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Cyclic Acetylenes. X. A Transannular Hypochromism Observed in a Cyclic Diacetylene Containing a Naphthalene Nucleus

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A cyclic diacetylene (XIa) has been synthesized by the oxidative coupling of 1, 5-bis(propargyloxymethyl)naphthalene (X) with a cyclic dimer (XIb) and a cyclic trimer (XIc). The electronic spectra of XIb and XIc have been found to be almost identical with that of naphthalene with respect to the location of the absorption maxima and the intensities. On the other hand, a marked decrease in the absorption intensities has been observed in the spectrum of the cyclic monomer (XIa). An inspection of the Dreiding model of XIa indicates that the two conformations (A and B) can retain the maximum distance between the dyine unit and the naphthalene nucleus. On the basis of the molecular model, the distance between the two chromophores and the angle between the short axis of the nucleus and the bridging chain have been estimated to be 2.26 Å, 21° for A and 2.12 Å and 38° for B. Employing these data, the hypochromic effect exerted by the diyne chromophore on the absorption of the naphthalene nucleus has been calculated according to the theory of Tinoco and Rhodes, resulting in a fairly good agreement with the observed values. Inversely, the calculation of the distance and the angle between the two chromophoric groups using the observed hypochromic effect has also given reasonable values. Therefore, the hypochromism observed in the cyclic diacetylene (XIa) has been attributed to the operation of dispersion-force interaction between diyne unit and the naphthalene chromophore.

An acetylenic bond incorporated in a cyclic system exerts a prominent effect on the conformation of the compound as a result of the linear arrangement of four atoms concerned with the linkage (–C–C≡C–C–). As a result of the restriction of the conformation, a cyclic acetylene is apt to be fixed in a definite molecular geometry. Accordingly, the acetylenic linkage in an adequate cyclic system seems to be held in a fixed spatial position proximate to another functional group in the molecule, thus offering an appropriate means for the study of the transannular interaction between the two groups.

The bathochromic shift in the electronic spectrum of cyclotetradeca-1, 3, 8, 10-tetrayne, as compared with those of such higher homologues as cyclo-octadeca-1, 3, 10, 12-tetrayne and cyclo-hexadeca-1, 3, 9, 11-tetrayne, has been attributed by Sondheimer to a transannular interaction between the two diyne units fixed closely in parallel in the molecule.[1]

The object of the present investigation is to study the transannular interaction between the acetylenic linkage and the aromatic nucleus.*[1] In order to obtain the desired information, we have investigated the synthesis of cyclic acetylenes containing the aromatic nucleus, in which the acetylenic linkage is held closely above the plane of the aromatic ring.

Synthesis

The preparation of the cyclic diacetylene (II) was attempted according to the sequence of reactions illustrated in Scheme 1. 1, 4-Bis(hydroxymethyl)benzene dipropargyl ether (I), which had been derived from 1, 4-bis(hydroxymethyl)-benzene or 1, 4-bis(chloromethyl)benzene, was subjected to oxidative coupling under various conditions. The sole identified product was proved to be the cyclic dimer (III) instead of the desired cyclic monomer (II). On the basis of the available data,[2] the distance between the two carbon atoms of the methylene groups in the bridging chain ($-CH_2-C\equiv C-C\equiv C-CH_2-$) is found to be approximately 6.70 Å, indicating that the bridging chain is probably too long to accomodate itself to the 1, 4-position of the *p*-xylylene group.

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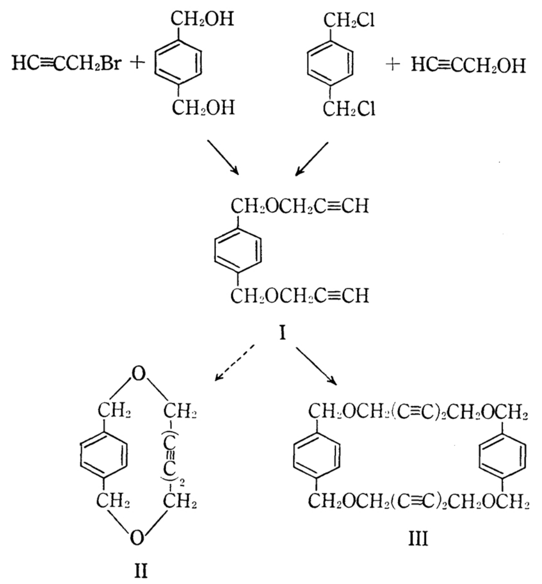
[1] F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **79**, 6263 (1957).

