2434 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *2434—2440 (1982)* [Vol. 55, No. 8

Synthesis of Paracyclo(1,8)napthalenophane and Paracyclo(5,6)acenaphthenophane[1)]

Akira KASAHARA,* Taeko IZUMI, Iwao SHIMIZU, Masahiro SATOU, and Takao KATOU
Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992

(Received December 5, 1981)

[2]Paracyclo[2]paracyclo[2](1,8)naphthalenophan-9-ene-1,17-diyne, [0]paracyclo[2]paracyclo[0](5,6)acenaphthenophan-7-ene, and [2]paracyclo[2]paracyclo[2](5,6)acenaphthenophan-9-ene-1,17-diyne, were synthesized by intramolecular reductive coupling reaction of the corresponding carbonyl compounds with low-valent titanium reagent. The structures of the compounds were elucidated by NMR analyses, and the transannular π-electronic interactions between two benzene rings were examined on the basis of electronic spectra.

Recently, a wide variety of [2.2]phanes containing benzene or heteroaromatic rings has been synthesized in order to study the effect of transannular π-electronic interactions on their physical and chemical properties.[2)] However, there are only a few investigations of paracyclonaphthalenophane having a bridged system in a peri-position of the naphthalene ring: the only compounds of this class which have been described are [0]paracyclo[2]paracyclo[0](1,8)naphthalenophane[3)] (**1**) and [0]paracyclo[2]paracyclo[0](1,8)naphthalenophan-7-ene[3)] (**2**). The distance between atoms 1 and 8 in naphthalene is 2.44 Å, while the van der Waals separation in the parallel π-system is 3.4 Å.[4)] Thus, in compounds **1** and **2**, substantial repulsive interactions must exist between the two peri-aryl rings, which are bound closely by ethano bridges at both ends. These results have prompted us to study the synthesis of [2]paracyclo[2]paracyclo[2](1,8)naphthalenophan-9-ene-1,17-diyne (**3**), [0]paracyclo[2]paracyclo[0](5,6)-acenaphthenophane (**4**), [0]paracyclo[2]paracyclo[0]-(5,6)acenaphthenophan-7-ene (**5**), and [2]paracyclo-[2]paracyclo[2](5,6)acenaphthenophan-9-ene-1,17-diyne (**6**).

Experimental

Materials and Measurement. All the melting points are uncorrected. 1,8-Diiodonaphthalene (**7**),[5)] 5,6-dibromoacenaphthene (**8**),[6)] 5,6-diiodoacenaphthene (**9**),[7)] 5-iodoacenaphthene (**10**),[7)] (p-bromophenylethynyl)trimethylsilane (**11**),[8)] and p-bromobenzaldehyde ethylene acetal (**12**)[9)] were prepared as described in the literature. The IR, NMR, mass, and electronic spectra were recorded with a Hitachi 260-10, a Hitachi R-22, a Hitachi RMU-6M, and a Hitachi 200-10 spectrometer, respectively.

p-*Ethynylbenzaldehyde Diethyl Acetal (15).* The Grignard reagent prepared from **11** (10.2 g, 0.04 mol) and 1.0 g (0.042 mol) of magnesium turning in 80 ml of dry THF was cooled to 20 °C; a solution of 2.8 g (0.038 mol) of anhydrous N,N-dimethylformamide in 20 ml of dry THF was then added dropwise over a 0.5 h period. After the addition was complete, the reaction was stirred for 4 h and then was allowed to remain overnight under a nitrogen atmosphere. The mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride, the organic layers were separated, and the aqueous layers were extracted twice with a 50 ml portion of ether. The organic layers and ether extracts were combined and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was chromatographed in benzene on silica gel. Colorless crystals of (p-formylphenylethynyl)-trimethylsilane (**13**), mp 56—58 °C, were obtained in 80% yield (6.5 g). IR (KBr): 2150 (–C≡C–), 1700 $\mathrm{cm^{-1}}$ (–CHO). NMR ($CDCl_3$): δ=0.18 (s, 9H, $-C\underline{H}_3$), 7.47 (d, 2H, Ar–$\underline{H}$), 7.68 (d, 2H, Ar–$\underline{H}$), 9.87 ppm (s, 1H, $-C\underline{H}O$). Found: C, 71.08; H, 6.86%. Calcd for $C_{12}H_{14}OSi$: C, 71.23; H, 6.97%.

A solution of **13** (5.6 g, 0.028 mol), triethyl orthoformate (5.5 g, 0.037 mol), and p-toluenesulfonic acid (0.16 g) in ethanol (20 ml) was refluxed for 5 h under stirring. After pouring into an aqueous solution of ammonia (50 ml), the mixture was extracted with ether. The extracts were then washed successively with aqueous ammonia and a saturated sodium chloride solution, dried over potassium carbonate, and evaporated to give a dark red liquid: [p-(diethoxymethyl)phenylethynyl]trimethylsilane (**14**). The liquid shows no IR absorption due to a formyl group, but it does show that due to an acetal. IR (neat): 1100, 1070, 1050 $\mathrm{cm^{-1}}$.

