# Chemical Modifications of Furan-Based Calixarenes by Diels – Alder Reactions

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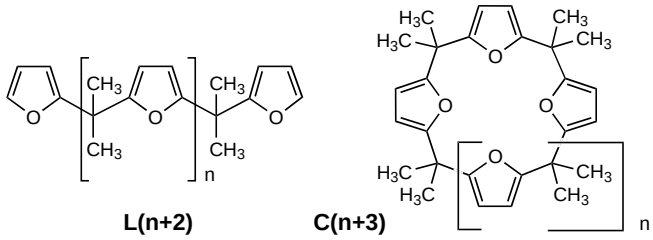
**Abstract:** The simple chemical modification by Diels – Alder reactions of the cyclic hexamer of furan and acetone, utilising two readily accessible dienophiles, benzyne and dimethylacetylenedicarboxylate (DMAD), is described. The studies have explored the ease with which different furan units within the macrocycle can be converted into either naphthalenes, *o*-phthalic ester residues or 3,4-furandicarboxylate units. The cycloaddition products are shown to differ as a function of stoichiometry, regiochemistry and stereochemistry. The problems encountered in the attempts to aromatise the benzyne adducts to their corresponding naphthafurophanes hamper the exploitation of these compounds as acenophane precursors. Similarly, the DMAD adducts are not suitable precursors for derivatives containing phthalic acid units. On the other hand, they readily provide access to furanophanes containing carboxyl substituents. The X-ray crystal structures of a variety of key derivatives have been determined and their conformations analysed and compared.

**Keywords:** calixarenes · Diels – Alder reactions · furan · macrocycles

## Introduction

Over recent decades, the development of supramolecular chemistry has been largely dominated by the design and synthesis of macrocyclic compounds with potential receptor capabilities.[1] Calixarenes are among some of the most studied representatives of such compounds.[2] Extensive research has been carried out on the chemical modification of these macrocycles, which permits a degree of tuning of both their physical properties and of their ability to act as molecular receptors.[2, 3] To a large extent, the rapid development of calixarene chemistry has resulted from the relative ease with which these self-assemble upon the cyclooligomerisation of phenol derivatives and carbonyl compounds under appropriate reaction conditions.[2] This self-assembling capability is also a property of some of the furan-based analogues of calixarenes, which can be synthesised by the acid-promoted condensation of furan and selected aldehydes and ketones.[4] However, their chemical modification has been little explored or exploited.[5] The cyclic tetramer of furan and acetone **C4** is the most well known and accessible member of this series,[4] but larger oligomers up to **C8** have been described in the literature[4c] prior to our recent investigation, which has now extended the current limit to **C9**.[6]




The Diels – Alder reactivity of the furan units provides a means for the chemical modification of these macrocycles. The aromatisation of the adducts can in principle also be exploited for the synthesis of other phanes containing acene moieties linked at the 1,4-positions of their benzene subunits.[7] However, an initial attempt by Hart and Takehira to convert **C4** into the corresponding [1$_4$](1,4)naphthalenophane was unsuccessful, because the intermediate tetra-adduct with benzyne could not be aromatised.[5a] More recently, we reinvestigated this process,[8] confirmed this result and found that only the monoaddition product of **C4** and benzyne can be converted into the corresponding naphthafurophane. This limitation was ascribed mainly to steric effects. On the basis of these results, we decided to extend our studies to larger homologues of **C4**, which can be expected to be considerably

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more flexible, and to include other dienophiles besides benzyne in our work.

Here we provide a full account of the results obtained so far along this route, which includes the synthesis of several benzyne and dimethylacetylenedicarboxylate (DMAD) adducts with **C6**. We also describe the aromatisation leading to naphthafurophanes of some of the benzyne adducts, the aromatisation of the DMAD adducts to furanophanes containing carboxyl functional groups and the structural characterisation of several of these compounds.

## Results and Discussion

We focused our attention on the cyclic oligomers of furan and acetone, because the $[1_n](2,5)$furophanes **Cn**, in which the link between the furan units is an unsubstituted carbon atom, are not readily obtainable.[9] Moreover, those obtainable from aldehydes (in which the linking carbon atom is monosubstituted) exist as groups of stereoisomers, which adds an undesired degree of complexity at the initial stages of our investigation. We decided to focus our investigation on **C6** rather than **C5**, because the former can be synthesised much more easily.[6] In fact **C6** can be prepared by the cyclodimerisation of **L3**, which is readily available. On the other hand, an efficient synthesis of **C5** can only be achieved by the cyclisation of **L5** (which is not as easily synthesised and purified as **L3**), since the condensation of **L2** with **L3** yields a mixture of **C4**, **C5** and **C6**, in which **C5** is only a minor component.[6] The macrocycle **C6** has also been characterised by X-ray crystallography (Figure 1) and an analysis of its solid-state structure reported in a preliminary communication.[6]

Key features of the structure include the presence of a crystallographic $C_2$ axis of symmetry passing through the furan rings in the 1- and 4-positions. Despite the relatively large ring size, there is no central void as two of the furan rings, with oxygen atoms numbered 1 and 4, are oriented codirectionally and are approximately coplanar with the mean plane of the macrocycle. The other four furan rings adopt a near orthogonal up–down–up–down geometry. The six isopropylidene carbon atoms are coplanar to within 1.1 Å and thus the macroring can be considered to have an overall discoid shape. The only feature of interest in the packing of the structure is that crystallisation has occurred in a non-centrosymmetric polar space group; there are however, no notable intermolecular interactions.

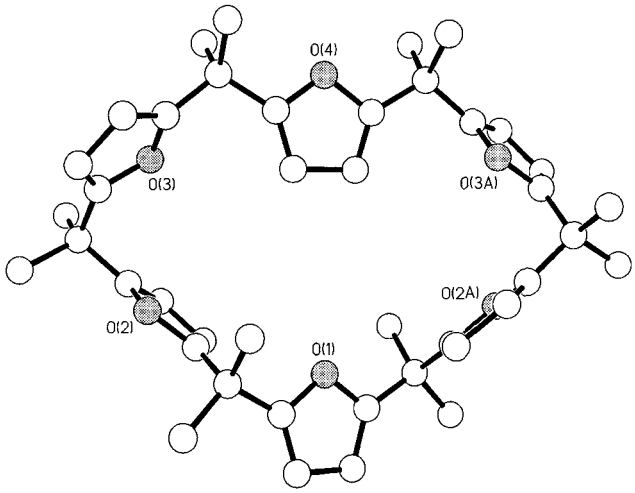


Figure 1. The X-ray crystal structure of the cyclic hexamer of furan and acetone **C6**. The tilt angles[10] of the furan rings containing O(1), O(2), O(3) and O(4) are 26, 95, 67 and 168° respectively.

**Reaction of C6 with benzyne**: Extending our initial study[8] on the conversion of the furan units of **C4** into acene units, we subjected **C6** to multiple cycloaddition with benzyne generated by the pyrolysis of benzenediazonium-2-carboxylate.[11] The choice of benzyne as the dienophilic component was prompted by its high reactivity, low cost and absence of *exo*/*endo* stereoisomerism of the adducts.

The cycloaddition products of **C6** (and its homologues) with benzyne can differ as a function of:

1) the number of furan units, which have undergone cycloaddition (stoichiometry)
2) the relative position of the furan units, which have reacted (regiochemistry)
3) the relative orientations of the various cycloadditions (stereochemistry), which, for convenience, can be referred to as either *syn* or *anti* with respect to a plane containing the macrocycle in an ideal flattened-out and all oxygen atoms 'in' conformation.

The complexity arising from the existence of all these possibilities is considerably reduced in the aromatised adducts, where the configurational *syn*/*anti* stereochemistry may become merely conformational if the 2,3-carbon atom bridge of the naphthalene units can pass through the central cavity of the macrocycle.[11] For example, penta- and hexa-adducts of **C6** with benzyne can exist as ten and six stereoisomers respectively (including enantiomers). However, when aromatised, each group should yield just a single compound.

**Abstract in Italian:** *Si descrive la semplice funzionalizzazione, mediante reazioni Diels–Alder con due dienofili facilmente disponibili, il benzino ed il dimetilacetilendicarbossilato (DMAD), dell'esamero ciclico ottenuto da furano ed acetone. In questo studio è stata investigata la facilità con cui le unità furaniche del composto macrociclico possono essere convertite in unità naftaleniche, esteree o-ftaliche, o unità furaniche contenenti funzioni carbossilato alle loro posizioni 3,4. I prodotti di cicloaddizione si differenziano per il rapporto stechiometrico, la regiochimica e la stereochimica. Le difficoltà incontrate nel tentativo di aromatizzare gli addotti con il benzino per ottenere i corrispondenti naftafurofani ne limitano lo sfruttamento quali precursori di acenofani. Analogamente gli addotti con DMAD non sono precursori adatti ad ottenere derivati contenenti residui o-ftalici, tuttavia essi possono essere facilmente convertiti in furanofani contenenti funzioni carbossilato. Le strutture di svariati derivati di rilievo ottenuti nel corso delle varie trasformazioni sono state determinate ai raggi X e le loro conformazioni analizzate e confrontate.*

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The crude mixtures obtained from the reaction of **C6** with benzyne in various stoichiometric proportions were analysed by thin layer chromatography (tlc) on $SiO_2$ with toluene/hexane (1:3) (Scheme 1). The cycloaddition products were

| Chromatographic mobility and composition ⇑ | 6/A mono-adduct | 9/A fraction almost absent | 12/A fraction almost absent |
|---|---|---|---|
| | 6/B several bis-adducts | 9/B several bis- and tris-adducts | 12/B fraction almost absent |
| | 6/C fraction almost absent | 9/C several tris- and tetra-adducts | 12/C several tetra-adducts |
| | 6/D fraction almost absent | 9/D several tetra - and penta-adducts | 12/D several tetra- and penta-adducts |
| | 6/E fraction almost absent | 9/E fraction almost absent | 12/E several penta- and hexa-adducts |
| Ratio benzyne/**C6** ⇨ | 6 | 9 | 12 |

Scheme 1. The crude mixtures from the cycloaddition of **C6** with 6, 9 and 12 moles of benzyne contain five chromatographic fractions in varying proportions and compositions as indicated. In each case, the isolated fractions are identified by a code (for example, 6/A for the first fraction to be eluted in the reaction of **C6** with 6 moles of benzyne, 6/B for the second and so on). $R_f$ values ($SiO_2$, toluene/hexane 1:3) for fractions A, B, C, D and E were 0.60, 0.40, 0.30, 0.25 and 0.20 respectively.

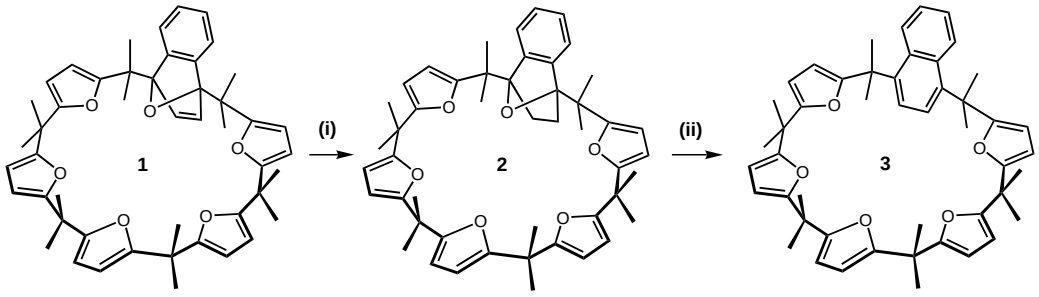
grouped into five chromatographic fractions. The yield of the most chromatographically mobile fractions decreased and that of the less mobile ones increased proportionally with the amount of benzyne used in each reaction. However, as revealed by positive-ion FAB-MS and $^1$H NMR data, these fractions did not correspond to five different stoichiometric proportions of cycloadded benzyne on **C6**, their composition being partly dependent upon the regio- and stereochemistry of the cycloadditions. Assuming that the multiple cycloadditions of benzyne on **C6** take place in sequence, the large excess of benzyne required to obtain significant quantities of polyaddition products could result from a progressive decrease of the reactivity of the adducts as a function of the cycloadded benzo units.

