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Triquinane-Derived Macrocyclic Lactones and a [2]-Catenane: Synthesis and Characterization

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Abstract: *cis,syn,cis*-Triquinane diol **1**, with its folded topology, hydrophobic posterior and inwardly directed *endo,endo*-hydroxy groups, readily enters into cyclooligomerization reaction with terephthaloyldichloride **4**. As many as nine cyclic oligomers **A-I**, with macrocyclic ring size varying from 28- to 98-membered, have been isolated and characterized. The cyclic oligomers exhibit interesting spatial relationships through the relative orientation of methylene groups on the central five membered ring of the triquinane moiety. Employing X-ray crystallography and symmetry considerations, in conjunction with NMR data, stereostructures of dimers **5** and **6**, trimers **7** and **8** and tetramers **9-12** could be delineated. The crystal packing in the case of **5**, **6** and **7** shows some interesting motifs and many short C-H...O contacts. From the reaction of **1** and **4**, a novel [2]-catenane **16**, constituted through aromatic spacers and a bulky triquinane entity, has also been isolated and characterized, through the incisive analysis of the mass spectral data.

Key words: Macrocycles; lactones; polyquinanes; catenanes; X-ray crystal structures.

Introduction

Macrocyclic systems, particularly those having interspersed aromatic spacers and binding sites like ethers, amides and lactones have aroused considerable attention in recent years, in the context of the study of supramolecular interactions [1]. The inherent flexibility, with regard to shape, ring size and binding sites, present in the macrocyclic systems make them versatile host systems. Consequently, a diverse range of macrocyclic compounds have been prepared through different synthetic protocols and their properties ranging from artificial receptors of biological substrates to neutral ionophores for selective alkaline-earth ion extraction investigated [1,2]. More recently, attempts towards the synthesis of macrocyclic hosts composed mainly of aromatic spacers have resulted in the formation and characterization of novel systems with mechanical bonds *e.g.* [n]-catenanes *via* self-assembly processes, promoted through π-π and H-bonding interactions [3]. However, examples of mixed macrocyclic systems constituted through rigid, globular, polycyclic entities and aromatic spacers are very limited and those of [n]-catenanes from such building-blocks are practically unknown [3]. In this context, our attention was drawn to the readily available *cis,syn,cis*-triquinane diol **1** [4] with rigid, convoluted topology and *endo,endo*-hydroxyl groups suitably poised for cyclofunctionali-

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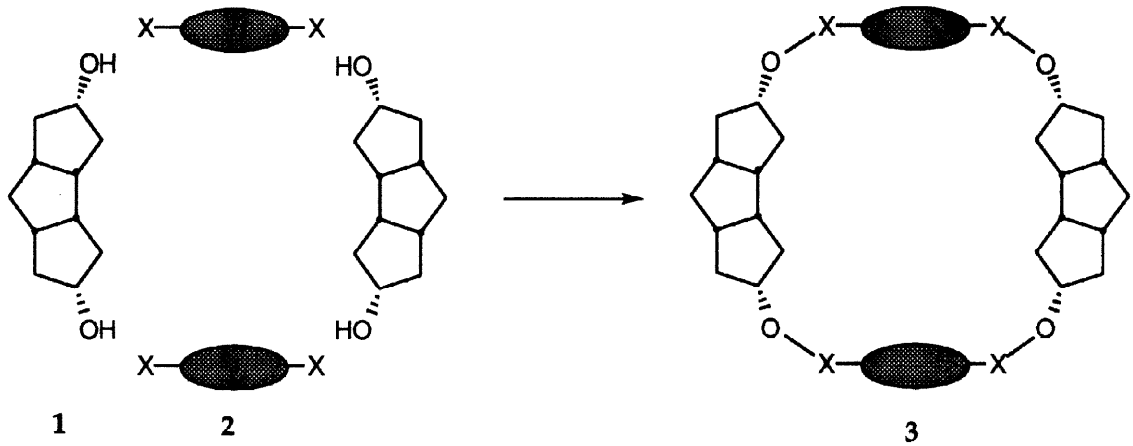
zation, with a range of aromatic spacers like **2** of complimentary functionalities, to furnish space enclosing macrocycles *e.g.* **3** [5], Scheme 1. It was anticipated that an ensemble like **3** with clearly defined alicyclic posterior and flat aromatic segments would be intrinsically interesting. Herein, we report that **1** indeed engages an activated terephthalic acid derivative, which functions as aromatic 'cavity wall' to assemble huge macrocyclic lactones as well as a [2]-catenane through multi-molecular inter- and intra-molecular esterification processes.

Scheme 1

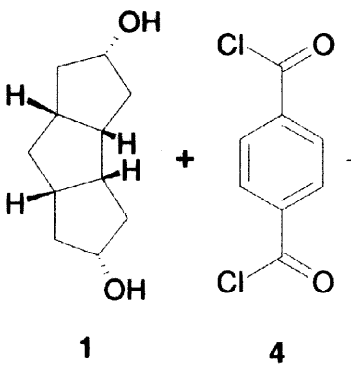


Results and Discussion

Reaction between *endo,endo*-triquinane diol **1** [4] and terephthaloyldichloride **4**, in equimolar amounts, at room temperature, in the presence of DMAP resulted in the complete consumption of both **1** and **4** and tlc examination revealed the presence of a complex mixture of less polar products in which a few compounds appeared to be more abundant. This reaction mixture, on extensive column chromatography and plc on appropriately pooled fractions led to the isolation of ten compounds **A-J** in a combined yield of ~30%, Scheme 2. Compounds **A-J** were all neat solids, some of which could be crystallized (*vide experimental*) and were found to be homogeneous by tlc. The elemental composition, FT-IR and ^{1}H NMR spectra of **A-J** revealed that they were all 1:1 coupled products of **1** and **4** and neither hydroxy nor carboxylate end groups were discernible. Further, the ^{1}H and ^{13}C NMR spectra of nine of them *i.e.*, **A-I** were nearly identical and in conjunction with strong ester carbonyl absorption in the FT-IR spectra, indicated that they were all cyclic oligomers of **1** and **4**. This was corroborated by LSIMS which additionally showed incremental change of 312 amu between oligomers. While the lowest mass $[M]^+$ observed was 625 amu indicating a coupling of two molecules each of **1** and **4** and formation of 28-membered macrocycle, the highest mass $[M+H]^+$ encountered was 2187 amu showing a union of seven units of **1** and **4** and formation of a giant oligomer with a 98-membered ring. It was also observed that each oligomer was formed in more than one stereoisomeric form and a symmetry based analysis indicated that some of the stereoisomeric oligomers could be differentiated on the basis of number of ^{13}C NMR lines. The ^{1}H NMR spectra of the compound **J** on the other hand were significantly different from **A-I** and marked it as a structurally distinct entity. All the macrocycles, despite their high molecular weight and functionalization show very good solubility in common organic solvents, due to the presence of lipophilic triquinane moieties. Another characteristic feature of diagnostic value in **A-I** was that the

orientation of the triquinane moieties in the macrocycle had a profound effect on their relative polarity. The structure elucidation of oligomers **A-J** is presented below.

