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CHARGE TRANSFER INTERACTION IN SOME TROPYLIOCYCLOPHANE TETRAFLUOROBORATES1)

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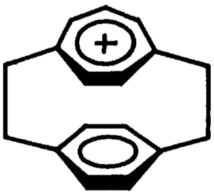
Three isomeric [2.2]tropyliocyclophanes were synthesized. The similarity of their structures to those of [2.2]metapara- and metacyclophanes and a relationship between the structures and the intramolecular CT interaction are discussed on the basis of the NMR and electronic spectra, respectively.

Recently much attention has been paid to intramolecular charge transfer type of cyclophanes, in which a donor and an acceptor moieties are forced to stack face-to-face with each other by methylene bridges. [2.2](1,4)Tropylioparacyclophane tetrafluoroborate 1, an example of CT cyclophanes, was independently synthesized through different routes by Keehn's group2) and our group3). It showed a remarkable CT transition in its electronic spectrum. In addition, we reported much stronger CT interaction in the triple-layered analogue 2 due to increasing transannular π-π interaction. In this communication we wish to report on the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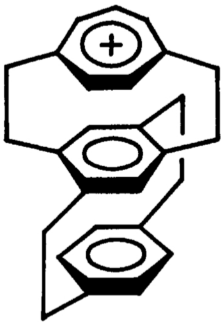
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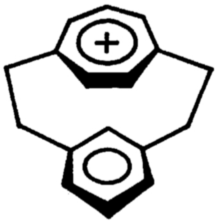
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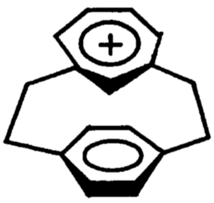
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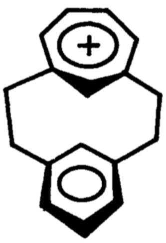
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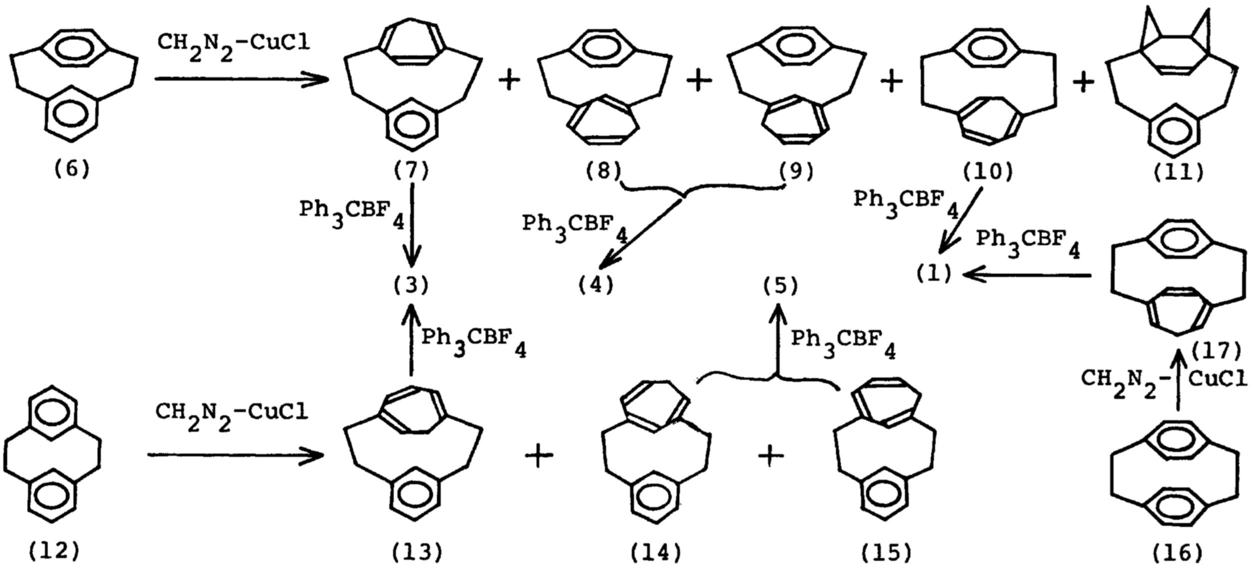
synthesis and the CT interaction of three structural isomers of 1, that is, [2.2]-(1,4)tropyliometacyclophane 3, [2.2](1,3)tropylioparacyclophane 4, and [2.2](1,3)-tropyliometacyclophane 5.

