

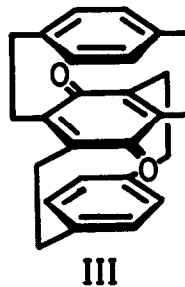
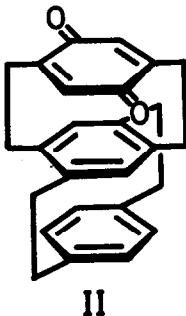
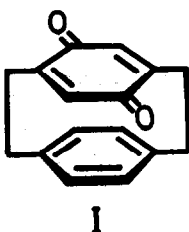
LAYERED COMPOUNDS. XXVII.<sup>1)</sup> THE SYNTHESSES OF TWO ISOMERIC  
TRIPLE-LAYERED [2.2]PARACYCLOPHANEQUINONES

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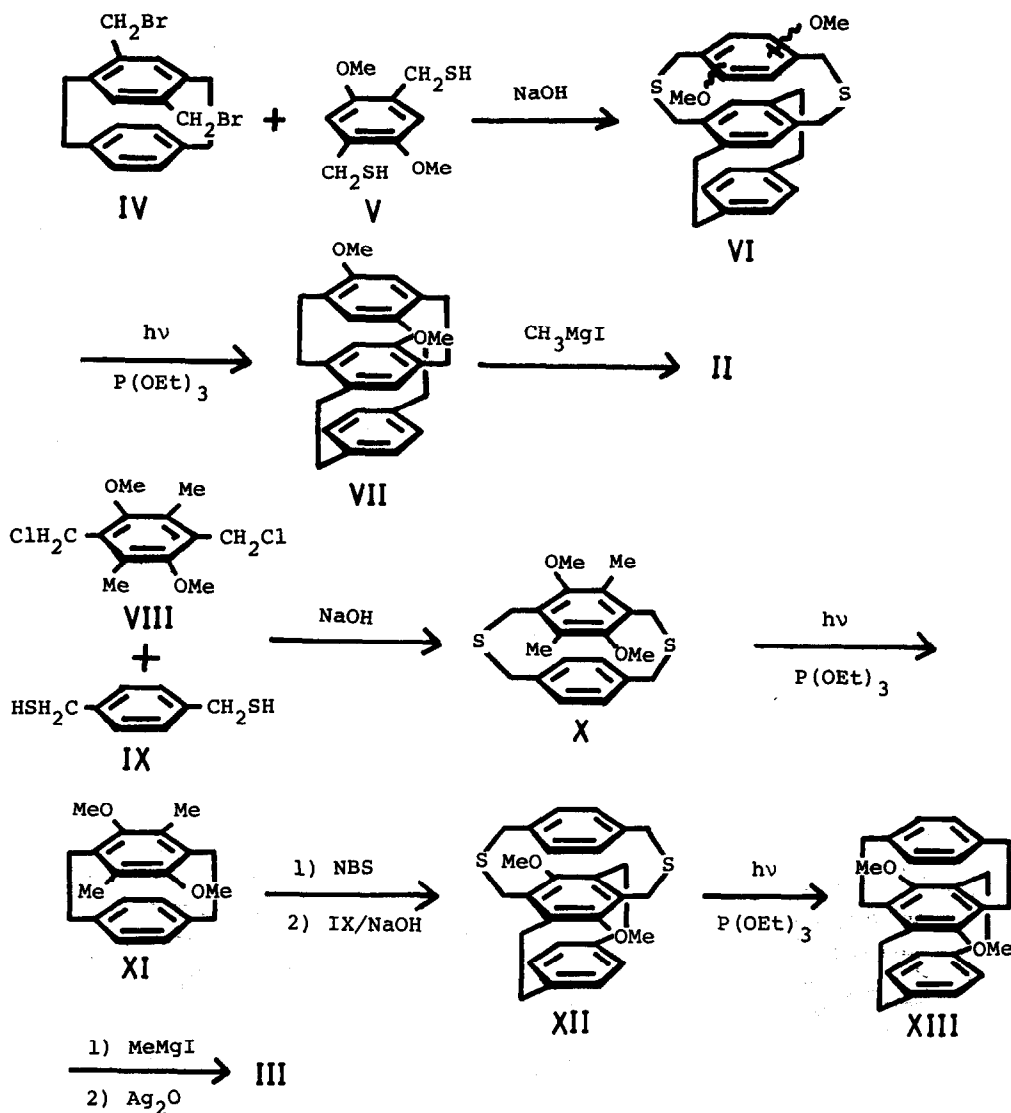
(Received in Japan 28 June 1975; received in UK for publication 17 July 1975)

