Synthesis and conformational studies of 2,11-dithia[3]metacyclo-[3](1,3)pyrenophanes: the ring current interactions derived from pyrene ring

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A series of 2,11-dithia[3]metacyclo[3](1,3)pyrenophanes are obtained by the coupling reaction of the corresponding 1,3-bis(bromomethyl)pyrene and bis(sulfanylmethyl)benzenes in ethanol under the high dilution conditions. The conformational studies of dithia[3]metacyclo[3](1,3)pyrenophanes as well as the ring current interactions derived from pyrene ring are described.

Keywords: cyclophanes, pyrenes, conformations, ring current effect, charge transfer complex

Although many cyclophanes having a pyrene skeleton and related compounds have been prepared,[1–9] there have been few investigations of their chemical nature in spite of a large number of reports on their spectroscopic properties. Such investigation has been limited, because the preparation of pyrene having the substituents at 1- and 3-positions is not easy. We have reported the $AlCl_3$-catalysed acetylation of 2,7-di-*tert*-butylpyrene with acetyl chloride using the *tert*-butyl group as a positional protective group to afford only the 4,9-diacetylated product, 4,9-diacetyl-2,7-di-*tert*-butylpyrene[10] and this strategy is also suitable for the preparation of 1,3-disubstituted pyrenes, which afforded convenient starting materials for the preparation of 1,3-bridged benzenopyrenophanes, 8-substituted [2]metacyclo[2](1,3)pyrenophanes.[11] Mitchell and his coworker have reported that 9,18-dimethyl-2,11-dithia[3.3]MCP (MCP = metacyclophane) exists in *syn*-and *anti*-conformers, which do not interconvert below 200 °C.[12–16] Vögtle and Schunder[17] have made extensive studies of *syn-anti* conversions in other dithia[3.3]MCPs, especially in relation to the size of the substituents. Although the study on the *syn* and *anti* conformers of dithia[3.3]MCPs was reported, the conformational analysis of dithia[3.3]MCPs having an expanded π-conjugated aromatic ring in spite of the much larger ring current interactions of π-conjugated system. Freezing conformational equilibrium, which is the common method of analysis, is often not effective in highly flexible molecules. Fukazawa *et al.*[18] developed a useful and very reliable method for the conformational analysis of flexible molecules using a combination of molecular mechanics calculations and chemical shift simulation of certain protons without the use of the freezing technique.

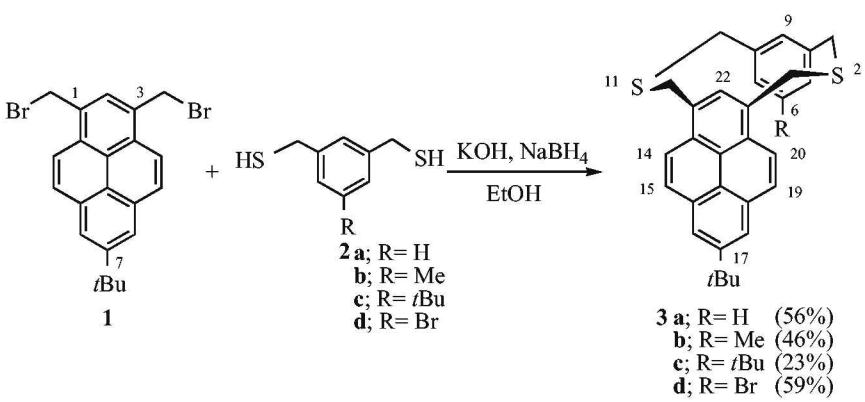
Although there exist two possible conformational isomers in dithia[3.3]MCPs,[8,9] the conformations regarding dithia[3.3]MCPs having a pyrene skeleton are not known so far. Thus, there is substantial interest in investigating the substituent effects at the 6 position on the conformations of the dithia[3]metacyclo[3](1,3)pyrenophanes **3**. We describe here the synthesis of pyrenophanes such as the titled MCPs using the above method, as well as studies of their conformation by the ring current interactions derived from pyrene ring.

