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A TRANSANNULAR HYPOCHROMISM OBSERVED IN A CYCLIC DIACETYLENE CONTAINING NAPHTHALENE NUCLEUS

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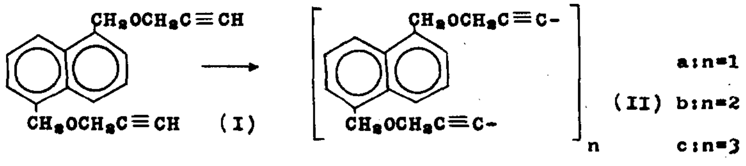
The absorption intensity in the electronic spectrum of a native nucleic acid has been found to be weaker than the sum of the intensities of individual mononucleotides constituting the nucleic acid[1]. This phemomenon has been explained in terms of the dispersion-force interaction between the transition moment dipoles stacked in parallel position and a quantitative treatment of this theory has been advanced by Tinoco[2] and Rhodes[3].

1,5-Bis(propargyloxymethyl)naphthalene (I, m.p. 79.9-80.5°C) which was derived from disodio derivative of 1,5-bis-(hydroxymethyl)naphthalene and propargyl bromide was subjected to the Eglinton's oxidative coupling under a high dilution condition. A chromatography on alumina of the reaction products afforded three cyclic acetylenes, i.e., the cyclic monomer (II_a,



3.8%, m.p. 160-170°C (decom.), Mol. wt., 246 (osmometry in benzene), calcd. for $(C_{18}H_{14}O_2)_1$ 262), the cyclic dimer (II_b, 3.7%, m.p. 190-200°C (decom.), Mol. wt., 546 (Rast), calcd. for $(C_{18}H_{14}O_2)_2$ 525) and the cyclic trimer (II_c, 4.8%, gradual decomposition was observed from 130°C, Mol. wt., 732 (Rast), calcd. for $(C_{18}H_{14}O_2)_3$ 787).

The electronic spectral data and the absorption curves of the cyclic acetylenes ($II_{a\sim c}$) are shown in Table 1 and Fig. 1, respectively. The absorption curves of these compounds closely related to that of naphthalene. The absorption curves of II_b and II_c were found to be almost identical with that of the open chain parent compound (I) excepting the increased absorption intensity at ca. 245 mμ indicating the minor contribution of the diacetylenic chromophore in II_b and II_c. Whereas, a remarkable hypochromism was observed in the spectrum of II_a. The relative absorption intensities of each of the three absorption bands as compared with those of II_c are summarized in Table 2.

TABLE 1

The Electronic Spectral Data of $II_{a\sim c}$

II_a	λ_{max}	230	278	288.5	300	315.5 mμ
	ε	53,100	4,760	5,780	4,110	410
II_b	λ_{max}	231	278	288	298.5	315
	ε	123,400	13,380	16,380	11,380	1,180
II_c	λ_{max}	230	277.5	287.5	298.5	315
	ε	190,200	21,420	26,490	18,540	1,750

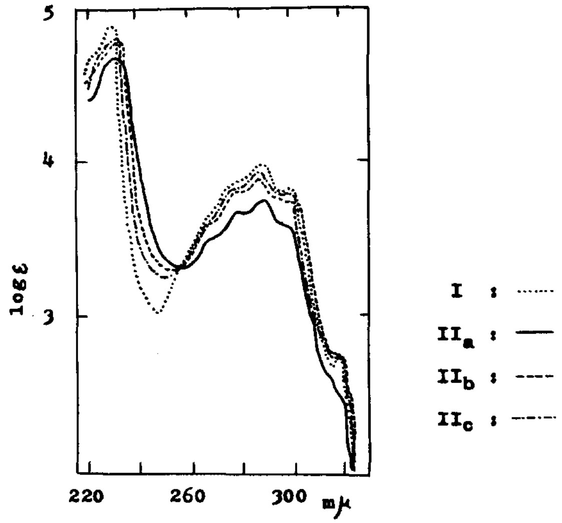


Fig. 1. The Electronic Spectra of $II_{a\sim c}$ and I

The curves of II_b and II_c were drawn using the reduced ε-values corresponding to the unit chromophore, i.e., ε/2 and ε/3 , respectively. (solvent: dioxane)

TABLE 2

The Relative Intensities*

absorption band**	β-(~230mμ)	para-(~280mμ)	α-(~315mμ)
II_c	100	100	100
II_b	97	93	101
II_a	84	65	70

* The reduced ε-values of II_b and II_c corresponding to the unit chromophore were compared with the ε-values of II_a taking the reduced values of II_c as unity.
** Clar's nomenclature.

The examination of Dreiding model of II_a indicates that two conformations are possible to retain the maximum distance between the diyne unit and the naphthalene nucleus. The projection of the molecular geometry corresponding to these two conformations (A and B) are shown in Fig. 2. The distance (R) between the diyne unit and the aromatic nucleus, and the angle (θ) between the short axis of the nucleus and the bridging chain were estimated to be R=2.26 Å, θ=21° for (A) and R= 2.12 Å and θ=38° for (B).

