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syn- and *anti*[3.3](1,4)Naphthalenophanes[1)]

Minoru YOSHINAGA, Tetsuo OTSUBO, Yoshiteru SAKATA, and Soichi MISUMI*

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565

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Synopsis. The title compounds were prepared by pyrolysis of disulfones. The absorption spectra depend rather on the stacking mode between two naphthalene rings than ring-to-ring distance, whereas for the emission spectra the reverse is the case. A [4+4]photocycloaddition and a reverse reaction were observed between *anti*-form and its photoisomer.

In order to clarify the effects of ring-to-ring distance and stacking mode between two naphthalene rings on the naphthalene excimer emission,[2,3)] the title compounds were studied as more suitable models than *syn*- and *anti*[2.2](1,4)naphthalenophanes (**1** and **2**)[4)] because the [3.3]phane system with longer ring-to-ring distance must be less strained than the [2.2]phane system.

The two isomeric [3.3](1,4)naphthalenophanes (*syn* **3** and *anti* **4**)[5)] were prepared by our method in which pyrolytic desulfurization of disulfone was the key step of [3.3]phane formation.[6)] 1,4-Bis(bromomethyl)naphthalene **5**[7)] was converted to 1,4-bis(2-mercaptoethyl)-naphthalene **10** in the conventional way of five steps. A coupling of **5** with mercaptan **10** gave 2,17-dithia[4.4]-(1,4)naphthalenophane **11**. The NMR spectrum of **11** shows the *anti*-conformer to be predominant though both conformers are easily interconvertible. After **11** was oxidized with *m*-chloroperbenzoic acid, pyrolysis of the resulting disulfone **12** led to a mixture of the desired phanes **3** and **4** with a 2: 3 ratio. The separation into the two isomers was performed by fractional crystallization and column chromatography on silica gel.

The structures of **3** and **4** were determined by NMR data characteristic of *syn*- and *anti*-conformers, respectively. Thus, the ring current effect due to the opposite naphthalene ring brings about upfield shifts of all the aromatic protons for *syn*-form **3** and of only H_a proton for *anti*-form **4**. These upfield shifts are, as expected, a little less, compared to those of *syn*- and *anti*[2.2]analogs **1** and **2**.

Fig. 1 shows electronic absorption spectra of **1**—**4**. Evidently, the spectra depend rather on the stacking mode of two naphthalene rings than on the ring-to-ring distance. Thus, the spectral shapes of both conformers **3** and **4** are markedly different, whereas each spectrum is quite similar to that of the same conformer of [2.2]-analog. This phenomenon can be interpreted by only exciton interaction of the two chromophores although a contribution of charge-transfer interaction is not neglected.[3,8)]

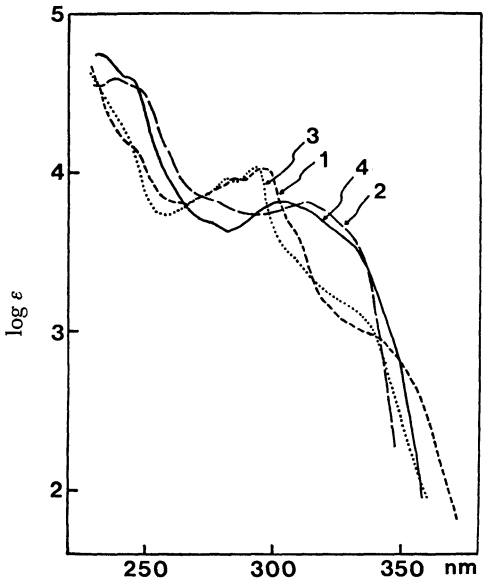
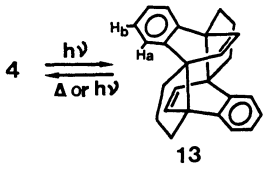
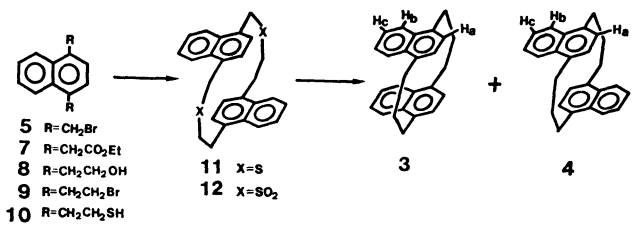


Fig. 1. Electronic spectra of **1**—**4** in tetrahydrofuran.





