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REGARDING THE STRUCTURE OF [2.2](2,6,2′,7′)-NAPHTHALENOPHANE-1,11-DIENE AND ITS CONFORMATIONAL MOBILITY[1]

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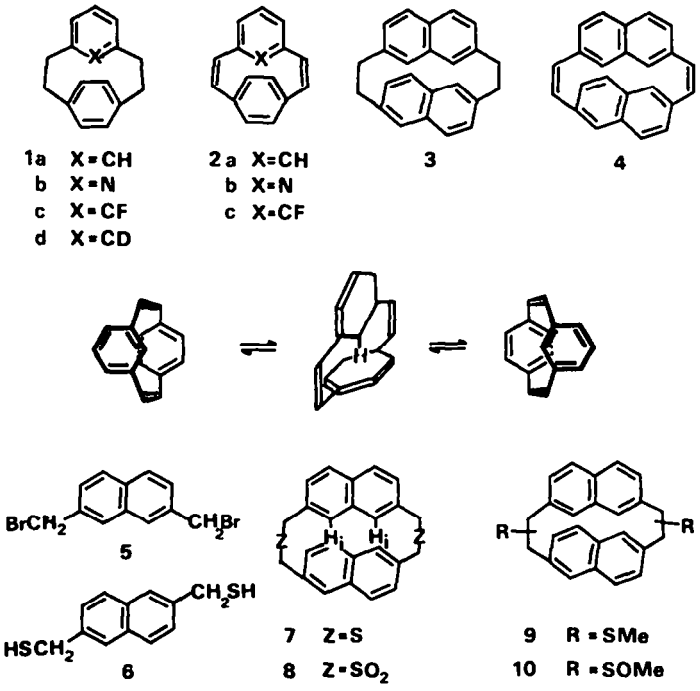
Abstract—The synthesis of [2.2](2,6,2′,7′)naphthalenophane - 1,11 - diene **4** has been effected by pyrolysis of the bis-sulphoxide **10**, in turn prepared by a ring-contraction procedure of the [3.3]dithiacyclophane **7**. The diene **4** has been fully characterized by spectroscopic and chemical methods. The variable-temperature ^{1}H NMR spectra of the diene **4** indicated that the compound undergoes conformational flipping in solution and has a conformational energy barrier $\Delta G^{\ddagger}_{T_c}$ 14.9 kcal mol^{-1} and a coalescence temperature T_c 38° for the internal protons H_c and H_c' (at 100 MHz). These results differ from those previously recorded. A complete assignment of the pmr spectrum of the cyclophane diene **4** at 270 MHz is presented together with the spectrum of the corresponding saturated [2.2]cyclophane **3**.

Considerable information regarding the conformational flipping of metaparacyclophanes (for example, **1** and **2**) has been obtained[2] and rationalized in terms of, (i) the energy-barrier requirements of a given substituent, X, and (ii) the hybridization of the bridging carbons between the two aromatic rings. Generally, it has been found that the unsaturated analogs **2** undergo a higher rate of conformational flipping than do the corresponding saturated compounds **1** and in one extreme case,[2c] compounds **1b** and **2b**, it has been found that the ground state of the diene **2b** is, in fact, one in which the aromatic moieties lie perpendicular to each other. It is thought that the lower energy-barrier to conformational flipping observed in the dienes is due to various factors[2c] including, (i) larger C–C–C bond angles within the bridging function which increases the distance between the interacting aromatic rings, (ii) stabilization of the transition state by conjugative interaction between the *meta*-bridged ring and the olefinic linkages, and (iii) a decrease in hydrogen–hydrogen non-bonded interactions along the bridges in the transition state.

As part of our investigations into cyclophanes derived from naphthalenes, we undertook the synthesis of [2.2](2,6,2′,7′)naphthalenophane **3** and [2.2]-(2,6,2′,7′)naphthalenophane - 1,11 - diene **4**, compounds which are closely related in structure to the [2.2]*metaparacyclophanes* (**1** and **2**) with respect to the relative stereochemistry of the constituent aromatic rings. The *metaparacyclophanediene* **2a** undergoes conformational flipping as shown in Scheme 1 and we anticipated that the naphthalenophanediene **4** should undergo similar conformational changes. We were particularly interested



Scheme 1.

to determine the energy barriers to flipping for both 3 and 4 and to relate these to those values previously determined for compounds 1a and 2a.