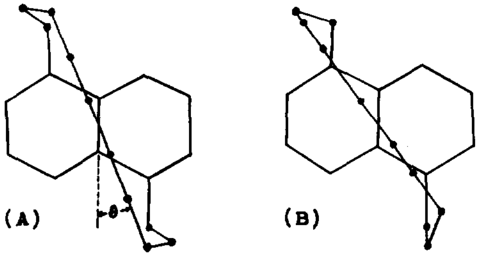


Fig. 2. The Possible Conformations of II_a

As summarized in Table 2, the hypochromism of the para-band ($^1L_a \leftarrow {}^1A$) was found to be stronger than that of β-band ($^1B_b \leftarrow {}^1A$). As the direction of the transition moment of para-band has been assigned to be perpendicular to the long axis of naphthalene nucleus, and the direction of the transition moment of diyne chromophore is obviously parallel to the long axis of the linear linkage, the pronounced hypochromism of para-band seems to indicate an operation of the dispersion-force interaction between the transition moment dipoles.

The original equation proposed by Rhodes[3] is designed for a polymeric substance bearing large number of chromophores.

For a molecule having two chromophoric groups, we can convert the original formula into the following equation (1), which represents the change of the oscillator strength (f) of the absorption band of chromophore A by the interaction of light induced dipoles of the absorption bands of chromophore B.

$$\frac{f_A'}{f_A} = 1 - 4K\sum_{B} \frac{f_B}{\tilde{\nu}_B^2 - \tilde{\nu}_A^2} \times G_{AB}\, \mathbf{e}_B \cdot \mathbf{e}_A \qquad \text{----------(1)}$$

where f_A' : the oscillator strength of an absorption band in chromophore A under the hypochromic effect.

f_A : the inherent oscillator strength of the absorption band in chromophore A.

K : $\dfrac{3e^2}{8\pi^2 c^2 m} = 1.07 \times 10^{10}\ \text{A}^3 \cdot \text{cm}^{-2}$

c represents light velocity in vacuo. e and m are the charge and the mass of an electron.

$\tilde{\nu}$: the transition energies in terms of wavenumbers.

$$G_{AB} = \left[\frac{\mathbf{e}_A \cdot \mathbf{e}_B}{R_{AB}^3} - 3\,\frac{(\mathbf{e}_A \cdot \mathbf{R}_{AB})(\mathbf{e}_B \cdot \mathbf{R}_{AB})}{R_{AB}^5} \right]$$

$\mathbf{e}_A, \mathbf{e}_B$: unit vectors in the direction of the respective transition moments in chromophore A and B.

$\mathbf{R}_{AB}$: the vector distance between the centers of the two chromophores.

The change of two absorption bands (β- and para-bands) of the cyclic monomer (II_a) by the interaction with the three absorption bands of diacetylenic chromophore were calculated according to the equation (1). The hypochromism of α-band was not taken into consideration, as the α-band was partly submerged in the tail of the para-band. The electronic spectral data of tetradeca-6,8-diyne [226 mμ (ε 360); 240 (350); 254 (200)] in iso-octane[4] and those of the cyclic trimer (II_c) were used as the references of diyne and naphthalene chromophores, respectively. The oscillator strength was approximately estimated according to the equation, $f = \varepsilon \times \nu / 0.464 \times 10^9$. R= 2.26 Å and θ =21° were substituted to the geometry dependent term in (1), and the two chromophoric groups were assumed to be perpendicular to the vector distance between the centers of the two groups. These assumptions correspond to the conformation (A) in Fig. 2. The results of the calculation are summarized in Table 3 (a). The agreement with the observed values appears to be rather good, even if it is not entirely satisfactory, in view of the crude estimation of R and θ basing on the molecular model. Inversely, R and θ were calculated employing observed f'/f . The results are shown in Table 3 (b). The angle between the two chromophoric groups (θ) agreed fairly well with the estimated value, but the distance (R) was larger than the estimated value. This results seem to be reasonable taking the repulsion of the π-electron clouds of the bridging chain and the aromatic nucleus into consideration.

TABLE 3

The Results of Calculation

	β -band	para-band
f'/f	calcd. 0.88	0.50
	obsd. 0.84	0.65

(a)

	θ	R
calcd.	28°	2.46 Å
est'd.	21°	2.26 Å

(b)

The hypochromism attributable to the interaction between transition moment dipoles was observed recently in spirochroman derivative[5] and diphenylsiloxanes[6]. The hypochromism observed in the cyclic diacetylene (II_a) afforded another interesting example of the same phenomenon, because the molecule is constrained to keep a fairly definite geometry holding the chromophoric groups in the fixed spatial positions and also the electronic transitions of the two chromophores are rather well understood.

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