Treatment of Dimethoxyparacyclophanes with Ammonium Cerium(IV) Nitrate

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The treatment of dimethoxy[*n*]paracyclophanes (*n*=7—12) (**5**), [2]paracyclo[2]thiophenophane (**13**), and dimethoxy[2.2]paracyclophane (**8**) with CAN in MeCN–water afforded 2,4-cyclohexadien-1-ones **9**, [8]paracyclophanedione **10**, the ring-opened esters **11**, and ketones **12**. When the *n* value of **5** was 7, 8, or 9, rearrangement of the methylene bridge occurred and **9** was obtained as the main products. With the *n* value of 12, quinone **10** was the main product. Whereas, treatment of **13** with CAN afforded the ring-opened ester **14** as the sole product. These results show that formation of **9** is dependent on the strain of the paracyclophanes. Epoxide **A** was proposed as an intermediate of these reactions.

Ammonium cerium (IV) nitrate (CAN) has been widely used in organic chemistry because of its strong oxidizing power and ease of availability.[1] Oxidation of *p*-dimethoxybenzenes with CAN is one of the useful methods to give the corresponding *p*-benzoquinones under mild conditions.[2] A mechanistic study of this reaction was investigated[2a] using $H_2{}^{18}O$, but there has been no report about the effect of molecular strain during oxidation of dimethoxybenzenes with CAN. By the way, it is possible to change molecular strain of [*n*]paracyclophanes by varing the length of the methylene chain. Herein, we synthesized several types of dimethoxyparacyclophanes, which have several methylene chain lengths or stacked aromatic rings, and studied the effect of molecular strain and the stacked aromatic ring on oxidation of these cyclophanes with CAN.

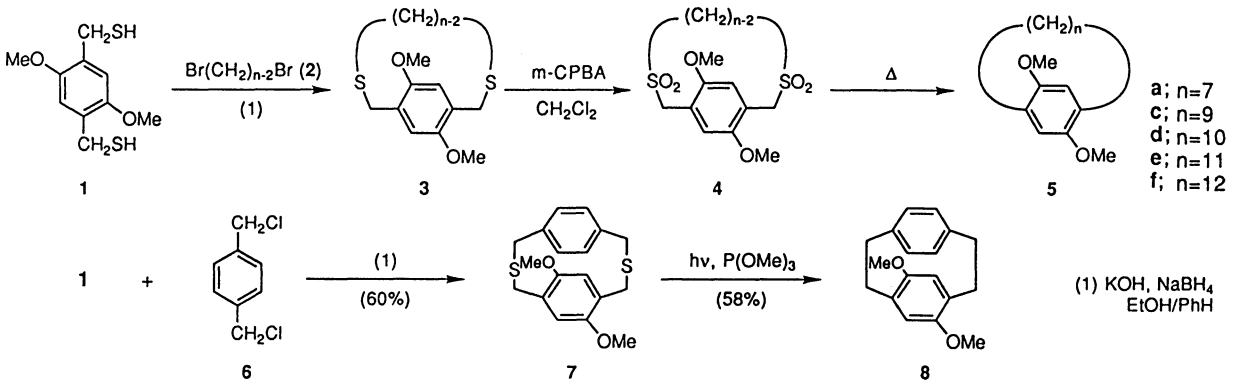
Results and Discussion

Dimethoxy[*n*]paracyclophanes **5** were prepared according to the route shown in Scheme 1 and the yields of the products are summarized in Table 1. The cyclophanes **5** with *n*=7, 9, 10, 11, and 12 were synthesized by pyrolysis of disulfones **4**,[3] which were obtained by oxidation of the corresponding dithiacyclophanes **3**. The low yields of cyclophanes with *n*=7 and 9 were assumed to be due to the higher strain of the cyclophanes. Preparation of the [8]paracyclophane **5b** has already been reported.[4] 4,7-Dimethoxy[2.2]paracyclophane (**8**) was prepared from dithia[3.3]paracyclophane **7** by irradiation using a high-pressure Hg lamp in $P(OMe)_3$.[4,5] The preparation of [2]paracyclo[2]thiophenophane **13** has also been reported.[4]

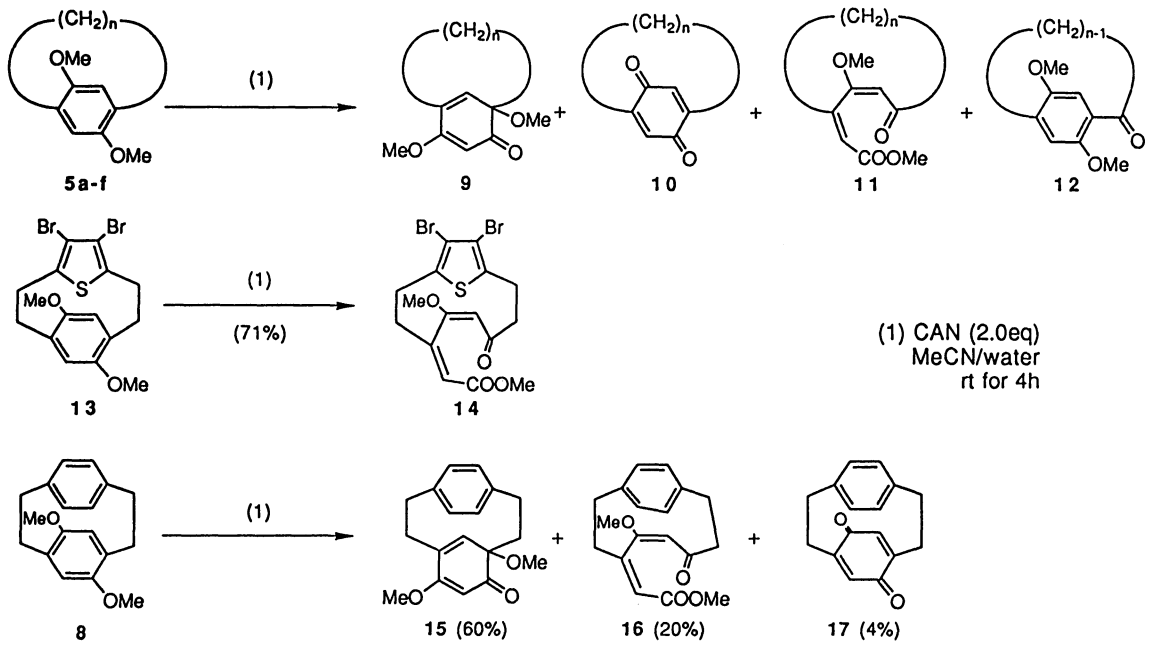
Compounds **5a**—**f** were treated with 2 equiv of CAN in a manner similar to that described in the literature.[2a]

Table 1. Yields of [*n*]Paracyclophanes

	n	3	4	5 (%)
a	7	33	91	10
c	9	30	88	23
d	10	59	89	22
e	11	69	78	57
f	12	70	84	68



Scheme 1.



