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LAYERED COMPOUNDS. XLVIII.[1] SYNTHESIS OF CHARGE TRANSFER CYCLOPHANES SANDWICHING A BENZENE RING

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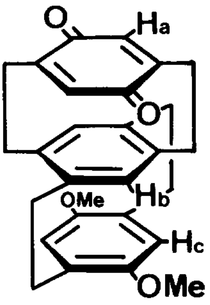
Triple-layered charge transfer(CT) cyclophane where a benzene ring is sandwiched between a donor and an acceptor has been interested in connection with our previous studies on intramolecular charge transfer complexes.[2] Such a new type of cyclophane is expected to show some physical properties different from double-layered CT cyclophanes.[3] We now wish to report the synthesis of three isomeric triple-layered CT cyclophanes 1-3.[4]



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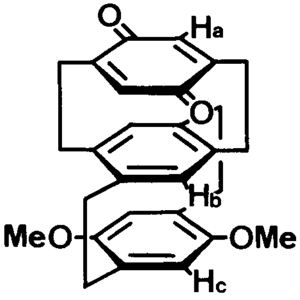

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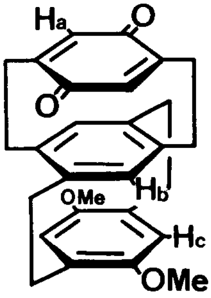
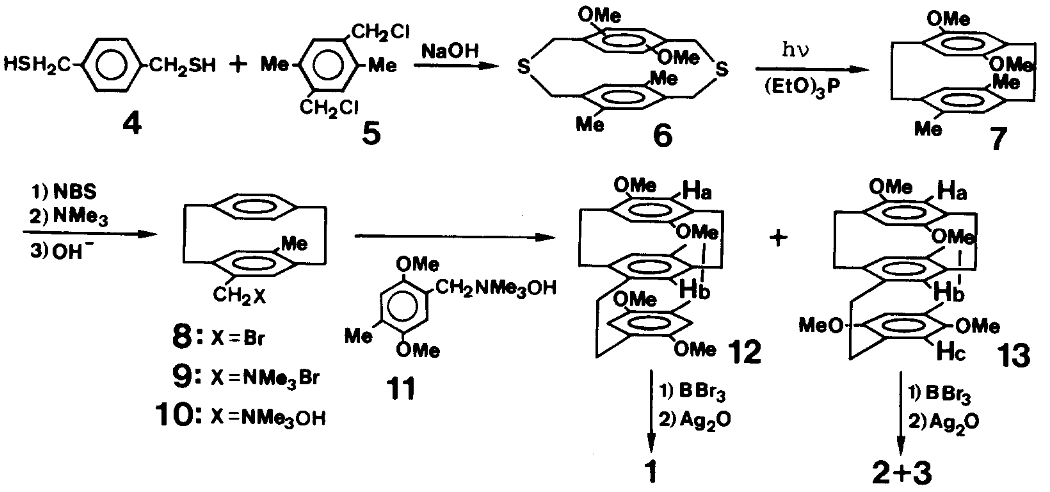


3

Photodesulfurization of a mixture of isomeric disulfides 6, prepared by coupling of 4 and 5, gave only a stagger type isomer 7 of two possible structures in a yield of 63.3%. 7 was treated with NBS in carbon tetrachloride followed with trimethylamine in carbon tetrachloride-ether to yield an ammonium salt 9. Cross-breeding pyrolysis of 10, derived from 9 by ion exchange, with 11 in boiling xylene gave a mixture of tetramethoxy double-, triple-, and quadruple-layered [2.2]paracyclophanes. The mixture was separated by means of gel permeation liquid chromatography into double-, triple-(6.1% yield based on 9), and quadruple-layered cyclophane(2.6% based on 9). Although the separation of the quadruple-layered cyclophane into two isomers is in progress, the triple-layered one could be separated into two isomers 12 and 13 by recrystallization from ethanol [12: colorless needles, mp 204.0-204.5°C. 13: colorless needles,



