Layered Compounds. LXIV.[1] Syntheses and Charge Transfer Spectra of Multilayered Paracyclophanequinones[2]

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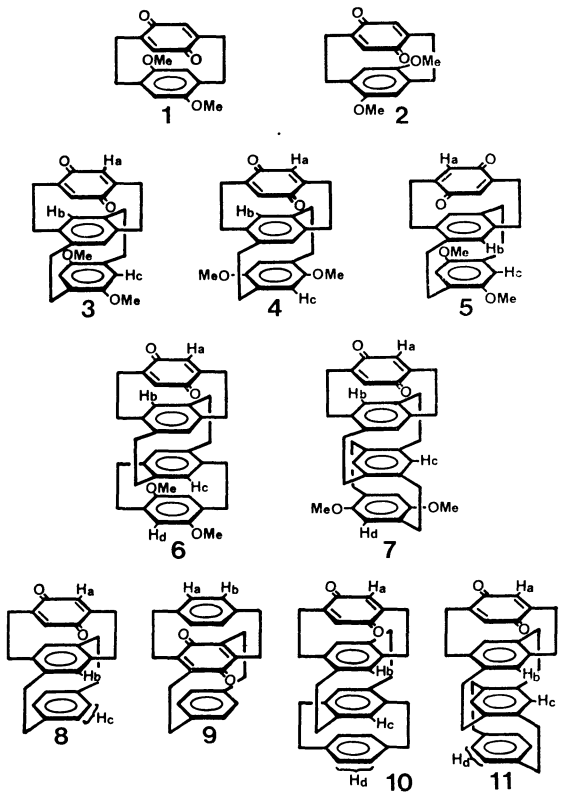
Three isomeric triple-layered and two isomeric quadruple-layered charge transfer cyclophanes containing benzoquinone and dimethoxybenzene moieties have been synthesized together with two triple-layered and two quadruple-layered paracyclophanequinones. The structures of the isomers were determined by ^{1}H- and ^{13}C-NMR spectra and/or alternative syntheses. By comparing the CT bands of a series of dimethoxycyclophanequinones with those of the corresponding cyclophanequinones, it is concluded that the CT stabilization of multilayered dimethoxyquinones should be attributed mainly to the π-basicity of the durene ring which faces the acceptor quinone ring and partly to the decreasing π-basicity of dimethoxybenzene ring as the layer number increases. No orientational dependence of quinone and dimethoxybenzene moieties on CT transition was observed in the multilayered series.

A wide variety of charge transfer (CT) cyclophanes with both donor and acceptor moieties have been synthesized for studying the relationship between the structure and the CT interaction on intermolecular CT complexes.[3] A marked difference, dependent upon the donor-acceptor orientation, was observed in the electronic spectra of double-layered CT cyclophanes, *e.g.*, **1** and **2**.[4] In the previous paper of this series, we reported that a series of multilayered [2.2]paracyclophanes showed the increase of the transannular interaction with an increase of layer number.[5] This change in their electronic spectra was interpreted as due to the configurational interactions of charge transfer and neutral excitation states.[6] The CT cyclophanes, in which the two outer benzene rings of the multilayered paracyclophanes are replaced by a donor and an acceptor moiety, are particularly interesting in connection with both the CT and the transannular interactions. We now report the syntheses and properties of three isomeric triple-layered (**3**—**5**) and two isomeric quadruple-layered CT cyclophanes (**6** and **7**) having parabenzoquinone moiety as an acceptor as well as two isomers of triple-layered (**8** and **9**) and two isomers of quadruple-layered quinones (**10** and **11**) as spectral references.



For the same purpose, we previously reported other examples of triple-layered CT cyclophanes which have tetracyanoquinodimethane moiety as an acceptor.[7] During the course of the present study, Staab and his coworkers independently reported the syntheses of **3**,[8] **4**,[8] **6**,[9] and **7**.[9]

Results and Discussion

Syntheses. The synthetic routes of dimethoxyquinones (**3**—**7**) and quinones (**8**—**11**) are shown in Schemes 1—3. A key intermediate of the routes, dimethoxy double-layered cyclophane **15b**, was prepared by two general methods, *i.e.*, the Hofmann elimination and the photodesulfurization.[10] Thus, the pyrolytic cross-breeding reaction of two quarternary ammonium hydroxides, **16** and **17**,[11] gave **15b** in 11.7% yield, whereas sulfur photo-extrusion from a mixture of isomeric disulfides, **14a** and **14b**, prepared by coupling of dithiol **12**[12] and dichloride **13**, gave the identical compound **15b** in 63% yield. The product by the latter method consisted of only the staggered isomer **15b**, indicating the intramolecular overcrowding of methyl and methoxyl groups in the eclipsed isomer **15a**.

Pyrolysis of **16** with ammonium hydroxide **20**, derived from **15b**, afforded a mixture of tetramethoxy triple-layered paracyclophane, **21** of D_2 symmetry and **22** of C_2 symmetry, in 6.1% yield, together with 7.7% of tetramethoxy double-layered and 2.5% of tetramethoxy quadruple-layered paracyclophanes. The separation of **21** and **22** was accomplished by repeated

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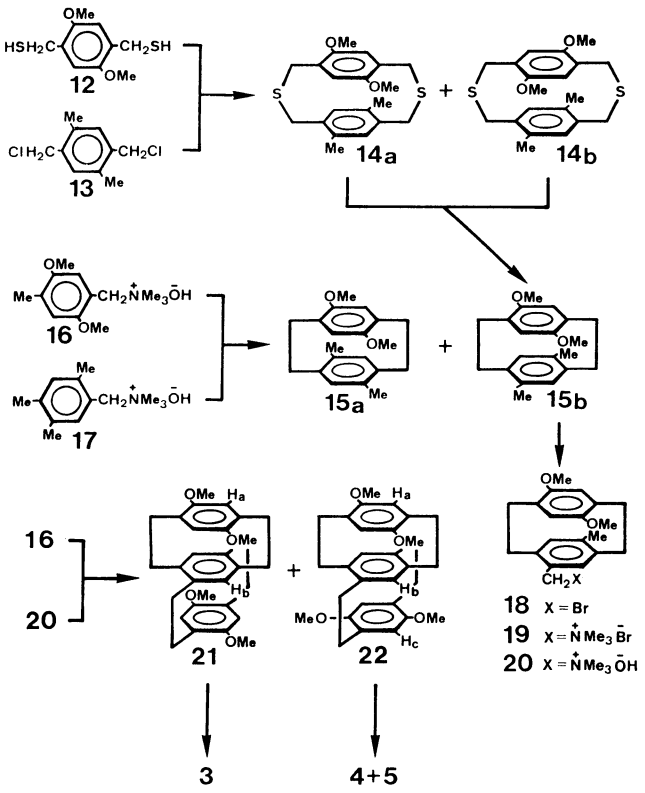
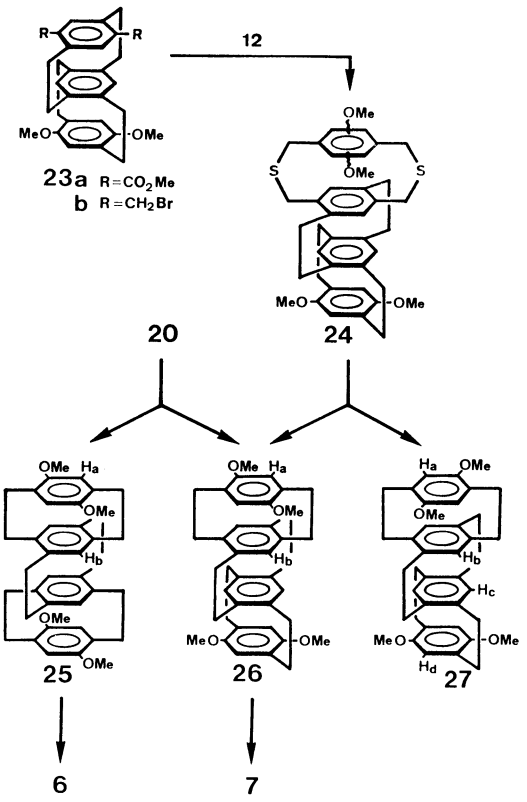


Scheme 1.