Scheme 2.

Table 2. Yields of the Products Obtained by Treatment of [*n*]Paracyclophanes with CAN

Substrate		Products/%				
	n	**5**	**9**	**10**	**11**	**12**
5a	7	—	73	—	—	—
5b	8	—	76	—	—	—
5c	9	—	56	—	—	—
5d	10	—	11	5	18	—
5e	11	27	—	7	16	26
5f	12	19	—	23	—	11

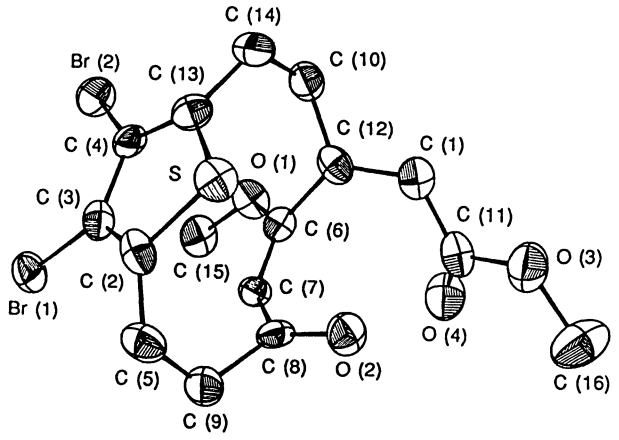
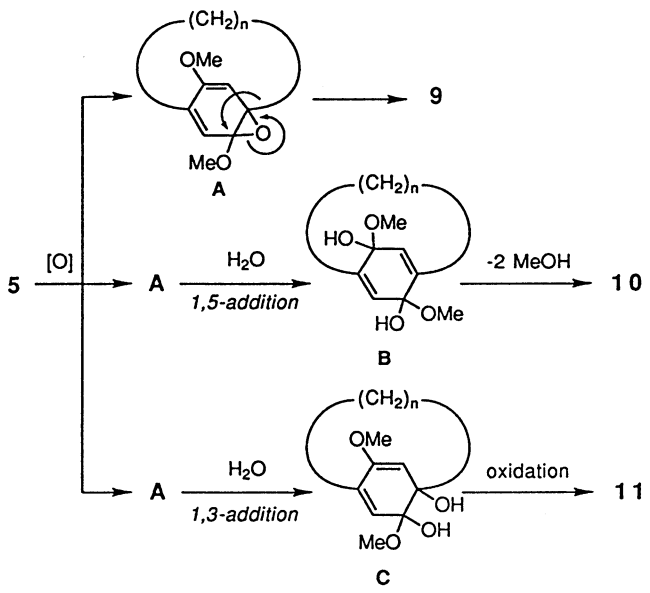


Fig. 1. ORTEP drawing of **14**.

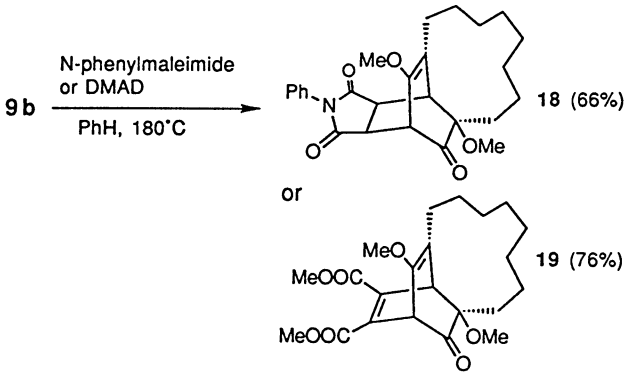
When an aqueous solution of CAN was added dropwise to a solution of **5** in acetonitrile, color of the reaction mixture immediately changed to black, and then changed to pale yellow. Disappearance of the black color occurred faster as the ring size decreased. The mixture was stirred for 4 h and poured into brine. The products were separated by silica-gel column chromatography. The results are summarized in Scheme 2 and Table 2. Interestingly, in the cases of smaller cyclophanes, 2,4-cyclohexadien-1-ones **9** were obtained as the sole product. Treatment of the larger cyclophanes, especially the [12]paracyclophane **5f**, with CAN afforded cyclic ketones **12** and quinones **10**. For the medium-sized compounds (n=10, 11), a ring-opened ester **11** were obtained. These results indicate that the products obtained from smaller cyclophanes, which have larger strain, are different from those of the large cyclophanes. Treatment of the paracyclothiophenophane **13** with CAN afforded an [8]thiophenophane **14** as the sole product. Its structure was confirmed by an X-ray crystallographic analysis (Fig. 1).[#] The reaction of the [2.2]paracyclophane **8** under similar conditions gave a mixture of [2.2]metaparacyclophane-4(3*H*)-one **15**, [8]paracyclophane **16**, and [2.2]paracyclophanedione **17**.

The reaction pathway for the formation of cyclohexadienones **9** was proposed as follows (Scheme 3). When **5** was treated with CAN, the epoxide **A** was produced first.[6] In the highly strained cyclophanes (n=7, 8, 9, 10), methylene bridge rearrangement occurred following ring opening of the epoxide to the bridge side to give the cyclohexadienones **9** in order to reduce the ring strain. It is well-known that rearrangement of [*n*]paracyclophanes to [*n*]metacyclophanes easily occur when [*n*]paracyclophanes are treated with acid.[7,8] When the dimethoxy[9]paracyclophane **5c** was treated with 25% H_2SO_4, only the starting material was recovered. This

[#] The complete F_o—F_c data are deposited as Document No. 9021 at the Office of the Editor of Bull. Chem. Soc. Jpn.