The crude product (**14**) in methanol (200 ml) was stirred with a solution of potassium hydroxide (3.6 g) in water (36 ml). The mixture was then heated under reflux for an additional 3 h, poured into water (1000 ml), and extracted with ether. The extracts were washed with a saturated sodium chloride solution and dried over potassium carbonate. The dark red liquid which remained after the evaporation of the solvents was distilled under reduced pressure to give **15**, a colorless liquid, bp 98—103 °C/2 mmHg,† 4.1 g (72% yield based on **13**). IR (neat): 3350 (–C≡C–H), 2150 (–C≡C–), 1100, 1040 $\mathrm{cm^{-1}}$ (–C–O–C–). NMR ($CDCl_3$): δ=1.16 (t, 6H, $-C\underline{H}_3$), 3.02 (s, 1H, $-C\equiv C-\underline{H}$), 3.54 (q, 4H, $-C\underline{H}_2-$), 5.47 (s, 1H, $-C-\underline{H}$), 7.06 (d, 2H, Ar–$\underline{H}$), and 7.68 ppm (d, 2H, Ar–$\underline{H}$). Found: C, 76.35; H, 7.81%; M^+, 204. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89%; M, 204.

*1,8-Bis(*p*-formylphenylethynyl)naphthalene (17).* A mixture of **7** (9.6 g, 25 mmol), **15** (10.2 g, 50 mmol), copper(I) iodide (0.048 g, 0.25 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.70 g, 1 mmol), and diethylamine (180 ml) was heated under nitrogen in an autoclave at 80 °C for 10 h. After the removal of diethylamine under reduced pressure, ether and water were added to the residue. The ether phase was separated, washed thoroughly with 10% hydrochloric acid, a saturated sodium hydrogencarbonate solution, and a saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography (silica gel–benzene). First elution with benzene gave 1-(p-formylphenylethynyl)-8-iodonaphthalene (**16**), colorless needles, mp 113—115 °C in 42% yield (4.05 g): IR (KBr): 2200 (–C≡C–), 1700 $\mathrm{cm^{-1}}$ (–CHO). NMR ($CDCl_3$): δ=7.36—7.93 (m, 10H, Ar–$\underline{H}$), 9.95 ppm (s, 1H, $-C\underline{H}O$). Found: C, 59.55; H, 2.78%; M^+ 382. Calcd for $C_{19}H_{11}IO$: C, 59.70; H, 2.90%; M, 382.

A second elution with benzene afforded 3.39 g (35% yield) of **17**, colorless needles, mp 168—169 °C. IR (KBr): 2200

---

† 1 mmHg ≈ 133.322 Pa.

(–C≡C–), 1700 cm^{-1} (–CHO). NMR ($CDCl_3$): δ=7.42—7.95 (m, 14H, Ar–$\underline{H}$), 9.98 ppm (s, 2H, –C$\underline{H}$O). Found: C 87.40; H, 4.68%; M$^+$, 384. Calcd for $C_{28}H_{20}O_2$: C, 87.48; H, 4.79%; M, 384.

5,6-Bis(p-formylphenyl)acenaphthene (19). Under a nitrogen atmosphere, the Grignard reagent prepared from **12** (9.1 g, 40 mmol) and magnesium turnings (1.2 g, 49 mmol) in dry THF (60 ml) was dropwise added to a mixture of **8** (2.5 g, 8 mmol) and dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (0.9 g, 1.6 mmol) in dry THF (60 ml) at 0 °C with stirring over 2.5 h. The reaction mixture was stirred for 4 h at 0 °C and then was allowed to remain overnight at room temperature. The mixture was hydrolyzed with 10% hydrochloric acid under cooling with an ice bath. The organic layers and ether extracts from the aqueous layer were combined, washed with 10% hydrochloric acid, water, a saturated sodium hydrogencarbonate solution, and water again, and then dried over anhydrous $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography (silica gel–benzene). The first elution with benzene gave 5-(*p*-formylphenyl)-6-bromoacenaphthene (**18**), colorless needles, mp 115—116 °C, in 37% yield (1.00 g). IR (KBr): 1690 (–CHO), 1600, 810 cm^{-1}. NMR ($CDCl_3$): δ=3.36 (s, 4H, –C$\underline{H}_2$–), 7.09 (d, *J*=7 Hz, 2H, Ar–$\underline{H}$), 7.47 (d, *J*=8 Hz, 2H, Ar–$\underline{H}$), 7.62 (d, *J*=7 Hz, 2H, Ar–$\underline{H}$), 7.83 (d, *J*=8 Hz, 2H, Ar–$\underline{H}$), 10.02 ppm (s, 1H, –C$\underline{H}$O). Found: C, 67.58; H, 3.80%; M$^+$, 337. Calcd for $C_{19}H_{13}BrO$: C, 67.67; H, 3.88%; M, 337.

The second elution with benzene afforded 0.37 g (13% yield) of **19**, colorless needles, mp 244—245 °C. IR (KBr): 1695 (–CHO), 1600, 810 cm^{-1}. NMR ($CDCl_3$): δ =3.49(s, 4H, –C$\underline{H}_2$–), 7.07 (d, *J*=7 Hz, 4H, Ar–$\underline{H}$), 7.33 (d, *J*=8 Hz, 2H, Ar–$\underline{H}$), 7.39 (d, *J*=7 Hz, 4H, Ar–$\underline{H}$), 7.45 (d, *J*=8 Hz, 2H, Ar–$\underline{H}$), 9.97 ppm (s, 2H, –C$\underline{H}$O). Found: C, 86.02; H, 4.88%; M$^+$, 362. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%; M, 362.

5,6-Bis(p-formylphenylethynyl)acenaphthene (21). In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substitution of **9** with **15** was carried out in the same way as described for **17**, and 5-(*p*-formylphenylethynyl)-6-iodoacenaphthene (**20**) (colorless needles, mp 154—155 °C) and **21** (pale yellow needles, mp 175—176 °C) were obtained in 24 and 50% yields, respectively.