During the course of this work, Boekelheide and Tsai[3] reported their results on a series of naphthalenophanes also based on the 2,6,2',7'-substitution pattern and which differed markedly both to the initial results that we had obtained, and to the general conclusions regarding saturated and unsaturated *metaparacyclophanes* indicated above. We record here the synthesis and characterization of [2.2](2,6,2',7') - naphthalenophane - 1,11 - diene 4 and the investigation of its conformational mobility as determined by variable-temperature proton magnetic resonance studies.

Synthetic route

The synthetic approach chosen was basically similar to that of Boekelheide and Tsai[3] and involved firstly the formation of the dithiacyclophane 7 in 68% yield by reaction of the 2,7 - bis(bromomethyl)naphthalene[4] 5 with the dianion of 2,6 - bis-(mercaptomethyl)naphthalene[5] 6 under conditions of high dilution. Compound 7 was ring-contracted to the [2.2]cyclophane 9 under Wittig reaction conditions[6] (*n*-butyl lithium followed by methyl iodide). The spectral data were consistent with the compound being a mixture of the possible structural/stereo isomers. Oxidation of 9 with sodium periodate in aq. methanol/dichloroethane gave a high yield of the bissulphoxide 10 (again, as a mixture of isomers) and this on pyrolysis at 300°/5 × 10^{-4} mm yielded [2.2](2,6,2',7')naphthalenophane - 1,11 - diene 4 as light yellow plates, m.p. 134–135°, in 40% yield. The generation of the diene by pyrolysis of the sulphoxide was the one major difference in our synthetic route to the previously recorded attempt.[3] We also prepared the bis-sulphone 8 and converted it to the [2.2]-cyclophane 3 by pyrolytic elimination of the $-SO_2-$ functions, and found the physical properties of the latter two compounds to be largely in agreement with those previously published.[3]

NMR data

At 270 MHz and −40°, the diene 4 dissolved in acetone-d_6 showed a well resolved first-order proton NMR spectrum (Fig. 1). The spectrum consisted of four sets of magnetically non-equivalent protons, each set consisting of resonances due to to an ABX system and a vinylic proton as shown in the partial structure 11, characteristic of that portion of a 2-substituted naphthalene. We have designated the protons in the 2,7-substituted ring (top ring in structure 4a) as being the a, b and c protons, those in the 2,6-substituted ring as being the d, e and f protons, and the vinylic protons as v and w. It was possible to assign most of the resonances by inspection (Table 1), and those in doubt were subsequently assigned by comparison with the high temperature spectrum (Fig. 2a) and also by selective homonuclear decoupling at low temperatures. In particular, homonuclear decoupling established the relationship between the peaks assigned to (i) Hc and Hc', (ii) Hd and Hd', (iii) He and He' and (iv) Hf and Hf'. There is some doubt in the assignment of the Hv/v' and Hw/w' protons. By direct comparison with the vinylic protons of [2.2](2,7)naphthalenophane - 1,11 - diene 12[7] (Hv, δ 6.57) and those of [2.2](2,6)naphthalenophane - 1,11 - diene 13[5] (Hv, δ 7.20) we suggest that the high-field pair of doublets Hv/v' are adjacent to the 2,7-disubstituted ring and the low-field pair Hw/w' are adjacent to the 2,6-disubstituted naphthalene.

At temperatures greater than 100° the proton NMR spectrum (100 MHz) of the diene 4 (in DMSO-d_6) simplified considerably into a first-order spectrum containing approximately half the number of resonances (Fig. 2a). Once again, the assignments could be made by inspection and are listed in Table 2 together with the chemical shift values for the calculated spectrum obtained by arithmetic averaging of the chemical shifts of the appropriate interchanging pairs as seen in the frozen conformers at −40°. The calculated chemical shifts deviate from the observed values by an average of 0.09 ppm downfield for all protons except Hc. We can only attribute this to a solvent shift in changing from