Scheme 3.



Scheme 4.

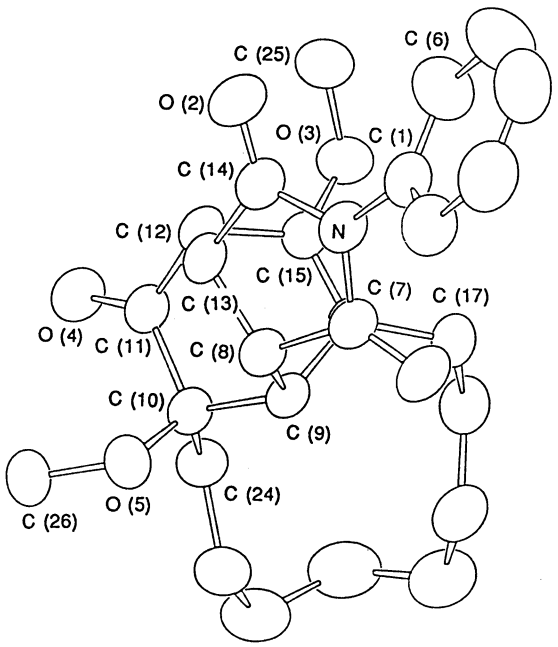


Fig. 2. ORTEP drawing of **18**.

result indicates that protonation to **5** was not the first stage of this rearrangement to give **9**. It was reported that the treatment of [6]paracyclophane with *m*-chloroperbenzoic acid (MCPBA) afforded the dimeric product which formed via rearrangement of the methylene bridge following the epoxidation of the cyclophane.[9] In the cases of n=7—9, also epoxide **A** is considered to be an intermediate for cyclohexadienone **9**. In the larger [n]cyclophanes (n=10, 11, 12), the 1,4-addition of H_2O to epoxide **A** gave a diacetal intermediate **B** which produced the quinones **10** by elimination of 2 moles methanol. When there was some steric hindrance of the methylene chain, the 1,2-addition of H_2O occurred and the 1,2-diol **C**, which might be oxidized to ring-opened keto esters **11** by CAN, was formed. A similar oxidation of [6]paracyclophane with OsO_4 to give the 1,2-diol is reported.[10] In the case of thiophenophane **13**, one side of the benzene ring was assumed to be sterically hindered by the dibromothiophene ring, and addition of H_2O could not occur at the 1,4-position, so the ring-opened ester **14** was formed as the sole product via a 1,2-diol type intermediate. Although the reason why cyclohexadienone was not formed from the thiophenophane **13** is still unknown, rearrangement of the methylene chain of **13** might not reduce its strain. The steric effect of compound **8** may be smaller than that of **13**, therefore, several kinds of compounds were formed during the same oxidation. Formation of ketone **12** is the result of oxidation, which is similar to that described in the literature[11] at the benzylic position of cyclophanes.

In order to obtain more information about the structure of the **9b**, the reaction of **9b** with *N*-phenylmaleimide or dimethyl acetylenedicarboxylate (DMAD) was carried out at 180 °C to give the corresponding [4+2] adducts as shown in Scheme 4. The structure of compound **18** was confirmed by X-ray crystallographic analysis (Fig. 2).

Experimental

All melting points were uncorrected. IR (KBr or NaCl), JASCO IR-700; ^{1}H NMR and ^{13}C NMR JEOL GSX-270 (270 MHz and 68 MHz) in $CDCl_3$, TMS as the reference at 300 K; UV, Hitachi 220A spectrophotometer; MS, JEOL JMS-01-SG-2; EA, Yanaco MT-5.

Synthesis of 11,14-Dimethoxy-2,8-dithia[9]paracyclophane (3a): To a refluxing solution of 2.2 g (40 mmol) of KOH and 190 mg (5 mmol) of $NaBH_4$ in 4 L of EtOH was added dropwise a solution of 2.3 g (10 mmol) of 1,5-dibromopentane (**2a**) and 2.3 g (10 mmol) of 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene (**1**)[12] in 100 mL of PhH–EtOH (1 : 1) over 17 h. The solvent was distilled off, and the residue was poured into ice/water. The mixture was extracted with CH_2Cl_2, the extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residue was subjected to column chromatography (silica gel,

hexane-CH_2Cl_2 (1 : 1)). Recrystallization of the eluate afforded 980 mg (3.3 mmol, 33%) of **3a**: Colorless prisms (hexane), mp 120.0—121.0 °C; IR (KBr) ν 2918, 1510, 1461, 1407, 1044, 865 cm^{-1}; ^1H NMR δ=0.74—0.92 (6H, m), 2.12—2.31 (4H, m), 3.40 (2H, d, J=13 Hz), 3.85 (6H, s), 4.16 (2H, d, J=13 Hz), 6.83 (2H, s); MS m/z 298 [M^+]; Anal. Calcd for $C_{15}H_{22}O_2S_2$: C, 60.36; H, 7.43%. Found: C, 60.41; H, 7.38%.

The dithia[n]paracyclophanes described below were prepared in a manner similar to that described for **3a**.

13,16-Dimethoxy-2,10-dithia[11]paracyclophane (3c): Colorless prisms (hexane), mp 85.0—87.0 °C; IR (KBr) ν 2918, 1506, 1463, 1403, 1044, 863 cm^{-1}; ^1H NMR δ=0.93—0.99 (6H, m), 1.07—1.17 (4H, m), 2.43—2.64 (4H, m), 3.32 (2H, d, J=14 Hz), 3.84 (6H, s), 4.13 (2H, d, J=14 Hz), 6.83 (2H, s); MS m/z 326 [M^+]; Anal. Calcd for $C_{17}H_{26}O_2S_2$: C, 62,53; H, 8.03%. Found: C, 62.68; H, 7.96%.

