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DOUBLE- AND TRIPLE-LAYERED CHARGE TRANSFER CYCLOPHANES CONTAINING TETRACYANOQUINODIMETHANE AND DIMETHOXYBENZENE GROUPS1)

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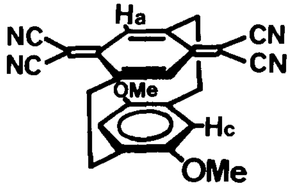
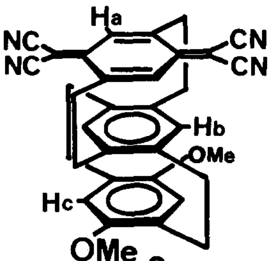
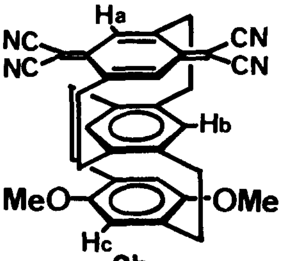
In the previous papers of this series, we reported some double- and triple-layered charge transfer cyclophanes.2) Cyclophane containing 7,7,8,8-tetracyanoquinodimethane(TCNQ) group known well as a very strong π-acceptor has been particularly expected to exhibit pronounced intramolecular CT interaction. A few TCNQ-cyclophanes remarkably showed, in fact, CT bands in long wavelength region.1,2b) We now wish to report syntheses and properties of double- and triple-layered TCNQ-cyclophanes with a dimethoxybenzene group as a π-donor.