20: IR (KBr): 2190 (–C≡C–), 1690 cm^{-1} (–CHO). NMR ($CDCl_3$): δ=3.33 (s, 4H, –C$\underline{H}_2$–), 7.05—7.77 (m, 8H, Ar–$\underline{H}$), 9.96 ppm (s, 1H, –C$\underline{H}$O). Found: C, 61.63; H, 3.13%; M$^+$, 408. Calcd for $C_{21}H_{13}IO$: C, 61.78; H, 3.21%; M, 408.

21: IR (KBr): 2200 (–C≡C–), 1690 cm^{-1} (–CHO). NMR ($CDCl_3$): δ=3.41 (s, 4H, –C$\underline{H}_2$–), 7.29 (d, *J*=7 Hz, 2H, Ar–$\underline{H}$), 7.41 (d, *J*=8 Hz, 4H, Ar–$\underline{H}$), 7.55 (d, *J*=7 Hz, 2H, Ar–$\underline{H}$), 7.78 (d, *J*=8 Hz, 4H, Ar–$\underline{H}$), 9.90 ppm (s, 2H, –C$\underline{H}$O). Found: C, 87.70; H, 4.33%; M$^+$, 410. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42%; M, 410.

The Intramolecular Reductive Coupling of 17 with $TiCl_4$–$LiAlH_4$. To a solution of $TiCl_4$ (9.5 g, 0.05 mol) in dry THF (200 ml) was added $LiAlH_4$ (0.90 g, 0.024 mol) with cooling under a nitrogen atmosphere. The mixture was refluxed for 2 h; to the metal complex solution thus obtained, was added dropwise a solution of **17** (3.84 g, 0.01 mol) and tributylamine (1.86 g, 0.01 mol) in dry THF (250 ml) over 8 h under refluxing, followed by an additional 10 h period of reflux. The reaction mixture was then cooled to room temperature and quenched with 20% aqueous K_2CO_3 solution. After filtration, the filtrate was extracted with chloroform. The chloroform extracts were washed with water and dried over anhydrous $MgSO_4$. After removal of the solvents, the residue was dissolved in hexane and chromatographed on silica gel.

The first fraction, eluted with hexane, gave colorless needles, mp 115—117 °C, in 35% yield, which were identified as 1,8-bis(*p*-tolylethynyl)naphthalene (**22**) by a comparison of the IR, NMR, and mass spectra and by a mixed-melting-point determination with an authentic sample (lit,[10] mp 116—117 °C).

The second fraction, eluted with hexane, gave 1,8-bis[[(*p*-hydroxymethyl)phenyl]ethynyl]naphthalene (**23**) (from CH_3OH), colorless needles, mp 166—167 °C, in 11% yield. IR (KBr): 3300 (–OH), 2150 (–C≡C–), 1600, 1500, 860 cm^{-1} *p*-disubstituted benzene ring). NMR ($CDCl_3$): δ=2.32 (br-s, 2H, –O$\underline{H}$), 4.58 (s, 4H, –C$\underline{H}_2$–), 7.14—7.54 ppm (m, 10H, Ar–$\underline{H}$). Found: C, 86.46; H, 5.07%; M$^+$, 388. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19%; M, 388.

The third fraction, eluted with hexane, gave **3** (from benzene–hexane), pale yellow needles, mp 239—241 °C (decomp), in 7.5% yield. IR (KBr): 1660, 1600, 1500, 830, 770, 750, 720, 690 cm^{-1}. Found: C, 95.28; H, 4.51%; M$^+$, 352. Calcd for $C_{28}H_{16}$: C, 95.42; H, 4.58%; M, 352.

The Intramolecular Reductive Coupling of 19 with $TiCl_4$–Zn. To a solution of $TiCl_4$ (2.6 g, 14 mmol) in dry THF (70 ml) was added Zn dust (1.8 g, 28 mmol) with cooling. The mixture was refluxed 1.5 h under a nitrogen atmosphere to give a deep black solution. To the metal complex solution thus obtained was added a solution of **19** (1.0 g, 2.8 mmol) and dry pyridine (0.20 g) in dry THF (150 ml) over 9.5 h under refluxing, followed by an additional 10 h period of refluxing. The reaction mixture was then cooled to room temperature and quenched with 20% K_2CO_3 solution. After filtration, the filtrate was extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with water and dried over $MgSO_4$. After removal of the solvents, the residue was dissolved in hexane and chromatographed on silica gel.

