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Synthesis, Structure, and Properties of Triple-Layered [2.2][2.2]Naphthalenophane[1]

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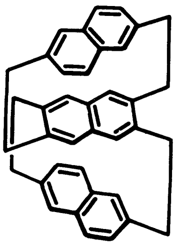
The title compound was synthesized in a similar manner to a simple access to triple-layered [2.2][2.2]paracyclophane. Its structure was elucidated by X-ray crystallographic analysis. The outer naphthalene rings are bent into a boat form and the inner naphthalene ring is bent into a twist form. These naphthalenes are stacked in layers within van der Waals contact. Therefore, there is a strong transannular π-electronic interaction between them, which brings about characteristic bathochromism, hyperchromism, and broadening in the electronic spectrum. These effects are more prominent than those of the double-layered homologue.

Multilayered cyclophanes are one of the most interesting compounds in the field of cyclophane chemistry.[2] They show more unusual physical and chemical properties than double-layered phanes because their transannular π-electronic interactions between aromatic nuclei increase with an increase of the layers.[3] However, the previous study has been limited only to benzene series.[2] The extensive studies to fused aromatic ring series might be helpful in a comprehensive understanding of the transannular electronic interactions of cyclophanes which serve as an excimer model.[4] In this report, we would like to present triple-layered [2.2][2.2]naphthalenophane (**1**) as the first example of multilayered phanes composed of fused aromatic nuclei. There have been some double-layered [2.2]naphthalenophanes of different stacking types mainly depending on the substitution mode of the bridging ethylenes. Haenel and Staab reported chiral [2.2](2,6)naphthalenophane (**2**), in which two aromatic rings were bridged at the 2- and 6-positions and obliquely overlapped each other.[5] Blanck and Haenel later reported achiral isomer (**3**), which had the exact overlap of the two aromatic rings and accordingly was less stable than **2**.[6] A study of a series of multilayered [2.2]paracyclophanes revealed that there was observed a dramatic enhancement in the electronic interaction with an increase in stacking layers from double to triple.[3] Therefore, triple-layered naphthalenophane (**1**) is expected to show characteristic properties as compared to double-layered one **2** or **3**.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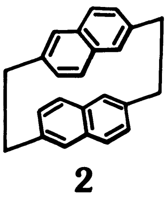
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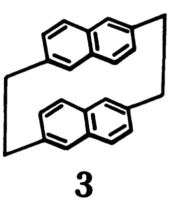
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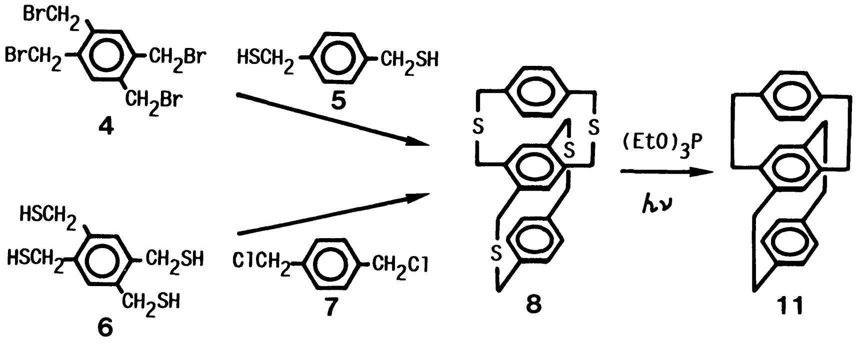
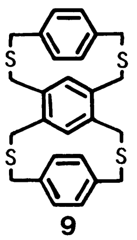
Results and Discussion

Synthesis. Multilayered cyclophanes were previously synthesized in multisteps via double-layered ones.[3,7] The same pathway is inapplicable to fused aromatic phanes because the functionalized double-layered intermediates are not readily accessible. Boekelheide et al., however, reported that a termolecular coupling of 1,2,4,5-tetrakis(bromomethyl)benzene



Scheme 1.

and 2 equiv of 2,6-bis(mercaptomethyl)pyridine followed by ring contraction using the Wittig rearrangement led to triple-layered pyridinoparacyclophane.[8] Such a termolecular reaction appears to provide a direct entry to triple-layered phanes, though it has a possibility of not only a low yield but also the formation of some regioisomers. Then, we have first examined its approach to triple-layered [2.2][2.2]paracyclophane (**11**) prior to the present target molecule **1**. As shown in Scheme 1, a termolecular coupling reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (**4**) and 2 equiv of 1,4-bis(mercaptomethyl)benzene (**5**) in ethanol solution containing potassium hydroxide at room temperature gave triple-layered tetrathia[3.3]-[3.3]paracyclophane (**8**) in only 4.2% yield. On the other hand, a reaction of 1,2,4,5-tetrakis(mercaptomethyl)benzene (**6**) and two 1,4-bis(chloromethyl)-benzenes (**7**) in refluxing ethanol gave the same compound **8** in 12% yield. There was no evidence for the formation of the other possible isomers **9** and **10**.



