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FURTHER EXAMPLES OF TETRACYANOQUINODIMETHANOCYCLOPHANE[1)]

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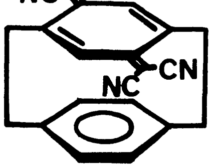
Three tetracyanoquinodimethanocyclophanes **2**-**4** were synthesized from the corresponding dimethyl cyclophanes. They show stronger charge transfer bands than TCNQ-paracyclophane **1** in the electronic spectra and no distinct difference in those of two isomeric TCNQ-naphthalenophanes **3** and **4**.

In connection with the dependences of orientation and distance of donor-acceptor pair for charge-transfer interaction, various charge-transfer (CT) cyclophanes have been extensively studied.[2)] Previously, we reported the preparation of CT cyclophane **1** containing a 7,7,8,8-tetracyanoquinodimethane (TCNQ) moiety, which is well known as a very strong π-acceptor. However, the compound **1** shows the CT band only as a shoulder submerged partially in the strong absorption band of the TCNQ chromophore itself. It is expected from the above result that distinct CT band will be displayed by some TCNQ-phanes where a TCNQ moiety is stacked with donors having lower ionization potential than benzene. In this communication we wish to report on the syntheses and CT interactions of three TCNQ-phanes **2**-**4**.



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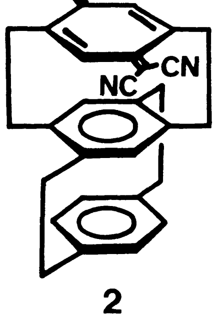

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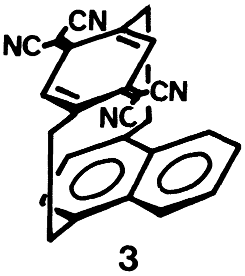

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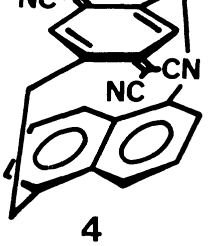

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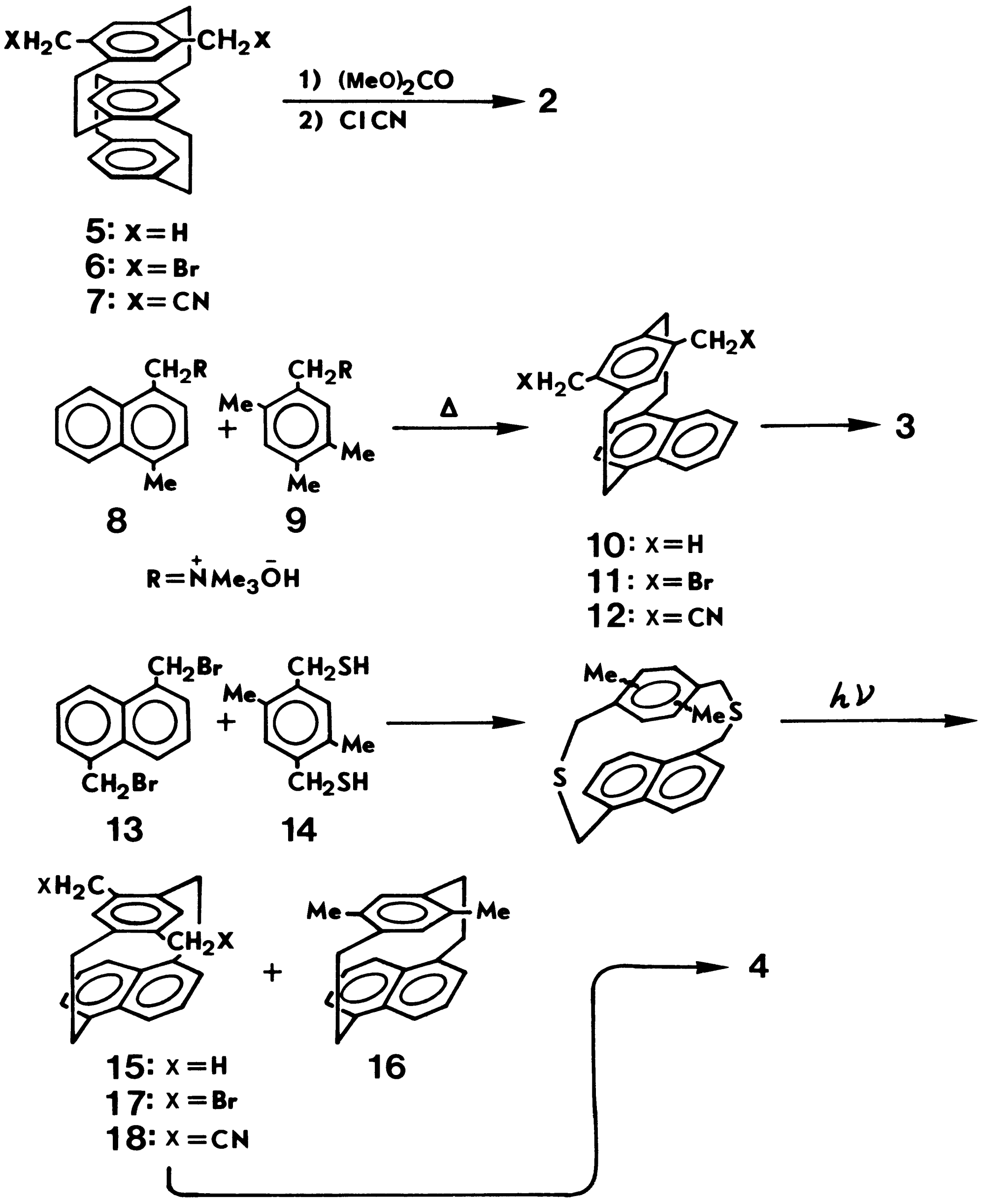

