Layered Compounds. V.[1] Synthesis and Properties of [*m.n*]Paracyclophadiynes

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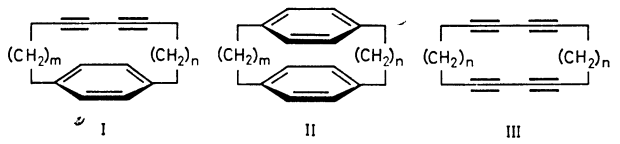
A series of bisethynyl compounds, IX and XII, were prepared by a modified ethynylation using *N*-methyl-2-pyrrolidone in good yields. Intramolecular oxidative coupling of the bisethynyl compounds has been achieved with high-dilution technique to give relatively good yields of highly strained or strainless [*m.n*]paracyclophadiynes I and cyclic diacetylenes XIII. From the comparison of the electronic spectra of these diacetylenic compounds, it is concluded that abnormal spectra of Ic and Id are attributed to the transannular π-electronic interaction between benzene nucleus and diacetylenic unit rather than the ring strain in the molecules. In addition, a marked down-field shift of aromatic protons in Ic compared with the other paracyclophadiynes is explained in terms of the transannular shielding effect of diacetylenic linkage.

In various types of bridged systems[2], two or more chromophoric groups separated from each other frequently exhibit anomalous behavior when they are forced to bring close together as in the case of [*m.n*]-paracyclophanes. Since an increased proximity of the groups necessarily brings about a severe strain in the molecule owing to a mutual π-orbital repulsion, the resulting strain sometimes makes it difficult to explain the anomalous physical properties of such distorted molecules in terms of a transannular interaction of π-orbitals.

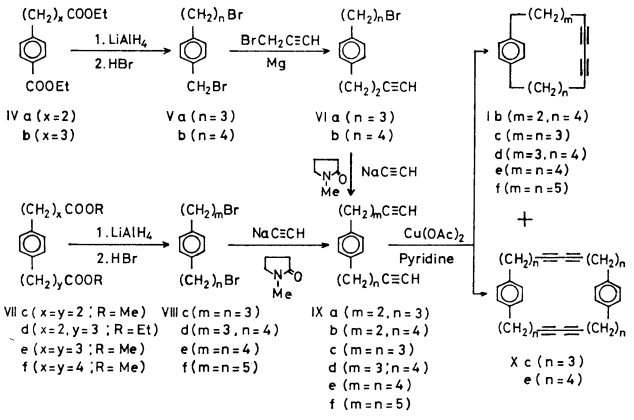


There have been systematic surveys of [*m.n*]paracyclophanes (II),[3] cyclic tetraacetylenes(III),[4] and multilayered cyclophanes[5] in view-points of the transannular interaction and the strain effect. They showed unambiguous evidences supporting the transannular interaction. On the other hand, there are only a few studies on the interaction in bridged compounds containing different chromophoric groups, since a superposition of absorption bands due to both groups often makes a spectral elucidation difficult. Cram and Antar[6] reported two of [*n*]paracyclophyne containing a monoacetylene group in its bridge chain. However, any evidence for transannular electronic interaction could not be observed there.

From examinations of scale models, it has been expected that paracyclophadiynes I are well suitable model compounds for the study of the transannular electronic interaction between a benzene nucleus and a conjugated diacetylene group. It is well known that a variety of highly strained diacetylenic compounds could have been prepared by oxidative coupling reaction of terminal bisethynyl compounds like IX.[7] Thus we have undertaken to investigate a relationship among methylene chain length and the physical properties of paracyclophadiynes I. In this paper we report the synthesis and the spectral properties of I. The name "[*m.n*]paracyclophadiyne" is used here in place of *a,b*-[*n'*]paracyclophadiyne for convenience, in which *m* and *n* are numbers of methylene group, *e.g.* for Ic [3.3]paracyclophadiyne instead of 4,6-[10]paracyclophadiyne.

Results and Discussion

Synthesis. All of the paracyclophadiynes (I) were prepared by the general synthetic sequence outlined in Scheme 1. Cyclic diacetylenes XIII and tetraacetylenes XIV were synthesized as spectral reference compounds (Scheme 2).



Scheme 1. A synthesis of paracyclophadiynes.

In some preliminary experiments, bisethynyl compounds IX were obtained by bisethynylation of dibromides VIII in ether with liquid ammonia solution of sodium acetylide in autoclave at room temperature in reasonable yields, 79% for $m=n=3$ and

1) The paper by T. Matsuoka, Y. Sakata, and S. Misumi (*Tetrahedron Lett.*, **1970**, 2549) is to be considered Part IV of this series.

2) B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y. (1964).

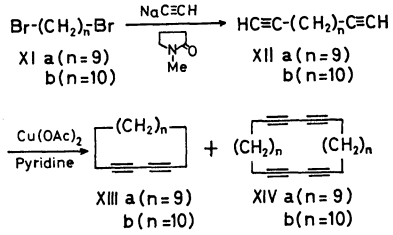
3) For review; D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959).

4) F. Sondheimer, Y. Amiel, and R. Wolovsky, *J. Amer. Chem. Soc.*, **79**, 6263 (1957).

5) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, *Chem. Commun.*, **1971**, 678; *Tetrahedron Lett.*, **1971**, 4803; S. Mizogami, T. Otsubo, Y. Sakata, and S. Misumi, *ibid.*, **1971**, 2791.

6) D. J. Cram and M. F. Antar, *J. Amer. Chem. Soc.*, **80**, 3109 (1958).

7) O. M. Behr, G. Eglinton, A. R. Galbraith, and A. R. Raphael, *J. Chem. Soc.*, **1960**, 3614; M. Morimoto, S. Akiyama, S. Misumi, and M. Nakagawa, This Bulletin, **35**, 857 (1962); A. J. Hubert and J. Dale, *J. Chem. Soc.*, **1963**, 86; R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965); R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968).



Scheme 2. A synthesis of cyclic acetylenes.

74% for $m=n=4$, accompanied with a small amount of olefinic compounds. After examining several experimental conditions, we observed a more convenient procedure by which the bisethynyl compounds IX were likewise afforded in good yields at atmospheric pressure by the use of *N*-methyl-2-pyrrolidone in place of ether as a co-solvent. This facile procedure was also applied to permit good yields of bisethynyl alkanes XII as shown in Table 1.

On the other hand, bisethynyl compounds, IXa and IXb, each containing a butynyl group were synthesized through stepwise ethynylations as shown in Scheme 1. Thus monoethynyl bromoderivatives VI (a and b) were obtained by the reaction of dibromides V with propargylmagnesium bromide in 80 and 96% yields, respectively. The following ethynylation of VI gave bisethynyl compounds IX (a and b), 77% and 89%, in a same manner stated above. Analytical data and the physical properties of the bisethynyl compounds IX and XII are shown in Table 1.

