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Tris-β-diketones and related keto derivatives for use as building blocks in supramolecular chemistry

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Abstract—The synthesis of three new tris-β-diketones and some derivatives is reported. In two cases facile alkaline hydrolysis of the diketone moieties yielded the corresponding keto compounds. These are readily functionalised to provide tripodal ligands.

1. Introduction

The β-diketone motif is a versatile metal coordinating ligand that is readily derivatised and able to form complexes with a wide range of metal ions. It has also been shown to be an attractive ligand for incorporation into metallo-supramolecular structures.[1,2] For example, many of the latter investigations have focused on systems in which two β-diketone ligands are linked to a central spacer by their terminal carbon atoms.[1,3–5] Pairs of these ligands have been shown to coordinate copper(II) ions in a square planar geometry resulting in the formation of planar di- and trinuclear scaffolds, with the uncoordinated axial sites on each metal centre available for further coordination.

The synthesis of scaffolds that bear more than two β-diketone groups will provide building blocks for the self-assembly of structures of higher dimensionality. In particular, scaffolds bearing three β-diketone ligands have the potential to form molecular cages and/or capsules upon the addition of suitable metal ions. We now report the synthesis of some tris-β-diketones based on a 1,3,5-trimethyl-2,4,6-trisubstituted benzene (mesitylyl) core, together with attempts to form molecular capsules from these ligands through metal coordination of the β-diketone groups.

The 1,3,5-trisubstituted benzyl moiety has been employed as a convenient scaffold in the design and synthesis of many supramolecular assemblies, including structures that resemble cages and/or capsules.[6–9] Use of the 1,3,5-trimethyl-2,4,6-trisubstituted benzene derivative has in some instances been proposed to favour the desirable preorganisation of the three pendant 'arms' towards the same face of the benzene core.[10–13] Another benefit of use of the mesitylyl moiety is that the required 1,3,5-trimethyl-2,4,6-tri(bromomethyl)benzene starting material is more readily prepared than 1,3,5-tris(bromomethyl)benzene itself.[14,15] We thus chose to employ this mesitylene derivative as our starting material for the synthesis of a number of tris-β-diketone derivatives.

2. Results and discussion

Compounds **2**–**4** were readily prepared in high yield (>80%) from tris(bromomethyl)mesitylene (**1**) and the corresponding β-diketone by refluxing in *tert*-butanol in the presence of *t*-BuOK (Scheme 1). The resulting β-diketones were all readily purified and their ^{1}H and ^{13}C NMR spectra are in accord with the presence of high levels of symmetry. In all cases, only a single tautomer, the diketone form, was observed by both ^{1}H and ^{13}C NMR spectroscopies in deuterochloroform. This is in contrast to similar bis-β-ketone derivatives in which a substantial percentage of the enol tautomer is observed.[16]

The X-ray crystal structure analysis of **4** (Fig. 1) revealed that this compound exists in the solid state as the keto tautomer only, with the central carbon atoms of the β-diketone groups all being sp^3 hybridised. In addition, the oxygen-to-oxygen distances for the three β-diketone groups are all greater than 3.17 Å, whereas oxygen-to-oxygen distances in enolic β-diketone derivatives are typically less than 2.54 Å.[17]

Keywords: β-Diketone; Tripodal scaffold; Alkaline hydrolysis; Tris-ketone.
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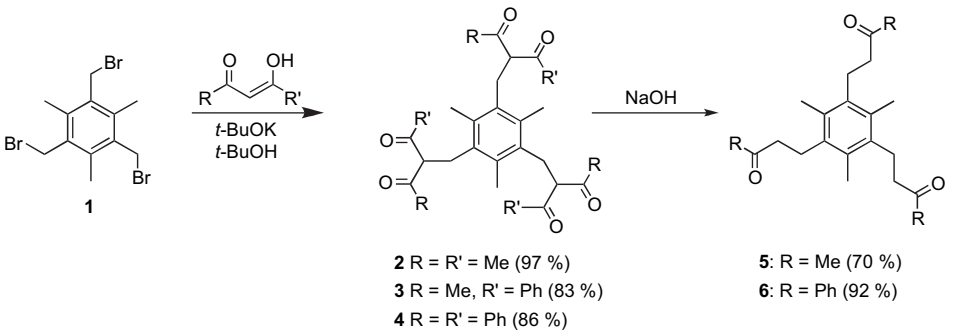


Scheme 1.

