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Synthesis and X-ray structural analysis of an acyclic bifunctional vicinal triketone, its hydrate, and its ethanol-adduct



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Morio Yonekawa ^{a, b}, Yoshio Furusho ^a, Yoshihisa Sei ^c, Toshikazu Takata ^b, Takeshi Endo ^{a,*}

^a Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan

^b Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 1-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan ^c Chamical Basaurose Laboratory, Tokyo Institute of Technology, 4350 Magatauta, Midari Iu, Yakabama 236, 8502, Japan

^c Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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ABSTRACT

We have synthesized and fully characterized an acyclic bifunctional vicinal tricarbonyl compound, its hydrate, and its ethanol-adduct, which could be converted to one another by utilizing the reversible addition—elimination of water or ethanol. X-ray single crystal study revealed that the bistriketone expanded and contracted by 10–30% in length during the interconversion.

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1. Introduction

Vicinal tricarbonyl compounds, such as alloxan, 1,2,3indanetrione, dehydroascorbic acid, and diphenylpropanetrione (DPPT, **1**, Scheme 1a), are known to have a highly electrophilic nature due to the three contiguous carbonyl groups, which are activated by the adjacent two carbonyl groups.^{1,2} Consequently, they are highly reactive toward various nucleophiles, such as water and alcohols, to afford the corresponding hydrate or alcohol-adduct. These covalently-bonded water or alcohols can be eliminated to give pure free tricarbonyls by heating under vacuum,^{3,4} sublimation,^{4,5} distillation,^{6–8} crystallization,⁷ azeotropic removal,⁸ and utilization of molecular sieves or P_2O_5 .^{5,8,9} Of particular interest is that the hydration and alcohol-addition processes are reversible¹⁰ and are accompanied by disappearance and appearance of the distinctive yellow–orange color due to the collapse and recovery of the contiguous three carbonyl groups, respectively, hence being detectable by the naked eye.¹

We have started our studies to develop new polymer materials based on the vicinal tricarbonyl structures, motivated by the characteristic features of vicinal tricarbonyl compounds. Recently, we reported design and synthesis of a polystyrene bearing acyclic vicinal tricarbonyl structures in the side chains and detailed investigation of reversible addition—elimination behavior of water or alcohols to the vicinal tricarbonyl moiety of the polymer.^{11–13} Moreover, we have successfully constructed the reversible cross-linking and de-cross-linking system that can be controllable at ambient conditions, utilizing the direct water—alcohol exchange reaction on the vicinal tricarbonyl groups.¹⁴

Several bifunctional vicinal polycarbonyl compounds have been reported to date. For example, Wasserman and Baldino synthesized bifunctional α , β -diketoesters tethered by phenylene, naphthylene, and decamethylene linkers and found that these compounds acted as dielectrophiles toward the amino groups of DNA bases, effectively cross-linked the DNA strands.¹⁵ Gleiter and Schang synthesized two bifunctional cyclic vicinal triketones (1,2,3,5,6,7-shydrindacenehexone, and 1,2,3,6,7,8-pyrenehexone), which formed 1:1 donor–acceptor complexes with pyrene.¹⁶ The same group also reported the synthesis and structure of a cyclic bifunctional vicinal tetraketone, and disclosed the presence of some intra-annular interactions in the solid state by X-ray single crystal structure analysis.¹⁷ Thus, bifunctional vicinal polycarbonyl compounds are of interest from a viewpoint of not only their molecular structures but also their chemical properties that could lead to the application to cross-linking agents. Another important feature of the vicinal tricarbonyl compounds is their relatively large structural changes accompanied by the addition of water and alcohols, which could be applied to polymer systems to create new stimuli-responsive



^{*} Corresponding author. Tel.: +81 948 22 7210; fax: +81 948 21 9132; e-mail addresses: tendo@moleng.fuk.kindai.ac.jp, tendo@me-jsr.fuk.kindai.ac.jp (T. Endo).

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Scheme 1. (a) Structure of DPPT 1, (b) synthesis of the bistriketone 3, its hydrate 4, and its ethanol-adduct 5.

materials or supramolecular systems such as molecular machines or molecular muscles.¹⁸ Investigation on the structural changes of bifunctional vicinal tricarbonyl compounds is an important, preliminary step toward future design and synthesis of such stimuli-responsive supramolecular systems consisting of vicinal tricarbonyl polymers. Herein, we report the facile synthesis, structures, and chemical properties of an acyclic bifunctional vicinal tricarbonyl compound (bistriketone, **3**), its hydrate **4**, and its ethanol-adduct **5** together with the drastic structural changes accompanying their reversible interconversion.