Scheme 2



1 4

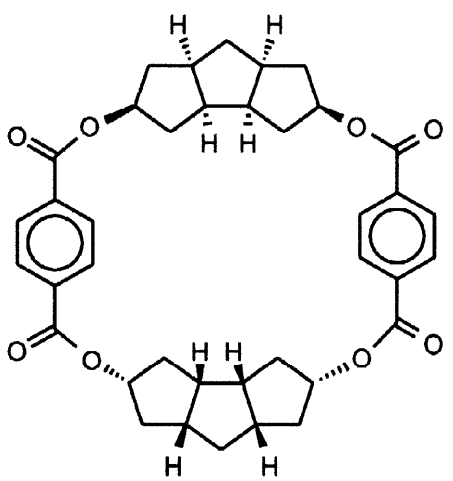
A + **B** + **C** + **D** +
(dimer, 10.2%) (dimer, 11.3%) (trimer, 5.2%) (trimer, 1.2%)

E + **F** + **G** +
(tetramer, 0.4%) (tetramer, 1.4%) (pentamer, 0.6%)

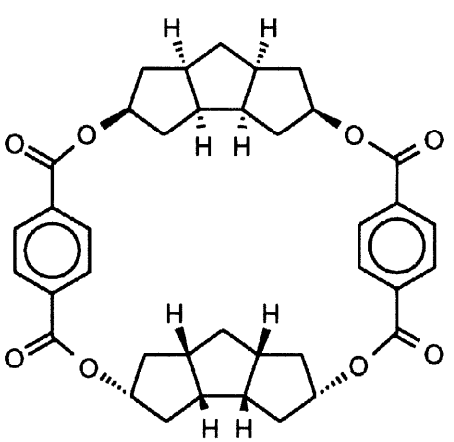
H + **I** + **J**
(hexamer, 0.5%) (heptamer, 0.2%) ([2]-catenane, 0.3%)

Structure of Dimers A and B:

The LSIMS of both **A** and **B** exhibited $[M]^+$ at 625 amu indicating a dimeric structure composed of two molecules each of **1** and **4**. The ^1H NMR spectra of **A** and **B** were essentially identical and ^{13}C NMR spectrum of each exhibited nine resonances, six due to alicyclic carbons and three due to aromatic and ester-carbonyl carbons, indicating the presence of a symmetry element. These characteristics pointed to the dimers **A** and **B** being stereoisomers of different symmetry, with a 28 membered cyclic tetra-lactone structure. The two stereoisomeric structures could be **5** (C_{2h}-symmetry, methylenes of the central five-membered ring of the two triquinane moieties pointing in opposite directions i.e. *up-down* isomer) and **6** (C_{2v}-symmetry, methylenes of the central five-membered ring of the two triquinane moieties disposed in the same direction i.e. *up-up* or *down-down* isomer). But, neither their spectral data nor any incisive NMR experiments (COSY, NOESY, etc.) helped in differentiating between **5** and **6**. Thus, recourse was taken to X-ray crystallography and both **A** and **B** yielded crystals good enough for such a solution. The X-ray crystal structure determination on the least polar compound **A** led to its identification as the *up-down* isomer **5** and its ORTEP plot is shown in Fig.1. The molecule defines an elliptical shape, fenced by triquinane and



5 (C_{2h}, *up-down*)



6 (C_{2v} *up-up*)

aromatic moieties and with a macrocyclic cavity of size ~9.76 x 6.75Å. All the four carbonyl groups of the lactone functionalities in **5** project outside the macrocycle. The aromatic rings in **5** are nearly parallel and off-set to each other. The packing diagram, Fig.2, reveals that the molecules are packed in a face-to-face manner along *b* axis. Thus, the off-set kind of arene-arene arrangement present in the molecule of **5** repeats intermolecularly with phenyl-phenyl separation of 3.64Å. Along *a* axis, the molecules are stacked, one over the other, with weak non-covalent edge-to-edge Π-Π interactions between the phenyl rings which form the walls of the infinite channels. In addition, several inter- and intramolecular C-H...O interactions [6] are also observed and are displayed in Table 1. Of particular interest is the intramolecular C8–H8b...O3 interaction between the non-acidic *endo*-hydrogen of the methylene group on the central five-membered ring of the triquinane moiety and the neighbouring ester oxygen (five bonds away). An intermolecular C6–H6a...O1 interaction between the *exo*- hydrogen of the methylene on the peripheral ring of the triquinane and the carbonyl group of the neighbouring molecule is noteworthy as its parameters (Table 1) fall well within the currently acceptable limits of a C-H...O hydrogen bond[6]. Similarly, intermolecular C5–H5...O4 interaction also involves a *exo*-cyclopentane hydrogen (attached to ester oxygen) and the carbonyl group of a neighbouring molecule. Thus, all the four ester carbonyl groups appear to be involved in C-H...O interactions, considering that the structure **5** has an inversion centre.