Results and discussion

1,3-Bis(bromomethyl)-7-*tert*-butylpyrene (**1**) was prepared according to our reported procedure[11] from pyrene using *tert*-butyl group as a positional protecting group on the aromatic ring. 1,3-Bis(sulfanylmethyl)benzenes **2** are prepared according to the reported procedure[19] starting from the corresponding 1,3-bis(bromomethyl)benzenes, which are brominated with *N*-bromosuccinimide in the presence of 2,2'-azobis(2,4-dimethylpentanenitrile) in a methylene dichloride solution, followed by treatment with thiourea and potassium hydroxide in ethanol.[20–24]

The dithia[3]metacyclo[3](1,3)pyrenophanes **3** were synthesised by coupling the 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **1** with bis(sulfanylmethyl)benzenes **2** under highly diluted conditions in 10% ethanolic potassium hydroxide in the presence of a small amount of sodium borohydride as shown in Scheme 1.[20–24] 2,11-Dithia[3]metacyclo[3](1,3)pyrenophanes **3** are obtained and the yields of **3** are compiled in Scheme 1.

The structures of **3** has been elucidated by elemental analyses and spectral data. For instance, the mass spectral data for **3b** (M^+ = 466) strongly support cyclic structure. It was assigned the *syn*-stereochemistry **3b** on the basis of its ^1H NMR spectrum by comparison to the known *syn*-cyclophanes **4** and **5**, since the 9- and 22-aryl proton of **3b**



Scheme 1

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appear at δ 6.50 and 6.73 ppm (those for **4** are at δ 6.82 ppm; those for **5** are at δ 6.73 and 6.94 ppm),[25,26] whereas if **3b** existed as the *anti* conformer they might be expected to be shielded by the opposite ring to *ca* δ 5.[11] Furthermore, the 5-, 7-aryl hydrogens and methyl protons at the 6-position can clearly be seen to be shielded at δ 6.68 and 1.67 ppm by the adjacent ring, a common consequence of face-to-face benzene ring.[26] The same upfield shift of the 5-, 7-aryl hydrogen was observed in **3a**, **3c** and **3d**. Also one of the *tert*-butyl protons of **3c** was observed at upper field, δ 0.58 ppm due to the strong shielding effect of pyrene ring.[27–29] These observations strongly suggest that compounds **3a–d** all adopt *syn*-conformations.

All the bridge protons of the above-prepared cyclophanes **3** are observed as a singlet in ^{1}H NMR spectra at 25 °C. The conformation of **3** has been evaluated by dynamic ^{1}H NMR spectroscopy. However, for instance, the protons of the ArCH_2SCH_2Ar methylene groups of 6-methyl-2,11-dithia [3]metacyclo[3](1,3)pyrenophane **3b** appear each as a singlet even below –60 °C ($CDCl_3/CS_2$ 1/3), and the rate of conformational ring flipping of **3b** is faster than the NMR time scale above this temperature. Similar findings were obtained in dithia[3]metacyclo[3](1,3)pyrenophanes **3a, 3c** and **3d**. These results indicate that the dithia[3]metacyclo[3] (1,3)pyrenophanes **3** are highly flexible molecules like dithia[3.3]MCPs.[17,25,26]

In order to obtain more detail informations concerning on the conformations of 2,11-dithia[3]metacyclo[3](1,3) pyrenophanes **3**, we have prepared 9-methoxy derivative **7** in 52% yield by coupling the 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **1** with 2,6-bis(sulfanylmethyl)-4-methylanisole **6** under highly diluted conditions in 10% ethanolic potassium hydroxide in the presence of a small amount of sodium borohydride as shown in Scheme 2.

In the case of **7**, the methyl protons at the 6 position appeared up-field shifts at δ 0.97 ppm due to the ring current effect of the opposite pyrene ring. The ^{1}H NMR spectrum of the CH_2SCH_2 bridge of **7** showed a pair of doublets at δ 3.52, 4.42 ppm (J = 14.1 Hz) and δ 4.29, 4.57 ppm (J = 15.0 Hz) at room temperature. With increasing temperature in DMDO-d_6, the doublets do not coalesce below 150 °C, respectively, and the energy barriers of flipping are both above 25 kcal mol^{-1}. These observations strongly suggest that compound **7** also