With the aim of converting all the adducts into the corresponding naphthafurophanes, we initially focused our attention on those which contained fewer cycloadded benzo units, so that we could follow the chemical transformations leading to the aromatised products more easily. Catalytic hydrogenation of the olefinic double bond of the mono-adduct **1** (fraction 6 A, Scheme 1) gave **2**, which was aromatised to give **3** (Scheme 2) by acid-promoted dehydration[5a, 12a–c] with TsOH in toluene. Other reagents such as $Ac_2O$/HCl, $HClO_4$/EtOH and HCl/MeOH gave complex mixtures and extensive decomposition of the products.[12a–c] Attempts to aromatise the mono-adduct **1** by direct deoxygenation with a variety of methods, which included the use of $TiClO_4/LiAlH_4/Et_3N$,[12d,e] $NaBH_4/CF_3COOH$[12f] and trimethylsilyl iodide in acetonitrile[12g], were also unsuccessful.

Crystallisation of fraction 6/B (Scheme 1) with acetone gave a product, which was characterised as the *anti*-1,4-bis-adduct **5** (Scheme 3). The mother liquor was concentrated and the residue was crystallised with ethyl acetate to give another crystalline product, which was characterised as the (±)-*anti*-1,3-bis-adduct **4** (Scheme 3). Their spectroscopic NMR data allowed unambiguous assignments of their regiochemistry, however their *anti* stereochemistry could only be established by X-ray analysis (Figure 2 and Figure 3). We could not isolate as pure compounds any other isomers of **4** and **5**, which are presumably also present in fraction 6/B.

Hydrogenation of the olefinic double bonds of **4** and **5** gave compounds **6** and **7** respectively. These were aromatised to the corresponding naphthafurophanes **8** and **9** (Scheme 3) by acid-promoted dehydration, as described for the mono-adduct **1**. The naphthafurophane **8** also gave single crystals, which were subjected to X-ray analysis (Figure 4).

Encouraged by the results obtained for the bis-adducts, we extended the study to adducts of **C6** containing more than two benzo units. Slow crystallisation of fraction 9/B (Scheme 1) from ethyl acetate – hexane afforded only a few single crystals of a tris-adduct. The X-ray analysis shows that the isolated tris-adduct **10** has a 1,2,4-epoxynaphthalene constitution and with an *anti-anti-syn* configuration (Figure 5). However, due to the very low yield, we found it impracticable to pursue the synthesis and the isolation of this tris-adduct in the quantities necessary for further synthetic work. The isolation of tris-adduct **10** from a mixture, which certainly contained numerous isomers, was probably due to its extremely low solubility in most conventional organic solvents (including $CHCl_3$, toluene, methanol and acetone). Its $^1$H NMR spectrum could be recorded only in [$D_6$]DMSO at 100 °C. The lack of symmetry in **10** is substantiated by the presence of 12 resonances (one overlapping) for the methyl groups, one AB system and two AX systems for the pairs of protons on the three different furan units. However, the resonances for the




Scheme 2. The conversion of the mono-adduct **1** of **C6** with benzyne to the aromatised naphthafurophane **3**: i) Pd/C, $H_2$, $CHCl_3$; ii) TsOH, PhMe.



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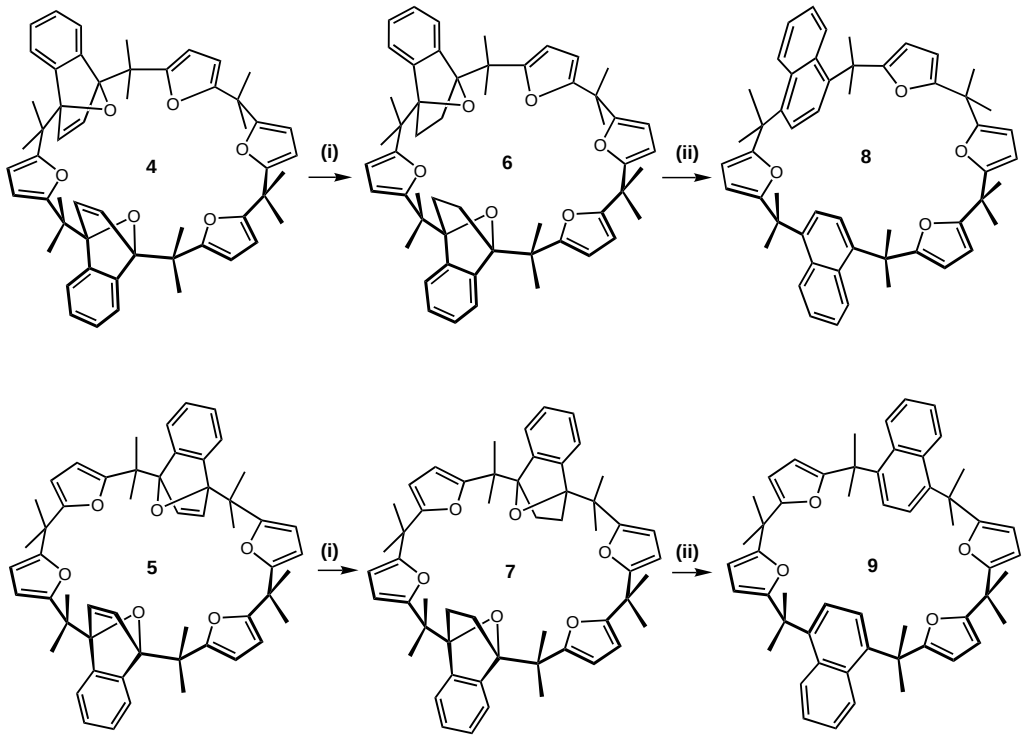


Scheme 3. The conversion of the bis-adducts **4** and **5** of **C6** with benzyne to the aromatised naphthafurophanes **8** and **9**: i) Pd/C, $H_2$, $CHCl_3$; ii) TsOH, PhMe.

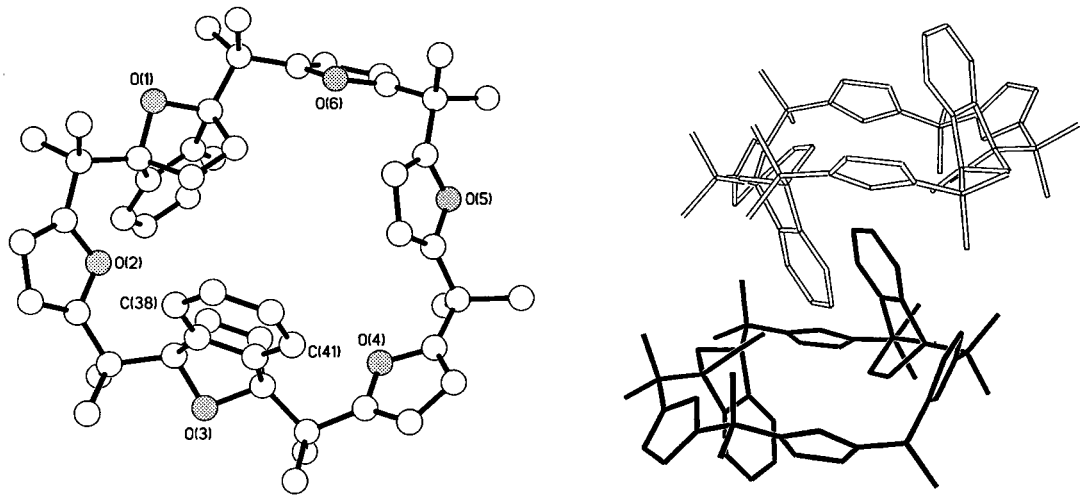


Figure 2. Left: X-ray crystal structure of the *anti*-1,3-bis-adduct **4**. The tilt angles[10] of the furan rings containing O(2), O(4), O(5) and O(6) are 35, 44, 133 and 71° respectively. The corresponding tilt angles for the benzo units associated with O(1) and O(3) are 74 and 70° respectively. CH···π interactions: C(38)–H···[O(2) furan ring] and C(41)–H···[O(4) furan ring]; H···π distances and C–H···π angles are 2.71 Å, 135° and 2.95 Å, 132°. Right: The packing of a $C_i$ related pair of molecules showing the insertion of the benzo ring of one molecule into the cavity of the other and vice versa.

olefinic protons partly overlap with those of the benzo protons.

The X-ray analyses of **4**, **5** and **10** provide valuable information on the structural behaviour of the macrocyclic system **C6** as a consequence of multiple cycloaddition with benzyne.

In **4** and **5**, adjacent furan rings adopt an up–down orientation of their oxygen atoms with respect to the macroring plane. In **10**, all the furan rings have their oxygen atoms oriented toward one face of the macrocyclic mean plane and the two adjacent ones in the 5- and 6-positions adopt a *gauche* orientation with respect to each other. A similar *gauche* relationship also exists between the 1,2-located epoxynaphthalene units, a conformation that is stabilised by an intramolecular C–H···O hydrogen-bonding interaction between the benzo ring C(38)–H group of one unit and the epoxy oxygen atom O(1) of the other. There is also a short contact (2.29 Å) between one of the methyl hydrogen atoms attached to C(5A) and the epoxy oxygen atom O(2). In all three benzyne adducts, there is an *anti* coplanar arrangement of a C–O bond in the furan rings and the C–$CH_3$ bond of at least one adjacent isopropylidene unit. This feature is also

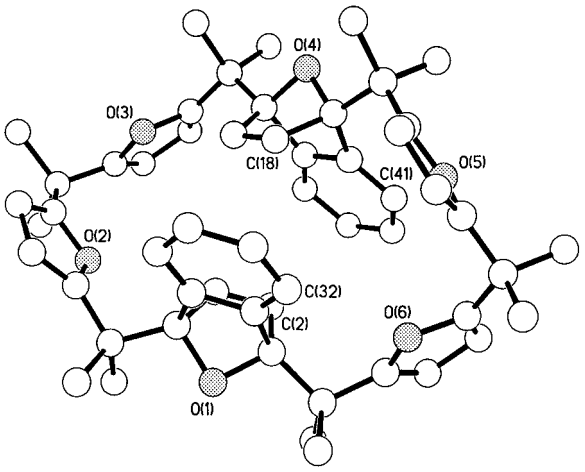


Figure 3. X-ray crystal structure of *anti*-1,4-bis-adduct **5**. The tilt angles[10] of the furan rings containing O(2), O(3), O(5) and O(6) are 83, 75, 90 and 86° respectively. The corresponding tilt angles for the benzo units associated with O(1) and O(4) are 67 and 66° respectively. Intramolecular CH···O interactions: C(32)–H···O(6) and C(41)–H···O(5); C···O, H···O distances and C–H···O angles: 3.03, 2.31 Å, 132° and 3.04, 2.29 Å, 134° respectively. Transannular CH···π interactions: olefinic C(2)–H···['O(1)' benzo ring] and olefinic C(18)–H···['O(1)' benzo ring], the H···π distances and C–H···π angles are 2.76 Å, 140° and 2.82 Å, 140° respectively.

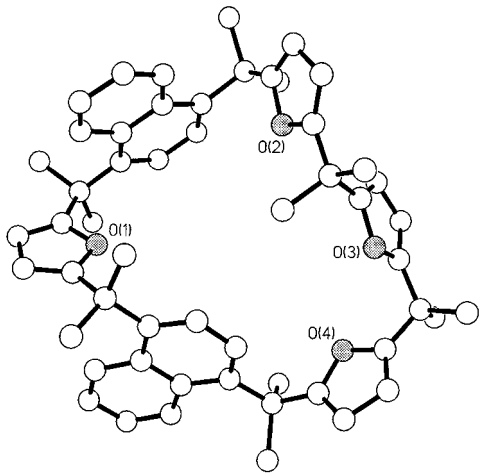


Figure 4. X-ray crystal structure of the naphthafurophane **8**. The tilt angles[10] of the furan rings containing O(1), O(2), O(3), O(4) are 50, 44, 66 and 48° respectively. The analogous angles for the naphthalene units between O(1) and O(2) and between O(1) and O(4) are 158 and 108° respectively.

present in **C4**,[13] **C6** and all of the other furan-containing macrorings described in this paper and examined by X-ray analysis.