The paracyclophadiynes I were obtained by Eglinton's oxidative reaction[8] of IX with a high-dilution

Table 1. Analytical data and physical properties of IX and XII

Compound	Mol. Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	[Mp] or Bp/mmHg °C	Yield %	ν_{max} (-C≡CH) cm^{-1}
IXa	$C_{15}H_{16}$	91.78	91.67	8.22	8.36	92—94/0.15	76.9	3286, 2119[f]
IXb	$C_{16}H_{18}$	91.37	91.03	8.63	8.49	124—126/2	88.9	3268, 2110[f]
IXc	$C_{16}H_{18}$	91.37	91.10	8.63	8.61	[49.5—50.5][a]	85.7	3247, 3231, 2108[g]
IXd	$C_{17}H_{20}$	91.01	90.94	8.99	9.27	112—114/0.07	77.6	3269, 2110[f]
IXe	$C_{18}H_{22}$	90.70	90.67	9.30	9.34	[18—19][a]	87.7	3266, 2110[f]
IXf	$C_{20}H_{26}$	90.16	90.08	9.84	10.00	[51—52][b]	86.0	3239, 3222, 2104[g]
XIIa	$C_{13}H_{20}$	88.56	88.63	11.44	11.56	81—83/2	87.6 (81)[e]	3275, 2112[f]
XIIb	$C_{14}H_{22}$	88.35	87.89	11.65	11.97	[32.5—33.5][c] [33—34][d]	90.5 (57)[d]	3283, 3257, 2106[g] (3274, 2100)[d]

a) From petroleum ether at −20°C. b) From *n*-pentane at −20°C. c) From ethanol at −20°C. d) From Ref. 8. e) From Ref. 9. f) Liquid film. g) Nujol mull.

Table 2. Molecular weight, analytical data, and physical properties of I, X, XIII, and XIV

Compound	Mol. Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Mol wt Calcd	Mol wt Found	Mp °C	Yield %	Crystal Form	ν_{max}(-C≡C-) cm^{-1}
Ib	$C_{16}H_{16}$	92.26	92.32	7.74	7.58	208	205[a] 208[b]	69.5—70.5	41.1	prisms[g]	2243[k], 2248[l]
Ic	$C_{16}H_{16}$	92.26	92.00	7.74	7.82	208	207[a] 208[b]	134—135	21.3	thick plates[h]	2247, 2153[k]
Id	$C_{17}H_{18}$	91.84	91.99	8.16	8.18	222	214[a] 222[b]	86—87.5	37.2	prisms[h]	2253, 2160[k]
Ie	$C_{18}H_{20}$	91.47	91.32	8.53	8.49	236	214[a] 236[b]	72—73[c] 76—77[c]	46.6	plates[g] thick plates[g]	2248, 2156[k,m] 2257, 2163[l]
If	$C_{20}H_{24}$	90.85	90.64	9.15	9.23	264	260[a] 264[b]	108—109	26.1	plates[h]	2252, 2164[k]
Xc	$C_{32}H_{32}$	92.26	92.14	7.74	7.73	416	417[a] 416[b]	158—159	10.6	plates[i]	2249, 2142[k]
Xe	$C_{36}H_{40}$	91.47	91.31	8.53	8.47	472	469[a] 472[b]	163—164	12.4	needles[l]	2253, 2162[k] 2262, 2167[l]
XIIIa	$C_{13}H_{18}$								55.2	liquid[j]	2246, 2163[n]
XIIIb	$C_{14}H_{20}$	89.29	89.01	10.71	11.14	188	188[b]	d	71.7 (17)[f]	liquid	2250, 2151[n] (2215, 2132)[f]
XIVa	$C_{26}H_{36}$	89.59	89.32	10.41	10.48	348	348[b]	141.5—142 (142)[e]	*ca.* 1	needles[i]	2258, 2162[k]
XIVb	$C_{28}H_{40}$	89.29	89.29	10.71	10.57	376	376[b]	100—101 (101—102)[f]	*ca.* 2	needles[g]	

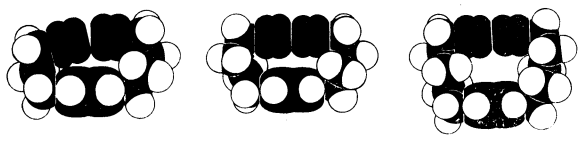
a) By vapor pressure osmometry. b) By mass spectrometry. c) Dimorphism. d) Evaporative distillation, *ca.* 100°C (bath temp.)/1 mmHg. e) From Ref. 9. f) From Ref. 8. g) From *n*-pentane at −20°C. h) From petroleum ether at −20°C. i) From cyclohexane. j) After chromatography. k) Nujol mull. l) CCl_4 soln. m) For the higher melting point crystals. n) Liquid film.

technique for intramolecular cyclization. The oxidative coupling reaction was achieved with dropwise addition of dilute ether solution of IX for a period of 80—110 hr to anhydrous cupric acetate in pyridine at 85—95°C under nitrogen atmosphere. Chromatography of the coupling products on alumina gave the desired cyclic monomers Ib—f in relatively good yields (47—21%) together with by-product, cyclic dimers X. It is noteworthy that nitrogen atmosphere during the oxidative coupling is presumably necessary to avoid air oxidation of the coupling products, because the coupling reaction of IX in air atmosphere gave a low yield of I, *e.g.* only 8% yield of Ie from IXe. As cyclic diacetylenes, XIIIa and XIIIb, were also afforded by this procedure in 55 and 72% yields, the procedure is excellently applicable to general preparation of cyclic conjugated diacetylenes. The latter compound XIIIb had been previously synthesized under normal Eglinton's condition in a 17% yield.[8] A new compound XIIIa, 1,3-cyclotridecadiyne, is the smallest one of monocyclic conjugated diacetylenes known so far and is highly strained on consideration with a skeletal model. It was observed that this compound is thereby unstable and becomes rapidly orange after isolation, but the dilute solution can be kept for a month at −20°C. All of the paracyclophadiynes I obtained above can be kept without decomposition in diffused light at room temperature.

An attempted synthesis of extremely strained paracyclophadiyne I with $m=2$, $n=3$ failed, but afforded a mixture of cyclic dimer X consisted of two possible isomers.

Analytical data and the physical properties of cyclic di- and tetra-acetylenes I, X, XIII, and XIV are summarized in Table 2.