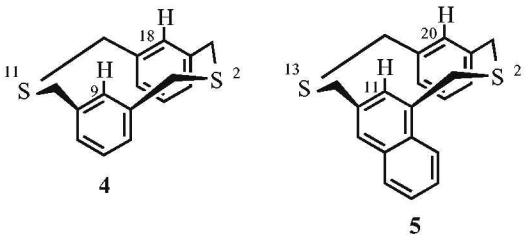
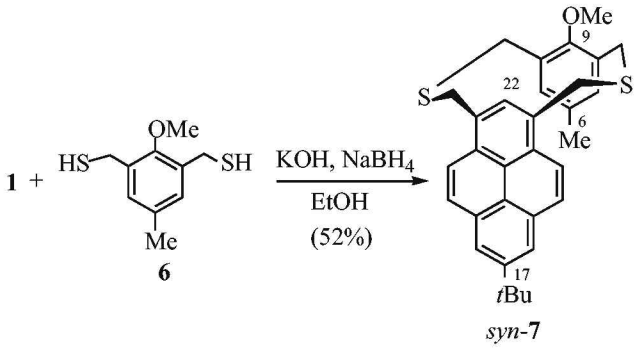


Fig. 1 Structures for [3.3]metacyclophane **4** and [3]metacyclo-[3]naphthalenophane **5**.



Scheme 2

adopts rigid *syn*-conformation. However, the internal pyrene proton (H_{22}) and methoxy protons at 9 position appeared at δ 7.65 ppm and δ 3.65 ppm different from those observed in 2,11-dithia[3]metacyclo[3](1,3)pyrenophanes **3a–d**. No ring current effects of the opposing benzene and pyrene ring was observed. These finding might attributable to the different structures between **3** and **7**.

The chemical shifts (δ) of the benzene protons and pyrene protons as well as the substituent (R) protons at 6-position of 2,11-dithia[3]metacyclo[3](1,3)pyrenophanes **3a–d** and *syn*-**7** are compiled in Table 1. The chemical shift differences (Δδ = $\delta_{cyclophane} - \delta_{reference}$) with the aromatic protons at position 2 of 1,3-dimethyl-5-substituted benzenes **8** and 7-*tert*-butyl-1,3-dimethylpyrene **9** are also summarised in Table 1. The ring current effect of the opposite aromatic ring on the internal protons can be judged by the values of the chemical shift differences (Δδ).[27–29] As shown in Table 1, the internal pyrene proton (H_{22} for **3a** and H_{22} for **3b**) on the pyrene ring is clearly shifted upfield (Δδ_H –0.86 ppm for **3a** and –0.90 ppm for **3b**) by the ring current in the opposite benzene ring.

Also, the internal proton at 9-position of **3a** and **3b** shows upfield shifts (Δδ_{H9} –0.19 for **3a** and –0.28 for **3b**) due to the ring current based on the pyrene ring of **3**. The value of Δδ_{H9} of cyclophane having 6-*tert*-butyl group **3c** (Δδ_{H9} –0.03) is smaller than those of cyclophanes **3a** and **3b**. This fact suggests

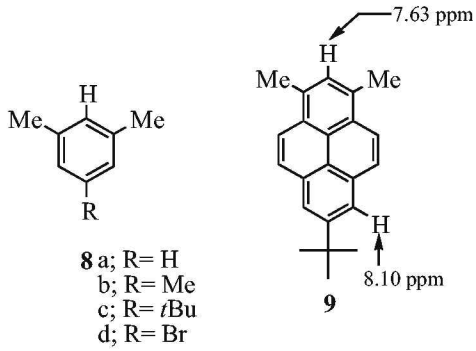


Fig. 2 Chemical shifts of reference compounds for **8** and **9**.

