Reaction and Spectra of [*n*.2.1](1,2,3)Cyclophanes

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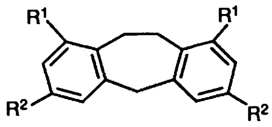
Novel triply bridged [*n*.2.1](1,2,3)cyclophanes, which contain a dibenzo[*a*,*d*]cycloheptene unit as a basic structure, were prepared. The mobility of the molecule and the orientation of two aromatic rings were deduced from the NMR and UV spectra. Each aromatic ring can flip with conformational inversion on the NMR time-scale at 27 °C when the length of the third methylene chain (*m* or *n*) is longer than five for the dithiacyclophanes **9** and ten for the cyclophanes **3**. Red shifts of λ_{max} for the aromatic rings and upfield shifts of aromatic protons are observed when the methylene chain becomes shorter. An X-ray study showed the benzene rings of the cyclophane **11c** to be slightly bent. Pyrolysis of the sulfones **10a** and **b** gave the anthracene **7a** rather than the cyclophanes **3a** and **b**. Transalkylation of the cyclophanes **3a** and **b** with $AlCl_3$–$MeNO_2$–benzene did not afford the de-*tert*-butylated cyclophanes **11a** and **b** but instead gave the phenylated products **13a** and **b**.

Although the preparation of multibridged cyclophanes which have two aromatic rings has been reported,[1] in most cases they have been obtained by the introduction of additional bridges to [2.2]paracyclophane derivatives. The other approaches seem to be too complicated and structurally limited. To the best of our knowledge, only a few examples[2–6] of triply bridged cyclophanes in which two aromatic rings are connected by other than an ethano bridge have been reported. Obviously this is due to difficulties in obtaining suitable intermediates for the introduction of the third bridge. We have reported the preparation of many types of metacyclophanes by utilizing a *tert*-butyl group as the protective function.[7] In the course of our studies we have developed a convenient preparation of the dibenzocycloheptene **1a**. We believe compound **1a** would be a convenient, useful candidate as a basic skeleton, since it can be obtained in one step in large quantities and it has a methylene bridge by which the molecule's conformational properties can be assessed by ^1H NMR spectroscopy. We herein describe the preparation of [*n*.2.1](1,2,3)cyclophanes by utilizing compound **1a** as an intermediate. Their reactivity and spectral properties are also discussed.



1a; $R^1 = CH_2Cl$, $R^2 = Bu^t$
b; $R^1 = CH_2SH$, $R^2 = Bu^t$
c; $R^1 = Me$, $R^2 = H$
d; $R^1 = Me$, $R^2 = Bu^t$
e; $R^1 = R^2 = H$

Results and Discussion

Unexpectedly, chloromethylation of the diphenylethane **2** with chloromethyl methyl ether and $TiCl_4$ afforded the dibenzocycloheptene **1a** in good yield (Scheme 1).

The best result was obtained when chloromethyl methyl ether was used at 11 mol equiv. to substrate **2** (97%). The details were reported previously.[8] One-step synthesis of the cyclophane **3k** by Wurtz coupling of compound **1a** was tried; however, the dimerized product **4** was isolated in 17% yield. When compound **1a** was treated with Na_2S, the dimerized dithiacyclophane **6** was the only product isolated (35%), instead of the thiacyclophane **5** (Scheme 1).

Table 1 Yields of cyclophanes **9**, **10**, **3** and **11**

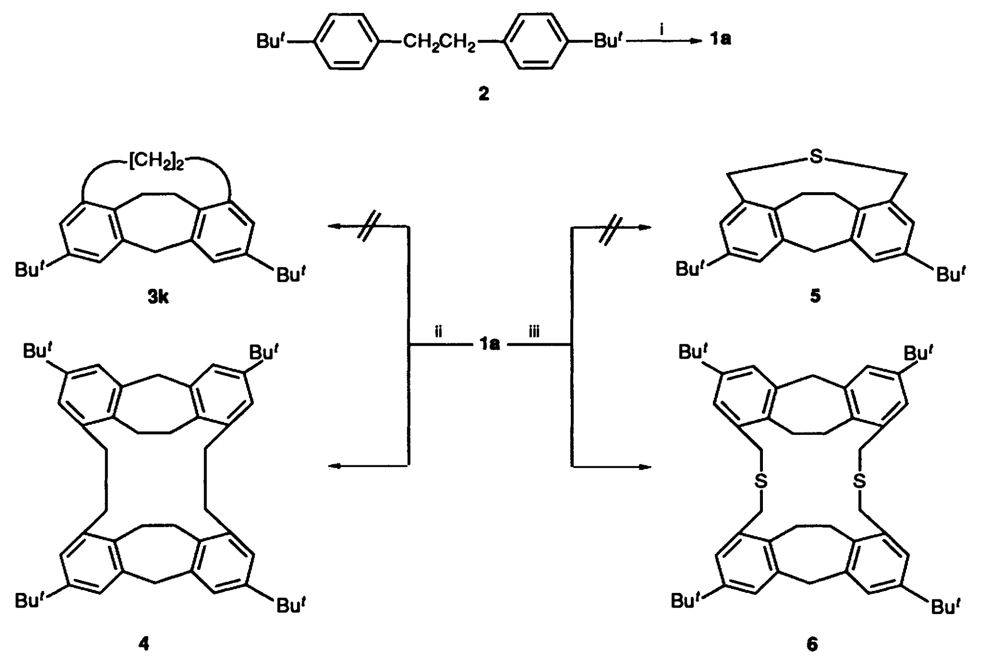
	Yield (%)[a]			
(*n*)	**9**	**10**	**3**	**11**
a (*n* = 3)	6	87	12	
b (*n* = 4)	41	97	16	
c (*n* = 5)	39	100	62	74
d (*n* = 6)	48	100	50	87
e (*n* = 7)	43	86	60	94
f (*n* = 8)	43	81	55	74
g (*n* = 9)	47	88	63	77
h (*n* = 10)	48	98	56	79
i (*n* = 11)	67	81	11	
j (*n* = 12)	47	96	48	

[a] Isolated yield.

