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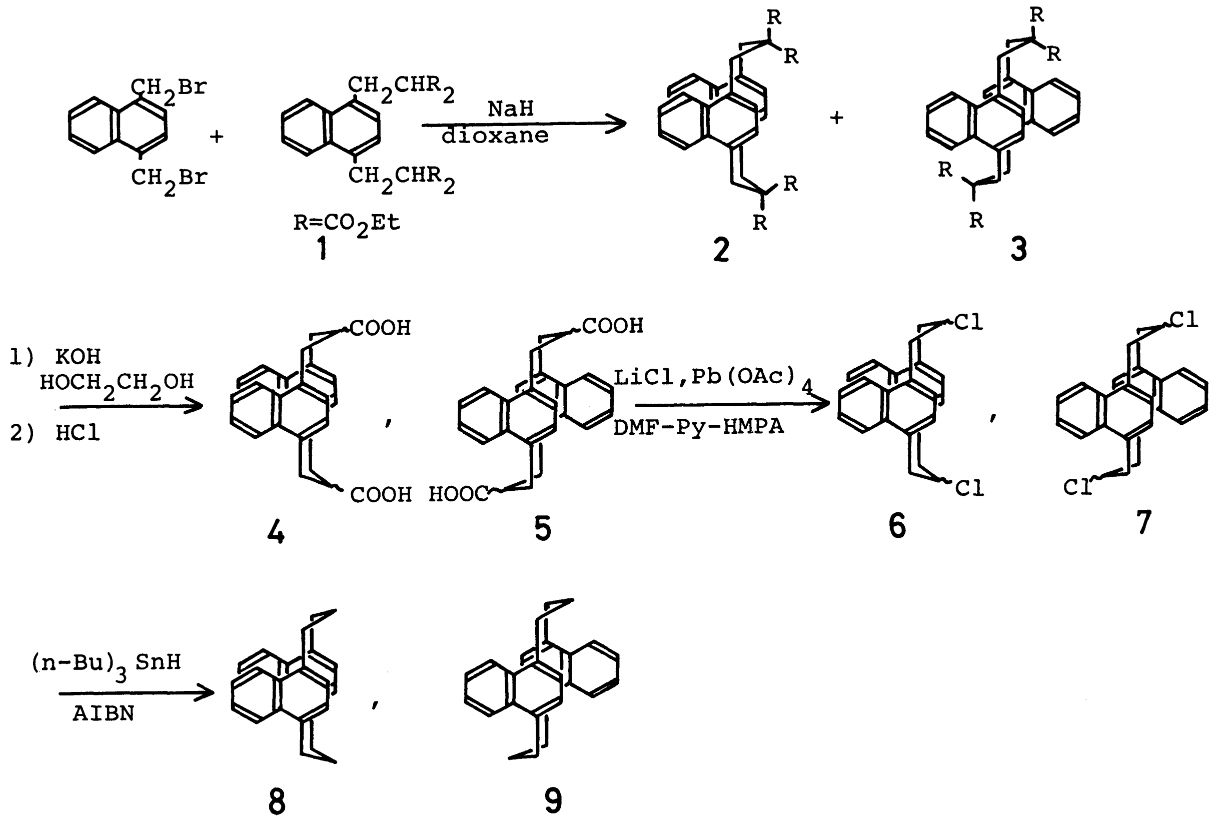
SYNTHESES1) OF *SYN*- AND *ANTI*-[3.3](1,4)NAPHTHALENOPHANE AND INTRAMOLECULAR CYCLOADDITION PRODUCTS OF *SYN*- AND *ANTI*-[3.3](1,4)-NAPHTHALENOPHANE DERIVATIVES

Takeo KAWABATA, Teruo SHINMYOZU, Takahiko INAZU, and Tamotsu YOSHINO
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812

Two isomeric [3.3](1,4)naphthalenophanes, *syn* and *anti* (8 and 9), were synthesized. The absorption maxima 237 and 330 nm for 8, as well as 231, 241, and 325 nm for 9 may be ascribed to the transannular π-electronic interaction between two naphthalene moieties. On irradiation, *syn*- and *anti*-[3.3](1,4)naphthalenophane derivatives were transformed to the photoisomers (10 and 11) which were reconverted to the original compounds (2 and 3) when heated in the solid phase at 175°C.