Table 1 Chemical shift (δ ppm) of internal aryl and pyrene protons of **3** and **7**[a]

Compd	Aryl protons δ_{ArH} (Δδ_{ArH}[b])				R protons δ_{sub}(Δδ_{sub})
	H_9	H_{22}	$H_{5,7}$	$H_{16,18}$	
3a	6.77 (–0.19)	6.77 (–0.86)	6.98 (+0.04)	8.19 (+0.09)	6.80 (–0.32)[c]
3b	6.50 (–0.28)	6.73 (–0.90)	6.68 (–0.10)	8.17 (+0.07)	1.67 (–0.59)
3c	6.76 (–0.03)	7.00 (–0.63)	6.80 (–0.20)	8.16 (+0.06)	0.58 (–0.71)
3d	6.44 (–0.42)	6.64 (–0.99)	6.93 (–0.17)	8.17 (+0.07)	–
7	–	7.65 (+0.02)	6.39 (–0.61)	8.16 (+0.06)	0.97 (–1.29)

[a]Determined in $CDCl_3$ using $SiMe_4$ as a reference. [b]–The down field shift; + the upfield shift due to ring current. [c]Midpoint value of multiplet.

that the internal H_9 proton on the benzene rings of **3c** is not effectively shielded by the opposite pyrene ring attributable to the bulkiness of the *tert*-butyl group which would increase the distance between benzene ring and pyrene ring. In contrast, in the case of 6-bromo derivative **3d** the highest up-field shift of the internal benzene proton ($\Delta\delta_{H9}$ –0.42 ppm) was observed, which might be attributable to the π–π-stacking charge-transfer-type interaction between the benzene ring with electron-withdrawing group and the electron rich pyrene ring. Thus, depending on the substituents at 6-position of dithia [3]metacyclo[3](1,3)pyrenophanes **3** different preferential conformations might be proposed.

It was also found that the introduction of the substituents at the internal position 9 tends to increase the value of the chemical shift difference at the 6-methyl protons in **7** from Δδ –0.56 ppm in **3b** to Δδ –1.26 ppm. Thus the ring current effect of internally substituted 9-methoxy-6-methyl-2,11-dithia [3]metacyclo[3](1,3)pyrenophane **7** is much larger than that of internally unsubstituted 6-methyl-2,11-dithia[3]metacyclo [3](1,3)pyrenophane **3b**. Considering the molecular model, it is concluded that the conformation of the 2,11-dithia[3] metacyclo[3](1,3)pyrenophanes should be strongly affected by the size of the substituents at position 9. As shown in Fig. 3, the overlapping between benzene ring and opposite pyrene ring might be much more favourable for the 9-substituted derivative **7** than unsubstituted one **3b**. Thus, the through-space interaction between the non-bonding electron pairs of the oxygen atom of the methoxy group and the opposite pyrene π-electrons of the *syn*-conformer may shorten the distance between the 6-methyl group and the opposite pyrene ring, whereas the H–π interaction could make this distance longer in the case of **3b**. The different structures are possible in the 2,11-dithia[3]metacyclo[3](1,3)pyrenophanes **3** and **7** depending on the substituents at the 9 position.

A solution of 6-methyl-2,11-dithia[3]metacyclo[3](1,3) pyrenophane **3b** and TCNE in CH_2Cl_2 presents a reddish brown colour and the charge-transfer band at 540 nm (log ε = 1.442) was observed in its UV spectrum. This absorption is due to the formation of 1 : 1 charge-transfer complex among the electron donor, **3b** and the electron acceptor, TCNE. The position of absorption maximum and the shape of absorption curve remain unchanged when a 4–12-fold excess of TCNE was added. The charge transfer band positions of other 1,3-dimethyl-5-methylbenzene **8b** and 7-*tert*-butyl-1,3-dimethyl-pyrene **9** with TCNE complexes are summarised in Table 2.

TCNE complexes have often been used in studies on the relative π-base strength of various methyl-substituted benzenes.[30] The π-basicity of the donor molecules increases with an increase in the number of substituted methyl groups and/or stacking benzene rings and an increase in the face-to-face overlapping between aromatic nuclei. In contrast to the cyclophanes having symmmetric donor-sites, unsymmetric cyclophanes containing non-equivalent donor-sites such as 4-acetyl- and 4-methoxy[2.2]paracyclophanes[31] can be expected

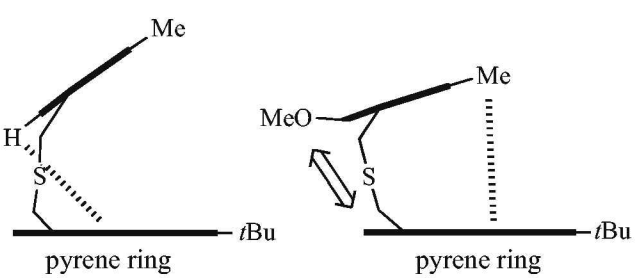


Fig. 3 Structures of dithia[3]metacyclo[3](1,3)pyrenophanes **3b** and **7**.