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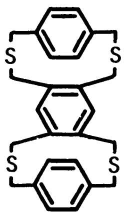

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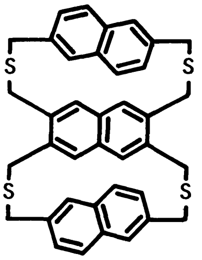
The photoinduced desulfurization of **8** with triethyl phosphite smoothly proceeded to give the desired compound **11** in 93% yield. The coupling yield is quite low, but the steps are few and the reactants **4**—**7** are readily available. As a result, this access constitutes the simplest one to **11**.

A similar method was applied to the synthesis of triple-layered [2.2][2.2]naphthalenophane (**1**) (Scheme 2). 2,3,6,7-Tetramethylnaphthalene (**12**) was prepared from 2,3-dimethylsuccinic anhydride and *o*-xylene according to the procedure of Dozen and Hatta[9] and brominated with *N*-bromosuccinimide to 2,3,6,7-tetrakis(bromomethyl)naphthalene (**13**) in 69% yield. A termolecular coupling reaction of **13** and two 2,6-bis(mercaptomethyl)naphthalenes (**14**) gave triple-layered tetrathia[3.3][3.3]naphthalenophane (**17**) in 9% yield. Alternatively, **13** on treatment with thiourea followed by alkaline hydrolysis was converted to 2,3,6,7-tetrakis(mercaptomethyl)naphthalene (**15**), which was coupled with two 2,6-bis(bromomethyl)naphthalenes (**16**) to give the same product **17** in 17% yield. The ^{1}H NMR spectrum demonstrates that the inner naphthalene protons resonate as a multiplet at δ 6.1—6.4. This indicates that **17** consists of an isomeric mixture of **17a**—**c**, which are quite difficult to separate. Another possible isomer **18** with a different substitution mode was not detected. The inner aromatic protons of **18** might be situated just above the outer naphthalene rings, so that the ^{1}H NMR spectrum should show a characteristic



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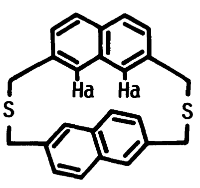

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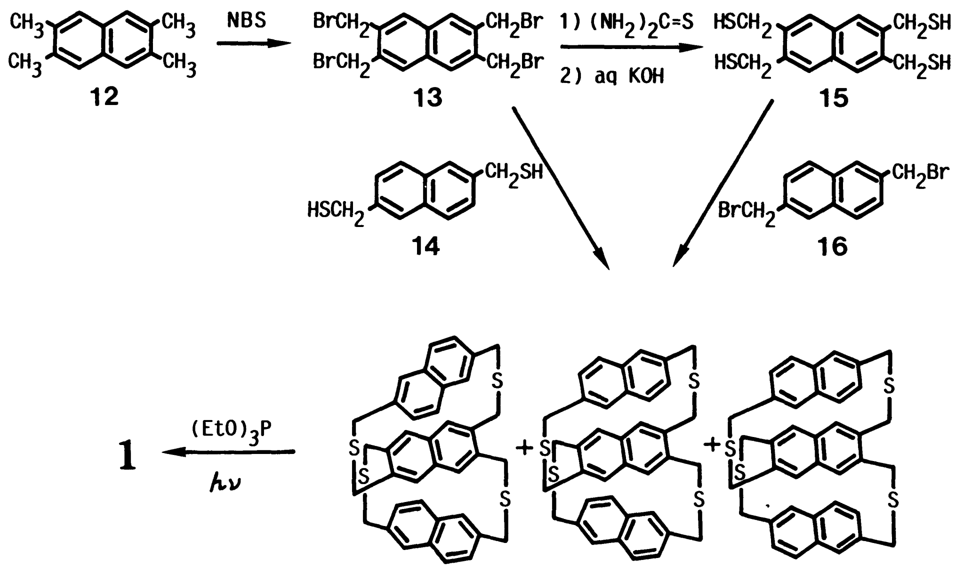

Scheme 2.

upfield shift like H_a protons (δ 5.82) of 2,15-dithia[3.3](2,6)(2,7)naphthalenophane (**19**) as a double-layered homologue.[10] The photolytic sulfur extrusion of **17** with triethyl phosphite gave the desired product **1** in 32% yield. Its structure was characterized by elemental analysis, spectroscopic measurements, and finally X-ray crystallographic analysis. No desulfurized isomers corresponding to the stacking types of **17b** and **17c** were observed. Probably a ring rotation occurred during the C–S bond fission on photolysis, leading to the sole formation of the more stable isomer **1**.

