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LAYERED COMPOUNDS. LIV.[1)] SYNTHESES OF TRIPLE-LAYERED [m.m][n.n]PARACYCLOPHANES

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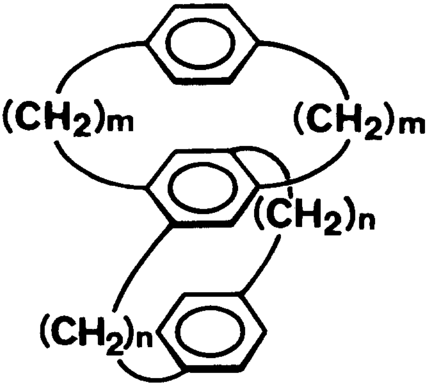
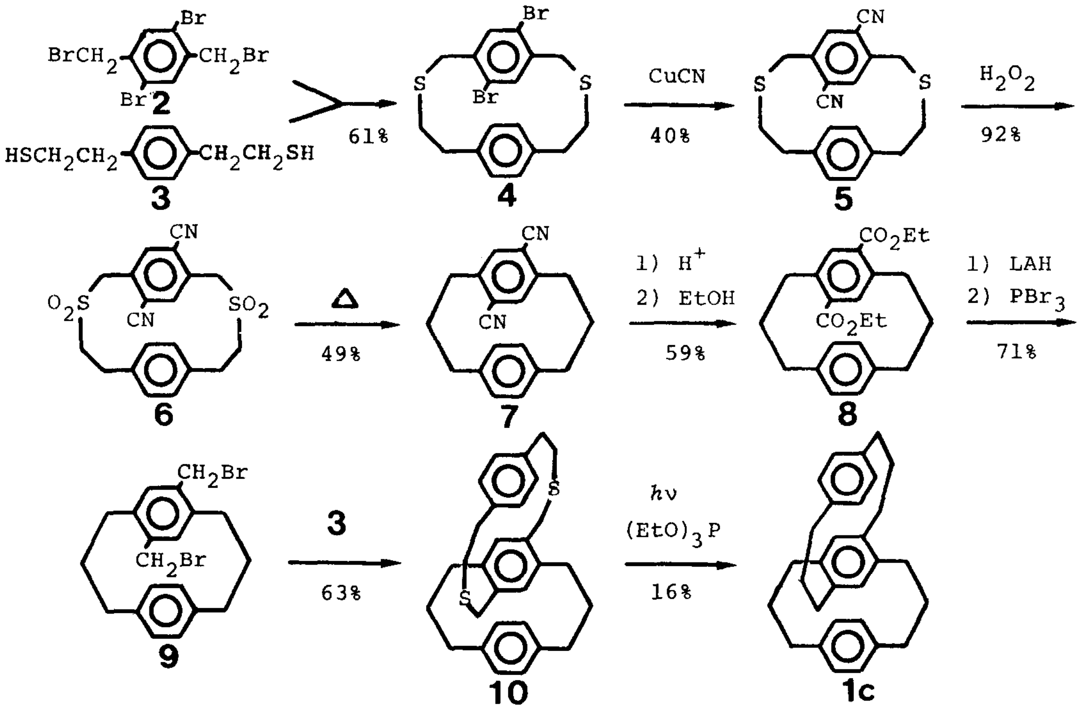
In the study of a series of multilayered [2.2]paracyclophanes including the triple-layered one 1a, we disclosed significant transannular electronic interaction with an increase of the layer number.2) Multilayered [3.3]- and [4.4]-paracyclophanes are expected to reveal unique behaviors concerning only the transannular π-π interaction in contrast to the [2.2]homologs which undergo a variety of intriguing properties based on both the interaction and their severe strain.3) Here we wish to report on the syntheses and properties of a series of triple-layered [m.m][n.n]paracyclophanes 1b-1e.