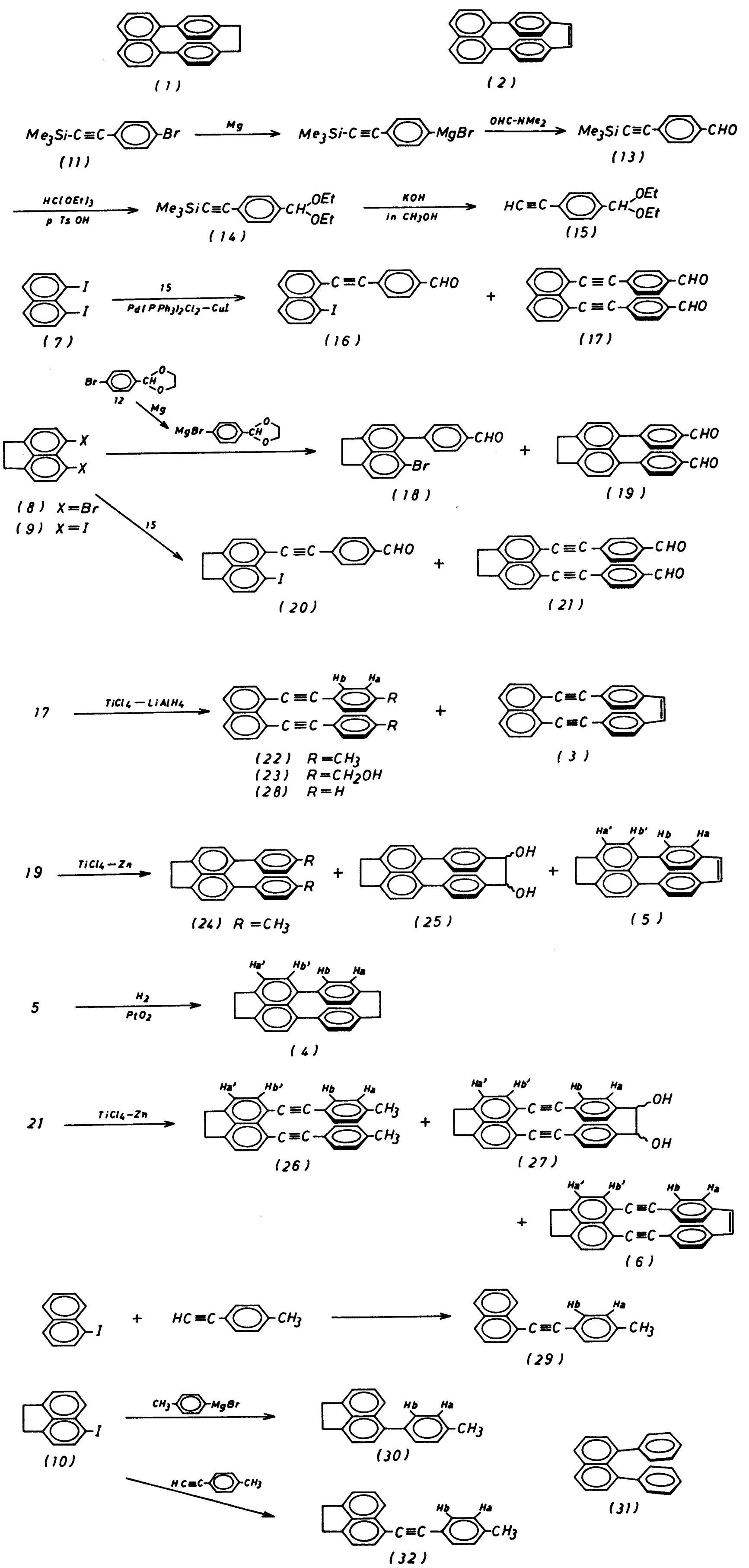
The first fraction, eluted with hexane, gave 5,6-di-*p*-tolylacenaphthene (**24**), colorless needles, mp 142—144 °C, in 12.5% yield. IR (KBr): 1600, 1510, 820, 800 cm^{-1}. Found: C, 93.32; H, 6.57%; M$^+$, 334. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63%; M, 334. The compound **24** is identical in all respects with 5,6-di-*p*-tolylacenaphthene, which was prepared by the nickel-phosphine catalyzed Grignard cross coupling reaction of **8** with *p*-tolylmagnesium bromide.

The second fraction, eluted with hexane, gave **5**, pale yellow needles, mp 186—188 °C, in 24% yield. IR (KBr): 1600, 1490, 825, 805, 720, 690 cm^{-1}. Found: C, 94.44; H, 5.40%; M$^+$, 330. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49%; M, 330.

The third fraction, eluted with benzene, gave [0]paracyclo[2]paracyclo[0](5,6)acenaphthenophane-7,8-diol (**25**), colorless needles, mp 210—211 °C (decomp), in 2.5% yield. IR (KBr): 3420 (–OH), 1610, 1600, 1500, 835, 810, 715, 690 cm^{-1}. Found: C, 85.60; H, 5.45%; M$^+$, 364. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%; M, 364.

The Catalytic Hydrogenation of 5 to 4. In the mixture of THF (10 ml) and ethanol (70 ml), **5** (0.4 g) was hydrogenated with PtO_2 (0.1 g) at room temperature under ordinary pressure. The reaction mixture was filtered to remove the catalyst and the filtrate was evaporated. The residue was chromatographed on silica gel with hexane to give 0.35 g (87.5% yield) of **4**, colorless needles, mp 263—265 °C. IR (KBr): 1600, 1500, 820, 800, 725, 695 cm^{-1}. Found: C, 93.87; H, 6.58%; M$^+$, 332. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%; M, 332.

The Intramolecular Reductive Coupling of 21 with $TiCl_4$–Zn. The reductive coupling of **21** was carried out in the same way as described for the reaction of **19** with $TiCl_4$–Zn, and the products were separated by chromatography on silica gel. The first fraction, eluted with hexane, gave 5,6-bis(*p*-tolylethynyl)acenaphthene (**26**), pale yellow needles, mp 179—180 °C, in 8.5% yield. IR (KBr): 1590, 1490, 830, 800 cm^{-1}.