Molecular Structure. The crystal of **1** is triclinic with space group $P\bar{1}$ and the unit cell contains four molecules which form two distinct enantiomeric pairs. Table 1 lists final atomic parameters for the molecules (I) and (II). No essential difference in structure between the two distinct molecules is observed, so that only molecular structure I is discussed below. Figure 1 shows the side view of the ORTEP drawing. The three naphthalenes diagonally overlap each other and, on the whole, take a spiral structure. As seen from the top view of Fig. 2, the diagonal angle between the neighboring ones is 34°. The bridging ethylene bonds are torsional to avoid the eclipsing form. The torsional angle around C(1)–C(2) bond is 39°. Table 2 summarizes the C–C bond lengths and C–C–C bond angles. As a whole, they hold values close to normal except for a little elongation of the bridged ethylene bonds. On the other hand, Figs. 3 and 4 demonstrate that the outer naphthalene rings are bent into a boat form and the inner naphthalene ring is bent into a twist form. A mean plane (A) defined by C(4), C(5), C(11), and C(12) atoms inclines by 8.1° from a plane (molecular horizon) defined by C(5), C(6), C(10), and C(11), a plane (B) defined by C(3),

Table 1. Final Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses and Thermal Parameters (Å^2)[a] for Carbon Atoms of **1**

Atom	Molecule I				Molecule II			
	x	y	z	B_{eq}	x	y	z	B_{eq}
C(1)	6404(4)	7180(2)	1613(4)	4.02	6430(4)	−1529(2)	6698(4)	3.80
C(2)	6770(4)	7787(2)	2740(4)	3.98	6830(4)	−1907(2)	7842(4)	4.44
C(3)	6816(3)	7412(2)	3932(3)	3.40	6907(4)	−1470(2)	9028(4)	4.06
C(4)	7787(3)	7458(2)	4668(3)	3.35	7891(4)	−1011(2)	9729(4)	4.21
C(5)	7868(3)	6937(2)	5567(3)	3.30	7975(3)	−421(2)	10593(4)	3.79
C(6)	8859(3)	6909(2)	6223(4)	4.11	8981(4)	127(3)	11195(4)	4.77
C(7)	8908(3)	6270(3)	6788(4)	4.43	9025(4)	807(3)	11727(4)	4.74
C(8)	7963(4)	5619(3)	6730(3)	4.13	8076(4)	970(3)	11702(3)	4.25
C(9)	6983(3)	5685(2)	6286(3)	3.71	7103(4)	402(3)	11298(3)	4.29
C(10)	6906(3)	6338(2)	5691(3)	3.34	7010(3)	−313(2)	10738(3)	3.85
C(11)	5905(3)	6371(2)	5058(4)	3.80	6005(3)	−863(2)	10156(4)	4.39
C(12)	5856(3)	6887(2)	4214(4)	3.71	5955(4)	−1429(2)	9330(4)	4.25
C(13)	8039(4)	4845(3)	6964(4)	5.14	8145(4)	1788(3)	11881(4)	4.59
C(14)	8501(4)	4555(2)	5943(4)	4.49	8554(4)	2262(2)	10810(4)	4.09
C(15)	8015(3)	4749(2)	4699(3)	3.11	8051(3)	1784(2)	9599(3)	2.83
C(16)	8566(3)	5407(2)	4228(3)	2.84	8599(3)	1392(2)	9128(3)	2.45
C(17)	8049(3)	5758(2)	3314(3)	2.31	8060(3)	761(2)	8243(3)	2.21
C(18)	8589(3)	6386(2)	2696(3)	2.98	8594(3)	395(2)	7614(3)	2.65
C(19)	8052(3)	6760(2)	1937(3)	3.16	8052(3)	−273(2)	6890(3)	2.93
C(20)	6925(3)	6593(2)	1904(3)	3.00	6936(3)	−670(2)	6918(3)	2.66
C(21)	6370(3)	5920(2)	2346(3)	2.55	6386(3)	−271(2)	7368(3)	2.46
C(22)	6909(3)	5466(2)	2999(3)	2.13	6919(3)	469(2)	7973(3)	2.03
C(23)	6370(3)	4729(2)	3350(3)	2.49	6386(3)	937(2)	8319(3)	2.45
C(24)	6911(3)	4344(2)	4090(3)	2.85	6940(3)	1619(2)	9032(3)	2.83
C(25)	6422(3)	3482(2)	4057(4)	4.00	6430(4)	2222(2)	9001(4)	3.80
C(26)	6857(4)	3109(2)	3120(4)	4.48	6849(4)	2799(2)	8033(4)	4.28
C(27)	6935(4)	3535(2)	1984(4)	4.09	6906(3)	2388(2)	6893(4)	3.75
C(28)	7927(4)	3995(2)	1781(4)	4.31	7885(3)	2418(2)	6656(4)	3.59
C(29)	8029(4)	4572(2)	949(4)	4.06	7963(3)	1875(2)	5821(3)	3.34
C(30)	9036(4)	5115(3)	842(4)	5.39	8964(3)	1835(2)	5695(4)	3.87
C(31)	9099(4)	5787(3)	333(4)	5.36	9011(4)	1182(2)	5191(4)	4.18
C(32)	8152(4)	5953(3)	−127(4)	4.98	8064(3)	529(2)	4783(3)	3.58
C(33)	7169(4)	5386(3)	−221(3)	4.66	7078(4)	604(2)	4706(3)	3.72
C(34)	7079(4)	4681(2)	310(3)	4.00	7000(3)	1275(2)	5225(3)	3.29
C(35)	6059(4)	4134(3)	383(4)	4.35	5989(4)	1320(3)	5327(4)	4.05
C(36)	6000(4)	3583(2)	1193(4)	4.40	5947(4)	1861(2)	6127(4)	4.16
C(37)	8226(4)	6771(3)	−271(4)	5.81	8143(4)	−250(3)	4649(4)	4.57
C(38)	8595(4)	7245(3)	1007(4)	5.06	8557(4)	−499(3)	5932(4)	4.19