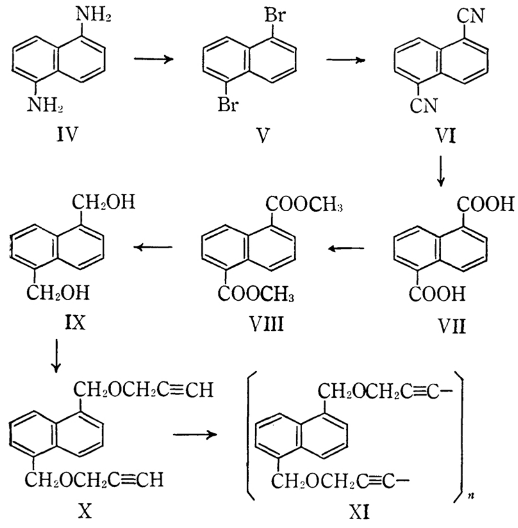
*[1] Previously, one of the present authors (M. N.) and F. Toda reported on the synthesis and spectral properties of the cyclic *p*-xylylene ether of *o, o'*-dihydroxydiphenyldiacetylene; they attributed the anomalous electronic spectrum to the operation of a transannular interaction between the diyne unit and the benzene ring in the *p*-xylylene bridge (This Bulletin, **34**, 874 (1961)). However, later work along this line has revealed that in reality the compound previously reported was not the cyclic monomer, but the cyclic dimer. The details of these later findings will be reported in the near future.

[2] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, New York (1966), p. 695.



Scheme 1. An attempted synthesis of the cyclic hexadiynylene ether of *p*-xylylene glycol.

The above-mentioned results prompted the present authors to study the cyclic acetylene containing a naphthalene nucleus. The interatomic distance (6.35 Å) between the two carbon atoms of the methylene groups of the 1- and 5-positions of naphthalene seemed to be adequate to link with the above-stated hexadiynylene chain. The sequence of the reaction used for the synthesis is outlined in Scheme 2.



a: $n=1$, b: $n=2$, c: $n=3$

Scheme 2. A synthesis of cyclic acetylenes containing naphthalene nucleus.

1, 5-Bis(hydroxymethyl)naphthalene (IX) was prepared by the lithium aluminum hydride reduction of the dimethyl ester (VIII), as the reaction of formaldehyde³⁾ with the bis-Grignard derivative of V⁴⁾ yielded only a trace of the glycol (IX). The dipropargyl ether (X), which had been prepared by the reaction of propargyl bromide with the disodio-derivative of IX, was treated with cupric acetate in pyridine⁵⁾ under ordinary reaction conditions, thus yielding a mixture of cyclic acetylenes. Chromatography of the products on alumina afforded the cyclic dimer (XIb), the cyclic trimer (XIc), and the cyclic tetramer (XI, $n=4$), or a mixture of the tetramer and the higher cyclic polymer. The absence of the absorption peak arising from terminal acetylene (~3300 cm^{-1}) in their infrared spectra indicates the cyclic nature of the products.

The desired cyclic monomer (XIa) was obtained, together with XIb and XIc, by the oxidative coupling of the diethynyl compound (X) in a highly diluted solution. The cyclic monomer (XIa) was found to be fairly unstable. A rapid development of a purple color on the surface of the crystals was observed on exposure to light. However, a solution of XIa in a dark and cold place could be kept without change for a long time. The infrared spectra of the cyclic acetylenes, XIa—XIc, and the dipropargyl ether (X) are shown in Fig. 1.

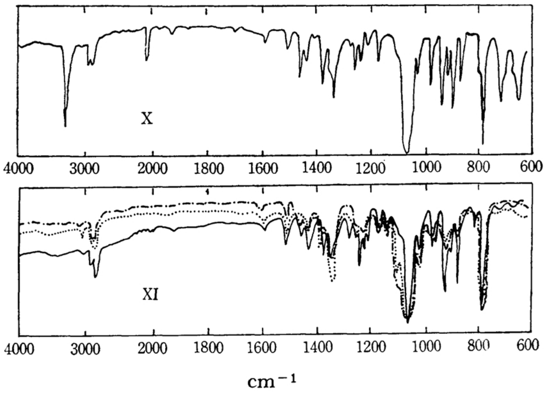


Fig. 1. The infrared spectra of X and XIa—XIc. XI: a ——; b ······; c -·-·

All attempts to prepare the 2, 6-isomer of XIa were fruitless. The oxidative coupling of 2, 6-bis(propargyloxymethyl)naphthalene, which had been derived from 2, 6-dimethylnaphthalene in four steps, resulted in two kinds of unstable cyclic acetylenes. The molecular-weight determinations revealed that none of the cyclic acetylenes was the cyclic monomer, but the fluctuating results, presumably resulting from their unstable

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3) K. Ziegler, *Ber.*, **54**, 739 (1921).
4) J. Salkind, *ibid.*, **67**, 1031 (1934).
5) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

