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Triple-layered Orthonaphtho[3.3]orthobenzeno[3.3]orthonaphthophane

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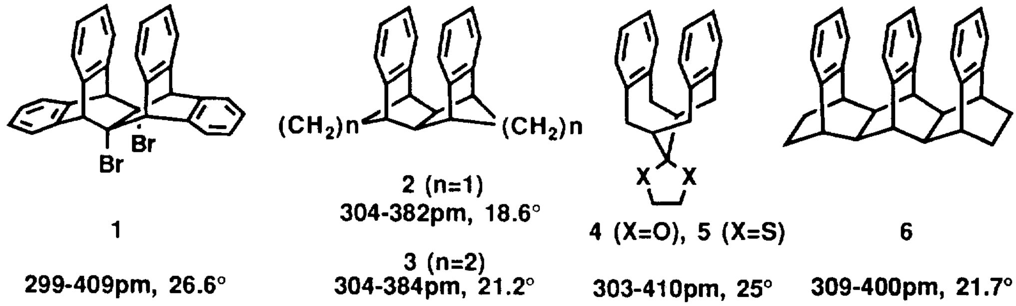
Abstract: Triple-layered [3.3][3.3]orthocyclophane of the *anti*-type was prepared for the first time, and its structure, in which two naphthalene rings sandwitch one benzene ring, was established by X-ray crystallographic analysis.

In the last decade, extensive work has been done on multilayered para- and meta-cyclophanes.[1-2] This interest is attributed mainly to the fact that, in many cases, the properties of [m.n]cyclophanes were found to be amplified in multilayered structures. Thus, very often a dramatic change in electronic spectra of multilayered paracyclophanes is observed when the number of layers is increased, for example, from [2.2]- to [2.2][2.2]- and from [3.3]- to [3.3][3.3]-paracyclophanes.[3] Layered [3.3]orthocyclophanes[4-8] **1-5** with additional bridge(s) show a π-π through-space interaction between the two undistorted benzene rings held rigidly face to face. Recently, it was found that [3.3][3.3]orthocyclophane **6**,[6] in which the three benzene rings are stacked in a *syn*-orientation, showed λmax at a similar wavelength (272 nm) with ca.1.5-folds of intensity to that (273 nm) of **3**.

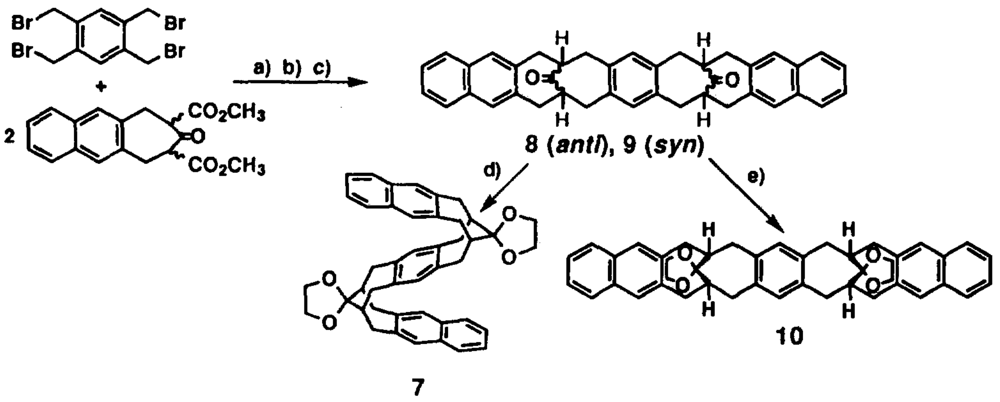


Scheme 1

In connection with our work[7-11] on the layered [3.3]orthocyclophane system, this communication reports the synthesis, X-ray structure analysis, and spectral properties of orthonaphto[3.3]orthobenzeno[3.3]orthonaphthophane **7**, an *anti*-type of the triple-layered [3.3][3.3]orthocyclophane.

Our strategy for the synthesis of **7** follows the route of our earlier preparation of [3.3]orthocyclophane **4-5**.[7,8] In the reaction of tetrakis(bromomethyl)benzene with naphthocycloheptenonedicarboxylate, two isomeric tetrakiscarboxylates, *anti*-ester and *syn*-one, were produced as a 1:1-mixture. Each ester was isolated (26% and

32% yields), hydrolyzed (97% and 98% yields), and decarboxylated at 310 °C, giving the corresponding ketones, *anti*-**8** (89% yield) and *syn*-**9** (68% yield). Bisacetalization of **8** and **9** with ethylene glycol was carried out in benzene or a mixed solvent of benzene and nitrobenzene under reflux and the expected bisacetals, **7** (60% yield) and **10** (58% yield),[12] precipitated when the reaction mixture was cooled.