The synthetic methods are shown in the following scheme. Thus the reaction of [2.2]metaparacyclophane 6 with diazomethane gave monomethylenated products 7-10 and bismethylenated one 11.[4] A similar reaction of [2.2]metacyclophane 12 gave monomethylenated products 13-15.[5] After separation by column chromatography,[6] these tropylidenecyclophanes were treated with trityl fluoroborate to yield the desired tropyliocyclophanes; 3, yellow semisolid which gradually decomposed on exposure to air, overall yield 1% based on 6 or 12; 4,[7] pale yellow prisms from ether-acetonitrile, mp 200-201°C (dec), overall yield 3% based on 6; 5,[7] yellow needles from methylene chloride-ether, mp 116-117°C (dec), overall yield 2% based on 12. Tropylioparacyclophane 1 was also derived from 10 (overall yield 1% based on 6) and its physical data agreed with those of the authentic sample previously prepared from [2.2]paracyclophane 16.



The NMR spectra give us an instructive information as to the stacking mode of

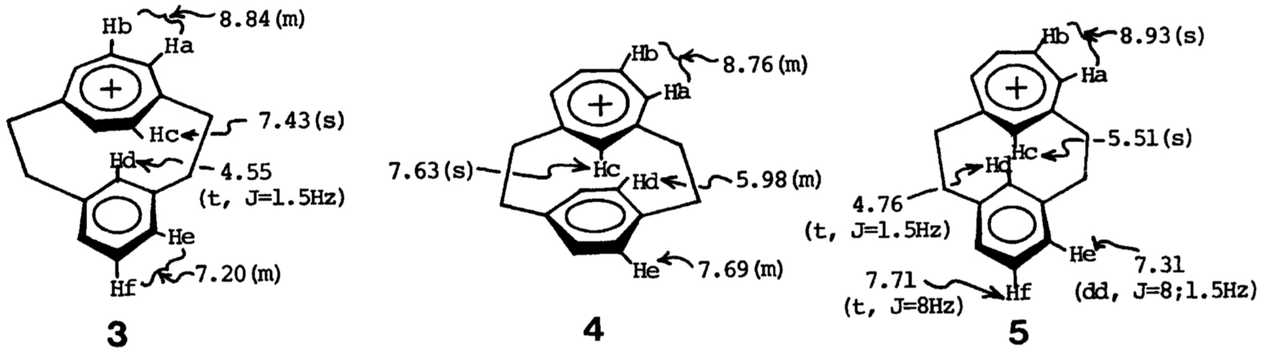
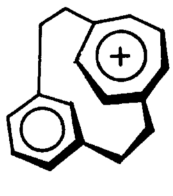
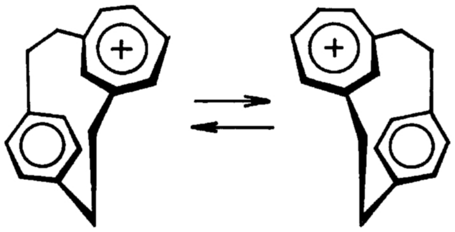


Fig. 1 ^{1}H-NMR spectra of tropyliocyclophanes 3-5 (δ values in CD$_2$Cl$_2$).

the benzene and the tropylium rings. As seen in Fig. 1, the NMR data of 3 and 4 reveal two features: 1) significant upfield shifts of the inner aromatic protons, Hd of 3 and Hc of 4; 2) nonequivalent chemical shifts of tropylium protons, Ha,b vs Hc in 3, and of benzene protons, Hd vs He in 4. Since these NMR patterns are characteristic of [2.2]metaparacyclophanes, it is considered that the geometries of 3 and 4 are similar to that of [2.2]metaparacyclophane 6, that is, 3a for 3 and 4a or 4b for 4. The NMR measurement at variable temperature showed that no ring flipping between 3a and 3b occurred up to 120 °C and only a rapid decomposition were observed over that temperature and thereby that 3 existed only in the stable form 3a. On the other hand, 4 exhibited the ring flipping between equivalent comformers 4a and 4b (Tc = 67°C). The energy barrier of the flipping, 16 Kcal/mol, is lower by ca. 5 Kcal/mol than that of 6,8) indicating the decrease in the molecular strain accompanied by enlargement of hexagonal benzene ring to heptagonal tropylium ring. The NMR spectrum of 5 is characterized by extraordinary upfield shifts of both the inner protons Hc and Hd. This suggests the structure of 5 to be similar to that of [2.2]metacyclophane 12. It is noteworthy that 1 may have a geometry analogous to [2.2]paracyclophane 16 but with slight displacement of the two aromatic rings in palallel.3)


3a


3b


4a 4b

The electronic spectra are shown in Fig. 2. The broad bands above 300 nm are associated with intramolecular charge transfer transition from the benzene to tropylium ion, because of their considerable blue shifts with an increase of solvent polarity (about 15 nm blue shift from methylene chloride to acetonitrile). These CT bands obviously differ from one another in intensity and wavelength.

