# Conformational study of the higher [n.n]paracyclophanes: evaluation as potential hosts for molecular halogens and benzenes

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**A fundamental study of the conformations of [7.7]-, [8.8]-, [9.9]-, [11.11]- and octamethyl[8.8]-paracyclophanes in the solid state shows that the [odd.odd] members of the series possess parallel, symmetrically disposed benzene rings. A new genre of inclusion phenomenon based on donor–halogen EDA interactions is also defined and the potential of cyclophanes to act as hosts both in this capacity and to benzenes is discussed.**

Host–guest chemistry is now a mature discipline, and countless examples of inclusion phenomena based on metal–ligand, ion-pairing, hydrogen bonding, hydrophobic and aromatic stacking interactions have been described.[1] Related to these interactions is the noncovalent bonding between n or π electron donors and halogen acceptors, typified by the solid state structures of trimethylamine–$I_2$ and benzene–$Br_2$ (Fig. 1). Commonly referred to as 'face-centred donor–acceptor' complexes,[2] these interactions can be of the same energetic magnitude as hydrogen bonds, and yet do not seem to have been the basis for the design of a host–guest system. We were intrigued particularly by the latter of these species (Fig. 1), and thus undertook a study of macrocycles with parallel aromatic rings at fixed distances which might serve as receptors for molecular halogens.

Although examples[3] of molecules which possess parallel benzene rings at distances in the range between 8.55 Å (the Ar–Ar distance in Ar · · · Cl–Cl · · · Ar)[4] and 9.65 (the predicted Ar–Ar distance in Ar · · · I–I · · · Ar) could be found in a search of the Cambridge Crystallographic Databasc,[5] the presence in every case of heteroatoms such as N and O which can act as n-donors complicates matters and does not allow one to isolate the potential coordinating effect of the aromatic π system.

We therefore turned to cases where all-hydrocarbon molecules satisfy the conditions defined above. The simplest of these would be where two benzene rings are linked by alkyl spacers, preferably in a *para* fashion (Fig. 2). Molecules of this description, the '[n.n]paracyclophanes', were first reported by Cram in 1951,[6] who prepared examples to a maximum dimension of $n = 6$.[7] Molecular mechanics studies show that the members of this series where $n$ is an odd number should find an energy minimum where the two benzene rings are face to face, in agreement with Dale's postulate that cycloalkanes with diametrically opposed alkene, alkyne or phenylene functions linked by chains with an odd number of methylene units are nearly strain-free, while those with an even number are conformationally unstable.[8] The minimized (MM3)[9] structures of the [7.7]- and [9.9]-paracyclophanes are presented in Fig. 3. The predicted Ar–Ar distances are 7.8 and 10.3 Å, respectively. Two points emerge on examination of these structures: first, that the cavity dimension of [7.7]paracyclophane is too small for $Cl_2$ while that of the [9.9] is too big for $I_2$, and second, that the protons of the alkyl chains already occupy the cavities to some extent. Modelling of the [8.8]paracyclophane showed that a structure with parallel benzene rings could exist with an Ar–Ar distance of about 9 Å, although this conformer was located in a cluster of minima about 3 kJ $mol^{-1}$ above the lowest energy structure, which was twisted and irregular in shape (Fig. 4). Its long dimension matched that reported for

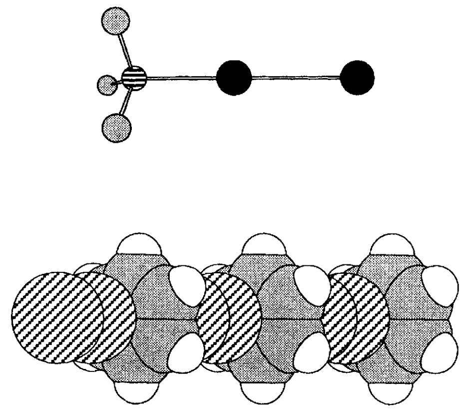
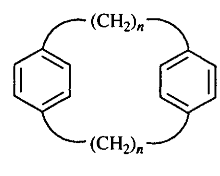


**Fig. 1** Top, the trimethylamine–$I_2$ EDA complex; bottom, the benzene–$Br_2$ EDA complex




**1** $n = 7$
**2** $n = 8$
**3** $n = 9$
**4** $n = 10$
**5** $n = 11$

**Fig. 2**

Ar–$Br_2$–Ar (9.0 Å)[10] and, unlike the above cases, the protons on the bridging alkyl chains point away from the cavity. The [10.10] shows similar behaviour, with an Ar–Ar distance of 11.6 Å. Although the cavities of the [9.9]- and [10.10]-cyclophanes are too large for halogen inclusion, the former appears to be a nearly ideal match for a perpendicular aromatic interaction with a benzene ring (Fig. 5), with centroid to centroid distances of just over 5 Å.[11] Again, this would allow the observation of a weak interaction in isolation from other more dominant forms of noncovalent bonding, with which it is virtually always found in combination. The effect of the partial occupancy of the cavity by the alkyl chain protons on any potential host–guest interaction would also have to be addressed in this case.

It was decided on the above grounds to prepare the series of paracyclophanes from [7.7] to [11.11]. Our interest was not only in their potential for molecular recognition, but also in

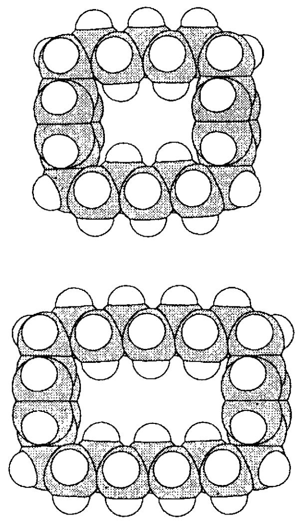


Fig. 3

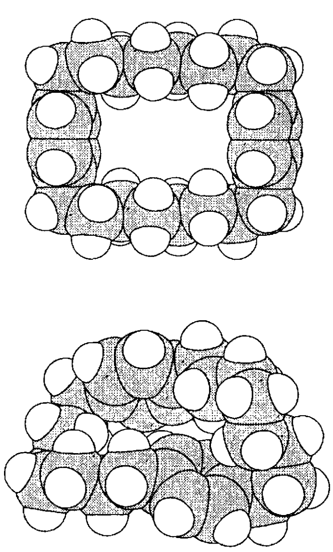


**Fig. 4** Top, minimized [8.8] structure possessing a cavity (E = 121 kJ mol$^{-1}$); bottom, lowest energy [8.8] structure from simulation (E = 118 kJ mol$^{-1}$)

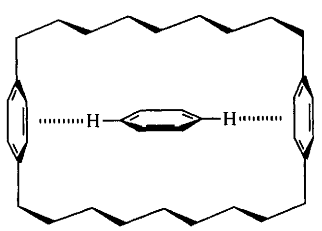
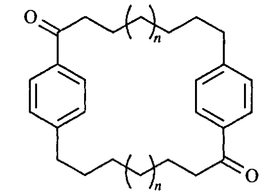
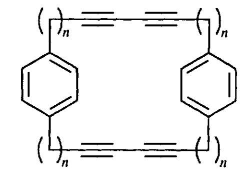



Fig. 5

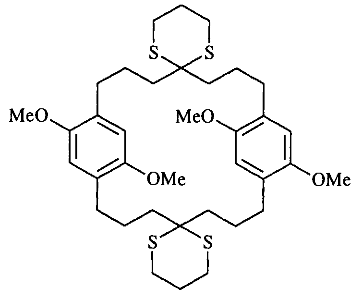
testing the findings of the modelling studies and in the fundamental structural appeal of these 'molecular boxes'. A literature review showed that none of the target cyclophanes **1**–**5** (Fig. 2) were known compounds, although a few examples of molecules possessing the higher (*i.e.* ⩾ [7.7]) paracyclophane framework were identified. Of these, most were functional derivatives noted as 'dimerization' products of annelation reactions. For example, the observation of paracyclophanediones **6** ($n$ = 1, 3, 4) in up to 12% yield was reported during the preparation of benzocycloalkanones by Friedel–Crafts acylation.[12,13] Intermolecular Dieckman[14] and acyloin[15] condensations have also resulted in oxygenated cyclophanes, again in about 10% yield. Acetylenic coupling reactions give 'dimers' **7** ($n$ = 2, 3; 10–12%),[16,17] and a [7.7]paracyclophane derivative **8** was obtained in a relatively good yield of 17% by the coupling of a bis(dithiane) with a diiodide.[18] Interestingly, the [7.7] system is also found in nature. The cylindrocyclophanes and nostocyclophanes (*e.g.* **9**) are cytotoxins associated with the blue-green algae *Cylindrospermum licheniforme* and *Nostoc linckia*, respectively.[19]



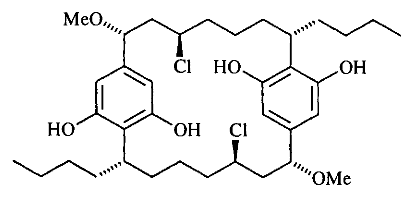

**6**




**7**




**8**




**9**

## Results and discussion

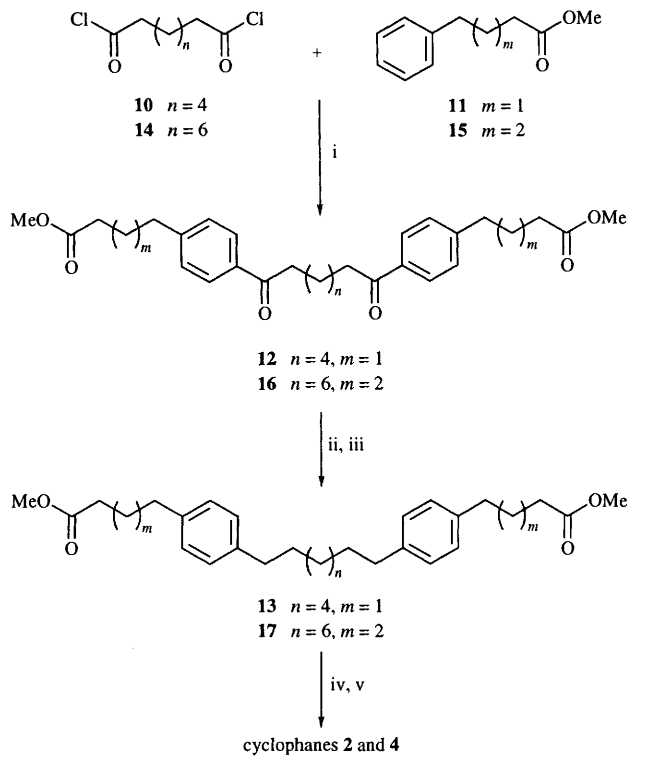
The synthetic approach originally developed by Cram[6] for the synthesis of the smaller [$n.n$]- and [$n.m$]-paracyclophanes involved an intramolecular acyloin condensation, and a modernized version of this method was used in preparation of the higher analogues. For the members of the series where $n$ was an even number of carbons, this was a straightforward matter of preparing the symmetric diesters **13** and **17** and cyclizing with sodium in the presence of trimethylsilyl chloride (Scheme 1). Clemmensen reduction without isolation of the intermediate bis(silyloxy)alkenes then provided the [8.8]- and [10.10]-cyclophanes **2** and **4** in 18 and 12% yields, respectively.

Synthesis of the [odd.odd]cyclophanes was effected by the same method but required asymmetric diester precursors. These were prepared by sequential Friedel–Crafts acylations on the relevant α,ω-diphenylalkanes (Scheme 2). Wolff–Kishner reduction and re-esterification of the resulting acids gave **24**, **31** and **38** which were cyclized to the products **1**, **3** and **5** in 21, 16 and 24% yields, respectively.

Of the two members of the [even.even] series, only compound **2** was a crystalline solid (mp 43–44 °C). Compound **4** was a waxy material which became liquid above 25 °C, and no attempt to obtain crystals thereof was successful. Slow evaporation of solutions of **2** in hexane gave colourless plates suitable for X-ray diffraction which yielded the structure shown in Fig. 6. Unfortunately no cavity is defined, but neither does the structure correspond to the predicted minimum in Fig. 4. According to MACROMODEL,[9] the structure generated from the crystal coordinates is 77 kJ mol$^{-1}$ above the lowest energy conformer (118 kJ mol$^{-1}$),[20] although relaxation to a nearby saddle point involves relatively small distortions of the overall structure and brings the energy down to 124 kJ mol$^{-1}$. This conformer, however, was not among the minima found during the simulation.