All the compounds **2-4** were prepared according to a recently developed procedure3) from the corresponding dimethyl cyclophanes as previously described for **1**.2i) Thus, reaction of dibromide **6**4) with sodium cyanide in DMSO yielded dicyanide **7** in 53% yield. The dicyanide **7** was treated with potassium t-butoxide in benzene-dimethyl carbonate, followed by azeotropic distillation of subsidiarily yielded methanol with benzene, and finally by blowing of cyanogen chloride into the reaction mixture with the aid of nitrogen stream. The crude product was passed through a short column of silica gel to give desired TCNQ-phane **2**, 26% yield, deep violet thin plates from acetone, dec> 250°C.5) In a similar manner, TCNQ-

(1,4)naphthalenophane **3** was derived from 4,7-dimethyl[2]paracyclo[2](1,4)naphthalenophane **10**, which was prepared by cross-breeding reaction of quaternary ammonium bases, **8**$^{6)}$ and **9**$^{7)}$, in 13% yield; **10** : colorless scales from hexane, mp 147.5-148.5°C; **3**: 24% yield based on **12**, deep violet thin plates from acetone, dec > 250°C.$^{5)}$

Coupling reaction of dibromide **13**$^{8)}$ and dimercaptan **14**$^{9)}$, followed by photodesulfurization in triethylphosphite gave two isomeric dimethyl[2]paracyclo[2]-(1,5)naphthalenophanes **15** and **16** in a ratio of 8-10:1. The same reaction procedure of isomer **15**, which was separated by recrystallization from benzene-hexane and confirmed by NMR spectrum, afforded TCNQ-(1,4)naphthalenophane **4**; **15**: colorless needles from hexane, mp 238.0-239.5°C with dec ; **16**: colorless prisms from hexane, mp 257.0-259.5°C with dec; **4**: 9.1% yield based on **18**, deep violet plates from benzene-hexane, dec > 250°C.$^{5)}$

The electronic spectra of **1**-**4** are shown together with that of dimethyl TCNQ as a reference in Fig. 1. The compounds **2-4** exhibit broad, intensive CT bands in the region of 500-900 nm, corresponding to lower ionization potentials of their donor moieties (I_P: naphthalene 8.1 eV, [2.2]paracyclophane 8.4 eV,$^{10)}$ and benzene 9.1 eV); λ_{max} (ε), 552 nm(3,150) for **2**, 626 nm(860) for **3**, and 660 nm(640) for **4**. A marked increase of absorption intensity rather than a red shift of the CT band maximum of **2** is observed by comparing with that of **1**, just as the CT bands of double- and triple-layered [2.2]paracyclophanequinones.$^{2g)}$

