and electron affinities, A, of the carbon and nitrogen atoms are taken as follows.

$I(C) = 11.16\,eV$	$A(C) = 0.03\,eV$
$I(N^{+1}) = 14.12\,eV$	$A(N^{+1}) = 1.78\,eV$
$I(N^{+2}) = 26.70\,eV$	$A(N^{+2}) = 9.26\,eV$

The two center core integrals $\beta_{\mu\nu}$ are calculated by the variable β method:[8]

$$\beta_{\mu\nu}(C\text{-}C) = -1.90 - 0.51\,P_{\mu\nu}\ eV$$

$$\beta_{\mu\nu}(C\text{-}N) = -2.09 - 0.53\,P_{\mu\nu}\ eV.$$

In the CI calculation, all possible singly excited configurations are included.

Results and Discussion

Determination of Orientation Axis. Indole and 3-indolebutyric acid show very similar spectra (Figs. 1(a) and 1(b)). From a comparison of the Rd curves, we see that the absorption in the range 240—300 nm consists of two bands with different polarizations. Let us denote the bands for the long and short wavelength side by bands (I) and (II). The apparent orientation angles are 49.5° (I) and 46.1° (II) for indole, and 52.7° (I) and 48.7° (II) for 3-indolebutyric acid, both orientation angles increasing with the substituent effect. On the other hand, the apparent angle for a third band (III) at *ca.* 220 nm decreases from 42.2° to 41.5°. Such changes suggest that the orientation axis rotates and approaches the polarization direction of the third band away from those of the first and second transitions. Thus, the polarization direction of bands I and II is on one side of the orientation axis of the molecule and that of band III on the opposite side.

In dichroism analysis, when an absorption band is isolated from the others, the Rd value for the band should be constant in the band region. However, the value for band III (max. 224 nm) of 3-indolebutyric acid, for example, is not constant but decreases from maximum at 230 nm toward the short wavelength for the band region observed. The decrease in Rd indicates that band IV penetrates into the band III region. The orientation angle for band III would become smaller than 41.5° if no penetration takes place.

The same situation is considered for band III of indole; the true orientation angle should be less than 42.2°. Since bands I and II overlap each other, their specific orientation angles should be >49.5° and <46.1° for indole and >52.7° and <48.7° for 3-indolebutyric acid, respectively.

Figure 2 shows the dichroic spectra and Rd curve for benzimidazole. From a comparison of Fig. 2 with Figs. 1(a) and 1(b), we see that bands, I and II (Fig. 2) are isolated from each other and correspond

to bands I and II of indole, respectively, and also band III of benzimidazole corresponds to that of indole. The apparent orientation angles for I(45°) and III(44.6°) of benzimidazole are nearly equal to each other and differ from that of II(49.7°), suggesting that their transition moments are on one side of the orientation axis of the molecule while band II is on the opposite side, in contrast to the case for indole. This indicates that the direction of the transition moment of band I of indole has been moved from one side to the other of the orientation axis by the substituent effect of aza-nitrogen at the 3-position of indole molecule.

The orientation axis of molecule can be determined by a comparison of the experimental orientation angles of band polarizations and the calculated absolute angles of corresponding transition moment.

In the dichroism analysis, the induced orientation axis (OA) of molecule in the stretched PVA substrate is assumed to take a specific direction in the molecular plane. Let us denote the angle between OA and the molecular coordinate axis X by $\theta_{OA}(X)$, where $-90° \leq \theta_{OA}(X) \leq 90°$ ($\theta_{OA}(X)$ is defined as positive for anticlockwise direction). If we denote the theoretically calculated angle of the moment of the n-th singlet transition (S_n) against the X-axis by $\theta_n(X)$, and the angle of S_n against OA by $\theta_n(OA)$, we have

$$\theta_n(OA) = 90° \pm (90° - |\theta_n(X) - \theta_{OA}(X)|), \qquad (7)$$

where the signs $+$ and $-$ are taken for negative and positive values, respectively. $\theta_n(OA)$ should be compared with the experimental orientation angle $\theta_N(OA)$ of the band number N corresponding to the n-th transition.