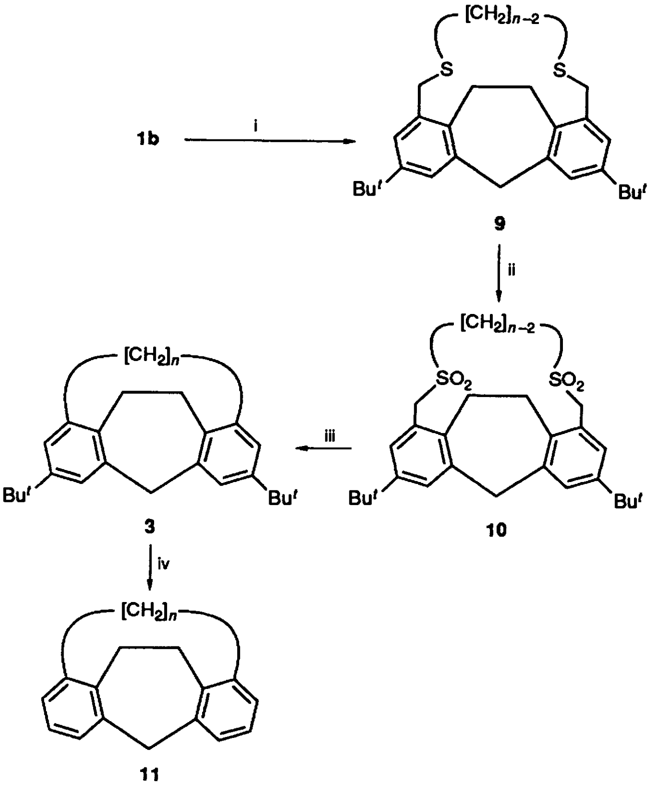
These results reflect the fact that both chloromethyl groups cannot simultaneously approach to within the appropriate distance for coupling to occur. High-dilution coupling of the mercaptomethyl product **1b**, prepared from the chloromethyl product **1a** and thiourea, with dibromoalkanes afforded the corresponding dithiacyclophanes **9**. Oxidation of (**9**) with *m*-chloroperbenzoic acid (MCPBA) afforded the disulfones **10** in almost quantitative yield, which were pyrolysed at 450–550 °C under reduced pressure to give the expected cyclophanes **3** (Scheme 2). The yields in these procedures are summarized in Table 1.

In pyrolysis of the sulfones **10a** (at 460 °C) and **10b** (at 510 °C), a small amount of the anthracene **7a** (1–3%) was isolated besides the expected products **3a** and **3b**, respectively.

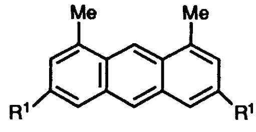
When pyrolysis of the dibenzocycloheptene **1c** was carried out at 730 °C in order to elucidate the mechanism of production of the anthracene **7a**, dimethylanthracene **7b** was confirmed together with recovery of **1c** (85%). In this case a benzyl radical



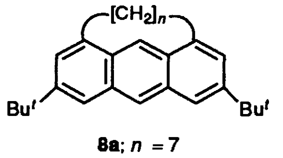
Scheme 1 *Reagents:* i, $ClCH_2OMe$, $TiCl_4$; ii, Na, THF; iii, Na_2S, MeOH



Scheme 2 *Reagents and conditions:* i, $Br[CH_2]_{n-2}Br$, KOH; ii, MCPBA; iii, heat; iv, $AlCl_3$, $MeNO_2$, benzene



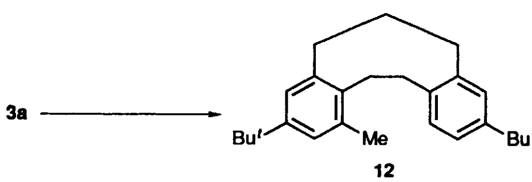
7a; $R^1 = Bu^t$
b; $R^1 = H$



8a; $n = 7$
b; $n = 8$

formed by cleavage of the ethano bridge in substrate **1c** might attack the *ipso* position, then aromatization might occur, resulting in formation of the anthracene structure. This implies that the anthracene structure was derived from the dibenzo[*a*,*d*]cycloheptene skeleton in the sulfones **10**. On the other hand pyrolysis of the sulfones **10e** and **f** afforded the cyclophanes **3e** and **f** and a trace amount of the anthracene **7a** and [*n*]anthracenophanes **8a** and **b**, which are supposedly obtained similarly to formation of compound **7a**.

Pyrolysis of the sulfones **10c** and **d** and **10g–j** afforded the expected cyclophanes **3c** and **d** and **3g–j** in the yields shown in Table 1. When heated at 550 °C, compound **3f** gave the [*n*]anthracenophane **8b** (1.5%), which indicates that cyclophanes are precursors for the anthracenes **8**. During this process, cleavage of ethano bridge and formation of a diradical are evidently involved[9] as shown here. This result reminded us of the pyrolysis of [2_n]cyclophanes in solvents. For example,[10,11] the pyrolysis of [2.2.2](1,2,4)cyclophane in thiophenol or *p*-diisopropylbenzene has been reported to yield 2,9-dimethyldibenzo[*a*,*e*]cyclooctadiene, which undoubtedly is attributed to H-abstraction of the diradical intermediate from the solvent. Thus, the cyclophane **3a** was subjected to pyrolysis in *p*-diisopropylbenzene at 260 °C for 44 h to afford the [2.3]orthocyclophane **12** (Scheme 3), in which the methylene bridge is cleaved.