Table 2 Charge transfer bands of π–π salts of **3b**, **7** and reference compounds **8b**, **9** with TCNE in CH_2Cl_2[a]

Compd	λCT (nm)	log ε
3b	540	1.442
7	549	1.825
8b	422	1.364
9	545	1.596

[a]The complexes were prepared in CH_2Cl_2 using equimolar quantities of substrate and TCNE at 25 °C.

to form two isomeric one-to-one complexes with TCNE, *i.e.*, pseudo-configurational isomers.[32] An important factor for determining which isomeric compex is more predominant or exclusive is the magnitude of ionisation potentials of the constituent donor moieties. Similarly, two possible pseudo-configurational isomers **A** and **B** are also expected for the one-to-one complex of 2,11-dithia[3]metacyclo[3](1,3)pyreno-phane **3b** as shown in Fig. 4.

In contrast to 7-*tert*-butyl-1,3-dimethylpyrene **9**, which exhibits the charge-transfer absorption band with TCNE at 545 nm (log ε = 1.596),[33] a mixture of TCNE and the reference compound, 1,3,5-trimethylbenzene (**8b**) exhibits the charge transfer absorption band at at 422 nm (log ε = 1.364). Thus the observed CT-band of **3b**–TCNE complex should be attributed to the pyrene-site complex, but not to the benzene-site one. Although the charge-transfer of **3b**–TCNE complex exhibits an absorption peak at 540 nm, that of the 9-methoxy derivative **7** is shifted to 549 nm. Such a redshift could be due to the benzene ring at the other side of the molecule which tends to work as a π-electron donor. Introduction of the electron-donating group such as methoxy group at the 9-position causes a larger redshift as indicated by the 9 nm shifts for the CT-band of **7**, due to the increased transannular π-electron donation from the non-complexed benzene ring to the complexed pyrene ring. This finding is strongly supported by shortened distance between the benzene ring and the opposite pyrene ring by the through-space interaction between the non-bonding electron pairs of the oxygen atom of the methoxy group and the opposite pyrene π-electrons of **7**. In conclusion, the present study indicates that the substituent effect at 9-position does exist in the complexation of 9-methoxy[3] metacyclo[3](1,3)pyrenophane **7** with TCNE and through space electronic interaction of the opposite uncomplexed benzene ring must be considered.

Conclusions

We conclude that preparation of *syn*-6-substituted [3]metacyclo [3](1,3)pyreno-phanes are obtained by the coupling reaction of 1,3-bis(bromomethyl)pyrene and the corresponding bis (sulfanylmethyl)benzenes in ethanol under the high dilution conditions. We have also demonstrated for the first time a

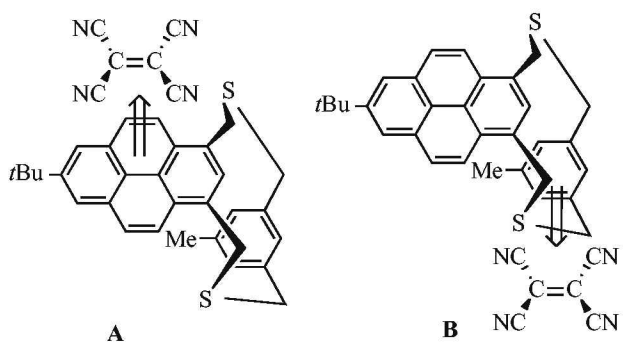


Fig. 4 Possible structures of charge transfer complex for 6-methyl-2,11-dithia[3]metacyclo[3](1,3)pyrenophanes **3b** with TCNE.

through-space interaction between the non-bonding electron pairs of the oxygen atom of the methoxy group and the opposite aromatic π-electrons which may disfavour formation of the *anti*-conformer during the coupling reaction of the corresponding 1,3-bis-(bromomethyl)pyrene and 4-methyl-2,6-bis (sulfanylmethyl)anisole to afford *syn*-9-methoxy[3]metacyclo-[3](1,3)pyrenophane. Further chemical and structural properties of the present novel *syn*-[3]metacyclo[3](1,3)pyrenophane derivatives are currently under study in our laboratory.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. UV-Vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Materials

Preparation of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **1** was previously described.[11] The preparations of 2,6-bis(sulfanylmethyl) benzenes **2** and **6** were carried out as previously reported.[20,21] The TCNE was recrystallised twice from chlorobenzene and sublimed twice at 125 °C (4 mmHg).