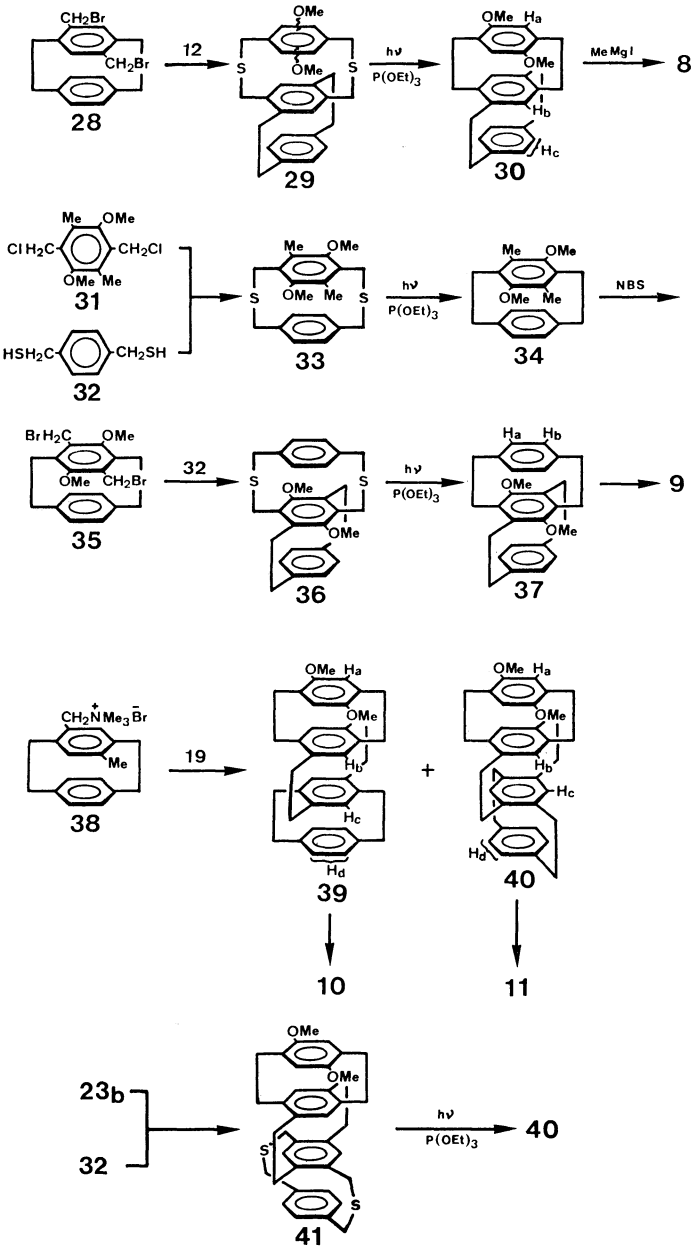


Scheme 2.

recrystallization from ethanol. Their structures were easily assigned by ^{1}H-NMR spectra, as described later. Treatment of **21** with boron tribromide followed by oxidation with silver oxide gave triple-layered dimethoxyquinone **3** in 33% yield. According to the same procedure, on the other hand, **22** gave two isomeric triple-layered dimethoxyquinones, **4** and **5**, in 41.7% total yield. The preparation of dimethoxyquinones **3** and **4** was also reported by Staab *et al.*[8] but with no isolation of the third isomer **5**. The formations of a single dimethoxyquinone from **21** and of two isomeric dimethoxyquinones from **22** provide chemical evidence to support the NMR assignment of **21** and **22**.

Pyrolysis of quarternary ammonium hydroxide **20** in boiling xylene gave a mixture of two isomeric tetramethoxy quadruple-layered paracyclophanes, **25** of C_{2h} symmetry and **26** of D_2 symmetry, in 21.8% total yield. The separation of these isomers was barely accomplished by fractional recrystallization from toluene, after many unfruitful attempts using column and liquid chromatographies. The structures of the isomers could not be unequivocally determined by ^{1}H- and ^{13}C-NMR spectra, although they were tentatively assigned by the chemical shifts of methylene carbons as described later. To confirm this ^{13}C-NMR assignment, an alternative synthesis of **26** was carried out. Here a photodesulfurization of a mixture of two isomeric disulfides **24**, prepared by coupling of dithiol **12** and triple-layered dibromide **23b**, which has a well-determined structure,[7] gave a mixture of two isomeric tetramethoxy quadruple-layered paracyclophanes (1 : 1 ratio) in 47% yield. The less soluble isomer, separated by repeated recrystallization of the mixture from hexane, was identical with **26** on the basis of various spectral data; thus **26** undoubtedly has the D_2 symmetric structure. The other two isomers, **25** and **27**, are, consequently, assigned to C_{2h} and C_2 symmetric structures, respectively. Demethylation and oxidation of **25** and **26** in a similar manner as done for the triple-layered analogues gave dimethoxy quadruple-layered paracyclophanequinones, **6** and **7**, in 10 and 9% yields, respectively. Staab and Zapf[9] also reported the preparation of **6** and **7** from **25** and **26** in the same way, after an X-ray crystallographic determination that the precursor **25** had a centrosymmetric structure.

Triple-layered paracyclophane derivatives, **30** and **8**, were prepared for spectral reference, as shown in Scheme 3. A mixture of two isomeric disulfides **29**, prepared by coupling of dibromide **28**[13] with dithiol **12**, was irradiated with a high pressure mercury lamp to give one of two possible isomers of dimethoxy compound, **30**, in 75% yield. Treatment of **30** with methylmagnesium iodide afforded, without oxidation with silver oxide, reddish orange quinone **8** in 72% yield. Dichloride **31** obtained by chloromethylation of 2,5-dimethoxy-*p*-xylene[14] was coupled with dithiol **32** to afford disulfide **33** in 65% yield. Sulfur photo-extrusion of **33** gave 60% yield of dimethoxydimethyl[2.2]-paracyclophane **34**. Disulfide **36** was obtained by bromination (86%) of **34** with NBS, followed by coupling (49%) with **32**. Photodesulfurization of **36** was performed in a similar manner to give dimethoxy triple-layered paracyclophane **37** in 69% yield. Demethylation of **37** with methylmagnesium iodide at 160 °C, followed by treatment with silver oxide, afforded yellow



Scheme 3.

inner-quinone **9** in 12.3% yield.

Dimethoxy quadruple-layered cyclophanes, **39** and **40**, were prepared by cross-breeding pyrolysis of a mixture of two quarternary ammonium hydroxides prepared from ammonium bromides, **19** and **38**.[5] After removal of non-substituted and tetramethoxy quadruple-layered cyclophanes from the reaction mixture by column chromatography, a mixture of the desired dimethoxy compounds, **39** and **40**, was separated by fractional crystallization from hexane. The structures of both isomers were assigned by ^{13}C-NMR spectra. In order to confirm this assignment, isomer **40** was prepared by an alternative route, as shown in Scheme 3. Photodesulfurization of disulfide **41**, prepared by coupling of dibromide **23b** and dithiol **32**, gave dimethoxy quadruple-layered paracyclophane in 25% yield. This product was identical, in all respects, with a more soluble isomer **40** obtained by the cross-breeding pyrolytic method. Quadruple-layered paracyclophanequinones **10** and **11** were obtained as red needles in 28 and 29% yields, respectively, by successive demethylation and oxidation from **39** and **40** in a similar manner as done for dimethoxy triple-layered one **6**.