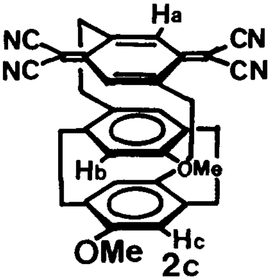
1



2a

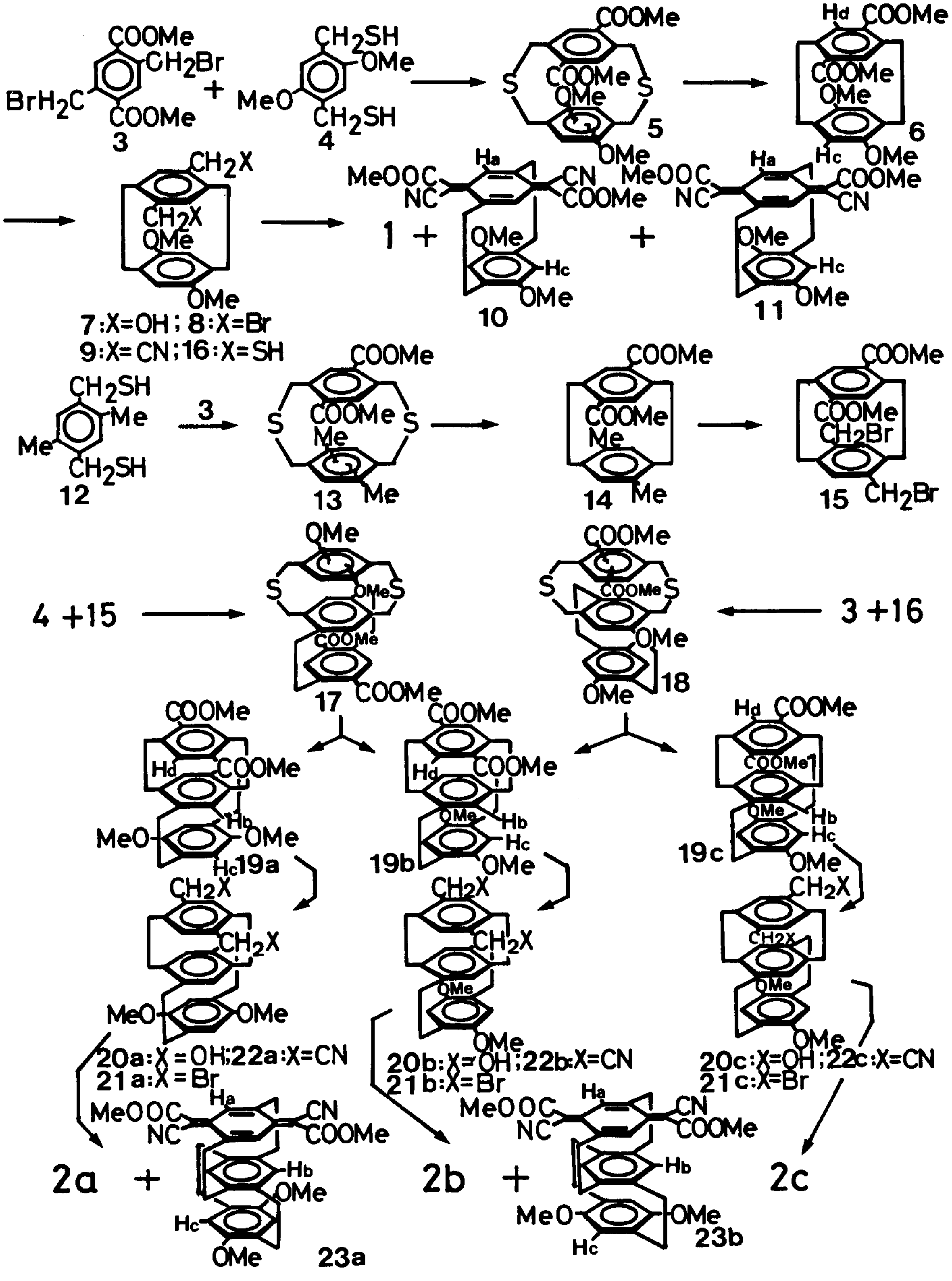


2b



2c

Coupling of dibromide 33) with dimercaptan 4 gave a mixture of two isomeric disulfides 5 in 58.5% yield (a ratio of 3:2 by NMR). The mixture of 5 was irradiated with high-pressure mercury lamp in triethylphosphite(TEP)-benzene (1:1) for 5 hr to give pseudo-ortho cyclophane 6 in 41.0% [yellow prisms from benzene, mp 159-160°C]. Reduction of 6 with $LiAlH_4$ in tetrahydrofuran, followed by treatment with PBr_3 in benzene, afforded dibromide 8 in 54.6% based on 6 [colorless prisms from benzene, dec.>180°C]. Treatment of 8 with potassium cyanide in DMSO gave biscyanomethyl compound 9 in 72.7% [colorless prisms from benzene, mp 208-210°C]. 9 was reacted with dimethyl carbonate in the presence of potassium t-butoxide under nitrogen stream and the volatile components in the reaction mixture were evaporated under vacuum. After cyanogen bromide gas was introduced into a DMSO solution of the residue in the aid of nitrogen stream, TCNQ-cyclophane 1 and two isomeric cyano-esters 10 and 11 were isolated by column chromatography on silica gel. When cyanogen chloride was used instead cyanogen bromide, only 10 was isolated in 9.1% yield [1: 36.4%, dark violet needles from benzene, dec.>270°C. 10: 11.5%, deep violet prisms from benzene-haxane, mp 192-


COOMe
CH2Br
BrH2C
COOMe
3
+
CH2SH
OMe
MeO
CH2SH
4
S
COOMe
COOMe
OMe
S
OMe
5
Hd
COOMe
COOMe
OMe
Hc
OMe
6
CH2X
CH2X
OMe
OMe
7:X=OH ; 8:X=Br
9:X=CN ; 16:X=SH
1 +
Ha
MeOOC
NC
CN
COOMe
OMe
Hc
OMe
10
+
Ha
MeOOC
NC
COOMe
CN
OMe
Hc
OMe
11
CH2SH
Me
Me
CH2SH
12
3
S
COOMe
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COOMe
Me
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COOMe
CH2Br
CH2Br
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OMe
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OMe
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COOMe
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MeO
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19b
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Hb
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21b:X=Br
CH2X
CH2X
OMe
OMe
20c:X=OH;22c:X=CN
21c:X=Br
2a
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Ha
MeOOC
NC
CN
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OMe
Hc
OMe
23a
2b
+
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MeOOC
NC
CN
COOMe
Hb
MeO
OMe
Hc
23b
2c