(1)
(2)
Me3Si-C≡C-⟨⟩-Br
(11)
Mg
Me3Si-C≡C-⟨⟩-MgBr
OHC-NMe2
Me3Si C≡C-⟨⟩-CHO
(13)
HC(OEt)3
p Ts OH
Me3SiC≡C-⟨⟩-CH(OEt)2
(14)
KOH
in CH3OH
HC≡C-⟨⟩-CH(OEt)2
(15)
(7)
15
Pd(PPh3)2Cl2-CuI
-C≡C-⟨⟩-CHO
-I
(16)
(17)
12
Mg
MgBr
X
(8) X=Br
(9) X=I
-CHO
-Br
(18)
(19)
(20)
(21)
17
TiCl4-LiAlH4
Hb Ha
R
(22) R=CH3
(23) R=CH2OH
(28) R=H
(3)
19
TiCl4-Zn
(24) R=CH3
OH
(25)
Ha' Hb' Hb Ha
(5)
5
H2
PtO2
(4)
21
TiCl4-Zn
CH3
(26)
(27)
(6)
HC≡C-⟨⟩-CH3
I
(29)
(10)
CH3-⟨⟩-MgBr
(30)
HC≡C-⟨⟩-CH3
(31)
(32)

Scheme 1.

Found: C, 94.07; H, 5.71%; M+, 382. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%; M, 382. The compound **26** is identical in all respects with 5,6-bis(*p*-tolylethynyl)acenaphthene, which was prepared by the palladium-catalyzed substitution of **9** with *p*-tolylacetylene.

The second fraction, eluted with hexane, gave **6**, yellow needles, mp 219—220 °C, in 32% yield. IR (KBr): 1630, 1600, 1500, 900, 840, 810, 765, 720, 690 cm^{-1}. Found: C, 95.08; H, 4.68%; M+, 378. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%; M, 378.

The third fraction, eluted with benzene-$CHCl_3$ (4 : 1), gave [2]paracyclo[2]paracyclo[2](5,6)acenaphthenophane-9,10-diol (**27**), yellow needles, mp 219—221 °C, in 15% yield. IR (KBr): 3350 (-OH), 1590, 1490, 1020, 820, 715, 690 cm^{-1}. Found: C, 87.24; H, 4.80%; M+, 412. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89%; M, 412.

*1-*p*-Tolylethynylnaphthalene (29).* In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substitution of 1-iodonaphthalene with *p*-tolylacetylene was carried out in the same way as described for **17**, and the compound **29**, colorless needles, mp 61—63 °C (from CH_3OH), was obtained in 78% yield. IR (KBr): 1600, 1500, 810, 790, 765 cm^{-1}. Found: C, 94.04; H, 5.77%; M+, 242. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82%; M, 242.

*5-*p*-Tolylacenaphthene (30).* In the presence of dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II), the cross coupling reaction of **10** with *p*-tolylmagnesium bromide in dry THF was carried out in the same way as described for **19**, and the compound **30**, colorless needles, mp 55—57 °C (from CH_3OH) was obtained in 63% yield. IR (KBr): 1600, 1500, 840, 790, 760, 720 cm^{-1}. Found: C, 93.28; H, 6.51%; M+, 244. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60%; M, 244.

*5,6-Di-*p*-tolylacenaphthene (24).* In the presence of nickel phosphine complex, the cross coupling reaction of **8** with *p*-tolylmagnesium bromide in dry THF was carried out in the same way as described for **19**, and the compound **24**, mp 142—144 °C, was obtained in 65% yield.

*5-*p*-Tolylethynylacenaphthene (32).* In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substitution of **10** with *p*-tolylacetylene was carried out in the same way as described for **17**, and the compound **32**, colorless needles, mp 116—118 °C (from ethanol) was obtained in 67% yield. IR (KBr): 1600, 1500, 830, 800 cm^{-1}. Found: C, 93.92; H, 5.89%; M+, 268. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%; M, 268.

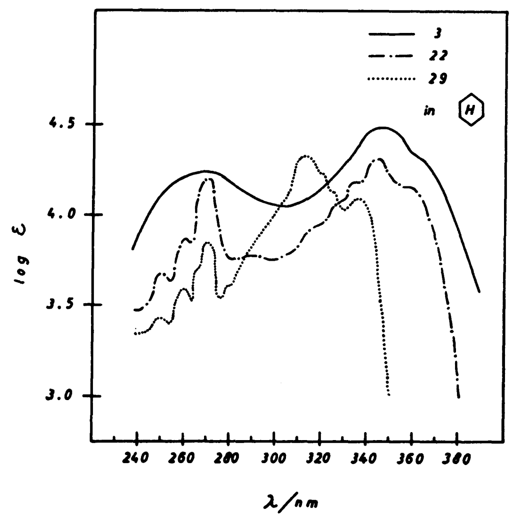


Fig. 1. Electronic spectra of **3**, **22**, and **29**.

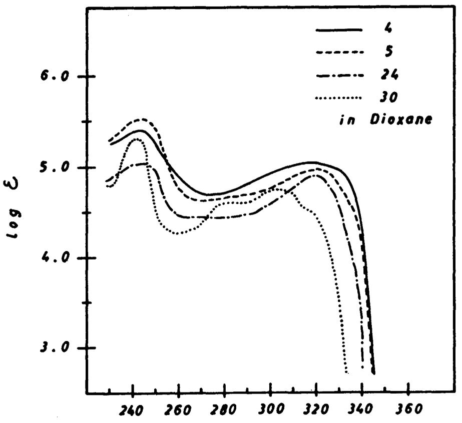


Fig. 2. Electronic spectra of **4**, **5**, **24**, and **30**.