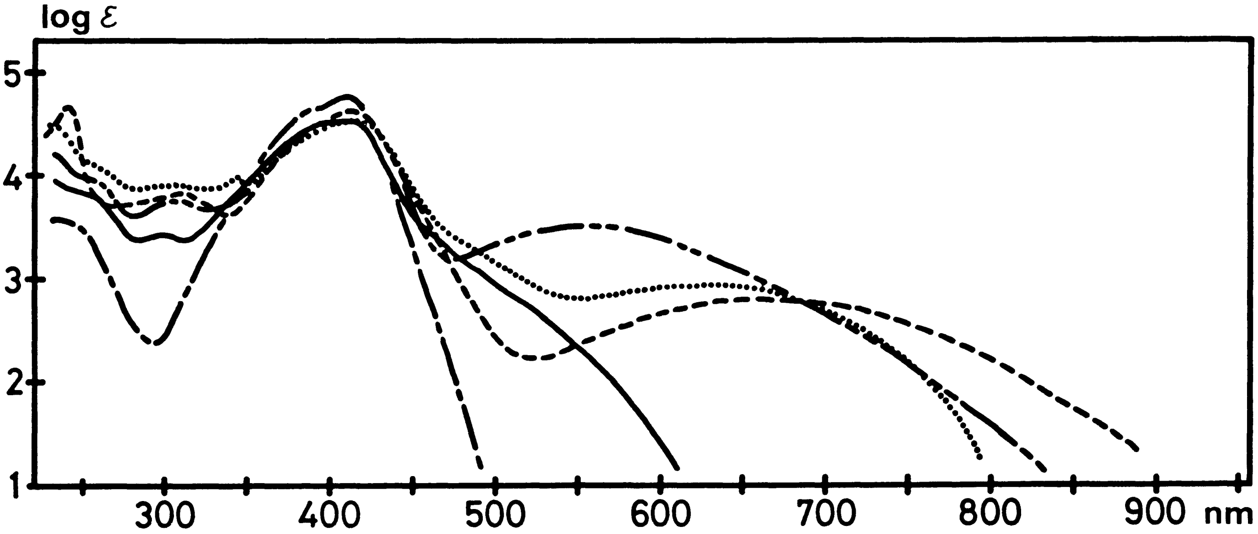

Fig. 1. Electronic spectra of **1** (———), **2** (—··—··), **3** (·········), **4** (- - - - -), and 2,5-dimethyl TCNQ (—·—·—) in CH_2Cl_2.

In contrast to pronounced donor-acceptor orientation dependence of CT interaction in double-layered CT cyclophanes,[2b-2e] there is not great difference in the spectra of two isomeric TCNQ-naphthalenophanes, **3** and **4**, except slight red shift of the CT band of **4**. It means the extent of donor-acceptor overlap to be less important for the intramolecular CT interaction in this case. The CT band maximum of **4** is located at the longest wavelength among those of CT cyclophanes ever reported.[2)]

References and Notes

1) Layered Compounds LVI. Part LV: H. Horita, T. Otsubo and S. Misumi, Chem. Lett. (1978) in press.
2) a) H. A. Staab and C. P. Herz, Angew. Chem., 89, 839 (1977); b) H. A. Staab and W. Rebafka, Chem. Ber., 110, 3333 (1977); c) H. A. Staab, C. P. Herz and H.-E. Henke, ibid., 110, 3351 (1977); d) H. A. Staab and H. Haffner, ibid., 110, 3358 (1977); e) H. A. Staab and V. Taglieber, ibid., 110, 3366 (1977); f) H. A. Staab and A. Gurke, Angew. Chem., 89, 841 (1977); g) H. Tatemitsu, T. Otsubo, Y. Sakata and S. Misumi, Tetrahedron Lett., 1975, 3059; h) H. Horita, T. Otsubo, Y. Sakata and S. Misumi, ibid., 1976, 3899; i) M. Yoshida, H. Tatemitsu, Y. Sakata and S. Misumi, ibid., 1976, 3821; j) H. Horita, T. Otsubo and S. Misumi, Chem. Lett., 1977, 1309; k) H. Masuhara, N. Mataga, M. Yoshida, H. Tatemitsu, Y. Sakata and S. Misumi, J. Phys. Chem., 81, 879 (1977); l) H. Machida, H. Tatemitsu, Y. Sakata and S. Misumi, Tetrahedron Lett., 1978, 915; m) T. Shinmyozu, T. Inazu and T. Yoshino, Chem. Lett., 1977, 1347.
3) R. C. Wheland and E. L. Martin, J. Org. Chem., 40, 3101 (1975).
4) N. Kannen, T. Otsubo and S. Misumi, Bull. Chem. Soc. Jpn., 49, 3208 (1976).
5) Satisfactory elemental analyses and spectral data were obtained. NMR data (100 MHz, δ, $CDCl_3$) **2**: 2.3-3.9(m,16H,CH_2), 5.87(s,2H,inner ArH), 6.16(d, J=0.98Hz,2H,olefinic), 6.38(AB,4H,outer ArH). **3**: 2.6-4.2(m,8H,CH_2), 5.51(bs, 1H,endo-olefinic), 6.47(bs,1H,exo-olefinic), 6.89(AB,1H,ArH), 7.06(AB,1H, ArH), 7.53-8.12(m,4H,ArH). **4**: 3.2-4.1(m,8H,CH_2), 5.91(bs,2H,olefinic), 7.68-7.18(m,6H,ArH).
6) D. J. Cram, C. K. Dalton and G. R. Knox, J. Am. Chem. Soc., 85, 1008 (1963); H. H. Wasserman and P. M. Keehn, ibid., 91, 2374 (1969).
7) D. T. Longone and H. S. Chow, J. Am. Chem. Soc., 86, 3898 (1964); ibid., 92, 994 (1970).
8) W. Ried and H. Boden, Chem. Ber., 91, 1981 (1958).
9) F. Imashiro, M. Oda, T. Iida, Z. Yoshida and I. Tabushi, Tetrahedron Lett., 1976, 371.
10) S. Pignataro, V. Mancini, J. N. A. Ridyard and H. J. Lempka, J. Chem. Soc., Chem. Commun., 1971, 142.

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