TABLE 1. THE ELECTRONIC SPECTRAL DATA OF XIa—XIc

XIa	λ_{max} (mμ) ε	230 53100	278 4760	288.5 5780	300 4110	315.5 410
XIb	λ_{max} (mμ) ε	231 123400	278 13380	288 16380	298.5 11380	315 1180
XIc	λ_{max} (mμ) ε	230 190200	277.5 21420	287.5 26490	298.5 18540	315 1750

natures, made difficult the discrimination between the cyclic dimer and trimer.[*2]

Results and Discussion

The electronic spectral data of the cyclic acetylenes (XIa—XIc) are summarized in Table 1, while their absorption curves, together with that of the parent diethynyl compound (X), are illustrated in Fig. 2. The curves of XIb and XIc were drawn using the reduced ε-values corresponding to the unit chromophoric group, *i. e.*, $\varepsilon/2$ and $\varepsilon/3$ respectively.

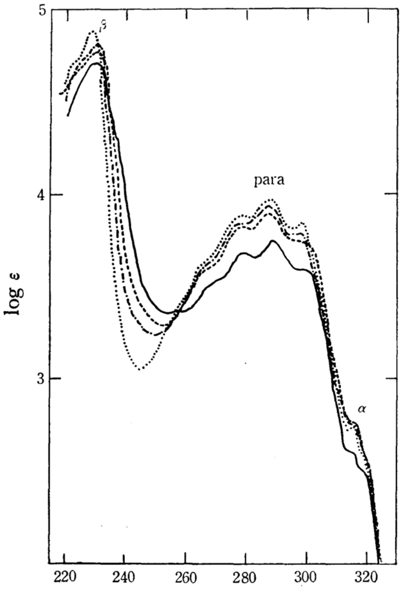
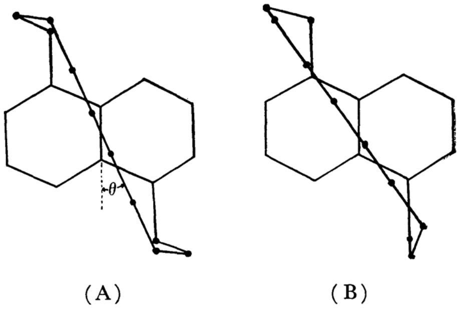


Fig. 2. The electronic spectra of X (……), XIa (——), XIb (----) and XIc (-·-·) (in dioxane).

The absorption curves of these compounds are closely related to that of naphthalene. The only difference was found in the increase in the absorption intensity at the λ_{min} around 245 mμ in the case of the spectra of the cyclic acetylenes (XIa—XIc); this indicates the contribution of the diacetylenic chromophore. The bathochromic shifts of the absorption maxima have been observed in the spectra of some paracyclophanes[6] and cyclic tetraynes,[1] and have been attributed to the operation of a p-σ type transannular interaction between two π-electron systems in proximate positions in these molecules. On the contrary, the cyclic acetylene (XIa) exhibited only a slight red shift (*ca.* 1.5 mμ) as compared with the cyclic dimer (XIb) and the trimer (XIc); this indicates the absence of appreciable p-σ type interaction between the diyne unit and the naphthalene nucleus.

The examination of the Dreiding model of the cyclic monomer (XIa) indicates that two conformations can retain the maximum distance between the diyne unit and the aromatic nucleus. The projections of the molecular geometry corresponding to these two conformations (A and B) are shown in Fig. 3. The distance between the diyne unit and the nucleus, and the angle (θ) between the short axis of the nucleus and the bridging chain were estimated to be 2.26 Å, and $\theta=21°$ for A and 2.12 Å and $\theta=38°$ for B respectively.



(A) (B)

Fig. 3. The possible conformations of XIa.

The transannular interaction between the two benzene rings in paracyclophane was observable when the two nuclei were held face to face in a parallel position within 3.4 Å.[6a] As the van der Waals radius of an acetylenic linkage may reasonably be assumed to be almost the same as that of a benzene ring, the above-mentioned distance between the diyne unit and the naphthalene

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[*2] The experiments on the 2, 6-isomer were performed by Mr. K. Nakasuji, to whom the authors' thanks are due.

6) a) D. J. Cram, N. L. Allinger and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954); b) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter and E. Heilbronner, *ibid.*, **81**, 5977 (1959).

nucleus in XIa seems to be close enough to manifest the p-σ type transannular interaction. However, not only should the two interacting groups be held in proximate position, but also the atoms in each group must lie one upon another and the sign of the orbitals of the groups must be the same in the excited states for a transannular interaction due to electron exchange or orbital overlapping to arise. As is clearly illustrated in Fig. 3, the atoms in the diyne unit in XIa are not placed in the appropriate position with regard to the atoms of the aromatic ring for the appearance of the abovementioned transannular interaction. Moreover, there is no necessity for the signs of the orbitals of the two chromophores in the excited states to be the same. These arguments seem to account for the minor red shift of the electronic spectrum of XIa regardless of the proximate position of the two chromophores.