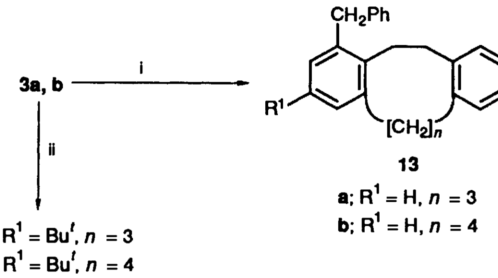
Scheme 3 *Conditions:* heat

Table 2 UV and ^{1}H NMR data of cyclophanes

Compound	λ_{max}(nm) (log ε)[a]	δ_H[b] ArCH_2Ar	δ_H[b] ArH	T_c (°C)	$\Delta G^‡$ (kcal mol^{-1})[c]
9a	291 (2.87) 282 (2.85) 234 (3.99)	3.44, 4.33	6.88, 6.98		
9b	288 (2.90)[d] 278 (2.96) 232 (3.99)	3.44, 4.53	7.02, 7.08		
9c	285 (2.94)[d] 279 (3.02)[d] 233 (3.09)	3.42, 3.70	7.01, 7.06	>150	>20.4
9d	285 (2.88)[d] 279 (3.04) 276 (3.04) 232 (3.99)	br s[e]	7.10, 7.13	50	15.6
9e	280 (3.03) 272 (3.00) 231 (3.97)	br s	7.13	−30	11.4
9f	280 (2.95) 272 (3.00) 231 (3.97)	4.15	7.14	−100	8.1
9j	280 (2.95) 272 (2.97) 230 (3.96)	4.14	7.13, 7.18		
3a	304 (2.32)[d] 262 (3.49)[d] 243 (4.01) 226 (3.97)	3.27, 4.27	6.48, 6.56		
3b	289 (2.55)[d] 274 (2.87)[d] 235 (3.99)	3.33, 4.20	6.53, 6.80		
3c	273 (2.79) 232 (3.97)	3.38, 4.18	6.67, 6.88		
3d	273 (2.86) 232 (3.97)	3.38, 4.35	6.84, 6.91		
3e	271 (2.78) 231 (3.96)	3.36, 4.58	6.88, 6.96		
3f	270 (2.78) 229 (3.94)	3.45, 4.74	6.96, 7.04	>120	>18.4
3g	268 (2.82) 228 (3.93)	br s[e]	7.01, 7.06	20	13.7
3h	267 (2.78) 229 (3.92)	4.13	7.00, 7.08	−50	10.4
1d	267 (2.73) 227 (3.93)	4.13	7.03, 7.07		

[a] In cyclohexane. [b] In CDCl$_3$ at 27 °C. [c] 1 cal = 4.184 J. [d] Shoulder. [e] Broad singlet.

To remove the protective group the cyclophanes **3** were treated with AlCl$_3$–MeNO$_2$ in benzene. When compounds **3c–h** were treated under these conditions, the corresponding cyclophanes **11c–h** were easily obtained; however, the same reaction for compounds **3a** and **b** afforded the phenylated products **13a** and **b**, respectively, as shown in Scheme 4.



Scheme 4 *Reagents:* i, AlCl$_3$, MeNO$_2$, benzene; ii, TiCl$_4$

In order to determine whether benzylation occurs prior to *trans-tert*-butylation or *vice versa*, TiCl$_4$, which is a weaker catalyst, was employed. When the cyclophanes **3a** and **b** were treated with TiCl$_4$ in benzene, the phenylated products **13c** and **d** were obtained, respectively (Scheme 4).

Thus, it is expected that benzylation precedes *trans-tert*-butylation. From these results the methano bridge of the cyclophanes in which the length of methylene chain is shorter than 4 is easily cleaved, which is presumably due to their strained structure.

Spectral data of the cyclophanes are summarized in Table 2. Methylene-bridge protons appear as a pair of doublets in the dithiacyclophanes **9a–c** and the cyclophanes **3a–f**, and as a sharp singlet in compounds **9f–j** and **3h**, suggesting that at 27 °C inversion occurs very rapidly on the NMR time-scale in the dithiacyclophanes **9** with n exceeding 8 and the cyclophanes **3** with n exceeding 10.

Coalescence temperature (T_c) and $\Delta G^‡$ are also shown in Table 2. Compounds **9e** and **3g** have the same bond numbers in the methylene chain. Comparing them, the latter shows a higher T_c and a larger $\Delta G^‡$, which could result from the slightly longer C–S bond distance. It was found that the difference of one methylene unit could cause an increase of T_c by ~100 °C (for example, comparing **9c** with **9d**, or **3f** with **3g**); however, such a dynamic property is scarcely affected by the existence of an external *tert*-butyl group.

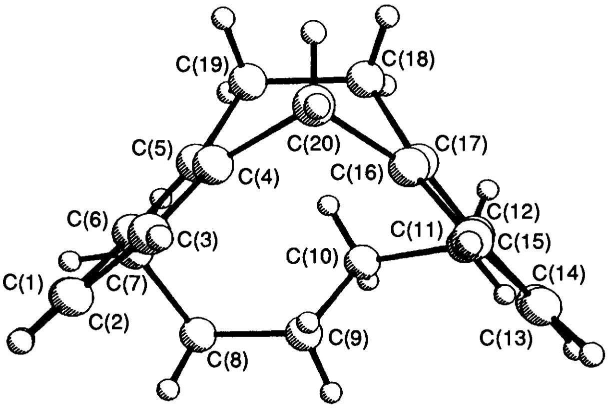


Fig. 1 Perspective view of compound **11c**

In general, red shifts for λ_{max} and upfield shifts of the aromatic protons can be seen as the methylene chain becomes shorter, which implies that the two aromatic rings of the cyclophanes **3** ($n \leqslant 8$) can approach each other closely enough to interact with and distort each other. On the other hand, the data of compounds **3** ($n \geqslant 9$) are almost identical with those of the corresponding noncyclic compound **1d**, suggesting no specific interaction between the two aromatic rings. UV and ^{1}H NMR spectra of the de-*tert*-butylated cyclophanes **11** exhibited a similar trend to that of the cyclophanes **3**.

A perspective view of compound **11c** is shown in Fig. 1. Fractional atomic co-ordinates are given in Table 3, and bond lengths and angles in Table 4.

Table 3 Fractional atomic co-ordinates for compound **11c**

	x	*y*	*z*
C(1)	0.9060(3)	0.2060(3)	0.7549(1)
C(2)	0.8254(3)	0.2874(4)	0.7009(1)
C(3)	0.7472(3)	0.4213(3)	0.7155(1)
C(4)	0.7609(3)	0.4817(3)	0.7842(1)
C(5)	0.8554(2)	0.4070(3)	0.8387(1)
C(6)	0.9191(2)	0.2605(3)	0.8252(1)
C(7)	0.9875(3)	0.1488(3)	0.8828(1)
C(8)	0.8817(3)	0.0137(3)	0.8972(1)
C(9)	0.7345(3)	0.0678(3)	0.9169(1)
C(10)	0.7417(3)	0.1497(3)	0.9891(1)
C(11)	0.6005(3)	0.2352(4)	1.0030(1)
C(12)	0.5314(3)	0.3348(3)	0.9413(1)
C(13)	0.3932(3)	0.2957(3)	0.9079(2)
C(14)	0.3329(3)	0.3705(4)	0.8466(2)
C(15)	0.4145(3)	0.4787(3)	1.8137(1)
C(16)	0.5527(3)	0.5201(3)	0.8457(1)
C(17)	0.6076(2)	0.4574(3)	0.9120(1)
C(18)	0.7502(3)	0.5233(3)	0.9488(1)
C(19)	0.8845(3)	0.4906(3)	0.9097(2)
C(20)	0.6560(3)	0.6093(3)	0.8083(2)