1a, m=n=2
1b, m=2, n=3
1c, m=n=3
1d, m=2, n=4
1e, m=3, n=4

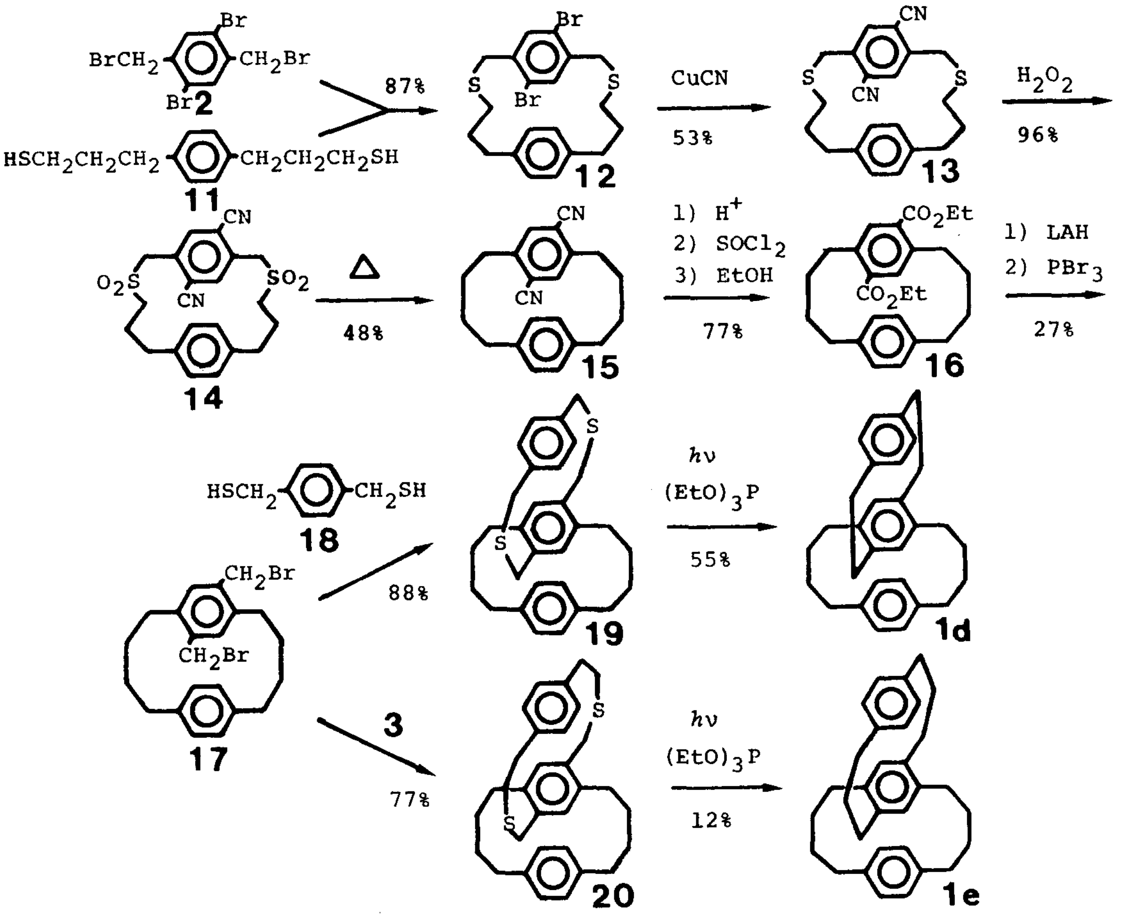
The synthesis of [2.2][3.3]paracyclophane 1b was reported in a recent communication where a general synthetic method of [3.3]cyclophanes was described.4) [3.3][3.3]Paracyclophane 1c was prepared by application of the same method. Thus, a coupling reaction between 2,5-dibromo-1,4-bis(bromomethyl)benzene 2 and 1,4-bis(mercaptoethyl)benzene 3 gave 16,19-dibromo-2,13-dithia[4.4]paracyclophane 4 in 61% yield, m.p. 181.5-182.5°C. Treatment of 4 with cuprous cyanide in N-methylpyrrolidinone led to the corresponding dicyano derivative 5 in 40% yield, m.p. 259.5-261.5°C. Oxidation of 5 with hydrogen peroxide to disulfone 6, followed by pyrolysis (650°C, 0.2 mmHg), gave 5,8-dicyano[3.3]paracyclophane 7, m.p. 190.5-191.5°C, which was converted to 5,8-bis(bromomethyl)[3.3]paracyclophane 9 in a conventional method. The dibromide



9 was treated with dithiol 3 to give cyclophane 10 in 63% yield, m.p. 204-205°C Photodesulfurization of 10 in triethylphosphite with a high pressure mercury lamp for 6 hrs under nitrogen afforded the desired [3.3][3.3]paracyclophane 1c5) in 16% yield, colorless plates from hexane, m.p. 166-168°C.

According to the same reaction sequence, 6,9-bis(bromomethyl)[4.4]paracyclophane 17 was obtained by the use of 1,4-bis(mercaptopropyl)benzene 11 instead of 3 as a starting material. A coupling reaction of 17 with 1,4-bis(mercaptomethyl)benzene 18 gave cyclophane 19 in 88% yield, which was irradiated with a high pressure mercury lamp for 7 hrs to afford [2.2][4.4]paracyclophane 1d5) in 55% yield, colorless prisms from hexane, m.p. 129-130°C. Similarly, cyclophane 20 was prepared in 77% yield by treatment of 17 with 3. However, the subsequent photochemical sulfur extrusion of 20 with a high pressure mercury lamp was quite sluggish. The use of a low pressure mercury lamp proved much effective, and after irradiation for 12 hrs [3.3][4.4]paracyclophane 1e5) was obtained in 12% yield, colorless columns from pentane, m.p. 170-171°C.