Compared to the furan rings in **5**, the planes of the furan rings in **4** and **10** are tilted at smaller angles with respect to the best plane through the six isopropylidene carbon atoms. The planes of the benzo rings in **4** and **5** are oriented at steeper angles than in **10** where they adopt a more equatorially flattened out conformation.

The bis-adduct **4** has a more opened-up cavity than **5**. Inspection of the packing of the molecules of **4** (Figure 2 right) reveals that one of the benzo rings of one molecule is partially inserted into the macrocyclic cavity of its $C_i$ related counterpart, the rings overlapping with a mean planar separation of approximately 3.2 Å. This indicates π···π stabilisation of the supramolecular structure, thus providing evidence for the potential of **4** to act as a π-complexing agent for aromatic substrates. The bis-adduct **5** adopts a folded conformation, with noncrystallographic $C_2$ symmetry about an axis passing through a pair of diametrically oppositely positioned isopropylidene carbon atoms. This geometry is stabilised by intramolecular C–H···O and C–H···π interactions, which result in the self filling of the central cavity. In the tris-adduct **10**, the combined effect of the variously oriented furan and epoxynaphthalene units is to produce a macrocyclic conformation that, although not totally self-filling, does not have any significant free pathway through its centre.

In **5** and **10**, there are no significant intermolecular C–H···O or π–π stabilising interactions.

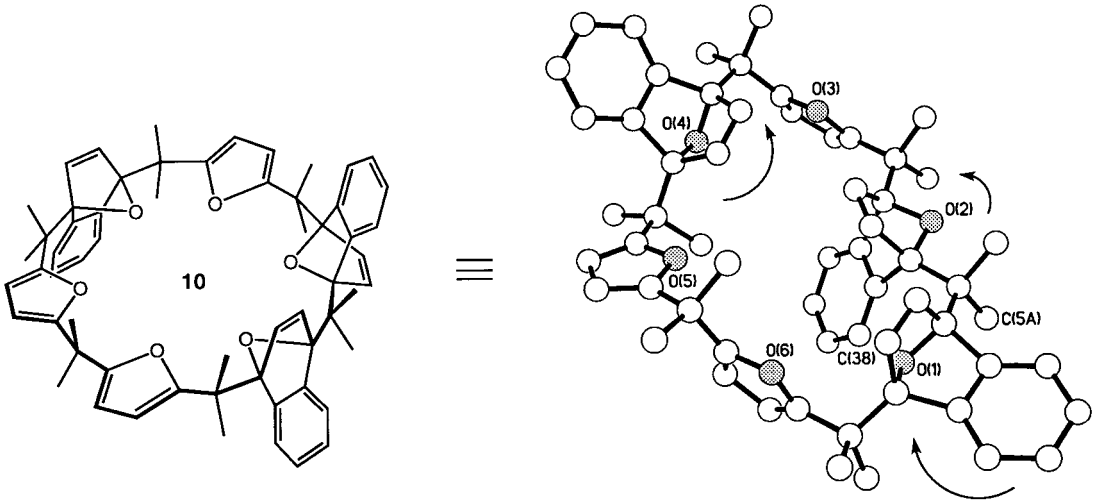


Figure 5. Left: Diagram of the 'all oxygen atoms in' conformation of the (±)-*anti-anti-syn*-1,2,4-tris-adduct **10** of **C6** with three benzynes emphasising the relative stereochemistry of the multiple cycloadditions observed in the X-ray crystal structure (right). The arrows indicate the major conformational flips assumed to obtain the representation shown on the left. The tilt angles[10] of the furan rings containing O(3), O(5) and O(6) are 62, 26 and 98°. The corresponding tilt angles for the benzo units associated with O(1), O(2) and O(4) are 14, 63 and 39° respectively. There is a hydrogen-bonding interaction C(38)–H···O(1): C···O and H···O distances are 3.02, 2.33 Å and the C–H···O angle is 129°.



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A common feature for the adducts **4**, **5** and **10** is that the six isopropylidene carbon atoms show only relatively small deviations from their mean plane values (0.6, 0.8 and 1.1 Å for **4**, **5** and **10** respectively), which are not substantially different from that observed for **C6** (1.1 Å). Thus, the discoid shape of **C6** is essentially retained in the benzyne adducts described here.

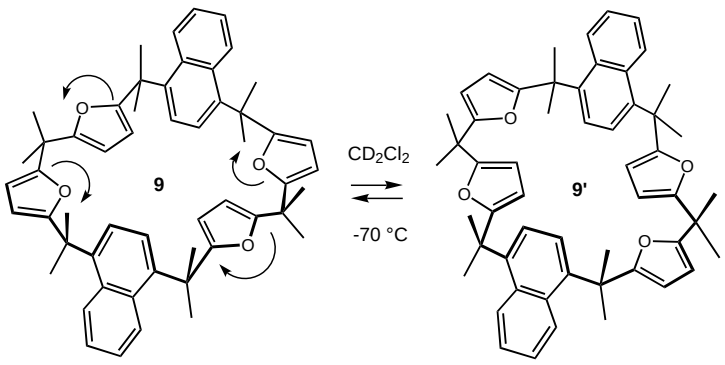
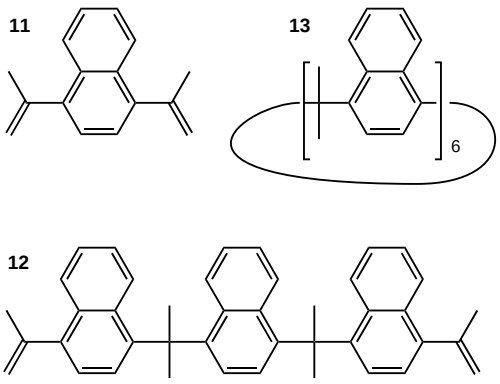



Figure 6. The degenerate conformational inversion observed by dynamic NMR spectroscopy for the naphthafurophane **9**. The orientation of the benzo rings of the naphthalene units cannot be assigned on the basis of NMR data and it is arbitrarily assumed as *anti*.

Crystals of naphthafurophane **8** contained two crystallographically independent molecules, both of which had the same chirality and essentially identical conformations with their naphthalene rings in an *anti* orientation (Figure 4). In solution, the naphthafurophane **8** exists as a racemic mixture, thus spontaneous resolution has occurred upon crystallisation. The three adjacent furan units adopt the up–down–up orientation of their oxygen atoms with respect to the macroring plane, as observed in **4**. The solid-state conformation shows that although the four furan rings are oriented with their oxygen atoms directed inwards, together with the naphthalene rings, they are inclined to the macrocyclic ring plane, so as to create a bowl-like shape. The macrocyclic ring is helically twisted relative to the plane of the furan ring containing O(1). As a result, the naphthalene residues are skewed by approximately 80° with respect to each other, about a vector passing through the two isopropylidene carbon atoms bonded to the O(1) furan ring. The cavities within these bowl-shaped molecules are occupied by acetone solvent molecules.

Although the solid-state structure of the naphthafurophane **9** could not be determined due to a lack of suitable single crystals, data on its conformational behaviour were obtained by dynamic NMR specroscopy. The $^1$H NMR spectrum of **9** in $CDCl_3$ at room temperature shows broad signals. However, a set of sharp signals corresponding to a time-averaged planar conformation is observed at $+90\,^\circ$C in $CDCl_2CDCl_2$. On cooling in $CD_2Cl_2$, the spectrum changes dramatically and at $-70\,^\circ$C, the furan protons appear as two different AB systems of equal intensity ($\delta = 3.26$ and 4.20, $J_{AB} = 3.1$ Hz; $\delta = 6.09$ and 6.33, $J_{AB} = 3.1$ Hz). The protons at the 2,3-positions of each naphthalene unit also resonate as one AB system ($\delta = 7.52$ and 7.64, $J_{AB} = 7.9$ Hz), whilst those at the 6,7- and 5,8-positions appear as a multiplet ($\delta = 7.03 - 6.97$) and as a separate set of signals ($\delta = 7.96$ and 7.54). We believe that these data are consistent with the molecule undergoing a degenerate conformational inversion, as represented in Figure 6. This is also consistent with the high-field resonances observed for one set of furan protons: two diametrically opposite furan units effectively fill the cavity with their H–C(3)–C(4)–H moieties. The NMR data are not sufficient to define the relative orientation (*syn* or *anti*) of the benzo rings of the naphthalene units, which are assumed as *anti* in Figure 6.

We attempted to obtain analogues of **8** and **9** containing more than two naphthalene units. We subjected crude mixtures from the reactions of **C6** with 9 and with 12 moles of benzyne to the hydrogenation acid-promoted dehydration as described for the adducts **1**, **4** and **5**. However, extensive decomposition occurred and we were unable to isolate any of the expected aromatised adducts. In another set of experiments, chromatographic fractions obtained from the reaction of **C6** with 9 and 12 moles of benzyne were hydrogenated and treated with acid individually. Although the successful hydrogenation of the olefinic double bonds in the various adducts could be unambiguously confirmed by positive-ion FAB-MS, no evidence of the presence of naphthafurophanes could be found in either the FAB-MS or the EI-MS spectra of all the mixtures obtained after treatment with acid. Attempts at direct deoxygenation by a variety of methods[12d–g] were equally unsuccessful. When a mixture of penta- and hexa-adducts (fraction 12/E, Scheme 1) was subjected to catalytic hydrogenation followed by treatment with acid, the only products which could be isolated from the mixture as minor components were the two fragments **11** and **12**, containing one




and three naphthalene units respectively. We cannot tell if they originate from the decomposition of the starting materials, or of partly aromatised compounds, or from the cleavage of the $[1_6](1,4)$naphthalenophane **13**.

The naphthalene trimer **12** gave single crystals from benzene/hexane. The X-ray analysis shows (Figure 7) that **12** adopts a *syn*, horseshoe-like conformation in the solid state

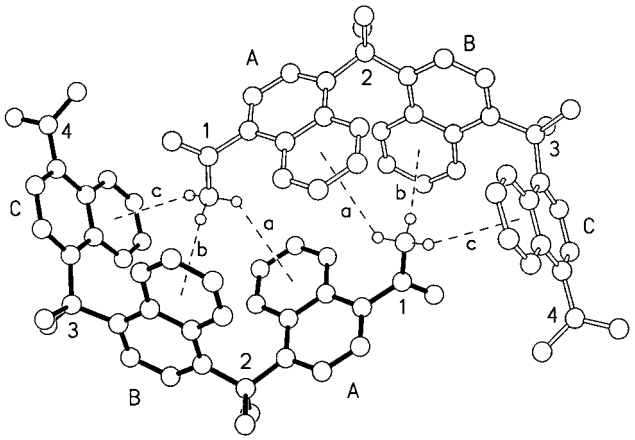



Figure 7. The solid state structure of the naphthalene trimer **12**, showing an interlocking pair of molecules. The geometries of the cooperative intermolecular CH$\cdots\pi$ interactions are [H$\cdots\pi$ distances (Å) and C–H$\cdots\pi$ angles (°)]: a) 3.1, 136; b) 3.0, 175; c) 2.9, 153.

in which the planes of the naphthalene rings are inclined alternately above and below the plane defined by the four backbone carbon atoms (1, 2, 3 and 4) by 57, 53 and 34° for rings A, B and C respectively. The molecular torsion angle formed by the backbone atoms is approximately 15°. Surprisingly, the two terminal vinyl groups are oriented almost orthogonally (74 and 81° to the planes of their attached naphthalene rings, that is minimum conjugation). An interesting consequence of the respective orientation of the three naphthalene rings is the formation of a cleft with approximate $C_3$ symmetry between the three unsubstituted benzo components. Inspection of the packing of the molecules reveals (Figure 7) an elegant utilisation of this cleft whereby pairs of $C_i$-related molecules are oriented such that one of the methyl groups in one molecule inserts itself into the cleft of another and vice versa. The orientation of each methyl group is such that it forms three weak, but cooperative, C–H$\cdots\pi$ interactions (2.9, 3.0 and 3.1 Å) with the unsubstituted benzo components of each naphthalene unit.