Table 4 Intramolecular distances (Å) and angles (°) for compound **11c**

(a) Distances			
C(1)–C(6)	1.401(4)	C(14)–C(15)	1.381(4)
C(1)–C(2)	1.367(4)	C(16)–C(15)	1.386(4)
C(4)–C(5)	1.411(4)	C(16)–C(20)	1.521(4)
C(4)–C(3)	1.391(4)	C(9)–C(10)	1.527(4)
C(4)–C(20)	1.523(4)	C(9)–C(8)	1.531(4)
C(6)–C(5)	1.400(4)	C(7)–C(8)	1.544(4)
C(6)–C(7)	1.514(4)	C(11)–C(10)	1.545(4)
C(5)–C(19)	1.513(4)	C(18)–C(19)	1.556(4)
C(3)–C(2)	1.385(4)	C(4) ··· C(16)	2.407(4)
C(17)–C(12)	1.402(4)	C(17) ··· C(5)	2.872(4)
C(17)–C(16)	1.398(4)	C(12) ··· C(6)	4.506(4)
C(17)–C(18)	1.514(4)	C(1) ··· C(13)	5.942(4)
C(12)–C(13)	1.391(4)	C(2) ··· C(14)	5.690(4)
C(12)–C(11)	1.510(4)	C(3) ··· C(15)	3.843(4)
C(13)–C(14)	1.375(4)		
(b) Angles			
C(6)–C(1)–C(2)	121.6(3)	C(17)–C(12)–C(11)	122.0(2)
C(5)–C(4)–C(3)	119.9(3)	C(13)–C(12)–C(11)	119.6(2)
C(5)–C(4)–C(20)	119.0(2)	C(12)–C(13)–C(14)	121.7(3)
C(3)–C(4)–C(20)	120.2(3)	C(13)–C(14)–C(15)	119.8(3)
C(1)–C(6)–C(5)	118.3(3)	C(17)–C(16)–C(15)	120.3(3)
C(1)–C(6)–C(7)	117.7(2)	C(17)–C(16)–C(20)	118.6(2)
C(5)–C(6)–C(7)	123.6(2)	C(15)–C(16)–C(20)	120.1(3)
C(4)–C(5)–C(6)	119.3(2)	C(14)–C(15)–C(16)	119.7(3)
C(4)–C(5)–C(19)	118.0(2)	C(10)–C(9)–C(8)	114.8(2)
C(6)–C(5)–C(19)	122.7(2)	C(6)–C(7)–C(8)	111.5(2)
C(4)–C(3)–C(2)	119.9(3)	C(12)–C(11)–C(10)	113.8(2)
C(1)–C(2)–C(3)	120.0(3)	C(9)–C(10)–C(11)	115.2(2)
C(12)–C(17)–C(16)	119.5(2)	C(9)–C(8)–C(7)	115.8(2)
C(12)–C(17)–C(18)	122.5(2)	C(17)–C(18)–C(19)	114.8(2)
C(16)–C(17)–C(18)	118.0(2)	C(4)–C(20)–C(16)	104.5(2)
C(17)–C(12)–C(13)	118.2(2)		

It was found that two aromatic rings face each other; however, compared with 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (DDCH) **1e**,[12] the distances are quite different.

The distance C(4) ··· C(16) is 2.407 Å which is 0.137 Å shorter than the corresponding distance in compound **1e**. The distance C(1) ··· C(13) (5.942 Å) is much shorter than the corresponding distance (7.300 Å) in **1e**. The internal ring C atom [C(17)] is raised above the mean plane of two *ortho* and *meta* C atoms by 0.098 Å, whereas C(14) is raised from the same plane by 0.052 Å. On the other hand the other ring C atoms [C(5) and C(2)] are positioned 0.103 Å and 0.049 Å above the C(1), C(3), C(4), C(6) plane, respectively. Such aromatic rings adopting an approximately boat shape might cause particular reactions of the cyclophanes **10a** and **b** and **3a** and **b**. Unfortunately, attempted X-ray analyses for more strained compounds such as **3a** and **b** were unsuccessful.

Experimental

General.—M.p.s were measured on a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a JEOL GSX-270 NMR spectrometer at 270 MHz in $CDCl_3$. *J*-Values are given in Hz. Mass spectra were obtained at 75 eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300). The amounts of silica gel used were from 5 to 100 g.

*3,7-Di-*tert*-butyl-1,9-bis(chloromethyl)dibenzo*[a,d]*cycloheptene* **1a**.—To a solution of compound **2** (16g, 54.3 mmol) and chloromethyl methyl ether (48.1 g, 0.6 mol) in CS_2 (320 cm^3) at −5 °C was added dropwise $TiCl_4$ (20.6 g, 0.11 mol). After the resulting mixture had been stirred for 4 h, it was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to give a residue, which was chromatographed with dichloromethane–hexane (1:3) as eluent to afford *title compound* **1a** (21.2 g, 97%) as needles, m.p. 133–138 °C (from hexane) (Found: C, 74.6; H, 8.0%; M$^+$, 402. $C_{25}H_{32}Cl_2$ requires C, 74.43; H, 7.99%; M, 402); δ_H 1.30 (18 H, s), 3.30 (4 H, s), 4.16 (2 H, s), 4.18 (4 H, s), 7.19 (2 H, d, *J* 2.2) and 7.22 (2 H, d, *J* 2.2).

Wurtz Coupling of Compound **1a**.—To a mixture of sodium (0.63 g, 27 mmol) and dry tetrahydrofuran (THF) (50 cm^3) was added dropwise a solution of compound **1a** (0.5 g, 1.24 mmol) in dry THF (50 cm^3) for 2 h. The reaction mixture was stirred for an additional 40 h, filtered, and evaporated under reduced pressure to leave the residue, to which dichloromethane (50 cm^3) was added and washed with 1 mol dm^{-3} HCl. After the organic layer had been dried ($MgSO_4$), it was concentrated under reduced pressure to give a residue, which was chromatographed. From the second fraction, eluted with dichloromethane–hexane (1:5), *compound* **4** (60 mg, 17%) was obtained as needles, m.p. 380 °C (decomp.) (Found: C, 90.5; H, 9.7%; M$^+$, 664. $C_{50}H_{64}$ requires C, 90.30; H, 9.70%; M, 664); δ_H 1.34 (36 H, s), 2.54–3.11 (8 H, s), 3.77 (8 H, s), 4.10 (4 H, s) and 7.12–7.15 (8 H, m).