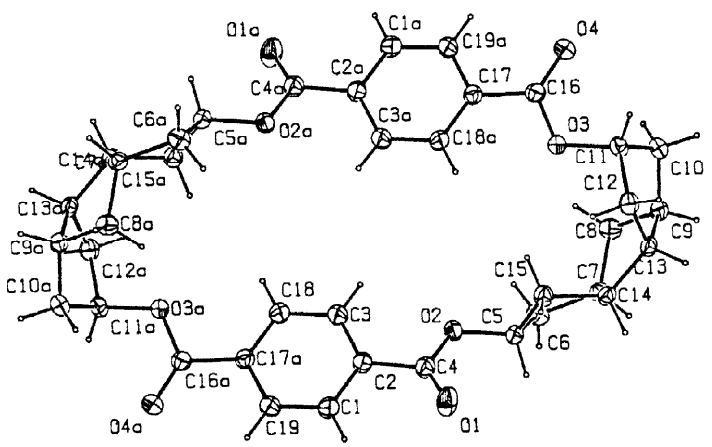


Fig. 1: ORTEP plot of **5**

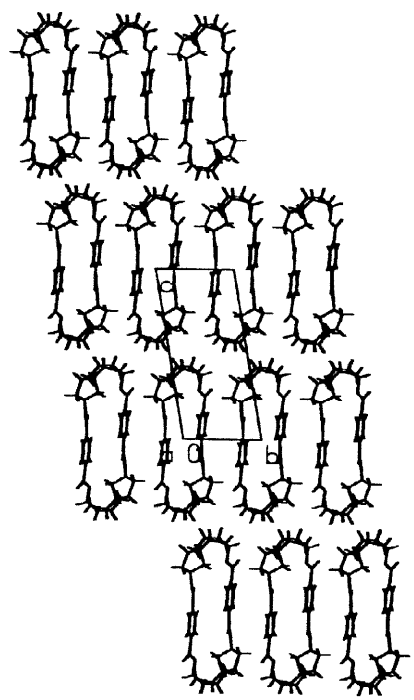


Fig.2: Packing diagram of **5**; view down *a* axis

The more polar compound **B** was revealed to be the *up-up*-isomer **6** by X-ray crystallography and its ORTEP plot is displayed in Fig.3. The shape of **6** resembles a distorted elliptical macrocycle with a cavity size of ~9.91 x 5.95Å. All the ester carbonyl groups were again pointing outside the macrocyclic cavity. The two phenyl rings in **6** are held nearly perpendicular(~100°) to each other and an edge-to-face arene-arene interaction is discernible. The packing pattern in **6**, Fig.4, is significantly different from the dimer **5** and highlights the fact that distal variation in stereochemical disposition of

methylene groups on the triquinane moiety can have a profound consequence on the packing arrangement. In **6**, many C-H...O interactions are present and are summarized in the Table 1. Once again, as in **5**, the non-acidic hydrogens on the triquinane moiety are involved in C-H...O interactions with the carbonyl groups on the neighbouring molecules.

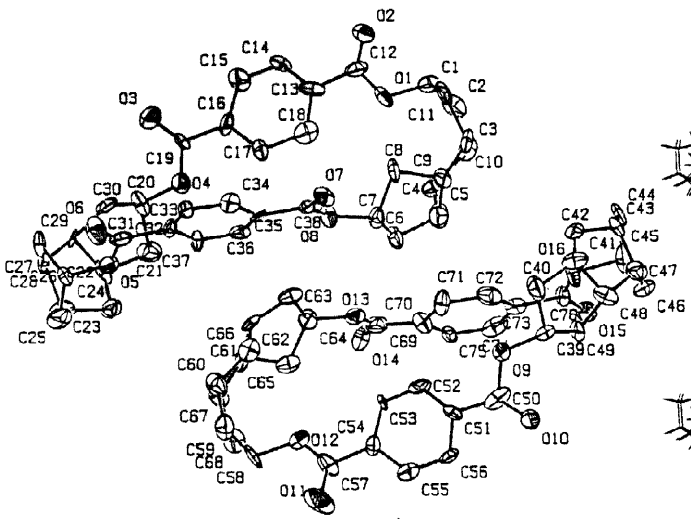


Fig. 3: ORTEP Plot of **6**

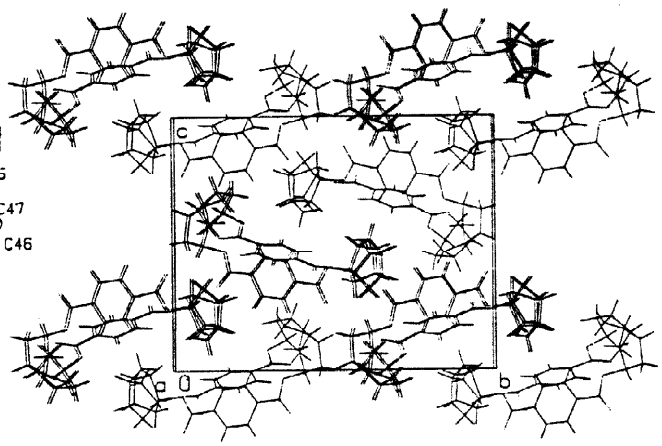


Fig.4: Packing diagram of **6**; view down *a* axis

Table 1. Selected inter- and intramolecular C-H...O interactions in **5** and **6**

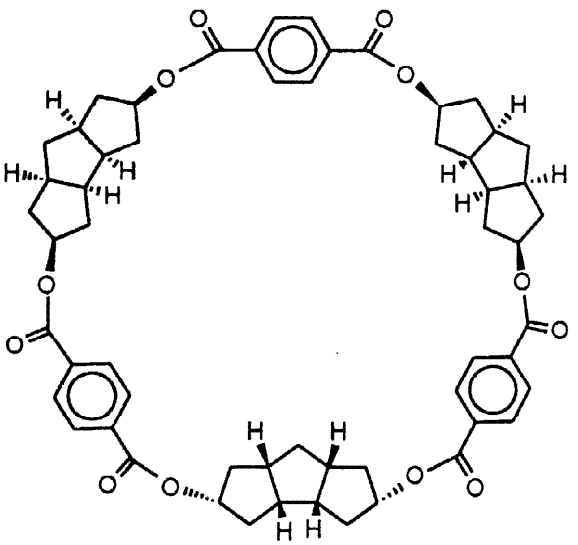
Compound	Ca – Hb...Oc	Type	*d*(H...O)/Å	*D*(C...O)/Å	Angle C-H...O/°
5	C8–H8b...O3	intra	2.5870	3.2379	124.60
	C5–H5...O4	inter	2.6163	3.4468	146.62
	C6–H6a...O1	inter	2.6956	3.6597	172.62
	C12–H12a...O4	inter	2.6575	3.4649	140.93
	C15–H15b...O3	intra	2.7352	3.5537	142.46
6	C4–H4a...O1	intra	2.5709	3.2149	123.96
	C24–H24...O7	inter	2.5000	3.3627	146.73
	C26–H26...O14	inter	2.5617	3.3229	134.49
	C42-H42b...O16	intra	2.5257	3.2133	127.83
	C45–H45...O7	inter	2.3559	3.1343	135.86
	C61–H61a...O12	intra	2.4994	3.1637	125.57
	C64–H64...O6	inter	2.5176	3.4906	171.94
	C65–H65b...O12	intra	2.5699	3.4138	145.50

Structure of Trimers C and D:

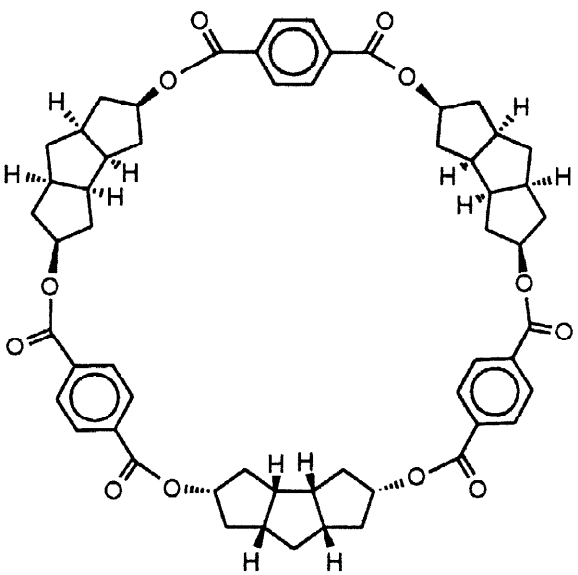
The second most abundant pair of compounds formed were **C** and **D** to which structures **7** and **8** were assigned. The LSIMS of **C** and **D** exhibited $[M]^+$ peak at 937 amu, indicating that both of them are trimers formed from the union of three molecules each of **1** and **4**. For the 42-membered macrocyclic hexalactones, two stereoisomeric forms with C_{3v} (*up-up-up*) **7** and C_s (*up-up-down*) **8** symmetry are possible, which can be differentiated by the number of ^{13}C NMR signals due to the triquinane moiety. Though the ^1H NMR spectra of the isomers **7** and **8** were nearly identical, the ^{13}C NMR

spectra were of diagnostic value and showed six and seventeen lines, respectively, due to the triquinane moiety and in consonance with the symmetry element present in them.

Among **7** and **8**, the former being more polar, readily furnished crystals good enough for X-ray crystal structure determination. An ORTEP diagram of **7** is shown in Fig.5, which confirmed its structure as the *up-up-up*-isomer with a circular cavity of ~14Å diameter. The crystal lattice of **7** has an interesting interpenetrating layered structure, with alternate layers in the 'bc' plane displaced with respect to each other, to give rise to a common cavity (~9Å) which grows into infinite channels along the *a* axis, Fig.6. The less polar isomer of the trimer was therefore recognized as **8**.



7 (C_{3v},*up-up-up*)



8 (C_s, *up-up-down*)

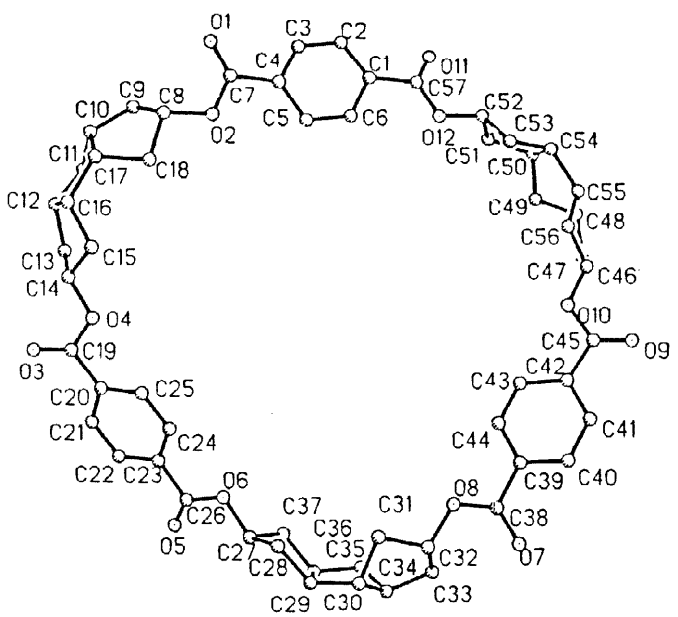


Fig. 5: ORTEP plot of **7**

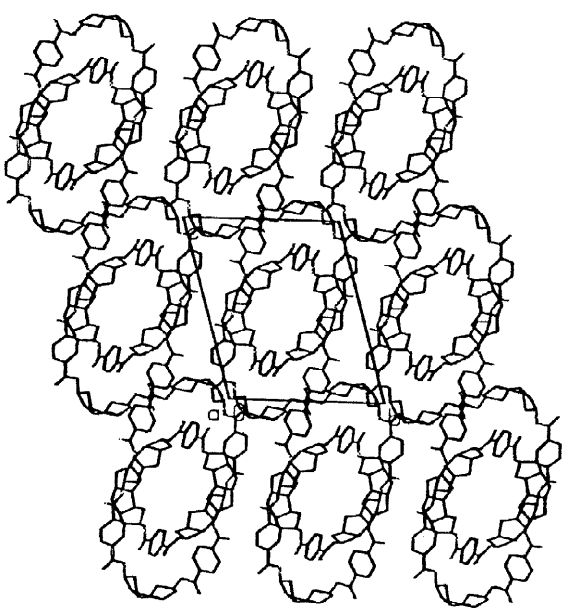
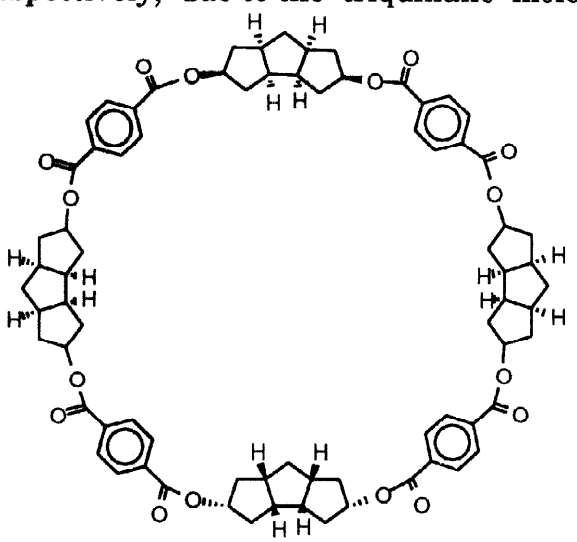


Fig.6: Packing diagram of **7**; view down *a* axis

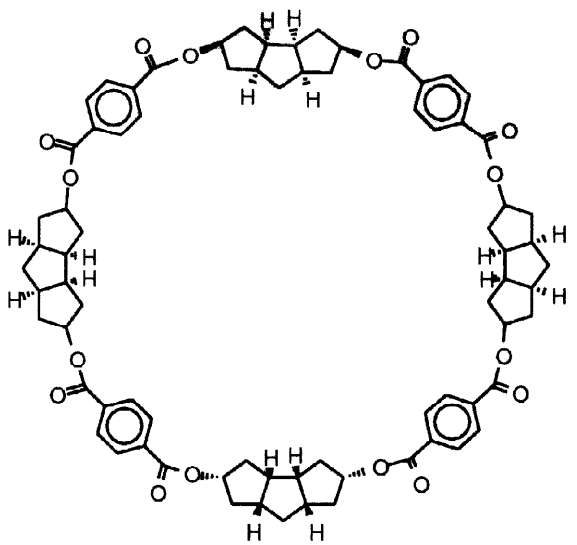
Structure of Tetramers E and F:

The LSIMS of **E** and **F** showed $[M+Na]^+$ and $[M]^+$ peaks at 1272 and 1249 amu, respectively, corresponding to a 56-membered tetrameric structure derived from four

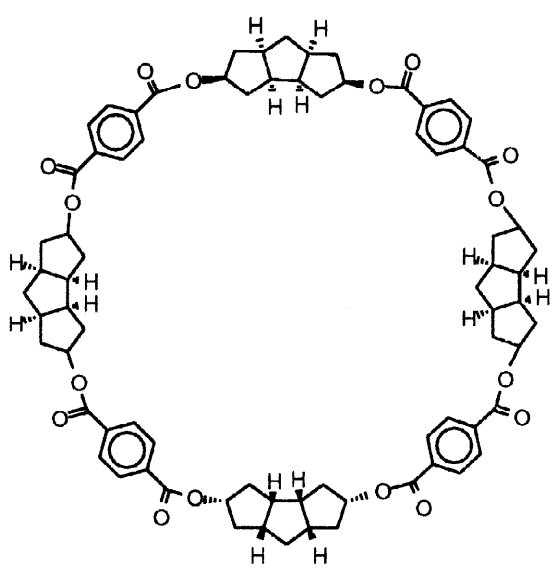
units each of **1** and **4**. The ^{1}H NMR spectra of both **E** and **F** were similar and of little diagnostic value. A symmetry based analysis indicated that the tetramers derived from **1** and **4** could exist in four stereoisomeric forms with respect to the disposition of the methylene group on the central five-membered ring of the triquinane moieties, i.e., C_{4v} (*up-up-up-up*), D_{2d} (*up-down-up-down*), C_{2h} (*up-up-down-down*) and C_s (*up-up-up-down*), and were amenable to differentiation on the basis of number of lines in the ^{13}C NMR spectra. Thus, the tetramers with C_{4v} (*up-up-up-up*) and D_{2d} (*up-down-up-down*) symmetry were expected to exhibit six lines each, while those with C_{2h} (*up-up-down-down*) and C_s (*up-up-up-down*) symmetry would exhibit eleven and twenty three lines, respectively, due to the triquinane moieties. The ^{13}C NMR spectrum of **E** showed



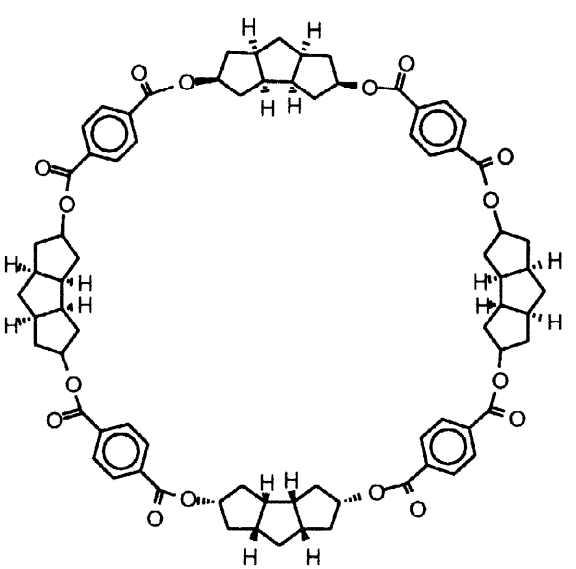
9 (C_{4v}, *up-up-up-up*)



10 (D_{2d}, *up-down-up-down*)



11 (C_{2h}, *up-up-down-down*)



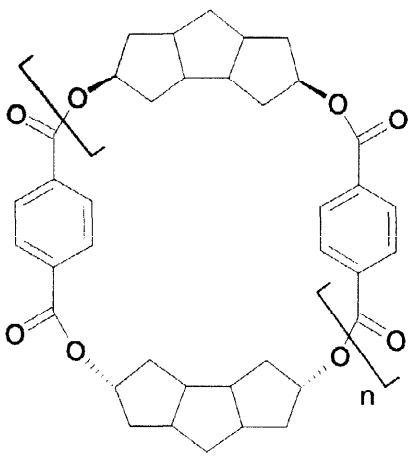
12 (C_s, *up-up-up-down*)

nine lines, six of them assignable to the triquinane portion and led to the assignment of structure **9** (C_{4v}) or **10** (D_{2d}) to this isomer. A distinction between **9** and **10** was not possible through spectral data and this isomer did not yield crystals suitable for X-ray

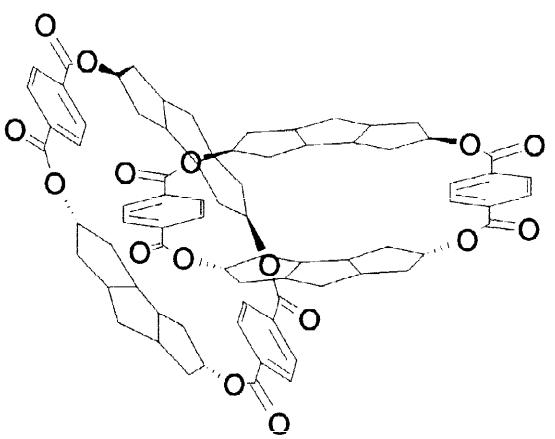
structure determination. However, on the basis of statistical considerations and trends in the polarity behaviour of these compounds, structure **10** is preferred. The tetramer **F**, which appeared homogeneous by tlc, showed forty lines in the high-field ^{13}C NMR spectrum (*vide experimental*), implying that it was a mixture of **9** (C_{4v}), **11** (C_{2h}) and **12** (C_s). Tetramer **F** could not be purified for complete characterization of **9**, **11** and **12**.

Structure of pentamers G, hexamers H and heptamers I:

The LSIMS of oligomers **G**, **H** and **I** were found to be $[M+H]^+$ 1563 amu, $[M+H]^+$ 1875 amu and $[M+H]^+$ 2187 amu, respectively. This indicated 70-, 84- and 98-membered macrocyclic structures for **G**, **H** and **I**, respectively. A symmetry based analysis indicated that pentamer **G** can exist in four stereoisomeric forms (three of C_s symmetry and one with C_{5v} symmetry), which could be identified through the number of lines in the ^{13}C NMR spectrum (28 for C_s and 6 for C_{5v}). The ^{13}C NMR spectrum of pentamer **G** showed more than 30 lines due to the triquinane moiety, thus identifying it as a mixture of stereoisomers **13**. The hexamer **H** and heptamer **I** can exist in eight (C_{6v}, D_{3d}, C_{2v}, C_{2h}, C_2 and three C_s) and nine (C_{7v}, C_1 and seven C_s) stereoisomeric forms, respectively. Once again, the hexamer and heptamer showed over 30 lines in the ^{13}C NMR spectrum, not corresponding to any single stereoisomeric forms, and implying that they were mixtures of stereoisomers **14** and **15**.