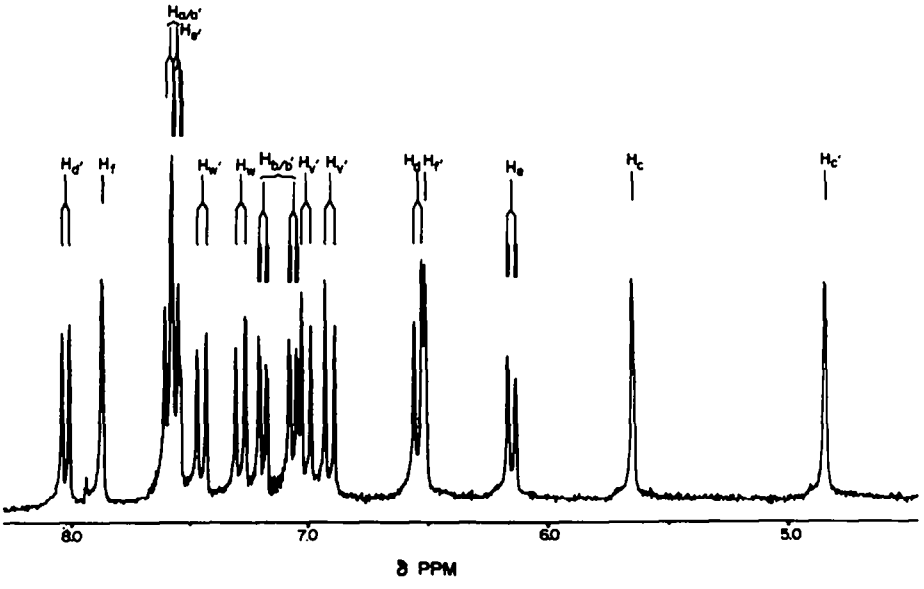


Fig. 1. 270 MHz PMR spectrum of the diene 4 at −40° in acetone-d_6.