14,17-Dimethoxy-2,11-dithia[12]paracyclophane (3d): Colorless prisms (MeOH), mp 31.0—33.0 °C; IR (KBr) ν 2914, 1508, 1466, 1404, 1210, 1044 cm^{-1}; ^1H NMR δ=0.85—0.93 (4H, m), 1.10—1.21 (4H, m), 1.24—1.35 (4H, m), 2.34—2.51 (4H, m), 3.30 (2H, d, J=14 Hz), 3.82 (6H, s), 4.15 (2H, d, J=14 Hz), 6.91 (2H, s); MS m/z 340 [M^+]; Anal. Calcd for $C_{18}H_{28}O_2S_2$: C, 63.48; H, 8.29%. Found: C, 63.81; H, 8.19%.

15,18-Dimethoxy-2,12-dithia[13]paracyclophane (3e): Colorless oil; IR (NaCl) ν 2904, 1505, 1462, 1400, 1212, 1045 cm^{-1}; ^1H NMR δ=0.95—1.13 (6H, m). 1.15—1.25 (4H, m), 1.32—1.40 (4H, m), 2.47 (4H, t, J=7 Hz), 3.30 (2H, d, J=14 Hz), 3.81 (6H, s), 4.11 (2H, d, J=14 Hz), 6.89 (2H, s); MS m/z 354 [M^+]; Anal. Calcd for $C_{19}H_{30}O_2S_2$: C, 64.36; H, 8.53%. Found: C, 64.16; H, 8.19%.

16,19-Dimethoxy-2,13-dithia[14]paracyclophane (3f): Colorless oil; IR(NaCl) ν 2924, 1510, 1462, 1398, 1208, 1044 cm^{-1}; ^1H NMR δ=1.04—1.16 (8H, m), 1.22—1.33 (4H, m), 1.45—1.57 (4H, m), 2.26—2.48 (4H, m), 3.32 (2H, d, J=14 Hz), 3.81 (6H, s). 4.16 (2H, d, J=14 Hz), 6.94 (2H, s); MS m/z 368 [M^+]; Anal. Calcd for $C_{20}H_{32}O_2S_2$: C, 65.17; H, 8.75%. Found: C, 65.39; H, 8.72%.

Synthesis of 5,8-Dimethoxy-2,11-dithia[3.3]paracyclophane (7): To a refluxing solution of 2.2 g (40 mmol) of KOH and 190 mg (5 mmol) of $NaBH_4$ in 4 L of EtOH was added dropwise a solution of 2.4 g (10 mmol) of **1** and 1.7 g (10 mmol) of 1,4-bis(chloromethyl)benzene (**6**) in 100 mL of PhH-EtOH (1 : 1) over 36 h. The solvent was distilled off, and the residue was poured into ice/water. The mixture was extracted with CH_2Cl_2, the extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residue was subjected to column chromatography (silica gel, hexane-$CHCl_3$(2 : 1)). Recrystallization of the eluate afforded 2.0 g (6.0 mmol, 60%) of **7**: Colorless prisms (EtOH-PhH), mp 167—171 °C; IR (KBr) ν 1506, 1463, 1401, 1209, 1044, 861 cm^{-1}; ^1H NMR δ=3.37 (2H, d, J=15 Hz), 3.75 (2H, d, J=15 Hz), 3.77 (6H, s), 3.84 (2H, d, J=15 Hz), 4.24 (2H, d, J=15 Hz), 6.46 (2H, s), 6.90 (2H, d d, J=2, 8 Hz), 6.96 (2H, d d, J=2, 8 Hz); MS m/z 332 [M^+]; Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.02; H, 6.06%. Found: C, 64.89; H, 6.00%.

Synthesis of 11,14-Dimethoxy-2,8-dithia[9]paracyclophane 2,2,8,8-Tetraoxide (4a): To a solution of 600 mg (2 mmol) of **3a** in 60 mL of CH_2Cl_2 was added portionally 1.7 g (10 mmol) of MCPBA and the mixture was stirred at room temperature for 13 h. The reaction mixture was poured into 20 ml of 2% aqueous NaOH solution, and the organic phase was separated. After washed with brine, the organic phase was dried ($MgSO_4$) and evaporated in vacuo. Recrystallization of the residue afforded 660 mg (1.8 mmol, 90%) of **4a**: Colorless prisms (benzene), mp 289 °C (decomp); IR (KBr) ν 2940, 1511, 1460, 1407, 1298, 1229, 1129, 883 cm^{-1}; ^1H NMR δ=0.86—1.24 (6H, m), 2.82—2.88 (4H, m), 3.92 (6H, s), 3.95 (2H, d, J=14 Hz), 4.92 (2H, d, J=14 Hz), 7.22 (2H, s); MS m/z 362 [M^+]; Anal. Calcd for $C_{15}H_{22}O_6S_2$: C, 49.71; H, 6.12%. Found: C, 49.72; H, 5.95.%

The dithia[n]paracyclophane S,S,S',S'-tetraoxides described below were prepared in a manner similar to that described for **4a**.

13,16-Dimethoxy-2,10-dithia[11]paracyclophane 2,2,10,10-Tetraoxide (4c): Colorless prisms, mp 236.0—238.0 °C; IR (KBr) ν 2934, 1511, 1460, 1410, 1289, 1224, 1116, 1040 cm^{-1}; ^1H NMR δ=0.84—1.08 (4H, m), 1.10—1.40 (6H, m), 2.86—3.12 (4H, m), 3.88 (2H, d, J=14 Hz), 3.90 (6H, s), 4.88 (2H, d, J=14 Hz), 7.20 (2H, s); MS m/z 390 [M^+]; Anal. Calcd for $C_{17}H_{26}O_6S_2$: C, 52.29; H, 6.71%. Found: C, 52.32; H, 6.57%.

14,17-Dimethoxy-2,11-dithia[12]paracyclophane 2,2,11,11-Tetraoxide (4d): Colorless prisms, mp 235.0—236.0 °C; IR (KBr) ν 2928, 1510, 1457, 1406, 1310, 1133, 1044 cm^{-1}; ^1H NMR δ=0.82—1.12 (4H, m), 1.25—1.60 (8H, m), 2.62—2.86 (4H, m), 3.88 (2H, d, J=14 Hz), 3.88 (6H, s), 4.88 (2H, d, J=14 Hz), 7.19 (2H, s); MS m/z 404 [M^+]; Anal. Calcd for $C_{18}H_{28}O_6S_2$: C, 53.44; H, 6.98%. Found: C, 53.90; H, 6.86%.