Our previous investigation on the aromatisation of adducts of **C4** with benzyne revealed that only the mono-adduct can be aromatised.[8] Since we ascribed this limitation mainly to steric factors, the successful aromatisation of the two bis-adducts **4** and **5** appeared to be a logical consequence of the increased conformational mobility of the larger macrocycle. Thus, an extension of the study to furanophanes larger than **C6** should allow the conversion into naphthalene units of more than two furan rings and this may constitute the subject of future studies.

**Reaction of C6 with DMAD**: The choice of DMAD as another suitable dienophile for the Diels–Alder reaction with **C6** was prompted by considerations similar to those mentioned for the benzyne. Moreover, we expected that the polar nature of the moiety introduced onto the macrocyclic structure by each cycloaddition with DMAD would have a greater influence on the chromatographic and other physical properties of the different adducts than that observed with the benzyne adducts. For this reason, the isolation of pure compounds was also expected to be easier. This prediction was later found to be correct.

When **C6** was treated with DMAD in excess, column chromatography with hexane/ethyl ether (7:3) afforded (Scheme 4), in order of elution, the mono-adduct **14** and four isomeric bis-adducts (±)-**15**, **16**, **17** and **18**. No attempt was made to optimise the yield of any of these adducts. These yields were 36, 17, 10, 8 and 12% respectively. We could not isolate any 1,2-bis-adducts.

The mono-adduct constitution of **14** was evident on the basis of its $^1$H NMR spectrum, which contained five resonances for the methyl groups (two overlapping) and two sets of AB systems for the furan units at the 2,6 and 3,5-positions of the macroring. The spectrum also contained singlets for the methyl esters, the newly formed olefinic units and the diametrically opposite furan protons. The $^{13}$C NMR spectrum displayed 24 resonances as expected. The EI-MS spectrum was characterised by the loss of methyl groups and by a peak corresponding to the elimination of DMAD by a retro Diels–Alder reaction. Crystallisation of **14** from toluene gave single crystals suitable for X-ray analysis.

The X-ray structure of **14** (Figure 8a) reveals that, in the solid state, the molecule has approximate non-crystallographic $C_s$ symmetry about a plane passing through the epoxy oxygen O(1) and bisecting the diametrically opposite O(4) furan ring. A dominant feature of the overall conformation is an almost regular alternating in–out tilting of the five furan rings, relative to the mean plane of the macrocycle. All six ring oxygen atoms are coplanar to within 0.05 Å and lie on one face. This arrangement coupled with the retention of a 'preferred' *anti* geometry for at least one of the isopropylidene C–$CH_3$ bonds with respect to one of the adjacent furan C–O bonds,[6, 13] which here is present for the rings containing O(2), O(4) and O(6), results in an all-axial arrangement for six of the isopropylidene C–$CH_3$ bonds. The six isopropylidene carbon atoms are coplanar to 0.2 Å. There is an absence of any intramolecular C–H$\cdots$O and or C–H$\cdots\pi$ interactions. The crystal structure contains toluene solvent molecules, which are not readily lost. Analysis of the packing reveals the formation of an hexagonal prismatic cage by $C_i$ related pairs of molecules. The cage is bounded by the six isopropylidene carbon atoms of each molecule and their associated axial C–$CH_3$ bonds and has a toluene molecule trapped inside it (Figure 8b).

The 1,3-regiochemistry and the bis-adduct composition for (±)-**15** was evident from its $^1$H NMR spectrum, which contained six resonances for the methyl protons of the isopropylidene units, two singlets and one AB system for the furan protons, as well as one AB system for the protons on the newly formed olefinic bonds. Moreover the methoxy groups gave two singlets. Taken together, these data do not allow the assignment of the *anti* stereochemistry, which was subsequently established by X-ray crystallography. Suitable single crystals were obtained from toluene (Figure 9).

The X-ray crystal structure of (±)-**15** reveals the macrocycle to have a folded self-filling geometry. Three of the furan oxygen atoms O(2), O(4) and O(6) are directed inwards, whilst that containing O(5) is directed outwards. All six ring



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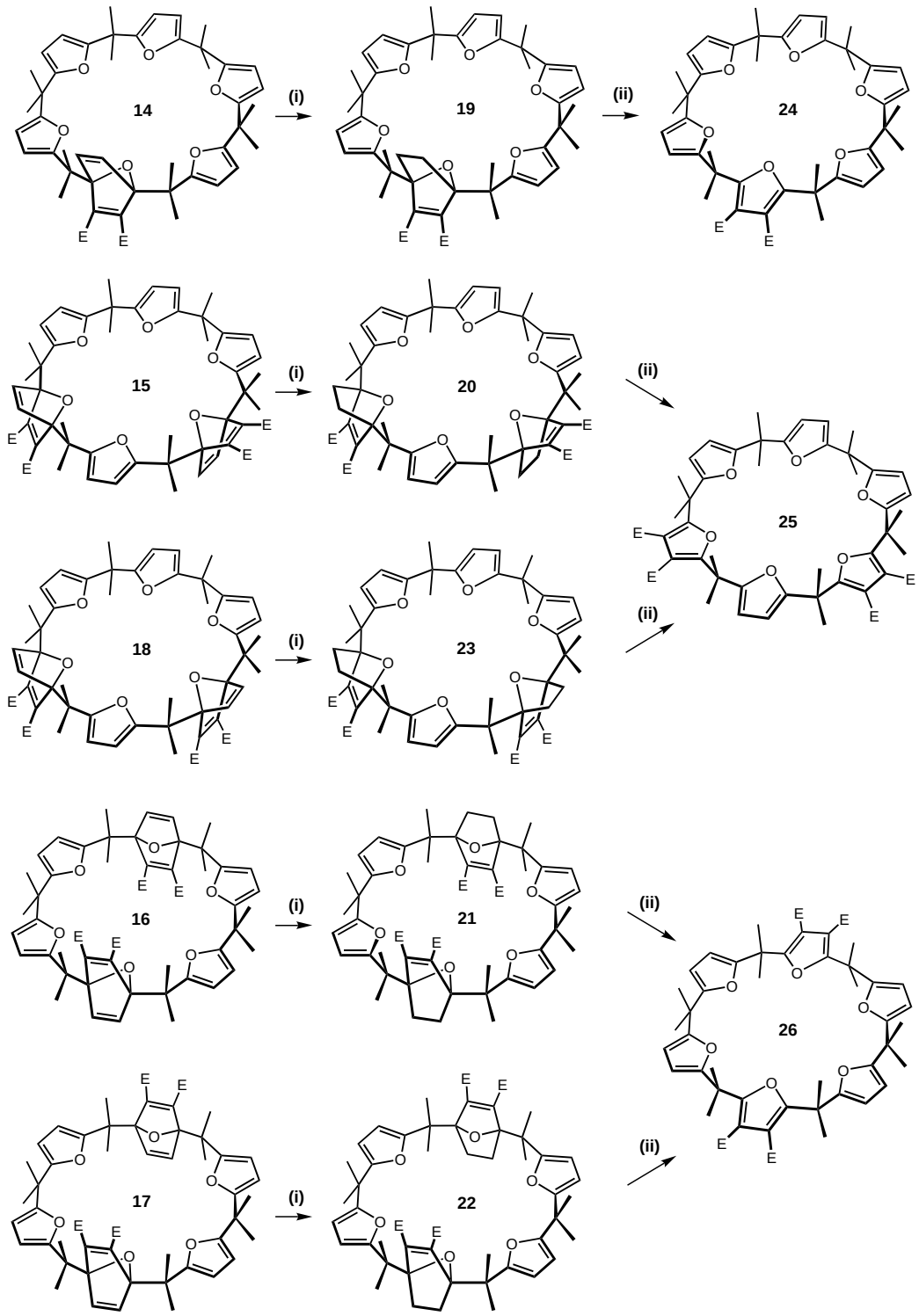


Scheme 4. The isolated adducts of **C6** with DMAD and their aromatisation by way of hydrogenation (i: $Pd/CaCO_3$, MeOH) followed by thermally promoted retro Diels–Alder (ii: Δ, 200 °C). $E = CO_2CH_3$ in all cases.

oxygen atoms are coplanar to within 0.5 Å. The six isopropylidene carbon atoms are coplanar to only 1.5 Å, reflecting the increased degree of folding in this structure, when compared with that of **14**. In common with the previously described structures, all the furan rings have at least one adjacent isopropylidene C–Me bond oriented *anti* to the ring CO bond.[6, 11, 13] Indeed when we compare this structure with that of the closely related (±)-**4** analogue, we see that the conformation of the portion of the macrocycle containing the O(4,5,6) furan rings matches very closely. The overall geometry is stabilised by an intramolecular C–H···O hydrogen bond between one of the ester carbonyl oxygen atoms O(36) and one of the C–H groups of the adjacent C(5A) isopropylidene moiety. There is also a C–H···π interaction (2.61 Å), between C(12)–H and

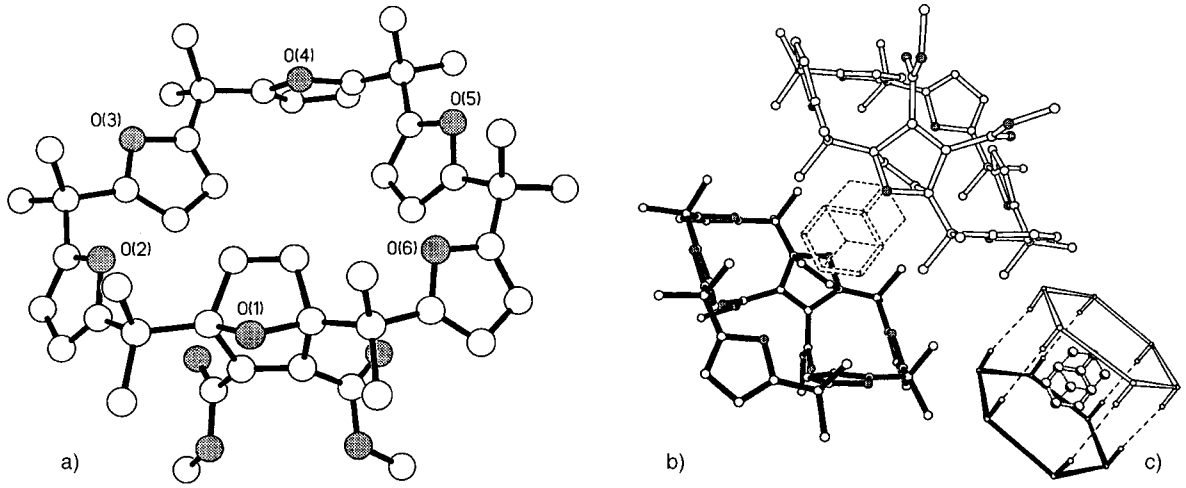


Figure 8. a) X-ray crystal structure of the mono-adduct **14** of **C60** with DMAD. The tilt angles[10] of the furan units containing O(2), O(3), O(4), O(5) and O(6) are 44, 141, 52, 139 and 46° respectively; b) The enclathration of a toluene solvent molecule by a symmetry-related pair of molecules of **14**; c) Schematic diagram outlining the geometry of the cage generated by the methyl groups of the two molecules of **14**, within which the toluene molecule is held.

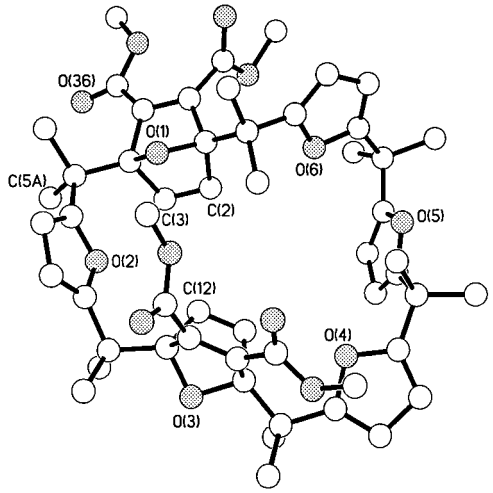


Figure 9. The X-ray crystal structure of (±)-**15**. The tilt angles[10] of the furan rings containing O(2), O(4), O(5) and O(6) are 51, 13, 108 and 54° respectively. There is a hydrogen-bonding interaction C(5a)–H–O(36): C–O and H–O lengths are 3.07, 2.23 Å, and the C–H–O angle is 145°. CH–π interaction: C(12)–H–[C(2)=C(3)], H–π length 2.61 Å, C–H–π angle 160°.

the opposite olefinic bond C(2)=C(3). There is an absence of any significant intermolecular packing interactions.