2. Results and discussion

The bifunctional vicinal tricarbonyl compound 3 (bistriketone), its hydrate 4, and its ethanol-adduct 5 were synthesized according to Scheme 1b. Treatment of dimethyl terephthalate and acetophenone with NaH in THF at 50 °C afforded the bifunctional 1,3diketone 2. Oxidation of the two 1,3-diketone moieties of 2 by Nbromosuccinimide (NBS) in DMSO at 80 °C for 1 day resulted in the formation of the corresponding bistriketone **3**, confirmed in situ with the orange coloration of the reaction mixture originating from the vicinal tricarbonyl structures. Since the tricarbonyl compound 3 is labile to hydration by moisture in solvents or air during isolation processes, we isolated its hydrate form 4 instead of 3; on addition of an excess of water to the reaction mixture, the color of the solution immediately turned light yellow indicating hydration of 3. After 1 h, a large amount of water was added to the solution and the resulting suspension was filtered. The residue was washed with water and chloroform to obtain bis(gem-diol) 4 as a colorless solid. Heating 4 at 100 °C in vacuo for 4 h resulted in quantitative generation of orange-colored bistriketone 3. Conversely, hydration of 3 proceeded smoothly upon treatment with water/acetone (1/9, v/v) for 1 h and 4 was quantitatively obtained after evaporation of the volatile components. The ethanol-adduct 5 was obtained by treatment of 3 with hot ethanol; when a suspension of bistriketone 3 in ethanol was heated at 70 °C, it became homogeneous. The solution was then cooled to rt, to form a white precipitate, which was collected by suction filtration and washed with *n*-hexane to obtain the ethanol-adduct 5. The white microcrystalline solid of 5 contained ethanol molecules included in the crystalline lattice, which were hardly removed by simply heating in vacuo. The ethanol-containing solid of 5 was subjected to recrystallization from ethyl acetate to give pure **5** as a white microcrystalline solid that did not contain any solvent molecules. Similarly to the hydrate 4, elimination of the ethanol from 5 proceeded by heating; 3 was regenerated quantitatively by heating **5** at 120 °C in vacuo for 1 h.

The structures of bistriketone **3**, its hydrate **4**, and its ethanoladduct **5** were confirmed unambiguously by NMR, IR, and UV/vis spectroscopies. Four peaks assignable to the phenyl and *p*-phenylene protons were observed in the ¹H NMR spectrum of bistriketone **3** in CDCl₃, whereas an additional singlet peak due to the *gem*-diol protons was observed at 7.88 ppm for hydrate **4** in DMSO-d₆ (Fig. S1, Supplementary data (SD)). Similarly, the signals assignable to the hemiketal hydroxyl protons along with the ethoxy groups were observed in addition to those due to the aromatic protons in the ¹H NMR spectrum of **5** in CDCl₃. In the ¹³C NMR spectrum of bistriketone **3**, the three sequential carbonyl carbons gave three peaks at 191.9, 191.8, and 187.2 ppm (Fig. S2, SD). On the other hand, only two carbonyl signals along with one signal for the quaternary carbon for the *gem*-diol or hemiketal signal were observed in the ¹³C NMR spectra of **4** or **5**, respectively.

The IR and UV/vis spectra of **3** showed characteristic absorptions originating from its vicinal tricarbonyl structure. As for IR, the bistriketone 3 exhibited the diagnostic absorption of the stretching vibration of its vicinal tricarbonyl groups at 1723 cm⁻¹, a close value to that of the monofunctional triketone DPPT 1 (1715 cm⁻¹, Fig. S3, SD). On the other hand, the hydrate **4** and the ethanol-adduct **5** offered absorption peaks at around 3400 cm⁻¹ due to the O-H groups of the gem-diol or hemiketal structures instead of the tricarbonyl absorption at around 1720 cm^{-1} . UV/vis absorption spectra of **3**. **4**. and **5** together with that of DPPT **1** were shown in Fig. 1. A solution of the bistriketone **3** in dry 1.4-dioxane exhibited an absorption in the region from 400 to 500 nm with a maximum ε value of 128 M⁻¹ cm⁻¹ at 456 nm arising from the carbonyl $n-\pi^*$ transitions. The maximal absorption wavelength of 3 approximately coincided with that of DPPT **1** (450 nm),¹¹ indicating clearly that the conjugated system of the vicinal tricarbonyl structure was not elongated. In contrast to the bistriketone 3, the hydrate 4 in 1,4dioxane/water (97/3, v/v) and the ethanol-adduct **5** in 1,4-dioxane/ ethanol (97/3, v/v) showed a negligible absorption in the same region, which is attributable to the collapse of the conjugate systems consisting of the three sequential carbonyl groups as a result of the addition of water or ethanol to the central ones.