The most interesting characteristic of the electronic spectrum of the cyclic monomer (XIa) was found in the marked decrease in the absorption intensities of the maxima as compared with the corresponding absorption intensities of the cyclic dimer (XIb) and trimer (XIc) (*cf.* Table 1 and Fig. 2). The latter two compounds showed absorption curves almost identical with that of the open chain dipropargyl ether (X), as is illustrated in Fig. 2. The fact that the repeated measurements of the spectrum employing various samples of XIa which had been purified according to different methods always gave identical spectra excluded the possibility of a contamination of XIa by an impurity causing the decrease in the absorption intensities. The relative absorption intensities of each of the three absorption bands as compared with those of the cyclic trimer (XIc) are summarized in Table 2.

TABLE 2. THE RELATIVE ABSORPTION INTENSITIES†

Absorption band††	β ($\sim$230 mμ)	para ($\sim$288 mμ)	α ($\sim$315 mμ)
XIc	100	100	100
XIb	97	93	101
XIa	84	65	70

† The ε-values of XIa were compared with the reduced ε-values of XIb and XIc, taking the reduced values of XIc as unity.

†† Clar's nomenclature.

It is well known that the absorption intensity in the electronic spectrum of a native nucleic acid with a double-stranded helix structure is weaker than the sum of the absorptions of the individual nucleotides constituting the nucleic acid. The denaturation of the nucleic acid by heat or by acid treatments, thus destroying the helical structure, causes the increase in the absorption intensity.[7] This phenomenon has been explained in terms of the dispersion-force interaction between the excited dipoles; *i. e.*, the parallel stacking of the transition moments should cause a decrease in the absorption intensity (hypochromism), while the colinear alignment of the transition moments should result in an increase in the absorption intensity (hyperchromism). The effective overlapping of atoms or the same signs of the orbitals in the excited states of the chromophoric groups are not the decisive factors for the manifestation of the interaction between the transition moment dipoles. A quantitative treatment of this theory has been developed by Tinoco[8] and Rhodes[9]; they also succeeded in the calculation of the hypochromism of deoxyribonucleic acid.[*3]

As is summarized in Table 2, the hypochromism of the para-band was found to be stronger than that of the β-band. The transition moment of the β-band ($^1B_b \leftarrow {}^1A$) has been assigned to be parallel to the long axis of the naphthalene nucleus. On the other hand, the transition moment of the para-band ($^1L_a \leftarrow {}^1A$) meets the long axis of the nucleus at right angles. The direction of the transition moment of a diacetylenic chromophore is obviously parallel to the long axis of the linear linkage. Therefore, the pronounced diminution in the absorption intensity of the para-band seems to suggest the operation of the dispersion-force between the transition-moment dipoles.

The original equation proposed by Rhodes[9] was designed for a polymeric substance bearing a large number of chromophores. For a molecule with two chromophores, we can convert the original fomula into the following equation (1), which represents the change in the oscillator strength of the absorption band of the A chromophore by the interaction of light-induced dipoles of the absorption bands of the B chromophore:

$$\frac{f'_A}{f_A} = 1 - 4K \sum_B \frac{f_B}{\tilde{\nu}_B^2 - \tilde{\nu}_A^2} \times G_{AB}\boldsymbol{e}_B \cdot \boldsymbol{e}_A \qquad (1)$$

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

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

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

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[7] G. H. Beaven, E. R. Holiday and E. A. Johnson, "The Nucleic Acid," Vol. I, Academic Press, New York (1955), p. 493; P. D. Lawley, *Biochim. Biophys. Acta,* **21**, 481 (1956); R. Thomas, *ibid.,* **14**, 1231 (1954); K. K. Reddi, *ibid.,* **27**, 1 (1958).

[8] I. Tinoco, Jr., *J. Am. Chem. Soc.,* **82**, 4785 (1960).

[9] W. Rhodes, *ibid.,* **83**, 3609 (1961).

[*3] The absorption intensity of deoxyribonucleic acid has been found to be 60% that of the mononucleotide.

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

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

$$\boldsymbol{G}_{\mathrm{AB}}=\left[\frac{\boldsymbol{e}_{\mathrm{A}}\cdot\boldsymbol{e}_{\mathrm{B}}}{R^3{}_{\mathrm{AB}}}-3\frac{(\boldsymbol{e}_{\mathrm{A}}\cdot\boldsymbol{R}_{\mathrm{AB}})(\boldsymbol{e}_{\mathrm{B}}\cdot\boldsymbol{R}_{\mathrm{AB}})}{R^5{}_{\mathrm{AB}}}\right]$$

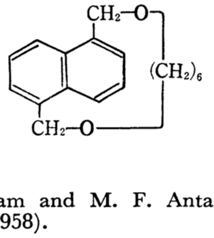
$\boldsymbol{e}_{\mathrm{A}}, \boldsymbol{e}_{\mathrm{B}}$: unit vectors in the direction of the respective transition moments in the A and B chromophores.