Geometry of Paracyclophadiynes. An examination of Stuart-Briegleb model for paracyclophadiynes Id—f reveals that in each molecule a benzene nucleus is held parallel to a diacetylene group in the bridge chain and its mutual distance becomes shorter with decreasing number of methylenes in the diacetylene bridge as shown in Fig. 1. [3.3]- and [2.4]-Paracyclophadiynes can not be constructed with this type of model. On the other hand, examination with Dreiding model suggests that two isomeric forms should be present in a highly strained molecule, [3.3]-paracyclophadiyne Ic (Fig. 2). The cyclophadiyne Ic, however, exhibits no evidence for the presence of such isomers on the NMR spectrum even at low temperature as described below. Therefore, it is quite interesting to investigate the mutual arrangement of



Id Ie If

Fig. 1. The molecular models of I. (Stuart-Briegleb model)

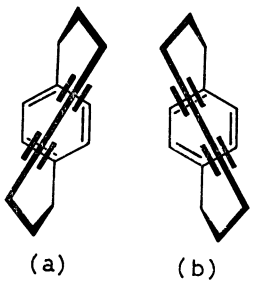


Fig. 2. Two possible isomeric forms of Ic on a consideration of Dreiding Model.

the benzene nucleus and the diacetylene group in the molecule.

Recently the exact molecular structure of [3.3]-paracyclophadiyne was determined with X-ray by Tanaka *et al.*[10] (Fig. 3 and 4). The figures show that the structure of the molecule is characterized as follows: a) atomic group C–C≡C–C≡C–C in Ic is forced to bend by 6—11° from its normal linear arrangement. Both the triple bonds are held with shorter bond lengths than that (1.208 Å)[11] in dimethyldiacetylene, b) the benzene nucleus is less distorted than the benzene nuclei in [3.3]paracyclophane, c) a particular bond angle in the trimethylene chain is unusually greater than the normal, *i.e.* 120.1° or 126.7°, d) the C–C≡C–C≡C–C group is parallel to an axis linked through substituted benzene atoms, C_{11} and C_{14}, as opposed to the examination of Dreiding model (see Fig. 4), e) two shortest distances between

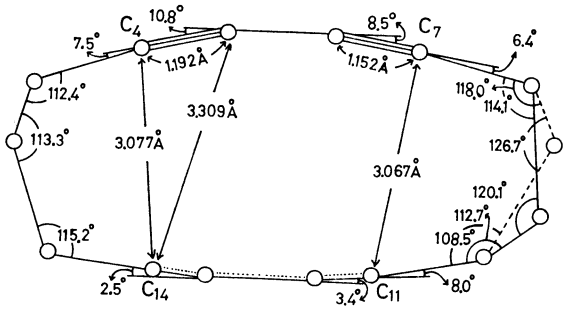


Fig. 3. Profile of crystal structure of [3.3]paracyclophadiyne.

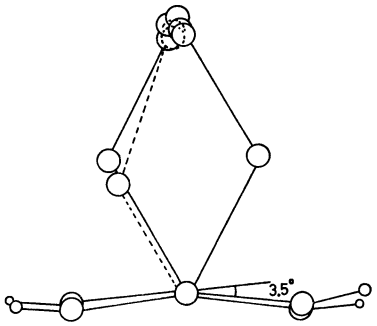


Fig. 4. Profile of crystal structure of [3.3]paracyclophadiyne.

8) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.
9) J. Dale, A. J. Hubert, and G. S. D. King, *ibid.*, **1963**, 73.
10) T. Aono, C. Katayama, K. Sakabe, T. Sakabe, and J. Tanaka, The 24th Annual Meeting of The Chemical Society of Japan, Summary 13330, Osaka, April, 1971.
11) A. Almenningen, O. Bastriansen, and T. Munthe-Kaas, *Acta Chem. Scand.*, **10**, 261 (1956).

both π-electron systems, 3.067 and 3.077 Å, are much shorter than a minimum distance (3.14 Å)[12] between two benzene nuclei in [3.3]paracyclophane.

The structural features of [3.3]paracyclophadiyne above-stated are most likely interpreted on the basis of a repulsive force arising from enormous π-orbital overlap between the diacetylene group and the benzene nucleus. Of several highly strained cyclic compounds containing a diacetylenic linkage isolated from the other chromophoric groups, [3.3]paracyclophadiyne is the first one of which exact structure was determined.

Nuclear Magnetic Resonance Spectra. The NMR spectra of [*m.n*]paracyclophadiynes I, cyclic dimers X, and open chain compound IX are illustrated in Table 3. It shows that chemical shifts of aromatic protons other than the Ic aromatic protons are about the same as that of the open chain compounds IX. Thus it can be considered that there is no appreciable effect of diacetylenic linkage on the chemical shifts of Id—f because of elongated distances. The aromatic protons of [2.4]homologue Ib appeared also at nearly the same position, indicating that the magnetic effect of diacetylenic linkage is negligible even in such a highly strained molecule. It was observed in a series of [*n*]paracyclophanes[13] that the chemical shift of aromatic protons was little varied even if the benzene ring is highly distorted.

Table 3. The chemical shifts of the aromatic protons of I[a], IXc[a], and X[b] in CCl_4 at room temperature

Compound	τ-Value	Pattern	No.
Ib	3.01	s	4
Ic	2.81	s	4
Id	2.97	AA'BB'	4
Ie	2.99	s	4
If	2.99	s	4
IXc	3.01	s	4
Xc	2.88	s	8
Xe	3.01	s	8

Concentration a) 0.14 M, b) 0.06 M.

In the other strained cyclophadiyne Ic, on the other hand, the aromatic protons were found to appear at down-field by *ca.* 0.2 ppm compared with strainless homologues (Table 3). Therefore, this down-field shift should be attributed to the transannular shielding effect from magnetic anisotropy of diacetylenic bond. It remains questionable that the aromatic protons of Id appeared as an expected AA'BB' pattern but those of Ib unexpectedly as a sharp singlet, in same relationship observed for the aromatic protons of [2.4]- and [3.4]-paracyclophanes.[14]

The spectra of methylene protons in I are showed in Fig. 5. The three signals in Ie and If are respectively assigned to benzylic, propargylic, and the rest methylene protons from lower field. The benzylic protons of I appear in a range of 6.9—7.7 τ as complexed multiplets. Unsymmetric paracyclophadiyne Id showed two multiplets at 7.1—7.3 and 7.3—7.6 τ, in which benzylic protons in trimethylene bridge and in tetramethylene bridge respectively were assigned from comparison with [3.3]- and [4.4]-homologues. In the spectrum of Ib a complexed signal at 7.3—7.7 τ is explainable by which the higher field counterpart of A_2B_2 pattern of the dimethylene bridge protons is superimposed with the benzylic protons in the tetramethylene bridge. The propargylic protons in the tetramethylene bridge appeared at 8.1 τ. A remarkable difference between the chemical shifts of two pairs of propargylic protons in Ib seems to be attributed to a difference in shielding effect of benzene ring due to methylene bridge length.