Fig. 1. UV/vis absorption spectra of **3** in 1,4-dioxane, **4** in 1,4-dioxane/water (97/3, v/v), and **5** in 1,4-dioxane/ethanol (97/3, v/v) along with DPPT **1** in 1,4-dioxane.

Finally, the structures of these three species were determined by X-ray crystallographic analysis.¹⁹ Fig. 2 shows the ORTEP drawings of **3**, **4**, and **5**; single crystals of **3**, **4**, and **5** suitable for X-ray analysis were grown from chloroform, acetone, and ethyl acetate, respectively. In the crystal structure of the bistriketone **3**, the sequential three carbonyl groups adopt helical conformations with slightly shorter bond lengths (ca. 0.01 Å) of the central carbonyl C8=O2 (1.209 Å) than those of the side ones C7=O1 (1.220 Å), and C9=O3 (1.217 Å), as often the case with other vicinal tricarbonyl



Fig. 2. Single crystal X-ray structures of (a) **3**, (b) **4**, and (c) **5**, top views (above) and side views (below) along with the distances between the centroids of the terminal phenyl rings. Thermal ellipsoids are drawn at 50% probability. Acetone molecules in the crystal structure of **4** are omitted for clarity.

compounds (Fig. 2a).¹ As a whole, the bistriketone molecule took a rod-like structure, in which the distance between the two terminal phenyl rings was 15.49 Å. The crystal structure of the hydrate 4 revealed that the two central carbon atoms (C8, C17) adopted sp^3 hybrid orbitals and the four hydroxyl groups formed intramolecular hydrogen bonds with the neighboring carbonyl oxygen atoms (01...02, 03...04, 05...06, 07...08) with lengths of 2.61–2.63 Å (Fig. 2b). Similarly to the hydrate **4**, the central carbonyl carbons (C8) of the ethanol-adduct 5 adopted tetrahedral configurations as a result of the addition of ethanol molecules (Fig. 2c). Intramolecular hydrogen bonds are also observed between the hemiketal hydroxyl moieties and the neighboring carbonyl oxygen atoms of 5 (01...03) with a length of 2.58 Å. In contrast to the rodlike structure of **3**, the molecules of **4** and **5** adopted zigzag-shaped structures in the solid state, in which the two terminal phenyl groups are located with distances of 10.76 Å and 13.77 Å, respectively. It follows from the changes in distance that the bistriketone molecule shrinks in length by 31% and 11% upon addition of the water and ethanol molecules, respectively.

The electrochemical properties of bistriketone 3 and its ethanoladduct 5 were evaluated by cyclic voltammetry (CV) analysis. The cyclic voltammograms of **3** and **5** in CH₂Cl₂ containing *n*-Bu₄NPF₆ are shown in Fig. 3 along with that of DPPT 1. Whereas the DPPT 1 showed almost reversible single-electron-transfer peak, the bistriketone 3 exhibited quasi-reversible, two-step, and twoelectron-transfer peaks. The half-wave reduction potentials of 3 were observed at $E^{1}_{1/2}$ =-0.84 V and $E^{2}_{1/2}$ =-1.11 V (vs Ag/Ag⁺), which were presumably attributed to the formation of anionic radical and dianion with *p*-quinodimethane structure,²⁰ respectively. The $E_{1/2}^1$ of **3** was less negative than $E_{1/2}$ of DPPT **1** $(-1.06 V vs Ag/Ag^+)$ because of the electron-withdrawing tricarbonyl moiety on the other side of 3. The decrease in the current intensity of the oxidation peak indicated that the anionic species generated from 3 was less stable than that of 1. In contrast to these triketones, ethanol-adduct 5 exhibited a completely irreversible reduction peak at $E_{1/2}$ =-1.12 V (vs Ag/Ag⁺).



