Cyclic Acetylenes. VI. Transannular and Proximity Effects in the Cyclic Derivatives of o, o′-Dihydroxydiphenyldiacetylene

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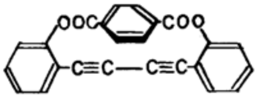
(Received December 9, 1960)

It was pointed out in Part II[1] of this series that the cyclic terephthalate of *o*, *o*′-dihydroxydiphenyldiacetylene (I) may be a suitable substance for the study of the transannular effect between the benzene ring of the bridging chain and the diacetylenic function. But the attempts to prepare I by the intramolecular oxidative coupling of 2-ethynylphenyl terephthalate gave unsatisfactory results. It was observed that the ester linkage is easily cleft during the course of oxidative coupling giving benzofurane derivatives. Therefore the authors have carried out the synthesis of an analogous substance of I in which the ester linkage is replaced by ether linkage.



I

Sodium *o*-ethynylphenoxide (II) was treated with *p*-xylylene dibromide to yield the terminal diacetylene III. Oxidative coupling of III, according to Eglinton's procedure[2], gave the cyclic diacetylene IV in 25% yield. The monomeric nature of IV was inferred from the molecular weight of the octahydroderivative V, since IV itself was found to have a poor solubility in camphor.

As illustrated in Fig. 1, the scale model of IV indicates that the molecule is almost strain

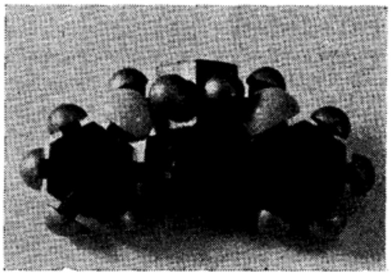
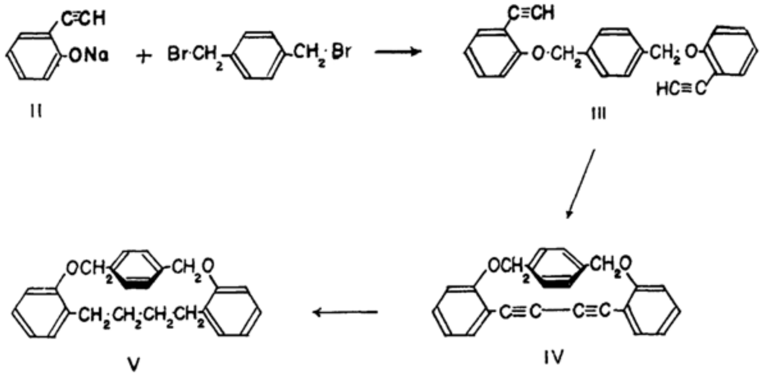


Fig. 1. The molecular model of IV (Courtauld model).



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[1] F. Toda and M. Nakagawa, This Bulletin, 33, 230 (1960).

[2] G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889.

free and the benzene nucleus in the bridging chain is held closely parallel to the diacetylenic linkage. A part of the infrared spectra of III, IV and V are recorded in Fig. 2. The absorption bands arising from the out-of-plane deformation of the adjecent two hydrogen atoms in the *p*-disubstituted benzene nucleus appeared at 814 cm^{-1} and 796 cm^{-1} in the case of III, whereas the corresponding absorption band shifted to 776 cm^{-1} and 785 cm^{-1} in IV and V, respectively. The infrared spectroscopic anomalousness of IV and V can be explained on the basis of a non-bonded interaction of hydrogen atoms in the benzene nucleus of the bridging chain with the diacetylenic linkage or with the $-(CH_2)_4-$ chain which is held in a proximate position to the hydrogen atoms. As indicated in Fig. 3 and Table I, the ultraviolet spectrum of IV also shows an anomalous feature. Loss of the sharpness and the marked decrease of the absorption intensities of the peaks at the longer wavelength region were observed in the spectrum of IV as compared with that of the open chain analogue, *o,o'*-dibenzyloxydiphenyldiacetylene (VI)[3].