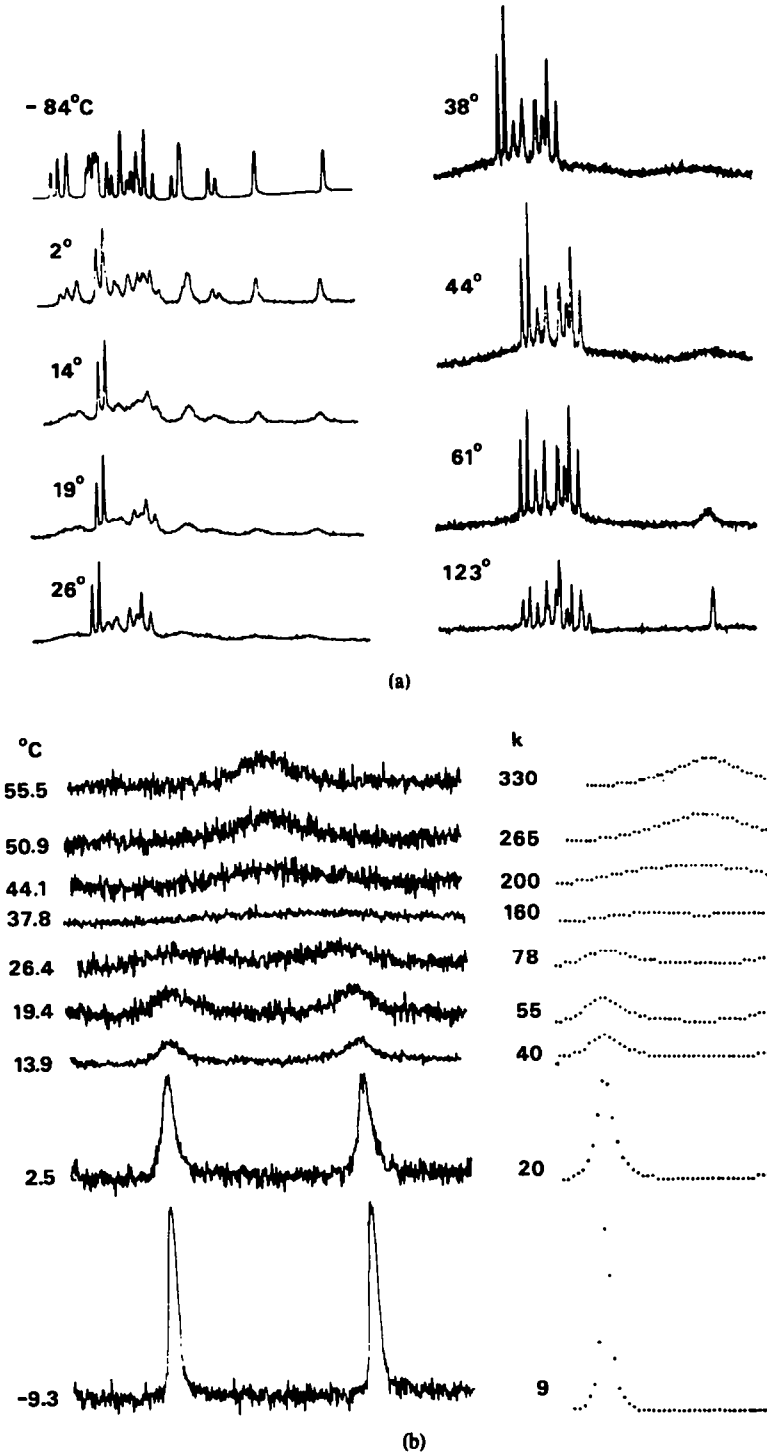


Fig. 2. (a) Variable temperature PMR spectra of the diene 4 at 100 MHz in acetone-d_6. (The spectrum at 123° was determined in DMSO-d_6.) (b) Observed and calculated spectra for the Hc and Hc' protons.

acetone-d_6 at low temperatures to DMSO-d_6 at high temperatures. It is of interest to note that only the peripheral protons experience the solvent shift; the two "inner protons" Hc/c' are apparently unperturbed by the effects of solvents. The coincidence of the calculated and observed chemical shifts in the high temperature spectrum further substantiates our assignments.

A series of variable temperature spectra of the diene 4 were determined at 100 MHz and over a temperature range of −9° to 55° and at intervals of 5° to 12°. These spectra are shown in Fig. 2 together with calculated spectra for the exchange-broadened signals of the Hc and Hc' protons.

The 100 MHz proton NMR spectrum of the

Table 1. 270 MHz PMR spectrum of diene 4 at −40° in acetone-d_6

δ		J(Hz)	Assignment
4.85	bs		Hc'
5.65	bs		Hc
6.15	dd	8.5, 1.5	He
6.51	bs		Hf'
6.54	d	8.6	Hd
6.91	d	10.8	Hv/v'
7.01	d	10.8	Hv'/v
7.07	dd	8.4, 1.7	Hb/b'
7.19	dd	8.4, 2.0	Hb'/b
7.28	d	10.8	Hw/w'
7.45	d	10.8	Hw'/w
7.56	dd	8.0, 1.6	He'
7.57	d	8.0	Ha/a'
7.60	d	8.0	Ha'/a
7.88	bs		Hf
8.03	d	8.6	Hd'

Table 2. 100 MHz PMR spectrum of diene 4 at 123° in DMSO-d_6

Observed				*Calculated δ	
δ		J(Hz)	Assign-ment	Arithmetic Average	Corrected Average**
5.24	bs		Hc	5.25	5.25
6.78	dd	8.5,2	He	6.86	6.77
6.89	d	11	Hv	6.96	6.87
7.04	dd	8.5,1.7	Hb	7.13	7.04
7.09	bs		Hf	7.20	7.11
7.17	d	8.1	Hd	7.29	7.20
7.30	d	10.7	Hw	7.37	7.28
7.49	d	8.8	Ha	7.59	7.50

* Calculated δ values are derived by averaging the δ values of the appropriate interchanging pairs of protons as observed at −40°C.

** Determined by subtracting 0.09ppm (due to solvent shift) from the Arithmetic Average for all protons other than Hc.

[2.2](2,6,2',7')naphthalenophane 3 at room temperature is recorded in Fig. 3 (which shows only the aromatic region and the aromatic protons have been designated as for the diene 4). The chemical shifts are included in the Experimental and the overall spectrum and assignments compare favorably with the other spectra already presented.