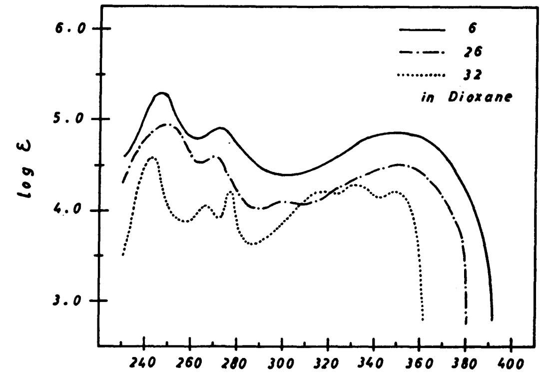


Fig. 3. Electronic spectra of **6**, **26**, and **32**.

Table 1. IR spectra of cyclophanes around 700 cm^{-1}

Compound	Wave number/cm^{-1}
3	720, 690
4	725, 700
5	700, 690
6	720, 690
25	715, 690
27	715, 690

*5,6-Bis(*p*-tolyethynyl)acenaphthene (26).* In the presence of $(Ph_3P)_2PdCl_2$ and CuI, the palladium-catalyzed substitution of **9** with *p*-tolylacetylene was carried out in the same way as described for **17**, and the compound **26**, mp 179—180 °C, was obtained in 58% yield.

Results and Discussion

A number of synthetic methods have been recently developed for [2.2]cyclophane.[11] The naphthalenophane **1** has been prepared by pyrolytic method of sulfone derivative **31**.[3] But a reductive coupling of carbonyl compounds with low valent titanium reagents[12] is still very convenient and advantageous for the synthesis of cyclophane because of the facile availability of the intermediary compounds.[13]

In the present work, we applied the same method for

TABLE 2. NMR SPECTRA OF THE CYCLOPHANE AND REFERENCE COMPOUNDS (δ, IN $CDCl_3$)

Compound	Aromatic protons	Naphthalene or acenaphthene ring	Other protons
3	$\left.\begin{matrix}\underline{H}_a\\ \underline{H}_b\end{matrix}\right\}$6.39(s, 8H)	7.40—7.76(m, 6H, Ar-$\underline{H}$)	7.18(s, 2H, -C$\underline{H}$=C$\underline{H}$-)
22	$\underline{H}_a$ 6.91(d, J=8 Hz, 4H) $\underline{H}_b$ 7.23(d, J=8 Hz, 4H)	7.12—7.81(m, 6H, Ar-$\underline{H}$)	2.28(s, 6H, -C$\underline{H}_3$)
29	$\underline{H}_a$ 7.17(d, J=8 Hz, 2H) $\underline{H}_b$ 7.53(d, J=8 Hz, 2H)	7.31—7.88(m, 7H, Ar-$\underline{H}$)	2.35(s, 3H, -C$\underline{H}_3$)
4	H_a 6.41(d, J=8 Hz, 4H) H_b 6.54(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.31(d, J=7 Hz, 2H) $\underline{H}_{b'}$, 7.49(d, J=7 Hz, 2H) $\underline{H}_{\text{-CH}_2}$-3.44(s, 4H)	3.07(s, 4H, bridged-C$\underline{H}_2$-)
5	$\underline{H}_a$ 6.56(d, J=8 Hz, 4H) $\underline{H}_b$ 6.62(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.34(d, J=7 Hz, 2H) $\underline{H}_{b'}$, 7.51(d, J=7 Hz, 2H) $\underline{H}_{\text{-CH}_2}$-3.43(s, 4H)	7.24(s, 2H, -C$\underline{H}$=C$\underline{H}$-)
24	$\underline{H}_a$ 6.65(d, J=8 Hz, 4H) $\underline{H}_b$ 6.74(d, J=8 Hz, 4H)	$\left.\begin{matrix}\underline{H}_{a'}\\ \underline{H}_{b'}\end{matrix}\right\}$7.30(br-s, 4H) $\underline{H}_{\text{-CH}_2}$-3.43(s, 4H)	2.16(s, 6H, -C$\underline{H}_3$)
25[a)]	$\underline{H}_a$ 6.77(d, J=8 Hz, 4H) $\underline{H}_b$ 6.95(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.35(d, J=7 Hz, 4H) $\underline{H}_{b'}$, 7.41(d, J=7 Hz, 4H) $\underline{H}_{\text{-CH}_2}$-3.46(s, 4H)	2.75(br-s, 2H, -O$\underline{H}$) 4.78(br-s, 2H, -C$\underline{H}$-)
30	$\underline{H}_a$ 7.26(d, J=7 Hz, 2H) $\underline{H}_b$ 7.68(d, J=7 Hz, 2H)	7.27—7.50(m, 5H, Ar-$\underline{H}$) $\underline{H}_{\text{-CH}_2}$-3.45(s, 4H)	2.38(s, 3H, -C$\underline{H}_3$)
6	$\underline{H}_a$ 6.58(d, J=8 Hz, 4H) $\underline{H}_b$ 7.07(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.21(d, J=7 Hz, 2H) $\underline{H}_{b'}$, 7.67(d, J=7 Hz, 2H) $\underline{H}_{\text{-CH}_2}$-3.38(s, 4H)	7.31(s, 2H, -C$\underline{H}$=C$\underline{H}$-)
26	$\underline{H}_a$ 6.88(d, J=8 Hz, 4H) $\underline{H}_b$ 7.20(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.22(d, J=7 Hz, 2H) $\underline{H}_{b'}$, 7.71(d, J=7 Hz, 2H) $\underline{H}_{\text{-CH}_2}$-3.37(s, 4H)	2.24(s, 6H, -C$\underline{H}_3$)
27[a)]	$\underline{H}_a$ 6.45(d, J=8 Hz, 4H) $\underline{H}_b$ 6.90(d, J=8 Hz, 4H)	$\underline{H}_{a'}$, 7.35(d, J=7 Hz, 4H) $\underline{H}_{b'}$, 7.70(d, J=7 Hz, 4H) $\underline{H}_{\text{-CH}_2}$-3.42(s, 4H)	2.78(br-s, 2H, -O$\underline{H}$) 4.86(br-s, 2H, -C$\underline{H}$-)
32	$\underline{H}_a$ 7.17(d, J=8 Hz, 2H) $\underline{H}_b$ 7.52(d, J=8 Hz, 2H)	7.08—8.04(m, 5H, Ar-$\underline{H}$) $\underline{H}_{\text{-CH}_2}$-3.38(s, 4H)	2.34(s, 3H, -C$\underline{H}_3$)