Cyclisation reaction of **1** *and* **2** *to give dithiapyrenophanes* **3**: *Typical procedure*

A solution of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **1** (2.0 g, 4.5 mmol) and 1,3-bis(sulfanylmethyl)benzene **2a** (811 mg, 4.5 mmol) in benzene (100 cm^3) was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of potassium hydroxide (700 mg, 12.4 mmol) and sodium borohydride (100 mg, 2.5 mmol) in ethanol (3.0 l). When addition was complete (6 h), the reaction mixture was concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 (500 cm^3). The CH_2Cl_2 extract was washed with water and dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Walo, C-300; 100 g) with hexane–CH_2Cl_2 1:1 as eluent to give a colourless solid, which was recrystallised from hexane to yield the desired 17-*tert*-butyl-2,11-dithia[3]metacyclo[3](1,3)pyrenophane **3a** (1.13 g, 56%) as pale yellow prisms (hexane); m.p. 226–227 °C; ν_{max} (KBr)/cm^{-1} 3030, 2960, 1590, 1480 and 1230; δ_H ($CDCl_3$) 1.57 (9H, s, 17-*t*Bu), 3.71 (4H, s, 1,12-CH_2), 4.29 (4H, s, 3,10-CH_2), 6.70–7.00 (5H, s, Ar*H*), 8.02 (2H, d, J = 9.5 Hz, 14,20-Ar*H*), 8.18 (2H, d, J = 9.5 Hz, 15,19-Ar*H*) and 8.19 (2H, s, 16,18-Ar*H*); *m/z* 452 (M$^+$) (Found: C, 79.60; H, 6.37. $C_{30}H_{28}S_2$ (452.68) requires C, 79.60; H, 6.23%).

Compounds **3b**, **3c** and **3d** were prepared in the same manner as described above for **3a**. The yields are compiled in Scheme 1.

17-tert-Butyl-6-methyl-2,11-dithia[3]metacyclo[3](1,3)pyrenophane **3b**: Pale yellow prisms [from hexane–CH_2Cl_2 (1:1)], m.p. 199–201 °C; ν_{max}(KBr)/cm^{-1} 2916, 1592, 1430 and 1010; δ_H ($CDCl_3$) 1.57 (9H, s, 17-*t*Bu), 1.67 (3H, s, 6-CH_3), 3.65 (4H, s, 1,12-CH_2), 4.26 (4H, s, 3,10-CH_2), 6.50 (1H, s, 9-Ar*H*), 6.68 (2H, s, 5, 7-Ar*H*), 6.73 (1H, s, 22-Ar*H*), 8.02 (2H, d, J = 9.2 Hz, 14,20-Ar*H*), 8.17 (2H, d, J = 9.2 Hz, 15,19-Ar*H*) and 8.17 (2H, s, 16, 18-Ar*H*); *m/z* 466 (M$^+$); HRMS (CI): *m/z* Calcd for $C_{31}H_{30}S_2$ (M$^+$) 466.1789. Found 466.1763 (Found: C, 79.52; H, 6.60. $C_{31}H_{30}S_2$ (466.70) requires C, 79.78; H, 6.48%).