DISCUSSION

The variable temperature proton NMR spectra of the diene 4 (Fig. 2) clearly shows that the molecule is undergoing conformational flipping. The two singlets at δ 4.85 and 5.65 suggest that the protons Hc and Hc' are considerably shielded and that the Hc' proton lies closer towards the centre of the π-cloud of the opposed 2,6-naphthalene ring than does Hc. On raising the temperature, the signals due to Hc and Hc' broaden and coalesce at 38°, and are observed as a single peak above this temperature. The diene molecule 4 must undergo conformational isomerism as shown in Scheme 2 in which one conformer **4a** interconverts to the other possible conformer **4c** via a transition state **4b** which has a C_2 rotation axis of symmetry.

From the exchange rates (k) calculated by line-shape analysis[8] using a two-site exchange program, we have calculated $\Delta G^{\ddagger}_{25°} = 14.9 \pm 1.0$ kcal mol^{-1}, $\Delta H^{\ddagger} 9.2 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17.3 \pm 1.0$ e.u. The value of $\Delta G^{\ddagger}$ is compared with those obtained for the related cyclophanes **1a**, **2a** and **3** in Table 3. It is apparent from Table 3 that cyclophanes 3 and 4 show the same general conformational behaviour as has been previously obser-

Table 3. Conformational energy barriers ($\Delta G^{\ddagger}$)

Compound	Tc°C (100MHz)	$\Delta G^{\ddagger}$ kcal.mol^{-1}		Ref.
[2.2]Metaparacyclophane (1a)	157	20.6	(157°C)	[2b,10]
[2.2]Metaparacyclophane-1,9-diene (2a)	-96	8.3	(-96°C)	[11]
Naphthalenophane-1,11-diene (4)	38	14.9	(25°C)	
Naphthalenophane(3)	160	20.6	(25°C)	[3]

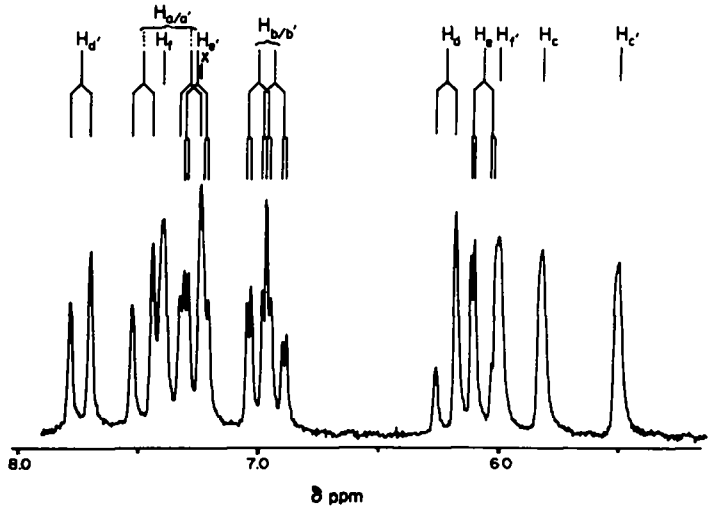
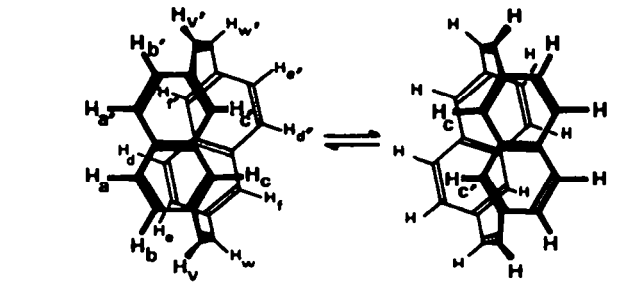
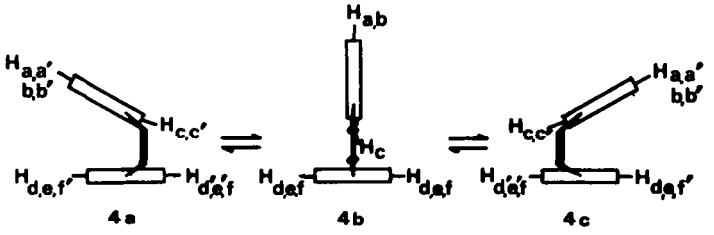


Fig. 3. 100 MHz PMR spectrum of the cyclophane 3 at 25° in $CDCl_3$ (X is due to $CHCl_3$).



