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# [3.3]- AND [4.4]-TROPYRIOPARACYCLOPHANE TETRAFLUOROBORATES[1]

## —INTRAMOLECULAR CHARGE-TRANSFER INTERACTION—

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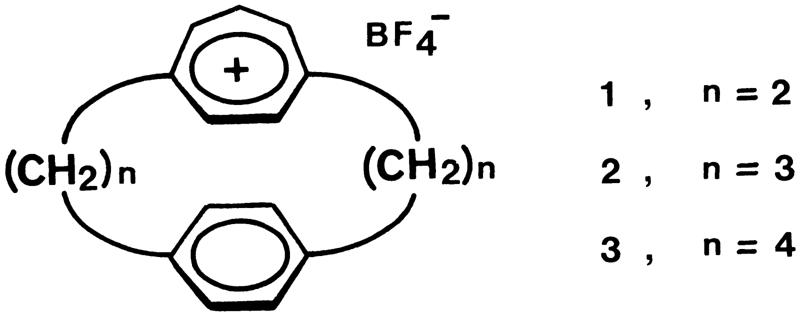
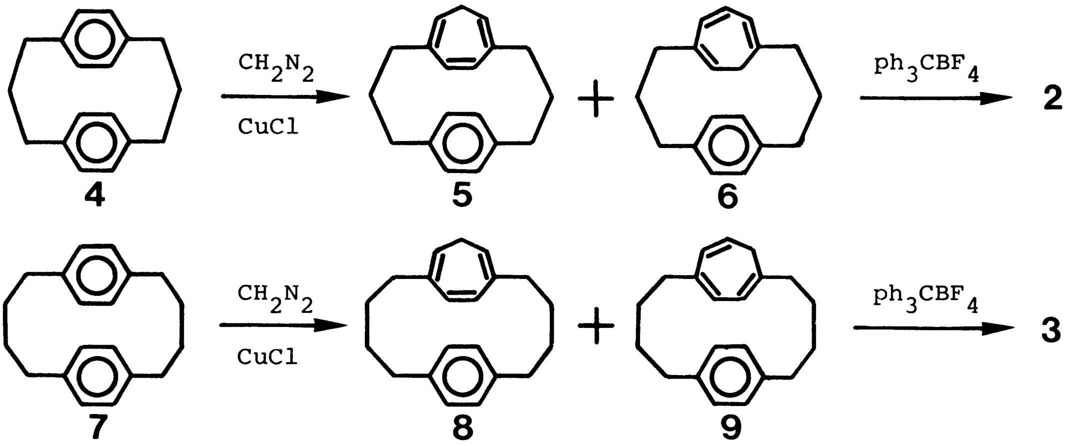
The title compounds were synthesized and their structures were confirmed by NMR spectra. The [3.3]cyclophane 2 shows significant charge-transfer bands in its electronic spectrum. The intramolecular CT interaction in three [n.n]tropylioparacyclophane homologues is compared.

In the study on tropyliocyclophanes as intramolecular charge-transfer models, we observed that the charge-transfer (CT) interaction increased with an increase in layer number of donor moiety[2] and depended largely on the geometry of donor-acceptor pair.[3] The CT interaction may be strengthened in a [3.3]system of cyclophane rather than in the corresponding [2.2]system where donor-acceptor pair is more closely fixed and more severely strained than the former. Recent examples involve [3.3]paracyclophanequinone[4] and dimethoxy[3.3]paracyclophanequinone,[5] although there is not so much difference between CT interactions in [2.2] and [3.3]systems of cyclophanequinone,[5] and dicyanodimethoxycyclophane.[6] In order to pursue this problem in the case of tropylioparacyclopahne, we have studied a series of [n.n](1,4)tropylioparacyclophane tetrafluoroborates 1-3. Now we wish to



report the syntheses of two higher homologues 2 and 3 and compare their properties with the corresponding property of the [2.2]system.[2,7)]



