Synthesis, Properties and Conformational Studies of *anti*-8-Fluoro-16-methyl-[2_2]metacyclophane and *anti*-8-Fluoro-16-methyl[2_2]metacyclophane-1,9-diene

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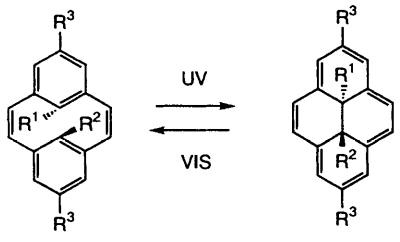
The protons of the *anti* and *syn* isomers, **5b** and **6b**, of 9-fluoro-18-methyldithia[3_2]metacyclophane have been assigned by 1D and COSY ^{1}H NMR spectral data. A Stevens rearrangement–Hofmann elimination sequence carried out with a mixture of **5b** and **6b** led only to the isolation of *anti* isomers of 8-fluoro-16-methyl[2_2]metacyclophane-1,9-diene **1f** and 8-fluoro-16-methyl-10-methylsulfanyl[2_2]metacyclophan-1-ene **11**. The photochemical and thermal decomposition of **1f** resulted in the formation of mainly pyrene and methylpyrenes. Dihydropyrene **2f** is probably the initial intermediate and the products are believed to be formed from subsequent carbocation formation and methyl shifts. The reduction of compound **11** led to the isolation of pyrene and *anti* cyclophane **17c**. The cyclophanene **16c** is believed to be the intermediate which undergoes 'disproportionation reactions' to give cyclophane **17c** and cyclophanediene **1f** (and thus pyrene). The protons in the bridges of **17c** could be assigned on the basis of NOE and decoupling experiments. Downfield shifts of the methyl signals are observed in passing from **17c** to **11** and **1f**, and going from **17a** to **17c**, **16a** to **11** and **1b** to **1f**, respectively. This is attributed to a change in molecular geometry resulting from the 'sliding' of the *anti*, stepped benzene rings.

Irradiation of cyclophanediene **1a** with light at 254 nm resulted in the formation of dihydropyrene **2a** which was readily oxidised to pyrene.[1,2] The dimethyl system **1b**[3] and other 8,16-dialkyl derivatives,[4] however, exhibit the unique photochemical valence isomerization **1b** ⇌ **2b** which could be

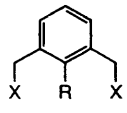


1 **2**

	R^1	R^2	R^3
a	H	H	H
b	Me	Me	H
c	H	Me	H
d	F	F	H
e	F	F	Bu^t
f	Me	F	H

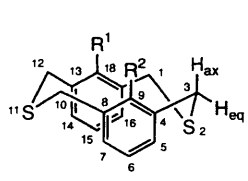
observed repeatedly.[3–6] In fact, the conversion **1b** ⟶ **2b** could also be achieved thermally—an example of an unusual concerted, symmetry-forbidden reaction.[6] The dimethyldihydropyrene system was found to be the more thermodynamically stable isomer. The monomethyl derivative **1c** also cyclized[7] readily to yield **2c** which eliminated methane to form pyrene. Synthesis of the difluoro derivative **1d** has been reported but unexpectedly **1d** failed to convert into **2d** readily.[8,9] Heating a sample of **1d** at 120 °C led to the isolation of 1-fluoropyrene believed to be formed *via* **2d**.[8] Photochemical interconversion between the di-*tert*-butyl derivatives, **1e** ⇌ **2e**, was, however, recently observed,[10] indicating that the bulky substituents may in some way affect the valence isomerization processes. Based on the significantly different isomerization behaviour of **1b** and **1d**, it would be interesting to synthesize the fluoro-methyl derivative **1f** and study its conversion into dihydropyrene **2f**. The chemistry of selected intraannular fluorine-containing cyclophanes has also recently been reviewed.[11] This paper reports the NMR and conformational properties of cyclophanediene **1f**, dithiacyclophanes **5** and **6**, and cyclophanene **11**.