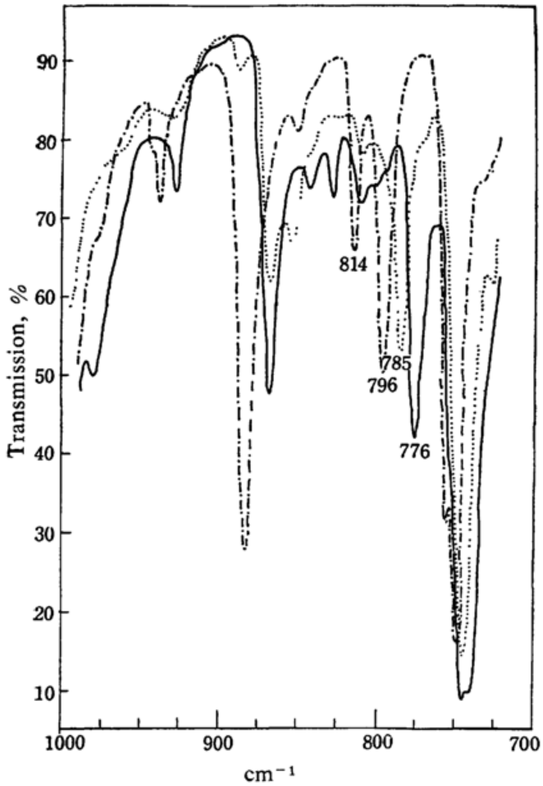


Fig. 2. The infrared spectra of III, IV and V.
-·-·- : III —— : IV ······ : V

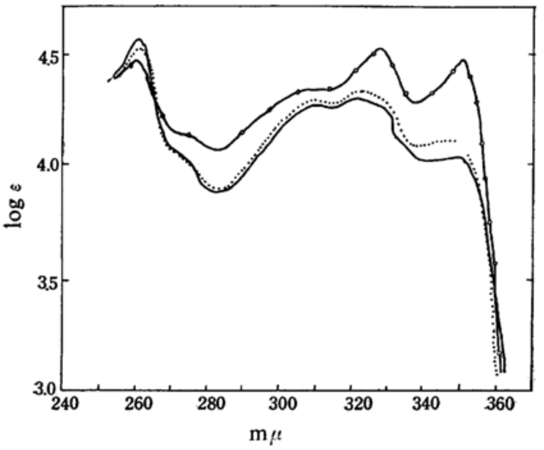
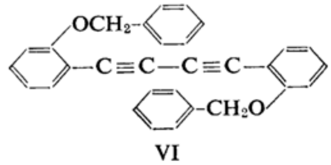


Fig. 3. The ultraviolet spectra of the cyclic diacetylene (IV), the cyclic tetraacetylene (IX) and the open chain analogue (VI) (in dioxane).
······ : IV —— : IX -○-○ : VI

TABLE I

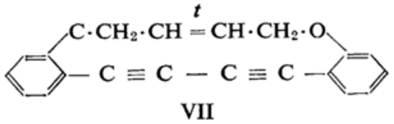
Compound	Absorption				
IV	261 (322)	**275** (105)	310 (189)	322 (208)	346 (127)
VI	261 (287)	**275** (130)	310 (212)	328 (323)	351 (285)
IX	261 (350)	**275** (105)	310 (185)	321 (196)	349 (115)

All spectra were measured in dioxane.
The figures indicate the λ_{max} in mμ.
The figures in parentheses are $\varepsilon_{max}\times10^{-2}$.
The bold figures indicate shoulders.



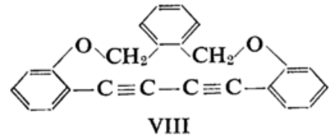
VI

It is to be noted that the ultraviolet spectrum of VII[3] also showed broad absorption peaks. On the other hand, the *ortho*-isomer of IV (VIII)[3] has a well defined, fine structure in



VII

the ultraviolet spectrum, in spite of the shifts in the absorption peaks. As already discussed in the preceding paper, the *trans*-ethylenic



VIII

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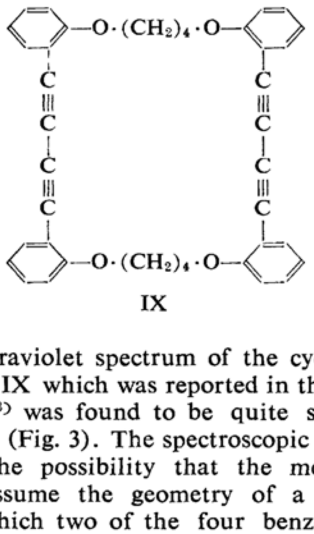
[3] F. Toda and M. Nakagawa, This Bulletin, 34, 862 (1961).

bond in VII is held closely to the diacetylenic function; on the contrary, the *o*-xylylene group in VIII is fixed fairly far apart from the diacetylenic linkage. Therefore the anomalousness in the ultraviolet spectra of IV and VII is probably associated with a transannular interaction of π-electrons in the bridging chain with those of the diyne function.