The regiochemistry of the two isomeric *anti*- and *syn*-1,4-bis-adducts **16** and **17** of **C60** with DMAD was established on the basis of their $^1$H NMR spectra. Both contained a single AB system for the furan units not involved in the cycloadditions and singlets for the newly formed olefinic residues and for the methoxy groups. The *anti* stereochemistry of the most chromatographically mobile isomer **16** was consistent with the presence of only three discrete resonances of equal intensity for the protons of the isopropylidene residues. In contrast, four resonances with relative intensities 1:1:2:2 were observed for these protons in the less chromatographically mobile isomer **17**. $^{13}$C NMR data were also fully consistent with these assignments.

The regiochemistry of the *syn*-1,3-bis-adduct **18** of **C60** with DMAD was evident on the basis of $^1$H NMR data. However, its stereochemistry was assigned by comparison with its *anti* isomer (±)-**15**, for which the X-ray crystal structure has been determined. The regioisomeric relationship between the two compounds was further supported by the subsequent chemical transformations (vide infra).

Initially, we attempted to aromatise these DMAD adducts of **C60** in order to obtain macrocycles containing phthalic ester units. Direct deoxygenation by a variety of methods[12d–g] was unsuccessful, leading to either extensive decomposition or to the recovery of unreacted starting materials. The olefinic units, which do not bear the ester functions, can be selectively hydrogenated with Pd/$CaCO_3$.[14] Thus **14**, (±)-**15**, **16**, **17** and **18** gave respectively **19**, (±)-**20**, **21**, **22** and **23** in quantitative yields. However, subsequent treatment with acids did not give the expected aromatised products by dehydration but resulted in extensive decomposition of these compounds. One 'alternative aromatisation process' was however successfully accomplished. This was the elimination of ethylene by a thermally promoted retro Diels–Alder reaction. This process produced furan-based calixarenes, in which the furan rings involved in the cycloadditions now contain carboxylate functions at their 3,4-positions. Thus, pyrolysis of **19** at 220 °C in an argon atmosphere gave **24**. The same reactions on individual samples of (±)-**20** and **23** gave the same tetra-ester **25** and similarly **21** and **22** gave the tetra-ester **26**. Yields were generally good and were not optimised.

## Conclusion

The feasibility of employing the Diels–Alder reactivity of furan in order to chemically modify furanophanes, obtained by the condensation of furan and acetone, has been explored with two readily accessible dienophiles (benzyne and DMAD) on the medium-sized system **C60**. The structural studies reported here provide a basis for the understanding of



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the conformational features of a range of furan-based calixarenes and their derivatives. These structural data partly fill the gaps in the literature on this topic, when compared to the vast amount of information available for the calixarenes.[2, 3]

Although several adducts of benzyne can be aromatised to provide naphthofuranophane, in which the naphthalene units are joined at the 1,4-positions of one benzo ring, yields are generally low. On the other hand, the use of DMAD, provides derivatives in which the newly formed 7-oxanorbornadiene moieties cannot be efficiently aromatised to benzo units. However, these can be re-converted, in an efficient and simple manner, into furan units now with carboxylate functions at their 3,4-positions. This process provides access to novel furanophanes, which cannot be synthesised by the condensation of acetone with 3,4-furandicarboxylate, due to the electron-withdrawing deactivating effect of the ester functions. The carboxylate units are susceptible to further chemical modification, including hydrolysis to acid and transesterification. Since polyaddition isomers of **C6** with DMAD having different regiochemistry can be easily separated, the cyclic oligomers of furan **C***n* can be exploited as a basis framework, on which to place sets of carboxyl functions in specific spatial relationships. This provides sites for supramolecular interactions with a variety of potential guests. We are currently pursuing these developments.

## Experimental Section

**General methods**: Tetrahydrofuran (THF) was distilled from the sodium ketyl of benzophenone. Furan was distilled from $CaH_2$. All other chemicals were standard reagent grade and were used without further purification. All air-sensitive and/or moisture-sensitive reactions were conducted under a dry argon atmosphere. Thin-layer chromatography was carried out on either glass or aluminium $SiO_2$ Carlo Erba Stratocrom SIF 254 or $Al_2O_3$ Carlo Erba Stratocrom ALF plates. Compounds were visualised with iodine or by examination under UV light. Column chromatography was conducted on Aldrich Si gel 230-400 mesh, 60 Å. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini 300 spectrometer in $CDCl_3$ using $(CH_3)_4Si$ as internal standard at 300 and 75 MHz respectively, unless otherwise stated. Mass spectra were measured by electron impact (EI) or positive fast atom bombardment (FAB) using *m*-nitrobenzyl alchool as matrix on a Finnigan Mat 90 spectrometer operated by Dr. Marcello Saitta. Melting points were determined on a Kofler hot stage apparatus and are not corrected.

**General procedure for the preparation of the adducts of C6 with benzyne**: Benzenediazoniumcarboxylate (1.37, 2.05 or 2.74 g, 6, 9 or 12 equiv respectively) was added as a solid to a solution of **C6** (1.00 g) in THF (50 mL). The mixture was refluxed for 2 h, concentrated under reduced pressure and extracted with $CH_2Cl_2/H_2O$ ($3 \times 50$ mL/50 mL). The organic phase was dried ($MgSO_4$) concentrated and subjected to column chromatography with toluene/hexane (35:65). The reaction of **C6** with benzyne (6 equiv) gave, in order of elution, the following products.

**Mono-adduct 1**: (569 mg, 54 %, m.p. 239–241 °C from $CHCl_3$); $^1$H NMR: $\delta = 1.34, 1.43, 1.47, 1.53, 1.56, 1.62$ (6 s, 1:1:1:1:1:1 ratio, 36 H; $CH_3$), 5.41 and 5.45 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.72 (s, 2 H; furan), 6.12–6.15 and 6.20–6.23 (AA′BB′ system, 4 H, Ar), 6.61 (br s, 4 H; furan), 7.13 (s, 2 H; olefin); $^{13}$C NMR: $\delta = 22.0, 25.7, 26.1, 26.3, 26.5, 26.6$ ($CH_3$), 37.2, 37.5, 37.7 ($C(CH_3)_2$), 94.6 ($C_q$–$O_{epox}$), 103.9, 104.1, 104.3, 104.5, 105.4 (furan CH), 120.2, 123.6 (Ar CH), 145.4 (olefin CH), 152.0 (Ar $C_q$), 158.0, 158.3, 158.7, 158.8, 159.0 (furan $C_q$); EI-MS: *m*/*z* (%): 724 ([$M^+$], 57), 709 (100), 681 (30), 365 (22), 279 (25), 257 (31); EI-HRMS calcd for $C_{48}H_{52}O_6$ 724.3764, found 724.3845; and a fraction characterised as a mixture of bis-adducts (246 mg, 40 %) on the basis of its EI-MS. Fractional crystallisation of this mixture with acetone gave the following product.

***anti*-1,4-Bis-adduct 5**: (83 mg, 14 %, m.p. 274–276 °C from acetone); $^1$H NMR: $\delta = 1.21, 1.34, 1.65$ (3 s, $3 \times 12$ H; $CH_3$), 5.35 (s, 4 H; olefin), 6.17 and 6.19 (AB system, $J_{AB} = 3.1$ Hz, 8 H; furan), 6.61–6.68 and 7.09–7.16 (AA′BB′ system, 8 H; Ar); $^{13}$C NMR: $\delta = 22.3, 24.7, 26.7$ ($CH_3$), 37.1, 37.3 [$C(CH_3)_2$], 94.5 ($C_q$–$O_{epox}$), 104.0, 106.5 (furan CH), 120.7, 123.5 (Ar CH), 143.2 (olefin CH), 151.6 (Ar $C_q$), 158.6, 159.5 (furan $C_q$); EI-MS: *m*/*z* (%): 800 ([$M^+$·], 27), 785 (32), 772 (21), 757 (13), 657 (24), 385 (57), 257 (100), 149 (40); EI-HRMS: calcd for $C_{54}H_{56}O_6$: 800.4077, found 800.4029. Crystallisation of the mother liquor from ethyl acetate gave the following product.

**(±)-*anti*-1,3-Bis-adduct 4**: (65 mg, 11 %, m.p. 259–260 °C from EtOAc); $^1$H NMR: $\delta = 1.18, 1.40, 1.47, 1.55$ (4 s, 1:1:2:2 ratio, 36 H; $CH_3$), 5.50 (s, 2 H; furan), 6.09 and 6.19 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 6.28 (s, 2 H; furan), 6.65–6.73 and 6.82–6.88 (2 m, 8 H and 4 H; Ar and olefinic); $^{13}$C NMR: $\delta = 22.1, 23.8, 25.6, 25.8, 26.1, 26.7$ ($CH_3$), 37.2, 37.5, 37.5 ($C(CH_3)_2$), 94.6, 94.8 ($C_q$–$O_{epox}$), 104.0, 104.5, 105.3, 105.7 (furan CH), 120.4, 120.7, 123.5, 123.6 (Ar CH), 144.7, 145.2 (olefin CH), 151.9, 151.9 (Ar $C_q$), 157.9, 158.7, 158.9, 159.4 (furan $C_q$) ; EI-MS: *m*/*z* (%): 800 ([$M^+$·] 60), 785 (38), 722 (64), 757 (36), 657 (36), 365 (90), 257 (97), 149 (100); EI-HRMS: calcd for $C_{54}H_{56}O_6$ 800.4077, found 800.4063.

The reaction of **C6** with benzyne (9 equiv) gave, in order of elution, fractions containing: bis- and tris-adducts (400 mg), other tris-adducts and tetra-adducts (740 mg) and tetra- and penta-adducts (262 mg), (corresponding to fractions 9/B, 9/C and 9/D in Scheme 1 respectively). The reaction of **C6** with benzyne (12 equiv) gave, in order of elution, fractions containing: tetra-adducts (347 mg), tetra- and penta-adducts (470 mg) and penta- and hexa-adducts (502 mg) (corresponding to fractions 12/C, 12/D and 12/E in Scheme 1 respectively).

**(±)-*syn*-*anti*-*syn*-1,2,4-Tris-adduct 10**: Slow crystallisation of fraction 9 B from ethyl acetate/hexane produced a few colourless crystals, (m.p. 200 °C (decomp)); $^1$H NMR ([D$_6$]DMSO at 100 °C): $\delta = 1.27, 1.41, 1.43, 1.45, 1.46, 1.50, 1.51, 1.52, 1.55, 1.56, 1.63$, (11 s, 2:1:1:1:1:1:1:1:1:1:1 ratio, 36 H; $CH_3$), 5.49 and 6.01 (AX system, $J_{AX} = 3$ Hz, 2 H; furan), 5.90 and 6.17 (AX system, $J_{AX} = 3$ Hz, 2 H; furan), 6.19 and 6.26 (AB system, $J_{AB} = 3$ Hz, 2 H; furan), 6.70–6.96 (m, 13 H; Ar–H and one olefin), 6.98–7.04, 7.29–7.33 and 7.43–7.48 (3 m, 1 H, 1 H and 3 H; olefin); EI-MS: *m*/*z* (%): 876 ([$M^+$·] 18), 848 (12), 549 (42), 441 (12), 401 (32), 293 (31), 257 (71), 149 (100); EI-HRMS: calcd for $C_{60}H_{60}O_6$ 876.4390, found 876.4380.

**General procedure for the hydrogenation of mono- and bis-adducts of C6 with benzyne**: Pd/C (10 % w/w, 20 % w/w catalyst/compound) was added to solutions of the adducts in $CHCl_3$. The mixtures were stirred under hydrogen (room temperature and pressure 24 h). The catalyst was filtered off and the solvent removed under reduced pressure. Yields were over 95 % in all cases.