The emission spectra of **3** and **4** show a broad fluorescence band of excimer type (λ_{max} 430 nm for **3** and 420 nm for **4**) and a phosphorescence band with fine structure (λ_{max} 494, 530, 570 nm for **3** and 530, 570 nm for **4**). These data suggest that the naphthalene excimer (λ_{max} 400—410 nm) has not necessarily a closely fixed sandwich structure, that is, the ease of the excimer formation is not correlated to the extent of overlapping between two naphthalene rings. The naphthalene excimer is presumed to be in a parallel slided conformation with a distance comparable to the ring-to-ring distance in [3.3]phane system.

Although *anti*-form **2** with [2.2]system undergoes two types of intramolecular photocycloaddition, *i.e.*, a formally two-fold [4+2]cycloaddition to dibenzoequinene[9)] and a [4+4]cycloaddition,[10)] *anti*-form **4** with [3.3]system undergoes onyl [4+4]photocycloaddition to afford photoisomer **13** in quantitative yield. Cycloadduct **13** is stable at room temperature and undergoes a reverse aromatization above 130 °C to regenerate **4**.[5)] The retro-conversion of **13** to **4** also was accomplished on irradiation with light at 253.7 nm.

Experimental

Melting points are uncorrected. NMR ($CDCl_3$), MS, UV, and emission (degassed EPA) spectra were recorded with a JEOL FX-100 (100 MHz), a Hitachi RMU-7, a Hitachi EPS-3T, and a Hitachi MPF-2A (HIV R-446 photomultiplier) spectrometers, respectively.

1,4-Bis(2-hydroxyethyl)naphthalene ***8***. The reduction of diester **7** (7.6 g, 25 mmol), which was derived by cyanation of 1,4-bis(bromomethyl)naphthalene **5**,[7] followed by esterification, in dry THF (200 ml) with $LiAlH_4$ (4.8 g, 127 mmol) in dry THF (270 ml) and recrystallization of the resulting glycol from ethyl acetate gave 89% (4.8 g) yield of **8**, colorless plates, mp 119.5—120 °C. NMR δ=3.31 (2H, t, J=6.1 Hz, CH_2), 3.97 (2H, t, J=6.1 Hz, CH_2), 7.30 (2H, s, ArH), 7.50 (2H, m, ArH), and 8.11 (2H, m, ArH). Found: C, 77.97; H, 7.54%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

1,4-Bis(2-bromoethyl)naphthalene ***9***. Dibromide **9** was obtained by refluxing a mixture of glycol **8** (3.5 g, 16 mmol), 47% HBr (200 ml), and conc H_2SO_4 (90 ml) for 2 h. The mixture was worked up and chromatographed on silica gel with benzene. **9**: colorless plates from benzene–hexane, yield 2.6 g (47%), mp 131—131.5 °C. NMR δ=3.65 (8H, m, CH_2), 7.35 (2H, s, ArH), 7.65 (2H, m, ArH), and 8.10 (2H, m, ArH). Found: C, 49.32; H, 4.41; Br, 46.27%. Calcd for $C_{14}H_{14}Br_2$: C, 49.15; H, 4.13; Br, 46.72%.

1,4-Bis(2-mercaptoethyl)naphthalene ***10***. A mixture of **9** (4.5 g, 13 mmol), thiourea (2.6 g, 34 mmol), and ethanol (180 ml) was treated in the same way as the preparation of 1,4-bis(2-mercaptoethyl)benzene.[1] The resulting oil crystallized after chromatography on silica gel with benzene, yield 1.0 g (31%), mp 108.5—109.5 °C. The dithiol was essentially pure and used in the next step without further purification. NMR δ=1.44 (2H, t, J=7.8 Hz, SH), 3.06 (4H, m, CH_2), 3.40 (4H, m, CH_2), 7.25 (2H, s, ArH), 7.49 (2H, m, ArH), and 8.05 (2H, m, ArH).