15,18-Dimethoxy-2,12-dithia[13]paracyclophane 2,2,12,12-Tetraoxide (4e): Colorless plates (EtOH), mp 215.0—216.5 °C; IR(KBr) ν 2930, 1511, 1458, 1405, 1306, 1224, 1134, 1042 cm^{-1}; ^1H NMR δ=0.95—1.06 (2H, m), 1.09—1.28 (6H, m), 1.38—1.47 (2H, m), 1.51—1.61 (4H, m), 2.81—2.94 (4H, m), 3.85 (2H, d, J=14 Hz), 3.88 (6H, s), 4.83 (2H, d, J=14 Hz), 7.13 (2H, s); MS m/z 418 [M^+]; Anal. Calcd for $C_{19}H_{30}O_6S_2$: C, 54.52; H, 7.22%. Found: C, 54.87; H, 6.97%.

16,19-Dimethoxy-2,13-dithia[14]paracyclophane 2,2,13,13-Tetraoxide (4f): Colorless plates (EtOH), mp 194.0—195.0 °C; IR (KBr) ν 2932, 1510, 1466, 1406, 1306, 1224, 1136, 1044 cm^{-1}; ^1H NMR δ=0.95—1.16 (8H, m), 1.23—1.35 (2H, m), 1.42—1.56 (2H, m), 1.72—1.85 (4H, m), 2.61—2.82 (4H, m). 3.87 (6H, s), 3.88 (2H, d, J=14 Hz), 4.84 (2H, d, J=14 Hz), 7.18 (2H, s); MS m/z 432 [M^+]; Anal. Calcd for $C_{20}H_{32}O_6S_2$: C, 55.53; H,7.46%. Found: C, 55.64; H, 7.25%.

Synthesis of 9,12-Dimethoxy[7]paracyclophane (5a): The pyrolysis of 550 mg (1.5 mmol) of **4a** was carried out in a manner similar to that described in the literature.[14] The organics were extracted with CH_2Cl_2, and the ash was filtered. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel, hexane-CH_2Cl_2 (3 : 1)). Recrystallization of the eluate afforded 36 mg (0.15 mmol, 10%) of **5a**: Colorless prisms (60% MeOH), mp 78.0—80.0 °C; IR (KBr) ν 2924, 1496, 1463, 1401, 1205, 1044 cm^{-1}; ^1H NMR δ=−0.35 to −0.10 (2H, m), 0.80 (2H, br. s), 1.20 (4H, br. s), 1.33 (2H, br. s), 2.24—2.34 (2H, m), 3.13—3.22 (2H, m), 3.80 (6H, s), 6.66 (2H, s); MS m/z 234 [M^+]; Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%. Found: C, 76.52; H, 9.38%.

The dimethoxy[n]paracyclophanes except for **5b** (n=8)[4] described below were prepared in a manner similar to that described for **5a**.

11,14-Dimethoxy[9]paracyclophane (5c): Colorless prisms (60% MeOH), mp 50.0—51.5 °C; IR (KBr) ν 2930, 1504, 1460, 1402, 1210, 1049 cm^{-1}; ^1H NMR δ=0.15—0.28 (2H, m), 0.51—0.70 (4H, m), 0.73—0.87 (2H, m), 1.12—1.27 (2H, m), 1.31—1.44 (2H, m), 1.48—1.62 (2H, m), 2.04—2.15 (2H, m), 3.14 (2H, d t, J=5, 13 Hz), 3.81 (6H, s), 6.61 (2H, s); MS m/z 262 [M^+]; Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%. Found: C, 77.52; H, 9.99%.

12,15-Dimethoxy[10]paracyclophane (5d): Colorless prisms (60% MeOH), mp 45.0—46.5 °C; IR (KBr) ν 2918, 1501, 1460, 1402, 1209, 1049 cm^{-1}; ^{1}H NMR δ=0.50—0.83 (8H, m), 1.05—1.22 (4H, m), 1.45—1.56 (2H, m), 1.61—1.75 (2H, m), 2.19—2.29 (2H, m), 3.03—3.13 (2H, m), 3.79 (6H, s), 6.65 (2H, s); MS m/z 276 [M$^+$]; Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21%. Found: C, 78.28; H, 10.09%.

13,16-Dimethoxy[11]paracyclophane (5e): Colorless prisms (60% MeOH), mp 48.5—49.5 °C; IR (KBr) ν 2926, 1507, 1460, 1404, 1211, 1049 cm^{-1}; ^{1}H NMR δ=0.76—0.92 (10H, m), 1.08—1.36 (4H, m), 1.47—1.74 (4H, m), 2.20—2.25 (2H, m), 2.99—3.08 (2H, m), 3.79 (6H, s), 6.65 (2H, s); MS m/z 290 [M$^+$]; Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41%. Found: C, 78.64; H, 10.11%.

14,17-Dimethoxy[12]paracyclophane (5f): Colorless oil; IR (NaCl) ν 2924, 2854, 1505, 1462, 1402, 1211, 1049 cm^{-1}; ^{1}H NMR δ=0.82—0.86 (4H, m), 0.93—1.15 (12H, m), 1.46—1.73 (4H, m), 2.15—2.26 (2H, m), 3.05—3.12 (2H, m) 3.77 (6H, s), 6.63 (2H, s); MS m/z 304 [M$^+$]; Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59%. Found: C, 78.67; H, 10.22%.

Synthesis of 4,7-Dimethoxy[2.2]paracyclophane (8): A solution of 1.3 g (4.0 mmol) of **7** in 50 mL of $P(OMe)_3$ was irradiated with a 100 W high-pressure mercury lamp at room temp for 2 h under bubling N_2. The reaction mixture was poured into 300 mL of water, stirred for 3 h, and extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was subjected to column chromatography (silica gel, hexane-CH_2Cl_2 (2:1)) and recrystallization of the eluate afforded 620 mg (2.3 mmol, 58%) of **8**: Colorless prisms (hexane), mp 184.0—185.0 °C; IR (KBr) ν 2936, 1212, 1047, 871 cm^{-1}; ^{1}H NMR δ=2.46—2.57 (2H, m), 2.95—3.14 (4H, m), 3.36—3.45 (2H, m), 3.69 (6H, s), 5.72 (2H, s), 6.38 (2H, d d, J=2, 8 Hz), 6.74 (2H, d d, J=2, 8 Hz); MS m/z 268 [M$^+$]; Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.92; H, 7.60%.