Attempts at forming transition-metal complexes of **2–4** using the normal procedure of heating with a metal salt in the presence of base were unsuccessful. In each case, rather than obtaining the desired metal complex upon cooling the reaction mixture, we isolated white solids that contained no metal ion. The difficulty in forming metal complexes is in accordance with these compounds being unable to easily tautomerise to the enolate derivative.[16] We therefore attempted to pre-form the sodium enolate of **2** since it has been shown previously that transmetallation of sodium acetylacetonate with a variety of transition metals can be used to form transition-metal complexes of acetylacetone without the need to add further base.[18,19] Attempts to form the sodium salt of **2**, by heating with NaOH in ethanol/water,[20] resulted in the crystallisation of fine white needles that exhibited a different habit to that of the starting compound. However, spectroscopic analysis and an X-ray crystal structure determination (Fig. 2) confirmed that this product was not the expected sodium salt, but was the tris-ketone derivative **5**, resulting from alkaline hydrolysis of each of the β-diketone groups (Scheme 1). The material isolated from the attempts to directly form transition-metal complexes of **2** was also identified spectroscopically as **5**.

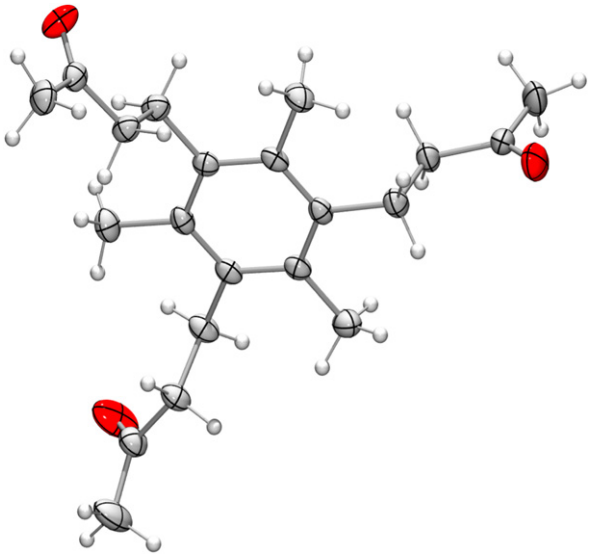


Figure 2. ORTEP of **5** with ellipsoids shown at the 50% probability level.

The alkaline hydrolysis of β-diketones has been reported previously,[21–23] but it was found that β-diketones with at least one proton on the central carbon position are somewhat protected from hydrolysis due to the presence of keto–enol tautomerism, which confers a partial double bond character to the C–C bond, making cleavage more difficult. However, for β-diketones with two non-hydrogen substituents on the central carbon atom, and hence unable to form an enol tautomer, alkaline hydrolysis has been shown to be more facile.[21–23] The ease of the alkaline hydrolysis of **2** is thus in accord with the enol tautomer not being readily accessible in this case. This is in agreement with our spectroscopic data, which show that only the keto tautomer is present, both in $CDCl_3$ solution and the solid state.