NMR Spectra. *^{1}H-NMR*: The chemical shifts of multilayered quinones **3**—**11** and related compounds are summarized in Table 1. We previously reported that there is an additivity among the chemical shifts of aromatic protons in a series of multilayered [2.2]-paracyclophanes and that the additivity is based on the anisotropic effect of facing benzene rings as well as the steric compression and magnetic anisotropic effects of pseudo-gem and pseudo-ortho substituents.[8] Reich and Cram also described such effects of various substituents on the chemical shifts of aromatic protons in a

Table 1. ^{1}H-NMR data of multilayered paracyclophanequinones and related compounds in deuteriochloroform (δ value)

Compd		Obsd Shift	Calcd Shift	Compd		Obsd Shift	Calcd Shift
3	Ha	5.56		**21**	Ha	5.51	
	Hb	6.12	6.19		Hb	5.98	6.02
	Hc	5.62			OCH_3	3.57	
	OCH_3	3.59		**22**	Ha	5.50	
4	Ha	5.57			Hb	5.65	5.74
	Hb	5.86	5.81		Hc	5.50	
	Hc	5.65			OCH_3	3.56	
	OCH_3	3.59		**25**	Ha	5.39	
5	Ha	5.63			Hb	5.48	
	Hb	6.04	6.04		OCH_3	3.50	
	Hc	5.63		**26**	Ha	5.39	
	OCH_3	3.59			Hb	5.47	
6	Ha	5.43			OCH_3	3.49	
	Hb	5.65		**27**	Ha	5.39	
	Hc	5.60			Hb	5.15	
	Hd	5.43			Hc	5.46	
	OCH_3	3.52			Hd	5.39	
7	Ha	5.43			OCH_3	3.49	
	Hb	5.65		**30**	Ha	5.47	
	Hc	5.61			Hb	5.71	
	Hd	5.43			Hc	6.24	
	OCH_3	3.51			OCH_3	3.54	
8	Ha	5.53		**37**	Ha	6.61	
	Hb	5.88			Hb	6.19	
	Hc	6.37			OCH_3	3.99	
9	Ha	6.56		**39**	Ha	5.38	
	Hb	6.33			Hb	5.41	
10	Ha	5.43			Hc	5.17	
	Hb	5.60			Hd	6.12	
	Hc	5.32			OCH_3	3.48	
	Hd	6.17		**40**	Ha	5.37	
11	Ha	5.42			Hb	5.41	
	Hb	5.61			Hc	5.19	
	Hc	5.34			Hd	6.12	
	Hd	6.17			OCH_3	3.47	

series of substituted [2.2]paracyclophanes.[9]

As seen in Table 1, the inner aromatic protons of three triple-layered dimethoxyquinones, **3**—**5**, and their precursors, two tetramethoxy compounds, **21** and **22**, show relatively large differences in chemical shift compared to the outer ring protons. In order to determine their structures, the magnetic effects ($\Delta\delta$) of dimethoxy and quinone groups on pseudo-ortho protons of facing benzene rings were evaluated from the observed chemical shifts of reference compounds, as shown in Fig. 1. Using these values, we calculated the chemical shifts of the inner aromatic protons of the above-mentioned triple-layered paracyclophane derivatives. For example, the calculated value of Hb in **4** is given from the chemical shift (δ 5.40) of the inner proton of **42** as follows;

$$\delta(\text{Hb of } \mathbf{4}) = \delta(\text{Hb of } \mathbf{42}) + \Delta\delta_{\text{H}\to\text{OMe}}(\text{pseudo-ortho effect}) + \Delta\delta_{\text{H}\to=\text{O}}(\text{pseudo-gem effect})$$
$$= 5.40 + 0.30 + 0.48 = 5.91 \text{ ppm}$$

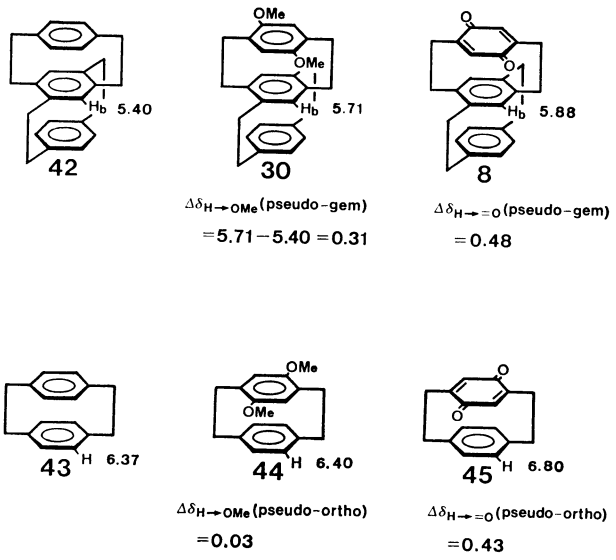


Fig. 1. ^{1}H-NMR chemical shifts of aromatic protons of five reference compounds in deuteriochloroform.

The calculated values in Table 1 are in good agreement with the observed values. The assignment of isomeric structures is consequently achieved.

On the other hand, the structures of four pairs of isomeric quadruple-layered cyclophanes, **6** and **7**, **10** and **11**, **25** and **26**, and **39** and **40**, could not be assigned only by ^{1}H-NMR spectra, because the chemical shifts of all corresponding protons are almost equal to each other in each pair. But the inner and outer aromatic protons of tetramethoxy compounds, **25**—**27**, were easily assigned on the basis of the solvent effect as described for non-substituted multilayered paracyclophanes.[8] As shown in Table 2, aromatic protons displaying larger chemical shift differences in two solvents, carbon tetrachloride and deuteriochloroform, were assigned to the outer benzene protons, while those displaying smaller differences (*ca.* 0.06 ppm) were assigned to inner benzene protons.

Table 2. Solvent effect of aromatic protons of tetramethoxy quadruple-layered paracyclophanes (δ value)

Compd		Solvent		$\Delta\delta$
		$CDCl_3$	CCl_4	($\delta_{CDCl_3}-\delta_{CCl_4}$)
25	outerH	5.39	5.23	0.16
	innerH	5.48	5.43	0.05
26	outerH	5.39	5.24	0.15
	innerH	5.47	5.41	0.06
27	innerH	5.15	5.08	0.07
	outerH	5.39	5.23	0.16
	innerH	5.46	5.40	0.06

^{13}C-NMR: To determine the structures of isomeric quadruple-layered cyclophanes, **25** and **26**, and **39** and **40**, ^{13}C-NMR spectra were examined. The data are shown in Fig. 2 together with those of reference compounds. The assignment was performed by an off-resonance technique and by comparing with the

