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TRIPLE-LAYERED [2.2]NAPHTHALENOPHANE

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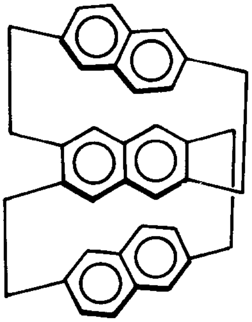
Abstract: The title compound 1 was synthesized via tetrathia[3.3]naphthalenophane 7 and showed a marked transannular interaction in the electronic spectrum.

Multilayered cyclophanes are particularly interesting in the field of cyclophane chemistry, for they have unusual physical and chemical properties due to the increased transannular π-electronic interactions between their aromatic nuclei, compared to double-layered cyclophanes.[1] However, these compounds so far studied have been limited only to benzenophanes. More extensive studies of multilayered cyclophanes composed of condensed aromatic nuclei might be of help toward understanding intermolecular interactions among aromatic nuclei and in the wide applications of layered compounds to other fields. In the present communication we like to report triple-layered [2.2]naphthalenophane 1 as the first example of triple-layered condensed aromatic phanes. Haenel and Staab reported chiral [2.2](2,6)naphthalenophane 2[2] as a double-layered homolog of several [2.2]naphthalenophanes.[3] Blank and Haenel recently reported the less stable achiral isomer 3.[4] A study of a series of multilayered [2.2]paracyclophanes revealed that an increase in stacked layers from double to triple gave rise to dramatic enhancement in the transannular electronic interactions.[5] Therefore, triple-layered naphthalenophane 1 is expected to show a similar marked interaction.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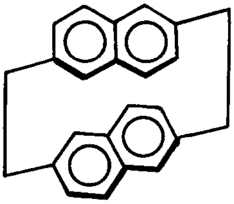
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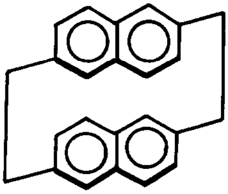
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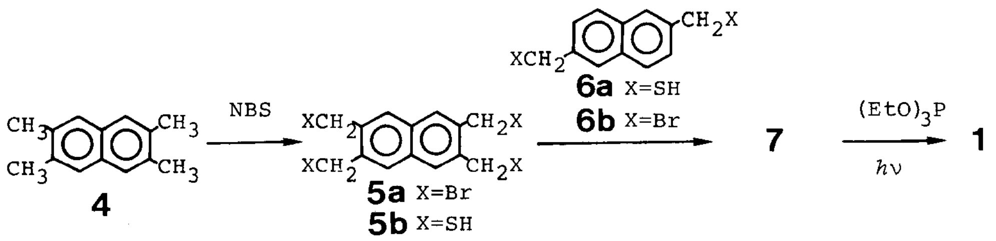
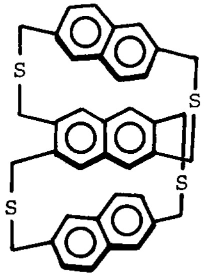
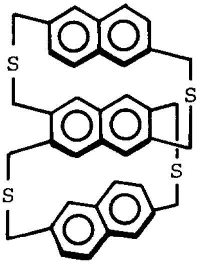
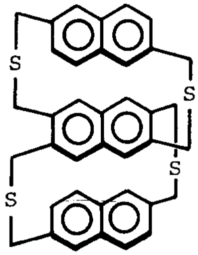




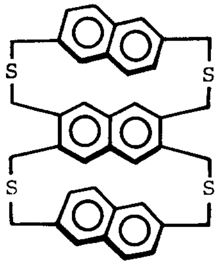
7a



7b



7c



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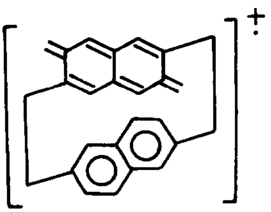
The synthesis of 1 is shown in the scheme. 2,3,6,7-Tetramethylnaphthalene 4 was prepared from 2,3-dimethylsuccinic anhydride and o-xylene according to the procedure of Dozen and Hatta,[6] and was converted to 2,3,6,7-tetrakis(bromomethyl)naphthalene 5a[7] in 69% yield by reaction with N-bromosuccinimide in carbon tetrachloride. A coupling reaction of 5a (one molecule) and 2,6-bis(mercaptomethyl)naphthalene 6a[2] (two molecules) in ethanol solution containing potassium hydroxide under high dilution gave tetrathia[3.3]naphthalenophane 7[8] in 9% yield. Altenatively, 5a was converted to 2,3,6,7-tetrakis(mercaptomethyl)naphthalene 5b[9] in 62% yield by reaction with thiourea followed by hydrolysis and then coupled with 2,6-bis(bromomethyl)naphthalene 6b[2] to give the same product 7 in 17% yield. The NMR spectrum of 7 demonstrates an apparent multiplet corresponding to the inner naphthalene protons,[8] suggesting an isomeric mixture of 7a, 7b, and 7c. The formation of another possible isomer 8 with a quite different stacked mode was not detected.[10] The photolytic sulfur extrusion of 7 in triethyl phosphite with a high pressure mercury lamp (12 hrs) gave the desired product 1 in 32% yield, colorless prisms from benzene, dec. p. 285°C.