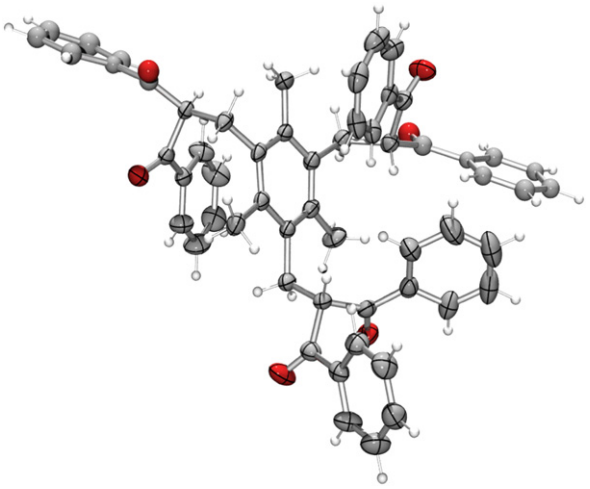
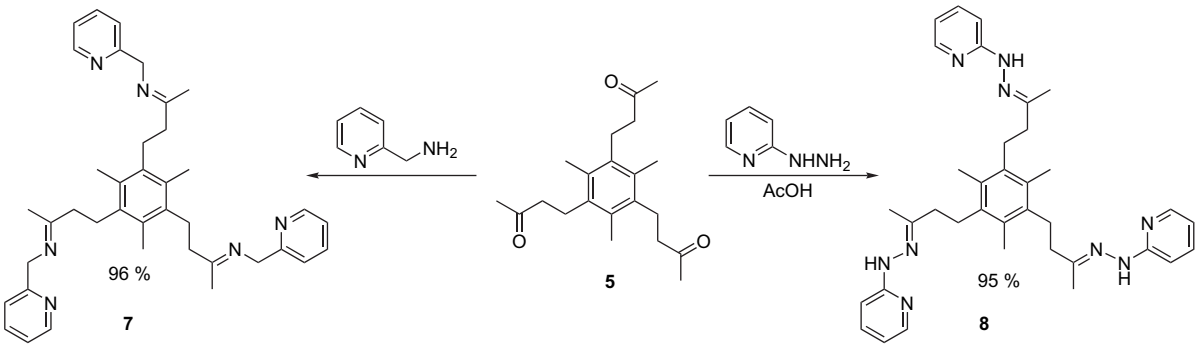


Figure 1. ORTEP of ligand **4** with ellipsoids shown at the 25% probability level. The benzoyl groups comprising atoms O3, C26–C32 and O5, C43–49 exhibit minor positional disorder and were modelled with two sites each. For clarity only one of these is shown.

Inspired by the ease and speed of the alkaline hydrolysis of **2** we found that **4** undergoes a similar reaction to yield the analogous tris-ketone **6** containing terminal phenyl groups on each arm (Scheme 1). Although a full investigation of the reaction mechanism has not been undertaken we propose that the ease of the alkaline hydrolysis in each of the above reactions is due to steric interactions between the β-diketone fragments and the aryl-bound methyl groups, that result in the predominance of the diketo tautomeric form of these compounds. Similar sterically hindered β-diketone derivatives have also been found to exist predominantly as their respective diketo tautomers.[16]



Scheme 2.

The inability to form the enolate derivatives of **2**–**4** has prevented an investigation of the self-assembly behaviour of these tripodal ligands. However, the ketone derivatives, **5** and **6**, obtained upon deacylation/debenzoylation of **2** and **4**, respectively, are readily functionalised allowing a variety of new compounds to be prepared. Indeed, there has been an interest in polyketones as precursors for the divergent approach to dendritic systems.[24] The tris-ketones can be employed as precursors in the formation of extended tripodal ligands, in which the functional groups are well separated from the aryl core. For example, we have prepared the pyridyl derivatives **7** and **8** by reaction of tris-ketone **5** with 2-picolylamine and 2-hydrazinopyridine, respectively (Scheme 2). An investigation of the coordination chemistry of these ligands has been conducted with a variety of transition-metal ions and the results of this study will be reported in due course.

3. Conclusions

Tris-β-diketone derivatives are readily prepared upon treatment of 1,3,5-trimethyl-2,4,6-tris(bromomethyl)benzene with β-diketones in the presence of base. These compounds are present as the keto tautomer, both in solution and the solid state. They do not readily form metal complexes and upon treatment with base, compounds **2** and **4** undergo a surprisingly facile hydrolysis, resulting in the formation of the corresponding tris-ketones **5** and **6** in high yield. Tris-ketones **5** and **6** are useful building blocks for the construction of larger tripodal ligands, in which the functional groups are positioned at a greater distance from the aryl core as evidenced by the formation of the tris-pyridyl derivatives **7** and **8**.