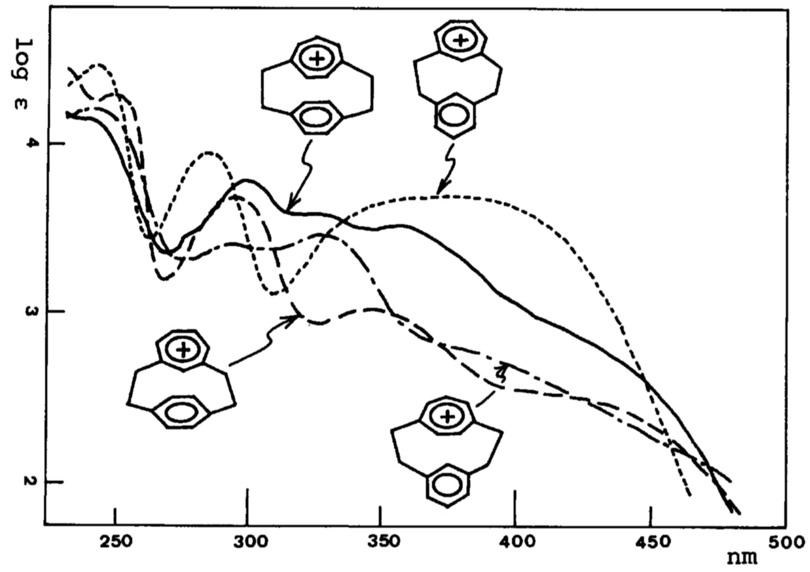


Fig. 2 Electronic spectra of 1 and 3-5 (in CH_2Cl_2).

Thus the compound 5 exhibits the most intensive CT band, despite the least overlapping between the donor and the acceptor rings. Very recently, Murata et al. have observed an intensive CT interaction in the spectrum of 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate, regardless of minimized overlap between the tropylium ion and the remote benzene rings.[9] This CT absorption shows incidentally a striking resembrance to the CT bands of 5. On the other hand, the other tropyliocyclophanes, 1, 3, and 4 with more extensively overlapped donor-acceptor pair demonstrate the CT bands extend to longer wavelength region than that of 5 or intermolecular p-xylene-tropylium complex.[10] These phenomena indicate that charge transfer transition depends largely on the geometry, i.e., orientation and distance, of donor-acceptor pair.

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4) NMR data (δ): 7 (CCl_4); 7.0-6.7 (m, 3H), 6.24 (t, J=1.5 Hz, 1H), 5.31 (s, 2H), 5.21 (t, J=7 Hz, 2H), 3.0-0.8 (m, 10H): 10 (toluene-d_8); 6.71 (dd, J=8 and 2 Hz, 1H), 6.53 (dd, J=8 and 2 Hz, 1H), 6.33 (dd, J=8 and 2 Hz, 1H), 6.26 (dd, J=8 and 2 Hz, 1H), 6.08 (dd, J=10 and 6 Hz, 1H), 5.92 (d, J=10 Hz, 1H), 5.42 (br d, J=6 Hz, 1H), 3.90 (t, J=7 Hz, 1H), 3.1-2.0 (m, 9H), 1.47 (dt, J=13 and 7 Hz, 1H): 11 (CCl_4); 7.02 (t, J=1.5 Hz, 1H), 7.0-6.7 (m, 3H), 4.74 (s, 2H), 2.8-0.8 (m, 10H), 0.42 (m, 2H), -0.47 (t, J=4 Hz, 2H). The NMR spectra of 8 and 9 were not assigned, because the two isomers could not be separated from each other.
5) NMR data of 13-15 are as follows (δ, CCl_4): 13; 7.07 (t, J=8 Hz, 1H), 6.74 (dd, J=8 and 1.5 Hz, 1H), 6.66 (dd, J=8 and 1.5 Hz, 1H), 6.55 (dd, J=11 and 5 Hz, 1H), 6.36 (d, J=11 Hz, 1H), 6.02 (br d, J=5 Hz, 1H), 5.31 (t, J=1.5 Hz, 1H), 3.05 (t, J=7 Hz, 1H), 3.1-1.3 (m, 10H): 14; 7.24-6.83 (m, 3H), 6.07 (d, J=10 Hz, 1H), 5.66 (t, J=1.5 Hz, 1H), 5.42 (dt, J=10 and 7 Hz, 1H), 5.05 (t, J=7 Hz, 1H), 4.08 (br s, 1H), 3.3-1.4 (m, 10H): 15; 7.22-6.80 (m, 3H), 6.20 (d, J=5 Hz, 1H), 6.09 (t, J=1.5 Hz, 1H), 5.80 (dd, J=10 and 5 Hz, 1H), 5.35 (ddd, J=10, 7, and 6 Hz, 1H), 3.50 (br s, 1H), 3.2-1.4 (m, 10H).
6) Even after purification by chromatography, the tropylidene compounds were contaminated with bismethylenated compound 11 or the starting material 6 or 12, but used without further purification.
7) Cyclophanes 4 and 5 gave satisfactory elemental analyses.
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