Dithia[3_2]*metacyclophanes* **5b** *and* **6b**.—The cyclophanedienes **1b** and **1d** were synthesized from dithiacyclophanes **6a**[2] and **5c**,[8,12] respectively. Preparation of a mixture of dithiacyclophanes **5b** and **6b** from the coupling reaction of **3**[8] and **4**[2] has been reported[8,13] but the yields were rather poor

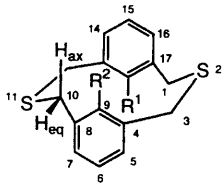


	R	X
3	F	Br
4	Me	SH

(17–25%). Under modified reaction conditions, a mixture of **5b** and **6b** was obtained in about 65% yield in our work. The ratio



5 *syn*



6 *anti*

	R^1	R^2
a	Me	Me
b	Me	F
c	F	F

of the integrated areas of the methyl protons at δ 2.45 and 1.51 in the ^{1}H NMR spectrum is 1.8:1.0, which corresponds to the ratio of *syn* and *anti* conformers **5b** and **6b**, respectively. The

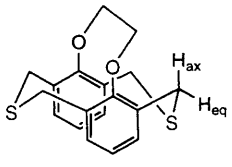
Table 1 ^1H and ^{19}F NMR chemical shifts (δ) for dithiacyclophanes **5a**, **5b**, **5c**, **6a** and **6b**

Phane	CH_3	F	5-,7-H	6-H	14-,16-H	15-H	3-,10-H_{ax}	3-,10-H_{eq}	1-,12-H_{ax}	1-,12-H_{eq}
5a[a]	2.51	—	6.59	6.59	6.59	6.59	4.00	3.80	4.00	3.80
5b	2.45[b]	−121.8	6.91[c]	6.67[c]	7.00[d]	6.70[c]	4.18[e]	3.37[e]	4.32[f]	3.63[f]
5c[a]	—	−126.7	6.98	6.70	6.98	6.70	4.34	3.43	4.34	3.43
6a[a]	1.30	—	7.27	7.06	7.27	7.06	3.68	3.68	3.68	3.68
6b	1.51[g]	−123.2	7.23[c]	7.02[c]	7.34[d]	7.19[c]	3.75[h]	3.32[i]	3.76[j]	3.80[j]

[a] Ref. 14. [b] Doublet; J 2.0 Hz. [c] Triplet; J 7.7 Hz. [d] Doublet; J 7.7 Hz. [e] Doublet; J 14.8 Hz. [f] Doublet; J 15.0 Hz. [g] Singlet. [h] Doublet; J 13.8 Hz. [i] Doublet of doublets; J 13.8, < 1 Hz. [j] Doublet; J 14.3 Hz.

presence of an equilibrium between the two conformers was earlier established by ^1H NMR studies.[13] All our attempts by fractional recrystallization and chromatography failed to isolate pure samples of **5b** or **6b**.

The interconversion between **5b** and **6b** has been studied[13] by dynamic ^1H NMR spectroscopy based on the methyl signals. Assignments of the other protons were, however, not possible in spectra reported earlier. A comparison of the proton chemical shifts of **5a**, **5c** and **6a** already reported[14] with the 1D and COSY ^1H NMR spectral data (500 MHz) of a mixture of **5b** and **6b** obtained in our work has allowed the assignment of most protons (Table 1). The aromatic protons of *syn* **5b** are expected to be shifted upfield, a common consequence of stacking two parallel aromatic rings.[2,15,16] In both **5b** and **6b**, 5-,7-H (a triplet) could be readily assigned due to the presence of F-coupling whereas the corresponding 14-,16-H appear as a doublet. The COSY spectra would then help assign the respective 6-Hs. Among the bridging methylene protons, those in close proximity to fluorine are expected to show $^4J_{HF}$ couplings. This, however, was only observed for 3-,10-H_{eq} of **6b**. Chemical shifts of the 3-,10-H_{eq} in **5b** and **6b**, relative to those in close proximity to the methyl groups, appear at higher field consistent with the fact that a decrease in ring current (fluorobenzene *versus* toluene) causes an upfield shift of an adjacent sp^2 or sp^3 benzylic proton.[17–19] The 3-,10-H_{ax} are however significantly deshielded by the anisotropic effect of the adjacent fluorine. Similar results could also be observed in **5c** (Table 1) and the oxo-derivative **7**.[20]



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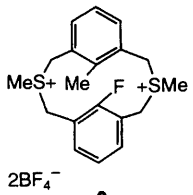
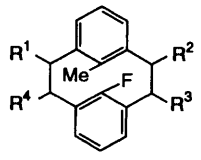