4. Experimental

4.1. General

Melting points were measured using a Gallenkamp Electrothermal apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker Avance DPX300 or DPX200 spectrometers operating at 300 and 200 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker Avance DPX300 spectrometer operating at 75.5 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane. DEPT spectra were used to aid in the assignment of ^{13}C signals. Low-resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Finnigan LCQ-8 spectrometer. High-resolution electrospray ionization mass spectra (HRMS-ESI) were obtained on a Finnigan MAT 900 XL spectrometer. FTIR spectra were determined on a Bio-Rad FTS-40 spectrometer. Elemental analyses were performed by the Microanalytical Unit, Australian National University, Canberra, Australia. Merck Kieselgel 60 silica gel (230–400 mesh) was used for column chromatography. All commercially available reagents were used as received.

4.1.1. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (1). Compound **1** was prepared by the literature method.[14] The ^{1}H NMR data (200 MHz, $CDCl_3$, 300 K): δ 2.46 (9H, s, CH_3), 4.58 (6H, s, CH_2) corresponded to that reported previously.

4.1.2. 1,3,5-Tris(3′-methyl-2′,4′-pentanedione)-2,4,6-trimethylbenzene (2). Acetylacetone (10.01 g, 100 mmol) was added to a refluxing solution of potassium *tert*-butoxide (8.4 g, 75 mmol) in *tert*-butanol (1250 mL). Trisbromide **1** (10.0 g, 25 mmol) was added in small portions followed by a catalytic amount of potassium iodide. After 20 h *tert*-butanol was removed under reduced pressure and the residue partitioned between dichloromethane (1250 mL) and water (500 mL). The organic phase was washed with water (2×500 mL) and dried over anhydrous Na_2SO_4. The dichloromethane was removed under vacuum to yield a white solid. This was recrystallised from ethanol/water (1:4) to give **2** as fine colourless crystals (11.40 g, 97%), mp 144–145 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 2.06 (18H, s, $COCH_3$), 2.19 (9H, s, $PhCH_3$), 3.25 (6H, d, J=7.4 Hz, CH_2), 3.84 (3H, t, J=7.4 Hz, COCHCO). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 17.4 (CH_3), 29.5 (CH_2), 30.6 (CH_3), 67.7 (CH), 134.2 (C), 134.7 (C), 204.2 (C=O). MS (ESI): m/z=479 $(M+Na)^+$. Found (%): C, 71.06; H, 8.09. $C_{27}H_{36}O_6$ requires: C, 71.03; H, 7.95. IR (KBr): $\nu_{(C=O)}$ 1711 cm^{-1}.

4.1.3. 1,3,5-Tris(2′-methyl-1′-phenyl-butane-1′,3′-dione)-2,4,6-trimethylbenzene (3). Benzoylacetone (3.2 g, 20 mmol) was added to a refluxing solution of potassium *tert*-butoxide (1.7 g, 15 mmol) in *tert*-butanol (250 mL). Trisbromide **1** (2.00 g, 5 mmol) was then added in small portions followed by a catalytic amount of potassium iodide. After 20 h of refluxing, *tert*-butanol was removed under reduced pressure and the residue partitioned between dichloromethane (150 mL) and water (100 mL). The organic phase