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

The first half of the second term in Eq. (1) is connected with the polarizability, while the latter half is the geometry-dependent term.

If there is no change in the shape of the absorption curve because of the influence of the hypochromic effect, the ratio of the absorption intensities, ε'/ε, should be equal to the ratio of the oscillator strength, f'/f. The change in two absorption bands (β- and para-bands)*4 of the cyclic monomer (XIa) because of the interaction with the three absorption bands of the diacetylenic chromophore were calculated according to Eq. (1). The electronic spectral data of tetradeca-6, 8-diyne [226 mμ (ε, 360); 240 (350); 254 (200)] in isooctane[10] were used as the reference of the diacetylenic chromophore. The spectrum of the cyclic trimer (XIc), in which no operation of the hypochromism seemed to be certain, was used as the reference of the naphthalene chromophore. The oscillator strength was estimated according to the equation; $f=\varepsilon\times\tilde{\nu}/0.464\times10^9$. $R=2.26$ Å and $\theta=21°$ were substituted for the geometry-dependent term in Eq. (1), and the two chromophoric groups were assumed to meet at right analges with the vector distance between the centers of the two groups. This assumption corresponds to the conformation A in Fig. 3; the latter half of the G term vanishes with this assumption. The calculation gave the following results: $f'_\beta/f_\beta=0.88$ for the β-band, and $f'_{\mathrm{para}}/f_{\mathrm{para}}=0.50$ for the para-band. The agreement with the observed values (0.84 and 0.65 respectively; *cf.* Table 2) appears to be rather good, even if it is not entirely satisfactory, in view of the crude estimation of R and θ based on the molecular model. Inversely, R and θ were calculated employing the observed f'/f ratio, resulting in $R=2.46$ Å and $\theta=28°$. The angle between the two chromophoric groups (θ) agreed fairly well with the estimated value, but the distance (R) was larger than the estimated one. These results seem to be reasonable in view of the repulsion of the π-electron clouds of the bridging chain and the aromatic nucleus. As has already been mentioned, the positions of the absorption maxima in the electronic spectrum of XIa were found to be almost identical with those of the cyclic trimer (XIc). Moreover, the infrared spectrum of XIa exhibited ordinary absorption peaks with regard to the naphthalene nucleus and the aromatic hydrogen atoms. On the other hand, appreciable changes were observed in the finger-print region of aliphatic carbon-hydrogen and carbon-carbon linkages in the spectrum of XIa as compared with those of XIb and XIc (Fig. 1). XIa exhibits much better-resolved bands than the larger rings (XIb and XIc). The strain inherent in XIa probably places certain restrictions on the stretching and bending vibrations of the various linkages in the bridging chain in XIa.[11] The above-mentioned facts seem to indicate that the ring strain in XIa accumulates in the bridging chain, leaving the naphthalene nucleus in the planar geometry. The absorption peak due to the stretching vibration of the acetylenic bond could not be observed in the spectra of XIb and XIc. The appearance of a group of weak bands in the 2100—2240 cm^{-1} region in the spectrum of XIa also seems to have some relation with the strain in the bridging chain.

The results of the above-mentioned calculation should be corrected if the electronic excitation of the diacetylenic chromophore is affected by the strain. However, the correction was inevitably ignored because of the difficulty of detecting or estimating the change in the spectrum of the diyne unit under the strain. As has been stated before, a planar geometry of the naphthalene nucleus in XIa was assumed on the basis of the infrared spectral evidence. However, it is desirable to confirm the effect of strain on the electronic spectrum of the nucleus. 1, 5-Bis(hydroxymethyl)naphthalene hexamethylene ether (XII), which is the saturated analogue of XIa bearing the bridging chain of nearly the same length, seemed to be an appropriate reference substance. Unfortunately, all attempts to prepare XII failed. The reduction of XIa over various catalysts under different conditions always resulted in the hydrogenolysis of the bridging chain.



(XII)

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*4 The change in the α-band was not taken into consideration, as the α-band was partly submerged in the tail of the para-band.

[10] C. J. Brown, *J. Chem. Soc.*, **1953**, 3265, 3279.

[11] D. J. Cram and M. F. Antar, *J. Am. Chem. Soc.*, **80**, 3103 (1958).

