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Layered Compounds. XLIII.[1] Syntheses and Properties of [2.2]Naphthaleno- and [2.2]Anthraceno-heterophanes

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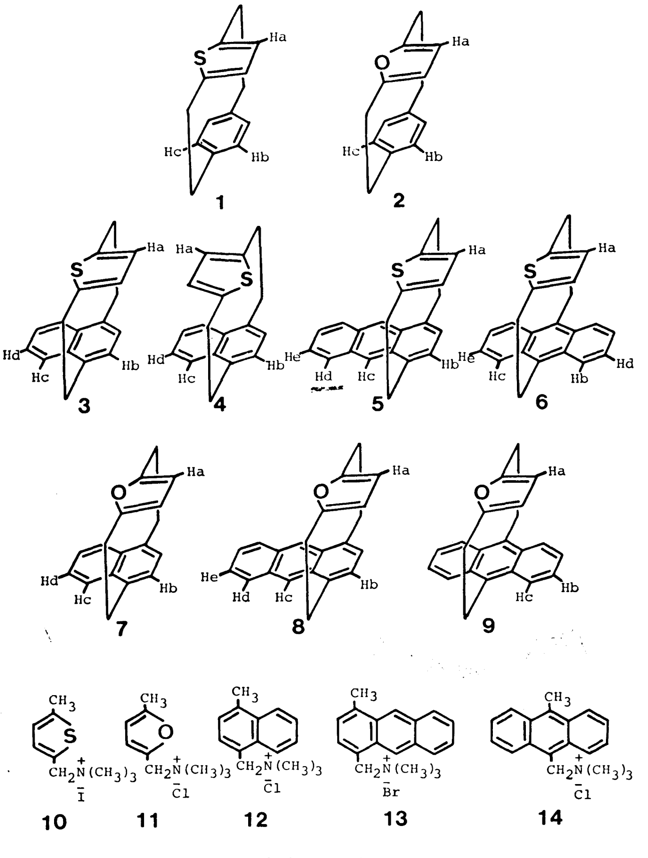
Several [2.2]naphthaleno- and [2.2]anthraceno-heterophanes were synthesized by cross-breeding Hofmann degradation of the corresponding two quaternary ammonium hydroxides. Two isomers, *anti*- and *syn*-forms, were obtained for [2.2](1,4)naphthaleno(2,5)thiophenophane, and one isomer, *anti*-form, for the [2.2](1,4)anthraceno homologue. The structures of the heterophanes were determined by variable temperature NMR analysis. Transannular π-electronic interactions between the condensed aromatic ring and the heteroaromatic ring were examined on the basis of electronic and emission spectra. The thiophene ring interacts more strongly with the condensed aromatic ring than the furan ring. For anthracenophanes, 9,10-bridged system shows more effective interaction than 1,4-bridged one.

The syntheses and properties of a series of multilayered paracycloheterophanes have been reported in the preceding paper.[1] A transannular π-electronic interaction has been observed between the benzene and the heteroaromatic ring in double-layered [2.2]paracycloheteropanes **1** and **2**, increasing with an increase in layer number of multilayered [2.2]paracycloheterophanes. The structures of the paracycloheterophanes, *i.e.*, facile flipping of the furanophane system and tight fixation of the thiophenophane system, and the addition reactions of the former series with benzyne as well as the NMR spectra and CT spectra of TCNE complexes have been reported. The present work was undertaken to study transannular electronic interaction between heteroaromatic and condensed aromatic rings. A series of naphthaleno- and anthraceno-heterophanes **3**—**9** were synthesized with expectation of marked interaction as compared with those of multilayered paracycloheterophanes.



Scheme 1.