was washed with water (2×100 mL) and dried over anhydrous Na_2SO_4. The dichloromethane was removed under reduced pressure to yield a pale yellow oil. This was purified via chromatography on silica gel (elution with dichloromethane followed by dichloromethane/methanol, 95:5) to yield **3** (R_f 0.6 in CH_2Cl_2) as a pale yellow glass (2.67 g, 83%), mp 50–55 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 1.97 (9H, s, $PhCH_3$), 2.19 (9H, s, CH_3CO), 3.35 (6H, d, J=6.4 Hz, CH_2), 4.44 (3H, t, J=6.4 Hz, COCHCO), 7.32–7.73 (15H, m, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 17.5 (CH_3), 29.3 (CH_3), 29.9 (CH_3), 63.3 (CH), 128.9 (CH), 129.2 (CH), 134.05 (CH), 134.1 (C), 135.1 (C), 136.9 (C), 197.1 (C═O), 203.6 (C═O). MS (ESI) m/z=665 $(M+Na)^+$. Found (%): C, 78.09; H, 6.71. $C_{42}H_{42}O_6$ requires: C, 78.48; H, 6.59. FTIR (KBr): $\nu_{(C=O)}$ 1717, 1669 cm^{-1}.

4.1.4. 1,3,5-Tris(2′-methyl-1′,3′-diphenyl-propane-1′,3′-dione)-2,4,6-trimethylbenzene (4). Dibenzoylmethane (6.3 g, 28 mmol) was added to a refluxing solution of potassium *tert*-butoxide (2.5 g, 23 mmol) in *tert*-butanol (280 mL). Trisbromide **1** (3.0 g, 7.5 mmol) was then added in small portions followed by a catalytic amount of potassium iodide. After 48 h of refluxing, *tert*-butanol was removed under reduced pressure and the residue partitioned between dichloromethane (150 mL) and water (100 mL). The organic phase was washed with water (6×100 mL) and dried over anhydrous Na_2SO_4. The dichloromethane was removed under vacuum to yield a pale yellow oil that solidified after two days. This was recrystallised from acetone to give the title compound as colourless crystals (5.35 g, 86%), mp 208–209 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 1.93 (9H, s, CH_3), 3.43 (6H, d, J=6.3 Hz, CH_2), 5.04 (3H, t, J=6.3 Hz, COCHCO), 7.25–7.71 (30H, m, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 17.6 (CH_3), 30.6 (CH_2), 58.7 (C), 129.0 (CH), 129.1 (CH), 133.9 (CH), 134.3 (C), 135.4 (C), 136.4 (C), 196.6 (C═O). MS (ESI) m/z=851 $(M+Na)^+$. Found (%): C, 82.54; H, 6.00. $C_{57}H_{48}O_6$ requires: C, 82.57; H, 5.84. FTIR (KBr): $\nu_{(C=O)}$ 1699, 1662 cm^{-1}. Crystals of sufficient quality for X-ray analysis were obtained by recrystallisation of the above product from ethyl acetate.

4.1.5. 1,3,5-Tris(3′-oxo-butyl)-2,4,6-trimethylbenzene (5). A solution of sodium hydroxide (0.26 g, 66 mmol) in water (10 mL) and methanol (10 mL) was added slowly to a suspension of **2** (1.0 g, 2.2 mmol) in warm methanol (20 mL). The resulting solution was stirred for 5 min without further heating and left to cool overnight. Compound **5** was crystallised from the reaction mixture as colourless needles (0.5 g, 70%), mp 143–144 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 2.19 (9H, s, CH_3), 2.22 (9H, s, CH_3), 2.58 (6H, t, J=8.3 Hz, CH_2), 2.94 (6H, t, J=8.3 Hz, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 16.1 (CH_3), 24.9 (CH_3), 30.25 (CH_2), 43.5 (CH_2), 132.6 (C), 136.4 (C), 208.5 (C═O). MS (ESI) m/z=329 $(M-H)^-$. Found (%): C, 75.66; H, 9.28. $C_{21}H_{30}O_3\cdot 1/4H_2O$ requires: C, 75.29; H, 9.18. FTIR (KBr): $\nu_{(C=O)}$ 1703 cm^{-1}. Crystals of sufficient quality for X-ray analysis were obtained by slow evaporation of an acetone/water solution of the product.