Although the cavity of the [8.8]paracyclophane is not 'preorganized' in the solid state for the accommodation of bromine, it remains true that the open cavity form of **2** (Fig. 4) is a low energy conformer (121 kJ $mol^{-1}$) and thus likely to be populated to some extent in solution. We therefore studied the interaction of **2** with $Br_2$, in hope that any complex formed might precipitate from solution. However, the reactivity of the halogen towards the benzylic positions of the cyclophane seriously interfered with this work, and it was therefore decided that these positions would be substituted to eliminate this problem. Thus a new target compound, 2,2,9,9,14,14,21,21-octamethyl[8.8]paracyclophane **45**, was identified.

The preparation of **45** was carried out as described in Scheme




**Scheme 1** *Reagents and conditions:* i, $AlCl_3$, $CS_2$; ii, $NH_2NH_2$, KOH, $HOCH_2CH_2OH$, heat; iii, $CH_2N_2$, $Et_2O$; iv, Na, $Me_3SiCl$, xylene, heat; v, Zn–Hg, conc. HCl, HOAc, heat

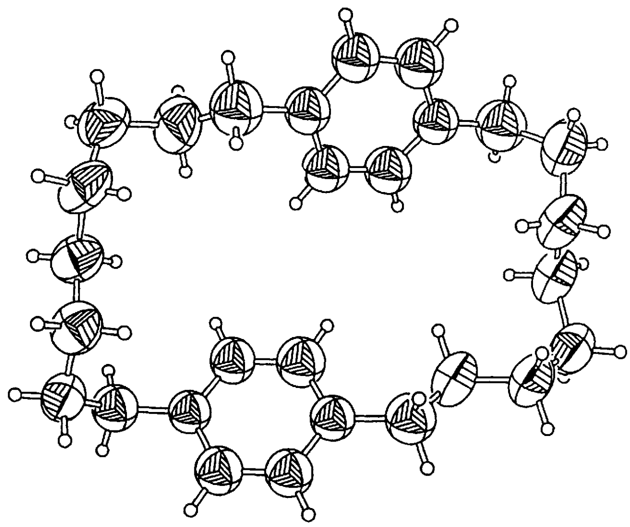
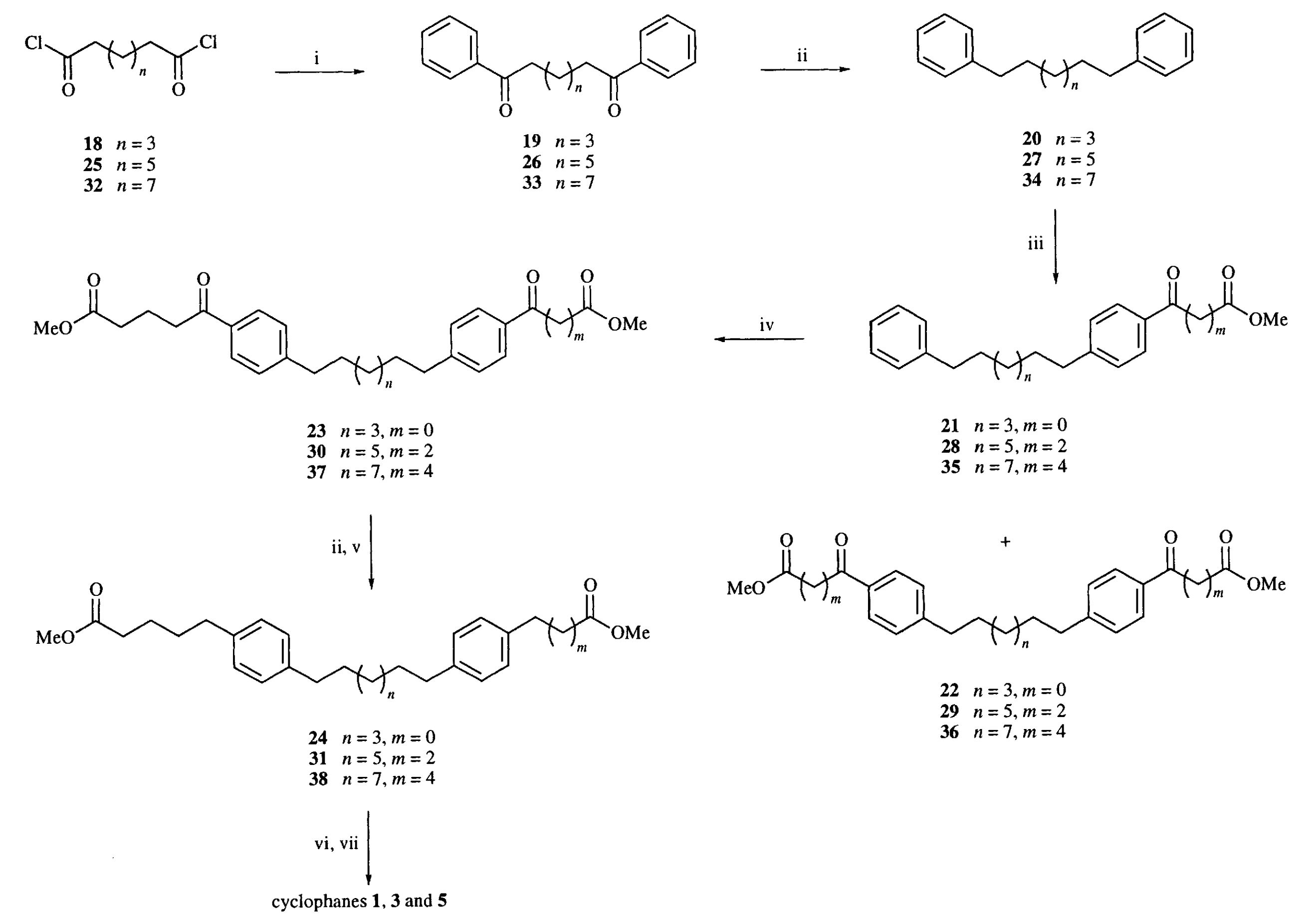


**Fig. 6** X-Ray crystal structure of **2**




**Scheme 2** *Reagents and conditions:* i, $AlCl_3$, PhH; ii, $NH_2NH_2$, KOH, $HOCH_2CH_2OH$, heat; iii, $MeO_2C(CH_2)_mCOCl$, $AlCl_3$, $Cl_2CHCHCl_2$; iv, $MeO_2C(CH_2)_3COCl$, $AlCl_3$, $CS_2$; v, $CH_2N_2$, $Et_2O$; vi, Na, $Me_3SiCl$, xylene, heat; vii, Zn–Hg, conc. HCl, HOAc, heat

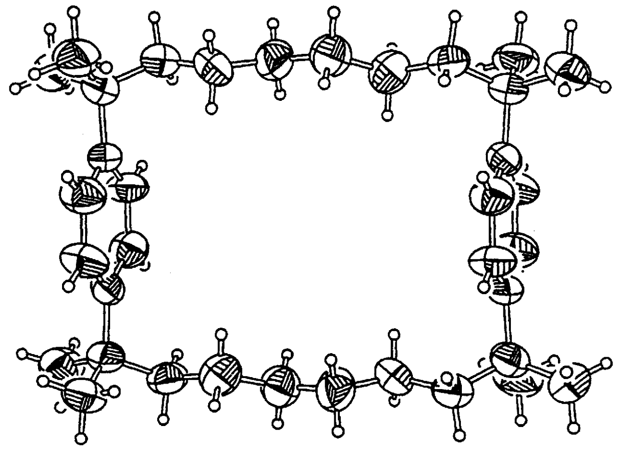
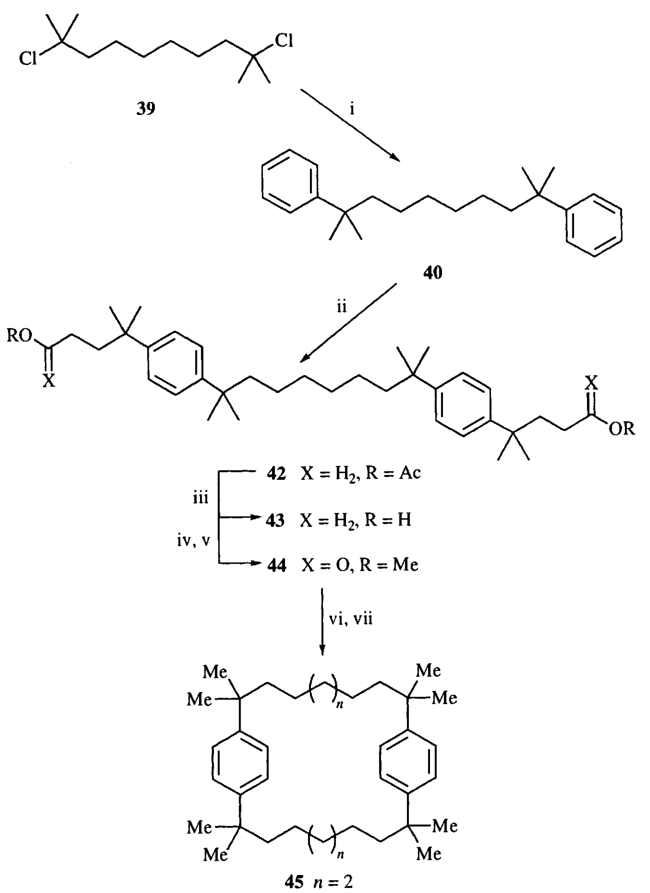


**Fig. 7** X-Ray crystal structure of **45**




**Scheme 3** *Reagents and conditions:* i, PhH, $FeCl_3$; ii, **41**, $FeCl_3$, $CH_2Cl_2$; iii, KOH, $HOCH_2CH_2OH$, heat; iv, $KMnO_4$, $MnSO_4$, $H_2SO_4$, adogen 464, $H_2O$, $CH_2Cl_2$; v, $CH_2N_2$, $Et_2O$; vi, Na, $Me_3SiCl$, xylene, heat; vii, Zn–Hg, conc. HCl, HOAc, heat

3. Successive Friedel–Crafts alkylations of benzene, first with reagent **39** and then 5-acetoxy-2-chloro-2-methylpentane **41** led to the diol acetate **42**. A hydrolysis-oxidation-esterification sequence then gave the substrate for the acyloin condensation **44**. Cyclization and reduction as usual afforded the target cyclophane **45** as a surprisingly high-melting (178–180 °C) white solid in 17% yield. The large gap in melting point between **2** and **45** indicated a difference in solid state structure, and therefore crystals of this material were submitted to X-ray analysis. Fig. 7 shows that **45**, unlike **2**, does indeed possess a cavity. However, the ring-to-ring distance is not the predicted 9.0 Å but is compressed to 8.64 Å, probably as a result of crystal packing forces. Attempts to observe an interaction between **45** and bromine unfortunately again led to chemical reaction. The addition of solutions of $Br_2$ ($CCl_4$, hexane) to the

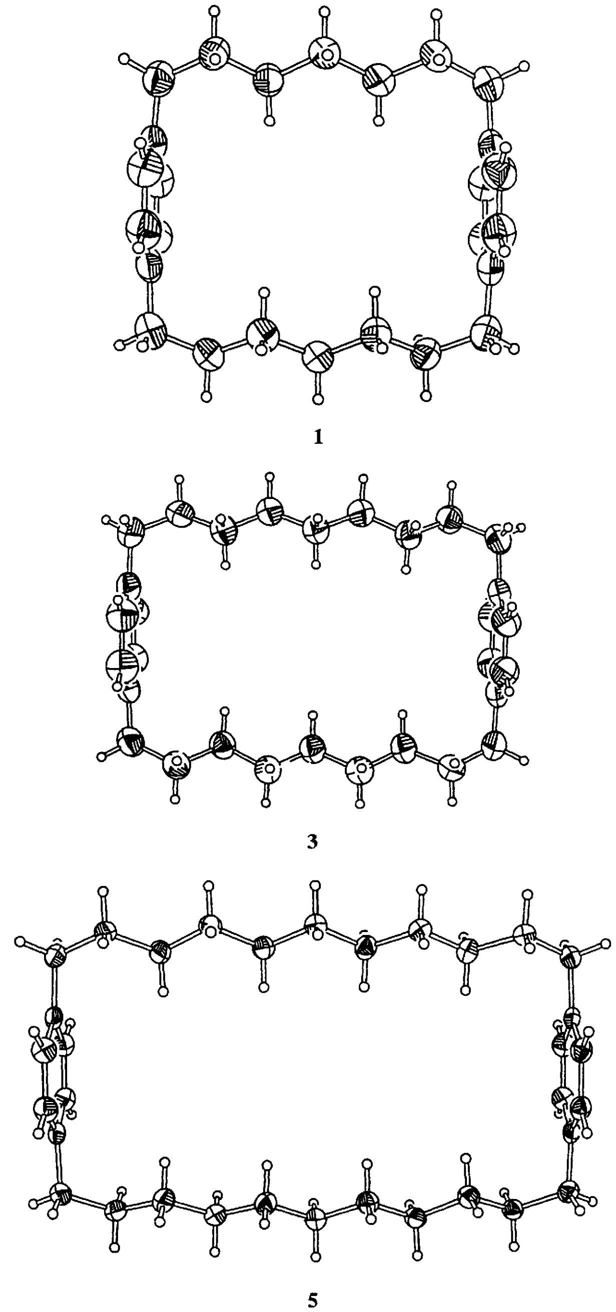



**Fig. 8** X-Ray crystal structures of **1**, **3** and **5**

cyclophane led to rapid decolouration, and subsequent analysis showed evidence of substitution both at the hydrocarbon bridges and the aromatic rings.