The interaction of transition-moment dipoles associated with electronic bands is reciprocal, as can be seen from the antisymmetric character of Eq. 1 to the permutation of A and B. If the excitation of the B chromophore caused a decrease in f_A, the excitation of the A chromophore should cause an increase in f_B. The above-mentioned argument is restricted to the interaction of the electronic bands of the bridging chain with the electronic bands of the naphthalene nucleus. On the contrary, the electronic bands of the diyne chromophore are necessarily affected by the interaction of the naphthalene nucleus. Therefore, the observed absorption curve must be regarded as the sum of the two effects. The calculation of the increase in intensity of an electronic band with a small oscillator strength as the result of the interaction of another chromophore with a large oscillator strength is accomplished only with a large error; thus only unreliable results are yielded. The change in the diyne chromophore was found to be too small to exert a marked change on the spectrum of XIa; therefore, the absorption of XIa can reasonably be regarded as the absorption of the naphthalene nucleus under the influence of the hypochromic effect.[†]

The hypochromism attributable to the interaction between transition-moment dipoles, which had been found for the first time in native nucleic acid[7] and polypeptide,[12] has recently been observed in a spirochroman.[13] Moreover, the hypochromism observed in the 270 mμ-band (the ^1L_b transition) of diphenylsiloxanes has been attributed to the restricted configurational randomization of the phenyl groups.[14] The fact that the hypochromism of the cyclic diacetylene (XIa) could be explained according to the theory of Tinoco[8] and Rhodes[9] afforded another interesting example of dispersion-force interaction between transition-moment dipoles, because the molecule is constrained to keep a fairly definite geometry, holding the chromophoric groups in the fixed spatial positions; also, the electronic transitions of the two chromophores are rather well understood.

Experimental[††]

1, 5-Dibromonaphthalene (V). 1, 5-Diaminonaphthalene was converted to the dibromo-compound according to the procedure of Hodgson.[15] Mp 131.2—131.8°C (lit. value, 131°C[16]).

1, 5-Dicarboxynaphthalene (VII). 1, 5-Dicyanonaphthalene (VI) was prepared according to the method of Friedman.[17] A stirred mixture of V (185.9 g, 0.65 mol), cuprous cyanide (139.7 g, 1.56 mol), and *N, N*-dimethylformamide (600 m*l*) was refluxed for 6 hr. The hot reaction mixture was then poured into a solution of ethylenediamine (300 m*l*) in water (1200 m*l*). After the mixture had been stirred for 30 min at 50—70°C, the insoluble material was collected on a sintered-glass filter funnel and washed successively with a 20% aqueous solution of ethylenediamine (500 m*l*), water, a warm 10% aqueous solution of sodium cyanide (500 m*l*), and water. The crude VI was recrystallized from ethanol, acetic acid, or dioxane to give pure VI, mp 268—269°C (lit. value, 270°C (in a sealed tube)[16]). The wet, crude dinitrile (146.6 g) was added to a mixture of concentrated sulfuric acid (390 m*l*) and water (230 m*l*), and the mixture was heated on an oil bath (170—180°C) for 3.5 hr while being stirred. Water (1500 m*l*) was added to the reaction mixture, and the precipitate formed was collected by filtration. The crude material thus obtained was dissolved in aqueous ammonia and treated with active charcoal. VII (127.0 g) was obtained by the acidification of the filtrate with concentrated hydrochloric acid.

1, 5-Bis(carbomethoxy)naphthalene (VIII). The dicarboxylic acid (VII, 127.0 g) was mixed with methanol (1870 m*l*) and concentrated sulfuric acid (295 g), and the mixture was refluxed for a period of 28 hr. The crystals deposited when the reaction mixture was cooled, were collected by filtration and washed successively with a small amount of methanol, a 10% aqueous potassium carbonate solution and water, thus yielding the dimethyl ester (VIII, 128.1 g, 80.9% from V). The second crop (11.5 g) was obtained on concentrating the mother liquor. Mp 117—118°C (from methanol); (lit. value, 120°C[16]).

1, 5-Bis(hydroxymethyl)naphthalene (IX). The dimethyl ester (VIII, 97.7 g, 0.4 mol) was introduced by a Soxhlet technique, over a 7 hr period, into a stirred and refluxing mixture of lithium aluminum hydride (41.0 g, 1.08 mol) and ether (1600 m*l*). The mixture was stirred for another hour and then cooled on an ice-bath, after which the reaction mixture was treated with wet ether and diluted sulfuric acid successively. The solvent was carefully distilled off, and the water layer was chilled, resulting in the deposition of crystals. These crystals were washed with water and recrystallized from ethanol, yielding IX (52.7 g, 70%). The second crop (7.9 g) was obtained from the mother liquor. The sublimation of the crystals gave a pure specimen mp 185.5—186.5°C

[†] The effect of the interaction of the naphthalene bands on the diyne chromophore was calculated employing R=2.46 Å and θ=28°. The socillator strengths of the naphthalene bands were estimated to be f=0.81 (the β-band) and f=0.17 (the para-band), considering the oscillator strength and the ε-values of naphthalene itself. The results may be summarized as follows: 226 mμ-band, f'/f=8.00, ε=2880; 254 mμ-band, f'/f=1.36, ε=270; 240 mμ-band, f'/f=−1.55, ε=−.