**Hydrogenated mono-adduct 2**: (m.p. 233 °C from $CHCl_3$); $^1$H NMR: $\delta = 0.90–0.96$ and 2.06–2.11 (2 m, $2 \times 2$ H; $CH_2$), 1.27, 1.41, 1.42, 1.47, 1.60, (5 s, 1:1:1:1:2 ratio, 36 H; $CH_3$), 5.33 and 5.66 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.71 (s, 2 H; furan), 6.09–6.12 and 6.15–6.18 (AA′BB′ system, 4 H; Ar), 6.84 (br s, 4 H; furan); $^{13}$C NMR: $\delta = 23.2, 23.7, 25.8, 25.8, 26.3, 26.3$ ($CH_3$), 30.8 ($CH_2$), 37.2, 37.6, 38.1 ($C(CH_3)_2$), 89.6 ($C_q$–$O_{epox}$), 103.6, 103.8, 104.0, 104.3, 105.2 (furan CH), 119.6, 125.3 (Ar CH), 147.2 (Ar $C_q$), 158.0, 158.2, 158.7, 158.8, 159.2 (furan $C_q$); EI-MS: *m*/*z* (%): 726 ([$M^+$·], 82), 711 (76), 698 (88), 683 (100), 554 (37), 365 (22), 334 (52), 257 (47), 149 (78); EI-HRMS: calcd for $C_{48}H_{54}O_6$ 726.3920, found 726.3945.

**Hydrogenated (±)-*anti*-1,3-bis-adduct 6**: (m.p. 223–225 °C from $CHCl_3$); $^1$H NMR: $\delta = 0.90–1.03$ and 1.94–2.05 (2 m, $2 \times 4$ H; $CH_2$), 1.11, 1.40, 1.48, 1.50, 1.54, 2.52 (6 s, 1:1:1:1:1:1 ratio, 36 H, $CH_3$), 5.36 (br s, 2 H; furan), 5.98 and 6.09 (AB system, 4 H; furan), 6.20 (s, 2 H; furan), 6.82–7.02 and 7.10–7.21 (2 m, 6 H and 2 H; Ar); $^{13}$C NMR: $\delta = 23.1, 23.5, 24.1, 24.1, 25.6, 26.8$ ($CH_3$), 31.1, 31.2 ($CH_2$), 37.6, 38.1, 38.5 ($C(CH_3)_2$), 89.9, 90.0 ($C_q$–$O_{epox}$), 104.0, 104.5, 105.0, 105.7 (furan CH), 119.9, 119.9, 125.2, 125.4 (Ar CH), 147.3, 147.3 (Ar $C_q$), 158.2, 158.5, 159.1, 159.7 (furan $C_q$); EI-MS: *m*/*z* (%): 804 ([$M^+$·], 88), 789 (21), 776 (100), 761 (67) 632 (30), 359 (30), 257 (22), 149 (56); EI-HRMS: calcd for $C_{54}H_{60}O_6$ 804.4390, found 804.4407.

**Hydrogenated *anti*-1,4-bis-adduct 7**: (m.p. 140–142 °C from $CHCl_3$); $^1$H NMR: $\delta = 0.93–1.00$ and 1.64–1.71 (2 m, $2 \times 4$ H; $CH_2$), 1.24, 1.40, 1.62 (3 s, $3 \times 12$ H; $CH_3$), 6.03 and 6.14 (AB system, $J_{AB} = 3.1$ Hz, 8 H; furan), 6.84–6.90 and 6.90–6.96 (AA′BB′ system, 8 H; Ar–CH); $^{13}$C NMR: $\delta =$

22.8, 24.0, 26.7 ($CH_3$), 31.2 ($CH_2$), 37.2, 38.2 ($C(CH_3)_2$), 89.6 ($C_q$–$O_{epox}$), 103.5, 105.9 (furan CH), 119.7, 125.4 (Ar CH), 147.3 (Ar $C_q$), 158.7, 159.4 (furan $C_q$); EI-MS: *m*/*z* (%): 804 ([$M^{+\cdot}$], 90), 789 (61), 776 (100), 761 (68), 632 (20), 387 (34), 359 (28), 257 (38), 149 (43); EI-HRMS: calcd for $C_{54}H_{60}O_6$ 804.4390, found 804.4392.

**General procedure for the hydrogenation of adducts containing more than two benzo units**: Pd/C (10% w/w, 20% w/w catalyst/compound) was added to a benzene solution of the adducts (5 mg mL$^{-1}$) containing methanol (1%). The mixtures were stirred under hydrogen (50 °C, 80 atm, 17 h). The catalyst was filtered off and the solvent removed under reduced pressure. The FAB-MS spectra of the mixtures obtained from these hydrogenations contained mainly the peaks at 960, 1038, and 1116, which correspond to the calculated masses for tetra-, penta- and hexa-adducts, in which the olefinic double bonds were fully hydrogenated.

**General procedure for the acid promoted dehydration**: The hydrogenated adducts were dissolved in toluene (10 mg mL$^{-1}$) and after addition of a catalytic amount of *p*-toluene sulfonic acid (0.1 mg mL$^{-1}$), the mixture was refluxed (until complete disappearance of the starting materials) and then extracted with aqueous $NaHCO_3$ (5%). The organic phase was dried ($MgSO_4$) and concentrated to yield a residue, which was subjected to column chromatography with toluene/hexane (5:95).

**Naphthafurophane 3**: From dehydration of **2** (370 mg, 0.51 mmol); white solid; yield 90 mg, 25%; m.p. 94–95 °C from acetone; $^1$H NMR: $\delta = 1.36$, 1.49, 1.83 (3 s, 3 × 12 H; $CH_3$), 5.01 and 5.41 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.83 and 5.96 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.93 (s, 2 H; furan), 7.12–7.18 and 7.92–7.98 (AA′BB′ system, 4 H; Ar), 7.54 (s, 2 H; Ar); $^{13}$C NMR: $\delta = 26.2$, 26.5, 30.0 ($CH_3$), 37.3, 37.5, 40.2 ($C(CH_3)_2$), 103.4, 103.7, 103.8, 104.4, 104.5 (furan CH), 122.9, 123.6, 126.3 (Ar CH), 132.7, 141.5 (Ar $C_q$), 157.9, 158.0, 158.0, 158.3, 162.0 (furan $C_q$); EI-MS: *m*/*z* (%): 708 ([$M^{+\cdot}$], 34), 693 (100), 585 (29), 432 (7), 417 (21), 339 (15), 149 (41); EI-HRMS: calcd for $C_{48}H_{52}O_5$ 708.3815, found 708.3822.

**Dinaphthafurophane 8**: From dehydration of **6** (94 mg, 0.12 mmol); white solid, yield 16 mg, 18%; m.p. 118–130 °C from toluene/hexane; $^1$H NMR: $\delta = 1.42$, 1.61, 1.79 (3 s, 3 × 12 H; $CH_3$), 5.48 (s, 2 H; furan), 5.82 (m, 4 H; furan), 6.23 (s, 2 H; furan), 6.93 and 7.04 (AB system, $J_{AB} = 8.1$ Hz, 4 H; furan), 7.13 and 8.02 (2 m, 2 × 4 H; Ar); $^{13}$C NMR: $\delta = 26.2$, 29.3, 29.7 ($CH_3$), 37.3, 40.4, 40.9 ($C(CH_3)_2$), 103.4, 103.7, 104.3, 104.5 (furan CH), 123.1, 123.3, 123.3, 123.5, 126.2, 126.8 (Ar CH), 132.4, 132.6, 141.5, 141.6 (Ar $C_q$), 158.0, 158.4, 161.6, 162.2 (furan $C_q$); EI-MS: *m*/*z* (%): 769 ([$M+1)^{+\cdot}$] (45)), 753 (100), 728 (24), 633 (11), 369 (14), 149 (83); EI-HRMS: calcd for $C_{54}H_{56}O_4$ 768.4179, found 768.4184

**Dinaphthafurophane 9**: From dehydration of **7** (106 mg, 0.13 mmol); white solid, yield 20 mg, 20%; m.p. 140–155 °C from acetone; $^1$H NMR (+20 °C, $CDCl_3$): $\delta = 1.50$ , 1.80 (2 s, 12 H and 24 H; $CH_3$), 4.80 and 5.40 (2 hump, 2 × 4 H; furan), 7.00–7.07 and 7.75–7.82 (AA′BB′ system, 8 H; Ar), 7.55 (s, 4 H, Ar); $^{13}$C NMR (+20 °C, $CDCl_3$): $\delta = 26.3$, 30.3 ($CH_3$), 37.5, 40.0 ($C(CH_3)_2$), 103.5, 104.0 (furan CH), 122.8, 123.7, 126.9 (Ar CH), 132.4, 141.6 (Ar $C_q$), 157.3, 160.0 (furan $C_q$); EI-MS: *m*/*z* (%): 768 ([$M^{+\cdot}$], 59), 753 (100), 369 (31); EI-HRMS: calcd for $C_{54}H_{56}O_4$ 768.4179, found 768.4178.

**1,4-di(1-methylethenyl)naphthalene 11 and 1,4-di(1-methyl-1(4-(1-methyl ethenyl)naphthyl)ethyl) naphthalene 12**: From dehydration of the hydrogenated mixture of penta- and hexa-adducts (fraction 12/E, Scheme 1), column chromatography as indicated in the general procedure gave in order of elution the following products.

**11**: colourless oil; $^1$H NMR: $\delta = 2.21$ (dd, $^4J = 1.3$ Hz, $^4J = 0.8$ Hz, 3 H; $CH_3$), 5.06 (dq, $^2J = 2.3$ Hz, $^4J = 1.3$ Hz, 2 H; $CH_2$), 5.40 (dq, $^2J = 2.3$ Hz, $^4J = 0.8$ Hz, 2 H; $CH_2$), 7.26 (s, 2 H; Ar), 7.42–7.50 and 8.02–8.10 (AA′BB′ system, 4 H; Ar); $^{13}$C NMR: $\delta = 25.2$ ($CH_3$), 116.0 ($CH_2$), 124.0, 125.0, 126.0 (Ar CH), 131.0, 141.3, 144.8 ($C_q$); FAB-MS: 208 ([$M^+$], 100), 193 (30), 167 (38); EI-HRMS: calcd for $C_{16}H_{16}$ 208.1252, found 208.1266.

**12**: white crystals, m.p. 244 °C from benzene/hexane; $^1$H NMR: $\delta = 2.10$ and 2.16 (2 br s, 12 H and 6 H; $CH_3$), 5.00 and 5.36 (2 br s, 2 H and 2 H; $CH_2$), 6.66–6.73 and 7.70–7.77 (AA′BB′ system, 4 H, H-6,7 and H-5,8 central naphthalene), 6.96–7.04 and 7.16–7.24 (2 m, 2 × 2 H, H-6 and H-7 external naphthalenes), 7.36 and 7.86 (AB system, $J_{AB} = 7.6$ Hz, 4 H, H-2,3 external naphthalenes), 7.83–7.95 (m, 4 H, H-5,8 external naphthalenes), 8.08 (s, 2 H, H-2,3 central naphthalene); $^{13}$C NMR: $\delta = 25.3$, 32.6 ($CH_3$), 44.2 ($C(CH_3)_2$), 115.9 ($CH_2$), 122.0, 122.5, 123.7, 124.2, 124.2, 124.7, 125.8, 126.1, 126.4 (Ar CH), 131.6, 131.9, 132.5, 141.2, 145.1, 145.7, 145.9 ($C_q$); EI-MS: *m*/*z* (%): 544 ([$M^{+\cdot}$], 6), 307 (21), 209 (15); EI-HRMS: calcd for $C_{42}H_{40}$ 544.3130, found 544.3131.

**Preparation of the adducts of C6 with DMAD**: The furanophane **C6** (1.00 g, 1.54 mmol) was suspended in DMAD (5.0 mL) and stirred at 110 °C for 6 h. The unreacted DMAD was removed under reduced pressure. Column chromatography of the residue with hexane/$Et_2O$ (5:1) gave, in order of elution, the following products.