4.1.6. 1,3,5-Tris(3′-oxo-3′-phenyl-propyl)-2,4,6-trimethylbenzene (6). A solution of sodium hydroxide (0.15 g, 3.6 mmol) in water (5 mL) and ethanol (5 mL) was added to a suspension of **4** (1.0 g, 1.2 mmol) in a minimum amount of hot ethanol. The resulting yellow solution was stirred for 5 min until the solution was colourless and then left to cool. Compound **6** was crystallised from the reaction mixture as a white solid (0.57 g, 92%), mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 2.34 (9H, s, CH_3), 3.16 (12H, s, CH_2), 7.47 (6H, m, C_6H_5), 7.57 (3H, m, C_6H_5), 7.98 (6H, m, C_6H_5). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 16.4 (CH_3), 25.4 (CH_2), 38.5 (CH_2), 128.4 (CH), 129.1 (CH), 133.6 (CH), 134.1 (C), 136.8 (C), 137.2 (C), 199.8 (C═O). MS (ESI) m/z=539 $(M+Na)^+$. Found (%): C, 83.79; H, 7.13. $C_{36}H_{36}O_3$ requires: C, 83.68; H, 7.03. IR (KBr): $\nu_{(C=O)}$ 1682 cm^{-1}.

4.1.7. Tris(pyridyl)imine (7). A solution of 2-picolylamine (0.63 g, 5.8 mmol) in toluene (10 mL) was added to a refluxing solution of tris-ketone **5** (3.00 g, 91 mmol) in toluene (15 mL). This solution was refluxed using a Dean–Stark trap for 4 h, before the solvent was removed under vacuum. This gave tris-imine **7** as a yellow oil (3.5 g, 96%), ^{1}H NMR ($CDCl_3$, 300 MHz, 300 K): δ 2.00 (9H, s, CH_3), 2.17 (9H, s, CH_3), 2.59 (6H, m, CH_2), 2.98 (6H, m, CH_2), 4.67 (6H, s, NCH_2Py), 7.13–7.74 (9H, m, C_5H_4N), 8.56 (3H, m, C_5H_4N). Found $(M+H)^+$ m/z=601.3994 (HRMS-ESI). $C_{39}H_{49}N_6$ requires 601.4013.

4.1.8. Tris(pyridyl)hydrazone (8). A warm solution of 2-hydrazinopyridine (0.99 g, 9 mmol) in ethanol (5 mL) was added to a refluxing solution of **5** (1.0 g, 3 mmol) in ethanol (10 mL). Six drops of glacial acetic acid were added and the solution was heated at reflux for 35 min before the ethanol was removed under vacuum, yielding a pale orange solid (1.9 g, 95%), mp 76–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 1.96 (9H, s, CH_3), 2.35 (9H, s, CH_3), 2.45 (6H, m, CH_2), 2.98 (6H, m, CH_2), 6.73 (3H, m, C_5H_4N), 7.31 (3H, m, C_5H_4N), 7.60 (3H, m, C_5H_4N), 8.06 (3H, m, C_5H_4N), 8.32 (3H, s, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 15.9 (CH_3), 16.2 (CH_3), 28.2 (CH_2), 38.9 (CH_2), 108.2 (CH), 115.4 (CH), 138.9 (CH), 146.9 (CH), 157.9 (CH), 132.6 (C), 136.9 (C), 148.8 (C). MS (ESI) m/z=604 $(M+H)^+$. Found (%): C, 67.32; H, 7.51; N, 19.18. $C_{36}H_{45}N_9\cdot 2\frac{1}{4}H_2O$ requires: C, 67.10; H, 7.74; N, 19.57.

4.2. Crystal structure data collection

For both compounds **4** and **5**, intensity data were collected at 150(2) K with ω scans to approximately 56° 2θ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo Kα radiation generated from a sealed tube (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP[25] and subsequent computations were carried out using WinGX-32 graphical user interface.[26] Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[27] Gaussian absorption corrections were applied using XPREP.[25] Structures were solved by direct methods using SIR97[28] then refined and extended with SHELXL-97.[29]

Unless otherwise stated, ordered non-hydrogen atoms were refined anisotropically while partial occupancy non-hydrogen atoms were refined isotropically. Hydrogen atoms attached to carbon atoms were included in idealised positions and a riding model was used for their refinement.