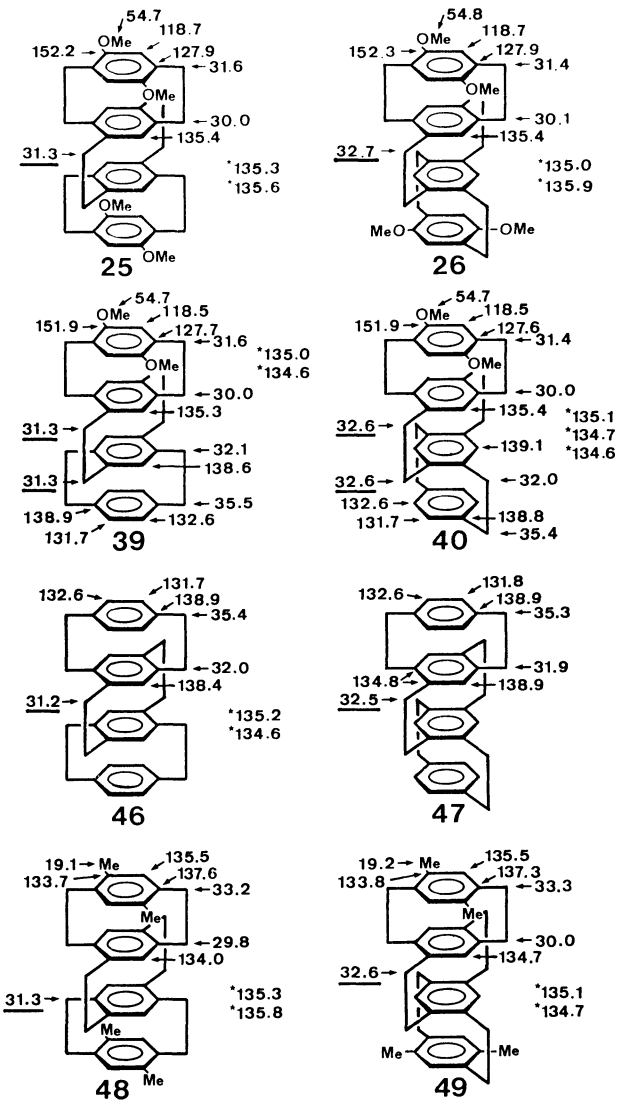


Fig. 2. ^{13}C-NMR data of quadruple-layered cyclophanes in deuteriochloroform. Values marked with star are difficult to assign.

chemical shifts which were calculated by adding the substituent effect to the chemical shifts of the parent hydrocarbons, **46** and **47**.[15] Each isomeric pair showed chemical shifts very close to each other, except for the underlined signals of the methylenes bridging two inner benzene rings.

The difference in carbon chemical shifts of the inner bridging methylenes, though slight, can be used to assign isomeric structures of reference compound pairs, **46** *vs.* **47** and **48** *vs.* **49**; these structures were clearly determined by X-ray analysis[16] or by an alternative stepwise synthesis.[5] Thus, the chemical shifts of the inner methylenes under consideration are 31.2 ppm for C_{2h} symmetric cyclophanes (**46** and **48**) and about 32.5 ppm for D_2 symmetric ones (**47** and **49**), though the relationship between structure and chemical shift is not clear. On the basis of this result, we assigned the cyclophanes displaying an inner methylene signal at 31.3 ppm to C_{2h} symmetric parent structure (**25** and **39**) and those having a signal around 32.6 ppm to D_2 symmetric parent structure (**26** and **40**). These assignments were satisfactorily supported by the alternative syntheses of **26** and **40** described before.

Electronic Spectra. The electronic spectra of **3**—**11** are shown in Figs. 3—5. All the broad and structureless bands in the longer wavelength region are associated with intramolecular charge transfer interactions, because neither the component chromophore nor the parent multilayered paracyclophane shows such an intensive band in the longer wavelength region.

It was reported that CT transitions of various double-layered CT cyclophanes such as **1** and **2** are markedly affected by the orientation of the donor and the acceptor moieties. However, the isomeric pairs (**3** *vs.* **5** and **6** *vs.* **7**) of the present triple- and quadruple-layered CT cyclophanes do not follow such a case. Thus, these isomeric pairs show nearly superimposable absorption curves, indicating no orientational dependence of the presumed main donor (dimethoxybenzene) and acceptor

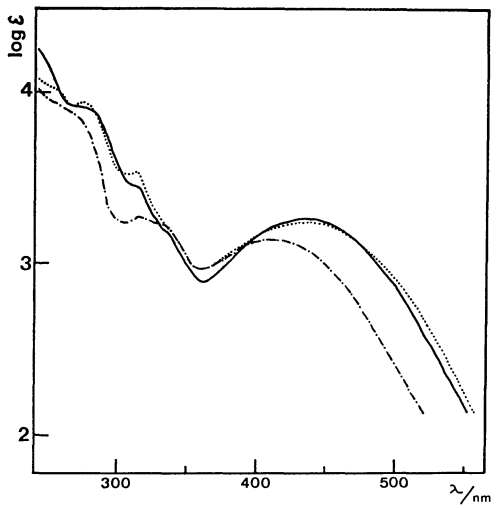


Fig. 3. Electronic spectra of three isomers of dimethoxy triple-layered [2.2]paracyclophanequinone in dichloromethane (**3**, ·····; **4**, -·-·-, **5**, ——).

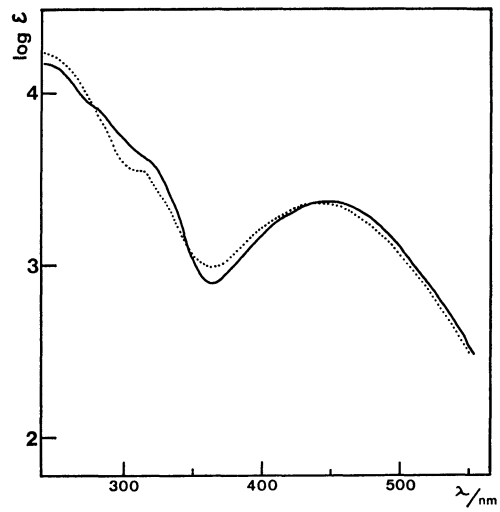


Fig. 4. Electronic spectra of two isomers of dimethoxy quadruple-layered [2.2]paracyclophanequinone in dichloromethane (**6**, ·····, **7**, ——).

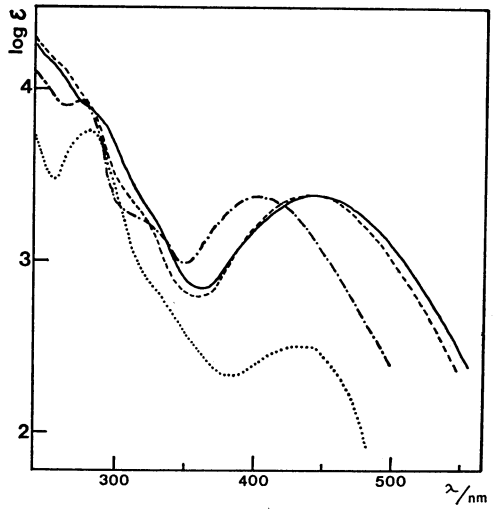


Fig. 5. Electronic spectra of two triple-layered (**8**, –·–·–; **9**, ·····) and two quadruple-layered [2.2]paracyclophanequinones (**10**, ----; **11**, ——) in dichloromethane.

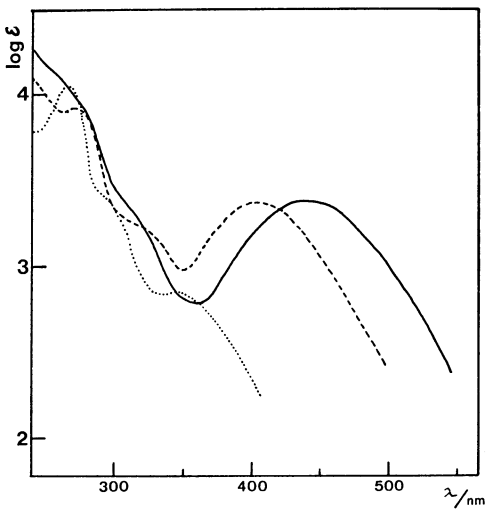
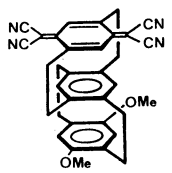


Fig. 6. Electronic spectra of double- to quadruple-layered [2.2]paracyclophanequinones in dichloromethane (**45**, ·····; **8**, ----; **10**, ——).