**Mono-adduct 14**: (428 mg, 36%, m.p. 165 °C from acetone, m.p. 159 °C from toluene); $^1$H NMR: $\delta = 1.31$, 1.48, 1.56, 1.61, 1.62 (5 s, 1:1:2:1:1 ratio, 36 H; $CH_3$), 3.40 (s, 6 H; $OCH_3$), 5.54 and 5.66 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 6.00 and 6.02 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 6.01 (s, 2 H; furan), 7.40 (s, 2 H; olefin); $^{13}$C NMR: $\delta = 22.1$, 25.6, 26.2, 26.4, 26.6, 26.7 ($CH_3$), 37.6, 37.7, 37.8 ($C(CH_3)_2$), 51.8 ($OCH_3$), 99.9 ($C_q$–$O_{epox}$), 103.9, 104.3, 104.5, 104.6, 105.3 (furan CH), 145.5 (olefin CH), 155.2, 157.9, 158.3, 158.5, 158.6, 158.8 ($C_q$), 165.2 (CO); EI-MS: *m*/*z* (%): 790 ([$M^{+\cdot}$], 53), 775 (100), 749 (22), 633 (79), 533 (20), 309 (37), 257 (21), 149 (40); elemental analysis calcd for $C_{48}H_{54}O_{10}$: (790.93) C 72.89, H 6.88; found C 72.67, H 6.90.

**(±)-*anti*-1,3-Bis-adduct 15**: (226 mg, 17%, m.p. 202 °C from $Et_2O$ and m.p. 213 °C from toluene); $^1$H NMR: $\delta = 1.16$, 1.41, 1.42, 1.43, 1.56, 1.59 (6 s, 1:1:1:1:1:1 ratio, 36 H; $CH_3$), 3.38 and 3.54 (2 s, 6 H; $OCH_3$), 5.77 (s, 2 H; furan), 5.99 (s, 2 H; furan), 5.99 and 6.05 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 7.38 and 7.49 (AB system, $J_{AB} = 5.3$ Hz, 4 H; olefin); $^{13}$C NMR: $\delta =$ 22.2, 23.6, 24.1, 26.1, 26.8, 27.0 ($CH_3$), 37.6, 37.7, 37.9 ($C(CH_3)_2$), 51.8, 51.9 ($OCH_3$), 99.8 ($C_q$–$O_{epox}$), 100.0 ($C_q$), 104.0, 104.5, 104.6, 105.7 (furan CH), 145.6, 145.7 (olefin CH), 158.2, 158.4, 158.6, 158.7 ($C_q$), 164.8, 165.3 (CO); EI-MS: *m*/*z* (%): 932 ([$M^{+\cdot}$], 12), 791(10), 775 (41), 633 (100), 365 (13), 309 (25), 257 (15), 149 (11); elemental analysis calcd for $C_{54}H_{60}O_{14}$ (933.05): C 69.51, H 6.48; found C 69.82, H 6.68.

***anti*-1,4-Bis-adduct 16**: 150 mg, 10%, m.p. 170–174 °C from MeOH); $^1$H NMR: $\delta = 1.32$, 1.49, 1.61 (3 s, 3 × 12 H; $CH_3$), 3.28 (s, 12 H; $OCH_3$), 5.90 and 6.00 (AB system, $J_{AB} = 1.4$ Hz, 8 H; furan) 7.43 (s, 4 H; olefin); $^{13}$C NMR: $\delta = 22.5$, 25.5, 26.3 ($CH_3$), 37.1, 37.7 ($C(CH_3)_2$), 51.8 ($OCH_3$), 99.9 ($C_q$–$O_{epox}$), 103.7, 105.5 (furan CH), 145.2 (olefin CH), 155.3, 158.0, 159.9 (Cq), 165.0 (CO); EI-MS: *m*/*z* (%): 932 ([$M^{+\cdot}$], 22), 917 (31), 970 (15), 775 (31), 633 (100), 309 (33), 257 (13), 149 (12); EI-HRMS: calcd for $C_{54}H_{60}O_{14}$ 932.3983, found 932.3982.

***syn*-1,4-Bis-adduct 17**: (120 mg, 8%, m.p. 180 °C from $Et_2O$); $^1$H NMR: $\delta =$ 1.36, 1.48, 1.56, 1.61 (4 s, 2:2:1:1 ratio, 36 H; $CH_3$), 3.49 (s, 12 H; $OCH_3$), 5.92 and 6.02 (AB system, $J_{AB} = 3.1$ Hz, 8 H; furan), 7.34 (s, 4 H; olefin); $^{13}$C NMR: $\delta = 22.9$, 25.2, 26.2, 27.5 ($CH_3$), 37.4, 37.8 ($C(CH_3)_2$), 51.9 ($OCH_3$), 100.2 ($C_q$–$O_{epox}$), 104.1, 105.7 (furan CH), 144.9 (olefin CH), 155.2, 157.9, 158.3 ($C_q$), 165.3 (CO); EI-MS: *m*/*z* (%): 932 ([$M^{+\cdot}$], 19), 917 (29), 791 (20), 775 (84), 633 (100), 309 (43), 257 (36), 149 (36); EI-HRMS: calcd for $C_{54}H_{60}O_{14}$ 932.3983, found 932.3994.

***syn*-1,3-Bis-adduct of C6 with DMAD 18**: (159 mg, 12%, m.p. 207 °C from $Et_2O$); $^1$H NMR ($CD_2Cl_2$): $\delta = 1.29$, 1.41, 1.44, 1.52, 1.53 (5 s, 1:1:2:1:1 ratio, 36 H; $CH_3$), 3.47 and 3.49 (2 s, 2 × 6 H; $OCH_3$), 5.75 (br s, 2 H; furan), 5.99 and 6.02 (AB system, $J_{AB} = 3$ Hz, 4 H; furan), 7.10 and 7.38 (AB system, $J_{AB} = 6$ Hz, 6 H; olefin); $^{13}$C NMR: $\delta = 22.5$, 23.5, 24.4, 24.4, 26.4, 26.4 ($CH_3$), 37.6, 37.7 ($C(CH_3)_2$), 51.9, 52.0 ($OCH_3$), 100.5 ($C_q$–$O_{epox}$), 103.7, 104.6, 105.2, 105.7 (furan CH), 144.2, 145.2 (olefin CH), 153.5, 156.7, 157.4, 158.1, 158.6, 159.2 ($C_q$), 165.0, 165.9 (CO); EI-MS: *m*/*z* (%): 932 ([$M^{+\cdot}$], 20), 917 (15), 790 (23), 775 (50), 633 (100), 365 (12), 309 (12), 257 (11), 149 (11); EI-HRMS: calcd for $C_{54}H_{60}O_{14}$ 932.3983, found 932.3981.

**General procedure for the selective hydrogenation of the olefinic double bonds not bearing carboxyl groups in the C6 adducts with DMAD**: Pd/$CaCO_3$ (10% w/w, 20% w/w catalyst/compound) was added to a methanol solution of the various adducts of **C6** with DMAD (1–4 mg mL$^{-1}$). The mixtures were stirred under $H_2$ at atmospheric pressure. The reaction was interrupted upon absorption of the appropriate volume of hydrogen, corresponding to the hydrogenation of all the olefinic double bonds not bearing carbonyl groups. The suspensions were filtered and the residues washed with $CH_2Cl_2$. In each case the combined MeOH solutions and the $CH_2Cl_2$ washings were concentrated. Yields were all over 95%.

**Hydrogenated mono-adduct 19**: (m.p. 172–173 °C from MeOH and 159 °C from toluene); $^1$H NMR: $\delta = 1.24$, 1.43, 1.54, 1.56, 1.57, 1.58 (6 s, 1:1:1:1:1:1 ratio, 36 H; $CH_3$), 1.36–1.44 and 2.04–2.10 (2 m, 2 × 2 H; $CH_2$), 3.48 (s, 6 H; $OCH_3$), 5.63 and 5.75 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.90 and 5.94 (AB system, $J_{AB} = 3.1$ Hz, 4 H; furan), 5.93 (s, 2 H; furan); $^{13}$C NMR: $\delta =$ 22.9, 23.7, 25.9, 26.1, 26.3, 26.3 ($CH_3$), 29.6 ($CH_2$), 37.3, 37.6, 38.2 ($C(CH_3)_2$),



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51.8 ($OCH_3$), 94.5 ($C_q$–$O_{epox}$), 103.3, 104.1, 104.2, 104.3, 105.3 (furan CH), 144.9, 158.0, 158.4, 158.5, 158.7 ($C_q$), 165.3 (CO); EI-MS: *m/z* (%): 792 ([$M^{+\cdot}$], 63), 777 (100), 749 (83), 633 (5), 367 (15), 257 (12), 233 (25), 149 (26); elemental analysis calcd for $C_{48}H_{56}O_{10}$ (792.95): C 72.70, H 7.12; found C 72.61, H 7.18.

**Hydrogenated (±)-*anti*-1,3-bis-adduct 20**: (m.p. 173 °C from MeOH and 213 °C from toluene); $^1$H NMR: $\delta = 1.28$, 1.38, 1.40, 1.45, 1.55, 1.59 (6s, 1:1:1:1:1:1 ratio, 36H; $CH_3$), 2.05–2.11 and 2.31–3.37 (2m, 2 × 2H; $CH_2$), 3.53 and 3.59 (2s, 2 × 6H; $OCH_3$), 5.56 and 5.90 (2s, 2 × 2H, furan), 5.93 and 5.98 (AB system, $J_{AB} = 3.1$ Hz, 4H; furan); $^{13}$C NMR: $\delta = 22.9$, 23.5, 23.7, 24.0, 26.1, 26.8 ($CH_3$), 29.8, 29.9 ($CH_2$), 37.7, 38.3, 38.4 ($C(CH_3)_2$), 51.8, 51.9 ($OCH_3$), 94.8, 94.9 ($C_q$–$O_{epox}$), 103.7, 104.7, 105.1, 105.2 (furan CH), 144.3, 146.0 (olefin $C_q$), 158.0, 158.4, 158.5, 158.8 ($C_q$), 165.3, 165.4 (CO); FAB-MS: *m/z* (%): 937 ([$M$+1]$^+$, 61), 921 (51), 893 (38), 865 (21); elemental analysis calcd for $C_{54}H_{64}O_{14}$ (937.08): C 69.22, H 6.88; found C 69.13, H 6.87.

**Hydrogenated *anti*-1,4-bis-adduct 21**: (m.p. 175 °C from MeOH); $^1$H NMR: $\delta = 1.26$, 1.46, 1.64 (3s, 1:1:1 ratio, 36H; $CH_3$), 1.75–1.78 and 2.17–2.19 (2m, 2 × 2H; $CH_2$), 3.31 (s, 12H; $OCH_3$), 5.89 and 5.94 (AB system, $J_{AB} =$ 3.1 Hz, 8H; furan); $^{13}$C NMR: $\delta = 22.8$, 24.1, 26.1 ($CH_3$), 29.9 ($CH_2$), 36.9, 38.4 ($C(CH_3)_2$), 51.7 ($OCH_3$), 94.3 ($C_q$–$O_{epox}$), 103.6, 106.0 (furan CH), 144.8 (olefin $C_q$), 157.6, 159.0 ($C_q$), 165.1 (CO); FAB-MS: *m/z* (%): 937 ([$M$+1]$^+$, 36), 921 (67), 893 (27), 865 (23); EI-HRMS: calcd for $C_{54}H_{64}O_{14}$ 936.4296, found 936.4306.

**Hydrogenated *syn*-1,4-bis-adduct 22**: (m.p. 197–198 °C from MeOH); $^1$H NMR: $\delta = 1.34$, 1.45, 1.57, 1.58 (4s and overlapping m, 40H; $CH_3$ and $CH_2$), 2.04–2.09 (m, 4H; $CH_2$), 3.57 (s, 12H; $OCH_3$) 5.87 and 5.94 (AB system, $J_{AB} = 3.1$ Hz, 8H; furan); $^{13}$C NMR: 22.9, 24.3, 26.2, 27.2 ($CH_3$), 29.7 ($CH_2$), 37.3, 38.6 ($C(CH_3)_2$), 52.0 ($OCH_3$), 94.9 ($C_q$–$O_{epox}$), 103.9, 105.8 (furan CH), 144.9, 157.8, 158.5 ($C_q$), 165.4 (CO); EI-MS: *m/z* (%): 936 ([$M^{+\cdot}$], 6), 921 (100), 893 (55), 865 (32), 233 (32), 149 (22); EI-HRMS: calcd for $C_{54}H_{64}O_{14}$ 936.4296, found 936.4325.