The compounds 2 and 3 were prepared by carbene ring expansion method from the corresponding [n.n]paracyclophanes[8)] as previously described for 1.[2)] Thus, 4 was treated with diazomethane to give a mixture consisted of two main isomeric tropylideneparacyclophanes 5 and 6.[9)] The subsequent treatment of the mixture with trityl fluoroborates produced tropylioparacyclophane 2, reddish yellow microcrystals from ether-acetonitrile, dec > 125°C, overall yield 7% based on 4. Similarly, 3 was derived via 8 and 9[10)] from [4.4]paracyclophane 7, pale yellow plates from ether-acetonitrile, mp 175-176°C with decomp., overall yield 10% based on 7.

Their structures were confirmed by NMR spectra as shown in Fig. 1 and elemental analyses. A comparison of the NMR data of 1-3 indicates that the anisotropy effects due to the two faced aromatic rings become marked as the length of the methylene bridges decreases. The ring-to-ring distances of 1-3, though both rings are not exactly centered, are roughly estimated to be comparable to those of the corresponding [n.n]paracyclophanes (2.83-3.09Å for [2.2]PC,[11)] 3.14-3.31Å for [3.3]PC,[12] and 3.73Å for [4.4]PC[13)]) and the values of both 1 and 2 are less than or equal to the value found for ordinary, intermolecular charge-transfer complexes.

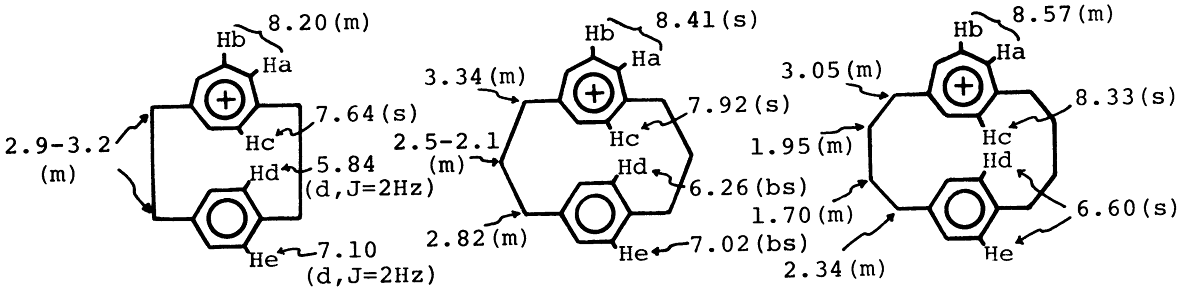


Fig. 1. NMR data of 1-3 in deuteriochloroform (δ value, 100MHz).

The two rings of 3 are apart enough to permit ring rotation as indicated by equivalence of Hd and He protons at room temparature. The singlet at $\delta$ 6.60 ppm, however, splits into two singlets at $\delta$ 6.40 and 6.49 ppm at a low temperature below -100°C, which corresponds to 8.9 kcal/mol (Tc = -100°C) of activation energy for ring rotation.14)

All the compounds 1-3 show intramolecular charge-transfer bands due to transitions from benzene to tropylium ion in a longer wavelength region of the electronic spectra (Fig. 2). The broad absorption bands above 340 nm for 1, 310 nm for 2, and 330 nm for 3 are shifted to shorter wavelength by about 15 nm accompanying the change from methylene chloride to acetonitrile, indicating the bands associated with charge-transfer transition.15) [4.4]Cyclophane 3 demonstrates a broad CT band at shorter wavelength and with weaker intensity than 1 and 2. The long donor-acceptor distance of 3 is responsible for this weak CT interaction. There are observed two CT bands in the spectra of 1 and 2, respectively, probably owing to a splitting of the degenerate highest occupied levels of donor benzene; $\lambda_{max}$ 410-430(sh) and 354 nm for 1 and 414 and 339 nm for 2. The first band of 2 is more intensive and extends to longer wavelength than that of 1, although the second bands of both compounds are nearly same in intensity.