4a 4c



4a 4b 4c

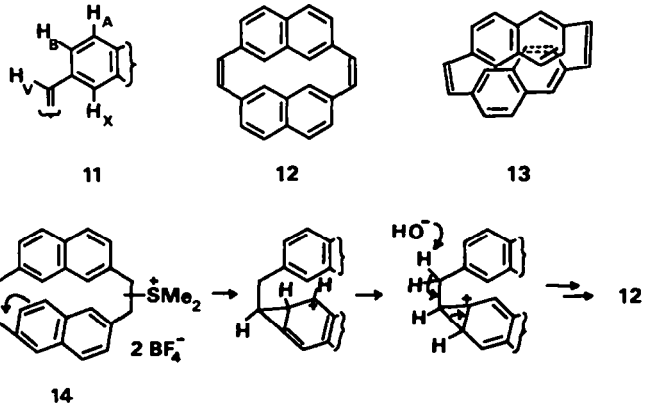
Scheme 2.

ved for similar pairs of compounds in that the diene **4** has a lower conformational energy barrier than the corresponding molecule having sp^3 bridging carbons **3**. Compound **4** also has a larger energy barrier to flipping than the diene **2a** in the *metapara*cyclophane series. This would indicate an increase in the steric crowding between the two internal aromatic protons Hc/c' with the aromatic π-electron cloud which is not effectively relieved by any increase in the flexibility of the molecule due to small incremental changes in bond angles and/or bond lengths within the larger naphthalene moieties.

The proton NMR data for the saturated cyclophane **3** was in accord with that of VB and CHT.[3] There is an overall similarity between the spectra of compounds **3** and **4**, (Figs. 3 and 1). The one major difference between the spectra is that the resonance frequencies for the aromatic protons of **3** encompass a range of 2.2 ppm whereas those of **4** are dispersed over 3.2 ppm. This, together with the relative downfield shift of the Hc/c' protons in compound **3** suggests that the two naphthalene rings in **3** are closer to being vertically stacked than in the case of **4**. Molecular models also support this conclusion.

The proton NMR spectrum of the Hofmann elimination product m.p. 247–248° reported by VB and CHT[3] suggested to us that they had obtained instead, [2.2]-(2,7)naphthalenophane - 1,11 - diene **12** which has a recorded m.p. 239–242°.[7] A direct comparison of these compounds has shown this to be correct.[9]

The isolation of the [2.2](2,7)naphthalenophane - 1,11 - diene **12**, from the [2.2](2,6,2',7')bis(methylfluoroborate) salt **14** precursor by a base initiated 1,2-elimination reaction[3] poses an interesting problem. The product **12** which was obtained in only 6% yield by heating the salt **14** with ethanolic KOH under reflux for 14 h, may well have resulted from a 1,2-rearrangement reaction through a [4.1.0]bicycloheptadienyl carbonium ion (Scheme 3) although this is largely open to conjecture. Rearrangements of cyclophanes are not without precedence; for example, the acid-catalyzed rearrangement of [2.2]-paracyclophane to [2.2]metaparacyclophane is a useful method of preparation of the latter compound.[12] From



11 12 13

14 12

Scheme 3.

the mass spectral data of the diene 4, we suspect that the first formed radical cation rearranges with a consecutive loss of four hydrogen atoms to produce the radical cation of coronene, and such a sequence would probably also involve [2.2](2,7)naphthalenophane intermediates.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were determined with a Perkin–Elmer 257 spectrophotometer. Proton NMR spectra at 270 MHz were determined on a Bruker HX-270 spectrometer at the National NMR Centre, ANU, Canberra, (Dr. A. J. Jones). A JEOL PS-100 PFT spectrometer was used to determine, (a) carbon magnetic resonance spectra at 25 MHz, (b) variable temperature proton magnetic resonance at 100 MHz, and the probe temperatures were measured with a calibrated thermistor. The high resolution mass spectra were determined on a JEOL D-100 double focusing spectrometer at 75 eV. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

