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SYNTHESIS AND PROPERTIES OF PARACYCLOPHADIYNES*

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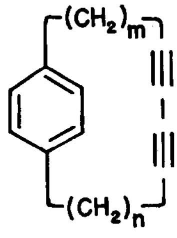
In various types of bridged systems[1], two chromophoric groups separated from each other frequently exhibit unusual behavior or transannular interaction, provided they are fixed at very closed positions in the same molecule as in the cases of paracyclophanes[2] and cyclic tetraacetylenes[3]. Furthermore, severe strain which forces to deform the aryl nucleus from its normal planar configuration in the ring system can cause anomalous behavior both in the chemical and in the physical properties of the systems.



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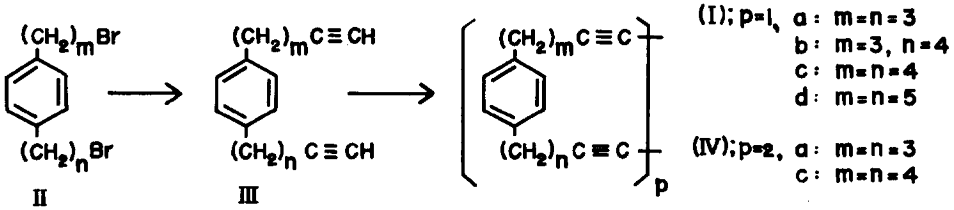
In this communication, we wish to report the synthesis and the properties of four paracyclophadiynes (I), in which each α-diacetylene unit and benzene nucleus are mutually close for electronic interaction to take place.

Bis-ethynyl compounds (III) were prepared in good yields by the reaction of dibromides (II) with sodium acetylide in N-methyl-2-pyrrolidone. The intramolecular cyclization of the compounds (III) was carried out by the Eglinton's oxidative coupling[4] with high-dilution technique under nitrogen atmosphere. The following chromatography on alumina of the coupling products afforded a cyclic monomer (I) with a cyclic dimer (IV). The structure of these cyclic compounds (I and IV) was established by NMR spectra,



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* This paper is dedicated to Emeritus Professor Munio Kotake in commemoration of his 75th birthday, Nov. 30, 1969.

elemental analysis and molecular weight determination. These data are listed in Table 1 and 2.

Table 1. Molecular Weight and Analytical Data of Ia∼Id, IVa and IVc

Compound	Mol. Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. Wt. Calcd.	Mol. Wt. Found*	m.p. °C	Yield*** %
(Ia)	$C_{16}H_{16}$	92.26	92.00	7.74	7.82	208	207	134-135	21.3
(Ib)	$C_{17}H_{18}$	91.84	91.99	8.16	8.18	222	214	86-87.5	37.2
(Ic)	$C_{18}H_{20}$	91.47	91.32	8.53	8.49	236	239	72-73** 76-77**	46.6
(Id)	$C_{20}H_{24}$	90.85	90.64	9.15	9.23	264	260	108-109	26.1
(IVa)	$C_{32}H_{32}$	92.26	92.14	7.74	7.73	416	417	158-159	10.6
(IVc)	$C_{36}H_{40}$	91.47	91.31	8.53	8.47	472	469	163-164	12.4

* Osmometry in benzene. ** Polymorphic forms. *** Based on III.

Table 2. NMR Spectral Data of Ia∼Id, IVa and IVc in Carbon Tetrachloride

Compound	Aromatic Protons τ-Value	Aromatic Protons Pattern	Aromatic Protons No.	Benzylic Protons τ-Value	Benzylic Protons Pattern	Benzylic Protons No.
(Ia)	2.83	s	4	7.1-7.4	m	4
(Ib)	2.96	A_2B_2	4	7.1-7.3* 7.3-7.6**	m m	2 2
(Ic)	3.00	s	4	7.3-7.6	m	4
(Id)	3.00	s	4	7.2-7.5	m	4
(IVa)	2.93	s	8	7.22	t	8
(IVc)	2.99	s	8	7.43	t	8

* Benzylic protons in trimethylene bridge. ** Benzylic protons in tetramethylene bridge.