One of the most remarkable features of multilayered paracyclophanes is marked bathochromic and hyperchromic shifts of the absorption bands in their



electronic spectra, which are theoretically explained in terms of the configuration interactions of charge-transfer and neutral excitation states.6) Figure 1 shows the electronic spectra of a series of triple-layered [m.m][n.n]paracyclophanes. Their bathochromic shifts decrease in order of [2.2][2.2] > [2.2][3.3] > [3.3][3.3] > [2.2][4.4] > [3.3][4.4]. It is concluded from the above result that [2.2]system contributes more strongly on the transannular interaction than [3.3] or [4.4]system in triple-layered paracyclophanes just as in double-layer series.

Cram et al. reported an interesting phenomenon that double-layered [3.3]-paracyclophane was a stronger π-donor than the corresponding [2.2]paracyclophane when complexed with tetracyanoethylene.7) A similar result was observed for the present triple-layer series. The CT absorption maxima of the TCNE complexes can be used as a measure of π-basicity of the donor cyclophanes; λmax in CH_2Cl_2, 630 nm for [2.2][2.2], 640 nm for [2.2][3.3], 655 nm for [3.3][3.3], 525 nm for [2.2][4.4], 546 and 625(sh) nm for [3.3][4.4]. Accordingly [3.3][3.3]system 1c is the strongest donor of all the triple-layered paracyclophanes.

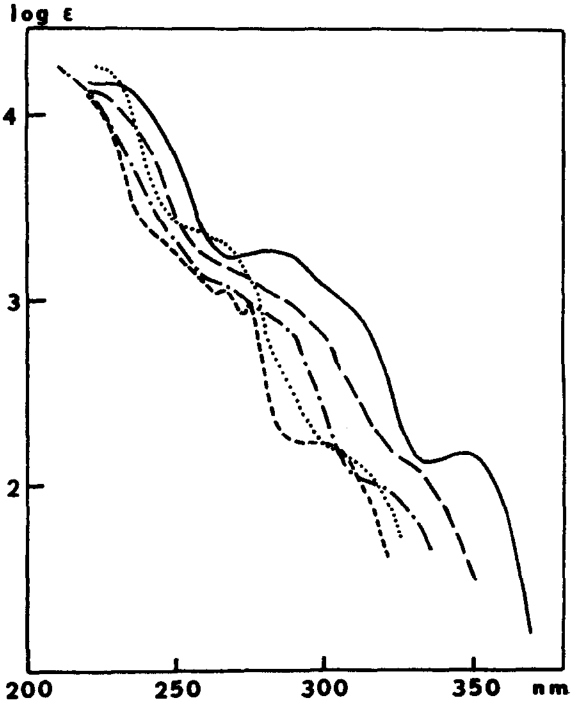


Fig. 1. The electronic spectra of 1a (———), 1b (— — —), 1c (—·—·), 1d (········) and 1e (-------) in THF.

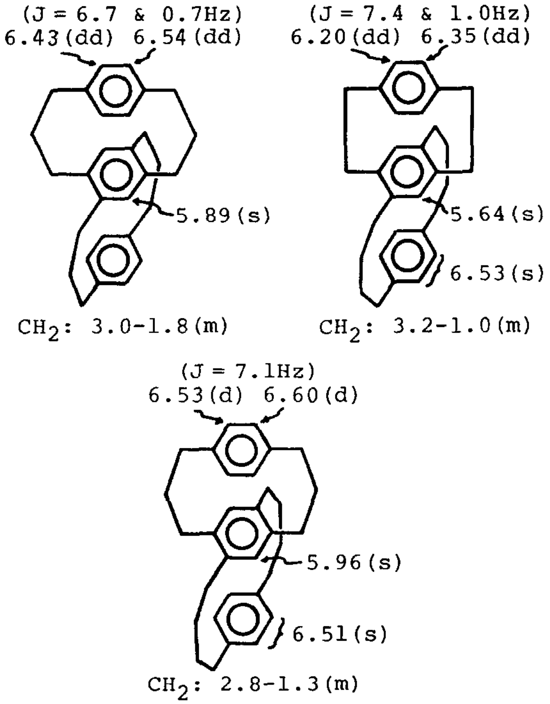


Fig. 2. The NMR data of 1c, 1d and 1e (100 MHz, δ in $CDCl_3$).

References and Notes

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5) Satisfactory NMR and MS spectra and elemental analyses were obtained. The NMR spectra (Fig. 2) exhibit marked upfield shifts characteristic of multi-layered cyclophanes (cf. T. Otsubo, S. Mizogami, Y. Sakata and S. Misumi, Bull. Chem. Soc. Jpn., 46, 3831 (1973).

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