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$.

C(4), and C(12) atoms makes a dihedral angle of 7.9° with the plane A, and the C(2)–C(3) bond makes an angle of 9.7° with the plane B. These values are fairly smaller than the bending angles of [2.2]paracyclophane[11] or the multilayered homologues,[12] indicating that the outer naphthalene effectively disperses a strain throughout the fused system. On the other hand, the twist angle of the inner naphthalene, defined by the dihedral angle between mean planes of the two

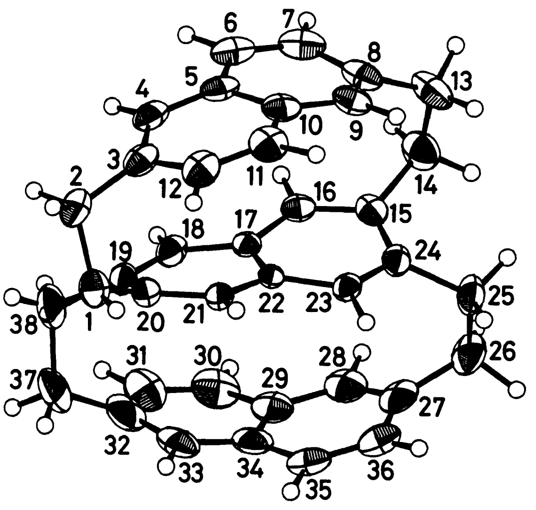

Fig. 1. A perspective view of molecule 1 with atom numbering scheme.

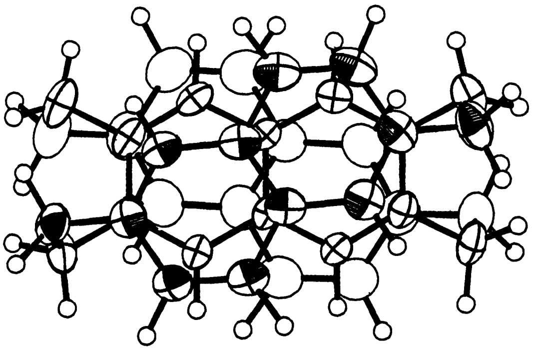

Fig. 2. A top view of molecule 1.