Results and Discussion

Syntheses. Five quaternary ammonium salts **10**—**14** were prepared according to the reported methods.[2—5] All the new cyclophanes were obtained by the cross-breeding Hofmann degradation of the corresponding two quaternary ammonium hydroxides in the same method as **1** and **2**. **2** shows the flipping of the furan ring at room temperature. However, **1** exhibits tight fixation of the thiophene ring even at 150 °C due to the bulkiness of sulfur atom.[1] Thus, both conformers, *anti* **3** and *syn* **4**, of [2.2](1,4)naphthaleno(2,5)thiophenophane are expected to be separated as stable ones. Actually the two isomers **3** and **4** were obtained by the pyrolysis of mixed quaternary hydroxides, derived from **10** and **12**, in boiling xylene. The mass spectra of **3** and **4** showed an identical pattern, indicating that both are isomeric with each other. Their structures were assigned on the basis of NMR analyses. The lower yield (0.3%) of *syn*-form **4** than that (4.2%) of *anti*-form **3** is ascribed to π-π repulsion between fused benzo group and thiophene ring in *syn* form. Although *syn*-[2.2](1,4)naphthalenophane and *syn*-[2.2](1,4)anthracenophane were thermally isomerized to *anti*-form, no isomerization of **4** to **3** was observed because of its ready decomposition. In the case of [2.2](1,4)anthraceno(2,5)thiophenophane, however, only one isomer was obtained in 2.8% yield by a cross-breeding reaction of two quaternary ammonium hydroxides derived from **10** and **13** in boiling xylene. Its structure was assigned to *anti*-conformer **5** by NMR spectrum. The *syn*-isomer could not be detected either when the pyrolysis was carried out in boiling toluene (pyrolysis at lower temperature). The *syn*-conformer seems to be very unstable due to both the increasing π-π repulsion and access of the reactive part of the anthracene ring to the thiophene ring. [2.2](9,10)Anthraceno(2,5)thiophenophane **6** and [2.2](1,4)anthraceno(2,5)furanophane **8** were synthesized by similar cross-breeding reactions in 5.5% yield from **10** and **14** and in 0.8% yield from **11** and **13**, respectively. As reference compounds, [2.2](1,4)naphthaleno(2,5)furanophane **7**[6] and [2.2](9,10)-anthraceno(2,5)furanophane **9**[5] were also prepared

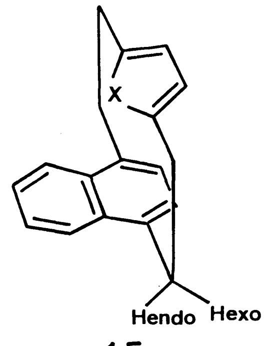
TABLE 1. NMR SPECTRA OF [2.2]NAPHTHALENO- AND [2.2]ANTHRACENO-HETEROPHANES (δ VALUE IN $CDCl_3$)

Compd	Aromatic proton	Calcd shift	Benzylic CH_2
1	Ha 6.34(s, 2H)	+0.11	2.5—3.3(m, 8H)
	Hb 6.20(d, J=2Hz, 2H)	+0.86	
	Hc 7.04(d, J=2Hz, 2H)	+0.02	
2	Ha 5.64(s, 2H), 5.49(s, 2H)[b]	+0.06	2.4—4.1(m, 8H)
	Hb Hc 6.79(s, 4H) {6.12(bs, 2H)[b] 7.07(bs, 2H)[b]}	+0.27 {+0.78[b] −0.17[b]}	
3	Ha 6.38(s, 2H)	+0.07	3.8—4.1(m, 2H)
	Hb 6.48(s, 2H)	+0.67	2.6—3.3(m, 6H)
	Hc 8.05(A_2B_2dd, J=6.5, 3.5 Hz, 2H)	−0.09	
	Hd 7.50(A_2B_2dd, J=6.5, 3.5 Hz, 2H)	−0.04	
4[a]	Ha 5.17(s, 2H)	+1.28	3.7—4.3(m, 2H)
	Hb 7.09(s, 2H)	−0.08	2.7−3.5(m, 6H)
	Hc 7.55(A_2B_2m, 2H)	+0.27	
	Hd 7.20(A_2B_2m, 2H)	+0.12	
5	Ha 6.38(s, 2H)	+0.07	3.8—4.1(m, 2H)
	Hb 6.42(s, 2H)	+0.77	2.6—3.2(m, 6H)
	Hc 8.44(s, 2H)	+0.07	
	Hd 8.00(A_2B_2dd, J=6.5, 3.5 Hz, 2H)	+0.02	
	He 7.46(A_2B_2dd, J=6.5, 3.5 Hz, 2H)	+0.01	
6	Ha 5.42(s, 2H)	+1.03	3.9—4.3(m, 4H)
	Hb 7.95(A_2B_2dd, J=7, 3.5 Hz, 2H)	+0.37	2.6—3.4(m, 4H)
	Hc 8.25(A_2B_2dd, J=7, 3.5 Hz, 2H)	+0.07	
	Hd He } 7.2—7.6(m, 4H)	−0.1—+0.3	
7	Ha 5.62(s, 2H)	+0.08	3.7—4.1(m, 2H)
	Hb 6.55(s, 2H)	+0.70	2.2—3.1(m, 6H)
	Hc 8.10(A_2B_2dd, J=6, 3 Hz, 2H)	−0.09	
	Hd 7.53(A_2B_2dd, J=6, 3 Hz, 2H)	+0.03	
8	Ha 5.65(s, 2H)	+0.05	3.6—4.1(m, 2H)
	Hb 6.52(s, 2H)	+0.67	2.4—3.1(m, 6H)
	Hc 8.59(s, 2H)	−0.08	
	Hd 8.00(A_2B_2dd, J=7, 3.5 Hz, 2H)	+0.02	
	He 7.47(A_2B_2dd, J=7, 3.5 Hz, 2H)	0	
9	Ha 4.98(s, 2H)	+0.72	3.8—4.2(m, 4H)
	Hb 8.15(A_2B_2dd, J=7, 3.5 Hz, 4H)	+0.17	2.4—2.7(m, 4H)
	Hc 7.35(A_2B_2dd, J=7, 3.5 Hz, 4H)	+0.14	