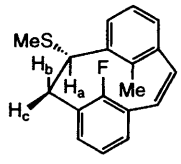
8

anti-8-*Fluoro*-16-*methyl*[2_2]*metacyclophane*-1,9-*diene* **1f**.—A mixture of dithiacyclophanes **5b** and **6b** was converted into their bis(methylsulfonium) salts **8** using dimethoxycarbonium tetrafluoroborate.[21] Rearrangement of **8** with potassium *tert*-butoxide in tetrahydrofuran gave a 90% yield of product **9** as a mixture of isomers. Based on the integrated areas of aromatic methyl signals (at *ca.* δ 2.2 and 0.7) in the ^1H NMR spectrum, the ratio of *syn* and *anti* isomers of **9** was estimated to be about 1:1, indicating that the rearrangement reaction might have effected some isomerization of **5b** (*syn*) to *anti*-**9**. Methylation of a mixture of **9** as for **8** afforded a mixture of the bis-salt **10** which was found to be hygroscopic. Treatment of **10** with potassium *tert*-butoxide in a mixture of dry tetrahydrofuran and *tert*-butyl alcohol (1:1) at 10 °C gave, after chromatography, pyrene, the *anti* monoene **11** and the *anti* diene **1f** in a 3:1:1 ratio.

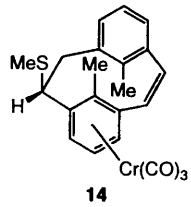
There was no evidence for the presence of *syn* diene **12c** or *cis*-dihydropyrene **13c** in the product mixture. The corresponding dienes **12a**[2] and **12b**[12] are known to undergo valence isomerization readily to afford the respective dihydropyrenes



	R^1	R^2	R^3	R^4
9a	SMe	SMe	H	H
9b	SMe	H	SMe	H
9c	H	H	SMe	SMe
10a	SMe_2^+	SMe_2^+	H	H
10b	SMe_2^+	H	SMe_2^+	H
10c	H	H	SMe_2^+	SMe^{2+}



11 *anti*



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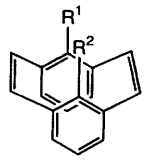
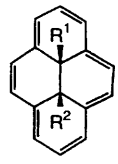


12 *syn*



13

	R^1	R^2
a	Me	Me
b	F	F
c	Me	F

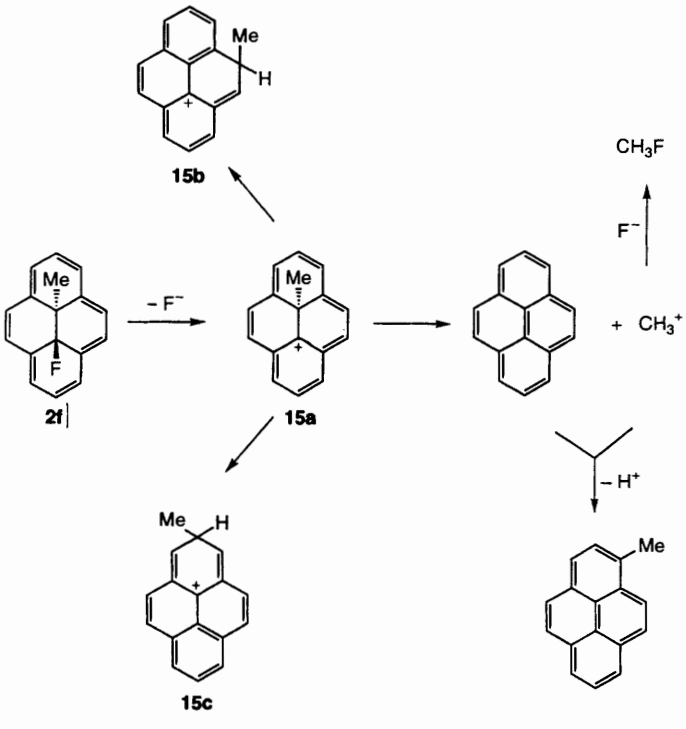
13a and **13b**, and the latter decomposes slowly to form 1-fluoropyrene.[12] The Hofmann elimination of *syn* isomers of **10** is thus expected to give **12c** which cyclizes to form **13c** followed by decomposition to yield pyrene (see later discussion on the conversion of **1f** into pyrene *via* **2f**).

