



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



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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 bistricketone expanded and contracted by 10–30% in length during the interconversion.

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1. Introduction

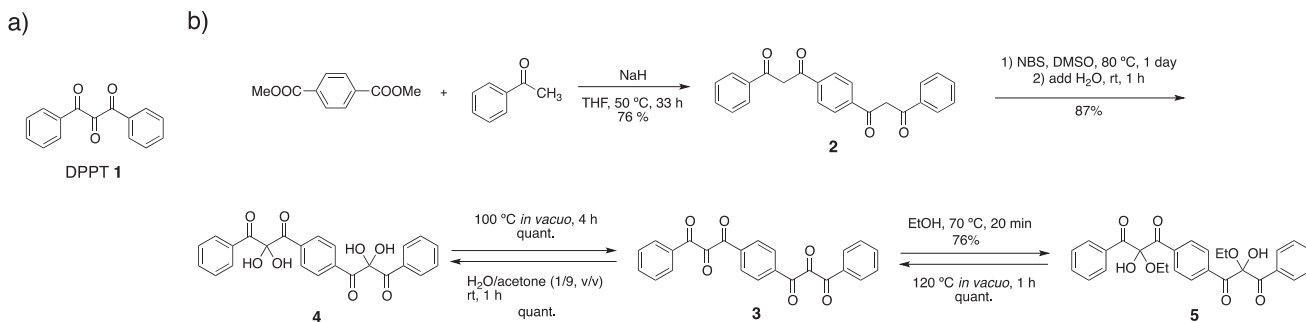
Vicinal tricarbonyl compounds, such as alloxan, 1,2,3-indanetrione, dehydroascorbic acid, and diphenylpropanetrione (DPPT, **1**, Scheme 1a), are known to have a highly electrophilic nature due to the three contiguous carbonyl groups, which are activated by the adjacent two carbonyl groups.^{1,2} Consequently, 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 P₂O₅.^{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-*s*-hydrindacenehexone, 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

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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 1,3-diketone **2**. Oxidation of the two 1,3-diketone moieties of **2** by *N*-bromosuccinimide (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 ethanol-adduct **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-*d*₆ (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*– π^* 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 1,4-dioxane/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.

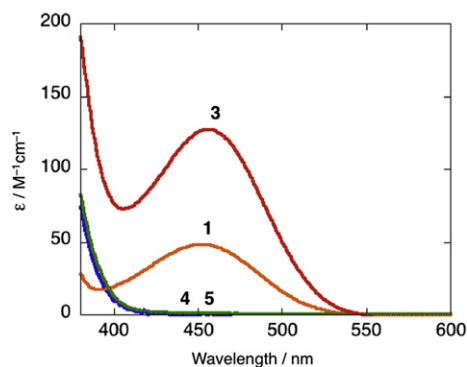


Fig. 1. UV/vis absorption spectra of **3** in 1,4-dioxane, **4** in 1,4-dioxane/water (97/3, v/v), and **5** in 1,4-dioxane/ethanol (97/3, v/v) along with DPPT **1** in 1,4-dioxane.

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