Table 2. C–C Bond Lengths (Å) and C–C–C Bond Angles (°) in 1

Bond length					
1-2	1.567(6),	2-3	1.508(6),	3-4	1.375(5)
4-5	1.419(5),	5-6	1.410(6),	6-7	1.372(7)
7-8	1.417(5),	8-9	1.365(7),	9-10	1.422(6)
10-5	1.425(5),	10-11	1.417(6),	11-12	1.361(6)
12-3	1.426(5),	8-13	1.511(8),	13-14	1.579(7)
14-15	1.514(5),	15-16	1.371(5),	16-17	1.413(5)
17-18	1.417(5),	18-19	1.361(6),	19-20	1.438(6)
20-1	1.505(7),	20-21	1.377(5),	21-22	1.416(5)
22-17	1.411(5),	22-23	1.420(4),	23-24	1.366(5)
24-15	1.437(5),	24-25	1.516(5),	25-26	1.565(7)
26-27	1.503(6),	27-28	1.385(6),	28-29	1.418(6)
29-30	1.417(6),	30-31	1.370(8),	31-32	1.418(8)
32-33	1.367(6),	33-34	1.427(7),	34-29	1.419(7)
34-35	1.423(6),	35-36	1.369(6),	36-27	1.418(7)
32-37	1.512(8),	37-38	1.568(7),	38-19	1.514(6)
Bond angle					
1-2-3	110.9(3),	2-3-4	121.1(4),	3-4-5	122.3(3)
4-5-6	123.5(3),	5-6-7	121.0(3),	6-7-8	121.0(4)
7-8-9	118.3(4),	8-9-10	121.1(4),	4-5-10	118.4(3)
6-5-10	117.4(4),	9-10-11	122.2(3),	9-10-5	119.4(4)
5-10-11	117.8(4),	10-11-12	121.5(4),	11-12-3	121.0(4)
2-3-12	120.4(3),	4-3-12	117.6(4),	7-8-13	120.7(5)
9-8-13	120.3(4),	8-13-14	111.4(4),	13-14-15	109.3(4)
14-15-16	119.6(3),	15-16-17	122.6(3),	16-17-18	125.0(3)
17-18-19	122.4(3),	18-19-20	118.7(3),	19-20-21	117.7(4)
1-20-19	121.7(3),	1-20-21	119.7(4),	2-1-20	109.6(3)
16-17-22	117.7(3),	18-17-22	117.4(3),	20-21-22	121.8(3)
21-22-23	123.9(3),	17-22-21	118.4(3),	17-22-23	117.7(3)
22-23-24	122.0(3),	23-24-25	119.6(3),	15-24-23	118.4(3)
15-24-25	120.9(4),	14-15-24	121.8(3),	16-15-24	117.5(3)
24-25-26	109.8(3),	25-26-27	111.4(4),	26-27-28	120.9(4)
27-28-29	121.1(5),	28-29-30	123.3(4),	29-30-31	121.1(5)
30-31-32	120.8(4),	31-32-33	118.5(5),	32-33-34	121.2(5)
28-29-34	118.6(4),	30-29-34	117.5(4),	33-34-35	121.7(5)
29-34-33	119.1(4),	29-34-35	118.4(4),	34-35-36	120.2(4)
27-36-35	122.0(4),	26-27-36	121.2(4),	28-27-36	117.1(4)
32-37-38	111.3(4),	31-32-37	120.1(4),	33-32-37	120.4(5)
19-38-37	109.6(3),	18-19-38	119.6(4),	20-19-38	121.0(4)

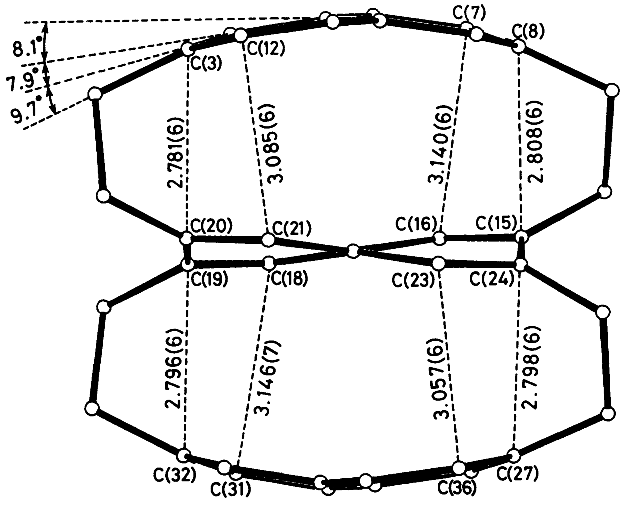

Fig. 3. A projection of the carbon skeleton of **1** along the transverse axis of the naphthalene with some short non-bonding atomic distances (Å).

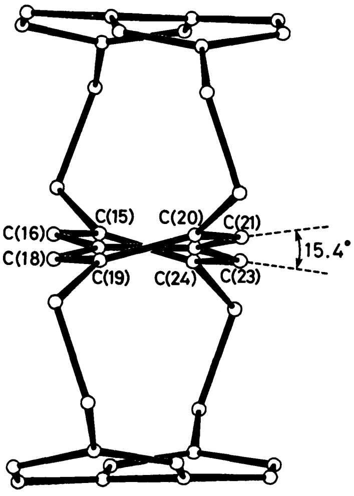

Fig. 4. A projection of the carbon skeleton of **1** along the longitudinal axis of the naphthalene.

benzene rings, is 15.4° so that a considerable strain exists in it. In addition, Fig. 3 shows the nearest nonbonded atomic distances between the neighboring aromatic rings to be situated in 2.8—3.1 Å. These values are quite smaller than van der Waals contact, causing a strong transannular interaction between the naphthalenes.