a) The spectra of **25** and **27** were observed in acetone-d_6.

the synthesis of cyclophanes **3**, **5**, and **6**. The synthesis of intermediates, dialdehydes **17** and **21**, were carried out by the palladium-catalyzed substitution[14)] of diiodo compounds **7** and **9** with acetylene derivative **15**; in the presence of phosphino nickel complex, dialdehyde **19** was obtained by the cross coupling reaction[15)] of **8** with a Grignard reagent prepared from **12**.

The intramolecular reductive coupling of **17** with a low valent titanium reagent ($TiCl_4$–$LiAlH_4$[12d)]) afforded a mixture of the reduction products (**22** and **23**) of carbonyl group and cyclophane **3**. On the other hand, the intramolecular reductive coupling of **19** or **21** with a low valent titanium reagent ($TiCl_4$–Zn[12a)]) gave a mixture of the reduction products (**24** or **26**), cyclophanes (**5** or **6**), and dihydroxycyclophane derivatives (**25** or **27**), respectively. It has already been reported that aldehydes and ketones were reduced by low valent titanium compounds, produced from $TiCl_4$ and Zn, to give the corresponding pinacols and olefins in high yields.[12a)] The cyclophane **4** was also obtained by the catalytic hydrogenation of **5**.

The structures of the compounds were assigned on the basis of the IR, NMR, and mass spectra and the elementary analyses.

The IR spectra of [2.2]paracyclophane system show these two obvious features. One is the increase of the intensity of the band in 1600—1580 cm^{-1}, which is related to the increased double bond character due to the distortion of the benzene rings.[16)] The other is the appearance of a strong new maximum near 710 cm^{-1} region. Longone and Warren[17)] reported that the strong maximum at 725 cm^{-1} in [2.2]paracyclophane and at 710 cm^{-1} in 4,7,12,15-tetramethyl[2.2]paracyclophane might be a characteristic band associated with the distorted benzene rings in the [2.2]paracyclophane system. Otsubo *et al.*[18)] reported the same phenomena in the multilayered [2.2]paracyclophane system. In practice, besides the strong peak around 1600 cm^{-1}, the cyclophanes (**3**—**6**, **25**, and **27**) also exhibit two strong peaks near 720 and 690 cm^{-1} (Table 1). This result indicates that the compounds all bear strained benzene rings.

The NMR spectral data of all the cyclophanes and the reference compounds are summarized in Table 2. The most remarkable feature is that the chemical shifts of all the benzene ring protons appear at high field, as in the case of [2.2]paracyclophane.[19)] For example, in the NMR spectrum of **3**, the signal of benzene protons (δ, 6.38 ppm) is shifted upfield by 0.53 and 0.84 ppm compared with that of the reference compound **22**

(δ, 6.93 and 7.23 ppm). Since the benzene ring protons of **3** are probably deshielded by the bridging vinylene group, this phenomenon indicates that the two benzene rings in **3** are held face to face in more close proximity by the vinylene bridge than in **22**. Staab and Ipaktschi[10] have previously reported from the X-ray analysis of 1,8-bis(phenylethynyl)naphthalene (**28**) that the nonbonding interaction between the two phenylethynyl groups of **28** results in a splaying out of the two phenylethynyl groups and, as a result, that the distance between the centers of two triple bonds is near the sum of van der Waals radii of π-systems. Similar to the case of **28**, the tolyl groups in **22** are relatively more distant from one another, compared with those of **3** in which the tolyl groups are bound together by vinylene bridges at both ends. Moreover, as in the electronic spectra of other cyclophanes, the electronic spectrum of **3** shows a general broadening of all bands in the spectrum and hyperchromic and bathochromic shifts of the long wavelength bands, compared with that of **22** (see Fig. 1). This result may be due to a more strong transannular π-electronic interaction in **3** than in **22**. On the other hand, the NMR signals of benzene ring protons in **22** are shifted somewhat upfield, compared with those of monosubstituted analog, 1-(*p*-tolylethynyl)naphthalene (**29**). In addition, in the electronic spectrum of **22**, the longest wavelength bands appear at a wavelength longer by 32 nm than those of **29**. This bathochromic shift and an increase of intensity in the spectrum of **22** may be caused by the transannular π-electronic interaction between the two chromophores in **22**.