13 n = 4, pentamer
14 n = 5, hexamer
15 n = 6, heptamer



16

Structure of [2]-catenane J:

The ^1H NMR spectrum of compound **J** was very different from **A-I** and was quite unusual for a simple macrocyclic structure. For example, the aromatic protons of the terephthaloyl moiety, which appeared as a singlet at δ ~8.1 in **A-I**, showed two AB-type quartets centred at δ 7.79 (J=8.1Hz) and 8.08 (J=8.4Hz) in **J**. Similarly, the ester attached protons of the triquinane moiety resonated as a multiplet at δ ~5.2-5.4 in **A-I**, but in **J** the same protons appeared as two multiplets of equal intensity at δ ~5.4-5.6 and δ ~5.0-5.35. These non-equivalences in the proton spectra were quite characteristic and indicative of a catenane-like structure **16** and this surmise was unambiguously established through incisive mass spectral studies. The LSIMS of **J** showed $[M+H]^+$ and $[M+Na]^+$ peaks at 1250 and 1272 amu, respectively. A comparison of mass spectra of dimers **5** and **6**, tetramer **10** and [2]-catenane **16** showed that the dimers gave abundant ions corresponding to $[M]^+$ at m/z 625 amu. The peaks corresponding to $[2M]^+$ and

$[2M+Na]^+$ were not prominent and also their abundance did not vary significantly at higher concentrations of the dimer. This indicated that the formation of $[2M]^+$ and $[2M+Na]^+$ under LSIMS conditions are negligible. The mass spectrum of the tetramer **10** gave $[M+Na]^+$ at m/z 1272 amu as an abundant peak as compared to $[M+H]^+$. The collision induced dissociation (CID) spectrum of the $[M+Na]^+$ ion showed peaks corresponding to trimer and dimer due to consecutive loss of m/z 312 amu. On the other hand, the mass spectrum of **16** showed peaks corresponding to $[M+H]^+$ and $[M/2]^+$ and their Na-adducts, with $[M/2]^+$ as the base peak. There were no significant fragment ion peaks in between $[M+H]^+$ and $[M/2]^+$. The CID spectrum of $[M+H]^+$ gave only the ion corresponding to $[M/2]^+$ (loss of one ring of the catenane) as the abundant ion. Under these conditions, the absence of peaks between $[M+H]^+$ and $[M/2]^+$ (*cf.* tetramer **10**) provided strong evidence for the [2]-catenane structure **16**. While the gross [2]-catenane structure for **16** was firmly established, the available data in the absence of suitable crystals for X-ray crystal structure determination did not permit complete assignment of stereostructure. Many catenanes are known to exhibit dynamical behaviour with subtle molecular motions and conformations. However, **16** appears to have a fixed structure with the bulky triquinane moieties blocking the movement within the interlocked rings.

In short, we have outlined a simple access to a range of macrocyclic lactones and a [2]-catenane, employing a flat aromatic precursor and a convoluted alicyclic substrate as the building-blocks. The tactic used here should be amenable to adaptation for the construction of macrocyclic lactams and many other structural variants.

Experimental

General: NMR spectra were recorded on Bruker AC-200 or on Varian UNITY- 400 Spectrometers in $CDCl_3$ using Me_4Si as internal standard. Chemical shift values are given in δ (ppm) units and J values are in Hz. In higher oligomers, many of the ^{13}C NMR resonances were overlapping. IR spectra were obtained with a JASCO FT-IR 5300 spectrophotometer. Liquid secondary ion mass spectra (LSIMS) were recorded using an AUTOSPEC-M mass spectrometer (Micromass, Manchester, UK) with an OPUS V3.1X data system. LSIMS spectra were taken by ionizing the sample with a primary beam of Cs^+ ions of 22kV energy at ambient temperature and recorded in continuum mode at a resolving power of 1000 (10% valley). m-Nitrobenzyl alcohol was used as the matrix and a chloroform solution of the sample was mixed with the matrix on the stainless steel target before the analysis. The collision induced dissociation (CID) spectra were recorded using linked scan technique at constant B/E and helium was used as the collision gas at a pressure for 50% main beam reduction. All the spectra reported are an average of 10-15 scans. Yields reported are isolated yields of material judged homogeneous by tlc.

Typical procedure for the oligomerisation of *cis*-triquinane diol 1 and terephthaloyl dichloride 4: To a stirred solution of *endo,endo*-triquinane diol **1** (0.5g, 2.75mmol) and dimethylaminopyridine (1.66g, 13.6mmol) in dry dichloromethane (DCM,150ml), terephthaloyldichloride **4** (0.56g, 2.75mmol) in dry DCM (30ml), was added dropwise over a period of 30 minutes under nitrogen. The mixture was stirred for about 40h at room temperature and filtered. The filtrate was successively washed with 0.6N HCl, saturated sodiumbicarbonate and brine. Drying over Na_2SO_4 and concentration furnished a solid residue (430mg). A careful tlc assay (eluent, $CHCl_3$:hexane, 4:1) resolved the mixture into at least 10 compounds with very close Rf values. The residue

was charged on a silica gel column(16g) and elution with $CHCl_3$-hexane (3:1) furnished dimer **5** (88mg, 10.2%) as colourless solid. An analytical sample was obtained by recrystallization from DCM/ethanol to afford colorless needles; mp. 268°C; IR (KBr): 1720, 1280, 729 cm^{-1}; ^1H NMR (200 MHz): δ 8.01 (s, 8H), 5.43-5.37 (m, -CH-OCO, 4H), 2.77-2.51 (m, 8H), 2.34-2.12 (m, 10H), 1.92-1.80 (m, 8H), 1.79-1.50 (m, 2H); ^{13}C NMR (50 MHz): δ 165.60, 134.30, 129.37, 79.88, 45.41, 45.20, 41.37, 37.47, 35.08; LSIMS: *m/z* 625 $[M]^+$. Anal. for $C_{38}H_{40}O_8$: calcd. C 73.06, H 6.45; found C 73.00, H 6.48.