195°C. **11**: 3.8%, green powder from benzene, mp 235-238°C with dec.].[4,5]

Coupling of **3** with **12** gave a mixture of two isomeric disulfides **13** in 67.7% (a ratio of 3:1). Photodesulfurization of **13** in TEP-benzene (1:1) for 6 hr afforded 55.8% yield of **14** which was converted with NBS to dibromide **15** in 57.8% [**14**: colorless scales from methanol, mp 108-109°C. **15**: colorless needles from benzene-hexane, mp 143.5-145.0°C]. **15** was coupled with **4** to give a mixture of two isomeric disulfides **17** in 48.3% (a ratio of 3:1). Photodesulfurization of **17** in TEP-benzene (4:1) for 3.5 hr to afford two isomeric triple-layered cyclophanes **19a** and **19b** in 75.2%, which were separated into the two isomers by fractional recrystallization from hexane [**19a**: less soluble isomer, yellow prisms from benzene, mp 178-178.5°C. **19b**: more soluble isomer, yellow prisms from benzene, mp 191.5-193.0°C]. On the other hand, a mixture of two isomeric disulfides **18** was obtained by coupling of **3** with dimercaptan **16** derived from **8** [**16**: 62.7%, colorless prisms from benzene, mp 125-127°C. **18**: 74.0%, a 2:3 ratio]. Photodesulfurization of **18** in TEP-benzene (4:1) for 4 hr to afford a mixture of **19b** and **19c** in 71.0%, which was separated into the two isomers by column chromatography on silica gel and fractional recrystallization from hexane. **19b** was identical with an isomer derived from **17** [**19c**: yellow columns from benzene, mp 191.5-193.0°C]. Three isomers **19a-c** were reduced with $LiAlH_4$ in THF followed by treatment on PBr_3 in benzene to give dibromides **21a-c**, respectively [**21a**: 66.5% based on **19a**, colorless microcrystals from benzene-hexane, dec.> 280°C. **21b**: 76.3% based on **19b**, colorless microcrystals from benzene-hexane, dec.>280°C **21c**: 63.8% based on **19c**, colorless needles from benzene, dec.>200°C].

Table ^{1}H-Chemical Shifts (δ ppm in Deuteriochloroform)

	1	2a	2b	2c	6	19a	19b	19c	10	11	23a	23b
Ha	6.66	6.21	6.20	6.26	—	—	—	—	7.40	6.60 7.47	6.94	6.98
Hb	—	5.83	6.06	6.15	—	5.41	5.73	5.79	—	—	5.80	6.09
Hc	6.11	5.66	5.64	5.64	5.77	5.44	5.47	5.46	6.13	6.12	5.60	5.63
Hd	—	—	—	—	7.44	6.94	6.98	6.97	—	—	—	—
OCH_3	3.77	3.60	3.62	3.62	3.67 3.91	3.51 3.86	3.52 3.89	3.54 3.86	3.68 3.87	3.70 3.77 3.91	3.56 3.84	3.59 3.85

Reaction of **21** with potassium cyanide in DMSO under nitrogen stream gave dinitrile **22** [**22a**: 63.4%, colorless prisms from benzene, mp 230-231°C. **22b**: 74.3%, colorless prisms from benzene, mp 232-233°C. **22c**: 88.1%, colorless needles from benzene, mp 220-221°C]. Three isomers of triple-layered TCNQ-cyclophane **2** were obtained from **22** in the same manner as in the case of **1** [**2a**: 2.9%, dark violet powder from benzene, dec.> 280°C. **2b**: 2.2%, dark violet powder from benzene, dec. >280°C. **2c**: 2.3%, dark violet powder from benzene, dec.>280°C].[7] Cyano-esters **23** were isolated by column chromatography on silica gel from the reaction mixture [**23a**: 37.6%, dark brown powder from benzene, dec.>200°C. **23b**: 13.6%, dark brown powder from benzene, mp 211-212°C with dec.]. The ^{1}H-NMR data of the TCNQ- and cyano-ester-cyclophanes as well as **6** and **19** are summarized in the Table.