Compounds **1**, **3** and **5** were all solids from which X-ray quality crystals could be grown. The structures (Fig. 8) were as predicted by modelling, with parallel Ar–Ar planes separated by 7.85, 10.33 and 12.88 Å, respectively. In all of these and in **45**, the number of molecules in the unit cell is half the number of general equivalent positions for the space group, implying the presence of molecular symmetry. In both *Pbca* and $P2_1/c$ the only special positions are inversion centres, therefore molecules of **1**, **3**, **5** and **45** possess crystallographically imposed $\bar{1}$ ($C_i$) symmetry. The molecular packing involves no end-to-end aryl stacking but rather takes on a herringbone motif, where the benzene rings abut the alkyl chains of neighbouring molecules. The box-like appearance of **1**, **3** and **5** gives the impression of open-cavitied structures, but any potential guest would violate the van der Waals radii of the alkyl-chain hydrogens which point into the cavity, as these are themselves less than 4 Å apart. Turning both alkyl chains through a *ca.* 30° angle serves

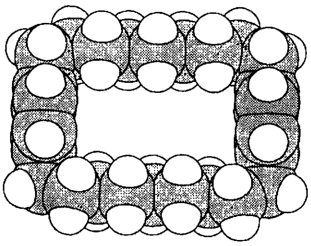


**Fig. 9** Minimized 'open-cavitied' structure of [9.9]paracyclophane

to 'open' the cavity to the extent that inclusion would be possible (Fig. 9), but at a cost of about 70 kJ $mol^{-1}$ (for the [9.9] system) according to MACROMODEL.[9] Indeed, no perpendicular π–π interaction could be detected (by NMR titration) between **3** and either benzene or 1,2,4,5-tetrafluorobenzene.

In summary, the higher paracyclophanes **1**, **2**, **3**, **4**, **5** and **45** have been prepared and the crystal structures of all but compound **4** determined. The [odd.odd]paracyclophanes **1**, **3** and **5** are all box shaped with symmetrically disposed benzene rings. The [even.even]paracyclophanes are conformationally unpredictable, with the [8.8] compound **2** being irregular in appearance while its octamethyl relative **45** again takes up a rectangular form. The cavity dimension of the idealized [8.8]paracyclophane matches closely the Ar–Ar distance in the bromine–benzene complex, while that of the [9.9] corresponds to the centroid–centroid distance in edge-to-face aromatic interactions. However, in the former case, the reactivity of the halogen was too great to allow the observation of any noncovalent bonding, and in the latter case, protons on the chains linking the two benzene rings partially occupied the cavity, the displacement of which to make room for a guest was energetically unfavourable.

It may be that no cyclophane host will be able to complex chlorine or bromine before chemical reaction occurs. However, a receptor for the less aggressive iodine molecule is still a possibility if the correct donor-to-iodine distance can be engineered into a macrocycle. Concerning the question of inclusion based on the perpendicular π–π interaction, this should be a matter of transporting the alkyl chains out of reach of the guest, perhaps by introducing extensions to the aryl residue (*e.g.* C≡C) to act as spacers. Work along these lines continues.

## Experimental

IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. $^1H$ NMR and $^{13}C$ NMR spectra were measured on Bruker WM 250 (250 MHz) and JEOL EX-270 (67.8 MHz) spectrometers, respectively. Samples were prepared in deuteriochloroform and referenced to an internal tetramethylsilane standard. Coupling constants (*J*) are given in Hz. Electron impact mass spectra were obtained on an AEI MS-902 or MM-701CF spectrometer. Silica gel was used for column chromatography. Carbon disulfide, 1,1,2,2-tetrachloroethane and dichloromethane were dried by distillation over $P_2O_5$. Benzene and xylene were dried by distillation over sodium. Cyclization reactions were performed under an argon atmosphere in oven dried glassware.

**Dimethyl 4,4′-[1,8-dioxooctane-1,8-diyldi(*p*-phenylene)]-dibutanoate 12**
The diacid chloride of suberic acid **10** (3.161 g, 14.97 mmol), freshly prepared from suberic acid and thionyl chloride, was added to a suspension of aluminium chloride (9.0 g, 67 mmol) in dry carbon disulfide (20 $cm^3$). Methyl 4-phenylbutyrate **11** (5.202 g, 29.19 mmol) was added dropwise to this mixture with vigorous stirring. The reaction mixture became brown in colour and the evolution of hydrogen chloride was observed. Approximately half of the carbon disulfide was then distilled off and the residual brown oil was stirred into a mixture of ice (100 g) and conc. hydrochloric acid (20 $cm^3$). Toluene (100 $cm^3$) was added, the mixture shaken, the phases were separated and the aqueous phase was re-extracted with toluene (100 $cm^3$). The combined organic extracts were washed with water (50 $cm^3$), saturated aq. sodium hydrogen carbonate (50 $cm^3$) and again with water (50 $cm^3$). The toluene phase was dried over $Na_2SO_4$ and then evaporated. The residue solidified on standing and was recrystallized from hexane to give the title compound **12** (3.748 g, 52%) as a fluffy white solid, mp 76–77 °C (Found: C, 72.7; H, 7.8. $C_{30}H_{38}O_6$ requires C, 72.85; H, 7.7%); $\nu_{max}/cm^{-1}$ 2947, 2858, 1731 ($CO_2Me$), 1681 (C=O), 1608, 1361, 1323, 1146 and 976; $\delta_H(CDCl_3)$ 1.42 (4 H, m, 8-H and 9-H), 1.75 (4 H, m, 7-H and 10-H), 1.98 (4 H, quint, *J* 7.3, 3-H and 14-H), 2.34 (4 H, t, *J* 7.3, 2-H and 15-H), 2.71 (4 H, t, *J* 7.3, 4-H and 13-H), 2.95 (4 H, t, *J* 7.3, 6-H and 11-H), 3.67 (6 H, s, OMe), 7.26 (4 H, d, *J* 8.1, 2′-H, 6′-H, 9′-H and 11′-H) and 7.89 (4 H, d, *J* 8.1, 3′-H, 5′-H, 8′-H and 12′-H); $\delta_C(CDCl_3)$ 24.3, 26.1, 29.2, 33.3, 35.1, 38.4 (6-C and 11-C), 51.6 (OMe), 128.3 (2′-C, 6′-C, 9′-C and 11′-C or 3′-C, 5′-C, 8′-C and 12′-C), 128.7 (2′-C, 6′-C, 9′-C and 11′-C or 3′-C, 5′-C, 8′-C and 12′-C), 135.1 (4′-C and 7′-C), 146.9 (1′-C and 10′-C), 173.7 (1-C and 16-C) and 200.1 (5-C and 12-C); *m*/*z* 494 ($M^+$, 18%), 327 (22), 275 (19), 220 (62), 205 (100), 146 (23) and 131 (34).

**Dimethyl 4,4′-[octane-1,8-diyldi(*p*-phenylene)]dibutanoate 13**
A mixture of compound **12** (1.00 g, 2.02 mmol), 85% hydrazine (5.0 $cm^3$, 135 mmol), potassium hydroxide (6.0 g, 107 mmol) and diethylene glycol (75 $cm^3$) was heated at reflux for 2 h. The mixture was distilled until the pot temperature rose to 190 °C and then allowed to reflux at that temperature for 17 h. The mixture was cooled and water (75 $cm^3$) was added. The pH was adjusted to 1 by the addition of conc. hydrochloric acid. The precipitated diacid was filtered, washed with water and dried. To a suspension of this material in methanol (10 $cm^3$) was added an excess of diazomethane in ether. The solvent was evaporated and the residue chromatographed (dichloromethane) to give the title compound **13** (0.750 g, 79%) as an oily white solid, mp 38–39 °C (Found: C, 77.15; H, 9.2. $C_{30}H_{42}O_4$ requires C, 77.2; H, 9.1%); $\nu_{max}/cm^{-1}$ 2931, 2856 and 1731 (C=O); $\delta_H(CDCl_3)$ 1.30 (8 H, br s, 7-H, 8-H, 9-H and 10-H), 1.57 (4 H, br s, 6-H and 11-H), 1.94 (4 H, quint, *J* 7.5, 3-H and 14-H), 2.32 (4 H, t, *J* 7.5, 2-H and 15-H), 2.58 (8 H, m, *J* 7.5, 4-H, 5-H, 12-H and 13-H), 3.65 (6 H, s, OMe) and 7.08 (8 H, s, ArH); $\delta_C(CDCl_3)$ 26.5, 29.3, 29.4, 31.6, 33.4, 34.7, 35.5, 51.5 (OMe), 128.4 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C), 138.5 (1′-C and 10′-C or 4′-C and 7′-C), 140.5 (1′-C and 10′-C or 4′-C and 7′-C) and 174.1 (1-C and 16-C); *m*/*z* 466 ($M^+$, 4%), 434 (5), 403 (4), 384 (4), 361 (9), 334 (9), 302 (10), 270 (15), 159 (18), 131 (19) and 117 (100).

**Tricyclo[20.2.2.2$^{10,13}$]octacosa-10,12,22,24,25,27-hexaene 2**
Sodium (0.250 g, 10.9 mmol) was pulverized by vigorous mechanical stirring in dry refluxing xylene (10 $cm^3$). Heating was discontinued and chlorotrimethylsilane (10.0 $cm^3$, 8.56 g, 78.8 mmol) was added dropwise to the still-hot mixture, which was then allowed to cool to room temperature with continuous stirring. A solution of the diester **13** (1.002 g, 2.15 mmol) in xylene (5 $cm^3$) was added dropwise over an 8 h period. The mixture was then heated at reflux for 8 h. The sodium chloride precipitate was filtered off and washed with xylene (2 × 5 $cm^3$) and these washings were added to the filtrate. Evaporation of the solvent gave a colourless oil. Zinc (10.0 g, 153 mmol) was amalgamated with mercuric chloride (1.0 g, 3.7 mmol), water (20 $cm^3$) and conc. hydrochloric acid (2 $cm^3$), and this was added to the above product along with glacial acetic acid (10 $cm^3$) and conc. hydrochloric acid (20 $cm^3$). The resulting mixture was heated at reflux for 70 h during which time 5

portions of conc. hydrochloric acid (1 $cm^3$) were added at regular intervals. The reaction mixture was cooled, diluted with water (20 $cm^3$) and extracted with hexane (2 × 20 $cm^3$). The hexane extracts were combined, washed with water (20 $cm^3$), dried over $Na_2SO_4$ and evaporated. The crude product was chromatographed (hexane) to give the title compound **2** (0.146 g, 18%) as white crystals, mp 43–44 °C (Found: $M^+$, 376.3127. $C_{28}H_{40}$ requires 376.3130); $\nu_{max}/cm^{-1}$ 2926, 2853, 1512 and 1459; $\delta_H(CDCl_3)$ 1.25 (16 H, m, 3-H, 4-H, 5-H, 6-H, 11-H, 12-H, 13-H and 14-H), 1.57 (8 H, quint, *J* 6.9, 2-H, 7-H, 10-H and 15-H), 2.55 (8 H, t, *J* 6.9, 1-H, 8-H, 9-H and 16-H) and 7.01 (8 H, s, ArH); $\delta_C(CDCl_3)$ 27.1, 28.1, 30.1, 34.7 (1-C, 8-C, 9-C and 16-C), 128.3 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C) and 139.6 (1′-C, 4′-C, 7′-C and 10′-C); *m/z* 376 ($M^+$, 100%), 374 (20), 146 (33), 131 (32), 117 (50), 105 (73), 104 (62) and 91 (50).