2,13 - *Dithia*[3.3](2,6,2',7')*naphthalenophane* 7. The title compound was prepared in a similar fashion to that previously recorded[3] and was obtained as white needles, m.p. 230–231 (yield 68%); PMR ($CDCl_3$), δ 3.73, s (4H, $-CH_2-S-$); 4.06, s (4H, $-CH_2-S$); 5.79, bs (2H, aromatic H_i); 7.13–7.55, m (10H, aromatic H). {^{1}H} CMR ($CDCl_3$/DMSO-d_6), singlets at 36.2, 38.1 (benzylic C) 125.0, 126.3, 126.6, 126.8, 127.3 (2 × C) (tertiary C); 128.8, 130.9, (Ç–CH_2–S); 132.0, 134.5, 137.0 (aromatic ring junction C). MS: $M^+ + 2$ at *m/e* 374 (9% rel. abund.), $M^+ + 1$ 373 (19), M^+ 372.1009 (63) [$C_{24}H_{20}S_2$ requires: 372.1006] and fragmentation ions at 187 (22), 186 (31), 156 (52), 155 (100), 154 (14) and 141 (22). (Found: C, 77.23; H, 5.38. Calc. for $C_{24}H_{20}S_2$: C, 77.38; H, 5.41%).

1,11 - (*or* 1,12 -)*Bis*(*methylthio*)[2.2](2,6,2',7')-*naphthalenophane* 9. *n*-Butyl lithium in ether (5 mmol) was added to a soln of the dithiacyclophane 7 (750 mg, 2 mmol) in dry THF (15 ml) under N_2 at 25°, and the mixture was stirred for 3 min. Methyl iodide (1.42 g, 10 mmol) was added which caused rapid decolourization of the solution. After the addition of water, the mixture was extracted with CH_2Cl_2. The dried extracts were concentrated and the residue chromatographed on silica gel (2.5 mm plate/hexane–benzene) yielding one main band from which was isolated 1,11 - (or 1,12 -)-bis(methylthio)[2.2](2,6,2',7')naphthalenophane 9 (690 mg, 86%) as a pale yellow glass m.p. 64–65°. PMR ($CDCl_3$), δ 1.99–2.26, m (6H, CH_3–S); 2.34–4.12, m (6H, benzylic H); 5.51–6.45 (5H; shielded aromatic H); 6.98–7.89 (7H; aromatic H). {^{1}H} CMR ($CDCl_3$), δ 15.4 (CH_3–S); singlets at 42.44–44.4 (benzylic $-CH_2-$) and 51.0–54.5 (benzylic C's); and singlets at 122.5–137.4 (aromatic C). MS: $M^+ + 2$ at *m/e* 402 (14% rel. abund.), $M^+ + 1$ 401 (31), M^+ 400.1319 (100) [$C_{26}H_{24}S_2$ requires 400.1319] and fragmentation ions at 385 (13), 353 (25), 246 (46), 245 (18), 231 (40), 201 (42), 200 (68) and 185 (32). (Found: C, 77.54; H, 6.09. Calc. for $C_{26}H_{24}S_2$: C, 77.97; H, 6.04%).

1,11 - (*or* 1,12 -)*Bis*(*methylthio*)[2.2](2,6,2',7')-*naphthalenophane* S,S' - *dioxide* 10. The compound 9 (300 mg, 0.75 mmol) and sodium periodate (320 mg, 1.5 mmol) were dissolved in a mixture of MeOH (20 ml), H_2O (1.5 ml) and $ClCH_2CH_2Cl$ (6 ml) and the solution was stirred for 20 hr at 25°. Excess water was added and the mixture extracted with 1,2-dichloroethane. Concentration of the dried extracts yielded the S,S'-dioxide 10 as a pale yellow glass (300 mg, 93%). PMR ($CDCl_3$), δ 2.52–2.80, m (6H, CH_3SO-); 2.97–4.24, m (6H, benzylic CH and CH_2); 5.41–6.43, m (5H, shielded aromatic H); 6.93–7.97, m (7H aromatic H). {^{1}H} CMR ($CDCl_3$), groups of singlets at δ 34.9–43.4 (ÇH_3–SO–) 68.9–72.5 (–SO–ÇH–); 121.9–135.6 (aromatic C). IR, ν_{max} 1040 cm^{-1} (strong, S = 0). MS: no M^+ could be observed, *m/e* 306 (8% rel. abund.), 305 (28), 304 (100) [$M^+ - 2 \times CH_3SOH$], 303 (10), 302 (15), 301 (16), 300 (21), 276 (13) and 150 (23). (Found: C, 70.0; H, 5.58. Calc. for $C_{26}H_{24}O_2S_2$: C, 72.19; H, 5.59%).