4.2.1. Crystal structure data for compounds 4 and 5. *Compound* ***4***: formula $C_{57}H_{48}O_6$; M=828.95; monoclinic; space group: $P2_1/c$(#14); a=12.2731(6), b=13.9649(7), c=26.3234(14) Å, β=102.0650(10)°; V=4412.0(4) Å^3; D_c=1.248 g cm^{-3}; Z=4; crystal size: 0.53 by 0.50 by 0.23 mm; colour: colourless; habit: multi-faced; temperature=150(2) K; λ(Mo Kα)=0.71073 Å; μ(Mo Kα)=0.080 mm^{-1}; T(SADABS)$_{min,max}$=0.917, 1.000; $2\theta_{max}$=56.64; *hkl* range: −16(15), −18(17), −34(33); N=43,322; N_{ind}=10,610 (R_{merge}=0.0207); N_{obs}=8469($I>2\sigma(I)$); N_{var}=555; residuals $R1(F)$=0.0687, $wR2(F^2)$=0.1853, GoF(all)=1.033; $\Delta\rho_{min,max}$=−0.536, 0.764 eÅ^{-3}.

$$R1 = \sum \frac{||F_o| - |F_c||}{\sum |F_o|} \quad \text{for } F_o > 2\sigma(F_o);$$

$$wR2 = \left(\frac{\sum w\left(F_o^2 - F_c^2\right)^2}{\sum \left(wF_c^2\right)^2} \right)^{1/2} \quad \text{for all reflections.}$$

$$w = \frac{1}{\left[\sigma^2\left(F_o^2\right) + (0.077P)^2 + 3.4339P\right]}, \quad \text{where}$$

$$P = \frac{\left(F_o^2 + 2F_c^2\right)}{3}.$$

Note: the benzoyl groups comprising atoms O3, C26–C32 and O5, C43–49 exhibit minor positional disorder and were modelled with two sites each. For clarity only one of these is shown in Figure 1.

Compound ***5***: formula: $C_{21}H_{30}O_3$; M=330.45; triclinic; space group: $P\bar{1}$(#2); a=4.9863(10), b=11.152(2), c=17.205(3) Å, α=81.184(4), β=84.908(3), γ=88.657(4)°; V=941.7(3) Å^3; D_c=1.165 g cm^{-3}; Z=2; crystal size: 0.605 by 0.214 by 0.088 mm; colour: colourless; habit: prism; temperature=150(2) K; λ(Mo Kα)=0.71073 Å; μ(Mo Kα)=0.076 mm^{-1}; T(Gaussian)$_{min,max}$=0.9745, 0.9947; $2\theta_{max}$=56.74; *hkl* range: −6(6), −14(14), −22(22); N=9354; N_{ind}=4366 (R_{merge}=0.0399); N_{obs}=3099($I>2\sigma(I)$); N_{var}=223; residuals $R1(F)$=0.0479, $wR2(F^2)$=0.1425, GoF(all)=1.047; $\Delta\rho_{min,max}$=−0.197, 0.269 eÅ^{-3}.

$$R1 = \sum \frac{||F_o| - |F_c||}{\sum |F_o|} \quad \text{for } F_o > 2\sigma(F_o);$$

$$wR2 = \left(\frac{\sum w\left(F_o^2 - F_c^2\right)^2}{\sum \left(wF_c^2\right)^2} \right)^{1/2} \quad \text{for all reflections.}$$

$$w = \frac{1}{\left[\sigma^2\left(F_o^2\right) + (0.0805P)^2 + 0.0000P\right]}, \quad \text{where}$$

$$P = \frac{\left(F_o^2 + 2F_c^2\right)}{3}.$$

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 626206 and CCDC 626207. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk).

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