The electronic spectra of TCNQ-cyclophanes are shown in the Figure. All

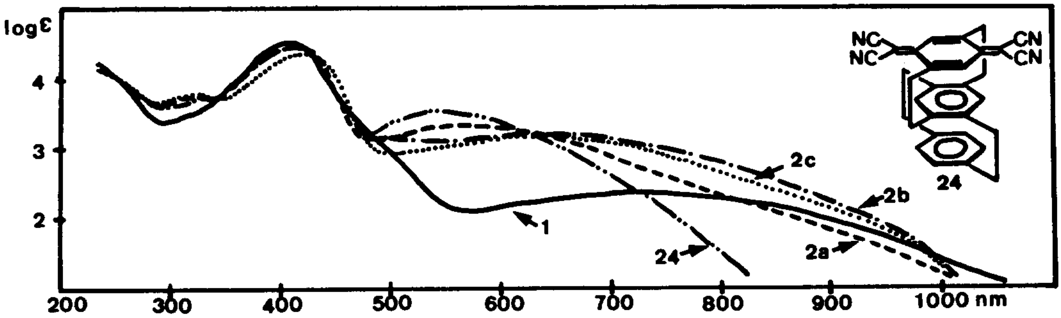

Fig. Electronic spectra of 1, 2, and 24 in CH_2Cl_2.

the compounds exhibit broad absorption bands (tailing to over 1000 nm) attributable to intramolecular charge transfer [λmax nm(ε) in CH_2Cl_2: **1** 720(250)(730nm, ε 260 in $CHCl_3$); **2a** 566(2450); **2b** 640(1880); **2c** 640(1680)]. A few marked features are observed in the spectra. The absorption maximum of double-layered TCNQ-cyclophane **1** is shifted to longer wavelength than those of triple-layered ones **2a-c**, while the integrated absorptions of the latter are larger than that of the former. The fact that CT bands of **2a-c** show marked red shift and long tailing to longer wavelength region compared to that of triple-layered TCNQ-cyclophane **24** [λmax nm(ε)(CH_2Cl_2) 552(3150)]$^{1)}$ clearly indicates that the dimethoxybenzene group functions as a strong π-donor through the sandwiched inner benzene ring.

References and Notes

1) Layered Compounds LVII. Part LVI: M. Yoshida, Y. Tochiaki, H. Tatemitsu, Y. Sakata and S. Misumi, submitted to *Chem. Lett.* (1978).

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3) R. Gray and V. Boekelheide, *Angew. Chem. Internat. Ed. Engl.*, **14**, 107 (1975).

4) Recently Staab and coworker reported the synthesis of **1** (1% yield) by use of ClCN; H. A. Staab and H.-E. Henke, *Tetrahedron Lett.*, 1955 (1978).

5) All the TCNQ-cyclophanes were obtained in situ without successive processes of alkaline hydrolysis, decarboxylation, and oxidation described in the TCNQ syntheses of Wheland and Martin, *J. Org. Chem.*, **40**, 3101 (1975).

6) The olefinic protons of **1** appear as a doublet(J=0.7 Hz) similar as in 2,5-dimethyl TCNQ(J=1.2 Hz). A singlet of the protons was reported in ref. 4.

7) All new compounds gave satisfactory elemental or mass spectral analyses. Found : **2a** 524.2211; **2b** 524.2211; **2c** 524.2210. Calcd. for **2a-c** 524.2212.

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