We can now determine the absolute angle $\theta_{OA}(X)$ of the orientation axis against the X axis of the molecule in the stretched PVA substrate. The relation between $\theta_n(OA)$ and $\theta_{OA}(X)$ for indole is shown in Fig. 3(a) where the lower limit $\theta_I(OA) > 49.5°$ and upper limits $\theta_{II}(OA) < 46.1°$ and $\theta_{III}(OA) < 42.2°$ are added. For $\theta_{OA}(X)$ satisfactory conditions are as follows: $\theta_I(OA) > 49.5°$ in the range $-36.2°$—$44.8°$, $\theta_{II}(OA) > 46.1°$ in the range from $43.5°$ to $-44.3°$ through $90°$, and $\theta_{III}(OA) < 42.2°$ in the range $-38.6°$ $\leq \theta_{OA}(X) \leq 45.8°$. The orientation axis (OA) associated with the indole molecule should be restricted to a common direction for which the three conditions are satisfied simultaneously. Such an angle $\theta_{OA}(X)$ ($44° \pm 1°$) can be found in the range $43.5°$—$44.8°$ (Fig. 4(a)).

In the same way, the orientation axis of the 3-indole-butyric acid molecule can be determined to be $\theta_{OA}(X) = 39° \pm 1°$, making use of the calculated result for methyl derivative of indole instead of the 3-(3-carboxypropyl) derivative.

In the case of benzimidazole, the range of angle $\theta_{OA}(X)$ which satisfies the experimental conditions is $5°$—$29°$ (Figs. 3(b) and 4(b)). The range is dependent on the experimental data for bands I and IV the orientation angles of which are $\theta_I(OA) \leq 45°$ and $\theta_{IV}(OA) > 54.7°$, respectively. However, band IV greatly overlaps band III of $\theta_{III}(OA) < 44.6°$ (Fig. 2). If band IV is isolated from band III, it will have
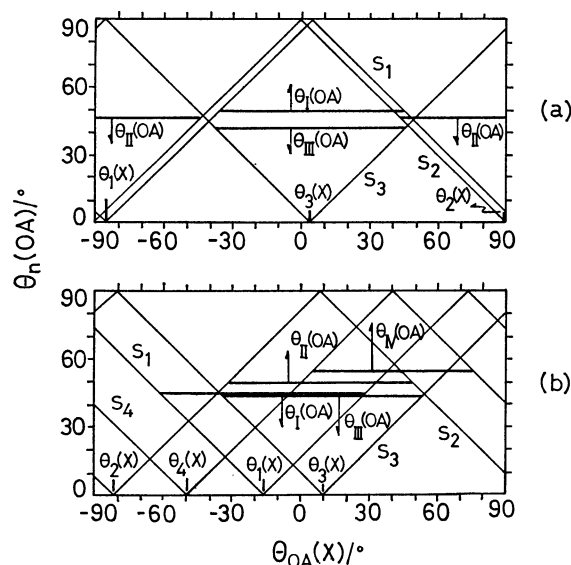

Fig. 3. The angle-relation between the moment of n-th transition (S_n) and the orientation axis (OA) of molecule when the angle of OA to the molecular axis (X) varies in the range $-90°$—$90°$.