Fig. 3. Cyclic voltammograms of bistriketone **3** (red line), its ethanol-adduct **5** (green line), and DPPT **1** (blue line) at 1.0 mM in CH_2Cl_2 solutions containing *n*-Bu₄NPF₆ (0.10 M). Sweep rate was 100 mV s⁻¹.

3. Conclusion

In summary, we have synthesized and fully characterized the acyclic bifunctional vicinal tricarbonyl compound **3**, its hydrate **4**, and its ethanol-adduct **5**. The bistriketone **3** was readily and quantitatively hydrated upon treatment with water-containing solvent. Conversely, the hydrate **3** was dehydrated quantitatively by heating in vacuo. Similarly, the bistriketone **3** was converted to

its ethanol-adduct by treatment with ethanol, from which the bistriketone **3** was quantitatively regenerated by heating under vacuum. As revealed by the X-ray crystallographic analysis, water and ethanol molecules added to the central carbonyl sp²-carbon atoms of the bistriketone 3 that changed to a tetrahedral configuration, so that the hydrate **4** and the ethanol-adduct **5** adopted a zigzag structure in contrast to the rod-shaped bistriketone **3**. The changes in the crystal structures indicated that the bistriketone **3** expanded and contracted by 10-30% in length as a result of the addition and elimination of water and ethanol molecules. The cyclic voltammogram of bistriketone indicated that the two vicinal tricarbonyl groups acted as two-electron acceptors though the generated dianion species is relatively labile when compared to its monofunctional counterpart **1**. As is evident from the bifunctional nature of the bistriketone **3**, it can be utilized as a reversible crosslinking reagent for multifunctional alcoholic polymers such as poly(vinyl alcohol) (PVA) or poly(2-hydroxyethyl methacrylate) (PHEMA). Moreover, we envisage that the chemistry of the bistriketone investigated herein, though a little premature, would be a first step toward a future design and synthesis of supramolecular systems that can undergo reversible extension and contraction motion in response to some external stimuli. These applications are currently underway in our laboratory.

4. Experimental section

4.1. General

Chloroform, chloroform-d (CDCl₃), dimethyl sulfoxide, dimethyl sulfoxide- d_6 (DMSO- d_6), and ethyl acetate were distilled over molecular sieves 4A (MS 4A). Acetone and acetophenone were distilled over CaCl₂. Ethanol was distilled over CaH₂. Tetrahydrofuran (THF) and 1,4-dioxane were distilled over sodium benzophenone ketyl. NaH (60% in oil) (WAKO, Japan) was washed with *n*-hexane before use. Diphenylpropanetrione (DPPT, **1**) was synthesized according to the literature.¹¹ Other reagents were used as received.

¹H and ¹³C NMR spectra were measured on a JEOL JNM-ECS 400 spectrometer at a resonance frequency of 400 and 100 MHz, respectively, with tetramethylsilane (TMS) as the internal standard. NMR chemical shifts were reported in delta unit (δ). IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer. UV/vis spectra were measured with a JASCO V-570 spectrophotometer in a 1-cm quartz cell. Melting points were measured on a Stuart Scientific SMP3 apparatus. Elemental analyses were carried out using a LECO CHNS-932. The single crystal X-ray data were collected on a Bruker Smart Apex CCD-based X-ray diffractometer with Mo-K α radiation (λ =0.71073 Å). Cyclic voltammograms were recorded at a scan rate of 100 mV/s on an ALS Electrochemical Analyzer Model 612D using a glassy carbon working, a Pt counter, and an Ag/Ag⁺ reference electrodes, and Bu₄NPF₆ (0.1 M) was used as supporting electrolyte for CH₂Cl₂ solutions.