Spectroscopic Properties. The ^{1}H NMR spectra of cyclophanes are characterized by the magnetic anisotropic effect of the adjacent aromatic rings.[13] When the chemical shifts of three kinds of the aromatic protons in [2.2](2,6)naphthalenophane (**2**), δ 6.41 (noncoupled α-ArH), 6.83 (coupled β-ArH), and 7.09 (coupled α-ArH) are compared to the corresponding ones of 2,6-dimethylnaphthalene, δ 7.57, 7.24, and 7.64, the upfield shift on the noncoupled α-protons is marked, because they are more subject to a shielding effect owing to the obliquely stacking structure.[5] The NMR spectrum of **1** suffers the additional anisotropy of the third naphthalene ring. The spiral stacking structure forces the noncoupled α-protons (δ 6.17) of the outer naphthalene to appear at a higher field than the coupled α-protons (δ 6.69) and β-protons (δ 6.91). The inner naphthalene protons are sandwiched between the two outer naphthalenes and accordingly the upfield shift of the signal (δ 5.55) relative to that (δ 7.44) of 2,3,6,7-tetramethylnaphthalene is especially large and corresponds to almost twice that for the α-protons of **2**.

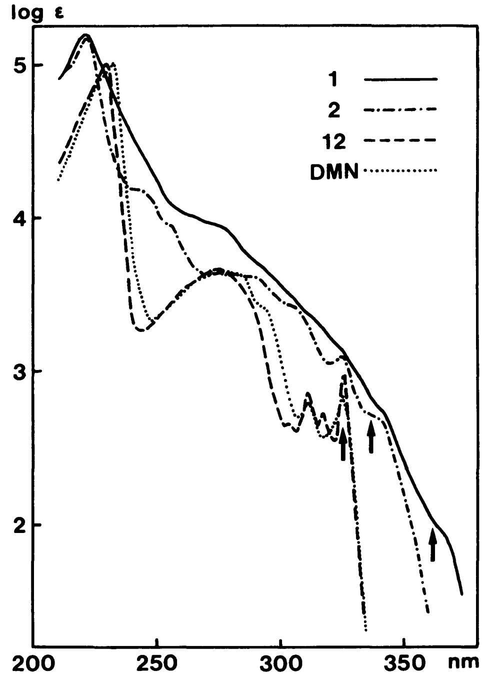

Fig. 5. The electronic spectra of triple-layered naphthalenophane (**1**), double-layered naphthalenophane (**2**), 2,3,6,7-tetramethylnaphthalene (**12**), and 2,6-dimethylnaphthalene (DMN) in tetrahydrofuran. The positions of the longest absorption bands are marked by arrows.

The transannular π-electronic interactions of layered cyclophanes can be best understood by electronic spectroscopy. Figure 5 shows the electronic spectra of naphthalenophanes **1** and **2** in tetrahydrofuran. When 2,6-dimethylnaphthalene (DMN) or 2,3,6,7-tetramethylnaphthalene (**12**) is chosen as a standard, both compounds demonstrate common spectral characteristics of layered cyclophanes, i.e., bathochromism, hyperchromism, and broadening.[3] These effects are more eminent with an increase of the layers. For example, the longest absorption peaks of 2,6-dimethylnaphthalene and 2,3,6,7-tetramethylnaphthalene appear at 326 and 325 nm, respectively. In contrast, **2** has a shoulder at 336 nm as the longest band. Further, **1** has its band at 362 nm, indicating a stronger transannular π-electronic interaction as expected from the above crystal structure.

The strong transannular π-electronic interaction of **1** was also confirmed by its charge-transfer absorption with tetracyanoethylene (TCNE) as an electron acceptor. 2,6-Dimethylnaphthalene with TCNE exhibited two broad CT bands at λ_{max} 478 and 609 nm in dichloromethane. On the other hand, **2** showed the corresponding CT bands at 500(sh) and 644 nm, and **1** at 514 and 683 nm. Evidently, the bathochromic shifts for these naphthalenophanes indicate the enhancement of their donor abilities due to the transannular electronic interactions, which is more eminent in **1** than in **2**.

Experimental

General. Elemental analyses were determined by Mr. H. Iwatani, Microanalytical Laboratory of Department of Applied Chemistry, Hiroshima University. Melting points are uncorrected. NMR measurements were made on a JEOL PMX-60 instrumet (60 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard. Mass spectra were taken on a JEOL JMS-DX 300 spectrometer at 70 eV using a direct insertion technique. Visible and ultraviolet spectra were measured with a Shimadzu UV-160 spectrophotometer.