For investigation of transannular π-electronic and steric effects, [3.3]cyclophanes are more suitable compounds because of less strain, more flexibility and more suitable transannular distances than [2.2]cyclophanes.2-5) As a part of our studies on [3.3]cyclophane chemistry, we wish to report the syntheses6) and properties7) of *syn*- and *anti*-[3.3](1,4)naphthalenophanes (8 and 9), which were prepared from corresponding dichlorides by a more suitable reduction method than previous one.8) A coupling reaction between 1,4-bis(bromomethyl)naphthalene and tetraester 1 gave a mixture of *syn*- and *anti*-isomers of desired cyclic tetraester in 14.5% yield (*syn*: *anti* ratio was 5:2; presumably because of steric effects of four ethoxycarbonyl groups, the *syn*-isomer yielded predominantly). By column chromatography on silica gel, using hexane-chloroform (3:1 v/v) as an eluent, the *syn*- and *anti*-isomers were isolated, respectively. 2: colorless plates, mp 204.5-205°C. Pmr (δ, CDCl$_3$): 1.37 (m,12H,-CH$_3$), 3.92(q,8H,ArCH$_2$), 4.40(m,8H,OCH$_2$), 6.87(s,4H,arom.Hc:H-2,-3), 6.90(m, 4H,arom.Ha:H-6,-7), 7.64(m,4H,arom.Hb:H-5,-8). 3: colorless needles, mp 213-214°C. Pmr: 1.36(t,12H,-CH$_3$), 3.93(q,8H,ArCH$_2$), 4.35(q,8H,OCH$_2$), 5.98(s,4H,arom.Hc:H-2,-3), 7.52(m,4H,arom.Ha:H-6,-7), 8.26(m,4H,arom.Hb:H-5,-8). After alkaline hydrolysis of 2, and followed by decarboxylation, the carboxylic acid 4 was obtained in 100% and in the same way 5 was obtained in 98% yield. 4 was treated with lead tetraacetate and lithium chloride in DMF-pyridine-HMPA to give the dichloride 6 in 36.8% and in the same way 7 was obtained in 30.9% yield. 6: white crystals, mp ca. 250°C dec. Pmr: 3.70(m,8H.ArCH$_2$), 5.20(m,2H,Cl-CH), 7.00(s,4H,arom.Hc:H-2,-3), 7.15(m,4H,arom.Ha:H-6, -7), 7.62(m,4H,arom.Hb:H-5,-8). 7 (a mixture of four isomers): white crystals, mp ca.270°C dec. Pmr: 3.55(m,8H,ArCH$_2$), 5.00(m,2H,Cl-CH), 5.82, 5.99, 6.23, 7.00(s, 4H,arom.Hc:H-2,-3), 7.65(m,4H,arom.Ha:H-6,-7), 8.08(m,4H,arom.Hb:H-5,-8). The reduction9) of the dichloride 6 with tributyltinhydride in the presence of azobisisobutyronitrile (AIBN) in toluene gave *syn*-[3.3](1,4)naphthalenophane (8) in 78.8%

and in the same way *anti*-[3.3](1,4)naphthalenophane (9) was obtained in 48.9% yield. 8: colorless plates from ethanol-chloroform, mp 229.5-230°C. 9: colorless crystals from ethanol-chloroform, mp 243-245°C



The nmr spectra provide strong support for the assigned structure as shown in Figure 1. The Hc protons (δ 5.98,s) in the *anti* form are situated above the transannular naphthalene ring, and their peaks are shifted significantly upfield. Whereas the Hc protons (δ 6.90,s) in the *syn* form have only the similar chemical shift as the corresponding protons of 1,4-dimethylnaphthalene. The Ha and Hb protons (δ 7.27,m) in the *syn* form and those (δ 7.77,m) in the *anti* form support the assignment.