4.1.1. 3,3'-(1,4-Phenylene)bis(1-phenylpropane-1,3-dione) (2). To a suspension of NaH (4.80 g, 200 mmol) in dry THF (100 mL), dimethyl terephthalate (9.71 g, 50.0 mmol) and acetophenone (11.7 mL, 100 mmol) were added and stirred for 20 min at ambient temperature under Ar atmosphere. Then the mixture was stirred at 50 °C for 33 h. After cooling the mixture to ambient temperature, the reaction was quenched by the addition of aqueous HCl (2 M, 100 mL) and a large amount of water. The resultant suspension was filtered and the collected solid was washed with water and chloroform, and dried in vacuo to yield **2**. The combined filtrate was extracted with chloroform and washed with water, dried over MgSO₄, filtered, and concentrated in vacuo. The crude material was recrystallized from toluene to yield **2** (14.0 g, 37.8 mmol, 76%) as a light yellow solid; mp 175.9–176.7 °C (lit. 176–177 °C).^{21 1}H NMR

(400 MHz, CDCl₃, 298 K): δ 16.84 (s, 2H, enol-OH), 8.10 (s, 4H, Ar–H), 8.05–7.99 (m, 4H, Ar–H), 7.63–7.56 (m, 2H, Ar–H), 7.56–7.49 (m, 4H, Ar–H), 6.93 (s, 2H, enol-CH) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 187.2, 183.6 (4C, C=O), 138.8, 135.5, 133.0, 128.9, 127.5, 127.5 (18C, Ar–C), 93.9 (2C, –CH₂–) ppm. IR (ATR): 3048 (C–H), 1524 (C=O) cm⁻¹.

4.1.2. 3.3'-(1.4-Phenylene)bis(2.2-dihydroxy-1-phenylpropane-1.3*dione*) (**4**). 3,3'-(1,4-Phenylene)bis(1-phenylpropane-1,3-dione) **2** (926 mg, 2.50 mmol) and NBS (890 mg, 5.00 mmol) were dissolved in DMSO (25 mL). The mixture was stirred at 80 °C for 24 h. After cooling to ambient temperature, distilled water (5.0 mL) was added to the solution and stirred for 1 h. The reaction was quenched by the addition of a large amount of water and the resultant suspension was filtered. The collected solid was washed with water and chloroform, and dried in vacuo to yield 4 (940 mg, 2.16 mmol, 87%) as a white solid; mp 98 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ 8.06 (s, 4H, Ar-H), 8.02 (d, J=7.6 Hz, 4H, Ar-H), 7.88 (s, 2H, -OH), 7.60 (t, J=7.4 Hz, 2H, Ar-H), 7.47 (dd, J₁=7.8 Hz, J₂=7.6 Hz, 4H, Ar–H) ppm. 13 C NMR (100 MHz, DMSO- d_6 , 298 K): δ 196.2, 196.1 (4C, C=0), 136.9, 133.8, 133.3, 130.2, 129.9, 128.7 (18C, Ar-C), 97.2 (2C, C(OH)₂) ppm. IR (ATR): 3368 (O–H), 1679 (C=O) cm⁻¹. Anal. Calcd for C₂₄H₁₈O₈: C, 66.36; H, 4.18; O, 29.47. Found: C, 65.83; H, 4.12; N, 0.17.

4.1.3. 3,3'-(1,4-Phenylene)bis(1-phenylpropane-1,2,3-trione) (**3**). 3,3'-(1,4-Phenylene)bis(2,2-dihydroxy-1-phenylpropane-1,3dione) **4** (1.53 g, 3.52 mmol) was heated at 100 °C for 4 h under reduced pressure (2 mmHg) to give **3** (1.40 g, 3.52 mmol, quant.) as an orange solid; mp 140.0–141.0 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.25 (s, 4H, Ar–*H*), 8.02 (d, *J*=6.8 Hz, 4H, Ar–*H*), 7.74 (t, *J*=7.4 Hz, 2H, Ar–*H*), 7.58 (dd, *J*₁=7.9 Hz, *J*₂=7.6 Hz, 4H, Ar–*H*) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 191.9, 191.8, 187.2 (6C, C=O), 136.6, 135.8, 132.0, 130.6, 130.4, 129.3 (18C, Ar–*C*) ppm. IR (ATR): 1723 (central C=O), 1675 (side C=O) cm⁻¹. Anal. Calcd for C₂₄H₁₄O₆: C, 72.36; H, 3.54; O, 24.10. Found: C, 71.80; H, 3.38; N, 0.00.

4.1.4. Hydration of **3**. To a solution of **3** (267 mg, 0.670 mmol) in acetone (6.3 mL), water (0.70 mL) was added and the solution was stirred at ambient temperature. After 1 h, the solvent of the resulting suspension was removed under reduced pressure to give **4** (291 mg, 0.670 mmol, quant.) as a white solid.