a) In CCl_4. b) In CS_2 at −60 °C.

according to the reported methods.

Structure and NMR Spectra. The NMR spectral data of all the naphthaleno- and anthraceno-heterophanes **3**—**9** as well as [2.2]paracycloheterophanes **1** and **2** are summarized in Table 1. Heterophanes **3**—**9** show the signals of all the bridged methylene protons to be roughly divided into two groups of multiplets. Of these, the lower field multiplet is associated with the endo proton (see **15**) of methylenes attached to condensed aromatic ring for 1,4-bridged systems (**3**, **4**, **5**, **7**, and **8**) or both protons of methylenes attached to the same ring for 9,10-bridged systems (**6** and **9**). The downfield shift of these protons is explained by the large deshielding effect of the neighbouring condensed aromatic ring. Most aromatic protons show more or less upfield shifts and are reasonably assigned by considering



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Scheme 2.

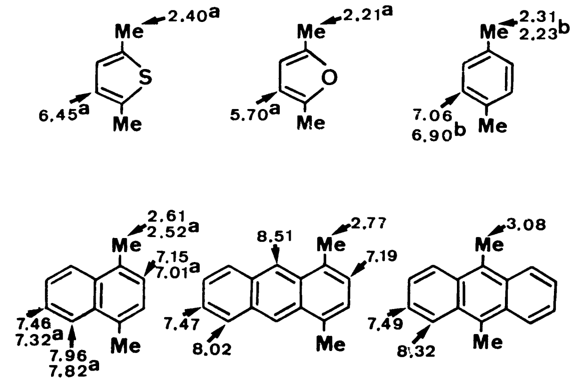


Fig. 1. NMR data of reference compounds, δ value in deuteriochloroform. a) in carbon tetrachloride. b) in carbon disulfide.

diamagnetic anisotropy of the opposite aromatic rings. As shown in Table 1, the magnitudes of the shifts are calculated using the chemical shifts (Fig. 1) of the aromatic protons of 2,5-dimethylfuran, 2,5-dimethylthiophene, *p*-xylene, 1,4-dimethylnaphthalene, 1,4-dimethylanthracene, and 9,10-dimethylanthracene as standards. The structural difference between **3** and **4** is unequivocally realized in the NMR spectra. The upfield shift (1.28 ppm) of thiophene proton Ha of **4** is drastic as compared with that of **1** (0.11 ppm) or **3** (0.07 ppm), suggesting that the proton is situated above the center of the opposite naphthalene ring. The naphthalene protons Hc and Hd show reasonable upfield shifts. However, Hb proton shows absorption at rather lower field. On the other hand, the shifts of Hc and Hd protons in **3** are negligible, the upfield shift (0.67 ppm) of Hb proton being marked and roughly the same as that (0.86 ppm) of Hb proton in **1**. These data are best accommodated by the *anti*-conformation for **3** and *syn*-conformation for **4**. The structure of 1,4-bridged anthracenothiophenophane **5** can be assigned to *anti*-conformation by a comparison of its NMR data with those of **3** and **4**. Thus the upfield shifts of Ha and Hb protons in **5** are identical with those of Ha and Hb in **3**, respectively. Small shielding effects on the Hc, Hd, and He protons are also explained by *anti* structure, but not by *syn* structure. The NMR pattern of 9,10-bridged anthracenothiophenophane **6** is in contrast to that of 1,4-bridged one **5**, and the chemical shifts are explained by considering both shielding effects of *anti*-form **3** and *syn*-form **4**.