**Dimethyl 5,5′-[1,10-dioxodecane-1,10-diyldi(*p*-phenylene)]-dipentanoate 16**

The diacid chloride of sebacic acid **14** (3.060 g, 12.80 mmol), freshly prepared from sebacic acid and thionyl chloride, was added to a suspension of aluminium chloride (5.0 g, 37 mmol) in dry carbon disulfide (20 $cm^3$). Methyl 5-phenylvalerate **15** (4.919 g, 25.59 mmol) was added and the same procedure was followed as described for the preparation of compound **12**. The crude product was chromatographed (1% methanol in dichloromethane) to give the title compound **16** (3.381 g, 48%) as a white solid, mp 65–67 °C (Found: C, 73.9; H, 8.6. $C_{34}H_{46}O_6$ requires C, 74.15; H, 8.4%); $\nu_{max}/cm^{-1}$ 2945, 2856, 1732 ($CO_2Me$), 1677 (C=O), 1607, 1355, 1315, 1139 and 980; $\delta_H(CDCl_3)$ 1.36 (8 H, br s, 9-H, 10-H, 11-H and 12-H), 1.67 (12 H, m, 3-H, 4-H, 8-H, 13-H, 17-H and 18-H), 2.34 (4 H, br t, *J* 6.4, 2-H and 19-H), 2.68 (4 H, br t, *J* 6.4, 5-H and 16-H), 2.93 (4 H, t, *J* 7.2, 7-H and 14-H), 3.66 (6 H, s, OMe), 7.25 (4 H, d, *J* 7.4, 2′-H, 6′-H, 9′-H and 11′-H) and 7.88 (4 H, d, *J* 7.4, 3′-H, 5′-H, 8′-H and 12′-H); $\delta_C(CDCl_3)$ 24.3, 29.2, 30.3, 33.7, 35.4, 38.3 (7-C and 14-C), 51.4 (OMe), 128.1 (2′-C, 6′-C, 9′-C and 11′-C or 3′-C, 5′-C, 8′-C and 12′-C), 128.4 (2′-C, 6′-C, 9′-C and 11′-C or 3′-C, 5′-C, 8′-C and 12′-C), 134.8 (4′-C and 7′-C), 147.5 (1′-C and 10′-C), 173.7 (1-C and 20-C) and 200.0 (6-C and 15-C); *m/z* 550 ($M^+$, 30%), 519 (6), 317 (28), 234 (77), 219 (100) and 202 (20).

**Dimethyl 5,5′-[decane-1,10-diyldi(*p*-phenylene)]dipentanoate 17**

Compound **16** (0.144 g, 0.26 mmol) was reduced with 85% hydrazine (0.50 $cm^3$, 13.5 mmol) and potassium hydroxide (0.8 g, 14 mmol) in diethylene glycol (10 $cm^3$) under conditions identical to those described for the preparation of compound **13**. After esterification with diazomethane the crude material was chromatographed (dichloromethane) to yield the title compound **17** (0.095 g, 70%) as a white solid, mp 44–45 °C (lit.,[21] 48–49.5 °C) (Found: $M^+$, 522.3698. $C_{34}H_{50}O_4$ requires 522.3709); $\nu_{max}/cm^{-1}$ 2940, 2852, 1732 (C=O), 1462, 1353, 1138 and 908; $\delta_H(CDCl_3)$ 1.28 (12 H, br s, 8-H, 9-H, 10-H, 11-H, 12-H and 13-H), 1.58–1.67 (12 H, br m, 3-H, 4-H, 7-H, 14-H, 17-H and 18-H), 2.33 (4 H, t, *J* 6.3, 2-H and 19-H), 2.57 (8 H, m, 5-H, 6-H, 15-H and 16-H), 3.66 (6 H, s, OMe) and 7.08 (8 H, s, ArH); $\delta_C(CDCl_3)$ 24.6, 29.3, 29.5, 30.9, 31.5, 33.9, 35.1, 35.5, 51.4 (OMe), 128.2 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C), 139.2 (1′-C and 10′-C or 4′-C and 7′-C), 140.3 (1′-C and 10′-C or 4′-C and 7′-C) and 174.1 (1-C and 20-C); *m/z* 522 ($M^+$, 6%), 490 (13), 472 (15), 458 (92), 430 (15), 361 (13), 205 (35), 173 (45), 160 (24), 145 (67), 131 (100), 117 (67), 105 (80) and 91 (48).

**Tricyclo[24.2.2.2$^{12,15}$]dotriaconta-12,14,26,28,29,31-hexaene 4**

A solution of the diester **17** (0.252 g, 0.48 mmol) in xylene (5 $cm^3$) was added to a mixture of finely divided sodium (0.247 g, 10.7 mmol) and chlorotrimethylsilane (5.0 $cm^3$, 4.28 g, 39.4 mmol) in xylene (5 $cm^3$) according to the procedure detailed for the preparation of compound **2**. After heating for 8 h at reflux and workup as described, reduction was carried out using half the quantity of reagents called for in the reduction of **2**. The crude product was chromatographed (hexane) to give the title compound **4** (0.025 g, 12%) as a waxy white solid, mp 25–27 °C (Found: $M^+$, 432.3731. $C_{32}H_{48}$ requires 432.3756); $\nu_{max}/cm^{-1}$ 2916, 2851, 1605, 1462, 1349 and 1117; $\delta_H(CDCl_3)$ 1.25 (24 H, br m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 13-H, 14-H, 15-H, 16-H, 17 H and 18-H), 1.58 (8 H, br quint, *J* 7.1, 2-H, 9-H, 12-H and 19-H), 2.56 (8 H, t, *J* 7.1, 1-H, 10-H, 11-H and 20-H) and 7.06 (8 H, s, ArH); $\delta_C(CDCl_3)$ 28.0, 28.4, 28.9, 30.6, 35.1 (1-C, 10-C, 11-C and 20-C), 128.3 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C) and 139.7 (1′-C, 4′-C, 7′-C and 10′-C); *m/z* 432 ($M^+$, 100%), 160 (34), 145 (24), 131 (47), 117 (59), 105 (98), 104 (60) and 91 (58).

**Methyl 2-oxo-2-[4-(7-phenylheptyl)phenyl]ethanoate 21 and dimethyl 2,2′-dioxo-2,2′-[heptane-1,7-diyldi(*p*-phenylene)]-diethanoate 22**

To a solution of monomethyl oxalyl chloride (2.430 g, 19.84 mmol) and 1,7-diphenylheptane **20**[22] (10.00 g, 39.62 mmol) in dry 1,1,2,2-tetrachloroethane (25 $cm^3$) at −10 °C was added aluminium chloride (8.0 g, 60 mmol). The mixture was allowed to warm to room temperature and after standing for 1.5 h was stirred into a mixture of ice (50 g) and conc. hydrochloric acid (10 $cm^3$). Toluene (100 $cm^3$) was added, the mixture shaken, the layers were separated and the aqueous layer was re-extracted with toluene (100 $cm^3$). The organic extracts were combined, washed with water, dried over $MgSO_4$ and evaporated. The residue was chromatographed (50% hexane in dichloromethane–1% methanol in dichloromethane) to give first unreacted starting material **20** (6.432 g) followed by **21** (2.475 g, 37%) as a colourless oil (Found: $M^+$, 338.1870. $C_{22}H_{26}O_3$ requires 338.1882); $\nu_{max}/cm^{-1}$ 2913, 2850, 1732 ($CO_2Me$), 1693 (C=O), 1608, 1461, 1322, 1161 and 996; $\delta_H(CDCl_3)$ 1.32 (6 H, br s, 5-H, 6-H and 7-H), 1.60 (4 H, br s, 4-H and 8-H), 2.59 (2 H, t, *J* 7.7, 9-H), 2.67 (2 H, t, *J* 7.7, 3-H), 3.96 (3 H, s, OMe), 7.17 (3 H, m, Ar-H), 7.27 (2 H, m, Ar-H), 7.29 (2 H, d, *J* 8.4, 3′-H and 5′-H) and 7.93 (2 H, d, *J* 8.4, 2′-H and 6′-H); $\delta_C(CDCl_3)$ 29.0, 29.2, 30.8, 31.3, 35.8 (3-C or 9-C), 36.0 (3-C or 9-C), 52.6 (OMe), 125.5 (10′-C), 128.1, 128.3, 128.9, 130.1, 130.2, 142.6 (7′-C), 151.1 (4′-C), 164.2 (1-C) and 185.6 (2-C); *m/z* 338 ($M^+$, 43%), 280 (99), 279 (100), 275 (18), 167 (42), 131 (23) and 91 (87). Continued chromatography gave **22** (1.640 g, 39%) as a white solid, mp 40–42 °C (Found: C, 70.8; H, 6.8. $C_{25}H_{28}O_6$ requires C, 70.7; H, 6.65%); $\nu_{max}/cm^{-1}$ 2933, 2858, 1739 ($CO_2Me$), 1684 (C=O), 1606, 1323, 1170 and 1005; $\delta_H(CDCl_3)$ 1.32 (6 H, br s, 5-H, 6-H and 7-H), 1.62 (4 H, br m, 4-H and 8-H), 2.67 (4 H, t, *J* 7.6, 3-H and 9-H), 3.97 (6 H, s, OMe), 7.30 (4 H, d, *J* 8.4, 3′-H, 5′-H, 8′-H and 12′-H) and 7.93 (4 H, d, *J* 8.4, 2′-H, 6′-H, 9′-H and 11′-H); $\delta_C(CDCl_3)$ 28.7, 28.9, 30.6, 35.8 (3-C and 9-C), 52.4 (OMe), 128.7, 129.8, 150.8 (4′-C and 7′-C), 164.0 (1-C and 11-C) and 185.5 (2-C and 10-C); *m/z* 365 ($M^+ - CO_2Me$, 17%), 337 ($M^+ - COCO_2Me$, 100) and 153 (25).

**Methyl 5-(4-{7-[4-(methoxydicarbonyl)phenyl]heptyl}phenyl)-5-oxopentanoate 23**

To a mixture of **21** (2.000 g, 5.91 mmol) and aluminium chloride (6.0 g, 45 mmol) in dry carbon disulfide (10 $cm^3$) was added monomethyl glutaryl chloride (2.503 g, 15.21 mmol). The evolution of hydrogen chloride was observed. Approximately half of the solvent was then distilled off and a mixture of ice (10 g) and hydrochloric acid (2 $cm^3$) was added. Toluene (20 $cm^3$) was added, the mixture shaken, the layers were separated and the aqueous layer was re-extracted with toluene (20 $cm^3$). The organic extracts were combined, washed with water, dried over $MgSO_4$ and evaporated. The solid residue was chromatographed (1% methanol in dichloromethane) to give the title compound **23** (2.118 g, 77%) as a colourless oil, (Found: C, 72.2; H, 7.5. $C_{28}H_{34}O_6$ requires C, 72.1; H, 7.3%); $\nu_{max}/cm^{-1}$ 2932, 2856, 1732 ($CO_2Me$), 1682 (C=O), 1606, 1458, 1362, 1322, 1168 and 1002; $\delta_H$($CDCl_3$) 1.32 (6 H, br s, 5-H, 6-H and 7-H), 1.61 (4 H, br s, 4-H and 8-H), 2.06 (2 H, quint, *J* 7.2, 12-H), 2.44 (2 H, t, *J* 7.2, 13-H), 2.65 (4 H, m, 3-H and 9-H), 3.03 (2 H, t, *J* 7.2, 11-H), 3.67 (3 H, s, $CO_2Me$), 3.96 (3 H, s, $COCO_2Me$), 7.24 (2 H, d, *J* 8.2, 8'-H and 12'-H), 7.30 (2 H, d, *J* 8.2, 3'-H and 5'-H), 7.88 (2 H, d, *J* 8.2, 9'-H and 11'-H) and 7.93 (2 H, d, *J* 8.2, 2'-H and 6'-H); $\delta_C$($CDCl_3$) 19.2, 28.9, 29.0, 30.7, 30.8, 33.0, 35.7 (3-C or 9-C), 36.0 (3-C or 9-C), 37.2 (11-C), 51.4 ($CO_2$*Me*), 52.5 ($COCO_2$*Me*), 128.0, 128.4, 128.8, 130.0, 130.1, 134.4 (10'-C), 148.4 (7'-C), 150.9 (4'-C), 164.1 (1-C), 173.6 (14-C), 185.6 (2-C) and 198.9 (10-C); *m/z* 466 ($M^+$, 5%), 435 (6), 407 (26), 375 (100), 337 (34), 333 (13), 279 (18), 217 (12), 153 (79), 131 (25), 118 (26), 91 (41) and 90 (36).