The *anti* stereochemistry of the monoene **11** is supported by a shielded aromatic methyl signal at δ 0.91. The methylsulfanyl group is evidently in a pseudoequatorial position adjacent to the aromatic methyl group supported by the splitting patterns of H_a (δ 3.79; doublet of doublets with a large $J_{a,b}$ = 11 Hz and a smaller $J_{a,c}$ = 2.7 Hz), H_b (δ 2.56; doublet of triplets with large $J_{a,b} = J_{b,c}$ = 11 Hz and a small $J_{c,F}$ = 0.8 Hz) and H_c (δ 2.95; doublet of doublets of doublets with large $J_{b,c}$ = 11 Hz and small $J_{a,c}$ = 2.7 Hz and $J_{c,F}$ = 1.1 Hz). Isolation of **11** is rather unexpected as the only other related monoene known, obtained from a similar reaction, is **14**,[19] which has the methylsulfanyl group in a pseudoaxial position adjacent to the relatively electron poor aromatic ring in contrast to that in **11**. The

monoene **11** was isolated in all repeated attempts but the reason for the selective formation of **11** is not understood.

The structure of **1f** was assigned on the basis of the mass spectrum molecular ion (M^+) at *m/z* 236 and its ^1H NMR spectrum, which showed the internal methyl protons at δ 1.61 (δ 1.55 for **1b**).[2] The vinyl protons of **1f** appeared as two doublets at δ 6.16 (1-,10-H; δ 6.28 for **1b**)[2] and δ 6.59 (2-,9-H; δ 6.41 for **1d**).[8] The diene **1f** decomposed slowly even at 0 °C in the solid state. Irradiation of a degassed solution of **1f** in [$^2H_6$]benzene resulted only in the isolation of a mixture of mainly pyrene and methylpyrenes. There was no evidence for the presence of dihydropyrene **2f** in the product mixture although it is believed to be the intermediate formed from valence isomerization of **1f**. The thermal decomposition of a degassed solution of **1f** at 50 °C was monitored by ^1H NMR spectroscopy. Rapid formation of fluoromethane was observed as evidenced by the increase in intensity of a doublet at δ 4.24 ($J_{H,F}$ = 46 Hz).[22] Chromatography of the product mixture again led to the isolation of a mixture of mainly pyrene and methylpyrenes, and small amounts of dimethylpyrenes. Although the methylated pyrenes could not be separated, their presence was clearly supported by the mass spectrum molecular ions (M^+) at *m/z* 216 (85%) and 230 (10%). The ^1H NMR spectrum of the product mixture also showed methyl proton signals at δ 2.8–3.0 which is consistent with those observed for a mixture of 1-, 2- and 4-methylpyrenes.[23,24]

The thermal decomposition of either *trans*-**2d**[8] or *cis*-**13b**[12] was reported to form 1-fluoropyrene. There was however no mention of any plausible mechanism to account for such reactions. The presence of alkyl radicals was noted in the conversion of **2c** into pyrene[7] but no formation of methylpyrenes was reported in this reaction. Thus, the decomposition of **2f** to form pyrene and methylpyrenes is unlikely to involve a radical mechanism. An attractive alternative is the formation of carbocation **15a** which is stabilized by extended conjugation.



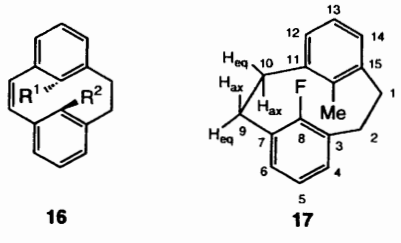
Pyrene could be formed from **15a** by the elimination of a transient methyl carbocation which then readily combines with a fluoride ion to form the fluoromethane observed in the NMR experiment mentioned earlier. The methyl carbocation could also undergo an electrophilic substitution with pyrene to yield 1-methylpyrene. The rearrangement of **15a** to **15b** and **15c** *via* methyl shifts might account for the formation of 2- and 4-methylpyrenes.