Intramolecular charge-transfer complexes where  $\pi$ -donor and  $\pi$ -acceptor are closely fixed in [2.2]paracyclophane system have been interested in the context of the investigations of transannular  $\pi$ -electronic interaction in layered aromatic compounds. Cram and Day<sup>2)</sup> prepared [2.2]paracyclophanequinone (I) containing p-benzoquinone nucleus, and Staab and his co-workers<sup>3)</sup> reported the syntheses of two isomeric "intramolecular quinhydrones" and 4,7-dimethoxy-12,15-dinitro[2.2]paracyclophanes having different orientation of donor and acceptor moieties.

We wish to report the syntheses of triple-layered [2.2]paracyclophanequinone (II) bearing a donor with increased  $\pi$ -basicity and its isomeric quinone (III), in which the quinone moiety is sandwiched with two  $\pi$ -donors. These compounds are expected to be suitable for studying the effects caused by a difference of the structure of CT-complexes in 2:1 donor-acceptor systems.



4,7-Bis(bromomethyl)[2.2]paracyclophane (IV)<sup>4)</sup> and 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene (V)<sup>5)</sup> were coupled to give a disulfide (VI, 4.8%, colorless prisms from benzene-hexane, m.p. 216-221°C with decomp.). The NMR spectrum of the disulfide showed to be a mixture of two isomers but an isomer could be isolated by recrystallization. Desulfurization of disulfide (VI) was achieved by irradiation with high pressure mercury lamp in triethylphosphite under nitrogen atmosphere for two hours and afforded one of two possible isomers of



dimethoxy compounds (VII, 75%, colorless prisms from benzene-hexane, m.p. ca. 250°C with decomp.). VII was demethylated by treatment with methylmagnesium-iodide at 160°C to give outer-quinone isomer (II, 72%, reddish orange prisms from benzene, ca. 220°C decomp.). On the other hand, 2,5-bis(chloromethyl)-3,6-dimethoxy-p-xylene (VIII) prepared by chloromethylation of 2,5-dimethoxy-p-xylene<sup>3b1</sup> was coupled with p-xylylenedimercaptane (IX) to afford 5,8-dimethoxy-6,9-dimethyl-2,11-dithia[3.3]paracyclophane (X, 65.5%, colorless prisms from methanol, m.p. 137-138°C). Ring contraction of X into XI was accomplished by

direct photodesulfurization in triethylphosphite (XI, 59.8%, colorless rhomboid crystals from methanol, m.p. 126-127°C). Disulfide XII was obtained by bromination (85.8%) of XI with NBS, followed by coupling (49.3%) with IX (XII, colorless fine crystals from benzene-methanol, m.p. 211-213°C). Photolytic desulfurization of XII was performed in a similar manner as above to yield XIII (68.5%, colorless prisms from hexane, ca. 230°C decomp.). Demethylation of XIII was carried out by stirring with methylmagnesiumiodide at 160°C for 30 min. followed by treatment with silver oxide in acetone to give the inner-quinone (III, 12.3%, yellow prisms from benzene-hexane, ca. 250°C decomp.).<sup>6)</sup>