Treatment of 10,13-Dimethoxy[8]paracyclophane (5b) with CAN. To a solution of 450 mg (1.8 mmol) of **5b** in 20 mL of MeCN was added dropwise a solution of 1.9 g (3.6 mmol) of CAN in 8 mL of water for 5 min and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into 50 mL of brine, and the organics were extracted with CH_2Cl_2 (20 mL×3) and washed with brine. After dried ($MgSO_4$), the solvent was evaporated in vacuo. The residue was subjected to column chromatography (silica gel, CH_2Cl_2). Recrystallization of the eluate afforded 360 mg (1.4 mmol, 76%) of **9b**.

10,13-Dimethoxybicyclo[8.3.1]tetradeca-1(14),12-dien-11-one (9b): Colorless prisms (hexane), mp 96.0—99.0 °C; IR (KBr) ν 2930, 1657, 1569, 1205, 1088 cm^{-1}; ^{1}H NMR δ=0.77—0.90 (1H, m), 0.92—1.60 (11H, m), 1.73—1.84 (1H, m), 2.03—2.23 (2H, m), 2.70—2.81 (1H, m), 3.08 (3H, s), 3.83 (3H, s), 5.62 (1H, s), 6.20 (1H, s); ^{13}C NMR δ=18.62, 25.13, 25.12, 25.76, 26.23, 27.80, 31.68, 39.91, 53.30, 56.28, 81.88, 101.94, 136.45, 140.90, 172.55, 201.95; UV (EtOH) λ_{max} (nm) (log ε) 317 (3.46); HRMS Found: m/z 264.1724 [M$^+$]. Calcd for $C_{16}H_{24}O_3$: M, 264.1728. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%. Found: C, 73.02; H, 9.04%.

Other products described below were obtained in a manner similar to that described for **9b**. The yields are shown in Table 2.

9,12-Dimethoxybicyclo[7.3.1]trideca-1(13),11-dien-10-one (9a): Colorless prisms (hexane), mp 112.0—114.0 °C; IR (KBr) ν 2936, 1651, 1564, 1455, 1389, 1206, 1090, 976 cm^{-1}; ^{1}H NMR δ=1.00—1.11 (1H, m), 1.15—1.76 (10H, m), 1.96—2.05 (1H, m), 2.12—2.22 (1H, m), 2.73—2.82 (1H, m), 3.15 (3H, s), 3.82 (3H, s), 5.54 (1H, s), 6.30 (1H, s); MS m/z 250 [M$^+$]; Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%. Found: C, 71.97; H, 8.59%.

11,14-Dimethoxybicyclo[9.3.1]pentadeca-1(15),13-dien-12-one (9c): Colorless prisms (hexane), mp 115.0—115.5 °C; IR (KBr) ν 2938, 1652, 1563, 1388. 1238, 1217, 1094 cm^{-1}; ^{1}H NMR δ=0.90—1.10 (1H, m), 1.15—1.55 (12H, m), 1.57—1.66 (2H, m), 1.91—2.06 (2H, m), 2.71—2.80 (1H, m), 3.12 (3H, s), 3.80 (3H, s), 5.54 (1H, s), 6.21 (1H, s); MS m/z 278 [M$^+$]; Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41%. Found: C, 73.53; H, 9.25%.

12,15-Dimethoxybicyclo[10.3.1]hexadeca-1(16),14-dien-13-one (9d): Colorless prisms (hexane), mp 132.0—134.0 °C; IR (KBr) ν 2930, 1649, 1563, 1453, 1393, 1229, 1096 cm^{-1}; ^{1}H NMR δ=1.12—1.45 (15H, m), 1.46—1.61 (2H, m), 1.85—1.94 (1H, m), 2.06—2.16 (1H, m), 2.66-2.78 (1H, m), 3.12 (3H, s), 3.80 (3H, s), 5.52 (1H, s), 6.16 (1H, s); MS m/z 292 [M$^+$]; Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65%. Found: C, 73.90; H, 9.37%.

[10]Paracyclophane-12,15-dione (10d): Yellow oil; IR (NaCl) ν 2926, 2854, 1661, 1455, 1260, 1194, 802 cm^{-1}; ^{1}H NMR δ=0.92—1.35 (14H, m), 1.56—1.73 (2H, m), 1.92—2.10 (2H, m), 2.95—3.05 (2H, m), 6.59 (2H, s); HRMS Found: m/z 246.1612 [M$^+$]. Calcd for $C_{16}H_{22}O_2$: M, 246.1619.

Methyl (2-methoxy-4-oxo-2-cyclotetradecenylidene)acetate (11d): Colorless prisms (50% MeOH), mp 84.0—86.0 °C; IR (KBr) ν 2920, 1730, 1550, 1402, 1200, 1170 cm^{-1}; ^{1}H NMR δ=1.22—1.45 (14H, m), 1.66—1.70 (2H, m), 2.27 (2H, t, J=7 Hz), 2.38 (2H, t, J=7 Hz), 3.65 (3H, s), 3.78 (3H, s), 5.62 (1H, s), 5.91 (1H, t, J=1 Hz); ^{13}C NMR δ=24.10, 24.16, 24.60, 24.68, 24.77, 25.80, 25.92, 26.10, 26.54, 34.84, 43.30, 51.22, 100.59, 119.48, 155.98, 165.49, 170.28, 199.42; MS m/z 308 [M$^+$]; Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15%. Found: C, 69.99; H, 8.82%.

[11]Paracyclophane-13,16-dione (10e): Yellow oil; IR (NaCl) ν 2924, 2852, 1657, 1460, 1401, 1209, 1046 cm^{-1}; ^{1}H NMR δ=0.85—1.77 (18H, m), 1.95—2.04 (2H, m), 2.87—2.95 (2H, m), 6.60 (2H, t, J=1 Hz); HRMS Found: m/z 260.1776 [M$^+$]. Calcd for $C_{17}H_{24}O_2$: M, 260.1775.