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The structure of 1 was assigned by MS and NMR measurements and elemental analysis. The MS spectrum clealy shows molecular ion peak m/e 488 (base peak) and a fragment peak m/e 334 corresponding to naphthoquinodimethane 9, in a similar manner as benzoquinodimethane characteristic of MS fragmentation of multilayered [2.2]paracyclophanes.[5] The NMR spectrum demonstrates signals at δ 2.3-3.3 (m, 16H,

CH_2), 5.55(s, 4H, inner ArH), 6.17(s, 4H, outer α-ArH), 6.69(d, J=8 Hz, 4H, outer β-ArH), and 6.91(d, J=8 Hz, 4H, outer α-ArH) in deteriochloroform. The aromatic protons absorb at very high fields due to the magnetic anisotropy of the adjacent naphthalene.[11] The upfield shift of the sandwiched naphthalene protons equals almost twice that of naphthalene α-protons of 2. On the other hand, there are observed no signals corresponding to the other isomers formed from the desulfurization of 7b and 7c.

The transannular π-electronic interactions of layered cyclophanes can be best understood by spectroscopic analysis. Figure 1 shows the electronic absorption spectrum of 1, together with those of 2 and 2,6-dimethylnaphthalene.[12] Both naphthalenophanes 1 and 2, as compared with 2,6-dimethylnaphthalene, demonstrate some common characteristic due to their electronic interactions, i.e., bathochromic and hyperchromic shifts and the disappearence of fine structure. As noted by the positions of the longest wavelength bands 362 nm (sh) for 1, 336 nm (sh) for 2, and 326 nm for 2,6-dimethyl napthalene, the more prominent effect of 1 indicates a strong transannular π-electronic interaction among the three naphthalene rings. Other spectral study is under way.

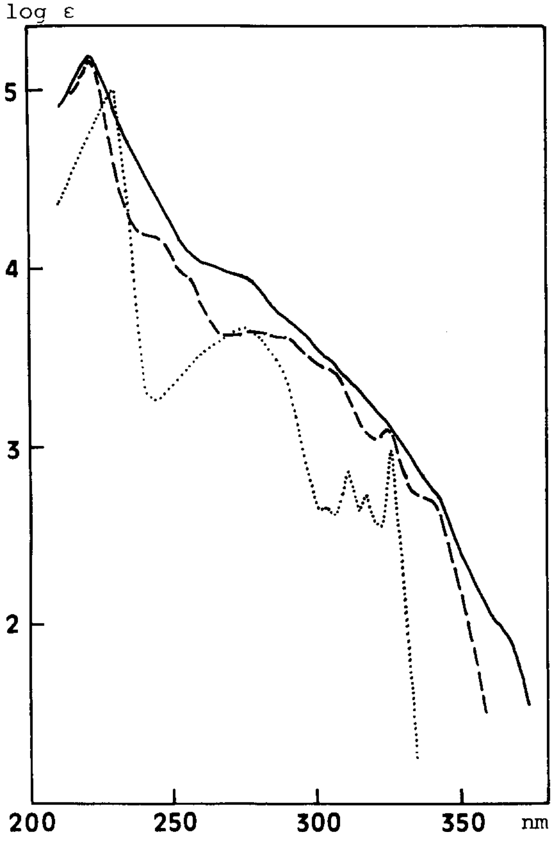

Fig. 1. The electronic spectra of triple-layered naphthalenophane 1 (———), double-layered naphthalenophane 2 (— — — —), and 2,6-dimethylnaphthalene (··········) in tetrahydrofuran.

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References and Notes

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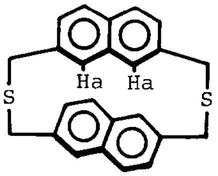
7) Compound 5a: colorless plates from benzene, mp 230°C with dec. NMR($CDCl_3$): δ 4.85(s, 8H, CH_2Br), 7.83(s, 4H, ArH).
8) Compound 7: colorless plates from benzene-chloroform, dec. p. 250°C. NMR($CDCl_3$): δ 3.5-4.5(m, 16H, CH_2S), 6.14, 6.21, 6.38(each s, 4H, inner ArH), 6.7-7.0(m, 12H, outer ArH). MS m/e 616(M^+).
9) Compound 5b: colorless scales from benzene, mp 181-182°C. NMR($CDCl_3$): δ 1.83(t, J=7 Hz, 4H, SH), 4.04(d, J=7 Hz, 8H, CH_2S), 7.69(s, 4H, ArH).
10) The NMR spectrum of double-layered dithia[3.3]naphthalenophane 10 shows characteristic upfield shift (δ 5.82) for Ha protons alone; V. Boekelheide and C. H. Tsai, Tetrahedron, 32, 423 (1976). Therefore, the formation of type 8 may be predicted by the observation of an NMR signal around δ 5.8 for the inner naphthalene protons. The NMR measurement of the present coupling products gave no such signal.



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11) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, Bull. Chem. Soc. Jpn., 46, 3831 (1973).
12) 2,3,6,7-Tetramethylnaphthalene 4 may be chosen as a standard for UV comparison, and its absorption spectrum is quite similar to that of 2,6-dimethylnaphthalene.

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