**Methyl 5-(4-{7-[4-(methoxycarbonylmethyl)phenyl]heptyl}-phenyl)pentanoate 24**

Compound **23** (1.187 g, 2.54 mmol) was reduced with 85% hydrazine (5.0 $cm^3$, 135 mmol) and potassium hydroxide (6.0 g, 107 mmol) in diethylene glycol (75 $cm^3$) under conditions identical to those described for the preparation of compound **13**. After esterification with diazomethane the crude material was chromatographed (dichloromethane) to yield the title compound **24** (0.977 g, 88%) as a colourless oil, (Found: $M^+$, 438.2766. $C_{28}H_{38}O_4$ requires 438.2770); $\nu_{max}/cm^{-1}$ 2929, 2855, 1732 (C=O), 1461, 1347, 1314, 1140 and 1002; $\delta_H$($CDCl_3$) 1.32 (6 H, br s, 5-H, 6-H and 7-H), 1.58–1.66 (8 H, br m, 4-H, 8-H, 11-H and 12-H), 2.33 (2 H, t, *J* 6.8, 13-H), 2.57 (6 H, br m, 3-H, 9-H and 10-H), 3.59 (2 H, s, 2-H), 3.65 (3 H, s, OMe), 3.68 (3 H, s, OMe), 7.07 (4 H, s, 8'-H, 9'-H, 11'-H and 12'-H), 7.12 (2 H, d, *J* 8.2, 2'-H and 6'-H or 3'-H and 5'-H) and 7.18 (2 H, d, *J* 8.2, 2'-H and 6'-H or 3'-H and 5'-H); $\delta_C$($CDCl_3$) 24.4, 29.0, 29.1, 30.7, 31.2, 31.3, 33.7, 34.9, 35.3, 40.5 (2-C), 51.2 (OMe), 51.7 (OMe), 128.0, 128.1, 128.4, 128.9, 130.9 (1'-C), 139.0 (4'-C, 7'-C or 10'-C), 139.9 (4'-C, 7'-C or 10'-C), 141.4 (4'-C, 7'-C or 10'-C), 172.0 (1-C or 14-C) and 173.8 (1-C or 14-C); *m/z* 438 ($M^+$, 7%), 407 (38), 406 (100), 378 (40), 374 (40), 347 (21), 345 (33), 163 (26), 145 (23), 139 (23), 131 (47), 117 (47), 105 (48), 104 (43), 91 (35) and 73 (44).

**Tricyclo[18.2.2.2$^{9,12}$]hexacosa-9,11,20,22,23,25-hexaene 1**

A solution of the diester **24** (0.198 g, 0.45 mmol) in xylene (5 $cm^3$) was added to a mixture of finely divided sodium (0.227 g, 9.87 mmol) and chlorotrimethylsilane (5.0 $cm^3$, 4.28 g, 39.4 mmol) in xylene (5 $cm^3$) according to the procedure detailed for the preparation of compound **2**. After heating for 8 h at reflux and workup as described, reduction was carried out using half the quantity of reagents called for in the reduction of **2**. The crude product was chromatographed (hexane) to give the title compound **1** (0.033 g, 21%) as white crystals, mp 102–104 °C (Found: $M^+$, 348.2818. $C_{26}H_{36}$ requires 348.2817); $\nu_{max}/cm^{-1}$ 2929, 2854, 1510, 1463, 1367, 1117 and 861; $\delta_H$($CDCl_3$) 0.95 (8 H, br quint, *J* 7.2, 3-H, 5-H, 10-H and 12-H), 1.18 (4 H, br quint, *J* 7.2, 4-H and 11-H), 1.47 (8 H, br quint, *J* 7.2, 2-H, 6-H, 9-H and 13-H), 2.53 (8 H, t, *J* 7.2, 1-H, 7-H, 8-H and 14-H) and 6.96 (8 H, s, ArH); $\delta_C$($CDCl_3$) 27.8, 29.3, 30.7, 35.0 (1-C, 7-C, 8-C and 14-C), 128.3 (2'-C, 3'-C, 5'-C, 6'-C, 8'-C, 9'-C, 11'-C and 12'-C) and 139.4 (1'-C, 4'-C, 7'-C and 10'-C); *m/z* 348 ($M^+$, 100%), 173 (23), 159 (23), 145 (24), 139 (38), 131 (44), 117 (68), 105 (85), 104 (70) and 91 (65).

**Methyl 4-oxo-4-[4-(9-phenylnonyl)phenyl]butanoate 28 and dimethyl 4,4'-dioxo-4,4'-[nonane-1,9-diyldi(*p*-phenylene)]-dibutanoate 29**

Reaction of monomethyl succinyl chloride (5.368 g, 35.65 mmol) with 1,9-diphenylnonane **27**[22] (20.00 g, 71.3 mmol) and aluminium chloride (9.0 g, 67 mmol) in 1,1,2,2-tetrachloroethane (50 $cm^3$) followed by workup with a mixture of ice (100 g) and conc. hydrochloric acid (20 $cm^3$) as described in the preparation of compound **21**, yielded a crude product which was chromatographed (50% hexane in dichloromethane–1% methanol in dichloromethane) to give first unreacted starting material **27** (13.605 g) followed by **28** (3.921 g, 28%) as a colourless oil (Found: C, 79.1; H, 9.0. $C_{26}H_{34}O_3$ requires C, 79.15; H, 8.7%); $\nu_{max}/cm^{-1}$ 2914, 2850, 1732 ($CO_2Me$), 1682 (C=O), 1607, 1461, 1356, 1324, 1155 and 975; $\delta_H$($CDCl_3$) 1.29 (10 H, br s, 7-H, 8-H, 9-H, 10-H and 11-H), 1.60 (4 H, br s, 6-H and 12-H), 2.61 (4 H, m, *J* 7.3, 5-H and 13-H), 2.75 (2 H, t, *J* 6.7, 2-H), 3.29 (2 H, t, *J* 6.7, 3-H), 3.70 (3 H, s, OMe), 7.15–7.18 (3 H, m, 9'-H, 10'-H and 11'-H), 7.25 (4 H, d, *J* 8.2, 3'-H, 5'-H, 8'-H and 12'-H) and 7.90 (2 H, d, *J* 8.2, 2'-H and 6'-H); $\delta_C$($CDCl_3$) 27.9, 29.1, 29.3, 30.9, 31.4, 33.1, 35.8 (5-C and 13-C), 51.6 (OMe), 125.4 (10'-C), 128.0, 128.1, 128.2, 128.5, 134.1 (1'-C), 142.7 (7'-C), 148.8 (4'-C), 173.3 (1-C) and 197.5 (4-C); *m/z* 394 ($M^+$, 33%), 362 (32), 307 (74), 187 (18), 174 (15), 167 (16), 131 (17), 117 (13), 105 (10) and 91 (100). Continued chromatography gave **29** (5.250 g, 58%) as a white solid, mp 68–69 °C (Found: C, 73.15; H, 8.1. $C_{31}H_{40}O_6$ requires C, 73.2; H, 7.9%); $\nu_{max}/cm^{-1}$ 2929, 2855, 1732 ($CO_2Me$), 1682 (C=O), 1607, 1356, 1324, 1162 and 975; $\delta_H$($CDCl_3$) 1.29 (10 H, br s, 7-H, 8-H, 9-H, 10-H and 11-H), 1.61 (4 H, br m, 6-H and 12-H), 2.65 (4 H, t, *J* 7.7, 5-H and 13-H), 2.76 (4 H, t, *J* 6.8, 2-H and 16-H), 3.30 (4 H, t, *J* 6.8, 3-H and 15-H), 3.70 (6 H, s, OMe), 7.26 (4 H, d, *J* 8.2, 3'-H, 5'-H, 8'-H and 12'-H) and 7.90 (4 H, d, *J* 8.2, 2'-H, 6'-H, 9'-H and 11'-H); $\delta_C$($CDCl_3$) 28.0, 29.1, 29.3, 31.0, 33.2 (3-C and 15-C), 35.9 (5-C and 13-C), 51.7 (OMe), 128.1, 128.6, 134.2 (1'-C and 10'-C), 148.8 (4'-C and 7'-C), 173.4 (1-C and 17-C) and 197.6 (4-C and 14-C); *m/z* 508 ($M^+$, 3%), 476 (15), 445 (20), 444 (20), 416 (13), 389 (49), 361 (37), 187 (22) and 167 (100).

**Methyl 5-(4-{9-[4-(4-methoxysuccinyl)phenyl]nonyl}phenyl)-5-oxopentanoate 30**

Reaction of compound **28** (0.500 g, 1.27 mmol), monomethyl glutaryl chloride (0.604 g, 3.67 mmol) and aluminium chloride (1.5 g, 11 mmol) in dry carbon disulfide (10 $cm^3$) as described for the preparation of compound **23** yielded a crude product which was chromatographed (1% methanol in dichloromethane) to give the title compound **30** (0.561 g, 85%) as a white solid, mp 43–45 °C (Found: $M^+$, 522.2982. $C_{32}H_{42}O_6$ requires 522.2981); $\nu_{max}/cm^{-1}$ 2928, 2854, 1732 ($CO_2Me$), 1682 (C=O), 1607, 1356, 1322, 1149 and 990; $\delta_H$($CDCl_3$) 1.29 (10 H, br s, 7-H, 8-H, 9-H, 10-H and 11-H), 1.61 (4 H, br quint, *J* 7.6, 6-H and 12-H), 2.06 (2 H, quint, *J* 7.1, 16-H), 2.43 (2 H, t, *J* 7.1, 17-H), 2.64 (4 H, t, *J* 7.6, 5-H and 13-H), 2.75 (2 H, t, *J* 6.6, 2-H), 3.02 (2 H, t, *J* 7.1, 15-H), 3.29 (2 H, t, *J* 6.6, 3-H), 3.67 (3 H, s, OMe), 3.69 (3 H, s, OMe), 7.25 (4 H, d, *J* 8.3, 3'-H, 5'-H, 8'-H and 12'-H), 7.88 (2 H, d, *J* 8.3, 2'-H and 6'-H or 9'-H and 11'-H) and 7.90 (2 H, d, *J* 8.3, 2'-H and 6'-H or 9'-H and 11'-H); $\delta_H$($CDCl_3$) 19.2, 27.8, 29.0, 29.2, 30.9, 32.9, 33.0, 35.8 (5-C and 13-C), 37.1 (15-C), 51.3 (OMe), 51.6 (OMe), 128.0, 128.4, 134.0 (1'-C or 10'-C), 134.3 (1'-C or 10'-C), 148.5 (4'-C or 7'-C), 148.7 (4'-C or 7'-C), 173.2 (1-C or 18-C), 173.5 (1-C or 18-C), 197.4 (4-C or 14-C) and 198.8 (4-C or 14-C); *m/z* 522 ($M^+$, 16%), 490 (13), 458 (19), 403 (16), 389 (30), 361 (18), 167 (100), 129 (63), 119 (44) and 91 (36).