Further elution with $CHCl_3$ furnished dimer **6** (97mg, 11.3%) as a colorless solid. Recrystallization from DCM/hexane afforded colorless needles; mp. 248°C; IR (KBr): 1722, 1277, 727 cm^{-1}; ^1H NMR (200 MHz): δ 8.10 (s, 8H), 5.53-5.47 (m, -CH-OCO, 4H), 2.90-2.51 (m, 8H), 2.30-2.12 (m, 10H), 2.00-1.83 (m, 8H), 1.71-1.55 (m, 2H); ^{13}C NMR (50 MHz): δ 165.43, 134.36, 129.35, 79.59, 45.34, 44.70, 42.31, 36.97, 34.95; LSIMS: *m/z* 625 $[M]^+$. Anal. for $C_{38}H_{40}O_8$: calcd. C 73.06, H 6.45; found C 73.10, H 6.42.

Subsequent elution with $CHCl_3$ furnished the [2]-catenane **16** along with small amounts of **6** and **8**. These fractions were concentrated and rechromatographed on a silica gel (3g) column using chloroform as the eluent to afford enriched fractions of compound **16** which were pooled and further purified by preparative tlc (eluent: $CHCl_3$/hexane, 4:1) to furnish pure **16** (3mg, ~0.3%), mp. 208-209°C (DCM/benzene); IR (KBr): 1716, 1275, 731 cm^{-1}; ^1H NMR (200 MHz): δ 8.12 (1/2 ABq, J=8.3Hz, 4H), 8.04 (1/2 ABq, J=8.2Hz, 4H), 7.92 (1/2 ABq, J=8.4Hz, 4H), 7.66 (1/2 ABq, J=8.1Hz, 4H), 5.65-5.45 (m, CH-OCO, 4H), 5.35-5.05 (m, CH-OCO, 4H), 3.00-1.37 (series of m, 56H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.51, 134.26, 134.05, 133.81, 129.47, 129.43, 129.27, 129.10, 80.90, 80.67, 78.11, 76.23, 47.72, 46.67, 46.04, 44.96, 43.68, 43.27, 43.15, 42.61, 42.35, 39.97, 38.40, 37.53, 36.90, 36.32, 36.13, 34.58, 33.83, 33.32. LSIMS: *m/z* 1272$[M+Na]^+$, 1250$[M+H]^+$, 625 $[M/2]^+$.

Further elution with $CHCl_3$ afforded trimer **8** (45mg, 5.2%) as colorless solid, which was crystallized from DCM/hexane to afford colorless needles; mp. 270°C; IR (KBr): 1716, 1273, 1120, 731 cm^{-1}; ^1H NMR (400 MHz): δ 8.08 (s, 12H), 5.39-5.31 (m, CH-OCO, 6H), 2.61-2.44 (series of m, 18H), 2.30-2.20 (m, 9H), 1.78-1.70 (m, 6H), 1.63-1.54 (m, 7H), 1.42-1.39 (m, 2H); ^{13}C NMR (100 MHz): δ 165.59(2C), 165.58, 134.15(2C), 134.14, 129.43(6C), 78.53, 78.52(2C), 44.29, 44.18, 44.05, 43.56, 43.49, 43.36, 41.60, 41.58, 37.91, 37.83, 37.75, 34.22, 34.20, 34.13. LSIMS: *m/z* 937 $[M]^+$. Anal. for $C_{57}H_{60}O_{12}$: calcd. C 73.06, H 6.45; found C 72.92, H 6.48.

Continued elution with $CHCl_3$ afforded a mixture of tetramer **10** and trimer **7**. On fractional crystallization from DCM/hexane, the trimer **7** crystallized out, thereby enriching the mother liquor with tetramer **10**, which was concentrated and chromatographed on silica gel (5g) using $CHCl_3$ eluent, to afford pure tetramer **10** (3.4mg, 0.4%), crystallized from DCM/hexane; mp.>280°C; IR (KBr): 1716, 1275, 731 cm^{-1}; ^1H NMR (200 MHz): δ 7.88 (s, 16H), 5.44-5.31 (m, CH-OCO, 8H), 2.82-1.38 (series of m, 56H); ^{13}C NMR (50 MHz): δ 165.24, 134.10, 129.31, 79.18, 45.24, 44.56, 41.48, 37.46, 34.83; LSIMS: *m/z* 1272 $[M+Na]^+$.

The above trimer **7** (10mg, 1.2%) was recrystallized from (DCM/hexane) to afford colorless needles; mp. 278°C; IR (KBr): 1720, 1275, 731 cm^{-1}; ^1H NMR (200 MHz): δ 8.09 (s, 12H), 5.42-5.28 (m, CH-OCO, 6H), 2.70-2.40 (m, 18H), 2.35-2.20 (m, 10H), 1.85-1.30 (m, 14H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.60, 134.21, 129.46, 78.53, 44.25, 43.57, 41.54, 37.94, 34.23; LSIMS: *m/z* 937$[M]^+$. Anal. for $C_{57}H_{60}O_{12}$: calcd. C 73.06, H 6.45; found C 73.04, H 6.46.

Further elution with $CHCl_3$ afforded a fraction which was homogeneous by tlc but high-field NMR showed it to be a mixture of three tetramers **9**, **11** and **12** (12mg, 1.4%), colorless solid; mp. 236-240°C; IR (KBr): 1716, 1275, 731 cm^{-1}; ^1H NMR (400 MHz): δ 7.95 (bs, 16H), 5.45-5.33 (m, C<u>H</u>-OCO, 8H), 2.80-2.44 (series of m, 16H), 2.40-2.25 (m, 6H), 2.20-2.12 (m, 8H), 1.95-1.40 (series of m, 26H); ^{13}C NMR (100 MHz): δ 165.30, 165.28, 165.23, 165.22, 134.13, 134.08, 129.38, 79.21, 79.18, 79.10, 79.04, 79.00, 45.27, 45.25, 45.16, 45.12, 44.95, 44.54, 44.41, 44.39, 44.32, 44.28, 44.24, 41.59, 41.48, 41.46, 41.39, 41.34, 37.74, 37.72, 37.58, 37.51, 34.83, 34.81, 34.75, 34.72, 34.68, 34.59; LSIMS: *m/z* 1249 $[M]^+$.

Continued elution with $CHCl_3$ afforded a mixture of pentamers **13** (5mg, 0.6%), as a white solid; mp. 160-162°C; IR (KBr): 1718, 1273, 731 cm^{-1}; ^1H NMR (400 MHz): δ 7.94 (s with sh, 20H), 5.34-5.31 (m, C<u>H</u>-OCO, 10H), 2.63-2.53 (series of m, 22H), 2.39-2.21 (m, 10H), 2.18-2.14 (m, 12H), 1.75-1.44 (series of m, 26H); ^{13}C NMR (100 MHz): δ 165.37, 134.02, 129.35, 79.02, 78.99, 78.97, 78.93, 78.90, 78.89, 78.88, 44.90, 44.86, 44.85, 44.84, 44.73, 44.17, 44.15, 44.12, 44.10, 44.08, 44.06, 41.29, 37.75, 37.73, 37.72, 37.69, 37.68, 37.66, 37.63, 34.59, 34.57, 34.55, 34.54, 34.52, 34.51, 34.49; LSIMS: *m/z* 1563 $[M+H]^+$.