Table 2 Assignment of bridging aliphatic protons in cyclophane **17c**

Proton	δ	*J*/Hz
1-,10-H_{ax}	2.72	12.0,[a] 12.0,[b] 3.8[c]
1-,10-H_{eq}	2.96	12.0,[a] 4.1,[c] 2.0[d]
2-,9-H_{ax}	2.63	12.0,[a] 12.0,[b] 3.8[c]
2-,9-H_{eq}	2.80	12.0,[a] 3.8,[c] 2.0,[d] 2.0[e]

[a] Geminal H_{ax}–H_{eq} coupling. [b] Vicinal H_{ax}–H_{ax} coupling. [c] Vicinal H_{ax}–H_{eq} coupling. [d] Vicinal H_{eq}–H_{eq} coupling. [e] $^4J_{H-F}$ coupling.

anti-8-*Fluoro*-16-*methyl*[2_2]*metacyclophane* **17c**.—Chromatography of the product mixture obtained from the treatment of the monoene **11** with Raney nickel in ethanol at reflux unexpectedly led to the isolation of pyrene and *anti* cyclophane **17c** in a 1 : 3 ratio. There was no evidence for the presence of the desired monoene **16c**. It is, however, believed that **16c** was



16 **17**

	R^1	R^2
a	Me	Me
b	F	F
c	Me	F

formed as an intermediate in the reaction. The conversion of the monoene **16a** into **1b** and thus **2b** was achieved by the use of a catalytic amount of palladium.[25] Oxidation of **16c** to give **1f** might be similarly effected by Raney nickel which has been reported in several examples to act as a dehydrogenation catalyst.[26] Valence isomerization of **1f** to **2f** followed by elimination of fluoromethane gave pyrene as described earlier. The monoene **16c** on the other hand could also be readily reduced (hydrogenated) in the presence of Raney nickel[27] to afford **17c**.

The aromatic protons in **17c** could be assigned readily (see Experimental section). Based on the coupling constants reported for geminal H_{ax}–H_{eq} coupling (12–14 Hz), vicinal H_{ax}–H_{ax} coupling (10–13 Hz), vicinal H_{ax}–H_{eq} coupling (2–5 Hz) and vicinal H_{eq}–H_{eq} coupling (2–5 Hz) in cyclohexane and its derivatives, the four axial and equatorial 1-,2-H (9-,10-H) in **17c** could be assigned accordingly (Table 2). *anti*-[2_2]metacyclophane **17a** has been shown by X-ray crystallographic analysis to have the two benzene rings in separate planes with the methyl groups extending over the face of the opposite benzene rings.[28] This stereochemistry results in a strongly shielded methyl signal at δ 0.56 in its ^1H NMR spectrum.[2] Thus, the *anti* stereochemistry of **17c** is also indicated by the shielded methyl signal at δ 0.67. An NOE experiment carried out with irradiation of the methyl signal of **17c** led to an enhancement of the doublet of triplets at δ 2.72 and confirms the assignment of 1-,10-H_{ax}, and thus, the other coupled protons (Table 2).

A downfield shift of the methyl signals is observed in passing from **17c** to **11** and **1f** (Table 3). This could be attributed to the following two factors: a change in molecular geometry resulting from the 'sliding' (due to a change in bond angles of the bridges) of the stepped benzene rings, and an increase in the dihedral

Table 3 ^1H and ^{19}F chemical shifts of selected cyclophanes, cyclophanenes and cyclophanedienes

Compound	δ(Me)[a]	δ(^{19}F)[b]
17a[2]	0.56	—
17c	0.67	−119.2
17b[9,12]	—	−125.1
16a[24]	0.79	—
11	0.91	−107.8
1b[2]	1.52	—
1f	1.61	−91.8
1d[9,12]	—	−95.0

[a] ppm Relative to TMS. [b] ppm Relative to $CFCl_3$.

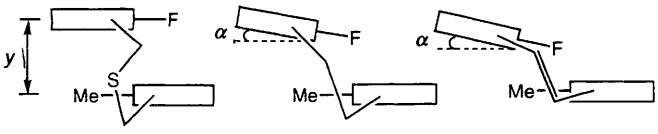


Fig. 1 Representations illustrating the outward sliding of benzene rings in going from **17c** to **11** to **1f**

angle α due to an increase in steric hindrance between the inner substituents and the respective opposite rings (Fig. 1). A similar observation has been reported in a related series of cyclophanes **17a**, **16a** and **1b**.[29] There seems also to be a downfield fluorine chemical shift going from **17c** to **11** and **1f** (Table 3) but this may be a coincidence as fluorine chemical shifts are relatively less sensitive to the ring current effect of a benzene ring. For example, the fluorine chemical shift (δ −98)[12] of *syn* **12b** is very similar to that (δ −95)[12] of *anti* **1d**. Downfield proton shifts of about 0.1 ppm are observed respectively going from **17a** to **17c**, **16a** to **11** and **1b** to **1f** (Table 3). A decrease in diatropicity going from toluene to fluorobenzene would lead to reduced shielding of the methyl protons in **17c**, **11** and **1f** by the opposite rings. The smaller spatial requirement of fluorine compared with that of a methyl group would result in a larger outward sliding effect of the rings (Fig. 1) in **17c**, **11** and **1f** moving the methyl groups further away from the shielding zone of the opposite rings. The observed trend is, however, expected to be a combined effect of the two factors. An upfield shift was however noted in the fluorine chemical shift going from **17c** to **17b** and **1f** to **1d**. This 'reverse' order again indicates that the fluorine chemical shift is relatively less sensitive to the ring current effect.