**Methyl 5-[4-(9-{4-[3-(methoxycarbonyl)propyl]phenyl}nonyl)-phenyl]pentanoate 31**

Compound **30** (2.512 g, 4.81 mmol) was reduced with 85% hydrazine (10.0 $cm^3$, 271 mmol) and potassium hydroxide (12.0 g, 214 mmol) in diethylene glycol (75 $cm^3$) under conditions identical to those described for the preparation of compound **13**. After esterification with diazomethane the crude material was chromatographed (dichloromethane) to yield the title compound **31** (1.712 g, 72%) as a colourless oil, (Found: C, 77.7; H, 9.3. $C_{32}H_{46}O_4$ requires C, 77.7; H, 9.4%); $\nu_{max}/cm^{-1}$ 2927, 2853, 1732 (C=O), 1461, 1354, 1319, 1141 and 998; $\delta_H$($CDCl_3$) 1.28 (10 H, br s, 7-H, 8-H, 9-H, 10-H and 11-H), 1.55–1.66 (8 H, m, 6-H, 12-H, 15-H and 16-H), 1.93 (2 H, quint, *J* 7.4, 3-H), 2.32 (4 H, t, *J* 7.4, 2-H and 17-H), 2.57 (8 H, m, 4-H, 5-H, 13-H and 14-H), 3.64 (6 H, s, OMe) and 7.07 (8 H, s, ArH);

$\delta_C(CDCl_3)$ 24.5, 26.4, 29.2, 29.4, 30.9, 31.5, 33.3, 33.8, 34.6, 35.0, 35.4, 51.3 (OMe), 128.1, 128.2, 128.3, 138.3, 139.1, 140.2, 140.4, 173.8 (1-C or 18-C) and 173.9 (1-C or 18-C); *m/z* 494 ($M^+$, 29%), 462 (51), 430 (56), 173 (22), 159 (20), 145 (34), 131 (53), 117 (100), 105 (43) and 91 (35).

**Tricyclo[22.2.2.2$^{11,14}$]triaconta-11,13,24,26,27,29-hexaene 3**
A solution of the diester **31** (0.200 g, 0.40 mmol) in xylene (5 $cm^3$) was added to a mixture of finely divided sodium (0.250 g, 10.9 mmol) and chlorotrimethylsilane (5.0 $cm^3$, 4.28 g, 39.4 mmol) in xylene (5 $cm^3$) according to the procedure detailed for the preparation of compound **2**. After heating for 8 h at reflux and workup as described, reduction was carried out using half the quantity of reagents called for in the reduction of **2**. The crude product was chromatographed (hexane) to give the title compound **3** (0.026 g, 16%) as white crystals, mp 84–86 °C (Found: $M^+$, 404.3458. $C_{30}H_{44}$ requires 404.3443); $\nu_{max}/cm^{-1}$ 2928, 2854, 1510, 1461, 1348, 1117 and 970; $\delta_H(CDCl_3)$ 1.18 (20 H, br s, 3-H, 4-H, 5-H, 6-H, 7-H, 12-H, 13-H, 14-H, 15-H and 16-H), 1.53 (8 H, br quint, *J* 7.2, 2-H, 8-H, 11-H and 17-H), 2.53 (8 H, t, *J* 7.2, 1-H, 9-H, 10-H and 18-H) and 7.02 (8 H, s, ArH); $\delta_C(CDCl_3)$ 28.2, 28.6, 29.0, 31.1, 35.2 (1-C, 9-C, 10-C and 18-C), 128.3 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C) and 139.8 (1′-C, 4′-C, 7′-C and 10′-C); *m/z* 404 ($M^+$, 77%), 153 (37), 145 (24), 131 (46), 117 (48), 105 (100), 104 (54) and 91 (56).

**1,11-Diphenylundecane-1,11-dione 33**
A mixture of undecanedioic acid (18.00 g, 83.23 mmol) and thionyl chloride (50.0 $cm^3$, 81.6 g, 685 mmol) was heated at reflux for 2 h. The excess thionyl chloride was removed under reduced pressure and the resulting diacid chloride **32** was added dropwise with vigorous stirring to a suspension of aluminium chloride (65.0 g, 487 mmol) in dry benzene (100 $cm^3$). The reaction mixture became brown in colour and the evolution of hydrogen chloride was observed. Approximately half of the benzene was distilled off and the residual brown oil was stirred into a mixture of ice (500 g) and conc. hydrochloric acid (100 $cm^3$). Toluene (100 $cm^3$) was added. The mixture was shaken, the layers were separated and the aqueous phase was extracted with toluene (100 $cm^3$). The combined organic extracts were washed with water (50 $cm^3$), saturated sodium hydrogen carbonate solution (50 $cm^3$) and again water (50 $cm^3$). The organic phase was dried over $Na_2SO_4$ and then evaporated. The crude product was recrystallized from hexane to give the title compound **33** (21.01 g, 75%) as white crystals, mp 50–52 °C (Found: C, 81.9; H, 8.55. $C_{23}H_{28}O_2$ requires C, 82.1; H, 8.4%); $\nu_{max}/cm^{-1}$ 2929, 2855, 1682 (C=O), 1589, 1449 and 1358; $\delta_H(CDCl_3)$ 1.34 (10 H, br s, 4-H, 5-H, 6-H, 7-H and 8-H), 1.73 (4 H, br quint, *J* 7.4, 3-H and 9-H), 2.96 (4 H, t, *J* 7.4, 2-H and 10-H), 7.42–7.55 (6 H, m, 3′-H, 4′-H, 5′-H, 9′-H, 10′-H and 11′-H) and 7.96 (4 H, d, *J* 8.5, 2′-H, 6′-H, 8′-H and 12′-H); $\delta_C(CDCl_3)$ 24.3, 29.3, 29.4, 38.5 (2-C and 10-C), 128.0, 128.5, 132.8 (4′-C and 10′-C), 137.0 (1′-C and 7′-C) and 200.5 (1-C and 11-C); *m/z* 336 ($M^+$, 1%), 232 (9), 217 (11), 202 (31), 154 (18), 133 (18), 120 (100), 105 (100) and 77 (51).

**1,11-Diphenylundecane 34**
A mixture of compound **33** (6.994 g, 20.79 mmol), 85% hydrazine (10.0 $cm^3$, 271 mmol), potassium hydroxide (12.0 g, 214 mmol) and diethylene glycol (75 $cm^3$) was heated at reflux for 2 h. The mixture was distilled until the pot temperature rose to 190 °C and then allowed to reflux at that temperature for 17 h. The mixture was cooled, diluted with water (75 $cm^3$) and extracted with ether (2 × 75 $cm^3$). The organic extracts were combined, washed with water (50 $cm^3$), dried over $CaCl_2$ and evaporated. The residual yellow liquid was chromatographed (hexane) to give the title compound **34** (6.089 g, 95%) as a colourless oil, (Found: C, 89.6; H, 10.6. $C_{23}H_{32}$ requires C, 89.55; H, 10.45%); $\nu_{max}/cm^{-1}$ 2908, 2853, 1603, 1496 and 1030; $\delta_H(CDCl_3)$ 1.26 (14 H, br m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H and 9-H), 1.59 (4 H, br m, 2-H and 10-H), 2.58 (4 H, t, *J* 7.8, 1-H and 11-H) and 7.14–7.25 (10 H, m, ArH); $\delta_C(CDCl_3)$ 29.3, 29.5, 29.6, 31.5, 36.0 (1-C and 11-C), 125.5 (4′-C and 10′-C), 128.2, 128.4 and 142.9 (1′-C and 7′-C); *m/z* 308 ($M^+$, 31%), 218 (10), 202 (9), 186 (55), 185 (34), 92 (100) and 91 (85).

**Methyl 6-oxo-6-[4-(11-phenylundecyl)phenyl]hexanoate 35 and dimethyl 6,6′-dioxo-6,6′-[undecane-1,11-diyldi(*p*-phenylene)]-dihexanoate 36**
Reaction of monomethyl adipyl chloride (0.872 g, 4.88 mmol) with 1,11-diphenylundecane **34** (3.00 g, 9.72 mmol) and aluminium chloride (2.0 g, 15 mmol) in 1,1,2,2-tetrachloroethane (10 $cm^3$) followed by workup with a mixture of ice (50 g) and conc. hydrochloric acid (10 $cm^3$) as described in the preparation of compound **21**, yielded a crude product which was chromatographed (50% hexane in dichloromethane–1% methanol in dichloromethane) to give first unreacted starting material **34** (2.069 g) followed by **35** (1.154 g, 52%) as a white solid, mp 33–34 °C (Found: C, 80.1; H, 9.6. $C_{30}H_{42}O_3$ requires C, 80.0; H, 9.4%); $\nu_{max}/cm^{-1}$ 2928, 2854, 1732 ($CO_2Me$), 1681 (C=O), 1590, 1362, 1140 and 991; $\delta_H(CDCl_3)$ 1.28 (14 H, br m, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H and 15-H), 1.60 (4 H, br s, 8-H and 16-H), 1.75 (4 H, m, 3-H and 4-H), 2.37 (2 H, t, *J* 6.9, 2-H), 2.59 (2 H, t, *J* 6.8, 17-H), 2.64 (2 H, t, *J* 6.7, 7-H), 2.96 (2 H, t, *J* 6.8, 5-H), 3.66 (3 H, s, OMe), 7.16–7.26 (7 H, m, 3′-H, 5′-H, 8′-H, 9′-H, 10′-H, 11′-H and 12′-H) and 7.87 (2 H, d, *J* 8.2, 2′-H and 6′-H); $\delta_C(CDCl_3)$ 23.5, 24.4, 29.0, 29.1, 29.2, 29.3, 29.4, 30.8, 31.3, 33.6, 35.7 (7-C and 17-C), 37.7 (5-C), 51.1 (OMe), 125.3 (10′-C), 127.9, 128.1, 128.3, 134.4 (1′-C), 142.5 (7′-C), 148.3 (4′-C), 173.4 (1-C) and 198.9 (6-C); *m/z* 450 ($M^+$, 14%), 418 (5), 373 (5), 363 (10), 350 (11), 335 (32), 260 (10), 245 (26), 213 (22), 187 (11), 167 (8), 147 (11), 131 (26), 105 (14) and 91 (100). Continued chromatography gave **36** (0.123 g, 8%) as a white solid, mp 67–68 °C (Found: $M^+$, 592.3805. $C_{37}H_{52}O_6$ requires 592.3764); $\nu_{max}/cm^{-1}$ 2929, 2854, 1731 ($CO_2Me$), 1680 (C=O), 1606, 1361, 1139 and 992; $\delta_H(CDCl_3)$ 1.27 (14 H, br m, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H and 15-H), 1.62 (4 H, br m, 8-H and 16-H), 1.74 (8 H, m, 3-H, 4-H, 20-H and 21-H), 2.37 (4 H, t, *J* 6.9, 2-H and 22-H), 2.65 (4 H, t, *J* 7.6, 7-H and 17-H), 2.97 (4 H, t, *J* 6.8, 5-H and 19-H), 3.67 (6 H, s, OMe), 7.25 (4 H, d, *J* 8.3, 3′-H, 5′-H, 8′-H and 12′-H) and 7.87 (4 H, d, *J* 8.3, 2′-H, 6′-H, 9′-H and 11′-H); $\delta_C(CDCl_3)$ 23.7, 24.5, 29.2, 29.3, 29.4, 31.0, 33.8, 35.9 (7-C and 17-C), 37.9 (5-C and 19-C), 51.4 (OMe), 128.1, 128.5, 134.6 (1′-C and 10′-C), 148.6 (4′-C and 7′-C), 173.8 (1-C and 23-C) and 199.4 (6-C and 18-C); *m/z* 592 ($M^+$, 56%), 514 (13), 492 (8), 431 (13), 417 (19), 401 (14), 189 (15), 181 (100), 131 (32), 91 (35) and 69 (36).