The abscissa represents the angle of OA to X, $\theta_{OA}(X)$, and the ordinate the angle of the moment of S_n to OA, $\theta_n(OA)$. The horizontal lines indicate the experimental orientation angles (lower or upper limit) of the band number N, $\theta_N(OA)$, which are compared with the theoretical values $\theta_n(OA)$. The allowed angles of $\theta_N(OA)$ are as follows. (a) indole: $\theta_I(OA) >$ $49.5°$, $\theta_{II}(OA) < 46.1°$, $\theta_{III}(OA) < 42.2°$. (b) benzimidazole: $\theta_I(OA) \leq 45°$, $\theta_{II}(OA) > 49.7°$, $\theta_{III}(OA) <$ $44.6°$, $\theta_{IV}(OA) > 54.7°$.
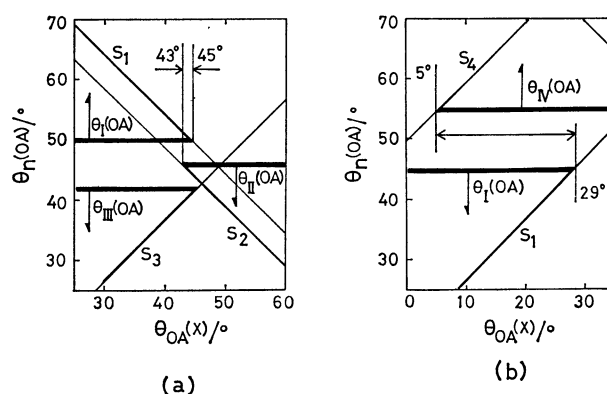

Fig. 4. Angle-relation of $\theta_n(OA)$ and $\theta_{OA}(X)$ of (a) indole and (b) benzimidazole. See the illustration of Fig. 3.

an angle much larger than $54.7°$. This will make the lower limit of $\theta_{OA}(X)$ shift from $5°$ toward $29°$ (Fig. 4(b)). Since the first peak of band I is considered to be pure electronic transition because of its isolation from band II, the value $\theta_I(OA) = 45°$ would be reliable and the angle of $\theta_{OA}(X)$ may be ca. $29°$.

The directions of OA of indole, 3-indolebutyric acid and benzimidazole determined experimentally are given in Table 1. $\theta_{OA}(X)$ is the absolute angle of OA against the molecular X(long) axis. The

TABLE 1. EXPERIMENTAL ORIENTATION ANGLE θ_N(OA) OF BAND N, CALCULATED ORIENTATION ANGLE θ_n(OA) OF n-TH TRANSITION AND DETERMINED DIRECTION θ_{OA}(X) OF ORIENTATION AXIS OA OF INDOLE, 3-INDOLEBUTYRIC ACID AND BENZIMIDAZOLE

N	θ_N(OA) $(\theta_n$(OA))		
	Indole	3-Indolebutyric acid	Benzimidazole
I	>49.5° (50.3°)	>52.7° (53.5°)	≦45° (45°)
II	<46.1° (45.6°)	<48.7° (47.3°)	>49.7° (71°)
III	<42.2° (40.4°)	<41.5° (34.5°)	>44.6° (19°)
IV	≫42.2°	≫41.5°	≫54.7° (79°)
θ_{OA}(X)[a]	44°±1°	39°±1°	ca. 29°

a) The angle against the X-axis of the molecule. See Figs. 4 and 5. For determination of θ_{OA}(X) for 3-indolebutyric acid, the calculated results for 3-methyl-indole were used.

TABLE 2. EXCITATION ENERGIES AND OSCILLATOR STRENGTHS OF π-π^* SINGLET STATES OF INDOLE, BENZIMIDASOLE, AND 3-METHYLINDOLE

Compound	Calculations		Experimental[a]	
	E/eV	f	E/eV	$\log(\varepsilon/1\,\mathrm{mol^{-1}\,cm^{-1}})$
Indole	4.48	0.024	4.1	≈3.2
	4.78	0.061	4.3	3.7
	6.02	0.886	5.5	4.5
	6.33	0.114		
	6.50	0.111		
3-Methyl-indole[b]	4.48	0.024	4.1	≈3.0
	4.81	0.067	4.3	3.7
	6.02	0.922	5.6	4.5
	6.40	0.077		
	6.52	0.124		
Benzimida-zole[c]	4.58	0.012	4.5	3.7
	5.05	0.086	5.0	3.7
	6.15	0.858	6.0	4.4
	6.51	0.249		
	6.72	0.046		

a) In aqueous solution. b) Experimental values are for 3-indolebutyric acid. c) pH of aqueous solution ca. 10.