6,17-Di-tert-butyl-2,11-dithia[3]metacyclo[3](1,3)pyrenophane **3c**: Pale yellow prisms (hexane), m.p. 165 °C; ν_{max}(KBr)/cm^{-1} 2932, 1594, 1444 and 1222; δ_H ($CDCl_3$) 0.58 (9H, s, 6-*t*Bu), 1.58 (9H, s, 17-*t*Bu), 3.80 (4H, s, 1,12-CH_2), 4.36 (4H, s, 3,10-CH_2), 6.76 (1H, s, 9-Ar*H*), 6.80 (2H, s, 5,7-Ar*H*), 7.00 (1H, s, 22-Ar*H*), 8.00 (2H, d, J = 9.2 Hz, 14,20-Ar*H*), 8.16 (2H, s, 16,18-Ar*H*) and 8.17 (2H, d, J = 9.2 Hz, 15,19-Ar*H*); *m/z* 508 (M$^+$); HRMS (CI): *m/z* Calcd for $C_{34}H_{36}S_2$ (M$^+$) 508.2258. Found 508.2255 (Found: C, 80.20; H, 7.15. $C_{34}H_{36}S_2$ (508.79) requires C, 80.27; H, 7.13%).

6-Bromo-17-tert-butyl-2,11-dithia[3]metacyclo[3](1,3)pyrenophane **3d**: Pale yellow prisms (hexane), m.p. 195–196 °C; ν_{max}(KBr)/cm^{-1} 2932, 1594, 1444 and 1222; δ_H($CDCl_3$) 1.56 (9H, s, 17-*t*Bu), 3.50 (4H, s, 1,12-CH_2), 4.18 (4H, s, 2,10-CH_2), 6.44 (1H, s, 9-Ar*H*), 6.64 (1H, s, 22-Ar*H*), 6.93 (2H, s, 5,7-Ar*H*), 7.80 (2 H, d, J = 9.2 Hz, 14,20-Ar*H*), 8.10 (2H, d, J = 9.2 Hz, 15,19-Ar*H*) and 8.17 (2H, s, 16,18-Ar*H*); *m/z* 530, 532 (M$^+$); HRMS (CI): *m/z* Calcd for $C_{30}H_{27}BrS_2$ (M$^+$) 530.0738. Found 530.0739 (Found: C, 67.90; H, 5.15. $C_{30}H_{27}BrS_2$ (531.57) requires C, 67.79; H, 5.12%).

Cyclisation reaction of **1** *and* **6** *to give dithiapyrenophanes* **7**: A solution of 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **1** (2.0 g, 4.5 mmol) and 2,6-bis(sulfanylmethyl)-4-methylamisole **2a** (964 mg, 4.5 mmol) in benzene (100 cm^3) was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of potassium hydroxide (700 mg, 12.4 mmol) and sodium borohydride (100 mg, 2.5 mmol) in ethanol (3.0 l). When addition was complete (6 h), the reaction mixture was concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 (500 cm^3). The CH_2Cl_2 extract was washed with water and dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Walo, C-300; 100 g) with hexane–CH_2Cl_2 1:1 as eluent to give a colourless solid, which was recrystallised from hexane to yield the desired *syn*-17-*tert*-butyl-9-methoxy-6-methyl-2,11-dithia[3]metacyclo[3](1,3) pyrenophane *syn*-**7** (1.24 g, 52%) as pale yellow prisms (MeOH); m.p. 120–123 °C; ν_{max} (KBr)/cm^{-1} 2904, 1592, 1432, 1206, 1002 and 870; δ_H($CDCl_3$) 0.97 (3H, s, 6-*Me*), 1.58 (9H, s, 17-*t*Bu), 3.52 (2H, s, J = 14.1 Hz, 1,12-CH_2), 3.72 (3H, s, 9-*OMe*), 4.29 (2H, s, J = 15.0 Hz, 3,10-CH_2), 4.42 (2H, s, J = 14.1 Hz, 1,12-CH_2), 4.57 (2H, s, J = 15.0 Hz, 3,10-CH_2), 6.39 (2H, s, 5,7-Ar*H*), 7.65 (1H, s, 22-Ar*H*), 8.01 (2H, d, J = 9.2 Hz, 14,20-Ar*H*), 8.16 (2H, s, 16,18-Ar*H*) and 8.16 (2H, d, J = 9.2 Hz, 15,19-Ar*H*); *m/z* 496 (M$^+$); HRMS (CI): *m/z* Calcd for $C_{32}H_{32}OS_2$ (M$^+$) 496.1895. Found 496.1883 (Found: C, 77.53; H, 6.37. $C_{32}H_{32}OS_2$ (496.73) requires C, 77.38; H, 6.49%).

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