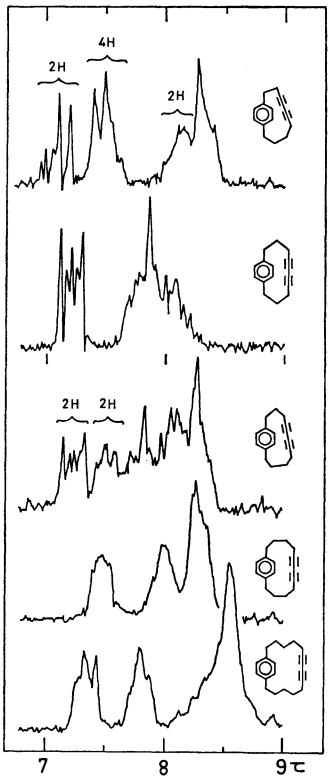


Fig. 5. The NMR spectra of the methylene protons in paracyclophadiynes (60 MHz, in CCl_4, at room temp.).

A long-range shielding effect of diacetylenic linkage is probably responsible to slight down-field shifts of benzylic protons in Ic and in shorter methylene bridges of Ib and Id. In order to confirm this shielding effect, cyclic diacetylenes XIII, in which the majority of protons might be located above the diacetylene linkage, were chosen to examine. Table 4 records the chemical shifts of the propargylic protons and the other methylene protons (τ-values at absorption maxima) in XIII and XIV together with cycloalkanes. Although the propargylic protons of XIII and XIVb

12) P. K. Gantzel, C. L. Coulter, and K. N. Trueblood, *Angew. Chem.*, **72**, 755 (1960); P. K. Gantzel and K. N. Trueblood, *Acta Crystallogr.*, **18**, 958 (1965).

13) D. J. Cram and M. Goldstein, *J. Amer. Chem. Soc.*, **85**, 1063 (1963); H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).

14) D. J. Cram and R. C. Helgeson, *ibid.*, **88**, 3515 (1966).

15) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

Table 4. The NMR spectral data of XIII and XIVb in CCl_4

Compound	Propargylic protons			Other methylene protons		
	τ-Value	Pattern	No.	τ-Value	Pattern	No.
XIIIa	7.80	br t	4	8.48	br s	14
XIIIb	7.80	br t	4	8.48	br s	16
XIVb	7.76	br t	8	8.65	br s	32
Cyclotridecane				8.64 (8.652)[a]		
Cyclotetradecane				8.66 (8.670)[a]		

a) From Ref. 15.

Table 5. The electronic spectral data of Ib—If and Xe in cyclohexane

Compound	λ_{max} in nm and $\varepsilon \times 10^{-2}$ in parentheses									
Ib	199	215[a]	222.5	227[a]	248	261.5	267	276		
	(189)	(61.0)	(56.1)	(47.5)	(4.07)	(4.22)	(4.02)	(3.34)		
Ic	206	233	265	273.5	282					
	(132)	(20.4)	(4.34)	(4.04)	(3.33)					
Id	200	227	245[a]	261	268	276.5				
	(154)	(41.8)	(5.11)	(4.11)	(3.70)	(3.24)				
Ie	214.5	221	225	241[a]	243.5	257.5	259.5	265	267[a]	273.5
	(66.4)	(67.6)	(58.4)	(3.03)	(3.04)	(3.36)	(3.36)	(3.56)	(3.02)	(3.40)
If	214.5	220	225	241	248[a]	257	260	265.5	268	274
	(85.2)	(88.7)	(79.5)	(3.61)	(2.59)	(3.54)	(3.39)	(4.04)	(3.42)	(4.30)
Xe	214	219.5	224	241.5	247[a]	255	259.5	265	267.5	273.5
	(181)	(181)	(153)	(8.58)	(6.14)	(8.28)	(7.89)	(8.85)	(8.26)	(9.34)

a) shoulder

appear at nearly the same position, the other methylene protons (broad singlet) of XIIIa and XIIIb are shifted by 0.17 ppm to down-field from those of XIVb and cycloalkanes. Since XIIIa would considerably be strained and XIIIb be strainless from the examination of model, same chemical shift for the methylene protons of XIIIa and XIIIb provided further evidence that the strain in diacetylenic linkage has little influence on the shielding effect of the linkage. Accordingly, the above-mentioned down-field shift should be mainly attributed to the shielding of diacetylenic linkage. And also the down-field shift (*ca.* 0.2 ppm) of aromatic protons in Ic stated before is possibly ascribed to the same effect.

The spectra of Ic were determined at 70, 35, and −70°C to study the conformational equilibrium (a⇄b in Fig. 2). But the signals of the aromatic protons were kept sharp singlet even at −70°C. This finding is consistent with that the molecule in solution has the same geometry as in crystals (Fig. 4). It is presumed that the relative arrangement of the benzene ring and the diacetylene linkage undergoes no significant change even if an interconversion between a chair form and a boat form arises from the conversion of both trimethylene bridges.

Electronic Spectra. Figure 6 and Table 5 record the electronic spectra of the [*m.n*]paracyclophadiynes I, in which the number of *m* and *n* are varied stepwise. In those spectra, a cyclic dimer Xe, 5,7,23,25-[12.12]paracyclophatetrayne, is a reference compound, in which the interaction between the two chromophores may be unexpected. The spectra show obvious features as follows: a) disappearance of vibrational fine structures with the decrease of

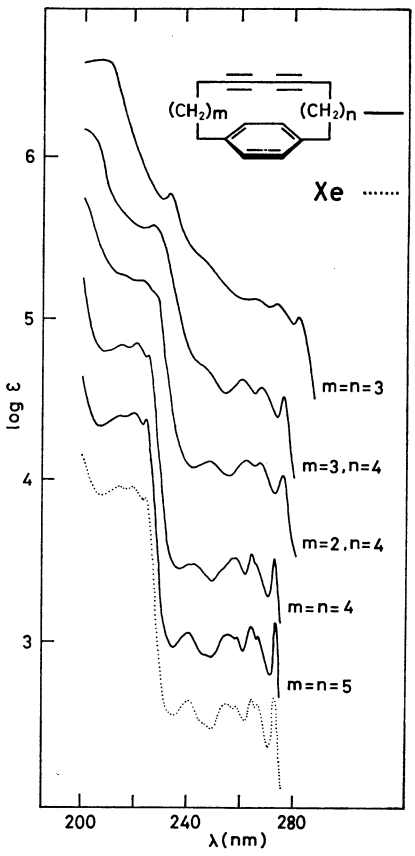


Fig. 6. The electronic spectra of paracyclophadiynes in cyclohexane. The ε-value of the cyclic dimer Xe is reduced to give the value for the unit chromophoric groups, *i.e.*, ε/2. The curves are displaced upward successively by 0.5 log ε unit from the curve immediately below.

methylene number, and then broadening of the curves, b) bathochromic shifts of the longest wavelength absorption bands, and c) appearance of a new peak at 233 nm for Ic and at 227 nm for Id, respectively.