geometrical relation of OA and the transition moments of S_n are shown in Fig. 5. Agreement between experimental and calculated results is satisfactory. In the case of indole the calculated angles of S_1 and S_2 are 50.3° and 45.6°, respectively. However, the angles observed are 49.5° and 46.1°, respectively, showing that the partial overlapping of the two bands makes the respective transition directions (absolute angles) approach each other (apparent angles). Similarly, the orientation angle of S_3 transition turns toward that of S_4 because of overlapping. The calculated and experimental results agree (Fig. 5).

Substituent Effect on the Electronic Transition Moment. The calculated π-π^* transition energies and oscillator strengths of indole, 3-methylindole, and benzimidazole are summarized in Table 2. Agreement between calculated and experimental results is satisfactory. The calculated transition moments, m_0 and $\tilde{m}$, and oscil-

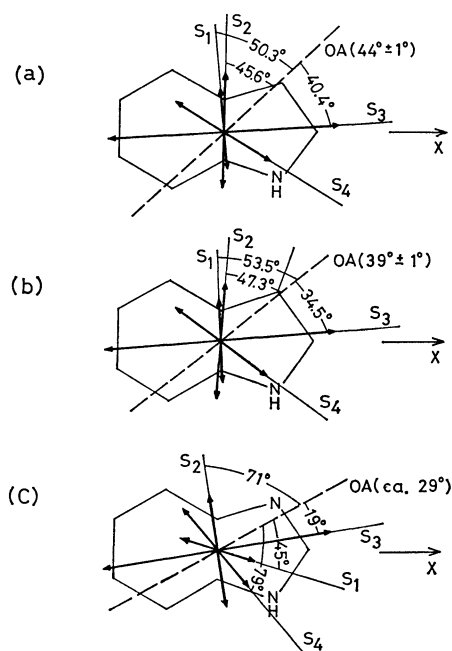(a)   OA(44°±1°)

(b)   OA(39°±1°)

(c)   OA(ca. 29°)

Fig. 5. Calculated transition moments (S_n) and orientation axis (OA) of (a) indole, (b) 3-indolebutyric acid and (c) benzimidazole. X means the molecular long axis.
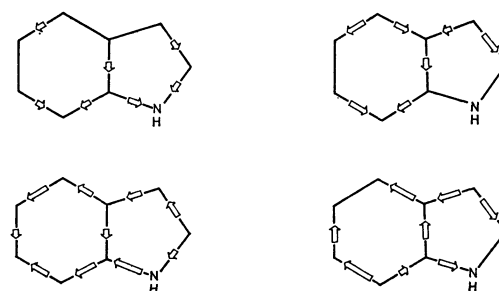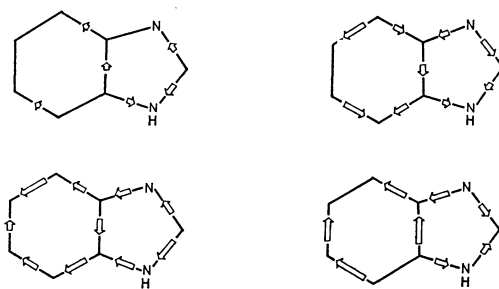

Fig. 6. The divided induced σ-polarization, Δm_{AB}'s, of indole.