A variable temperature NMR analysis of [2.2]paracyclofuranophane **2** exhibited the conformational flipping of the furan ring at room temperature and the fixation at low temperature (T_c, -39 °C).[1,7] Thus, 1,4-bridged naphthalenofuranophane **7** and anthracenofuranophane **8** are expected to show similar behavior, that is, consisting of one isomer at room temperature and two conformers, *syn* and *anti*, at low temperature. However, the NMR spectra exhibited no temperature-dependence, though the temperature was lowered to -100 °C. The upfield shifts of Hb protons of **7** and **8** are much larger than that of benzene proton of **2** at room temperature and close to that at ring fixation temperature. The furan protons Ha show no large shielding effect due to the fused aromatic ring. These data support the view that both **7** and **8** exist exclusively in the *anti*-conformation rather than in the *syn*-conformation owing to a π-π repulsive instabilization in the latter conformation.[8] The NMR spectrum of 9,10-bridged anthracenophane **9** is characterized by a symmetrical pattern, indicating a rapid flipping of the furan ring unlike **7** and **8**.

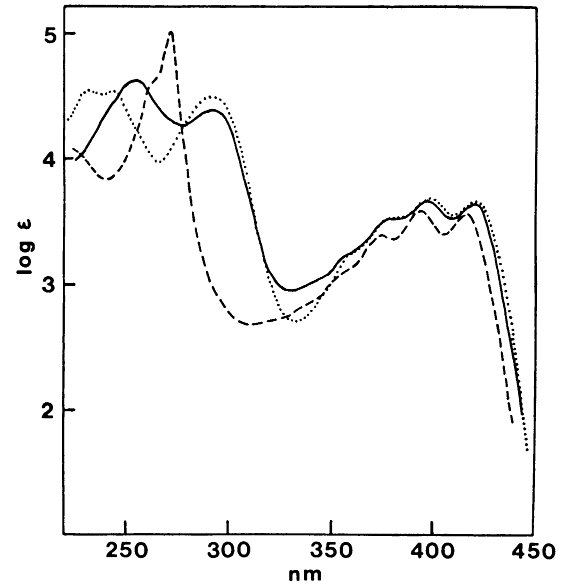


Fig. 2. Electronic spectra of **6** (——), **9** (----), and **18** (······) in tetrahydrofuran.

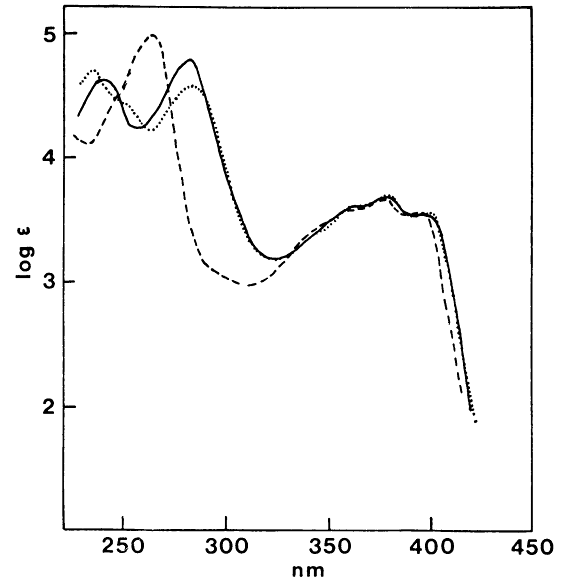


Fig. 3. Electronic spectra of **5** (——), **8** (----), and **17** (······) in tetrahydrofuran.

Electronic Spectra and Emission Spectra. Figures 2, 3, and 4 show the electronic spectra of naphthaleno- and anthraceno-heterophanes together with those of the corresponding paracyclophanes **16**—**18**.[9] All the absorption curves exhibit common features of cyclophanes, *viz.*, broadening, bathochromic and hyperchromic shifts,[10] caused by the transannular electronic interaction. A comparison of Fig. 2 with Fig. 3 shows that