The spectral features are explainable by two plausible elucidations, distortion in the two chromophores and transannular interaction between those. It was reported in the spectra of [*n*]paracyclophanes[16] that the distortion of benzene ring resulted in a disappearance of fine structure and a bathochromic shift of absorption band. However, there has not been investigated the spectral properties of distorted cyclic molecules containing only a conjugated diacetylenic linkage. Figure 7 shows that a strain-free cyclic diacetylene XIIIb exhibits a characteristic fine structure, whereas a strained one XIIIa does a broad absorption maximum, and that there is no significant difference between the positions of absorption bands of both spectra. Upon these facts, a) and b) may be explained by the strain effect of the chromophores, mainly of benzene ring, but c) not by only the strain effect. The reason is that the spectrum of less strained [3.4]paracyclophadiyne Id resembles the spectrum of more strained [3.3]homologue Ic, whereas highly strained one Ib shows an absorption curve similar to the reference compound Xe rather than to [3.3]homologue.

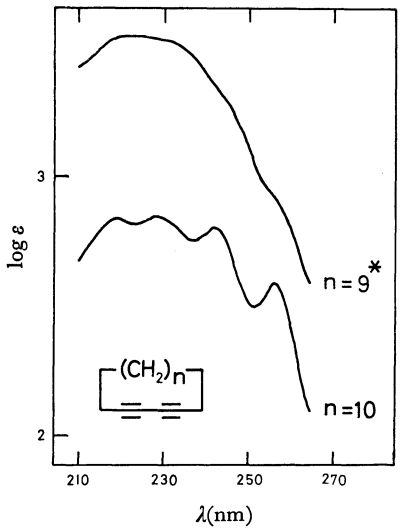


Fig. 7. The electronic spectra of cyclic diacetylenes in cyclohexane. * Qualitative.

Accordingly, it is suggested that new absorption peaks, at 233 nm of Ic and at 227 nm of Id, of the smaller paracyclophadiynes might be ascribed to the transannular interaction between the two chromophores. As is illustrated in Fig. 3, the closest interatomic distances between the two groups, 3.067 Å of C_7—C_{11} and 3.077 Å of C_4—C_{14}, are remarkably small as compared with a minimum interplanar distance of approximately 3.4 Å known for a variety of non-distorted aromatic substances. Thus the overlap of the π-electron orbitals must be particularly significant both at C_7—C_{11} and C_4—C_{14}. On the other hand, [2.4]homologue should be highly strained and less overlapped at the tetramethylene bridge site than in [3.3]homologue from the examination of molecular model. Consequently, it is concluded that the abnormal spectra of [3.3]- and [3.4]-paracyclophadiynes, Ic and Id, are best explained in terms of transannular π-electron interation caused by closely overlapped two chromophores.

[4.4]Paracyclophadiyne Ie shows absorption bands at about same wavelengths as those of the reference compound Xe, but with 0.7—0.8 times of the intensity ($\varepsilon/2$) for each pair of the chromophores as can be seen from Table 5. Such lower intensity was invariably observed on repeated measurements and with various runs of the specimen, indicating noncontamination of impurities. This phenomenon on the intensity has been also observed by Nakagawa and Ando[17] and explained in terms of the dispersion force interaction between excited dipoles by Tinoco[18] and Rhodes.[19] Accordingly, the intensity of the spectrum of Ie seems to be explained in terms of the dispersion force interaction or dipole-dipole interaction rather than the overlap of π-orbitals unlike in the cases of [3.3]- and [3.4]-homologues.

A similarity of the If spectrum to that of Xe is suggestive of the absence of the interaction between the two chromophores. Low intensity bands, occured at 285—295 nm in each spectrum of Ib, Ie, and If, at 285 nm for XIIIb and at 288 nm for XIVa, are considered as an excitation of the diacetylene bond alone.

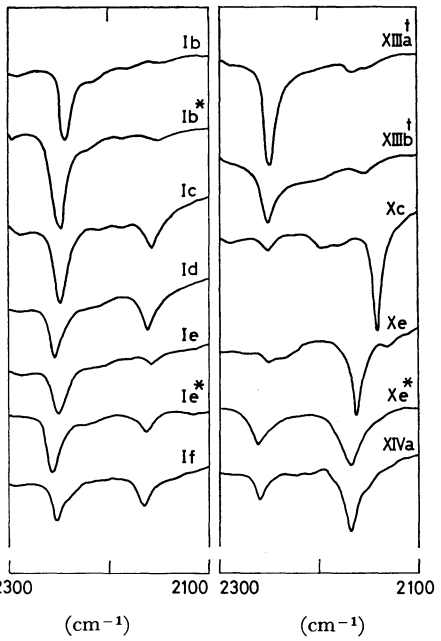


Fig. 8. The infrared spectra of I, X, XIII, and XIV (Nujol mull).
* CCl_4 soln. † Liquid film. The frequencies of the C≡C stretching bands in this figure are summarized in Table 2.

16) D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, **88**, 515 (1966).

17) T. Ando and M. Nakagawa, This Bulletin, **40**, 363 (1967).
18) I. Tinoco, Jr., *J. Amer. Chem. Soc.*, **82**, 4785 (1960).
19) W. Rhodes, *ibid.*, **83**, 3609 (1961).

The electronic spectra of paracyclophadiyne-tetracyanoethylene complexes will be reported in near future.

Infrared Spectra. Figure 8 shows the infrared spectra in a range of 2300—2100 cm^{-1} for cyclic acetylenic compounds, I, X, XIII, and XIV. The cyclic monomers I and XIII exhibit stronger higher-frequency band than lower-frequency one, whereas the cyclic dimers X and XIV are *vice versa*. This phenomenon is related probably to the very structure of the molecules and not to intermolecular interaction since the same relationship is observed between spectra of solid state and of solution.

Experimental

Melting points and boiling points are uncorrected. The UV, IR, NMR, and mass spectra were measured with a Hitachi EPS-3T autorecording spectrophotometer, a Hitachi EPI-G2 spectrometer, a Hitachi R-20 spectrometer, and a Hitachi RMU-7 spectrometer, respectively.

Ethyl p-*Ethoxycarbonylhydrocinnamate (IVa).* Acetylation of ethyl hydrocinnamate was accomplished by the procedure of Borshe and Sinn[20] except for using carbon tetrachloride as a solvent, yield 86.0%, bp 144—146°C/3 mmHg (lit,[20] bp 194—197°C/16 mmHg).