The NMR spectral data of the cyclic monomers and dimers are shown in Table 2. Table 2 indicates that as the methylene bridge becomes shorter, the bands of the aromatic protons of Ia∼Id tend to move toward slightly lower field. This shift should be attributed to the long-range shielding effect of the conjugated diacetylenic bond, because deformation of the benzene ring from a planar configuration shifts them to higher field. Further studies of the spectrum of Ia at variable temperature are in progress.

Fig. 1 records the electronic spectra of cyclic monomers (I) as well as that of a cyclic dimers (IVc) as a reference compound. A remarkable change is observed on the spectra of Ia and Ib in contrast with those of the others. Also, the absorption curves of Ia and Ib are similar

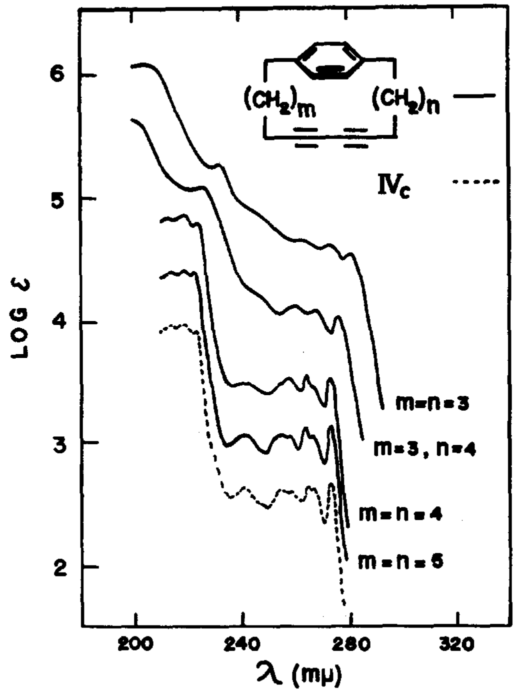

Fig. 1. Electronic spectra of paracyclophadiynes in cyclohexane. The ε-value of the cyclic dimer (IVc) at the bottom is reduced to give the value for the unit chromophoric groups, i.e., ε/2. The curves are displaced upward successively by 0.5 log ε unit from the curve immediately below.

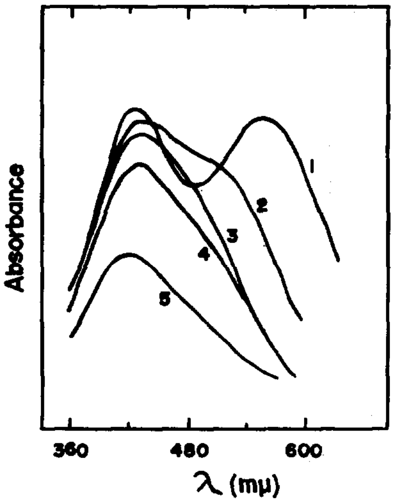

Fig. 2. Electronic spectra of the paracyclophadiyne-TCNE complexes in dichloromethane. Curves are identified by the π-base of the complex as follows: curve 1, paracyclophadiyne (I)(m=n=3); curve 2,(m=3,n=4); curve 3,(m=n=4); curve 4,(m=n=5); curve 5, cyclic dimer(IVc).

to each other, although they seem to possess highly and slightly strained structures, respectively, from the examination of skeletal model. It is inferred, from comparison with the spectra of [n]-paracyclophanes[5] and cyclic tetraacetylenes[6], that the anomalous behavior of these spectra is not caused solely by deformation of the benzene nucleus and the diyne unit. Consequently, it is obvious that the transannular interaction between a benzene nucleus and a conjugated diyne unit should arise in these paracyclophadiynes (Ia and Ib). In addition, the spectrum of Ic exhibits remarkable hypochromic effect in comparison with the similarity on the absorption curves of Ic and IVc.

The electronic spectra of the paracyclophadiyne-TCNE complexes in dichloromethane are shown in Fig. 2. The shorter wavelength maxima of these spectra occur at the nearly equal position, i.e.,~430 mμ. On the other hand, the longer wavelength bands, of which positions are uncertain except that of Ia, show bathochromic shifts and hyperchromic effects as shortening of the methylene chain. In particular, the longer wavelength band of the complex of Ia occurs at even longer wavelength than those of the others and further is distinctly separated from the shorter wavelength band. This interesting behavior, observed on the electronic spectra of Ia, Ib and the TCNE complexes, will be discussed with relation to those structures in a future paper.

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