4.1.5. 3,3'-(1,4-Phenylene)bis(2-ethoxy-2-hydroxy-1-phenylpropane-(5). 3,3'-(1,4-Phenylene)bis(1-phenylpropane-1,2,3-1.3-dione) trione) 3 (851 mg, 2.14 mmol) was suspended in ethanol (4.0 mL) at ambient temperature and then the suspension was heated to 70 °C. After 20 min, the resulting solution was cooled to ambient temperature and allowed to stand for 1 h. The resulting precipitation was filtered, washed with *n*-hexane, and dried in vacuo. The crude product was recrystallized in dry EtOAc to afford 5 (798 mg, 1.63 mmol, 76%) as colorless blocks; mp 103 °C (decomp.). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.25 (s, 4H, Ar–H), 8.18 (d, J=7.4 Hz, 4H, Ar-H), 7.61 (t, J=7.4 Hz, 2H, Ar-H), 7.46 (dd, J₁=7.8 Hz, $J_2=7.6$ Hz, 4H, Ar-H), 5.91 (s, 2H, -OH), 3.69-3.48 (m, 4H, $-OCH_2-$), 1.20 (t, J=6.9 Hz, 6H, $-CH_3$) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 195.7, 195.3 (4C, C=O), 136.7, 134.5, 132.5, 130.7, 130.5, 128.7 (18C, Ar-C), 99.6 (2C, C(OH)(OR)), 59.2 (2C, -OCH₂-), 15.5 (2C, -OCH₃) ppm. IR (ATR): 3419 (O-H), 2978 (C-H), 1694, 1674 (C=O) cm⁻¹. Anal. Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34; O, 26.09. Found: C, 67.99; H, 5.12; N, 0.00.

4.1.6. *Ethanol-elimination* from **5**. 3,3'-(1,4-Phenylene)bis(2ethoxy-2-hydroxy-1-phenylpropane-1,3-dione) (**5**) (123 mg, 0.250 mmol) was heated at 120 °C for 1 h under reduced pressure (2 mmHg) to give **3** (100 mg, 0.250 mmol, quant.) as an orange solid.

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Supplementary data

Detailed X-ray crystal data of **3**, **4**, and **5**, ¹H NMR, ¹³C NMR, and FT-IR spectra. The supplementary data can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.065.

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- 19. Crystal data for **3**: C₂₄H₁₄O₆: *F*_W=398.35, monoclinic, space group *P*2₁/*c*, *a*=11. 301 (3) Å, *b*=5.8285 (15) Å, *c*=14.258 (4) Å, *β*=108.868 (3), *V*=888.7 (4) Å³, *Z*=2, *D*_{calcd}=1.489, 3846 reflections measured, 1563 unique reflections, 1302 observations (*I*>2.0*σ*(*I*)), *R*=0.0330 (*I*>2.0*σ*(*I*)), *R*_W=0.0888 (*I*>2.0*σ*(*I*)). CCDC 917094. Crystal data for **4**: C₂₇H₂₄O₉: *F*_W=492.46, triclinic, space group *P*-1, *a*=9.4625 (13) Å, *b*=11.3827 (16) Å, *c*=11.5726 (17) Å, *a*=92.198 (2), *β*=110.599 (2), *γ*=98. 513 (2), *V*=1148.4 (3) Å³, *Z*=2, *D*_{calcd}=1.424, 5521 reflections measured, 3983 unique reflections, 3230 observations (*I*>2.0*σ*(*I*)), *R*=0.0381 (*I*>2.0*σ*(*I*)), R=0.037 (*I*>2.0*σ*(*I*)), CCDC 917095, Crystal data for **5**: C₂₈H₂₆O₈: *F*_W=490.49, triclinic, space group *P*-1, *a*=8.337 (3) Å, *b*=8.518 (4) Å, *c*=8.983 (4) Å, *a*=71.791 (5), *β*=77.809 (5), *γ*=80.783 (6), *V*=589.2 (4) Å³, *Z*=1, *D*_{calcd}=1.382, 2815 reflections measured, 2035 unique reflections, 1731 observations (*I*>2.0*σ*(*I*)), *R*=0.0582 (*I*>2.0*σ*(*I*)), *R*_w=0.1553 (*I*>2.0*σ*(*I*)). CCDC 917096. For more detail on the data, see Supplementary data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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