To an alkaline solution of sodium hypobromite, prepared from sodium hydroxide (230 g, 5.75 mol) and bromine (310 g, 1.94 mol) in water (1.9 *l*), 65 g (0.30 mol) of ethyl *p*-acetylhydrocinnamate was added over a period of 10 min with stirring keeping the temperature below 0°C. After the addition the mixture was kept at 60°C for 3 hr with stirring. The reaction mixture was cooled and washed well with ether and then acidified with 150 m*l* of conc. sulfuric acid, successively. The acid precipitate was collected, washed well with water and dried in vacuum over calcium chloride to give white crystals (53.7 g, 93%). For analysis a small amount of the sample was recrystallized from acetic acid and then sublimed (bath temp. *ca.* 200°C/3 mmHg) to give white powder, mp 296—297°C (in sealed tube), (Found: C, 61.39; H, 6.05%) (lit,[21] mp 284°C).

p-Carboxyhydrocinnamic acid was converted to diethyl ester *via* acid chloride according to the usual method. From 63.9 g of the dicarboxylic acid was obtained 70.0 g (84.5%) of the diethyl ester IVa as a colorless liquid, bp 148—153°C/4 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 157—158°C/4 mmHg. Found: C, 67.12; H, 7.26%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

p-*(3-Hydroxypropyl)benzyl Alcohol.* The ester IVa (81.0 g, 0.32 mol) in 200 m*l* of ether was added dropwise over a period of 1.5 hr with stirring to a suspension of 24.4 g (0.64 mol) of lithium aluminum hydride in 800 m*l* of ether. The mixture was kept at reflux with stirring for 4 hr. To the cooled reaction mixture a small amount of water was carefully added dropwise to decompose the excess reducing agent. After addition of 2 N hydrochloric acid (1.8 *l*) and salting out, the mixture was extracted with ether (500 m*l*). The ether solution was washed twice with succesive, 100 m*l* portions of saturated sodium chloride, dilute sodium bicarbonate solution saturated with sodium chloride, and saturated sodium chloride, respectively. The solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield an opaque pale yellow viscous oil (54.0 g).

The bis-*p*-nitrobenzoate of this material was prepared by the usual pyridine-*p*-nitrobenzoyl chloride method, mp 111.5—112.5°C (from ethanol). Found: C, 62.04; H, 4.42; N, 5.90%. Calcd for $C_{24}H_{20}N_2O_8$: C, 62.06; H, 4.34; N, 6.03%.

p-*(3-Bromopropyl)benzyl Bromide (Va).* *p*-(3-Hydroxypropyl)benzyl alcohol (54.0 g) was converted to the dibromide Va (41.5 g, 43.7%) according to the usual method,[22] bp 142—147°C/3 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 117—119°C/0.08 mmHg; IR (liquid film), 608 and 563 cm^{-1} (C-Br). Found: C, 41.38; H, 4.21%. Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14%.

*4-(*p-*(3'-Bromopropyl)phenyl)-1-butyne (VIa).* To a solution of propargylmagnesium bromide,[23] prepared from magnesium (1.3 g, 0.054 mol) and propargyl bromide (6.4 g, 0.054 mol) in ether (15 m*l*) under nitrogen atmosphere, a solution of the dibromide Va (8.7 g, 0.030 mol) in 20 m*l* of ether was quickly added with vigorous stirring. The mixture was stirred for 6 hr at room temperature and then poured into a mixture of crashed ice (100 g) and ether (100 m*l*), and 50 m*l* of 6 N hydrochloric acid was added. The resulting mixture was extracted with ether. The ether solution was washed with a saturated sodium chloride and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to yield an orange liquid (7.38 g). This residue was chromatographed on 30 g of neutral alumina using petroleum ether as an eluent to yield a colorless liquid (6.0 g, 80.0%). For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 108—110°C/0.08 mmHg; IR (liquid film), 3287, 2120 and 644 (-C≡CH), 573 cm^{-1} (C-Br); NMR (CCl_4), τ: 2.97 (s, 4H), 6.73 (t, J=6 cps, 2H), 7.1—8.1 (m, 8H), 8.19 (t, J=2 cps, 1H). Found: C, 62.22; H, 6.21%. Calcd for $C_{13}H_{15}Br$: C, 62.16; H, 6.02%.

Ethyl p-*(3-Ethoxycarbonylpropyl)benzoate (IVb).* *p*-(3-Ethoxycarbonylpropyl)acetophenone was obtained according to Baddeley and Williamson.[21]

Oxidation of the acetophenone derivative with sodium hypobromite was carried out in the same manner described for the preparation of *p*-carboxyhydrocinnamic acid. From 104 g of the acetophenone derivative was obtained 82.2 g (89.0%) of *p*-(3-carboxypropyl)benzoic acid, mp 184—190°C. A small amount of sample was recrystallized from 50% acetic acid to yield white needles, mp 195.5—196°C (lit,[21] mp 194—195°C).

The dicarboxylic acid was converted to diethyl ester *via* acid chloride according to the usual method. From 65.1 g of the acid was obtained 72.8 g (88.0%) of ethyl *p*-(3-ethoxycarbonylpropyl)benzoate(IVb) as a pale yellow liquid, bp 156—160°C/2 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 153—155°C/1 mmHg. Found: C, 68.00; H, 7.77%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

p-*(4-Hydroxybutyl)benzyl Alcohol.* Reduction of the ester IVb with lithium aluminum hydride was accomplished in a similar manner described for the preparation of *p*-(3-hydroxypropyl)benzyl alcohol. From 90 g of IVb was obtained 63.7 g of the crude diol as an opaque pale yellow viscous oil. The bis-*p*-nitrobenzoate of this diol was prepared, mp 99—100°C (from ethanol). Found: C, 63.00; H, 4.65; N, 5.75%. Calcd for $C_{25}H_{22}N_2O_8$: C, 62.76; H, 4.64; N, 5.86%.

p-*(4-Bromobutyl)benzyl Bromide (Vb).* *p*-(4-Hydroxybutyl)benzyl alcohol (62.0 g) was converted to the di-

20) W. Borsche and F. Sinn, *Ann. Chem.*, **553**, 260 (1942).
21) G. Baddeley and R. Williamson, *J. Chem. Soc.*, **1956**, 4647.

bromide Vb (63.5 g, 60.5%) according to the usual method,[22] bp 149—153°C/3 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 126—128°C/0.08 mmHg; IR (liquid film), 608 and 561 cm^{-1} (C–Br). Found: C, 43.34; H, 4.63; Br, 51.91%. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61; Br, 52.22%.