(benzoquinone). The only exception is the blue shifted CT band of dimethoxyquinone **4**, where the two methoxyl groups are substituted at the positions pseudogem to the bridged methylenes. The reason of the blue shift is probably the decrease of the π-basicity of dimethoxybenzene ring which results from the overcrowding interaction between the methoxyl and the methylene groups. A similar blue shift was also observed in the spectrum of TCNQ cyclophane **50**, which has the same steric relationship between dimethoxyl and bridged methylene groups.[7]



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The electronic spectra of CT cyclophane analogues with different numbers of layers are shown in Figs. 6 and 7. In a series of paracyclophanequinones (Fig. 6), the CT bands shifted to longer wavelengths as the number of layers increased. This indicates that the π-basicity of the benzene ring facing the acceptor quinone ring becomes larger with the increase of layer number. A similar result was observed in the spectra of intermolecular CT complexes between a series of multilayered [2.2]paracyclophanes and π-acceptors.[5]

For a series of dimethoxyquinones (Fig. 7), on the other hand, the order of CT band maxima does not correspond to that of layer number, that is, **1**>**6**>**3**. In compound **1**, the dimethoxydimethylbenzene moiety having a relatively lower ionization potential is so closely fixed to the acceptor quinone that the CT band of **1** shifts to a longer wavelength compared to those of the others, **3** and **6**. In contrast to **1**, multilayered dimethoxyquinones (**3** and **6**) have two types of donors: durene moiety (the inner benzene ring faced to quinone

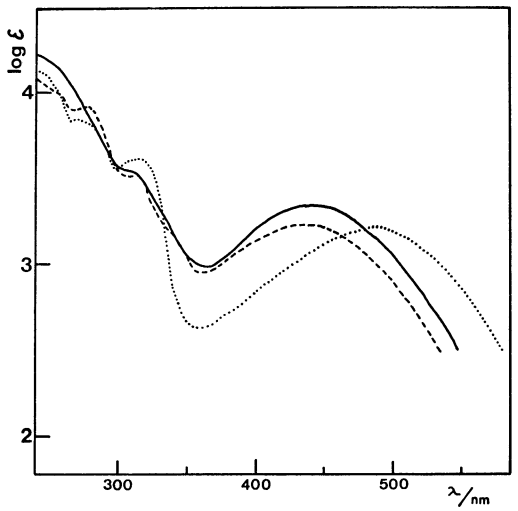

Fig. 7. Electronic spectra of double- to quadruple-layered dimethoxy[2.2]paracyclophanequinones in dichloromethane (**1**, ·····; **3**, ----; **6**, ——).

ring) and dimethoxydimethylbenzene moiety. In the case of the quadruple-layered compound **6**, the durene moiety is concluded to be the main donor, from the fact that the absorption curves of two quadruple-layered quinones, **6** and **10**, are roughly superimposable over each other. In other words, the two methoxyl groups show no contribution to the CT transition. The same conclusion for triple-layered compound **3** is obtained by comparing the spectra of **3** and **8**, but in this series, the dimethoxydimethylbenzene ring increases the π-basicity of the durene moiety by the transannular electron release. In conclusion, the blue shifts of CT bands of **3** and **6** are attributed to the durene moiety acting as the main donor in place of the dimethoxydimethylbenzene ring which has a lower ionization potential but is more remote from the acceptor. Undoubtedly, this is why there is no orientational dependence of the quinone and the dimethoxybenzene moieties on the CT transitions of **3**—**7** mentioned before.

Experimental

All melting points are uncorrected. The IR, NMR, mass and electronic spectra were recorded with a Hitachi EPI-G2, a JEOL JNM-FX-100 (100 MHz for ^1H; 25 MHz for ^{13}C) and a Hitachi R-20, a Hitachi RMU-7 or JEOL JMS-01SG-2 and a Hitachi EPS-3T spectrometer, respectively. Liquid chromatography was performed with a Nihonbunsekikogyo LC-08 of GPC type and a Waters Prep 500.

Staggered and Eclipsed 5,8-Dimethoxy-14,17-dimethyl-2,11-dithia-[3.3]paracyclophanes (14a and 14b). All the solvents were bubbled with nitrogen before use. A solution of 2,5-bis-(chloromethyl)-*p*-xylene **13** (8.13 g, 40 mmol) and 2,5-bis-(mercaptomethyl)-1,4-dimethoxybenzene **12** (9.22 g, 40 mmol) in benzene (800 ml) was added to a stirred solution of sodium hydroxide (3.92 g, 44 mmol) in water (50 ml) and ethanol (2 l) with reflux under nitrogen for 28 h. Reflux was continued for an additional 18 h. After removal of the solvents, the residue was taken up with benzene and chromatographed on silica gel with benzene–hexane (1 : 1). The crude product was recrystallized from benzene–hexane to give 9.82 g (68.1%) of **14a** and **14b**. The mixture was separated into the two isomers by repeated chromatography on silica gel.

14a: Colorless prisms, mp 188.0—189.0 °C. NMR ($CDCl_3$, δ): 6.71 (s, 4H, ArH), 3.79 (s, 6H, OCH_3), 2.33 (s, 6H, CH_3). Found: C, 66.38; H, 6.71; S, 17.50%. Calcd for $C_{20}H_{24}S_2O_2$: C, 66.63; H, 6.71; S, 17.79%.

14b: Colorless prisms, mp 202.0—202.5 °C. NMR ($CDCl_3$, δ): 6.86 (s, 2H, dimethylArH), 6.59 (s, 2H, dimethoxyArH), 3.71 (s, 6H, OCH_3), 2.20 (s, 6H, CH_3). Found: C, 66.48; H, 6.72; S, 17.79%. Calcd for $C_{20}H_{24}S_2O_2$: C, 66.63; H, 6.71; S, 17.79%.

4,7-Dimethoxy-12,15-dimethyl[2.2]paracyclophane (15a and 15b). *By Photodesulfurization*: A mixture of **14a** and **14b** (2.21 g, 5.8 mmol) in benzene–triethyl phosphite (300 ml, 1 : 1 vol ratio) was irradiated with a high pressure mercury lamp for 2 h while nitrogen was bubbled through the solution. After removal of the solvents, the residue oil was chromatographed on silica gel with benzene and recrystallized from methanol to give 1.15 g (63.3%) of **15b**.

15b: Colorless needles, mp 123.5—124.0 °C. NMR ($CDCl_3$, δ): 6.32 (s, 2H, dimethylArH), 6.08 (s, 2H, dimethoxyArH), 3.68 (s, 6H, OCH_3), 2.08 (s, 6H, CH_3). Found: C, 80.78; H, 8.03%. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%.

By Hofmann Elimination: An aq solution of (2,4,5-trimethylbenzyl)trimethylammonium chloride[11] (364 g, 1.6 mol) and (2,5-dimethoxy-4-methylbenzyl)trimethylammonium bromide (242 g, 0.8 mol) was passed through a column of anion exchange resin (Dowex 1-X8) to give an aq solution of quarternary ammonium hydroxides **16** and **17**. This solution was dropwise added to a boiling solution of phenothiazine (5 g) in xylene, (2.8 l) which was placed in a three-necked flask equipped with a condenser, a mechanical stirrer, and a water separater. During the reaction, the bath temperature was kept at 140 °C. After water removal was over, heating was continued for 3 h. To the mixture was added benzene (1 l) and the solution was filtered off to remove insoluble solid. The filtrate was concentrated to dryness and the residue was treated with boiling hexane (2 l) and filtered. After removal of the solvent, the residue was passed through a short column of silica gel with benzene. Evaporation of the solvent gave an oil, to which hexane (50 ml) was added, the mixture was left overnight. The resulting precipitate was recrystallized from benzene to give 5 g (2.3%) of the less soluble isomer **15a**.