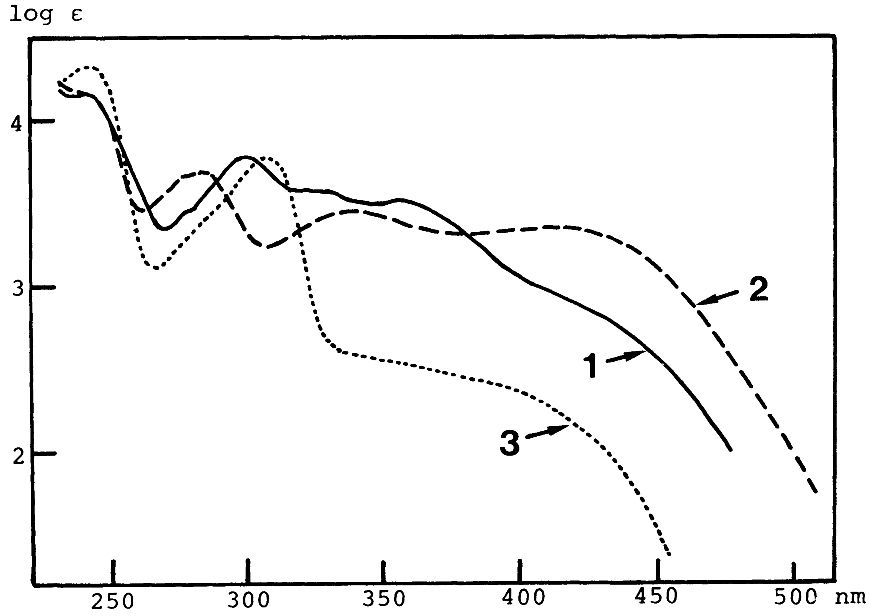


Fig. 2. Electronic spectra of 1-3 in methylene chloride.

The above results suggest that the CT interaction becomes stronger in an order of [4.4] < [2.2] < [3.3] and that the strainless, somewhat flexible geometry of [3.3] system enables a donor-acceptor orientation suitable to facilitate the CT transition.

## References and Notes

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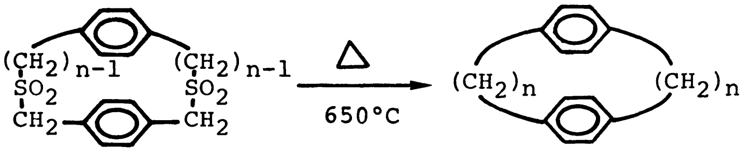

4 : n=3 74.5%

7 : n=4 75.9%

9) NMR data (δ value in $CCl_4$, 100 MHz). 5: 6.72(d, J=1.5Hz, 2H, ArH), 6.56(d, J=1.5Hz, 2H, ArH), 5.76(s, 2H, olefinic), 4.84(t, J=6Hz, 2H, olefinic), 3.0-1.2 (m, 14H, $CH_2$); 6: 7.0-6.6(m, 4H, ArH), 6.00(dd, J=10 and 5Hz, 1H, olefinic), 5.56(bd, J=5Hz, 1H, olefinic), 4.00(t, J=7Hz, 1H, olefinic), 3.0-1.2(m, 14H, $CH_2$).

10) NMR data (δ value in $CCl_4$, 100 MHz). 8: 6.80(s, 4H, ArH), 6.04(s, 2H, olefinic). 4.94(t, J=6Hz, 2H, olefinic), 2.6-1.2(m, 18H, $CH_2$); 9: 6.76(s, 4H, ArH), 5.78 (d, J=6Hz, 1H, olefinic), 5.60(d, J=10Hz, 1H, olefinic), 5.29(d, J=6Hz, 1H, olefinic), 4.88(dt, J=6, 6, and 10Hz, 1H, olefinic), 2.6-1.2(m, 18H, $CH_2$).

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