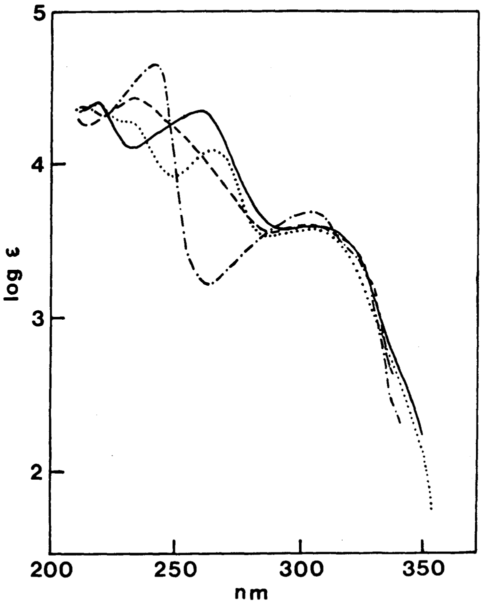
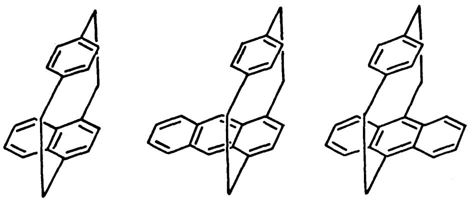


Fig. 4. Electronic spectra of **3** (——), **4** (----), **7** (—·—), and **16** (······) in cyclohexane.



16 **17** **18**

Scheme 3.

the interactions in 9,10-bridged anthracenophanes are more effective than those in 1,4-bridged analogues. The spectra of the thiophenophane are very similar to those of the corresponding paracyclophanes as in the case of multilayered paracyclothiophenophanes,[1] indicating a strong interaction between thiophene and condensed aromatic ring. The broad long wavelength band and the short wavelength band are due to ${}^1L_a$ and ${}^1B_b$ transitions of naphthalene or anthracene. The single band between them (260 nm for *anti*-form **3**, 281 nm for *anti*-form **5**, and 292 nm for **6**) is considered to be associated with a transition of the thiophene ring, showing a considerable bathochromic shift due to the strong interaction with the condensed aromatic ring, as compared with an absorption band (230 nm) of thiophene itself.[11] On the other hand, absorption of the thiophene ring in *syn*-form **4** exhibits no such large shift, being superposed on ${}^1B_b$ band of naphthalene at 233 nm. The difference between the *anti* and *syn* forms suggests that the d-orbitals of sulfur atom play an important role in the interaction, especially for the former.

Furan shows no absorption in the long wavelength region above 220 nm[11] In the present furanophanes, the absorption due to the furan ring is submerged by band ${}^1B_b$ of the naphthalene or anthracene ring. The presence of reasonable transannular electronic interaction in the furan series is supported by the broadening and bathochromic shift of the long wavelength band (${}^1L_a$ band). However, the shift value is smaller than that of the other cyclophanes. The interaction between furan ring and condensed aromatic ring is relatively weak.

Table 2. Emission spectra of layered heterophanes containing condensed aromatic nuclei at room temperature

Compound	Solvent	Fluorescence maximum
Thiophenophane		
3	EPA	342, 380 nm
5	THF	421,[a]437
6	THF	445, 460
Furanophane		
7	EPA	345,[a]357
8	THF	418,[a]432
9	THF	438, 455
Paracyclophane		
16	THF	418, 435
17	THF	440, 461
Naphthalene	Cyclohexane	322, 335
Anthracene	Cyclohexane	378, 400

a) Shoulder.

In order to obtain further informations on the interaction, emission spectra were measured (Table 2). Since the heteroaromatic ring shows about zero value of fluorescence quantum yield and, in the present cycloheterophanes, energy transfer is expected to take place transannularly from the excited state of the heteroaromatic ring to the lowest excited level of the condensed aromatic ring, only transitions ${}^1L_a \rightarrow {}^1A$ of the condensed aromatic rings are observed as fluorescence. Their fluorescence maxima show remarkable bathochromic shifts as compared with that of naphthalene or anthracene. The feature of the shifts agrees with that discussed on the electronic absorption spectra; the thiophenophanes and the 9,10-bridged anthracenoheterophanes show more effective interaction than the furanophanes and the 1,4-bridged analogues, respectively.