15a: Colorless prisms from benzene, mp 205.0—206.0 °C. NMR ($CDCl_3$, δ): 6.15 (s, 2H, dimethylArH), 5.87 (s, 2H, dimethoxyArH), 3.64 (s, 6H, OCH_3), 2.23 (s, 6H, CH_3). Found: C, 80.80; H, 8.04%. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%.

The more soluble isomer **15b** was obtained by addition of hexane to the filtrate of **15a** and by liquid chromatography of the second mother liquor: yield, 27 g (11.7%).

Quarternary Ammonium Bromide 19. A mixture of **15b** (3 g, 10 mmol) and NBS (1.44 g, 8.1 mmol) in carbon tetrachloride (40 ml) was refluxed for 2.5 h under irradiation with a tungsten lamp. The resulting imide was filtered off and the filtrate was cooled on ice. A cold ethereal solution (14 ml) of trimethylamine (4 ml, 45.5 mmol) was added to the above solution. After the mixture was allowed to stand overnight, the precipitate was collected and dried in vacuum to yield 3.2 g (73.7%) of **19**.

Tetramethoxy Triple-layered [2.2]Paracyclophanes (21 and 22). To a refluxing solution of phenothiazine (350 mg) in xylene (240 ml) was added dropwise an aq solution of two quarternary ammonium hydroxides, **16** and **20**, which was produced by passing an aq solution of ammonium bromides, **19** (28.5 g, 65.6 mmol) and (2,5-dimethoxy-4-methylbenzyl)trimethylammonium bromide (40.2 g, 132.1 mmol) through a column of anion exchange resin (Dowex 1-X8). After water was removed by azeotropic distillation, heating was continued for an additional 2 h. Benzene (500 ml) was added to the cooled reaction mixture and the polymer was filtered off. The solvent was evaporated and the residue was chromatographed on silica gel with benzene–hexane. The crude product was separated into two tetramethoxy double-layered (1.67 g, 7.7%), triple-layered (1.84 g, 6.1%), and quadruple-layered paracyclophanes (0.49 g, 2.5%) by liquid chromatography. Separation of two isomeric triple-layered cyclophanes was carried out by fractional crystallization from ethanol to give the sparingly soluble isomer **22** and the more soluble isomer **21**.

21: Colorless needles, mp 204.0—204.5 °C. Found: C, 78.80; H, 7.70%. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47%.

22: Colorless needles, mp 226.5—226.7 °C. Found: C, 78.36; H, 7.43%. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47%

Dimethoxy Triple-layered [2.2]Paracyclophanequinone (3). A solution of **21** (49.3 mg, 0.11 mmol) in dry dichloromethane (4 ml) was added dropwise for 10 min to a stirred solution of boron tribromide (120 mg, 0.48 mmol) in dry dichloromethane (0.5 ml) under ice-salt cooling. After the addition was over, the stirring was continued for 1.5 h; then the mixture was treated with water and extracted with diethyl ether. The extract was washed with water and dried on $MgSO_4$. After removal of the solvents, acetone (5 ml) and silver oxide (126 mg) were added to the residue and the mixture was stirred for 30 min at room temperature and then for 30 min at 50 °C. Insoluble material was filtered off and the filtrate was concentrated to dryness. The crude product was chromatographed on silica gel with benzene to give 15.2 mg (33.0%) of **3**.

3: Red needles from ethanol, dec>220 °C. Found: M^+, 428.19880. Calcd for $C_{28}H_{28}O_4$: 428.19874.

Dimethoxy Triple-layered [2.2]Paracyclophanequinones (4 and 5). A solution of **22** (48.7 mg, 0.106 mmol) in dry dichloromethane was added to a stirred solution of boron tribromide (100 mg, 0.4 mmol) in dry dichloromethane (0.5 ml) at −20 °C for 5 min. The stirring was continued at that temperature for 2.5 h and then at 0 °C for 50 min. The reaction mixture was worked up as described for **3**. Silica gel chromatography of the oxidation product with benzene gave **4** from the initial eluate and **5** from the following eluate in a total yield of 19.0

mg (41.7%).

4: Red needles from ethanol, dec>225 °C. Found: M+, 428.19933. Calcd for $C_{28}H_{28}O_4$: 428.19874.

5: Red needles from ethanol, dec>210 °C. Found: C, 78.24; H, 6.35%; M+, 428.19971. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%; M+, 428.19874.

Tetramethoxy Quadruple-layered [2.2]Paracyclophanes (25 and 26). Pyrolysis of quarternary ammonium hydroxide **20** was carried out as described for **15**. The crude product was chromatographed on silica gel with benzene–hexane to give a mixture of **25** and **26** in a total yield of 5.3 g (21.8%). Recrystallization of the mixture from toluene gave colorless plates of **25** and colorless needles of **26**, which were separated with a pincette and purified by recrystallization from ethyl acetate.

25: Colorless prisms, dec>260 °C. Found: C, 81.76; H, 7.58%. Calcd for $C_{40}H_{44}O_4$: C, 81.60; H, 7.53%.

26: Colorless needles, dec>260 °C. Found: C, 81.56; H, 7.36%. Calcd for $C_{40}H_{44}O_4$: C, 81.60; H, 7.53%.

4,7-Bis(bromomethyl)-20,23-dimethoxy Triple-layered[2.2]-Paracyclophane (23b). A solution of dimethoxy bis(methyl ester) **23a**[7] (316.1 mg, 0.6 mmol) in dry THF (20 ml) was dropwise added to a suspension of $LiAlH_4$ (1 g) in dry THF (10 ml) under reflux and stirring. After cooling, the mixture was worked up in the usual manner and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated to dryness. To the solution of the residue in benzene (30 ml) was dropwise added a solution of PBr_3 (700 mg) in benzene (10 ml). The mixture was stirred at 45 °C overnight and worked up in the usual manner to give dibromide **23b** (298.4 mg, 83.2%).

23b: Colorless fine crystals from benzene–hexane, dec >280 °C. NMR ($CDCl_3$, δ): 6.14 (s, 2H, ArH), 5.86 (s, 2H, ArH), 5.48 (s, 2H, ArH), 4.35, 4.07 (AB, J=10 Hz, 4H, CH_2Br), 3.54 (s, 6H, OCH_3).

Tetramethoxy Quadruple-layered [2.2]Paracyclophanes (26 and 27). A solution of dibromide **23b** (407.6 mg, 0.7 mmol) and dithiol **12** (160.6 mg, 0.7 mmol) in benzene (40 ml) was added to a stirred solution of potassium hydroxide (142.6 mg) in methanol (100 ml) for 5 h under reflux and nitrogen atmosphere. After an additional reflux for 2 h, the mixture was worked up in the usual manner. The crude product was chromatographed on silica gel with benzene to give colorless disulfide **24** (86.1 mg, 18.8%) as a mixture of two isomers.

A solution of **24** (86.1 mg, 0.13 mmol) in benzene (12 ml) and triethyl phosphite (40 ml) was irradiated with a high pressure mercury lamp under bubbling of nitrogen for 75 min. After removal of the solvents, the residue was chromatographed on silica gel to give a mixture of **26** and **27** (1: 1 ratio) in 47.0% yield (36.5 mg). The mixture was separated into the two isomers by fractional crystallization from hexane.