Experimental

All melting points were determined with a GALEN III Hot Stage Microscope and are uncorrected. ^1H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Bruker ACF300 (300 MHz; 16K data points; spectral width 3333 Hz) or AMX500 (500 MHz; 32K data points; spectral width 5555 Hz) spectrometer. All proton chemical shifts are reported in ppm downfield from tetramethylsilane, which was used as an internal standard. Fluorine chemical shifts are relative to $CFCl_3$. *J* values are given in Hz. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV using electron impact ionization. Relative intensities are given in parentheses. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. All evaporations were carried out under reduced presure on a rotary evaporator at about 40 °C and all organic layers were washed with water (unless otherwise stated) and dried with anhydrous magnesium sulfate.

9-Fluoro-18-methyl-2,11-dithia[3$_2$]metacyclophanes **5b** *and* **6b**.—A solution of **3** (0.56 g, 2 mmol) and **4** (0.37 g, 2 mmol) in benzene (200 cm^3) was added dropwise over a period of 12 h to a solution of potassium hydroxide (0.34 g, 6 mmol) in a mixture of benzene and 95% ethanol (1 : 1; 500 cm^3) at room temperature under nitrogen. The mixture was then stirred for a further 24 h and the bulk of the solvent was removed under reduced pressure. Water and dichloromethane were added to the residue and the mixture was stirred until all the solids had dissolved. The organic layer was separated, washed, dried and then evaporated to dryness. The residue was chromatographed on silica gel using a mixture of dichloromethane and cyclohexane (1 : 1) as eluent to afford a mixture of the title compounds **5b** and **6b** (0.39 g, 64%), m.p. 200–215 °C (lit.,[8] 200–205 °C); δ_H, see Table 1; *m/z* 304 (M^+, 80%), 149 (100) and 134 (20).

Stevens Rearrangement of Dithiacyclophanes **5b** *and* **6b** *to form Bis(methylsulfanyl)*[2$_2$]*metacyclophanes* **9**.—A solution of **5b** and **6b** (0.30 g, 1 mmol) in dichloromethane (10 cm^3) was added to a stirred suspension of dimethoxycarbonium fluoroborate[21] (0.81 g, 5 mmol) in dichloromethane (5 cm^3) kept at −30 °C under nitrogen. After the addition, the mixture was allowed to warm to room temperature and then stirred for an additional 5 h. Ethyl acetate (10 cm^3) was then added and the mixture stirred for 2 h. The white solid, 0.51 g (99%), was collected by filtration and dried to give the salt **8**, which was used directly for the subsequent reaction.

Powdered potassium *tert*-butoxide (0.34 g, 3 mmol) was added to a suspension of the salt **8** (0.51 g, 1 mmol) in dry THF (20 cm^3) at room temperature under nitrogen. The mixture was stirred for 1 h and then the solvent was evaporated under reduced pressure. Dilute HCl was added followed by dichloromethane. The organic layer was separated, washed, dried and then evaporated to dryness. The residue was chromatographed on silica gel using dichloromethane–hexane (1 : 2) as eluent to yield a mixture of isomers of **9** (0.30 g, 90%) as a thick yellow oil (Found: M^+, 332.1077. $C_{19}H_2FS_2$ requires *M*, 332.1069); δ_H(300 MHz) 7.2–7.8 (6 H, m, ArH), 6.2–7.1 (6 H, m, ArH), 3.8–4.0 (4 H, m, CHS), 2.3–3.3 (8 H, m, CH_2), 2.17–2.23 (3 H, multiple singlets, $ArCH_3$), 2.12–2.15 (12 H, multiple singlets, SCH_3) and 0.67–0.72 (6 H, multiple singlets, $ArCH_3$); the ratio of integrated areas of the two sets of aromatic methyl protons is about 1 : 1, which corresponds to the approximate ratio of *syn* and *anti* conformers, respectively; *m/z* 332 (M^+, 100%), 317 (17), 284 (60), 269 (90), 237 (50), 202 (30).