The structures of **4** and **5** can be also assigned to cyclophane structure by a comparison of their NMR data with those of the reference compounds: **24** and 5-*p*-tolylacenaphthene (**30**). Similar to the case of **3**, the upfield shifts of benzene ring protons in **4** (Δ, 0.24 and 0.20 ppm) and in **5** (Δ, 0.09 and 0.12 ppm), compared with those in **24**, are explained by cyclophane structure, in which the benzene ring protons in **4** and **5** lie in more close proximity to the π-cloud of the opposed moiety than in **24**. House *et al.*[5] have previously reported that the molecule of 1,8-diphenylnaphthalene (**31**) should be deformed to alleviate the nonbonding interaction between the two phenyl rings and that the approximately parallel planes of the two phenyls are at an angle of approximately 70° to the plane of the naphthalene ring. Similar to the case of **31**, in **24** the nonbonding interaction between the two aryl rings results in a splaying out of the two aryl rings and as a result, the aryl rings in **24** are relatively more distant from one another, compared with those of **4**. Furthermore, the NMR spectrum of saturated cyclophane **4** showed H_a at 6.41 ppm and H_b at 6.54 ppm, indicating a marginal upfield shift (0.06 and 0.15 ppm) with respect to the unsaturated cyclophane **5**; this is characteristic of such pairs of cyclophanes (with saturated and unsaturated bridges).[20] On the other hand, similar to the case of **22**, the NMR signals of aryl ring protons in **24** are shifted upfield, compared with those of **30**. Additionally, in the electronic spectrum of **24**, compared with that of **30**, all the absorption curves exhibit broadening, and bathochromic and hyperchromic shifts, caused by the transannular π-electronic interaction between the two aryl moieties in **24** (see Fig. 2).

The NMR and electronic spectra of **6** are also consistent with a cyclophane structure. The chemical shifts for H_a and H_b protons of benzene rings of **6** are found respectively at 0.30 and 0.13 ppm upfield relative to those (H_a and H_b) of the reference compound **26**. These upfield shifts are due to the fact that, as in the case of **3**, the two benzene rings in **6** are held face to face in more close proximity by the vinylene bridge at both ends than in **26**. Furthermore, the electronic spectrum of **6** shows a general broadening of all bands in spectrum and hyperchromic and bathochromic shifts of the long wavelength bands, compared with that of **26** (see Fig. 3). It is probably due to more strong transannular π-electronic interaction between the two aryl moieties in **6** than in **26**. On the other hand, in the NMR spectrum of **26**, the upfield shifts of H_a (Δ, 0.29 ppm) and H_b (Δ, 0.32 ppm) are also observed, compared with the corresponding ones in the reference compound: 5-*p*-tolylacenaphthene (**32**). Moreover, in the electronic spectrum of **26**, the electronic absorption curve becomes even more structureless with bathochromic shift and increased intensity of the band, compared with those of **32**. It indicates that the two aryl moieties in **26** interact strongly with each other, similar to the case of **22**.

This research was supported by Grant-in-Aid for Scientific Research No 554137 from the Ministry of Education, Science and Culture.

References

1) A preliminary report dealing with a part of this work has appeared: A. Kasahara, T. Izumi, and T. Katou, *Chem. Lett.*, **1979**, 1373.

2) S. Misumi and T. Otsubo, *Acc. Chem. Res.*, **11**, 251 (1978).

3) W. Bieber and F. Vögtle, *Angew. Chem.*, **89**, 199 (1977).

4) L.Pauling, "The nature of the Chemical Bond," 3rd ed, Cornell University Press., Ithaca, N. Y. (1960), p. 262.

5) H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972).

6) R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962).

7) R. L. Clough, P. Mison, and J. P. Roberts, *J. Org. Chem.*, **41**, 2252 (1976).

8) C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc., C*, **1967**, 1364.

9) J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, **31**, 2585 (1966).

10) H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **104**, 1170 (1971).

11) F. Vögtle and P. Neumann, *Synthesis*, **1973**, 85; S. Misumi, *Kagaku No Ryoiki*, **28**, 927 (1974); **32**, 651 (1978); Y. Sakata, *Yuki Gosei Kyokai Shi*, **38**, 164 (1980).

12) a) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, **1973**, 1041; b) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974): c) J. E. McMurry and L. R. Krepski, *J. Org. Chem.*, **41**, 3929 (1976); d) A. Ishida and T. Mukaiyama, *Chem. Lett.*, **1976**, 1127; e) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, **43**, 3255 (1978).

13) a) A. Kasahara and T. Izumi, *Chem. Lett.*, **1978**, 21;

b) A. Kasahara, T. Izumi, and I. Shimizu, *ibid.*, **1979**, 1119; c) A. Kasahara, T. Izumi, and H. Umezawa, *ibid.*, **1980**, 1039; d) D. Tanner and O. Wennerstrom, *Tetrahedron Lett.*, **1981**, 2313.

14) a) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **1975**, 4467; b) S. Takahashi, Y. Kuroyama, K. Sonogashira, and N. Hagihara, *Synthesis*, **1980**, 627.

15) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **49**, 1958 (1976).

16) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

17) D. T. Longone and C. L. Warren, *J. Am. Chem. Soc.*, **84**, 1507 (1962).

18) T. Otsubo, S. Mizogami, I. Otsubo, Z. Tozuka, A. Sakagami, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3519 (1973).

19) a) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963); b) T. Otsubo, S. Mizogami, Y Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3831 (1973).

20) a) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974); b) J. R. Davy and J. A. Reiss, *Aust. J. Chem.*, **29**, 163 (1976); c) J. R. Davy, M. N. Iskander, and J. A. Reiss, *ibid.*, **32**, 1067 (1979).