2,17-Dithia[4.4](1,4)naphthalenophane ***11***. The coupling of dibromide **5** (700mg, 2.3 mmol) with dithiol **10** (600 mg, 2.4 mmol) in benzene (400 ml) was carried out according to the general procedure in the preceding paper.[1] **11**: colorless plates from benzene–hexane, yield 200 mg (22%), mp 256—257 °C. NMR δ=3.18 (8H, A_2B_2m, CH_2), 3.78 (4H, s, CH_2), 6.00 (2H, s, ArH), 6.37 (2H, s, ArH), 7.47 (4H, m, ArH), and 7.90 (4H, m, ArH). Found: C, 77.72; H, 6.05; S, 16.29 %; MS *m/e* 400 (M^+). Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04; S, 16.01%; M 400.

2,17-Dithia[4.4](1,4)naphthalenophane 2,2,17,17-Tetraoxide ***12***. The preparation of disulfone **12** was carried out according to the general procedure (with *m*-chloroperbenzoic acid) in the preceding paper.[1] **12**: quantitative yield, mp 324 °C (dec). It was used for the next step without purification.

[3.3](1,4)Naphthalenophanes, syn ***3*** *and* anti ***4***. Pyrolysis of disulfone **12** (50 mg, 0.108 mmol) was carried out by the same method as previously reported (650 °C, 0.2 mmHg).[6] The collected product was purified by column chromatography on silica gel with benzene and then gel-permeation liquid chromatography to give a mixture of *syn*- and *anti*-isomers with a 2:3 ratio, yield 10 mg (28%). Recrystallization from hexane afforded pure *anti*-isomer **4**, colorless needles, mp 214—216 °C. NMR δ=2.32 (4H, m, CH_2), 2.72 (4H, m, CH_2), 3.43 (4H, m, CH_2), 5.99 (4H, s, H_a), 7.51 (4H, q, J=7.0, 2.0 Hz, Hc), and 8.06 (4H, q, J=7.0, 2.0 Hz, Hb). Found: C, 92.80; H, 7.21%, MS *m/e* 336 (M^+). Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%; M 336.

Careful column chromatography of the mother liquid of above recrystallization on silica gel with CCl_4 afforded pure *syn*-isomer **3** after the elution of *anti*-isomer. Recrystallization from ethanol gave colorless plates, mp 229—229.5 °C. NMR δ=2.80 (8H, m, CH_2), 3.60 (4H, m, CH_2), 6.93 (4H, s, H_a), 6.98 (4H, q, J=7.6, 2.0 Hz, H_c), and 7.12 (4H, q, J=7.6, 2.0 Hz, H_b). Found: *m/e* 336.18601. Calcd for $C_{26}H_{24}$: M, 336.18779.

Photoisomer ***13***. *anti*[3.3](1,4)Naphthalenophane **4** (1.6 mg) was dissolved in 5 ml of benzene in a Vycor tube. The solution was irradiated with a high pressure mercury lamp (400 W) for 2 h under a nitrogen atmosphere. Evaporation of the solvent gave colorless solid of photoisomer **13** in a quantitative yield. NMR δ=1.79 (4H, m, CH_2), 2.16 (4H, m, CH_2), 2.71 (4H, m, CH_2), 5.47 (4H, s, olefin), 7.16 (4H, q, J=6.1, 2.8 Hz, H_b), and 7.36 (4H, q, J=6.1, 2.8 Hz H_a). Found: *m/e* 336.18645. Calcd for $C_{26}H_{24}$: M 336.18779.

It melted at 130 °C, resolidified above the temperature, and remelted at the melting point of **4**. The regeneration of **4** was confirmed by heating **13** at 132 °C in DMSO for 20 min and also by irradiating **13** with a low pressure mercury lamp for 4 h under a nitrogen atmosphere.

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