8-Fluoro-16-methyl[2$_2$]*metacyclophane-1,9-diene* **1f** *and 8-Fluoro-16-methyl-10-methylsulfanyl*[2$_2$]*metacyclophan-1-ene* **11**.—The bis(sulfonium) salt **10** was prepared from compound **9** (0.3 g, 0.9 mmol) according to the procedure described for the preparation of the salt **8**. The hygroscopic salt **10**, obtained as a yellow powder (0.4 g, 70%), was filtered from the product mixture under nitrogen and was washed with freshly distilled ethyl acetate.

Powdered potassium *tert*-butoxide (0.3 g, 3 mmol) was added to a suspension of salt **10** in a mixture of dry THF and *tert*-butyl alcohol (1 : 1) maintained at 10 °C under nitrogen. The reaction mixture was stirred for 6 h at this temperature and the solvent was then removed under reduced pressure. Dilute HCl and benzene were added and the organic layer was separated, washed, dried and then evaporated to dryness. The residue was chromatographed on silica gel using hexane as eluent. First eluted was pyrene (80 mg, 57%), m.p. 145–148 °C (lit.,[24] 148–150 °C.

Next eluted was the diene **1f** (32 mg, 20%) obtained as a yellow solid (Found: M^+, 236.0986. $C_{17}H_{13}F$ requires *M*, 236.1001); δ_H(500 MHz) 7.16 (1 H, t, *J* 7.4, 13-H), 7.01 (1 H, t, *J* 7.4, 5-H), 6.82 (2 H, t, *J* 7.4, 4-,6-H), 6.78 (2 H, d, *J* 7.4, 12-,14-

H), 6.59 (2 H, d, *J* 11.2, 1-,10-H), 6.16 (2 H, d, *J* 11.2, 2-,9-H), 1.61 (3 H, s, CH_3); δ_F −91.8; *m/z* 236 (M^+, 18%), 220 (65), 216 (15), 202 (100).

Last eluted was a mixture of isomers (41 mg, 21%) of **11** obtained as a thick yellow oil; δ_F −109.8 and −107.8. Chromatography on silica gel resulted in the isolation of *anti*-**11** as the major isomer (Found: M^+, 284.1035. $C_{18}H_{17}FS$ requires *M*, 284.1035); δ_H(300 MHz) 7.68 (1 H, d, *J* 7.8, 12-H), 7.25 (1 H, t, *J* 7.8, 13-H), 6.94–7.17 (4 H, m, 4-,5-,6-,14-H), 6.80 (1 H, d, *J* 11, 1-H), 6.39 (1 H, d, *J* 11, 2-H), 3.79 (1 H, dd, *J* 2.7 and 11, 10-H), 2.95 (1 H, dq, *J* 1.1, 2.7 and 11, 9-H_{eq}), 2.56 (1 H, dt, *J* 0.8 and 11, 9-H_{ax}); δ_F −107.8; *m/z* 284 (M^+, 80%), 269 (10), 237 (40), 221 (90), 202 (100).

Desulfurization of Compound **11** *with Raney Nickel.*—A solution of **11** (150 mg, 0.5 mmol) was added to a suspension of an excess of W-7 Raney Nickel[30] in ethanol (30 cm^3). The reaction mixture was heated at reflux for 14 h. After removal of the catalyst and solvent, the residue was chromatographed on silica gel using hexane as eluent. First eluted was pyrene (20 mg, 19%), m.p. 149–150 °C (lit.,[24] 148–150 °C).

Next eluted was **17c** (80 mg, 63%) obtained as a white solid, m.p. 122–125 °C (Found: C, 85.1; H, 7.1%. M^+, 240.1321. $C_{17}H_{17}F$ requires C, 84.95; H, 7.1%. *M*, 240.1318); δ_H(500 MHz) 7.13 (2 H, t, *J* 6.9, 4-,6-H), 7.05–7.10 (3 H, m, 12-,13-,14-H), 6.91 (1 H, t, *J* 7.4, 5-H); for assignment of aliphatic protons, refer to to Table 2; δ_F −119.2; *m/z* 240 (M^+, 100%), 225 (95), 205 (48).

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