Reagents ; a) TBABr / CH_2Cl_2-23%NaOHaq., b) KOH / EtOH, c) Pyrolysis(310°C), d) TosOH, Excess Ethylene Glycol / Benzene-Nitrobenzene, e) TosOH, Excess Ethylene Glycol / Benzene

Scheme 2

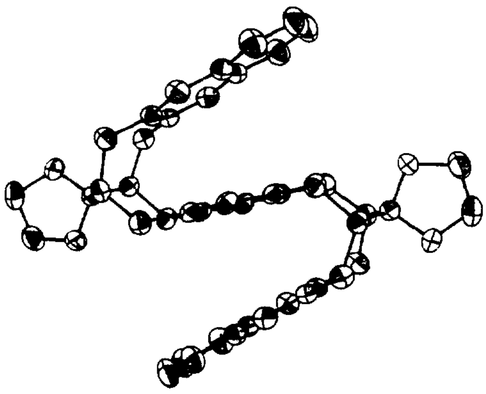
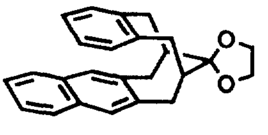


Fig. 1 ORTEP view of 7

The triple-layered [3.3][3.3]orthocyclophane structure of *anti*-bisacetal **7** was determined by X-ray crystallographic analysis (Fig. 1).[13,14] The two naphthalene rings and the benzene ring of **7** are not distorted. The nearest interplanar distance between the benzene and naphthalene rings is 300 pm. The dihedral angle between the planes of the benzene and naphthalene rings is 18.1°. The structure of **7** resembles that of **2** rather than orthobenzo[3.3]orthobenzenophane **4**-**5**[7,8,15]; however, a direct comparison of the triple-layered [3.3][3.3]orthocyclophane **7** with the corresponding double-layered ortho[3.3]-phanes awaits an X-ray structure analysis of **11**. The ^1H NMR spectrum (pyridine-d_5) reflects the symmetric triple-layered structure of **7**. The aromatic protons are strongly affected by anisotropic effects of the benzene and naphthalene rings. Signals of the protons of the two outer naphthalene rings of **7** appeared at $\delta = 7.15$ (s), 7.34-7.37 (m), and 7.67-7.71 (m) ppm, and that of the protons of the inner benzene ring at $\delta = 6.10$ ppm. The bridge methylenes were shown as two sets of double doublets and the bridgehead methine protons as a multiplet peak.



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The spectrum of *syn*-bisacetal **10** (pyridine-d_5) showed broad peaks due to the conformational change at room temperature. When the temperature was lowered to -40 °C, three singlet peaks, which are assignable to the inner phenyl ring, were observed at $\delta = 6.38$ (s), 6.70 (br s), and 7.06 (s) ppm, with an intensity ratio of 2:1:2. These facts suggest that **10** exists as an equilibrium mixture of three or more conformers and that two[16] of them have a layered [3.3]orthocyclophane sub-structure. Signals of the other aromatic protons and of the aliphatic bridges are complicated in the spectrum at -40 °C.

The electronic spectra of **7** and **10** are very similar in shape (Fig. 2), although a larger hyperchromic shift was observed. *Anti*-bisacetal **7** shows a long wavelength shift, as compared to the spectrum of the diketone **8**; however, the value of the shift (16 nm) is almost the same as that in the case of *syn*-bisacetal **10**, and similar to those (13 and 10 nm, respectively) reported for [3.3]orthophane **4** (X=O) and **5** (X=S).[7,8] No absorption of the C-T complex formation with TCNE was observed.[17]

These facts indicate that in triple-layered [3.3][3.3]orthocyclophane **7**, a through-space electronic interaction between the upper and the lower ring via the middle one is small, in sharp contrast with the large hyperchromic and long wavelength shifts of electronic spectra in a series of multilayered paracyclophanes.[18]

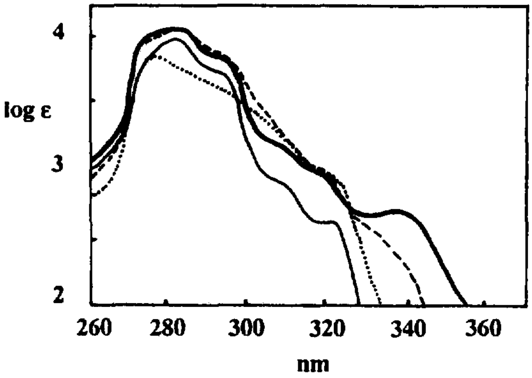

Fig. 2 UV spectra of **7**-**10**
7 —— , **8** ······ , **9** —— , **10** - - -

References

1. Vögtle, F. *Cyclophane Chemistry*; John Wiley and Sons Ltd, Chichester, 1993; pp 277-316.

2a. Misumi, S. Multilayered Cyclophanes. In *Cyclophanes*; Keehn, P. M. Rosenfeld, S. M. Eds.; Academic Press : New York, 1983; Vol. 2, Chapt. 10.