The less soluble isomer was in all respects identical with **26** obtained by pyrolysis of **20**. The more soluble isomer **27** was recrystallized from ethyl acetate.

27: Colorless columns, dec>260 °C. Found: M+ 588.32559. Calcd for $C_{40}H_{44}O_4$: 588.32394.

Dimethoxy Quadruple-layered [2.2]Paracyclophanequinone (6). A solution of boron tribromide (180 mg, 0.72 mmol) in dry dichloromethane (12 ml) was dropwise added to a stirred solution of **25** (104.5 mg, 0.18 mmol) in dry dichloromethane (3 ml) at 0 °C for 5 min and the stirring was continued at that temperature for 20 min. The reaction mixture was treated with water and extracted with diethyl ether. After drying ($MgSO_4$) and removal of the solvent, acetone (30 ml) and silver oxide (500 mg) were added to the residue, then the mixture was stirred at room temperature for 30 min and at 50 °C for 30 min. Insoluble material was filtered off and the filtrate was concentrated to dryness. The crude product was purified by column chromatography on silica gel with benzene–hexane to give 10.3 mg (10.4%) of **6**.

6: Red needles from ethanol, dec>220 °C. Found: M+, 558.2770. Calcd for $C_{38}H_{38}O_4$: 558.2771.

Dimethoxy Quadruple-layered [2.2]Paracyclophanequinone (7). Demethylation and oxidation of **26** were carried out as described for **6**. The crude product was chromatographed on silica gel with benzene to give **7** in 8.7% yield.

7: Red needles from ethanol, dec>230 °C. Found: M+, 558.2770. Calcd for $C_{38}H_{38}O_4$: 558.2771.

Triple-layered Dimethoxy Disulfide 29. A solution of 4,7-bis(bromomethyl)[2.2]paracyclophane **28**[13] (1.60 g, 4.06 mmol) in benzene (50 ml) and a solution of dithiol **12** (0.85 g 3.70 mmol) and potassium hydroxide (0.46 g) in aq ethanol (50 ml) were dropwise and simultaneously added to ethanol (150 ml) for 2.5 h under reflux and nitrogen atmosphere. After further reflux for 10 h, the solvents were evaporated and the residue was chromatographed on silica gel with benzene–hexane (1 : 1) to give a mixture of isomeric disulfide **29**.

29: Colorless prisms from benzene–hexane (1 : 1), mp 216—221 °C (dec). NMR ($CDCl_3$, δ): 6.6—6.1 (A_2B_2, 4H, ArH), 6.29 (s, 2H, ArH), 5.93 (d, 2H, ArH), 4.3—2.2 (m, 16H, CH_2), 3.64 (s, 6H, OCH_3); MS *m/e* 462 (M+), 263. Found: C, 72.98; H, 6.54; S, 14.00%. Calcd for $C_{28}H_{30}O_2S_2$: C, 72.69; H, 6.54; S, 13.86%.

4,7-Dimethoxy Triple-layered [2.2]Paracyclophane (30). A solution of disulfide **29** (56 mg, 0.12 mmol) in triethyl phosphite (15 ml) was irradiated with a high pressure mercury lamp for 2 h under nitrogen bubbling. After removal of the solvent, the residue was chromatographed on silica gel with benzene–hexane (1: 2) to give **30**, 36 mg (75%).

30: Colorless prisms from benzene–hexane (1: 1), mp 250 °C (dec). NMR ($CDCl_3$, δ): 6.24 (s, 4H, ArH), 5.71 (s, 2H, ArH), 5.47 (s, 2H, ArH), 3.54 (s, 6H, OCH_3), 3.4—2.1 (m, 16H, CH_2); MS *m/e* 398 (M+), 294, 234. Found: C, 84.13; H, 7.36%. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59%.

Outer Triple-layered [2.2]Paracyclophanequinone (8). A solution of dimethoxy compound **30** (21 mg, 0.06 mmol) and methylmagnesium iodide (from methyl iodide 410 mg and magnesium 100 mg) in dry diethyl ether (10 ml) was refluxed for 30 min. After removal of the solvent, the residue was heated at 160 °C for 1.5 h. To the cooled product were added diethyl ether (10 ml), water (10 ml), and dil HCl, successively. The ether layer was separated and the aqueous layer was extracted with ether several times. The combined ether solution was washed with water and dried over anhyd Na_2SO_4. After solvent removal the residue was chromatographed on silica gel to give **8**, 14 mg (72%).

8: Reddish orange crystals from benzene, mp *ca.* 225 °C (dec), MS *m/e* 368 (M+). NMR ($CDCl_3$, δ): 6.37 (s, 4H, ArH), 5.88 (s, 2H, ArH), 5.53 (s, 2H, quinone), 3.4—2.3 (m, 16H, CH_2). Found: C, 84.75; H, 6.51%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57%.

2,5-Bis(chloromethyl)-3,6-dimethoxy-p-*xylene (31).* Into a solution of 2,5-dimethoxy-*p*-xylene[14] (119.4 mg, 0.72 mmol) and paraformaldehyde (222.1 mg, 3.6 mmol) in dioxane (12 ml) and concd HCl (6 ml) was bubbled hydrogen chloride gas at room temperature and then at 70 °C under stirring for 5 h. In the course of this process, an additional amount (222 mg, 3.6 mmol) of paraformaldehyde was added to the mixture. After adding ice, the mixture was extracted with diethyl ether and the extract was washed with sodium hydrogencarbonate and sat NaCl aq solution and dried (Na_2SO_4). After removal of the solvent, the residue was chromatographed on silica gel to give a colorless solid of **31**

(151.1 mg, 80.0%).

31: Colorless needles from benzene–hexane (1 : 2), mp 168.0—168.5 °C, MS *m/e* 262 (M^+), 264. NMR ($CDCl_3$, δ): 4.71 (s, 4H, CH_2), 3.83 (s, 6H, OCH_3), 2.36 (s, 6H, CH_3). Found: C, 54.48; H, 5.91%. Calcd for $C_{12}H_{16}O_2Cl_2$: C, 54.76; H, 6.13%.

5,8-Dimethoxy-6,9-dimethyl-2,11-dithia[3.3]paracyclophane ***33***. A solution of dichloride **31** (1.048 g, 3.98 mmol) in benzene (100 ml) and a solution of dithiol **32** (681 mg, 4.00 mmol) and sodium hydroxide (399 mg, 9.97 mmol) in aq ethanol (104 ml) were simultaneously and dropwise added to a boiling ethanol (100 ml) for 1 h under nitrogen; the mixture was refluxed under stirring for 6 h. After removal of the solvent, the residue was chromatographed on silica gel (40 g) with benzene. Disulfide **33** was obtained as a colorless oil (941 mg, 65.5%) which crystallized on standing or by adding a small amount of hexane.

33: Colorless prisms from methanol, mp 137—138 °C, MS *m/e* 360 (M^+); UV (THF, λ_{max} nm): 303 (ε 1010), 279 sh (1390), 260.5 (4000), 223.5 (16900). NMR ($CDCl_3$, δ): 7.04 (A_2B_2, 4H, ArH), 4.13 (d, J=13.8 Hz, 2H, CH_2), 3.79 (s, 4H, CH_2), 3.56 (s, 6H, OCH_3), 3.51 (d, J=13.8 Hz, 2H, CH_2), 2.19 (s, 6H, CH_3). Found: C, 66.43; H, 6.55; S, 17.75%. Calcd for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71; S, 17.79%.