12) K. Imahori and J. Tanaka, *J. Mol. Biol.*, **1**, 359 (1959).

13) S. Smoliński, *Tetrahedron Letters*, **1965**, 457.

14) J. F. Brown, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1402 (1964).

[††] All melting points are uncorrected. The electronic spectra were measured on a Hitachi ESP-2 autorecording spectrophotometer, while the infrared spectra were obtained by the KBr-disk method on a Hitachi EPI-2 infrared spectrophotometer.

15) H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, **1947**, 80.

16) G. Lock, *Monatsh.*, **81**, 850 (1950).

17) L. Friedman and H. Sechter, *J. Org. Chem.*, **26**, 2522 (1961).

(lit. value, 191.5°C (corr.)[18]).

1, 5 - Bis(propargyloxymethyl)naphthalene (X). A mixture of sodium hydride dispersion (in mineral oil; hydride content: 50%, 28.8 g, 0.6 mol), the glycol (IX, 28.2 g, 0.15 mol), and diethylene glycol dimethyl ether (250 *ml*) was vigorously stirred at room temperature for 30 min. After the temperature had gradually been raised to 130°C, stirring was continued for 8 hr at that temperature. To the stirred reaction mixture, which was allowed to cool to room temperature, there was added a solution of 3-bromo-1-propyne (71.4 g, 0.6 mol) in the same solvent (100 m*l*) over a period of 30 min. After the vigorous reaction had subsided, the mixture was heated to 65°C and stirred for 8 hr. The solvent was then distilled in vacuo below 100°C. Wet ether and then water were added to the residue, which was extracted with ether. The ethereal solution was washed with water, filtered to remove any insoluble material, and dried. The residue obtained upon evaporating the solvent was treated with petroleum ether in order to remove the mineral oil. The insoluble part was recrystallized from ethanol with the aid of active charcoal, resulting in the dipropargyl ether (X, 28.5 g, 72%) in the form of yellow crystals. Mp 79.7—80.5°C (from ethanol, 21.9 g).

Found: C, 81.64; H, 5.99%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

The Oxidative Coupling of X. Exposure to light was avoided throughout the course of the following reactions, and the solvents were removed at a low temperature under reduced pressure in a stream of nitrogen.

1) Under Ordinary Conditions. A mixture of X (1.0 g), cupric acetate monohydrate (10 g), and pyridine (100 m*l*) was stirred at 70°C for 15 min.⁵⁾ The coolded mixture was then filtered to remove the inorganic material. Pyridine was removed from the filtrate; then benzene was added to the residue, and again the solvent was distilled off. The residue was mixed with water and extracted with benzene (100 m*l*). The extract was washed successively with an aqueous cupric acetate solution and with water, and filtered to remove any insoluble material. The dried extract was concentrated, resulting in the deposition of yellow-brown crystals (0.42 g). The crude material in carbon tetrachloride was subjected to chromatography on alumina (Woelm, neutral, activity III). The crystals (0.13 g) obtained from the carbon tetrachloride - benzene (1 : 1) eluate were recrystallized from benzene, yielding the crystals of XIb-C_6H_6. The recrystallization of the crystals from carbon tetrachloride - dichloromethane yielded the cyclic dimer, XIb, mp 190—200°C (decomp.). Found: C, 82.03; H, 5.31%. Calcd for $(C_{18}H_{14}O_2)_n$; C, 82.42; H, 5.38%. Mol wt, Found: 549 (Rast). Calcd for $(C_{18}H_{14}O_2)_2$: 525. The crystalline material (0.11 g) obtained from the fractions eluted with benzene was recrystallized from benzene, resulting in the cyclic trimer, XIc as fine crystals (gradual decomposition was observed from 130°C). Found: C, 82.50; H, 5.56%. Calcd for $(C_{18}H_{14}O_2)_n$: C, 82.42; H, 5.38%. Mol wt, Found: 723 (Rast). Calcd for $(C_{18}H_{14}O_2)_3$: 787. The fractions eluted with ether and tetrahydrofuran gave a scarcely soluble material. This material could not be purified. However, the infrared spectrum, which was found to be closely related to that of XIc in lacking the absorption of terminal acetylene, suggests that the material was the cyclic tetramer (XI, $n=4$) or a mixture with a higher cyclic polymer.