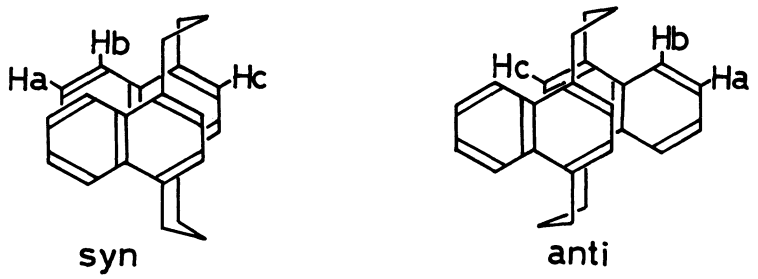
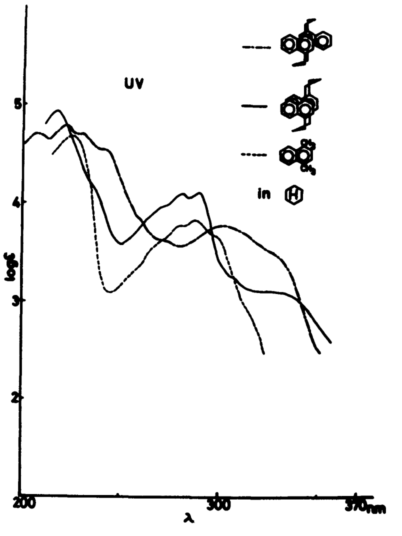


Figure 1

The electronic spectra of *syn*- and *anti*-[3.3](1,4)naphthalenophanes(8 and 9) have similar tendency to those of *syn*- and *anti*-[2.2](1,4)naphthalenophanes.10)



Compared with the electronic spectrum of 1,4-dimethylnaphthalene, 8 shows new absorption maxima at 237 and 330 nm and 9 shows at 231, 241 and 325 nm in cyclohexane, which could be ascribed to the transannular π-electronic interaction between two naphthalene chromophores. In the partly superposed *anti* form 9, compared with the well superposed form 8, the major peaks are observed to shift to longer wavelengths and to be weakened in intensity.

Compared to the *syn* form 8, loss of the fine structure around 300 nm in the *anti* form 9 is noticeable. *anti*-[2.2](1,4)Naphthalenophane11) has been known to undergo [4+4]photocycloaddition.

Recently, we have reported the cycloaddition of [3.3](1,4)naphthaleno(9,10)anthracenophane derivative.12) We found that *syn*- and *anti*-[3.3]-(1,4)naphthalenophane derivatives gave the similar [4+4]photocycloaddition products.11-14) Ultraviolet irradiation of 2 in chloroform flushed with nitrogen gas for 10 hours yielded 10 in 96.2%, after chromatography on silica gel and recrystallization from ether. Being heated at 175°C, 10 was completely reconverted to the original compound (2). Ultraviolet irradiation of 3 yielded 11 in 81.5% in the same way. Being heated at 175°C, 11 was also completely reconverted to the original compound (3). 10: colorless plates, mp 145.5°C. Found: C, 73.06; H, 6.47%, mol wt(MS,M^+) 624. 11: colorless prisms from ether-chloroform, mp 174°C. Found: C, 72.99; H, 6.49%; mol wt (MS,M^+) 624. Calcd for $C_{38}H_{40}O_8$; C, 73.06; H, 6.45%; mol wt 624.73. These photoproducts were characterized by nmr spectra (Figure 4). The shape of the electronic spectrum of 10 closedly resembles to that of 11.