Methyl (2-methoxy-4-oxo-2-cyclopentadecenylidene)acetate (11e): Pale yellow oil; IR (NaCl) ν 2932, 1721, 1574, 1437, 1211, 1078 cm^{-1}; ^{1}H NMR δ=0.81—0.96 (3H, m), 1.12—1.50 (12H, m), 1.61—1.70 (3H, m), 2.23 (2H, t, J=7 Hz), 2.44 (2H, t, J=7 Hz), 3.64 (3H, s), 3.77 (3H, s), 5.60 (1H, s), 5.88 (1H, t, J=1 Hz); HRMS Found: m/z 322.2145 [M$^+$]. Calcd for $C_{19}H_{30}O_4$: M, 322.2142.

13,16-Dimethoxy[11]paracyclophane-1-one (12e): Colorless prisms (50% MeOH), mp 78.0—80.0 °C; IR (KBr) ν 2926, 1672, 1501, 1461, 1401, 1211, 1039 cm^{-1}; ^{1}H NMR δ=0.74—1.25 (13H, m), 1.41—1.72 (3H, m), 2.21—2.30 (1H, m), 2.43—2.53 (1H, m), 3.08—3.17 (1H, m), 3.24—3.34 (1H, m), 3.80 (3H, s), 3.86 (3H, s), 6.77 (1H, s), 6.90 (1H, s); MS m/z 304 [M$^+$]; Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27%. Found: C, 74.82; H, 9.14%.

[12]Paracyclophane-14,16-dione (10f): Yellow prisms (hexane), mp 53.0—58.0 °C; IR (KBr) ν 2926, 2854, 1655, 1608, 1460, 1252, 928 cm^{-1}; ^{1}H NMR δ=1.04—1.26 (18H, m), 1.47—1.62 (2H, m), 1.97—2.06 (1H, m), 2.89—2.93 (2H, m), 6.56 (2H, s); MS m/z 274 [M$^+$]; Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%. Found: C, 78.72; H, 9.37%.

14,17-Dimethoxy[12]paracyclophane-1-one (12f): Colorless prisms (40% MeOH), mp 65.0—66.5 °C; IR (KBr) ν 2924, 1667, 1501, 1459, 1402, 1212, 1043 cm^{-1}; ^{1}H NMR δ=0.68—

0,73 (2H, m), 0.82—1.22 (12H, m), 1.41—1.72 (4H, m), 2.26—2.35 (1H, m), 2.39—2.50 (1H, m), 3.37—3.46 (1H, m), 3.81 (3H, s), 3.86 (3H, s), 6.75 (1H, s), 6.99 (1H, s); MS *m/z* 318 [M$^+$]; Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.49%. Found: C, 75.42; H, 9.34%.

Treatment of 13 with CAN. Treatment of 100 mg (0.24 mmol) of **13** with CAN and its work up was carried out in a manner similar to that described above for **5a**. The residue was subjected to column chromatography (silica gel, hexane—AcOEt (1 : 1)). Recrystallization of the eluate afforded 76 mg (0.17 mmol, 71%) of **14**.

12,13-Dibromo-5-methoxy-6-(methoxycarbonylmethylene)[8](2,5)thiophenophane-4-en-3-one (14): Colorless prisms (hexane-EtOH), mp 176.0—181.0 °C; IR (KBr) ν 2938, 1728, 1571, 1402, 1199, 1175 cm^{-1}; ^{1}H NMR δ=2.30—2.35 (1H, m), 2.40—2.50 (1H, m), 2.63—2.72 (1H, m), 2.93—3.05 (2H, m), 3.16—3.42 (3H, m), 3.57 (3H, s), 3.73 (3H, s), 5.02 (1H, s), 6.09 (1H, s); ^{13}C NMR δ=27.33, 28.99, 35.00, 41.86, 51.73, 55.58, 102.59, 111.77, 113.46, 127.83, 136.99, 139.12, 142.46, 162.07, 165.78. 197.73; UV (EtOH) λ_{max} (nm) (log ε) 291 (shoulder, 3.65); MS *m/z* 462, 464, 466 [M$^+$]; Anal. Calcd for $C_{16}H_{16}Br_2O_4S$: C, 41.40; H, 3.47%. Found: C, 41.61; H,3.84%. The structure of **14** was also confirmed by X-ray crystallographic analysis.

Treatment of 8 with CAN. Treatment of 270 mg (1.0 mmol) of **8** with 1.25 g (2.2 mmol) of CAN and its work up were carried out in a manner similar to that described above for **5a**. The residue was subjected to column chromatography (silica gel, hexane-AcOEt (10 : 1)). Recrystallization of the first eluate afforded 10 mg (0.04 mmol, 4%) of **17**, that of the second eluate afforded 170 mg (0.60 mmol, 60%) of **15**, the third eluate gave 60 mg (0.20 mmol, 20%) of **16**.

3,6-Dimethoxy[2.2]metaparacyclophane-4(3*H*)-one (15): Colorless prisms(hexane-benzene), mp 173.0—174.0 °C; IR (KBr) ν 2920, 1637, 1563, 1390, 1065 cm^{-1}; ^{1}H NMR δ=1.74—1.86 (2H, m), 2.26—2.33 (1H, m), 2.35—2.46 (2H, m), 2.60—2.68 (1H, m), 2.77—2.94 (2H, m), 2.87 (3H, s), 3.84 (3H, s), 4.53 (1H, s), 5.34 (1H, s), 6.69 (1H, d d, *J*=2, 7 Hz), 6.77 (1H, d d, *J*=2, 7 Hz), 7.05 (1H, d d, *J*=2, 7 Hz), 7.33 (1H, d d, *J*=2, 7 Hz); ^{13}C NMR δ=31.00, 33.69, 35.23, 43.67, 51.16, 56.07, 100.49, 128.33, 129.41, 129.74, 129.96, 130.13, 130.90, 139.85, 140.54, 143.49, 173.04, 197.93; MS *m/z* 284[M$^+$]; Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. Found: C, 76.18; H, 7.13%.