[2.2](2,6,2',7')*Naphthalenophane* - 1,11 - *diene* 4. The disulphoxide 10 (200 mg, 0.46 mmol) was heated in a silica tube at 500°/5 × 10^{-4} mm for 30 min. The pale yellow oil which condensed on the cool portion of the silica tube was chromatographed on a silica gel plate (2.5 mm) with hexane–benzene. The major band yielded the diene 4 as light yellow plates (55 mg, 40%) m.p. 134–135°. PMR (C_3D_6O at −40°), see Table 1. PMR (DMSO-d_6 at 123°), see Table 2. MS: $M^+ + 2$ at *m/e* 306 (5% rel. abund.), $M^+ + 1$, 305 (29), M^+ 304.1252 (100) [$C_{24}H_{16}$ requires: 304.1252] and fragmentation ions at 276 (25) and 150 (17). (Found: C, 94.80; H, 5.39. Calc. for $C_{24}H_{16}$: C, 94.70; H, 5.30%).

2,2,13,13 - *Tetraoxo* - 2,13 - *dithia*[3.3](2,6,2',7') - *naphthalenophane* 8. The dithiacyclophane 7 (300 mg, 0.81 mmol) was dissolved in a mixture of glacial acetic acid (25 ml) and benzene (25 ml) at 100°. Hydrogen peroxide (35%, 2 ml) was added over 30 min. The mixture was stirred for 6 hr, cooled, filtered and the powder was washed with benzene, methanol and dried at 100°/0.1 mm to yield the bis-sulphone 8 (330 mg, 94%) as a white powder m.p. > 340°. MS: $M^+ + 2$ at *m/e* 438 (0.7% rel. abund.), $M^+ + 1$ 437 (1.4), M^+ 436.0807 (6) [$C_{24}H_{20}O_4S_2$ requires: 436.0803], and fragmentation ions at 309 (13), 308 (50), 169 (24), 155 (100), 154 (86) and 153 (31). IR (Nujol): ν_{max} 1110 and 1310 cm^{-1} (strong, sharp, $-SO_2-$). Due to the compound's low solubility, no NMR data could be obtained. (Found: C, 66.29; H, 4.58. Calc. for $C_{24}H_{20}O_4S_2$: C, 66.03; H, 4.62%).

[2.2](2,6,2',7')*Naphthalenophane* 3. This compound was prepared after the method of Boekelheide[3] and was obtained as pale yellow prisms m.p. 181–182° (lit.[3] 170–172°). MS: $M^+ + 2$ at *m/e* 310 (7% rel. abund.), $M^+ + 1$ 309 (29), M^+ 308.1567 (100) [$C_{24}H_{20}$ requires: 308.1565] and fragmentation ions at 155 (25), 154 (89), 153 (40) and 152 (24). PMR ($CDCl_3$), δ 2.48–3.51, symmetrical m ($-CH_2-$, two superimposed ABCD patterns), 5.51, bs (Hc'), 5.83, bs (Hc), 6.01, bs (Hf'), 6.07, dd (*J* 8.3 and 1.5 Hz, He) 6.23, d (*J* 8.3 Hz, Hd), 6.94, dd (*J* 8.3 and 1.7 Hz, Hb/b'/e'), 7.01, dd (*J* 8.3 and 1.7 Hz, Hb'/e'/b'), 7.27, dd (*J* 8.3 and 1.7 Hz, He'/b/b'), 7.29, d (*J* 8.4 Hz, Ha/a'), 7.41, bs (Hf), 7.49, d (*J* 8.5 Hz, Ha/a'), 7.75, d (*J* 8.3 Hz, Hd). (Found: C, 93.35; H, 6.60. Calc. for $C_{24}H_{20}$, C, 93.46; H, 6.54%).

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