1,2,4,5-Tetrakis(mercaptomethyl)benzene (6). A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (**4**)[14] 1.35 g (3 mmol) and thiourea 0.99 g (13 mmol) was refluxed in 20 cm^3 of 95% ethanol for 5 h. The resulting tetrakis(thiouronium salt) was collected by filtration and washed with ethanol, 2.21 g. It was then refluxed with potassium hydroxide (4 g) in 15 cm^3 of water for 4 h under nitrogen. The reaction mixture was acidified with 50% sulfuric acid on ice-cooling and extracted with dichloromethane. The extract was washed with brine, dried ($MgSO_4$), and evaporated. Recrystallization of the residue from benzene gave colorless needles 0.65 g (83%), mp 132—133 °C. ^{1}H NMR δ=1.83 (t, J=7 Hz, 4H, SH), 3.80 (d, J=7 Hz, 8H, CH_2), 7.21 (s, 2H, ArH). Calcd for $C_{10}H_{14}S_4$: C, 45.76; H, 5.38%. Found: C, 45.74; H, 5.38%.

Triple-Layered Tetrathia[3.3][3.3]paracyclophane (8). A solution of 1,2,4,5-tetrakis(mercaptomethyl)benzene (**6**) 1.048 g (4 mmol) and 1,4-bis(chloromethyl)benzene (**7**) 1.40 g (8 mmol) in 200 cm^3 of benzene was slowly added into a refluxing solution of ethanol (1 dm^3) containing potassium hydroxide (1.44 g) in a nitrogen atmosphere. The addition took one and a half day. After treated under reflux for additional half a day, the reaction mixture was concentrated in vacuo. The residue was taken up in dichloromethane and chromatographed on silica gel with dichloromethane. Recrystallization of the solid in the first eluate gave colorless plates of **8**, 228 mg (12%), decomp 210 °C. ^{1}H NMR δ=3.57 (d, J=14 Hz, 4H, CH_2), 3.66 (s, 8H, CH_2), 4.16 (d, J=14 Hz, 4H, CH_2), 6.26 (s, 2H, ArH), 6.71 (ABq, J=8 Hz, 8H, ArH). MS *m/z* 466 (M$^+$). Calcd for $C_{26}H_{26}S_4$: C, 66.91; H, 5.61%. Found: C, 67.17; H, 5.29%.

The same product (**8**) was obtained from a similar coupling reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (**4**) 1.80 g (4 mmol) and 1,4-bis(mercaptomethyl)benzene (**5**) 1.36 g (8 mmol) at RT, yield 77 mg (4.2%).

Triple-Layered [2.2][2.2]Paracyclophane (11). A mixture of compound **8** 77 mg, triethyl phosphite 20 cm^3, and benzene 20 cm^3 was placed in a quartz tube and irradiated with a high-pressure mercury lamp (300 W) for 5 h in a nitrogen atmosphere. It was concentrated in vacuo, and the residue was chromatographed on silica gel with benzene to give the desired product **11** in the first eluate, 52 mg (93%). Recrystallization from carbon tetrachloride–acetone (1:3) gave colorless prisms, decomp 230 °C. It was consistent with the authentic sample in all respects.

2,3,6,7-Tetrakis(bromomethyl)naphthalene (13). 2,3,6,7-Tetramethylnaphthalene (**12**)[9] 3.68 g (20 mmol) was refluxed with *N*-bromosuccinimide 15.6 g (88 mmol) and a catalytic amount of benzoyl peroxide in 300 cm^3 of carbon tetrachloride for 30 min under sunlight. The mixture was concentrated to about 50 cm^3. The resulting solid was collected by filtration and thoroughly washed with hot water. The remainder was essentially pure product **13**, which was recrystallized from benzene to give colorless fine crystals, decomp 230 °C, 6.87 g (69%). ^{1}H NMR δ=4.85 (s, 8H, CH_2), 7.83 (s, 4H, ArH). Calcd for $C_{14}H_{12}Br_4$: C, 33.64; H, 2.42%. Found: C, 33.67; H, 2.36%.