Reaction of Compound **1a** *with* Na_2S.—To a solution of compound **1a** (1.0 g, 2.5 mmol) in methanol (150 cm^3) was added dropwise a solution of $Na_2S{\cdot}9H_2O$ (2.66 gg, 11 mmol) in water (10 cm^3) during 5 min. After the addition was completed the resultant solution was refluxed for 36 h, to which water (100 cm^3) was added, followed by extraction with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to leave a residue, which was washed with hexane to give compound **6** (0.32 g, 35%) as a powder, m.p. 275 °C (decomp.) (from EtOH–$CHCl_3$) (Found: M$^+$, 728. $C_{50}H_{64}S_2$ requires C, 82.37; H, 8.85%; M, 728); δ_H 1.31 (36 H, s), 3.11 (8 H, s), 3.77 (8 H, s), 4.10 (4 H, s) and 7.12–7.15 (8 H, m). Elemental analysis gave unsatisfactory results.

*3,7-Di-*tert*-butyl-1,9-bis(mercaptomethyl)dibenzo*[a,d]*cycloheptene* **1b**.—After a solution of compound **1a** (2 g, 5 mmol) and thiourea (0.9 g, 12 mmol) in dimethyl sulfoxide (DMSO) (20 cm^3) had been stirred at 25 °C for 18 h under nitrogen, it was poured into aq. 10% NaOH. The mixture was acidified with 1 mol dm^{-3} HCl and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to give *title compound* **1b** (1.88 g, 95%) as prisms, m.p. 126–128 °C (from hexane) (Found: C, 75.1; H, 8.85%; M^+, 398. $C_{25}H_{34}S_2$ requires C, 75.32; H, 8.60%; M, 398); ν_{max}/cm^{-1} 2560 (SH); δ_H 1.30 (18 H, s), 1.67 (2 H, t, *J* 7), 3.29 (4 H, s), 3.75 (4 H, d, *J* 7), 4.15 (2 H, s), 7.11 (2 H, d, *J* 2) and 7.14 (2 H, d, *J* 2).

Dithia[n + 2.2.1](1,2,3)*cyclophanes* **9**.—*General procedure; Preparation of compound* **9b**. A solution of compound **1b** (3 g, 7.6 mmol) and 1,2-dibromoethane (2.14 g, 11.4 mmol) in a mixture of EtOH and benzene was added dropwise from a Hershberg funnel to a stirred refluxing mixture of KOH (2 g, 30 mmol) and $NaBH_4$ (1.44 g, 38 mmol) in EtOH (4 dm^3). When addition was complete (15 h), the mixture was concentrated to leave a residue, to which water (500 cm^3) was added, then extracted with dichloromethane. After the extract had been washed with water, dried ($MgSO_4$), and evaporated, the resulting residue was chromatographed with hexane–chloroform (3:1) as eluent to yield *compound* **9b** (1.33 g, 41%) as needles, m.p. 209–211 °C (from hexane–chloroform) (Found: C, 76.5; H, 8.5%; M^+, 424. $C_{27}H_{36}S_2$ requires C, 76.36; H, 8.54%; M, 424); δ_H 1.26 (18 H, s), 2.07–2.45 (4 H, m), 3.09–3.28 (4 H, m), 3.44 (1 H, d, *J* 13), 3.49 (2 H, d, *J* 14), 4.14 (2 H, d, *J* 14), 4.53 (1 H, d, *J* 13), 7.02 (2 H, d, *J* 2.2) and 7.08 (2 H, d, *J* 2.2).

Compound **9a**: needles, m.p. 194–195 °C (Found: C, 76.2; H, 8.2%; M^+, 410. $C_{26}H_{34}S_2$ requires C, 76.04; H, 8.34%; M, 410); δ_H 1.20 (18 H, s), 1.58 (1 H, d, *J* 12), 2.88 (1 H, d, *J* 12), 2.93–3.01 (2 H, m), 3.44 (1 H, d, *J* 12), 3.56 (2 H, d, *J* 13), 3.61–3.69 (2 H, m), 4.20 (2 H, d, *J* 13), 4.33 (1 H, d, *J* 12), 6.88 (2 H, d, *J* 2.2) and 6.98 (2 H, d, *J* 2.2).

Compound **9c**: needles, m.p. 183–185 °C (Found: C, 76.5; H, 8.5%; M^+, 438. $C_{28}H_{38}S_2$ requires C, 76.56; H, 8.73%; M, 438); δ_H 1.10–1.26 (1 H, m), 1.28 (18 H), 1.44–1.60 (1 H, m), 2.20–2.30 (2 H, m), 2.50–2.60 (2 H, m), 3.12–3.28 (2 H, m), 3.41–3.57 (2 H, m), 3.42 (1 H, d, *J* 14.3), 3.70 (2 H, d, *J* 13.9), 3.94 (2 H, d, *J* 13.9), 4.70 (1 H, d, *J* 14.3), 7.01 (2 H, d, *J* 2) and 7.06 (2 H, d, *J* 2).

Compound **9d**: needles, m.p. 212–214 °C (Found: C, 77.0; H, 8.8%; M^+, 452. $C_{29}H_{40}S_2$ requires C, 76.93; H, 8.90%; M, 452); δ_H 1.10–2.20 (8 H, m), 1.30 (18 H, s), 3.13–3.35 (4 H, br s), 3.40–4.25 (5 H, m), 4.50–5.10 (1 H, br s), 7.10 (2 H, d, *J* 2) and 7.13 (2 H, d, *J* 2).

Compound **9e**: needles, m.p. 186–188 °C (Found: C, 77.25; H, 9.0%; M^+, 466. $C_{30}H_{42}S_2$ requires C, 77.19; H, 9.07%; M, 466); δ_H 1.32 (18 H, s), 1.42–1.50 (6 H, m), 2.40–2.48 (4 H, m), 3.35 (4 H, s), 3.81 (4 H, s), 4.10–4.20 (2 H, br s) and 7.13 (4 H, s).

Compound **9f**: prisms, m.p. 203–204 °C (Found: C, 77.2; H, 8.9%; M^+, 480. $C_{31}H_{44}S_2$ requires C, 77.44; H, 9.22%; M, 480); δ_H 1.24–1.64 (8 H, m), 1.30 (18 H, s), 2.52 (4 H, t, *J* 6), 3.35 (4 H, s), 3.77 (4 H, s), 4.15 (2 H, s) and 7.14 (4 H, s).