Experimental

Melting points are uncorrected. All the solvents are of reagent grade. NMR spectra were taken with a Hitachi-Perkin Elmer R-20 spectrometer (60 MHz) using tetramethyl silane as an internal standard. MS spectra were measured with a Hitachi RMU-7 spectrometer and UV spectra with a Hitachi EPS-3T spectrophotometer. Emission spectra were taken on a Hitachi MPF-2A spectrophotometer using 1×10^{-3}M degassed solution in tetrahydrofuran or EPA (5 : 5 : 2 volume ratio of ethyl ether–isopentane–ethanol) at room temperature. Emission spectra are uncorrected.

anti- *and* syn-*[2.2](1,4)Naphthaleno(2,5)thiophenophanes,* ***3*** *and* ***4***. 5-Methylthenyltrimethylammonium iodide **10** (8.2 g, 40 mmol) and (1-methyl-4-naphthylmethyl)trimethylammonium chloride **12** (5 g, 20 mmol) were dissolved in distilled water (*ca.* 300 ml) and passed through a column of strong anion exchange resin (Dowex 1-X8) which had been converted into hydroxide form with 3M sodium hydroxide solution. The eluted solution (*ca.* 700 ml) was mixed with xylene (150 ml) and phenothiazine (100 mg), water being removed by azeotropic distillation in a nitrogen atmosphere. After complete removal of water, reflux was continued for 7 h. The insoluble polymer was filtered and washed with xylene. The filtrate and the washings were combined and concentrated. The residue was taken up in benzene and subjected to column chromatography on silica gel. Elution with 1 : 9 benzene–hexane gave successively [2.2](2,5)thiophenophane,[2] *syn*-[2.2](1,4)naphthaleno(2,5)thiophenophane **4**, *anti*-[2.2](1,4)naphthaleno(2,5)thiophenophane **3**, and a mixture of *anti*- and *syn*-[2.2](1,4)naphthalenophanes.[3] Recrystallization of **3** from 1 : 1 hexane–benzene gave colorless prisms (222 mg, 4.2%), mp 182—183 °C.

MS *m/e* 264 (M^+). Found: C, 81.90; H, 6.04%. Calcd for $C_{18}H_{16}S$: C, 81.79; H, 6.10%.

Recrystallization of **4** from 1 : 1 hexane–benzene gave colorless plates (16 mg, 0.3%), mp 142—143 °C.

MS *m/e* 264 (M^+). Found: C, 81.59; H, 6.00%. Calcd for $C_{18}H_{16}S$: C, 81.79; H, 6.10%.

[2.2](1,4)Anthraceno(2,5)thiophenophane **5**. The method described above was used for the cross-breeding reaction of the quaternary hydroxides derived from 5-methylthenyltrimethylammonium iodide **10** (6 g, 29 mmol) and (1-methyl-4-anthrylmethyl)trimethylammonium bromide **13** (5 g, 14.5 mmol). The cross coupling product **5** was separated from homo coupling products, [2.2](2,5)thiophenophane,[2] [2.2.2](2,5)-thiophenophane,[1] *anti*-[2.2](1,4)anthracenophane,[4] and *syn*-[2.2](1,4)anthracenophane and its photoisomer[12] by careful column chromatography on silica gel using 1 : 9 benzene–hexane and recrystallized from 1 : 1 benzene–hexane to give pale yellow prisms (130 mg, 2.8%), mp 195 °C with decompn.

MS *m/e* 314 (M^+). Found: C, 84.25; H, 5.59%. Calcd for $C_{22}H_{18}S$: C, 84.05; H, 5.77%.

[2.2](9,10)Anthraceno(2,5)thiophenophane **6**. The method described for **3** and **4** was used for pyrolysis of the quaternary hydroxides derived from a mixture of two ammonium salts **10** (6 g, 29 mmol) and **14** (4.5 g, 15 mmol), giving cross coupling cyclophane **6**, together with homo coupling products, [2.2](2,5)thiophenophane,[2] [2.2.2](2,5)thiophenophane,[1] and [2.2](9,10)anthracenophane.[5,13] Column chromatography on silica gel with 1 : 9 benzene–hexane and recrystallization from pentane–dichloromethane gave pure greenish yellow needles **6** (260 mg, 5.5%), dec>100 °C.

MS *m/e* 314 (M^+). Found: C, 83.80; H, 5.57%. Calcd for $C_{22}H_{18}S$: C, 84.05; H, 5.77%.

[2.2](1,4)Anthraceno(2,5)furanophane **8**. The method described for **3** and **4** was used for the pyrolytic reaction of the quaternary hydroxides derived from a mixture of two ammonium salts **11** (8 g, 28 mmol) and **14** (5 g, 14 mmol), the desired cyclophane **8** being obtained. After removal of homo coupling cyclophanes by column chromatography, recrystallization of **8** from 1 : 1 benzene–hexane gave pale yellow prisms (34 mg, 0.8%), dec>154 °C.

MS *m/e* 298 (M^+). Found: C, 88.32; H, 5.97%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%.

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