2) Under Dilute Conditions. A solution of X (6.0 g) in pyridine (300 m*l*) was added into a stirred solution of cupric acetate monohydrate (60 g) in pyridine (1000 m*l*) at 60°C over a period of 20 hr. The reaction mixture was then concentrated to *ca.* 700 m*l*, and benzene was added to the concentrate in order to precipitate the inorganic material. After the inorganic material had been removed, the filtrate was concentrated to dryness. The residue was mixed with water and extracted with benzene. The extract was washed with an aqueous solution of cupric acetate and water. The dried extract was evaporated, and the solution of the residue in carbon tetrachloride was chromatographed on alumina (Woelm, neutral, activity III, 150 g). The fractions eluted with carbon tetrachloride - benzene (1 : 1) gave an unstable new substance (229 mg, 3.8%). The concentration of the solution of this substance in benzene-ethanol under reduced pressure at room temperature resulted in the deposition of crystals. The crystals were washed with ethanol and dried, yielding the cyclic monomer, XIa (193 mg), mp 160—170°C (decomp.). Found: C, 82.21; H, 5.40%. Calcd for $(C_{18}H_{14}O_2)_n$: C, 82.42; H, 5.38%. Mol wt, Found: 310 (Rast), 246 (osmometry in benzene)*, 246 (osmometry in tetrahydrofuran)*. Calcd for $(C_{18}H_{14}O_2)_1$: 262. XIb (220 mg, 3.7%) was obtained from the fractions eluted with carbon tetrachloride - benzene (1 : 2). The fractions eluted with benzene contained the crude XIc (288 mg, 4.8%).

1, 4-Bis(propargyloxymethyl)benzene (I). *1) From 1, 4-Bis(hydroxymethyl)benzene.* The 1, 4-glycol (8.6 g, 0.06 mol) in dioxane (80 m*l*) was converted to the disodio-derivative according to a procedure analogous to that described in the case of X, and then treated with propargyl bromide (14.3 g, 0.12 mol). The product was chromatographed on alumina, yielding crude I as pale yellow crystals (2.6 g, 20%).

2) From 1, 4-*Bis(chloromethyl)benzene.* The reaction of propargyl alcohol (6.7 g, 0.12 mol) with the dichlorocompound (8.8 g, 0.05 mol) in dioxane in the presence of finely-powdered potassium hydroxide (7.9 g, 0.14 mol) afforded I (3.15 g, 29.4%). Mp 34.2—34.7°C (from water-ethanol); colorless leaflets.

Found: C, 78.48; H, 6.61%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%. IR: 3300, 2105 cm^{-1}. UV: (in tetrahydrofuran) λ_{max} 225 (7340), 262 mμ (ε, 257).

The Oxidative Coupling of the Dipropargyl Ether (I). The oxidative coupling of I (1.0 g) according to Eglinton's method⁵⁾ (cupric acetate monohydrate, 10 g, pyridine, 120 m*l*, 20 min at 50°C) resulted in yellow crystals (0.4 g). Chromatography on alumina, followed by recrystallization from benzene, urnished the cyclic dimer, III (0.15 g), colorless prisms, mp 165.5—167°C (decomp.).

Found: C, 78.87; H, 5.69%. Calcd for $(C_{14}H_{12}O_2)_n$: C, 79.22; H, 5.70%. Mol wt, Found: 447 (Rast); 430 (isothermal distillation). Calcd for $(C_{14}H_{12}O_2)_2$: 425. UV: (in tetrahydrofuran) λ_{max} 226 (15560), 245 (1560), 259.5 mμ (ε, 1158).

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* A Mechrolab Model 301A vapor pressure osmometer was used.

2, 6-Bis(bromomethyl)naphthalene. The Wohl-Ziegler bromination of 2, 6-dimethylnaphthalene was carried out according a modification of the reported procedure.[19,20] Seventeen grams of 2, 6-dimethylnaphthalene afforded 19 g of the crude dibromo-compound (56%), which was then recrystallized from chloroform to give a pure specimen, mp 180—182°C (lit. value, 182°C[19]).

2, 6-Bis(hydroxymethyl)naphthalene. The dibromo-compound (104 g) was converted to the corresponding glycol *via* the diacetoxy derivative according to the method used for the preparation of the 2, 3-analogue.[21] The crude 2, 6-diacetoxymethyl-compound (75 g, 83.5%) was repeatedly recrystallized from ethanol, yielding a pure specimen, mp 130—132°C.

Found: C, 70.75; H, 6.00%. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%.

The hydrolysis of the diacetoxy-compound by means of an ethanolic solution of sodium hydroxide gave the crude glycol. The crude material was recrystallized from ethanol to give pure 2, 6-bis(hydroxymethyl)-naphthalene (37.6%) as colorless prisms, mp 169—170°C.

Found: C, 76.32; H, 6.35.%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

2, 6 - Bis(propargyloxymethyl)naphthalene. The reaction of the disodio-derivative of the 2, 6-glycol with propargyl bromide was carried out according to the procedure described in the case of the 1, 5-derivative, resulting in the 2, 6-dipropargyl ether in the form of thin plates, mp 77—78°C (78%).

Found: C, 81.47; H, 6.05%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

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