Compound **9g**: prisms, m.p. 172–174 °C (Found: C, 77.9; H, 9.1%; M^+, 494. $C_{32}H_{46}S_2$ requires C, 77.67; H, 9.37%; M, 494); δ_H 1.30 (18 H, s), 1.39–1.68 (10 H, m), 2.57 (4 H, t, *J* 6.4), 3.35 (4 H, s), 3.77 (4 H, s), 4.16 (2 H, s), 7.14 (2 H, d, *J* 2) and 7.17 (2 H, d, *J* 2).

Compound **9h**: needles, m.p. 128–131 °C (Found: C, 78.0; H, 9.2%; M^+, 508. $C_{33}H_{48}S_2$ requires C, 77.89; H, 9.51%; M, 508); δ_H 1.30 (18 H, s), 1.35–1.74 (12 H, m), 2.66 (4 H, t, *J* 6), 3.38 (4 H, s), 3.77 (4 H, s), 4.14 (2 H, s), 7.13 (2 H, d, *J* 2) and 7.16 (2 H, d, *J* 2).

Compound **9i**: prisms, m.p. 165–167 °C (Found: C, 78.3; H, 9.4%; M^+, 522. $C_{34}H_{50}S_2$ requires C, 78.10; H, 9.64%; M, 522); δ_H 1.29 (18 H, s), 1.34–1.76 (14 H, m), 2.61 (4 H, t, *J* 6.6), 3.33 (4 H), 3.75 (4 H, s), 4.15 (2 H, s), 7.13 (2 H, d, *J* 2) and 7.16 (2 H, d, *J* 2).

Compound **9j**: prisms, m.p. 148–150 °C (from hexane) (Found: C, 78.5; H, 9.7%; M^+, 536. $C_{35}H_{52}S_2$ requires C, 78.29; H, 9.67%; M, 536); δ_H 1.30 (18 H, s), 1.33–1.74 (16 H, m), 2.62 (4 H, t, *J* 6.6), 3.31 (4 H, s), 3.74 (4 H, s), 4.14 (2 H, s), 7.13 (2 H, d, *J* 2.2) and 7.16 (2 H, d, *J* 2.2).

Cyclophanes **3**.—*General procedure: oxidation of compound* **9a**. After **9a** and MCPBA in dichloromethane had been stirred at room temperature, the solvent was removed to give crude compound **10a**, which was used in pyrolysis without further purification.

Pyrolysis of Compound **10a**. Compound **10a** (5.4 g, 11.4 mmol) was pyrolysed at 460 °C under reduced pressure (0.5 Torr) in a horizontal quartz tube (15 mm diameter, 45 cm long). The resultant product was chromatographed with hexane as eluent to afford compound **7a** (0.11 g, 3%) from the first fraction. A yellow oil obtained from the second fraction was recrystallized to give *compound* **3a** (0.46 g, 12%) as prisms, m.p. 155–157 °C (from MeOH) (Found: C, 90.25; H, 9.7%; M^+, 346. $C_{26}H_{34}$ requires C, 90.11; H, 9.89%; M, 346); δ_H 0.46–0.61 (1 H, m), 1.11 (18 H, s), 1.93–2.06 (1 H, m), 2.52–2.83 (4 H, m), 2.88–3.25 (4 H, m), 3.27 (1 H, d, *J* 12), 4.27 (1 H, d, *J* 12), 6.48 (2 H, d, *J* 1.8) and 6.56 (2 H, d, *J* 1.8).

Compound **7a**: pale yellow needles, m.p. 184–187 °C (from MeOH) (Found: C, 90.45; H, 9.4%; M^+, 318. $C_{24}H_{30}$ requires C, 90.51; H, 9.49%; M, 318); δ_H 1.44 (18 H, s), 2.82 (6 H, s), 7.38 (2 H, s), 7.72 (2 H, s), 8.32 (1 H, s) and 8.48 (1 H, s).

Compound **3b**: (pyrolysed at 550 °C): needles, m.p. 146–147 °C (from MeOH) (Found: C, 89.7; H, 10.0%; M^+, 360. $C_{27}H_{36}$ requires C, 89.94; H, 10.06%; M, 360); δ_H 0.84–1.03 (2 H, m), 1.14 (18 H, s), 1.82–2.01 (2 H, m), 2.24–3.31 (8 H, m), 3.33 (1 H, d, *J* 12), 4.20 (1 H, d, *J* 12), 6.53 (2 H, d, *J* 2) and 6.80 (2 H, d, *J* 2).

Compound **3c**: prisms, m.p. 120–122 °C (from MeOH) (Found: C, 89.6; H, 10.0%; M^+, 374. $C_{28}H_{38}$ requires C, 89.78; H, 10.22%; M, 374); δ_H −0.82 to −0.64 (1 H, m), 0.46–0.64 (1 H, m), 1.17 (18 H, s), 1.26–1.80 (4 H, m), 2.29–2.40 (2 H, m), 2.86–2.95 (2 H, m), 3.05–3.16 (2 H, m), 3.31–3.40 (2 H, m), 3.38 (1 H, d, *J* 12.5), 4.18 (1 H, d, *J* 12.5), 6.67 (2 H, d, *J* 2) and 6.88 (2 H, d, *J* 2).

Compound **3d**: prisms, m.p. 125–126 °C (from MeOH) (Found: C, 89.8; H, 10.3%; M^+, 388. $C_{29}H_{40}$ requires C, 89.63; H, 10.37%; M, 388); δ_H 0.59–1.82 (8 H, m), 1.22 (18 H, s), 2.48–2.95 (4 H, m), 2.95–3.52 (4 H, m), 3.38 (1 H, d, *J* 13), 4.35 (1 H, d, *J* 13), 6.84 (2 H, d, *J* 2) and 6.91 (2 H, d, *J* 2).

Compound **3e**: prisms, m.p. 146–148 °C (from MeOH–$CHCl_3$) (Found: C, 89.7; H, 10.4%; M^+, 402. $C_{30}H_{42}$ requires C, 89.49; H, 10.51%; M, 402); δ_H 0.96–1.78 (10 H, m), 1.26 (18 H, s), 2.42–2.94 (4 H, m), 3.04–3.28 (4 H, m), 3.36 (1 H, d, *J* 14), 4.35 (1 H, d, *J* 14), 6.88 (2 H, d, *J* 2) and 6.96 (2 H, d, *J* 2).

