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LAYERED COMPOUNDS. XXXVIII.[1] SYNTHESIS OF AN INTRAMOLECULAR CHARGE TRANSFER COMPLEX CONTAINING A 7,7,8,8-TETRACYANOQUINODIMETHANE UNIT

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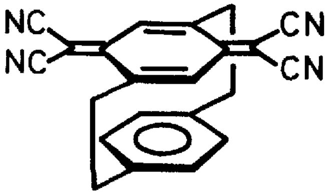
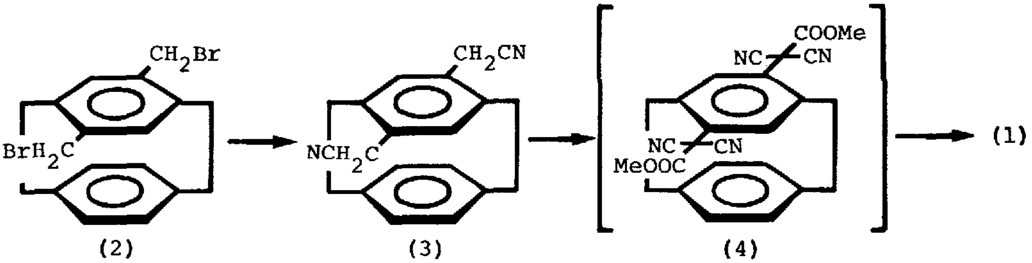
Several intramolecular charge transfer complexes of [2.2]paracyclophane system have been reported in the context of the study of transannular π-electronic interactions in layered compounds.[2] A typical π-acceptor 7,7,8,8-tetracyanoquinodimethane(TCNQ) is well known to form stable, highly conductive charge transfer complexes with some π-donors, particularly with tetrathiofulvalene[3] and tetraselenofulvalene.[4] We now wish to report the synthesis of an intramolecular charge transfer cyclophane(1) containing a TCNQ moiety, which was accomplished successfully by the application of new synthetic procedure of TCNQ.[5]



(1)

Reaction of 4,7-bis(bromomethyl)[2.2]paracyclophane(2)[6] with sodium cyanide in dimethyl sulfoxide gave dicyanide(3)[77.8%, faintly yellow fine plates from benzene-hexane, m.p. 173.5-174.5°C]. Treatment of 3 with dimethyl carbonate and sodium methoxide, azeotropic distillation of resulting methanol with benzene, and distillative addition of cyanogen chloride into the reaction



mixture were successively carried out according to Wheland and Martin.[5] A solution of the reaction product in benzene was passed through a column of silica gel to afford the desired compound(1)[7] without isolation of the intermediate(4)[1: 22.8% based on 3, purplish-red plates from benzene, decomp. over 260°C, Mass 344(M^+), IR(KBr disk) 2190 cm^{-1}(C≡N), NMR($CDCl_3$) δ 2.5-3.5(m, 4H, methylene), 3.8-4.1(m, 4H, methylene), 6.46(bs, 2H, vinyl), 6.83 ppm(s, 4H, aromatic)].

The electronic spectrum of 1 in the Figure shows strong, additional absorption in the region of 500-600 nm as compared with that of 2,5-dimethyl TCNQ, indicating that the absorption is attributable to the intramolecular charge transfer band. The studies on electrical conductivity and crystal structure of 1 are now in progress and will be reported elsewhere.

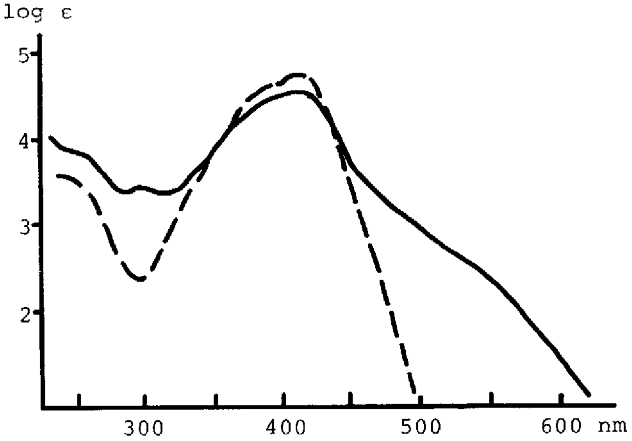


Figure. Electronic spectra of 1(——) and 2,5-dimethyl TCNQ(----) in CH_2Cl_2.

References

1) Part XXXVII: N. Kannen, T. Otsubo, and S. Misumi, Bull. Chem. Soc. Japan, in press.

2) D. J. Cram and A. C. Day, J. Org. Chem., 31, 1227(1966); W. Rebafka and H. A. Staab, Angew. Chem. internat. Edit., 12, 776(1973); ibid., 13, 203(1974); H. A. Staab and H. Haffner, Tetrahedron Lett., 4397(1974); H. Tatemitsu, T. Otsubo, Y. Sakata, and S. Misumi, ibid., 3059(1975).

3) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Amer. Chem. Soc., 95, 948(1973).

4) E. M. Engler and V. V. Patel, ibid., 96, 7376(1974).

5) R. C. Wheland and E. L. Martin, J. Org. Chem. 40, 3101(1975).

6) N. Kannen, T. Umemoto, T. Otsubo, and S. Misumi, Tetrahedron Lett., 4357(1973)

7) Satisfactory elemental analyses of 1 and 3 were obtained.