5-Methoxy-6-(methoxycarbonylmethylene)[8]paracyclophane-4-en-3-one (16): Pale yellow oil; IR (NaCl) ν 2932, 1727, 1677, 1583, 1197, 1078 cm^{-1}; ^{1}H NMR δ=2.40 (2H, t, *J*=7 Hz), 2.54 (2H, t, *J*=7 Hz), 2.86 (2H, t, *J*=7 Hz), 2.97 (2H, t, *J*=7 Hz), 3.59 (3H, s), 3.60 (3H, s), 5.83 (1H, s), 7.05 (2H, d, *J*=8 Hz), 7.11 (2H, d, *J*=8 Hz); ^{13}C NMR δ=34.18, 36.36, 37.80, 47.75, 51.60, 58.63, 108.39, 123.65, 129.66, 129.76, 139.62, 139.92, 150.95, 160.79, 165.77, 199.13; HRMS Found: *m/z* 300.13598 [M$^+$]. Calcd for $C_{18}H_{20}O_4$: M, 300.13604.

[2.2]Paracyclophane-4,7-dione (17): Yellow prisms (hexane), mp 185 °C (sub.), 240 °C (decomp), (lit,[14] 110 °C/0.1 Torr (sub.), 1 Torr=133.322 Pa): ^{1}H NMR δ=2.26—2.37 (2H, m), 3.00—3.29 (6H, m), 5.83 (2H, s), 6.73 (2H, d d, *J*=2, 8 Hz), 6.85 (2H, d d, *J*=2, 8 Hz); HRMS Found: *m/z* 238.0996 [M$^+$]. Calcd for $C_{16}H_{14}O_2$: M, 238.0993. Other spectral data were supported by the literature.[14]

Reaction of 9b with *N*-Phenylmaleimide. A solution of 53 mg (0.20 mmol) of **9b** and 53 mg (0.30 mmol) of *N*-phenylmaleimide in 2 mL of benzene in sealed tube under N_2 was heated at 190 °C for 5 h. The solvent was evaporated in vacuo and the residue was subjected to column chromatography (silica gel, CH_2Cl_2-AcOEt (10 : 1)). Recrystallization of the second eluate afforded 58 mg (0.13 mmol, 66%) of **18**.

16-Aza-3,19-dimethoxy-16-phenyltetracyclo[10.6.1.0^{3,13}.0^{14,18}]nonadec-12(19)-en-2,15,17-trione (18): Colorless prisms (hexane-benzene), mp 162.0—163.0 °C; IR (KBr) ν 2938, 1717, 1650, 1499, 1459, 1385, 1187, 1067, 747, 692 cm^{-1}; ^{1}H NMR δ=1.25—1.85 (14H, m), 1.98—2.10 (1H, m), 2.75—2.85 (1H, m), 3.32 (3H, s), 3.38 (1H, d d, *J*=3, 8 Hz), 3.50 (3H, s), 3.70 (1H, d, *J*=4 Hz), 3.76 (1H, d d, *J*=3, 8 Hz), 3.90 (1H, d, *J*=4 Hz), 7.12—7.15 (2H, m), 7.36—7.49 (3H, m); ^{13}C NMR δ=20.53, 21.41, 25.76, 26.08, 26.74, 27.05, 27.11, 28.11. 40.34, 41.32, 46.71, 49.31, 52.12, 56.86, 122.01, 126.48, 128.89, 129.31, 131.73, 146.06, 175.73, 177.33, 201.71; MS *m/z* 437 [M$^+$]; Anal. Calcd for $C_{26}H_{31}NO_5$: C, 71.37; H, 7.14; N, 3.20%. Found: C, 71.31; H, 7.11; N, 2.74%. The structure of **18** was also confirmed by X-ray crystallographic analysis.

Dimethyl 3,16-Dimethoxy-2-oxotricyclo[10.3.1.0^{3,13}]hexadeca-12(16),14-diene-14,15-dicarboxylate (19) was obtained from **9b** and dimethyl acetylenedicarboxylate in a manner similar to that described for **18**. **19**: Colorless prisms (hexane), mp 118.0—119.0 °C; IR (KBr) ν 2934, 1722, 1438, 1347, 1277, 1069 cm^{-1}; ^{1}H NMR δ=1.27—1.83 (14H, m), 1.96—2.08 (1H, m), 2.66—2.74 (1H, m), 3.21 (3H, s), 3.59 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 4.08 (1H, s), 4.38 (1H, s); MS *m/z* 406 [M$^+$]; Anal. Calcd for $C_{22}H_{30}O_7$: C, 65.01; H, 7.44%. Found: C, 65.23; H, 7.49%.

X-Ray Analysis of 14. Crystallographic Section: $C_{16}H_{16}Br_2O_4S$, M_m=464.19, monoclinic, space group $P2_1/n$, a=8.806(3), b=10.627(2), c=18.339(7) Å, α=90.00°, β=93.49°, γ=90.00°, V=1713 Å^3, Z=4, d_x=1.80 g cm^{-3}.

Data Collection: Diffractometer: CAD4 (ENRAF-NONIUS), crystal size: 0.45×0.30×0.40 mm, radiation: Mo$K\alpha$ (0.70930 Å), monochromator: graphite, data collecting mode: ω-θ scan, number of reflections: 2500 (observed), temperature 297 K.

Structural Analysis: Solution: Direct method, method of refinement: block-diagonal least-squares; R=0.083, R_w=0.098. software: SDP.

X-Ray Analysis of 18. Crystallographic Section: $C_{26}H_{31}NO_5$, M_m=437.54, triclinic, space group $P\bar{1}$, a=10.7750(7), b=11.394(1), c=10.0486(8) Å, α=96.465(7)°, β=95.927(6)°, γ=68.450(7)°, V=1137.38 Å^3, Z=2, d_x=1.277 g cm^{-3}.

Data Collection: Diffractometer: CAD4 (ENRAF-NONIUS), crystal size: 0.4 mm, radiation: Cu$K\alpha$ (1.54184 Å), monochromator: graphite, data collecting mode: ω-2θ scan, number of reflections: 3856 (observed), temperature 297 K.

Structural Analysis: Solution: Direct method, method of refinement: full matrix, R=0.05239, R_w=0.08784, software: SDP.

Supplementary Material Available. The tables of positional parameters, their estimated standard deviations, refined temperature factor expressions, bond distances, bond angles of X-ray crystallography of **14** and **18** (13 pages). Ordering information is given on any current masthead page.

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