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The Synthesis of [6.0.6.0]Paracyclophane

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It has been reported that 1,6,19,24-tetraaza[6.0.6.0]- and 1,6,19,24-tetraoxa[6.0.6.0]paracyclophane form an inclusion compound with benzene or dioxane.[1,2] These cyclophanes have nitrogen or oxygen atoms attached to biphenyl nuclei. To see if the presence of such hetero atoms had any effect on the inclusion of a guest molecule in an empty space of the macro cyclic compounds, [6.0.6.0]paracyclophane, I, constructed with two biphenyl nuclei and two hexamethylene bridges, was synthesized as a reference compound free from hetero atoms. No addition compound of the I cyclophane with benzene has been isolated under similar conditions. [6.0.6.0]Paracyclophane, I, and its open-chain model compound, XI, were synthesized as is shown in Figs. 1 and 2. We adopted the acyloin condensation of the diester, V, in the ring-closing step. In the NMR spectrum of I, the signals for aromatic protons showed an A_2B_2 pattern, and the peaks of I, centered at 7.15 ppm, were found to shift toward an upper field by 0.18 ppm compared with those of the open-chain model, XI.

The electronic spectrum of I (λ_{max} 255 nm, ε_{max} 2.9×10^4 in *n*-hexane) showed a slight blue shift and a hypochromic effect compared with that of the open-chain compound, XI, (λ_{max} 258 nm, ε_{max} 4.46×10^4 in *n*-hexane), the shapes of the curves being virtually the same. The shapes of the electronic spectra of 1:1 electron-donor-acceptor complexes of I and XI with tetracyanoethylene (TCNE) in dichloromethane were virtually the same. However, the λ_{max} at the longest wavelength in the spectra (λ_{max} 398, 418, 578 nm) of the I-TCNE complex showed a blue shift by 10 nm compared with that in the spectra (λ_{max} 400, 417, 588 nm; ε 588 nm 770) of the XI-TCNE complex. Accordingly, the I-TCNE complex appears, unexpect-

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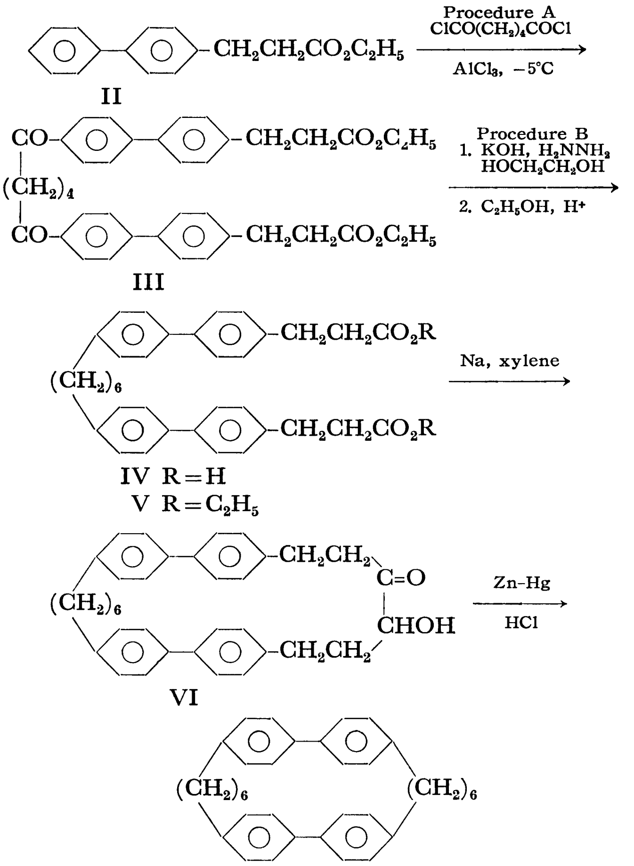
[1] H. Stetter and E. E. Roos, *Chem. Ber.*, **87**, 566 (1954).

[2] J. Nishikido, T. Inazu, and T. Yoshino, This Bulletin, to be published.

Table 1.

Compd	Cryst. form[a)]	Cryst. solv.[a)]	Mp, bp °C	Prd.	Formula	Analyses, % Found C	Found H	Calcd C	Calcd H	Yield %
I[b)]	w.n	Hx–Bz	157 —157.5		$C_{36}H_{40}$	91.22	8.51	91.47	8.52	70.0
II			bp 149.5—150/0.23							93.3
III	w.p	Bz	191 —192	A	$C_{40}H_{42}O_6$	77.85	7.03	77.64	6.84	78.9
V	w.pl	Bz	160	B	$C_{40}H_{46}O_4$	81.35	7.92	81.32	7.85	34.4[c)]
VI	w.p	Hx–Bz	198 —201[d)]		$C_{36}H_{38}O_2$	86.04	7.69	86.01	7.62	30.1
VIII	w.pl	Bz	220 —221	A	$C_{30}H_{26}O_2$	86.02	6.43	86.09	6.26	79.8
IX	w.n	$CHCl_3$	142	B	$C_{30}H_{30}$	92.34	7.82	92.26	7.74	91.0
X	cw.p	Hx–Bz	220[e)]	A	$C_{36}H_{38}O_2$	86.05	7.63	86.01	7.62	62.5
XI	cw.n	Bz–Et	157 —158	B	$C_{36}H_{42}$	91.10	8.79	91.08	8.92	86.3

a) cw=creamy white. n=needles. p=powder. pl=plates. w=white. Bz=benzene. Et=ethanol. Hx=*n*-hexane.
b) Found; mol wt, 457.8 in benzene (Hitachi Perkin-Elmer 115 model). Calcd; mol wt,. 472.7.
c) from the keto ester III.
d) turned yellow at 189—192°C.
e) began to sinter at 178°C.