Compound **3f**: needles, m.p. 214–215 °C (from EtOH–hexane) (Found: C, 89.0; H, 10.5%; M^+, 416. $C_{31}H_{44}$ requires C, 89.36; H, 10.64%; M, 416); δ_H 0.72–1.90 (12 H, m), 1.29 (18 H, s), 2.39–2.50 (2 H, m), 2.94–3.12 (4 H, m), 3.16–3.30 (2 H, m), 3.45 (1 H, d, *J* 14), 4.74 (1 H, d, *J* 14), 6.96 (2 H, d, *J* 2) and 7.04 (2 H, d, *J* 2).

Compound **3g**: needles, m.p. 151–153 °C (from EtOH) (Found: C, 89.4; H, 10.4%; M^+, 430. $C_{32}H_{46}$ requires C, 89.24; H, 10.76%; M, 430); δ_H 1.14–1.50 (14 H, m), 1.29 (18 H, s), 2.54–2.68 (4 H, m), 3.12–3.24 (4 H, br s), 7.01 (2 H, d, *J* 2) and 7.06 (2 H, d, *J* 2). Methylene protons (2 H) were not observed because the coalescence temperature is 20 °C.

Compound **3h**: needles, m.p. 179–181 °C (from EtOH–$CHCl_3$) (Found: C, 89.4; H, 10.6%; M^+, 444. $C_{33}H_{48}$ requires C, 89.12; H, 10.88%; M, 444); δ_H 1.20–1.51 (16 H, m), 1.30 (18 H, s), 2.61 (4 H, t, *J* 7), 3.18 (4 H, s), 4.13 (2 H, s), 7.00 (2 H, d, *J* 2) and 7.08 (2 H, d, *J* 2).

Compound **3i**: needles, m.p. 152–154 °C (from EtOH–$CHCl_3$) (Found: C, 88.9; H, 10.6%; M^+, 458. $C_{34}H_{50}$ requires C, 89.01; H, 10.99%; M, 458); δ_H 1.20–1.47 (18 H, m), 1.30 (18 H, s), 2.56–2.64 (4 H, m), 3.17 (4 H, s), 4.14 (2 H, s), 7.03 (2 H, d, *J* 2) and 7.08 (2 H, d, *J* 2).

Compound **3j**: powder, m.p. 136–138 °C (from EtOH) (Found: C, 89.0; H, 10.9%; M$^+$, 472. $C_{35}H_{52}$ requires C, 88.91; H, 11.09%; M, 472); δ_H 1.30 (18 H, s), 1.30–1.54 (20 H, m), 2.55–2.63 (4 H, m), 3.17 (4 H, s), 4.14 (2 H, s), 7.03 (2 H, d, *J* 2) and 7.08 (2 H, d, *J* 2).

Compound **8a**: pale yellow prisms, m.p. 214–218 °C (from MeOH) (Found: M$^+$, 386.2973. $C_{29}H_{38}$ requires M, 386.2973); δ_H 1.44 (18 H, s), 1.48–2.16 (10 H, m), 3.12–3.28 (4 H, m), 7.36 (2 H, d, *J* 1.5), 7.72 (2 H, d, *J* 1.5), 8.27 (1 H, s) and 8.69 (1 H, s).

Compound **8b**: prisms, m.p. 233–235 °C (from MeOH) (Found: C, 89.7; H, 9.7%; M$^+$, 400. $C_{30}H_{40}$ requires C, 89.94; H, 10.06%; M, 400); δ_H 1.43 (18 H, s), 1.56–2.10 (12 H, m), 3.08–3.19 (4 H, m), 7.37 (2 H, d, *J* 2), 7.70 (2 H, d, *J* 2), 8.29 (1 H, s) and 8.76 (1 H, s).

Pyrolysis of Compound **1c**.—Compound **1c** (0.35 g, 1.57 mmol) was pyrolysed at 730 °C as described above to give compound **7b** as yellow prisms, m.p. 133–134.5 °C (from MeOH) (lit.,[13] 130–131 °C) (Found: M$^+$, 206. Calc. for $C_{16}H_{14}$: M, 206); δ_H 2.85 (6 H, s), 7.32 (2 H, dd, *J* 6.6, 1), 7.38 (2 H, dd, *J* 8, 6.6), 7.88 (2 H, dd, *J* 8, 1), 8.43 (1 H, s) and 8.63 (1 H, s).

Pyrolysis of Compound **3a**.—A solution of compound **3a** (0.1 g, 0.29 mmol) in *p*-diisopropylbenzene (3 cm^3) was heated at 260 °C for 44 h. The resultant yellow oil was chromatographed with hexane as eluent to afford *compound* **12** (18 mg, 18%) as prisms, m.p. 120–122 °C (from MeOH) (Found: C, 89.6; H, 10.1%, M$^+$, 348. $C_{26}H_{36}$ requires C, 89.59; H, 10.14%; M, 348); δ_H 1.32 (9 H, s), 1.33 (9 H, s), 1.98 (2 H, br s), 2.39 (3 H, s), 2.60–3.30 (8 H, br s) and 7.06–7.23 (5 H, m).

trans-tert-*Butylation of Compounds* **3c**–**h**.—*General procedure*. To a solution of compound **3c** (0.2 g, 0.53 mmol) in benzene (20 cm^3) was added a solution of $AlCl_3$ (0.29 g, 2.15 mmol) in nitromethane (0.4 cm^3). After the reaction mixture had been stirred and heated for 2 h, and water (20 cm^3) had been added, it was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$) and evaporated to leave a residue, which was chromatographed with hexane as eluent to give *compound* **11c** (0.11 g, 74%) as needles, m.p. 107–108 °C (from EtOH) (Found: C, 91.6; H, 8.3%; M$^+$, 262. $C_{20}H_{22}$ requires C, 91.55; H, 8.45%; M, 262); δ_H −0.75 to −0.57 (1 H, m), 0.50–0.66 (1 H, m), 1.28–1.44 (2 H, m), 1.67–1.85 (2 H, m), 2.34–2.45 (2 H, m), 2.90–3.00 (2 H, m), 3.09–3.20 (2 H, m), 3.37–3.47 (2 H, m), 3.42 (1 H, d, *J* 12.5), 4.20 (1 H, d, *J* 12.5), 6.72 (2 H, dd, *J* 7.3, 1.8), 6.82 (2 H, dd, *J* 7.3, 7.4) and 6.87 (2 H, dd, *J* 7.3, 1.8).