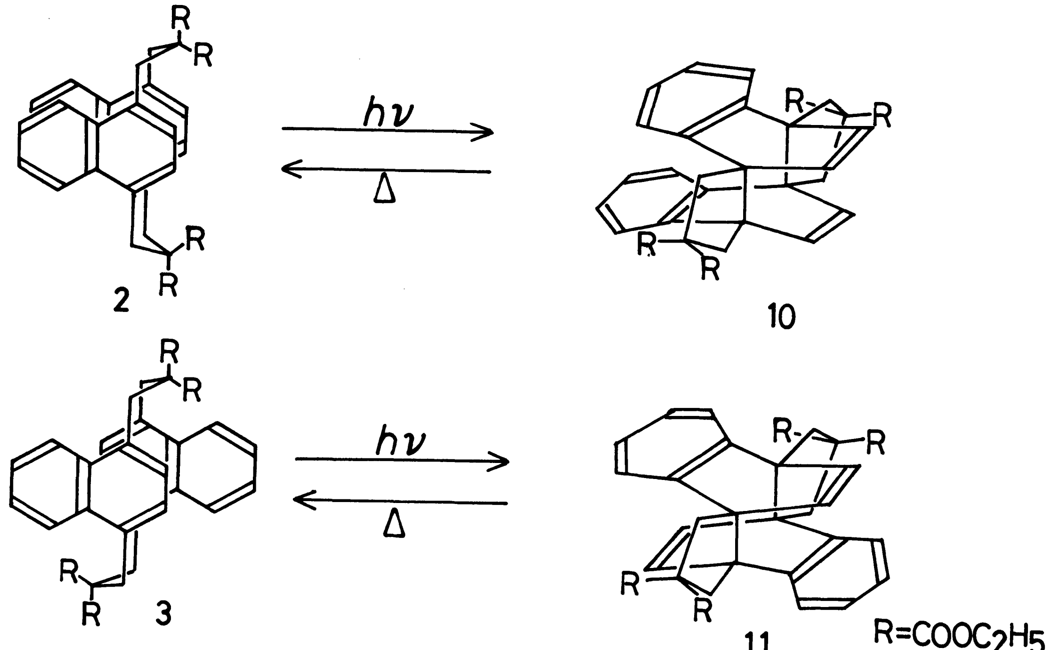


Figure 3

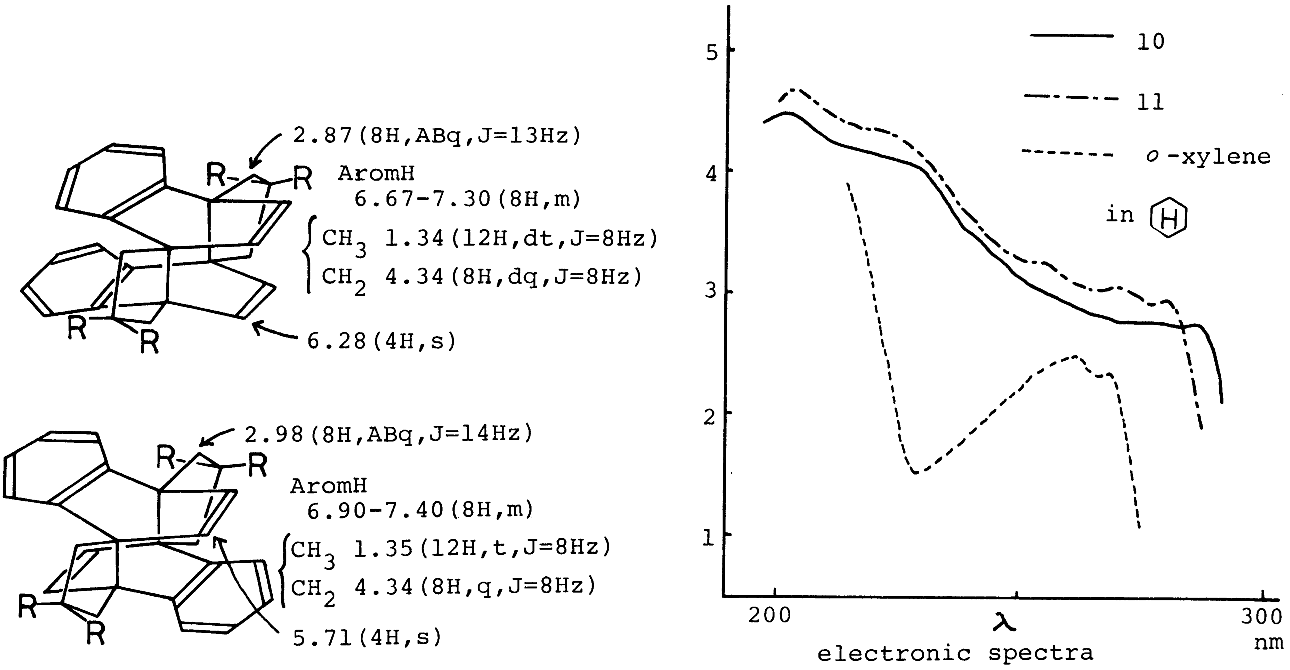


Figure 4

References and Notes

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