2,3,6,7-Tetrakis(mercaptomethyl)naphthalene (15). 2,3,6,7-Tetrakis(bromomethyl)naphthalene (**13**) 6.87 g (13.7 mmol) was refluxed with thiourea 5.03 g (66 mmol) in 100 cm^3 of 95% ethanol. The resulting tetrakis(thiouronium salt) was collected by filtration and washed with ethanol, 7.85 g. It was refluxed with potassium hydroxide (18 g) in 200 cm^3 of water for 6 h under nitrogen. After the insoluble material was removed by filtration, the filtrate was acidified with 50% sulfuric acid on ice-cooling. The resulting solid was collected by filtration and recrystallized from chloroform to give colorless scales, 2.64 g (62%), mp 181—182 °C. ^{1}H NMR δ=1.83 (t, J=7 Hz, 4H, SH), 4.04 (d, J=7 Hz, 8H, CH_2), 7.69 (s, 4H, ArH). Calcd for $C_{14}H_{16}S_4$: C, 53.80; H, 5.16%. Found: C, 53.52; H, 5.02%.

Triple-Layered Tetrathia[3.3][3.3]naphthalenophane (17). A solution of 2,3,6,7-tetrakis(mercaptomethyl)naphthalene (**15**) 312 mg (1 mmol) and 2,6-bis(bromomethyl)naphthalene (**16**)[5] 646 mg (2.06 mmol) in 400 cm^3 of benzene was slowly added into a refluxing solution of ethanol (800 cm^3) containing potassium hydroxide (0.6 g) in a nitrogen atmosphere. The addition took 3 days. The solution was concentrated in vacuo, and the residue was chromatographed on silica gel with dichloromethane to give the desired product **17** in the first eluate, 52 mg (17%), colorless plates from chloroform, decomp 250 °C. ^{1}H NMR δ=3.5—4.5 (m, 16H, CH_2), 6.14, 6.21, 6.35 (each bs, 4H, inner ArH), 6.7—7.0 (m, 17H, outer ArH). MS *m/z* 616 (M$^+$). Calcd for $C_{38}H_{32}S_4$: C, 73.98; H, 5.23%. Found: C, 73.71; H, 5.27%.

A similar coupling reaction using 2,3,6,7-tetrakis(bromomethyl)naphthalene (**13**) 200 mg (0.4 mmol) and 2,6-bis(mercaptomethyl)naphthalene (**14**)[5] 167 mg (0.76 mmol) gave the same product **17**, 21 mg (9%).

Triple-Layered [2.2][2.2]Naphthalenophane (1). Triple-layered tetrathia[3.3][3.3]naphthalenophane (**17**) 72 mg, triethyl phosphite 20 cm^3, and benzene 30 cm^3 were placed in a quartz tube. The suspension was irradiated with a high-pressure mercury lamp for 12 h in a nitrogen atmosphere. It was evaporated, and the residue was purified by column chromatography on silica gel with benzene and then gel-permeation liquid chromatography with chloroform to give the desired product **1**, 18 mg (32%), colorless prisms from benzene, decomp 285 °C. ^{1}H NMR δ=2.3—3.3 (m, 16H,

CH_2), 5.55 (s, 4H, inner ArH), 6.17 (s, 4H, outer ArH), 6.69 (d, J=8 Hz, 4H, outer ArH), 6.91 (d, J=8 Hz, 4H, outer ArH). MS m/z 488 (M^+). Calcd for $C_{38}H_{32}$: C, 93.40; H, 6.60%. Found: C, 93.24; H, 6.71%.

Crystal Structure Analysis. The X-ray diffraction data were collected by using a Rigaku automated four-circle diffractometer with Cu $K\alpha$ radiation monochromatized by a graphite plate. Independent reflections 5750 with 2θ values up to 126° ($|F_o| \geqq 3.0\sigma(F_o)$) were used for analysis. Crystal data are as follows; colorless prism, $C_{38}H_{32}$, M=488.68, triclinic, space group $P\bar{1}$, a=13.515(3), b=18.748(3), c=11.143(2) Å, α=90.38(2), β=101.62(2), γ=110.30(1)°, V=2584.8(9) Å^3, D_m=1.237, D_c=1.256 g cm^{-3} for Z=4, u=4.574 cm^{-1}, crystal size 0.18×0.18×0.23 mm^3. The structure was solved by the Monte Carlo direct method(15) using the MULTAN-78 program system(16) and refined on F^2 by the full-matrix least-squares method with the analytical absorption correction.(17) Atomic scattering factors were taken from International Tables for X-ray Crystallography.(18) Anisotropic temperature factors were used for the refinement of carbon atoms. All H atoms were located from difference Fourier maps and their coordinates were refined with the isotropic temperature factors equivalent to that of the bonded carbon atoms. The R value converged to 0.066. Computations were carried out partly at the Information Processing Center of Hiroshima University and mainly at the Computation Center of Nagoya University using the library program of CRYSTAN system. Tables of structure factors, anisotropic thermal parameters, and coordinates of hydrogen atoms are deposited as Document No. 8850 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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