**Hydrogenated *syn*-1,3-bis-adduct 23**: (m.p. 177 °C from MeOH); $^1$H NMR: $\delta = 1.30$, 1.36, 1.40, 1.51, 1.52 (5s and overlapping m, 38H; $CH_3$ and $CH_2$), 1.60–1.71, 1.87–1.98 and 2.00–2.10 (3m, 3 × 2H; $CH_2$), 3.55 and 3.57 (2s, 2 × 6H; $OCH_3$), 5.73 (brs, 2H; furan), 5.89 (s, 2H; furan), 5.92 and 5.95 (AB system, $J_{AB} = 3.1$ Hz, 4H; furan); $^{13}$C NMR: $\delta = 23.0$, 23.0, 23.4, 24.0, 26.5 ($CH_3$), 29.1, 30.2 ($CH_2$), 37.5, 38.3, 38.4 ($C(CH_3)_2$), 51.9, 51.9 ($OCH_3$), 94.8, 94.9 ($C_q$–$O_{epox}$), 103.6, 104.4, 105.4, 105.7 (furan CH), 144.7, 145.0 (olefin $C_q$), 157.6, 158.3, 158.6, 159.0 (furan $C_q$), 165.4, 165.8 (CO); FAB-MS: *m/z* (%): 937 ([$M$+1]$^+$, 10), 921 (5), 893 (3), 865 (1); EI-HRMS: calcd for $C_{54}H_{64}O_{14}$ 936.4296, found 936.4296.

**General procedure for the thermally promoted elimination of ethylene by retro Diels–Alder from the hydrogenated adducts of C60 with DMAD**: In each case, a solid sample of the compound to be pyrolysed was heated at 200 °C in an argon atmosphere for 30 min. The residues were then subjected to flash column chromatography ($SiO_2$, hexane/$Et_2O$ (7:3)). All yields were over 90% using 50–300 mg of starting materials.

**Diester 24**: (m.p. 110 °C from MeOH); $^1$H NMR: $\delta = 1.50$, 1.55, 1.60 (3s, 3 × 12H; $CH_3$), 3.62 (s, 6H; $OCH_3$), 5.67 and 5.71 (AB system, $J_{AB} = 3.2$ Hz, 4H; furan), 5.80 and 5.91 (AB system, $J_{AB} = 3.1$ Hz, 4H; furan), 5.87 (s, 2H; furan); $^{13}$C NMR: $\delta = 25.8$, 26.0, 26.4 ($CH_3$), 37.3, 37.5, 38.6 ($C(CH_3)_2$), 51.8 ($OCH_3$), 103.8, 103.9, 103.9, 104.1, 104.8 (furan CH), 113.8 ($C_q$ $\alpha$-ester), 156.9, 157.6, 158.2, 158.3, 158.5, 158.7 ($C_q$), 164.2 (CO); EI-MS: *m/z* (%): 764 ([$M^{+\cdot}$], 32), 749 (100), 367 (20), 233 (10), 149 (4); elemental analysis calcd for $C_{46}H_{52}O_{10}$ (764.90): C 72.23, H 6.85; found C 72.25, H 6.92.

**Tetraester 25**: (m.p. 160 °C from MeOH); $^1$H NMR: $\delta = 1.52$, 1.54, 1.61 (3s, 3 × 12H; $CH_3$), 3.60 and 3.63 (2s, 12H; $OCH_3$), 5.77 (s, 2H; furan), 5.83 and 5.94 (AB system, $J_{AB} = 3.1$ Hz, 4H; furan), 5.93 (s, 2H; furan); $^{13}$C NMR: $\delta = 25.5$, 25.8, 26.2 ($CH_3$), 37.3, 38.5, 38.6 ($C(CH_3)_2$), 51.8, 51.8 ($OCH_3$), 103.8, 103.9, 104.9, 104.9 (furan CH), 113.6, 113.7 ($C_q$ $\alpha$-ester), 156.8, 157.1, 157.4, 157.9, 158.2, 159.0 ($C_q$), 164.1, 164.2 (CO); FAB-MS: *m/z*(%): 880 ([$M$+1]$^+$, 29), 865 (100); EI-HRMS: calcd for $C_{50}H_{56}O_{14}$ 880.3670, found 880.3697.

**Tetraester 26**: (m.p. 145 °C from $Et_2O$); $^1$H NMR: $\delta = 1.42$, 1.54 (2s, 12H and 24H; $CH_3$), 3.56 (s, 12H; $OCH_3$), 5.70 and 5.82 (AB system, $J_{AB} =$ 3.1 Hz, 8H; furan); $^{13}$C NMR: $\delta = 25.6$, 26.2 ($CH_3$), 37.3, 38.6 ($C(CH_3)_2$), 51.8 ($OCH_3$), 103.8, 104.7 (furan CH), 113.8 ($C_q$ $\alpha$-ester), 156.8, 157.6, 158.6 ($C_q$), 164.2 (CO); FAB-MS: *m/z* (%): 880 ([$M$+1]$^+$, 27), 865 (100); EI-HRMS: calcd for $C_{50}H_{56}O_{14}$ 880.3670, found 880.3673.

**X-ray crystallography**: Crystal data, data collection and refinement parameters for those compounds analysed by X-ray crystallography are given in Table 1. All the structures were solved by direct methods and were refined by full matrix least-squares based on $F^2$. Except for the partial occupancy alternate orientations of the disordered *n*-hexane solvent molecules in **10**, all the non-hydrogen atoms throughout all eight structures were refined anisotropically. Disorder is also present in **14**, where the toluene solvent molecule is disordered over a centre of symmetry and in **15**, where one of the ester groups exhibits an approximately 180° rotational disorder about the C–COOMe bond. All of the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}$(C–Me)] and were allowed to ride on their parent atoms. For **8**, spontaneous resolution upon crystallisation has occurred, but it was not possible from the crystallographic data to determine which enantiomer the particular crystal contained. Computations were carried out using the SHELXTL PC program system.[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102311 (**10**), CCDC-102312 (**12**), CCDC-102313 (**14**) and CCDC-102314 (**15**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: teched@chemcrys.cam.ac.uk).

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Table 1. Crystal Data, Data Collection and Refinement Parameters. [a]

| data | **C6** | **4** | **5** | **8** | **10** | **12** | **14** | **15** |
|---|---|---|---|---|---|---|---|---|
| formula | $C_{42}H_{48}O_6$ | $C_{54}H_{56}O_6$ | $C_{54}H_{56}O_6$ | $C_{54}H_{56}O_4$ | $C_{60}H_{60}O_6$ | $C_{42}H_{40}$ | $C_{48}H_{54}O_{10}$ | $C_{54}H_{60}O_{14}$ |
| solvent | - | - | - | $1.5\,Me_2CO$ | $0.5\,C_6H_{14}$ | - | $0.5\,C_7H_8$ | - |
| formula weight | 648.8 | 801.0 | 801.0 | 856.1 | 920.2 | 544.7 | 837.0 | 933.0 |
| colour, habit | clear blocks | clear rhombic blocks | clear prisms | clear blocks | clear needles | clear blocks | clear prisms | clear prisms |
| crystal size [mm] | $0.50 \times 0.33 \times 0.23$ | $0.33 \times 0.33 \times 0.20$ | $0.12 \times 0.12 \times 0.08$ | $0.38 \times 0.21 \times 0.12$ | $0.43 \times 0.17 \times 0.10$ | $0.30 \times 0.27 \times 0.17$ | $0.30 \times 0.30 \times 0.13$ | $0.43 \times 0.37 \times 0.10$ |
| lattice type | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic | monoclinic |
| space group , number | *Aba*2, 41 | $P2_1/n$, 14 | *C*2/*c*, 15 | $P2_1$, 4 | $P2_1/n$, 14 | *I*2/*a*, 15 | $P\bar{1}$, 2 | *C*2/*c*, 15 |
| $T$ [K] | 293 | 293 | 293 | 203 | 293 | 293 | 293 | 293 |
| cell dimensions: | | | | | | | | |
| $a$ [Å] | 16.679(2) | 13.293(2) | 25.770(4) | 10.610(1) | 13.796(3) | 19.906(1) | 13.431(1) | 24.124(1) |
| $b$ [Å] | 12.136(2) | 14.594(2) | 12.394(2) | 43.406(1) | 13.700(2) | 11.564(1) | 13.619(1) | 14.705(1) |
| $c$ [Å] | 18.926(2) | 23.423(3) | 28.616(4) | 10.655(1) | 28.385(5) | 28.405(2) | 15.623(1) | 28.541(3) |
| $\alpha$ [°] | - | - | - | - | - | - | 108.48(1) | - |
| $\beta$ [°] | - | 93.89(1) | 94.65(1) | 96.93(1) | 97.43(2) | 100.84(1) | 95.52(1) | 92.31(1) |
| $\gamma$ [°] | - | - | - | - | - | - | 115.56(1) | - |
| $V$ [Å$^3$] | 3830.9(9) | 4534(1) | 9110(2) | 4871.2(4) | 5320(2) | 6422.1(6) | 2352.5(2) | 10116(1) |
| $Z$ | 4[b] | 4 | 8 | 4[c] | 4 | 8 | 2 | 8 |
| $\varrho_{calcd}$ [g cm$^{-3}$] | 1.125 | 1.174 | 1.168 | 1.167 | 1.149 | 1.127 | 1.182 | 1.225 |
| $F(000)$ | 1392 | 1712 | 3424 | 1840 | 1972 | 2336 | 894 | 3968 |
| radiation used | $Cu_{K\alpha}$ | $Cu_{K\alpha}$ | $Cu_{K\alpha}$[d] | $Cu_{K\alpha}$[d] | $Cu_{K\alpha}$ | $Cu_{K\alpha}$[d] | $Cu_{K\alpha}$ | $Cu_{K\alpha}$ |
| $\mu$ [mm$^{-1}$] | 0.59 | 0.59 | 0.59 | 0.57 | 0.57 | 0.47 | 0.66 | 0.72 |
| $\theta$ range [°] | 4.7 – 63.9 | 3.6 – 60.0 | 3.1 – 62.0 | 2.0 – 60.0 | 3.1 – 60.0 | 3.2 – 62.0 | 3.1 – 60.0 | 3.1 – 64.0 |
| no. of unique refln.: | | | | | | | | |
| measured | 1641 | 6719 | 7171 | 7489 | 7904 | 5056 | 6701 | 8410 |
| observed, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$ | 1583 | 5530 | 4881 | 6878 | 5270 | 3814 | 5122 | 5912 |
| no. of variables | 218 | 542 | 542 | 1153 | 641 | 384 | 575 | 623 |
| $R_1$[e] | 0.031 | 0.041 | 0.048 | 0.049 | 0.076 | 0.057 | 0.052 | 0.054 |
| $wR_2$[f] | 0.086 | 0.104 | 0.106 | 0.125 | 0.198 | 0.140 | 0.124 | 0.138 |
| weights $a$, $b$[g] | 0.050, 0.805 | 0.051, 1.300 | 0.049, 4.693 | 0.090, 1.022 | 0.115, 3.834 | 0.074, 3.155 | 0.062, 0.472 | 0.071, 5.635 |
| largest difference peak, hole [e Å$^{-3}$] | 0.11, – 0.15 | 0.20, – 0.18 | 0.15, – 0.15 | 0.36, – 0.29 | 0.58,-0.34 | 0.17,-0.21 | 0.19,-0.24 | 0.25,-0.20 |

[a] Details in common: graphite monochromated radiation, $\omega$ scans, Siemens P4 diffractometer, refinement based on $F^2$. [b] The molecule has crystallographic $C_2$ symmetry. [c] There are two crystallographically independent molecules in the asymmetric unit. [d] Rotating anode source; [e] $R_1 = \Sigma \lVert F_o\rvert - \lvert F_c \rVert / \Sigma \lvert F_o\rvert$. [f] $wR_2 = \sqrt{[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]}$. [g] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.


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[10] The tilt angles of the furan rings are given in relation to the mean plane of the six isopropylidene carbon atoms. When the oxygen atoms of the furan rings are directed away from the central core of the macrocycles, then the obtuse angle is given.

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