I

Fig. 1.

edly, to be less stabilized than the XI–TCNE complex; this is in contrast to the reports[3)] that the well-known [*m.n*]paracyclophane-TCNE complexes are generally more stabilized than their corresponding open-chain compound-TCNE complexes, where *m* and *n* range from 2 to 6.

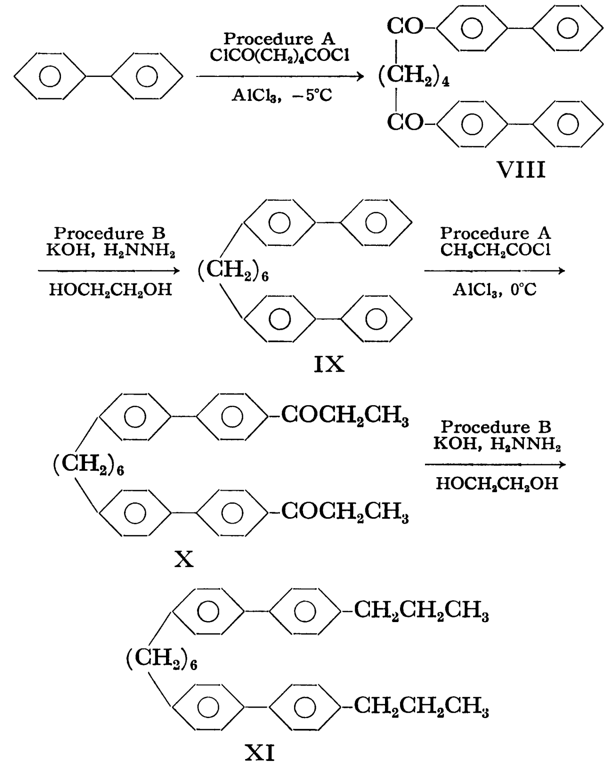


Fig. 2.

Experimental

All the melting and boiling points are uncorrected. The electronic spectra were measured on a Hitachi EPS-3T spectrophotometer. The NMR spectra were recorded on a Hitachi R-20 model at 60 MHz, using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent.

1,6-Bis[4′-(2-ethoxycarbonylethyl)-4-biphenylyl]-1,6-hexanedione, III. Procedure A: Ethyl biphenyl-4-acrylate[4)] was reduced to ethyl biphenyl-4-propionate, II, by catalytic hydrogenation with palladium-on-carbon in ethanol at room temperature. Into a mixture of 80.5 g of the ester, II, and 28.9 g of adipyl chloride in 500 ml of tetrachloroethane, we stirred

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3) D. J. Cram and R. H. Bauer, *J. Amer. Chem. Soc.*, **81**, 5971 (1959); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1080 (1963); D. J. Cram and M. Sheehan, *ibid.*, **91**, 3553 (1969).

4) D. H. Hey, *J. Chem. Soc.*, **1931**, 2478.

150 g of anhydrous aluminum chloride, portion by portion, at −10°C. The dark green reaction mixture was kept below 0°C for 7 hr and was then allowed to come to room temperature. The mixture was poured onto crushed ice. The organic layer was separated, and the solvent was removed by steam distillation. A light brown solid was thus obtained.

1,6-Bis[4′-(2-ethoxycarbonylethyl)-4-biphenylyl]hexane, V. Procedure B: A mixture of 6.2 g of the keto ester, III, and 70 g of 80% hydrazine hydrate in 400 ml of ethylene glycol was refluxed for an hour. Then potassium hydroxide was slowly added in small portions. The yellowish-gray mixture was refluxed for 24 hr, while two 50 ml portions of 80% hydrazine hydrate and 100 ml portions of ethylene glycol were added at 10 hr intervals. After the usual treatment, a crude reduction product, IV, was obtained. This reduction product, IV, was esterified by the usual method.

3-Hydroxy-4-oxo[6.0.6.0]paracyclophane, VI. A solution of 4.43 g of the diethyl ester, V, in 1 l of xylene was stirred into 2.90 g of dispersed sodium in 1 l of xylene over 41 hr under a nitrogen atmosphere. The usual work-up of the reaction mixture[5] then gave crude acyloin, 1.136 g (30.1%). A small sample was chromatographed on silica gel with benzene.

[6.0.6.0]Paracyclophane, I. Activated zinc was prepared by swirling 12 g of zinc with a solution of 1.5 g of $HgCl_2$ and 1.5 ml of concentrated HCl in 28.5 ml of water. To the zinc we then added 20 ml of glacial acetic acid, 40 ml of toluene, 20 ml of concentrated HCl, and 251 mg of the acyloin.

The mixture was refluxed for 10 hr, during which time two 30 ml portions of concentrated HCl were added. After the usual treatment, 165 mg of the crude I was obtained (70%). The crude cyclophane, I, was chromatographed on silica gel with benzene; the subsequent evaporation of the column filtrates gave solid residues. In the mass spectrum, the molecular ion peak was found as the base peak at *m/e* 472 (Hitachi RMS-4 model).

The equilibrium constant of the XI–TCNE complex was determined to be $K=1.53$ l/mol by a modified Benesi-Hildebrand plot.[6]

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[5] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).

[6] R. P. Lang, *ibid.*, **84**, 1185 (1962).