**Methyl 6-(4-{11-[4-(5-methoxyglutaryl)phenyl]undecyl}-phenyl)-6-oxohexanoate 37**
Reaction of compound **35** (1.280 g, 2.84 mmol), monomethyl glutaryl chloride (1.400 g, 8.51 mmol) and aluminium chloride (3.4 g, 25 mmol) in dry carbon disulfide (10 $cm^3$) as described for the preparation of compound **23** yielded a crude product which was chromatographed (1% methanol in dichloromethane) to give the title compound **37** (1.315 g, 80%) as a white solid, mp 67–68 °C (Found: C, 74.7; H, 8.8. $C_{36}H_{50}O_6$ requires C, 74.7; H, 8.7%); $\nu_{max}/cm^{-1}$ 2929, 2855, 1731 ($CO_2Me$), 1681 (C=O), 1606, 1460, 1362, 1319, 1145 and 992; $\delta_H(CDCl_3)$ 1.27 (14 H, br m, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H and 14-H), 1.62 (4 H, br m, 7-H and 15-H), 1.74 (4 H, br m, 19-H and 20-H), 2.07 (2 H, quint, *J* 7.1, 3-H), 2.37 (2 H, t, *J* 6.9, 21-H), 2.44 (2 H, t, *J* 7.1, 2-H), 2.65 (4 H, t, *J* 7.6, 6-H and 16-H), 2.97 (2 H, t, *J* 7.0, 18-H), 3.03 (2 H, t, *J* 7.2, 4-H), 3.67 (3 H, s, OMe), 3.68 (3 H, s, OMe), 7.25 (4 H, d, *J* 8.3, 3′-H, 5′-H, 8′-H and 12′-H), 7.87 (2 H, d, *J* 8.3, 2′-H and 6′-H or 9′-H and 11′-H) and 7.88 (2 H, d, *J* 8.3, 2′-H and 6′-H or 9′-H and 11′-H); $\delta_C(CDCl_3)$ 19.4, 23.7, 24.6, 29.2, 29.4, 29.5, 29.6, 31.1, 33.1, 33.9, 35.9 (6-C and 16-C), 37.3 (4-C), 38.0 (18-C), 51.5 (OMe), 128.1, 128.6, 134.5 (1′-C or 10′-C), 134.6 (1′-C or 10′-C), 148.7 (4′-C or 7′-C), 148.8 (4′-C or 7′-C),

173.7 (1-C or 22-C), 173.9 (1-C or 22-C), 199.0 (5-C or 17-C) and 199.5 (5-C or 17-C); $m/z$ 578 ($M^+$, 39%), 431 (44), 181 (100), 131 (56), 118 (33), 91 (50) and 55 (50).

**Methyl 6-[4-(11-{4-[4-(methoxycarbonyl)butyl]phenyl}-undecyl)phenyl]hexanoate 38**

Compound **37** (0.171 g, 0.295 mmol) was reduced with 85% hydrazine (0.5 $cm^3$, 13.5 mmol) and potassium hydroxide (0.8 g, 14 mmol) in diethylene glycol (10 $cm^3$) under conditions identical to those described for the preparation of compound **13**. After esterification with diazomethane the crude material was chromatographed (dichloromethane) to yield the title compound **38** (0.123 g, 76%) as a white solid, mp 31–32 °C (Found: $M^+$, 550.4026. $C_{36}H_{54}O_4$ requires 550.4022); $\nu_{max}/cm^{-1}$ 2928, 2854, 1731 (C=O), 1461, 1354, 1318 and 1136; $\delta_H(CDCl_3)$ 1.27 (16 H, br m, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H and 19-H), 1.55–1.67 (12 H, m, 3-H, 4-H, 7-H, 15-H, 18-H and 20-H), 2.30 (4 H, t, $J$ 7.4, 2-H and 21-H), 2.52–2.61 (8 H, m, 5-H, 6-H, 16-H and 17-H), 3.65 (6 H, s, OMe) and 7.07 (8 H, s, ArH); $\delta_C(CDCl_3)$ 24.5, 24.7, 28.7, 29.3, 29.5, 29.6, 30.9, 31.1, 31.5, 33.9, 35.1, 35.2, 35.5, 51.4 (OMe), 128.1, 128.2, 139.1, 139.5, 140.1, 140.2, 174.0 (1-C or 22-C) and 174.1 (1-C or 22-C); $m/z$ 550 ($M^+$, 9%), 518 (82), 486 (62), 173 (25), 159 (21), 145 (52), 131 (64), 117 (59), 105 (100) and 91 (57).

**Tricyclo[26.2.2.2$^{13,16}$]tetratriaconta-13,15,28,30,31,33-hexaene 5**

A solution of the diester **38** (0.197 g, 0.358 mmol) in xylene (5 $cm^3$) was added to a mixture of finely divided sodium (0.221 g, 9.61 mmol) and chlorotrimethylsilane (5.0 $cm^3$, 4.28 g, 39.4 mmol) in xylene (5 $cm^3$) according to the procedure detailed for the preparation of compound **2**. After heating for 8 h at reflux and work-up as described, reduction was carried out using half the quantity of reagents called for in the reduction of **2**. The crude product was chromatographed (hexane) to give the title compound **5** (0.039 g, 24%) as a white solid, mp 53–55 °C (Found: $M^+$, 460.4067. $C_{34}H_{52}$ requires 460.4069); $\nu_{max}/cm^{-1}$ 2928, 2854, 1715, 1683, 1462, 1361, 1312 and 1119; $\delta_H(CDCl_3)$ 1.23 (28 H, br m, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H and 20-H), 1.56 (8 H, br m, $J$ 7.4, 2-H, 10-H, 13-H and 21-H), 2.55 (8 H, t, $J$ 7.4, 1-H, 11-H, 12-H and 22-H) and 7.06 (8 H, s, ArH); $\delta_C(CDCl_3)$ 28.6, 28.9, 29.1, 29.2, 31.3, 35.4 (1-C, 11-C, 12-C and 22-C), 128.2 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C) and 139.9 (1′-C, 4′-C, 7′-C and 10′-C); $m/z$ 460 ($M^+$, 78%), 245 (28), 202 (7), 167 (23), 159 (37), 145 (30), 131 (48), 117 (48), 105 (100) and 91 (46).

**2,9-Dimethyl-2,9-diphenyldecane 40**

To a solution of 2,9-dichloro-2,9-dimethyldecane **39**[23] (2.775 g, 11.60 mmol) in dry benzene (50 $cm^3$) was added ferric chloride (1.1 g, 6.8 mmol). The evolution of hydrogen chloride was observed. When effervescence had ceased, the flask was cooled in ice and 2 mol $dm^{-3}$ hydrochloric acid (10 $cm^3$) was added. The solution was stirred for 1 h and the phases were separated. The aqueous layer was extracted with dichloromethane (20 $cm^3$) and the organic extracts were combined, washed with water (20 $cm^3$) and dried over $MgSO_4$. The solvent was evaporated and the resulting black oil distilled under reduced pressure to give the title compound **40** (2.886 g, 77%) as a colourless oil, bp 166 °C/0.6 mmHg (Found: $M^+$, 322.2667. $C_{24}H_{34}$ requires 322.2661); $\nu_{max}/cm^{-1}$ 2930, 2856, 1947, 1872, 1807, 1600, 1496, 1463, 1366 and 1315; $\delta_H(CDCl_3)$ 0.99 (4 H, br m, 4-H and 5-H), 1.10 (4 H, br m, 3-H and 6-H), 1.25 (12 H, s, 9-H, 10-H, 11-H and 12-H), 1.53 (4 H, br m, 2-H and 7-H), 7.15 (2 H, m, 4′-H and 10′-H) and 7.29 (8 H, m, 2′-H, 3′-H, 5′-H, 6′-H, 8′-H, 9′-H, 11′-H and 12′-H); $\delta_C(CDCl_3)$ 24.6, 28.9 (9-C, 10-C, 11-C and 12-C), 30.1, 37.6 (1-C and 8-C), 44.5 (2-C and 7-C), 125.2 (4′-C and 10′-C), 125.8, 127.9 and 149.7 (1′-C and 7′-C); $m/z$ 322 ($M^+$, 7%), 119 (100), 105 (33) and 91 (86).

**5-Acetoxy-2-chloro-2-methylpentane 41**

Thionyl chloride (10.0 $cm^3$, 16.3 g, 137 mmol) was added to 5-*O*-acetyl-2-methylpentane-2,5-diol[24] (0.102 g, 0.64 mmol) at 0 °C. The mixture was stirred for 1 h at that temperature and then heated at reflux for 30 min. The excess thionyl chloride was removed under reduced pressure and the residue distilled to give the title compound **41** (0.100 g, 87%) as a colourless liquid, bp 86 °C/25 mmHg (Found: C, 53.8; H, 8.7. $C_8H_{15}ClO_2$ requires C, 53.8; H, 8.5%); $\nu_{max}/cm^{-1}$ 2932, 2857, 1732 (C=O), 1457, 1363, 1285 and 1120; $\delta_H(CDCl_3)$ 1.59 (6 H, s, 5-H and 6-H), 1.82 (4 H, m, 2-H and 3-H), 2.06 (3 H, s, COMe) and 4.10 (2 H, t, $J$ 5.9, 1-H); $\delta_C(CDCl_3)$ 20.9 (COMe), 24.5 (2-C), 32.3 (5-C and 6-C), 42.2 (3-C), 64.2 (1-C), 70.1 (4-C) and 171.0 (C=O); $m/z$ 179 (M + 1, 54%), 118 (17), 101 (60), 83 (75), 82 (87), 77 (45), 67 (39), 61 (52), 55 (68) and 43 (100).

**{4,4′-[2,9-Dimethyldecane-2,9-diyldi(*p*-phenylene)]-4,4′-dimethyl}dipentyl diacetate 42**

To a solution of 2,9-dimethyl-2,9-diphenyldecane **40** (0.335 g, 1.04 mmol) and 4-chloro-4-methylpentyl acetate **41** (0.561 g, 3.14 mmol) in dry dichloromethane (1 $cm^{-3}$) was added ferric chloride (0.5 g, 3 mmol). The evolution of hydrogen chloride was observed. Exactly 5 min after the addition of the catalyst, the mixture was diluted with dichloromethane (20 $cm^3$), the flask was cooled in ice and 2 mol $dm^{-3}$ hydrochloric acid was added (5 $cm^3$). The mixture was stirred for 1 h, the phases were separated and the aqueous layer was extracted with dichloromethane (20 $cm^3$). The organic extracts were combined, washed with water (10 $cm^3$) and dried over $MgSO_4$. The solvent was evaporated and the residual oil chromatographed (dichloromethane) to give the title compound **42** (0.348 g, 55%) as a waxy white solid, mp 70–71 °C (Found: C, 79.3; H, 10.6. $C_{40}H_{62}O_4$ requires C, 79.2; H, 10.3%); $\nu_{max}/cm^{-1}$ 2931, 2857, 1729 (C=O), 1464, 1364 and 1277; $\delta_H(CDCl_3)$ 0.99 (4 H, br m, 8-H and 9-H), 1.12 (4 H, br s, 7-H and 10-H), 1.24 (12 H, s, 19-H, 20-H, 21-H and 22-H), 1.29 (12 H, s, 17-H, 18-H, 23-H and 24-H), 1.39 (4 H, br m, 2-H and 15-H), 1.52 (4 H, br m, 6-H and 11-H), 1.63 (4 H, m, 3-H and 14-H), 2.01 (6 H, s, COMe), 3.95 (4 H, t, $J$ 6.6, 1-H and 16-H) and 7.21 (8 H, s, ArH); $\delta_C(CDCl_3)$ 21.0 (CO*Me*), 24.2, 24.6, 28.8 (17-C, 18-C, 19-C, 20-C, 21-C, 22-C, 23-C and 24-C), 30.1, 36.9 (4-C and 13-C or 5-C and 12-C), 37.1 (4-C and 13-C or 5-C and 12-C), 40.5 (3-C and 14-C), 44.5 (6-C and 11-C), 65.1 (1-C and 16-C), 125.2, 125.4, 145.5 (1′-C and 10′-C or 4′-C and 7′-C), 146.9 (1′-C and 10′-C or 4′-C and 7′-C) and 171.1 (C=O); $m/z$ 505 [$M^+ - MeCO_2(CH_2)_3$, 15%], 261 (100), 202 (55), 201 (39), 159 (31), 145 (41), 131 (65) and 83 (31).