mp 226.5-226.7°C]. The NMR chemical shifts of 12 and 13 are shown in the Table

The isomer 12 was demethylated with BBr_3 in CH_2Cl_2 at 0°C for 2 hrs, followed by oxidation with Ag_2O in aceton at room temperature for 1 hr to give 1 in 33.0% yield [1: red needles from ethanol, deccomp. over 220°C; M^+ obs. 428.19880, calcd. 428.19874; IR(KBr disk) 1659, 1648 cm^{-1}]. The same reaction sequence for 13, on the other hand, gave 41.7% yield of two isomeric dimethoxyquinones(2 and 3) which were separated by careful column chromatography over silica gel [2: reddish brown needles from ethanol, decomp. over 225°C; M^+ obs.

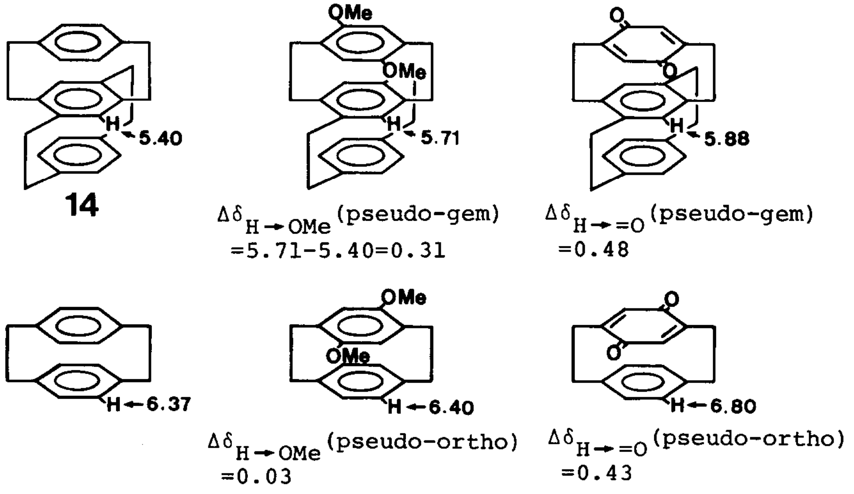


Fig. 1. Observed chemical shifts(δ ppm in $CDCl_3$) of reference cyclophanes and anisotropic effects(Δδ) of methoxy and quinonecarbonyl groups.

428.19933, calcd. 428.19874; IR(KBr disk) 1663, 1648 cm^{-1}. 3: red needles from hexane, decomp. over 210°C; M^+ obs. 428.19971, calcd. 428.19874; IR(KBr disk) 1658 cm^{-1}].

The structural assignment of 2 and 3 was done by comparing the chemical shifts of inner aromatic protons(Hb) with calculated values. Thus, the anisotropic effects of methoxy and quinonecarbonyl groups on pseudo-gem and pseudo-ortho aromatic protons on the faced benzene ring were evaluated from the observed chemical shifts of reference compounds in Fig. 1. By employing these values, the chemical shifts of Hb protons in 2 and 3 as well as those of 1, 12, and 13 were estimated (Table). The Table shows the observed values of Hb protons to be good agreement with the calculated values, suggesting that the structures assigned to these triple-layered compounds are justified.

Table. Observed chemical shifts(δ ppm in $CDCl_3$) of 1, 2, 3, 12 and 13. Values in parentheses are calculated ones for Hb.

	1	2	3	12	13
Ha	5.56	5.57	5.63	5.50	5.50
Hb	6.12	5.86	6.04	5.98	5.65
(calcd)	(6.19)	(5.91)	(6.14)	(6.02)	(5.74)
Hc	5.62	5.65	5.63	——	5.50
OCH_3	3.59	3.59	3.59	3.56	3.56 3.56

The electronic spectra of 1-3 are shown together with those of reference compounds in Fig. 2. The spectra of 1-3 are very similar with each other showing little influence of donor-acceptor orientation, in contrast to the related double-layered CT cyclophanes, e.g., 15.[3)] Marked red shift of the longest wavelength band was observed for 1-3 as compared with that of the parent triple-layered hydrocarbon 14. This broad and structureless band(350-450 nm) might be associated with intramolecular CT transition because of no existence of such a strong band in a combined spectrum of 2,5-dimethylbenzoquinone and 2,5-dimethoxy-p-xylene and in the spectrum of 14. The CT bands of 1-3, however, appear at relatively shorter wavelength than that of 15. On the basis of the above results, it is suggested that a sandwiched benzene ring functions as a sort of conductor for intramolecular donor-acceptor interaction and not as an insulator. Further studies on this problem is under way with other systems.