As already pointed out in the previous papers[3,4], the strained cyclic derivatives of *o*, *o*'-dihydroxydiphenyldiacetylene have a sharp and intense $\lambda_{\min}$ at ca. 260 mμ in their ultraviolet spectra, and the presence of this $\lambda_{\min}$ was attributed to a proximity effect of *o*, *o*'-bridging chain to the diacetylenic linkage. The ultraviolet spectrum of IV lacks the $\lambda_{\min}$, but has a $\lambda_{\max}$ at the same wavelength. An examination of the scale model of IV reveals that the methylene groups in the benzyl position of the bridging chain are fixed fairly far apart from the diacetylenic function owing to the presence of the rigid benzene nucleus. As the result of the above-mentioned spatial position of the methylene groups, there might be no proximity effect to operate in IV, in spite of the fact that the cycle has a short bridging chain.



IX

The ultraviolet spectrum of the cyclic tetraacetylene IX which was reported in the preceding paper[3] was found to be quite similar to that of IV (Fig. 3). The spectroscopic similarity suggests the possibility that the molecule of IX can assume the geometry of a puckered ring in which two of the four benzene rings are faced to the diacetylenic functions making it possible for some transannular effect to operate (Fig. 4).

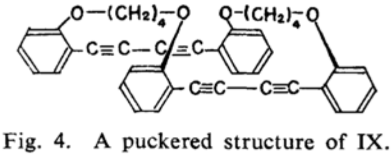


Fig. 4. A puckered structure of IX.

Experimental*

Synthesis of 1,4-Bis-(*o*-ethynylphenoxymethyl)-benzene (III).—*o*-Hydroxyphenylacetylene (3.54 g., 0.03 mol.) was dissolved in a solution of sodium ethoxide in ethanol (sodium, 0.69 g., 0.03 mol. and absolute ethanol, 10 ml.) and the solvent was removed in vacuo. The sodium phenoxide thus obtained was mixed with *p*-xylylene dibromide (3.96 g., 0.015 mol.), a catalytic amount of potassium iodide and dimethylformamide (25 ml.). After being refluxed for 2.5 hr., the mixture was cooled and poured into ice-water. The solid deposited was filtered and then washed with water and ethanol. The dried material was repeatedly recrystallized from ethanol giving III, colorless prisms or needles, m. p. 93~94°C, 3.90 g. (78%).

Found: C, 84.91; H, 5.40. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

IR max., 3280 (-C≡CH), 2940, 2880 (ν CH), 2110 (-C≡C-), 1470, 1386 (δ CH), 1242 (=C-O-), 814, 796 (*p*-disubst. benzene), 740 (*o*-disubst. benzene) cm^{-1}.

Oxidative Coupling of III.—The mixture of III (1.5 g.), cupric acetate monohydrate (15 g.) and pyridine (150 g.) was stirred for 4 hr. at 50°C. The reaction mixture was cooled and the crystals deposited were filtered and then washed with water and ethanol. The filtrate was concentrated under reduced pressure yielding crystals. The crystals were washed with water and ethanol, and combined with the first crop. Repeated recrystallization of the combined material from benzene afforded cyclic diacetylene IV, colorless needles, m. p. 274~275°C (decomp.), 370 mg. (25%).

Found: C, 85.34; H, 4.99, Mol. wt., 354. Calcd. for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%, Mol. wt., 336.

IR max., 2920, 2870 (ν CH), 2220, 2150 (-C≡C-), 1380 (δ CH), 1245, 1220 (=C-O-), 776 (*p*-disubst. benzene), 746 (*o*-disubst. benzene) cm^{-1}.

Hydrogenation of IV.—IV (210 mg.) was hydrogenated in benzene (100 ml.) over 5% palladium-on-charcoal (20 mg.). After removal of the catalyst, the solvent was distilled, resulting in crystals. On recrystallization from ethyl acetate-ethanol or benzene-petroleum ether (b. p. 60~70°C) the crystals afforded **V** in quantitative yield, colorless needles, m. p. 195~197°C.

Found: C, 83.67; H, 6.83, Mol. wt., 381. Calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02%, Mol. wt., 344.

IR max., 2930, 2860 (ν CH), 1380 (δ CH), 1230 (=C-O-), 785 (*p*-disubst. benzene), 745 (*o*-disubst. benzene) cm^{-1}.

The authors are grateful to the Ministry of Education for the Grant-in-Aid for fundamental scientific research.

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[4] F. Toda and M. Nakagawa, 33, 223 (1960).

[*] All melting points were not corrected. The infrared spectra were measured by KBr-disk method. The microanalyses were performed by Mr. M. Okumiya of the microanalytical laboratory of this Department.