**4,4′-[2,9-Dimethyldecane-2,9-diyldi(*p*-phenylene)]-4,4′-dimethyldipentan-1-ol 43**

A mixture of compound **42** (1.585 g, 2.61 mmol), diethylene glycol (100 $cm^3$), water (10 $cm^3$) and potassium hydroxide (5.0 g, 89 mmol) was heated at reflux for 20 min. The mixture was cooled to room temperature, diluted with water (100 $cm^3$) and adjusted to pH 1 by addition of conc. hydrochloric acid. The solution was extracted with dichloromethane (2 × 50 $cm^3$), the organic extracts were combined, washed with water (3 × 100 $cm^3$) and dried over $MgSO_4$. The solvent was evaporated and the residual viscous oil chromatographed (7% methanol in dichloromethane) to give the title compound **43** (1.162 g, 85%) as a white solid, mp 54–55 °C (Found: C, 82.4; H 11.4. $C_{36}H_{58}O_2$ requires C, 82.7; H 11.2%); $\nu_{max}/cm^{-1}$ 3303 (OH), 2932, 2857, 1657, 1465, 1362, 1116, 1005 and 835; $\delta_H(CDCl_3)$ 0.99 (4 H, br m, 8-H and 9-H), 1.11 (4 H, br m, 7-H and 10-H), 1.24 (12 H, s, 19-H, 20-H, 21-H and 22-H), 1.30 (12 H, s, 17-H, 18-H, 23-H and 24-H), 1.33 (4 H, m, 2-H and 15-H), 1.51 (4 H, m, 6-H and 11-H), 1.63 (4 H, m, 3-H and 14-H), 3.53 (4 H, t, $J$ 6.0, 1-H and 16-H) and 7.22 (8 H, s, ArH); $\delta_C(CDCl_3)$ 24.6, 28.2, 28.9 (17-C, 18-C, 19-C, 20-C, 21-C, 22-C, 23-C and 24-C), 30.1, 36.9 (4-C and 13-C or 5-C and 12-C), 37.1 (4-C and 13-C

**Table 1** X-Ray crystallographic data for compounds **1**, **2**, **3**, **5** and **45**

| Compound | 1 | 2 | 3 | 5 | 45 |
|---|---|---|---|---|---|
| Formula | $C_{26}H_{36}$ | $C_{28}H_{40}$ | $C_{30}H_{44}$ | $C_{34}H_{52}$ | $C_{36}H_{56}$ |
| *M* | 348.57 | 376.62 | 404.68 | 460.78 | 488.84 |
| Crystal system | Orthorhombic | Triclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | *Pbca* | $P\bar{1}$ | *Pbca* | *Pbca* | $P2_1/c$ |
| *a*/Å | 10.897(2) | 8.549(2) | 11.112(1) | 11.114(3) | 10.500(2) |
| *b*/Å | 10.371(1) | 11.232(3) | 10.405(2) | 10.297(4) | 12.194(3) |
| *c*/Å | 19.704(2) | 12.634(3) | 23.186(2) | 26.900(6) | 12.697(2) |
| $\alpha$/° | 90 | 91.97(2) | 90 | 90 | 90 |
| $\beta$/° | 90 | 103.84(2) | 90 | 90 | 98.87(1) |
| $\gamma$/° | 90 | 93.57(2) | 90 | 90 | 90 |
| $V$/Å$^3$ | 2226.8(5) | 1174.1(5) | 2680.8(6) | 3078.6(6) | 1606.2(6) |
| Reflections used | 25 | 25 | 25 | 28 | 25 |
| $\theta$ Range/° | 22–29 | 20–24 | 20–25 | 7.5–12.5 | 20–25 |
| *Z* | 4 | 2 | 4 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.04 | 1.06 | 1.00 | 0.99 | 1.01 |
| *F*(000) | 768 | 416 | 896 | 1024 | 544 |
| $\mu$/cm$^{-1}$ | 4.2 | 4.3 | 4.1 | 0.55 | 4.1 |
| Scan mode | $2\theta/\omega$ | $2\theta/\omega$ | $2\theta/3\omega$ | $2\theta/\omega$ | $\omega$ |
| Max. $\theta$/° | 66 | 60 | 60 | 25 | 60 |
| Unique data | 1939 | 3494 | 1979 | 2710 | 2381 |
| Obs. data $I > 2\sigma(I)$ | 796 | 822 | 1032 | 1713 | 800 |
| No. of variables | 119 | 174[a] | 137 | 193 | 163 |
| Data used | 1935 | 3486 | 1978 | 2710 | 2351 |
| Weighting scheme,[b] *a*, *b* | 0.062, 0.066 | 0.131, 0.822 | 0.089, 1.626 | 0.055, 0 | 0.006, 2.53 |
| Extinction,[c] x | 0.0039(4) | 0.0004(8) | 0.0013(5) | 0.015(1) | — |
| *R*(*F*), obs. data | 0.050 | 0.088 | 0.065 | 0.046 | 0.067 |
| $wR(F^2)$, all data | 0.169 | 0.381 | 0.219 | 0.112 | 0.187 |
| Goodness-of-fit | 1.013 | 0.997 | 1.074 | 0.893 | 1.010 |
| $\Delta\rho_{max}$/e Å$^{-3}$ | 0.14 | 0.23 | 0.16 | 0.27 | 0.16 |
| $\Delta\rho_{min}$/e Å$^{-3}$ | −0.14 | −0.20 | −0.16 | −0.21 | −0.16 |

[a] 60 restraints applied to $U_{ij}$. [b] Weights $w = [\sigma^2(F_o^2) + (a\cdot P)^2 + b\cdot P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$, if $F_c^2 < 0$, $P = 2F_c^2/3$. [c] Empirical (SHELXL) correction, $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$, where *x* was refined.

or 5-C and 12-C), 40.5 (3-C and 14-C), 44.5 (6-C and 11-C), 63.5 (1-C and 16-C), 125.3, 125.4, 145.8 (1′-C and 10′-C or 4′-C and 7′-C) and 146.8 (1′-C and 10′-C or 4′-C and 7′-C); *m*/*z* 522 ($M^+$, 2%), 219 (100), 201 (40), 159 (19), 145 (17) and 131 (14).

**Dimethyl 4-4′-[2,9-dimethyldecane-2,9-diyldi(*p*-phenylene)]-4,4′-dimethyldipentanoate 44**

To a solution of manganese(II) sulfate hydrate (0.011 g, 0.065 mmol), conc. sulfuric acid (1 cm$^3$) and glacial acetic acid (0.2 cm$^3$) in water (10 cm$^3$) was added potassium permanganate (1.0 g, 6 mmol). Dichloromethane (10 cm$^3$) containing adogen 464 (0.050 g) was then added and the biphasic system was stirred vigorously. A solution of diol **43** (0.203 g, 0.39 mmol) in dichloromethane (5 cm$^3$) was added dropwise and the mixture was stirred for an additional 15 min. Oxalic acid was added in portions until the purple colour of the reaction mixture was discharged. The mixture was then filtered and the solids were washed with dichloromethane (2 × 10 cm$^3$). The layers of the filtrate were separated and the aqueous phase was extracted with dichloromethane (10 cm$^3$). The organic extracts were combined, washed with water (10 cm$^3$), dried over $MgSO_4$ and evaporated. The resulting oil was stirred in ether (5 cm$^3$) and treated with an excess of diazomethane in ether. The solvent was evaporated and the residue chromatographed (dichloromethane) to give the title compound **44** (0.077 g, 34%) as an oily white solid, mp 55–56 °C (Found: $M^+$, 578.4334. $C_{38}H_{58}O_4$ requires 578.4335); $\nu_{max}$/cm$^{-1}$ 2947, 2849, 1732 (C=O), 1461, 1363, 1302 and 1116; $\delta_H(CDCl_3)$ 0.99 (4 H, br s, 8-H and 9-H), 1.13 (4 H, br s, 7-H and 10-H), 1.24 (12 H, s, 19-H, 20-H, 21-H and 22-H), 1.30 (12 H, s, 17-H, 18-H, 23-H and 24-H), 1.52 (4 H, m, 6-H and 11-H), 1.96 (4 H, m, 2-H and 15-H or 3-H and 14-H), 2.06 (4 H, m, 2-H and 15-H or 3-H and 14-H), 3.59 (6 H, s, OMe) and 7.22 (8 H, s, ArH); $\delta_C(CDCl_3)$ 24.6, 28.6 (17-C, 18-C, 23-C and 24-C or 19-C, 20-C, 21-C and 22-C), 28.8 (17-C, 18-C, 23-C and 24-C or 19-C, 20-C, 21-C and 22-C), 30.0, 30.1, 36.7 (4-C and 13-C or 5-C and 12-C), 37.1 (4-C and 13-C or 5-C and 12-C), 39.0 (3-C and 14-C), 44.5 (6-C and 11-C), 51.4 (OMe), 125.2, 125.5, 144.6 (1′-C and 10′-C or 4′-C and 7′-C), 147.0 (1′-C and 10′-C or 4′-C and 7′-C) and 174.5 (1-C and 16-C); *m*/*z* 578 ($M^+$, 2%) 491 (5), 247 (100), 202 (16), 129 (21), 97 (22) and 69 (27).

**2,2,9,9,14,14,21,21-Octamethyltricyclo[20.2.2.2$^{10,13}$]octacosa-10,12,22,24,25,27-hexaene 45**

A solution of the diester **44** (0.272 g, 0.47 mmol) in xylene (5 cm$^3$) was added to a mixture of finely divided sodium (0.272 g, 11.8 mmol) and chlorotrimethylsilane (5.0 cm$^3$, 4.28 g, 39.4 mmol) in xylene (5 cm$^3$) according to the procedure detailed for the preparation of compound **2**. After heating for 8 h at reflux and workup as described, reduction was carried out using half the quantity of reagents called for in the reduction of **2**. The crude product was chromatographed (hexane) to give the title compound **45** (0.039 g, 17%) as white crystals, mp 178–180 °C (Found: $M^+$, 488.4393. $C_{36}H_{56}$ requires 488.4382); $\nu_{max}$/cm$^{-1}$ 2929, 2856, 1463 and 1362; $\delta_H(CDCl_3)$ 0.89 (8 H, br m, 4-H, 5-H, 12-H and 13-H), 1.01 (8 H, br m, 3-H, 6-H, 11-H and 14-H), 1.25 (24 H, s, 17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H and 24-H), 1.51 (8 H, m, 2-H, 7-H, 10-H and 15-H) and 7.18 (8 H, s, ArH); $\delta_C(CDCl_3)$ 24.2, 29.1 (17-H, 18-H, 19-H, 20-H, 21-H, 22-H, 23-H and 24-H), 29.9, 37.3 (1-C, 8-C, 9-C and 16-C), 44.5 (2-C, 7-C, 10-C and 15-C), 125.3 (2′-C, 3′-C, 5′-C, 6′-C, 8′-C, 9′-C, 11′-C and 12′-C) and 145.9 (1′-C, 4′-C, 7′-C and 10′-C); *m*/*z* 488 ($M^+$, 9%), 245 (89), 202 (50), 159 (100), 145 (38) and 131 (34).

**X-Ray crystal structure determinations**

X-Ray single crystal diffraction experiments for **1**, **2**, **3** and **45** were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer (Ni-filtered Cu-K$\alpha$ radiation, $\lambda$ = 1.541 84 Å), while that for **5** was carried out at 150 K on a Siemens P4 diffractometer (graphite-monochromated Mo-K$\alpha$ radiation, $\lambda$ = 0.710 73 Å) using an Oxford Cryosystems open-flow $N_2$ gas cryostat.[25] The structures were solved by direct methods using MULTAN-80[26] (**1**, **2**, **3** and **45**) and SHELXS-86[27] (**5**), and refined by full-matrix least-squares against $F^2$. All refinements employed Chebyshev weighting schemes[28] in SHELXL-93.[29] In **1**, **3** and **45**, all carbon atoms were refined with anisotropic displacement parameters and all hydrogen atoms were treated as 'riding'. In **2**, the aromatic and adjacent methylene carbon atoms were refined isotropically, other carbon atoms anisotropically (with similarity restraints applied to the $U_{ij}$ components of neighbouring atoms) and with all hydrogen atoms 'riding'. In **5**, all carbon atoms were refined anisotropically, aromatic hydrogen atoms isotropically, and methylene hydrogen atoms treated as 'riding', although their isotropic thermal parameters were refined. Crystal data and experimental details are listed in Table 1; atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC), see Instructions for Authors, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/5.

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