Further elution with $CHCl_3$ afforded a mixture of hexamers **14** (4.5mg, 0.5%), as a colorless solid, which was recrystallized from DCM/hexane to afford colorless needles; mp. 170-171°C; IR (KBr): 1718, 1273, 731 cm^{-1}; ^1H NMR (400 MHz): δ 7.93 (s with sh, 24H), 5.36-5.33 (m, C<u>H</u>-OCO, 12H), 2.66-2.10 (series of m, 48H), 1.76-1.45 (series of m, 36H); ^{13}C NMR (100 MHz): δ 165.30, 134.06, 129.36, 79.06, 79.03, 78.99, 78.95, 78.94, 78.92, 78.90, 45.01, 44.99, 44.98, 44.94, 44.93, 44.92, 44.90, 44.19, 44.17, 44.16, 41.50, 41.48, 37.69, 37.64, 37.63, 37.61, 37.60, 37.58, 37.56, 34.68, 34.66, 34.63, 34.62, 34.60; LSIMS: *m/z* 1875 $[M+H]^+$.

Continued elution with $CHCl_3$ afforded a mixture of heptamers **15** (2mg, 0.2%) colorless solid, mp.153-154°C; IR (KBr): 1718, 1273, 731 cm^{-1}; ^1H NMR (400 MHz): δ 7.94 (s with sh, 28H), 5.40-5.32 (m, C<u>H</u>-OCO, 14H), 2.76-2.06 (series of m, 56H), 1.80-1.41 (series of m, 42H); ^{13}C NMR (100 MHz): δ 165.38, 165.35, 134.07, 129.37, 78.95, 78.89, 78.87, 44.79, 44.09, 44.07, 44.02, 41.46, 41.43, 37.68, 37.63, 34.66, 34.51, 34.46; LSIMS: *m/z* 2187 $[M+H]^+$. Further elution with $CHCl_3$-ethylacetate (9:1) afforded more polar compounds of polymeric nature, as indicated by spectral analyses.

Crystal data for 5: $C_{38}H_{40}O_8$, M=624.7, crystals from DCM/ethanol, triclinic, Space group $P\bar{1}$, a = 6.4052(18), b=7.4718(4) and c=16.5972(14)Å, α=100.063(6)°, β=96.837(13)°, γ=90.364(11)°, V=776.2(2)Å^3, Z=1, D_c=1.336Mg m^{-3}, T=293K, F(000)=332, μ(Mo-K_α) =0.093mm^{-1}, crystal dimensions 0.16 x 0.20 x 1.36 mm. Data were collected on Enraf-Nonius MACH-3 diffractometer, graphite-monochromated Mo-K_α radiation (λ=0.71073Å), by ω–scan method in the range $2 \leq \theta \leq 25°$, 2727 unique reflections [R_{int}=0.000], of which 1967 had $Fo > 4\sigma$ (F_o), were used in all calculations. At final convergence $R_1[I>2\sigma(I)]$=0.0377, wR_2=0.0947 for 208 parameters, GOF=1.052, $\Delta\rho_{max}$=0.168e Å^{-3}, $\Delta\rho_{min}$=-0.271e Å^{-3}. The data were reduced using XTAL (ver 3.4), solved by direct methods, refined by full-matrix least-squares on F^2 using SHELX 97 [7], with the non-H atoms anisotropic and H atoms isotropic.

Crystal data for 6: $C_{38}H_{40}O_8$, M=624.7, crystals from DCM/Hexane, monoclinic, Space group $P2_1/n$ a=10.7260(10), b=19.565(2) and c=15.4590(10)Å, β=90.800(10)°,

V=3243.8(5)Å^3, Z=4, D_c=1.279Mg m^{-3}, T=293K, F(000)=1328, μ(Mo-K$_\alpha$) =0.089mm^{-1}, crystal dimensions 0.13 x 0.16 x 0.11mm. Data was collected on SIEMENS R3m/V single crystal diffractometer, graphite-monochromated Mo-K$_\alpha$ radiation (λ=0.71073Å), by ω–2θ scan technique, in the range 2≤θ≤22.5°, 4500 unique reflections [R_{int}=0.0248], of which 2595 had $Fo > 4\sigma(F_o)$, were used in all calculations. At final convergence $R_1[I>2\sigma(I)]$=0.0465, wR_2=0.1208 for 829 parameters, GOF=1.134, $\Delta\rho_{max}$= 0.221e Å^{-3}, $\Delta\rho_{min}$=-0.182e Å^{-3}. Data corrected for Lorentz and polarization but not for absorption. The structure was solved by direct methods, refined by full-matrix least-squares on F^2 using SHELX 97 [7], with the non-H atoms anisotropic and H atoms isotropic.

Crystal data for 7: $C_{57}H_{60}O_{12}$, M=937.1, colourless crystals from DCM/Hexane, Triclinic, Space group $P\bar{1}$, a=10.664(2), b=14.472(2) and c=18.018(3)Å, α=103.66 (2)°, β=104.67(2)°, γ=97.10(2)°, V=2563.7(9)Å^3, Z=2, D_c=1.214Mg m^{-3}, T=293K, μ(Mo-K$_\alpha$) =0.08mm^{-1}, crystal dimensions 0.13 x 0.15 x 0.10mm, 7346 reflections measured, $2\theta_{max}$=45°, 7194 unique reflections [R_{int}=0.032] and 1291 observed with I≥3σ(I). Final R=0.088 and R_w=0.064 for 622 parameters, $\Delta\rho_{max}$=0.24e Å^{-3}, $\Delta\rho_{min}$=-0.21e Å^{-3}.Data were collected on SIEMENS R3m/V single crystal diffractometer, graphite-monochromated Mo-K$_\alpha$ radiation (λ=0.71073Å), by ω–2θ scan technique. Data corrected for Lorentz and polarization but not for absorption. The structure was solved by direct methods (SHELXTL- Plus 4.11/v) and anisotropically refined. The H atoms calculated to their idealized positions and refined as riding atoms with fixed isotropic temperature factors (U=0.08Å^2). As the observed-data-to-parameter ratio was low a relatively high R value was obtained. The final refinements were carried out with blocked matrix technique. However, the stereo structure of the molecule was clear, Fig.5.

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