4-(p-(4'-Bromobutyl)phenyl)-1-butyne (VIb). Propynylation of the dibromide Vb with propargylmagnesium bromide[23] was accomplished in a manner to that described for the propynylation of the dibromide Va. From 20 g of the dibromide Vb was obtained 16.6 g (96.0%) of the monoethynyl compound VIb as a pale yellow liquid after chromatographic treament. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 118—120°C/0.09 mmHg; IR (liquid film), 3287, 2120 and 645 (–C≡CH), 563 cm^{-1} (C–Br); NMR (CCl_4), τ: 3.03 (s, 4H), 6.70 (t, J=6 cps, 2H), 7.1—7.8 (m, 6H), 8.1—8.3 (m, 5H). Found: C, 63.24; H, 6.53%. Calcd for $C_{14}H_{17}Br$: C, 63.40; H, 6.46%.

p-*Bis(β-methoxycarbonylethyl)benzene (VIIc).* A mixture of 36.9 g of dimethyl β,β'-(*p*-phenylene)diacrylate,[24] 360 m*l* of tetrahydrofuran and 3.6 g of 5% palladium-carbon catalyst was shaken in an atmosphere of hydrogen for 3 hr at about 60°C to take up theoretical amount of hydrogen. The hot mixture was filtered through an extraction thimble and the residual material in the thimble was extracted with tetrahydrofuran using a Soxhlet extractor. The combined solution was cooled to 0°C. The precipitated diester VIIc was collected and dried in vacuum, brilliant white scaly crystals (36.6 g, 97.6%), mp 116—118°C (lit,[25] mp 117—118°C).

p-*Bis(3-bromopropyl)benzene (VIIIc).* Reduction of the dimethyl ester VIIc, which was slightly soluble in ether, with lithium aluminum hydride was carried out by the technique of Nystrom and Brown.[26] From 30 g of VIIc was obtained 20.5 g (88.0%) of *p*-bis(3-hydroxypropyl)-benzene as white crystals, mp 60—61.5°C. A small amount of the sample was recrystallized from benzene to give colorless plates, mp 60.5—61.5°C (lit,[27] mp 61°C).

Bromination of the above diol was accomplished by the method of Ruzicka *et al.*[24] From 20 g of the diol was obtained 24.9 g (75.5%) of the dibromide VIIIc as a colorless liquid, bp 156—160°C/1 mmHg (lit,[24] bp 158—162°C/1 mmHg).

Ethyl p-(3-Ethoxycarbonylpropyl)hydrocinnamate (VIId). 108 g of β-(*p*-(2-carboxyethyl)benzoyl)propionic acid[28] was reduced by the modified Wolff-Kishner method[29] to yield 76.4 g (75.0%) of the *p*-(3-carboxypropyl)hydrocinnamic acid, mp 142—144°C (lit,[28] mp 143—144°C).

This dicarboxylic acid (66.4 g) was converted to the diethyl ester (69.6 g, 85.0%) by the usual acid-ethanol method, bp 165—168°C/2 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 173—174°C/3 mmHg. Found: C, 69.73; H, 8.51%. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27%.

4-(p-(3'-Bromopropyl)phenyl)butyl Bromide (VIIId). Reduction of VIId with lithium aluminum hydride was accomplished in a similar manner described for the preparation of *p*-(3-hydroxypropyl)benzyl alcohol. From 64.5 g of VIId was obtained 47.9 g of 4-(*p*-3'-hydroxypropyl)-phenyl)butyl alcohol as an opaque pale yellow viscous oil. The bis-*p*-nitrobenzoate of this diol was prepared, mp 100.5—101.5°C (from ethanol). Found: C, 64.07; H, 5.22; N, 5.46%. Calcd for $C_{27}H_{26}N_2O_8$: C, 64.02; H, 5.17; N, 5.53%.

Bromination of the above diol was achieved by the usual dry hydrogen bromide method.[30] From 26.1 g of the diol was obtained 32.9 g (78.7%) of the dibromide VIIId as a colorless liquid, bp 151—155°C/1 mmHg. For analysis a sample was distilled under reduced pressure to give a colorless liquid, bp 174—176°C/3 mmHg. Found: C, 46.78; H, 5.34%. Calcd for $C_{13}H_{18}Br_2$: C, 46.73; H, 5.43%.

p-*Bis(4-bromobutyl)benzene (VIIIe).* A series of reactions leading to the formation of dibromide VIIIe *via* diethyl ester VIIe was carried out by the method of Cram *et al.*[31]

p-*Bis(5-bromopentyl)benzene (VIIIf).* Bromination of *p*-bis(5-hydroxypentyl)benzene, which was prepared from dimethyl ester VIIf by the method of Cram and Daeniker,[32] was accomplished by the usual method.[30] From 33.0 g of the diol was obtained 41.5 g (83%) of the dibromide VIIIf as a colorless liquid, bp 188—190°C/3 mmHg. For analysis a sample was chromatographed on alumina using petroleum ether as an eluent and then distilled under reduced pressure to give a colorless liquid, bp 144°C/0.02 mmHg. Found: C, 50.99; H, 6.50; Br, 42.28%. Calcd for $C_{16}H_{24}Br_2$: C, 51.08; H, 6.43; Br, 42.49%.

Ethynylation of VI, VIII, and XI. To a solution of monosodium acetylide, prepared from 3.6 g (0.16 mol) of sodium in liquid ammonia (100 m*l*), a solution of 10 g (0.029 mol) of dibromide VIIIe in 100 m*l* of *N*-methyl-2-pyrrolidone, which was distilled at atmospheric pressure, was added dropwise over a period of 50 min. During this period the bottom of the reaction flask was kept cool on a dry ice-alcohol bath, and vigorous stirring was continued with passage of a slow stream of acetylene. After the addition of VIIIe and the introduction of acetylene were over, stirring was continued overnight at room temperature to allow the evaporation of nearly all the ammonia. To the reaction mixture a small amount of water was carefully added to decompose excess sodium acetylide. After further addition of water (1 *l*) and salting-out, the reaction mixture was extracted with ether. The ether extract was washed well with water, dilute sulfuric acid, dilute sodium bicarbonate solution, and again with water, successively and dried over calcium chloride. The solution was concentrated under reduced pressure to yield 6.4 g of a yellow oil, for which Beilstein's test was negative. This residue was chromatographed on 50 g of alumina using petroleum ether as an eluent to yield 6.0 g (87.7%) of 6-(*p*-(4'-ethynylbutyl)phenyl)-1-hexyne (IXe) as a colorless liquid. For analysis a small amount of the sample was crystallized from petroleum ether at −20°C to give colorless crystals, mp 18—19°C. Bisethynyl compound IXc, IXd, IXf, XIIa, and XIIb were also prepared in good yields from corresponding dibromides by the method described above. VIa and VIb were also ethynylated in a similar method except that two gram atoms of sodium were

22) O. Kamm and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, p. 25 (1947).
23) F. Sondheimer *et al.*, *J. Amer. Chem. Soc.*, **82**, 755 (1960); **83**, 1686 (1961).
24) L. Ruzicka, J. B. Buijs, and M. Stoll, *Helv. Chim. Acta*, **15**, 1220 (1932).
25) H. Hopff and H. Diethelm, *Ann. Chem.*, **691**, 61 (1966).
26) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 1197 (1947).
27) K. Murayama, Y. Kato, and S. Morimoto, This Bulletin, **40**, 2645 (1967).
28) M. S. Ahmad and G. Baddeley, *J. Chem. Soc.*, **1961**, 2520.
29) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).
30) W. L. McEwen, "Organic Syntheses," Coll. Vol. III, p. 227 (1955).
31) D. J. Cram, M. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).
32) D. J. Cram and H. U. Daeniker, *ibid.*, **76**, 2743 (1954).