Compound **11d**: needles, m.p. 99–101 °C (from EtOH) (Found: C, 91.4; C, 8.7%; M$^+$, 276. $C_{21}H_{24}$ requires C, 91.25; H, 8.75%; M, 276); δ_H 0.62–1.84 (8 H, m), 2.52–2.96 (4 H, m), 3.01–3.10 (2 H, m), 3.43 (1 H, d, *J* 12.8), 3.44–3.53 (2 H, m), 4.38 (1 H, d, *J* 12.8) and 6.85–6.93 (6 H, m).

Compound **11e**: prisms, m.p. 102–104 °C (from MeOH) (Found: C, 91.05; 8.9%; M$^+$, 290. $C_{22}H_{26}$ requires C, 90.98; H, 9.02%; M, 290); δ_H 0.85–1.74 (10 H, m), 2.42–2.96 (4 H, m), 3.08–3.38 (4 H, m), 3.39 (1 H, d, *J* 13.6), 4.54 (1 H, d, *J* 13.6) and 6.85–6.98 (6 H, m).

Compound **11f**: prisms, m.p. 168–170 °C (from MeOH–$CHCl_3$) (Found: C, 90.9; H, 9.1%; M$^+$, 304. $C_{23}H_{28}$ requires C, 90.73; H, 9.27%; M, 304); δ_H 0.64–1.89 (12 H, m), 2.39–2.51 (2 H, m), 2.94–3.04 (2 H, m), 3.04–3.37 (4 H, m), 3.45 (1 H, d, *J* 14.3), 4.72 (1 H, d, *J* 14.3) and 6.90–7.04 (6 H, m).

Compound **11g**: needles, m.p. 103–105 °C (from EtOH) (Found: C, 90.65; H, 9.4%; M$^+$, 318. $C_{24}H_{30}$ requires C, 90.51; H, 9.49%; M, 318); δ_H 1.10–1.50 (14 H, m), 2.62 (4 H, t, *J* 7.3), 3.23 (4 H, s), 3.90–4.30 (2 H, br s) and 6.97–7.03 (6 H, m).

Compound **11h**: prisms, m.p. 109–110 °C (from EtOH) (Found: C, 90.6; H, 9.5%; M$^+$, 332. $C_{25}H_{32}$ requires C, 90.3; H, 9.70%; M, 332); δ_H 1.19–1.52 (16 H, m), 2.62 (4 H, t, *J* 7.2), 3.23 (4 H, s), 4.11 (2 H, s) and 6.95–7.06 (6 H, m).

trans-tert-*Butylation of Compounds* **3a** *and* **b**.—*General procedure*. To a solution of compound **3a** (83 mg, 0.24 mmol) in benzene (15 cm^3) was added a solution of $AlCl_3$ (0.13 g, 0.96 mmol) in nitromethane (0.2 cm^3). The reaction mixture was stirred at 55 °C for 12.5 h. After the addition of water (10 cm^3), followed by extraction with dichloromethane, the extract was washed with water, dried ($MgSO_4$), and concentrated to leave a residue, which was chromatographed with hexane as eluent to afford *compound* **13a** (43 mg, 57%) as needles, m.p. 140 °C (from MeOH) (Found: C, 92.6; H, 7.8%; M$^+$, 312. $C_{24}H_{24}$ requires C, 92.26; H, 7.74; M, 312); δ_H 1.93–2.05 (2 H, m), 2.27–2.36 (4 H, m), 2.60–3.00 (4 H, m), 4.11 (2 H, s) and 7.00–7.30 (12 H, m).

Compound **13b**: needles, m.p. 101–103 °C (from EtOH) (Found: C, 92.0; H, 7.9%; M$^+$, 326. $C_{25}H_{26}$ requires C, 91.97; H, 8.03%; M, 326); δ_H 1.62–1.74 (4 H, m), 2.42–2.56 (4 H, m), 2.78–3.06 (4 H, m), 4.13 (2 H, s) and 6.95–7.32 (12 H, m).

Reaction of Compounds **3a** *and* **b** *with* $TiCl_4$.—To a solution of compound **3a** (60 mg, 0.17 mmol) in benzene (5 cm^3) was added $TiCl_4$ (0.5 cm^3, 4.54 mmol). After the reaction mixture had been stirred at 55 °C for 0.5 h, it was quenched with water (10 cm^3). The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave a residue, which was chromatographed with hexane as eluent to give *compound* **13c** (24 mg, 33%) as prisms, m.p. 108–110 °C (from EtOH) (Found: C, 90.65; H, 9.45%; M$^+$, 424. $C_{32}H_{40}$ requires C, 90.51; H, 9.49%; M, 424); δ_H 1.31 (9 H, s), 1.32 (9 H, s), 1.92–2.04 (2 H, m), 2.10–2.60 (4 H, m), 2.60–3.30 (4 H, m), 4.11 (2 H, s) and 6.98–7.31 (10 H, m).

Compound **13d** (49%): prisms, m.p. 63–66 °C (from EtOH) (Found: C, 90.35; H, 9.6%; M$^+$, 438. $C_{32}H_{42}$ requires C, 90.35; H, 9.65%; M, 438); δ_H 1.29 (9 H, s), 1.30 (9 H, s), 1.62–1.74 (4 H, m), 2.40–2.52 (4 H, m), 2.69–2.98 (4 H, m), 4.12 (2 H, s) and 6.99–7.31 (10 H, m).

Crystal Structure Determination for Compound **11c**.—$C_{20}H_{22}$, M = 262.394, monoclinic, $a = 9.267(5)$, $b = 8.367(9)$, $c = 19.023(25)$ Å, $\beta = 97.70(7)°$, $V = 1461.61$ Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, $D_x = 1.147$ g cm^{-3}, prisms. Data were collected on an AFC5 diffractometer (Rigaku, Japan), ω scan width 0.50 + 0.26 tan θ, graphite-monochromated Cu-Kα radiation, λ 1.540 56 Å. Of 2426 independent reflections collected in th range $5 < 2\theta < 120°$ (2θ–ω scan type) 1783 with $I > 3\sigma(I)$ were taken as observed. Neither absorption nor decay correction was applied. The structure was solved by direct methods using the TEXSAN program system (Version 2.0, MJ201SP) and refined by full-matrix least-squares calculations with all non-hydrogen atoms treated anisotropically using the weighting scheme $w = 4F_0^2/\sigma^2(F_0^2)^2$ which resulted in the final residuals: R 0.0558, R_w 0.0703.*

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* *Supplementary publication* (see Instructions for Authors, section 5.6.3, January issue). Tables of bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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