4,7-Dimethoxy-5,8-dimethyl[2.2]paracyclophane ***(34)***. Disulfide **33** (102 mg, 0.29 mmol) in triethyl phosphite (10 ml) was irradiated with a high pressure mercury lamp under nitrogen bubbling for 2.5 h. The residue obtained by solvent removal was chromatographed on silica gel (15 g) with benzene–hexane (1 : 1) and then benzene. The benzene eluate was condensed and recrystallized from methanol to give **34** (50.1 mg, 59.8%).

34: Colorless prisms, mp 126—127 °C, MS *m/e* 296 (M^+); UV (THF, λ_{max} nm): 313 (ε 660), 291 (420), 254 sh (4260), 229 (17600). NMR ($CDCl_3$, δ): 6.64 (s, 4H, ArH), 3.52 (s, 6H, OCH_3), 2.93 (m, 8H, CH_2), 1.92 (s, 6H, CH_3). Found: C, 80.83; H, 8.04%. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%.

4,7-Dimethoxy-5,8-bis(bromomethyl)[2.2]paracyclophane ***(35)***. A mixture of **34** (309.8 mg, 1.05 mmol), NBS (413.3 mg, 2.32 mmol), and a catalytic amount of benzoyl peroxide in carbon tetrachloride (60 ml) was refluxed for 3 h. The mixture was worked up in the usual manner. The solid thus obtained was recrystallized from hexane to give dibromide **35** (407.2 mg, 85.8%).

35: Colorless cubic crystals from hexane, mp 176—177 °C, MS *m/e* 452 (M^+), 454, 456. NMR ($CDCl_3$, δ): 6.68, 6.36 (A_2B_2, J=8, 2 Hz, 4H, ArH), 4.59, 4.02 (AB, J=9.6 Hz, 4H, CH_2Br), 3.71 (s, 6H, OCH_3), 2.6—3.4 (m, 8H, CH_2). Found: C, 52.69; H, 4.69; Br, 35.29%. Calcd for $C_{20}H_{22}O_2Br_2$: C, 52.88; H, 4.88; Br, 35.19%.

Triple-layered Dimethoxy Disulfide ***(36)***. A solution of dibromide **35** (212.2 mg, 0.47 mmol) in benzene (25 ml) and a solution of dithiol **32** (81.4 mg, 0.48 mmol) and NaOH (56.8 mg, 1.42 mmol) in aq ethanol (24 ml) were added simultaneously and dropwise to a boiling ethanol (20 ml) for 67 min under nitrogen. The mixture was refluxed for 6.5 h and worked up as described for **33** to give disulfide **36**, 106.5 mg (49.3%).

36: Colorless fine crystals from benzene–methanol (1 : 3), mp 211—213 °C, MS *m/e* 462 (M^+); UV (THF, λ_{max} nm): 351 (ε 1140), 311 sh (950), 290 sh (2020), 225 (20300). NMR ($CDCl_3$, δ): 6.83 (s, 4H, ArH), 6.54, 6.26 (A_2B_2, J=8, 2 Hz, 4H, ArH), 3.96 (s, 6H, OCH_3), 3.72, 3.30 (AB, J=14 Hz, 4H, CH_2), 3.70 (s, 4H, CH_2), 2.82 (m, 8H, CH_2). Found: C, 72.43; H, 6.29; S, 13.87%. Calcd for $C_{28}H_{30}O_2S_2$: C, 72.69; H, 6.54; S, 13.86%.

12,15-Dimethoxy Triple-layered [2.2]Paracyclophane ***(37)***. Dimethoxy disulfide **36** (31.7 mg, 6.5 mmol) in triethyl phosphite (10 ml) was irradiated with a high pressure mercury lamp for 2 h. The mixture was worked up as described for **34**.

37: Colorless fine crystals from hexane, mp 230 °C (dec), MS *m/e* 398 (M^+); UV (THF, λ_{max} nm): 385 sh (ε 800), 375 (970), 315 sh (1280), 294 (1680), 226 (17500). NMR ($CDCl_3$, δ): 6.61 6.19 (A_2B_2, J=8, 2 Hz, 8H, ArH), 3.99 (s, 6H, OCH_3), 2.3—3.1 (m, 16H, CH_2). Found: C, 84.12; H, 7.57%. Calcd for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59%.

Inner Triple-layered [2.2]Paracyclophanequinone ***(9)***. A solution of dimethoxy compound **37** (52.6 mg, 0.13 mmol) in diethyl ether (30 ml) was worked up as described for **8**. The resulting brown oil in acetone (10 ml) was refluxed with silver oxide (0.5 g) and magnesium sulfate (1 g) for 1 h. After removal of insoluble material by filtration and washing with benzene, the combined solution was chromatographed on silica gel (5 g) with benzene to give yellow quinone **9**, 6.0 mg (12.3%) from benzene–hexane (1: 2).

9: Yellow prisms, dec>250 °C with sublimation, MS *m/e* 368 (M^+). NMR ($CDCl_3$, δ): 6.56, 6.33 (A_2B_2, J=8.0, 1.4 Hz, 8H, ArH), 3.3—2.2 (m, 16H, CH_2). Found: C, 84.54; H, 6.53%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57%.

Dimethoxy Quadruple-layered [2.2]Paracyclophanequinones ***(39 and 40)***. Cross-breeding reactions of quarternary ammonium bromides, **19** and **38**,[5] were done as described for **15**. After the reaction was over, benzene was added to the reaction mixture and the insoluble polymer was filtered off. The filtrate was condensed and passed through a short column of silica gel to remove the polymer. The crude product was chromatographed on silica gel with benzene–hexane to separate non-substituted and tetramethoxy quadruple-layered paracyclophanes from the desired dimethoxy compound. The dimethoxy compound was separated by recrystallization from hexane into two isomers, the less soluble isomer **39** and the more soluble one **40**.

39: Colorless prisms, mp 205.5—206.5 °C with decomp. Found: C, 86.14; H, 7.54%. Calcd for $C_{38}H_{40}O_2$: C, 86.32; H, 7.63%.

40: Colorless columns, mp 205.0—205.5 °C. Found: C, 86.10; H, 7.44%. Calcd for $C_{38}H_{40}O_2$: C, 86.32; H, 7.63%.

Alternative Synthesis of ***40***. Coupling of dibromide **23b** and dithiol **32** was carried out as described for **14**. The crude product was chromatographed on silica gel with benzene to give quadruple-layered disulfide **41** in 33.1% yield. Without further purification, **41** was used for the following reaction. A solution of **41** (117.1 mg) in benzene (30 ml) and triethyl phosphite (70 ml) was irradiated with a high pressure mercury lamp under bubbling of nitrogen for 1.3 h. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to give a 25.2% yield of **40** which was in all respects identical with the more soluble isomer described above.

Quadruple-layered [2.2]Paracyclophanequinone ***(10)***. To a methylmagnesium iodide solution (from 101.3 mg, 4.2 mmol of magnesium and excess of methyl iodide in dry diethyl ether, 50 ml) was added crystals of **39** (109.1 mg, 0.21 mmol) in a portion. After stirring for 40 min and removal of the solvent, the residue was heated at 160—170 °C for 50 min. The mixture was worked up as described for **6**. The crude product was chromatographed on silica gel with benzene to give 29.1 mg (28.3%) of **10**.

10: Red needles from ethanl, odec>235 °C. Found: M+, 498.2570. Calcd for $C_{36}H_{34}O_2$: 498.2558.

Quadruple-layered [2.2]Paracyclophanequinone ***(11)***. Demethylation and oxidation of **40** were carried out as described

for **6**. The crude product was chromatographed on silica gel with benzene to give **11** in 29.0% yield.

11: Red needles from ethanol, dec>230 °C. Found: M^+, 498.2558. Calcd for $C_{36}H_{34}O_2$: 498.2558.

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