2b. Very recently, a "molecular ribbon" containing six *syn*-[3.3]metacyclophane units was synthesised, in which seven fourfold-bridged benzene rings are accumulated. Breidenbach, S.; Ohren, S.; Nieger, M.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1237-1238.

3a. Otsubo, T.; Mizogami, S.; Otsubo, I; Tozuka, Z.; Sakagami, A.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.*, **1973**, *46*, 3519-3530.

3b. Otsubo, T.; Mizogami, S.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.*, **1973**, *46*, 3831-3835.

3c. Koizumi, T.; Toyoda, T.; Miki, K.; Kasai, N.; Misumi, S. *Bull. Chem. Soc. Jpn.*, **1986**, *59*, 239-242.

3d. Otsubo, T.; Aso, Y.; Otgura, F.; Misumi, S. *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 164-170.

4. Cristol, S. J.; Lewis, D. C. *J. Am. Chem. Soc.* **1967**, *89*, 1476-1487.

5. Prinzbach, H.; Sedelmeier, G.; Krüger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem.* **1978**, *90*, 297-305.

6. Grimme, W.; Kämmeerling, H. T.; Lex, J.; Gleiter, R.; Heinze, J.; Dieterich, M., Roth, W. R. *Angew. Chem. Int. Ed., Engl.* **1991**, *30*, 205-207.

7. Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M.; Imada, K. *J. Chem. Soc.,Chem. Commun.* **1985**, 973.

8. Mataka, S.; Takahashi, K.; Mimura, T.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M.; Imada, K.; Kuniyoshi, M. *J. Org. Chem.* **1987**, *52*, 2653-2656.

9. Mataka, S.; Mimura, Lee, S.-T.; Kobayashi, H.; Takahashi, K.; Tashiro, M. *J. Org. Chem.* **1989**, *54*, 5237-5241.

10. Mataka, S.; Lee, S.-T.; Tamura, Y.; Tsuge, A.; Tashiro, M. *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1107-1113.

11. Mataka, S.; Ma, J.; Thiemann, T.; Rudziñski, J. M.; Sawada, T.; Tashiro, M. *Tetrahedron Lett.* **1995**, *36*, 6105-6108.

12. Although stable in a solid state, **7** and **10** are sensitive to hydrolysis in $CHCl_3$. Their UV spectra were measured in $CHCl_3$ containing 1% of NEt_3.

13. X-ray crystallographic analysis of **7**: colorless prisms, $C_{44}H_{42}O_4$, F. W.= 634.8, monoclinic; a = 17.924 (1), b = 8.004 (1), c = 11.947 (1) Å, β = 108.85 (1)°, V = 1622.0 Å^3, Z = 2, D_c= 1.30 g cm^{-3}, space group P21/a. Data were collected on an Enraf-Nonius CAD4 diffractometer, $\omega - 2\theta$ scan type, graphite-monochromated Cu Kα radiation, λ = 1.54184 Å. Of 2756 independent reflections collected in the range $2 < \theta < 65°$, 1898 with $I_0 > 3\sigma(I_0)$ were taken as observed. The crystal did not show any significant decay during the data collection. Positional parameters were determined by direct methods using SIR 88 13) and were refined by full-matrix least-squares calculations with all nonhydrogen atoms treated anisotropically and hydrogen atoms treated isotropically using the scheme $w = 4F_0^2/(\sigma F_0^2)^2$ to give the final residuals: R = 4.2%, R_w = 5.2%.

14. Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **1989**, *22*, 389-393.

15. The crystal structures of acetal **4** (X= O) and dithoacetal **5** (X= S) are very similar.

16. Signals at δ = 6.38 and 6.70 ppm showed an up-field shift, compared to the aromatic proton signal of 1,2,4,5-tetramethylbenzene (δ = 6.89 ppm in pyridine-d_5).

17. Due to the poor solubility of 7, a C-T complexation study was made at a concentration of $1.0\text{x}10^{-4}$M. No charge-transfer band was observed in the absorption spectra of a mixture of TCNE ($1.0\text{x}10^{-4}$ M ~ $1.0\text{x}10^{-2}$) and 7 ($1.0\text{x}10^{-4}$ M) in CH_2Cl_2.

18. Otsubo, T.; Kohda, T.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 512-517.

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