The electronic spectra of I, II, III, and 2,5-dimethylbenzoquinone (XIV) are shown in the Figure 1 and the chemical shifts of aromatic protons of II, III, VII, and XIII in the Figure 2. The electronic spectra of II and III show broad, characteristic absorption bands due to intramolecular charge-transfer in the region of longer wavelength [ $\lambda_{\text{max}}$  ( $\epsilon$ ): II, 395 (2330); III, 435 nm (320)]. Both the charge-transfer bands shift markedly to longer wavelength compared with the corresponding one (ca. 340 nm)<sup>2)</sup> of I, indicating the increase of  $\pi$ -donor character of donor moieties in II and III. Broadening of these bands, in particular of III, is presumably due to mixing of  $n \rightarrow \pi^*$  transition band in

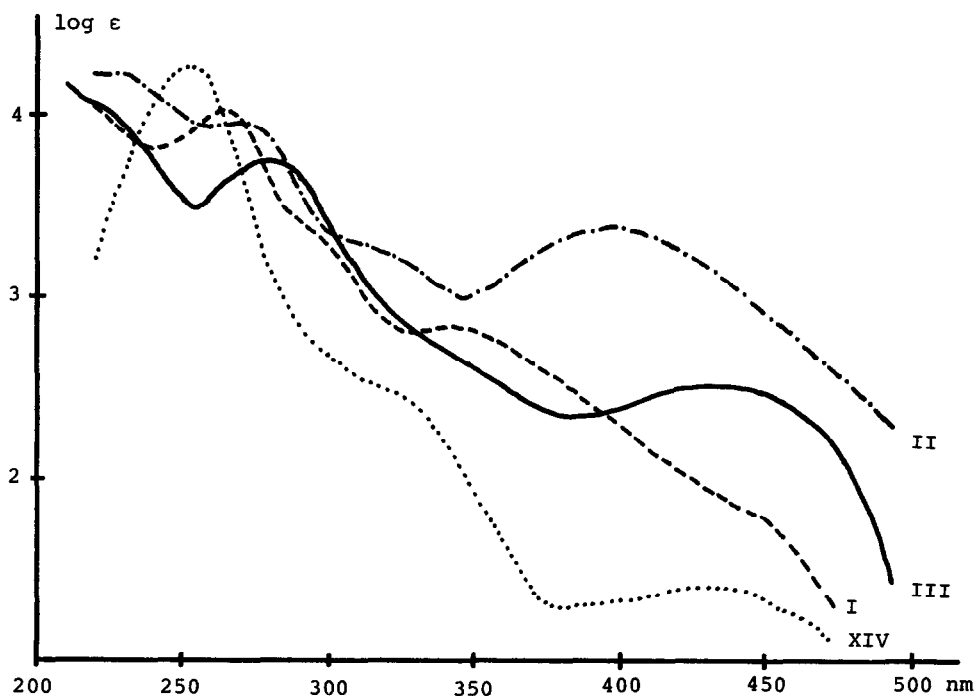


Figure 1. The electronic spectra of I, II, III, and XIV in tetrahydrofuran.

the longest wavelength region.

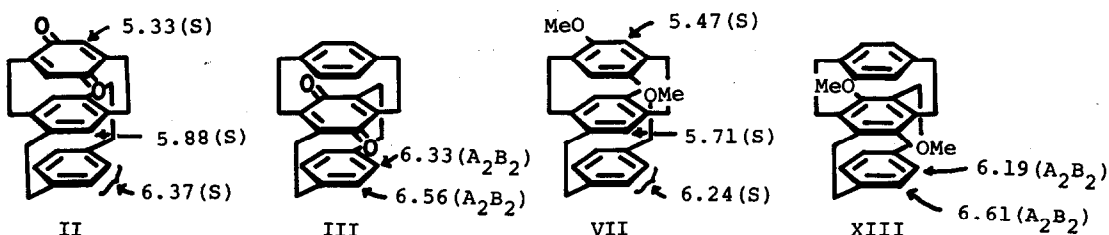


Figure 2. The chemical shifts of aromatic protons of II, III, VII, and XIII ( $\delta$  value in CDCl<sub>3</sub>).

#### References

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- 6) All new compounds were isolated by column chromatography on silica gel and gave satisfactory elemental analysis and mass, ir, and nmr spectra.