References

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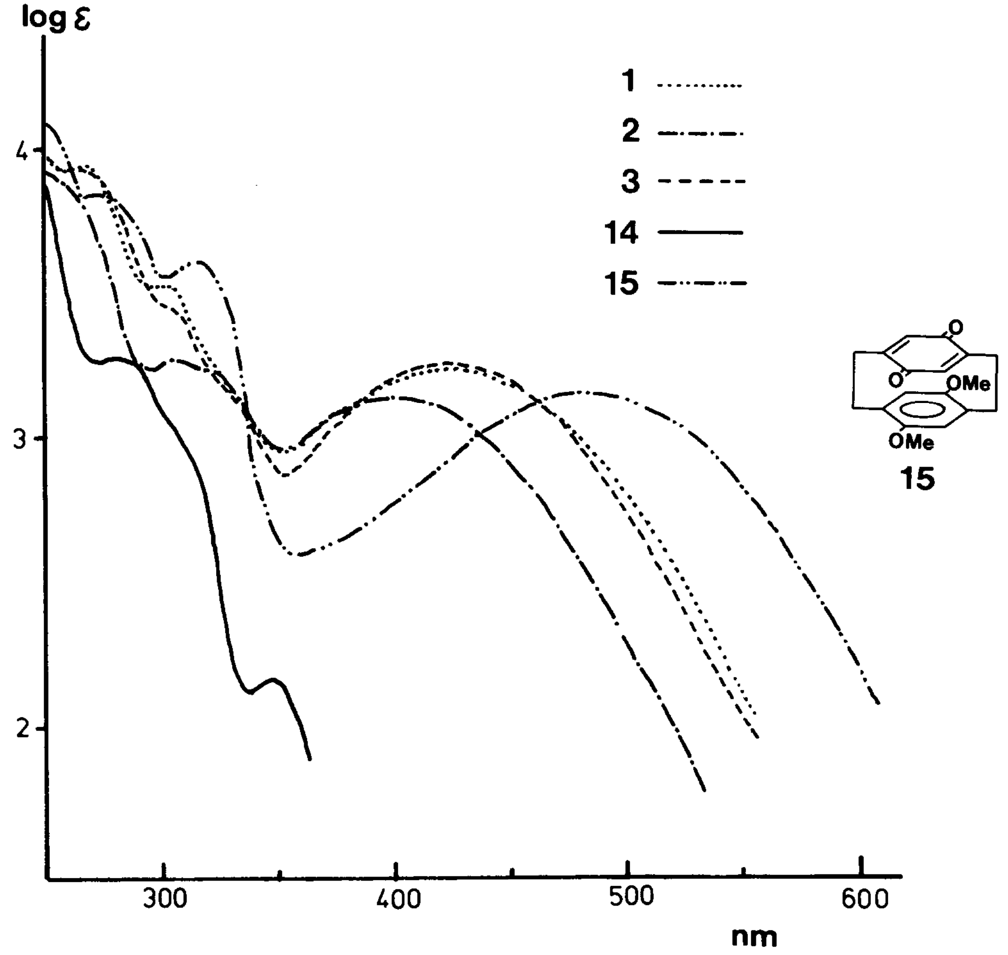

Fig. 2. Electronic spectra of **1**, **2**, **3**, **14** and **15**$^{3,*)}$ in CH_2Cl_2 (* in $CHCl_3$).

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4) We have just learned from Prof. Staab's private communication that the compounds **1** and **2** have also been prepared by his group [Angew. Chem., 89, 841 (1977)].