Fig. 7. The divided induced σ-polarization, Δm_{AB}'s, of benzimidazole.

lator strengths, f_0 and f, of these molecules are summarized in Table 3. The directions of m_0 and Δm are almost opposite each other, f being considerably reduced. It is of interest to study the effect of the methyl group on the transition moment of the methyl substituted systems. The induced σ-polarization of indole and that of 3-methylindole are illustrated in Figs. 6 and 8, respectively. In the case of 3-methylindole, a large induced σ-bond polarization is found

Table 3. Calculated transition moments and oscillator strengths of indole, benzimidazole, and 3-methylindole

States[a]	Transition moments[b]						Oscillator strengths[c]			
	m_0/eÅ		Δm/eÅ		$\tilde{m}$/eÅ					
	x	y	x	y	x	y	f_0	f	f/f_0	θ/° [d]
				Indole						
S_1	−0.029	0.392	0.010	−0.144	−0.019	0.248	0.061	0.024	0.39	−85.7
S_2	−0.004	0.587	0.007	−0.204	0.003	0.383	0.144	0.061	0.42	89.6
S_3	1.697	0.113	−0.403	−0.031	1.294	0.082	1.524	0.886	0.58	3.6
S_4	0.491	−0.341	−0.105	0.102	0.386	−0.238	0.198	0.114	0.58	−31.7
S_5	0.071	0.704	−0.018	−0.269	0.052	0.434	0.286	0.111	0.39	83.2
				Benzimidazole						
S_1	0.216	−0.067	−0.052	0.019	0.164	−0.048	0.020	0.012	0.60	−16.4
S_2	−0.096	0.682	0.024	−0.248	−0.072	0.435	0.210	0.086	0.41	−80.6
S_3	1.642	0.367	−0.398	−0.150	1.244	0.217	1.523	0.858	0.56	9.9
S_4	−0.560	0.726	0.133	−0.221	−0.427	0.505	0.479	0.249	0.52	−49.8
S_5	−0.263	0.340	0.055	−0.154	−0.208	0.185	0.108	0.046	0.43	−41.7
				3-Methylindole						
S_1	−0.026	0.383	0.016	−0.134	−0.011	0.249	0.058	0.024	0.41	−87.5
S_2	0.009	0.589	0.017	−0.190	0.026	0.399	0.146	0.067	0.46	86.3
S_3	1.727	0.094	−0.408	0.010	1.319	0.105	1.575	0.922	0.59	4.5
S_4	−0.376	0.370	0.073	−0.154	0.303	−0.216	0.156	0.077	0.49	35.6
S_5	0.048	0.722	−0.006	−0.257	0.042	0.465	0.299	0.124	0.41	83.2

a) Singlet states are placed in order of increasing the energy. b) x and y indicate components of the transition moment. c) f_0 and f are calculated by using m_0 and m, respectively. d) Angles of m from the molecular long axis shown in degrees are defined as positive for anticlockwise direction.
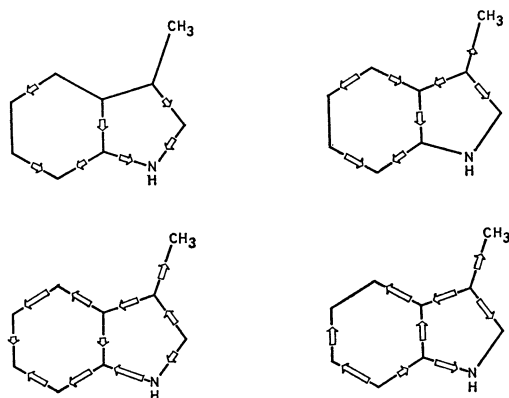

Fig. 8. The divided induced σ-polarization, Δm_{AB}'s, of 3-methylidole.

at C–CH₃ σ-bond, but its oscillator strength and the direction of transition moment of the π-π* excitation are almost the same as those of indole. It is thus concluded that in an alkyl derivative, the induced σ-bond polarization appearing at C–C (alkyl) σ-bond differs at each excited state. However, it has no appreciable effect on the direction of the transition moment of the π-π* excitation. For determination of the direction of transition moment, the alkyl substituted molecule is often used instead of the parent molecule because of its larger orientation

in the adsorption on the PVA film or in crystallization. The theoretical results support the pertinence of such experimental prescription. The induced σ-polarization are shown in Figs. 6—8 where, for the sake of simplicity, the π-π* transition moments are omitted. The gross features of the induced σ-bond polarizations of each molecule considered resemble each other.

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