Table 6. The experimental conditions for I, X, XIII, and XIV

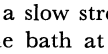
Reaction condition			Condition of chromatography		
Starting material (g)	Bath temp. °C	Dropping period (hr)	Alumina[b] (g)	Cyclic monomer eluent	Cyclic dimer eluent
IXa (3.0)	75	60[a]	200[c]		pet. ether–ether (20 : 1)
IXb (3.0)	85	92	200	pet. ether–ether (20 : 1)	
IXc (3.0)	85	77	200	pet. ether–ether (20 : 1)	pet. ether–benzene (2 : 1)
IXd (2.7)	90	84	200	pet. ether–ether (30 : 1)	
IXe (3.0)	95	110	200	pet. ether–ether (40 : 1)	pet. ether–benzene (2 : 1)
IXf (3.6)	90	114	200	pet. ether–ether (40 : 1)	
XIIa (3.0)	85	90[a]	150	pet. ether	pet. ether–benzene (50 : 3)
XIIb (3.0)	95	74	150	pet. ether	pet. ether–ether (20 : 1)

a) In darkness. b) Sumitomo activated alumina, KCG-30. c) Merck silica gel.

used to 1 mol of the monobromide VI.

Analytical data, yields, and physical properties of these bisethynyl compounds IX and XII were summarized in Table 1.

General Procedure for the Oxidative Coupling of IX and XII. In a 3 *l* separable flask, equipped with a vibromixer, a 1 *l* dropping funnel fitted with a capillary, and a gas inlet tube, are placed 1.3 *l* of pyridine and 20 g (0.11 mol) of anhydrous cupric acetate. The mixture was heated on an oil-bath with vigorous stirring and passage of a slow stream of nitrogen. Keeping the temperature of the bath at about 95°C, the solution of the bisethynyl compound IXe (3.0 g, 0.013 mol) in 2 *l* of ether was added dropwise through the capillary of the dropping funnel into the reaction flask. The addition was completed for 110 hr. During this period vigorous stirring and passage of nitrogen were continued and two 5 g portions of the cupric salt were added at nearly equal intervals. After the addition the reaction mixture was permitted to stand at room temperature for more than 6 hr and poured into a cooled mixture of crashed ice (2.4 kg), conc. sulfuric acid (540 m*l*) and ether (650 m*l*). Then brown insoluble material was filtered, the organic layer was separated and the water layer was extracted with 1 *l* of ether. The combined etherial solution was washed well with dilute sulfuric acid, dilute sodium bicarbonate solution and water, successively and dried over calcium chloride. The solution was concentrated under reduced pressure to yield a red oil (6.8 g) which gave no band at *ca.* 3300 cm^{-1} due to ethynyl group. The residue was dissolved in 10 m*l* of benzene and chromatographed on 200 g of alumina to yield two compounds. The first (1.39 g, 46.6%) was eluted with petroleum ether - ether (40 : 1); it was the cyclic monomer, [4.4]-paracyclophadiyne (Ie). For analysis a small amount of the sample was crystallized from *n*-pentane at −20°C, colorless plates, mp 72—73°C. On the crystallization, however, the alternative colorless thick plates were often obtained, they showed mp 76—77°C. The latter shows identical UV and NMR spectra with those of the former. Once the lower melting point crystals were melted and then solidified, it showed mp 76—77°C. On the other hand, in the case of the higher melting point crystals such phenomenon was not observed in this process. This phenomenon is explainable in terms of a polymorphism. Analytical data and physical properties of the cyclic monomer Ie are shown in Tables 2, 3 and 5 and Figs. 5, 6 and 8. The second substance (0.370 g, 12.4%) was eluted with petroleum ether - benzene (2 : 1); it was the cyclic dimer, 5,7,23,25-[12.12]paracyclophatetrayne (Xe). For analysis a small amount of the sample was recrystallized from cyclohexane, white needles, mp 163—164°C. Analytical data and physical properties of this cyclic dimer are shown in Tables 2, 3 and 5 and Figs. 6 and 8.

In a preliminary experiment, the linear dimer, (HC≡C–$(CH_2)_4$–  –$(CH_2)_4$C≡C–)$_2$, was obtained; colorless needles, mp 76—77°C; λ_{max} 219.5 nm (ε 20200), 241.5 (518) and 274 (936) (in cyclohexane); IR 3265, 2320 and 2110 cm^{-1} (KBr disk). Found: C, 91.37; H, 8.83%; mol wt, 457 (osmometry in benzene). Calcd for $C_{36}H_{42}$: C, 91.08; H, 8.92%; mol wt, 475.

The Oxidative Coupling of IXa. The oxidative coupling of IXa (Table 6) resulted in a red oil (7.1 g). Chromatography on silica gel, followed by recrystallization from cyclohexane gave a mixture of two possible cyclic dimers, 3,5,18,20-[9.9]- and 3,5,18,20-[8.10]-paracyclophatetraynes, in poor yield; white needles, mp 159—162°C. Found: C, 92.94; H, 7.35%. Calcd for $C_{30}H_{28}$: C, 92.74; H, 7.26%. Mol wt, Found: 388 (mass spectrometry). Calcd for $C_{30}H_{28}$: 388. UV: (in cyclohexane) λ_{max} 214, 220, 225, 242.5, 256.5, 264, and 273 nm.

Hydrogenation of XIII. 1,3-Cyclotridecadiyne (XIIIa, 704 mg), which was purified by chromatography in *n*-pentane on alumina at *ca.* 5°C, took up 96% of the calculated volume of hydrogen in ethyl acetate (5% Pd-C). The crude product was chromatographed in petroleum ether on alumina, followed by distillation (*ca.* 80°C (bath temp.)/2 mmHg), to give cyclotridecane[33] (430 mg, 60%) as a colorless oil. Found: C, 84.81; H, 14.99% mol wt (mass spectroscopy) 182.

1,3-Cyclotetradecadiyne[8] (XIIIb, 563 mg) similarly gave cyclotetradecane (419 mg, 73%, mp 48—52°C), which was recrystallized from ethanol as colorless needles, mp 56—56.5°C (lit,[33] 53.5—54°C). Found: C, 85.33; H, 14.62%, mol wt (mass spectroscopy) 196.

33) L. Ruzicka, Pl. A. Plattner, and H. Wild, *Helv. Chim. Acta*, **28**, 395 (1945).