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5-Arylidene derivatives of Meldrum's acid: Synthesis, structural characterization using single crystal and powder crystal X-ray diffraction, and electronic properties

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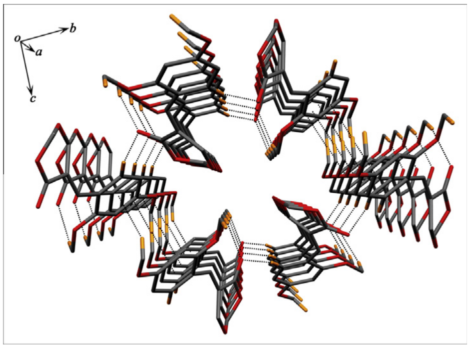
HIGHLIGHTS

- Crystal structures of 5-arylidene derivatives of Meldrum's acid.
- Structure determination from X-ray powder diffraction.
- Comparison of intermolecular interaction via Hirshfeld surface analysis.
- Electronic structure evaluation with DFT calculations.

GRAPHICAL ABSTRACT

Four 5-arylidene derivatives of Meldrum's acid have been synthesized, structurally characterized using single crystal and powder crystal X-ray diffraction and their intermolecular interactions are compared via Hirshfeld surface analysis. The electronic structures have been evaluated via DFT calculations.



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ABSTRACT

Four 5-arylidene derivatives of Meldrum's acid, 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**2**), 5-(3-hydroxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3**), 5-(3,4-dimethoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**) and 5-(2,4-dimethoxy benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**) have been synthesized and their crystal structures have been determined using single crystal X-ray diffractometry for **2**, **4** and **5** and X-ray powder diffraction for **3**. The nature of intermolecular interactions in **2**–**5** has been analyzed through Hirshfeld surfaces and 2D fingerprint plots. The DFT optimized molecular geometries in **2**–**5** agree closely with those obtained from the crystallographic studies. The crystal packing in **2**–**5** exhibits an interplay of O—H···O, C—H···O, C—H···Cl and C—H···π (arene) hydrogen bonds and $\pi \cdots \pi$ interactions, which assemble molecules into three-dimensional architecture in **2**, **3** and **5** and two-dimensional framework in **4**. The Hirshfeld surface analyses of **2**–**5**, Meldrum's acid (**1**) and a few related 5-arylidene derivatives of Meldrum's acid retrieved from the Cambridge Structural Database (CSD) indicate that about 85% of the Hirshfeld surface area (72% in **2** where H···Cl contribution is about 13%) in this class of compounds are due to H···H, O···H and C···H contacts. The HOMO–LUMO energy gap (>2.2 eV) in **2**–**5** indicates a significant degree of internal charge transfer within the molecule.

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Introduction

Meldrum's acid (MA), 2,2-dimethyl-1,3-dioxane-4,6-dione (**1**), is a cyclic isopropylidene ester of malonic acid with extensive synthetic potential [1–3]. The high value for C—H acidity of MA (pK_a 7.3 in DMSO at 25 °C) can be attributed to the presence of two hydrogen atoms of the methylene group adjacent to two electron withdrawing carbonyl groups, thus allowing simple alkylation and acylation of MA at the 5-position. The utility of MA as a starting scaffold in the synthesis of heterocyclic compounds with diverse substitution patterns has been well recognized [4,5]. Due to its unique reactivity, MA finds applications in the field of multi-component reactions, divergent oriented synthesis and flash vacuum pyrolysis [6,7]. It is well known that MA can undergo Knoevenagel condensation [8] with aromatic aldehydes to provide corresponding arylidenes, which are useful as intermediates toward synthesis of natural products and their analogs [9–12]. In this context, Knoevenagel condensation in environment-friendly conditions such as photochemical reactions prompted by infrared or micro-wave irradiation is considered as an attractive green procedure [13,14].

To study the effect of electron donating substitution at the methylene carbon atom of MA (**1**) on the resulting structures, particularly the role of weak hydrogen bonds in building molecular assemblies, we have synthesized four 5-arylidene derivatives of MA, 5-(4-chlorobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**2**), 5-(3-hydroxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3**), 5-(3,4-dimethoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**) and 5-(2,4-dimethoxy benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**) via photochemical condensation of MA with appropriate aromatic aldehydes. The crystal structures of **2**, **4** and **5** have been accomplished by single crystal X-ray analysis. Since our attempts to grow single crystal of **3** suitable for X-ray analysis resulted in assemblies of microcrystals, the structure determination of **3** was attempted using X-ray powder diffraction. The synthesis and crystallographic analyses of **2**–**5** are described in the present paper along with the DFT calculations to study the electronic structures. An investigation of close intermolecular interactions in compounds **2**–**5**, MA (**1**) and a few 5-arilydene derivatives of MA retrieved from the Cambridge Structural Database [15] via Hirshfeld surface analysis is also presented.

Experimental and computational methods

Materials and instrumentation

All chemicals were obtained from commercial sources (Sigma–Aldrich). Solvents were dried using standard methods, and chromatographic purifications were performed using silica gel (60–120 mesh). Elemental analysis was carried out with a Perkin–Elmer 240C elemental analyzer. Fourier Transform infrared (FTIR) spectra were measured on a Perkin Elmer Spectrum BX II spectrometer as KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded at 22 °C using a Bruker DPX-300 spectrometer using $CDCl_3$ as solvent. Melting points were determined using a sulfuric acid bath method and were uncorrected.

Synthesis

Equi-molar quantities of Meldrum's acid (**1**) (10 mmol) and different aromatic aldehydes (**2a**–**5a**) were taken in aqueous ethanol mixture (20 ml, 1:1 v/v) and irradiated with a 150 W tungsten lamp (Philips India Ltd.). The reaction time varied on an average from 10 to 20 min for different aromatic aldehydes (monitored by TLC after 5 min interval). Upon completion of reaction, the reaction mixture was cooled and the crystalline products (**2**–**5**) so obtained (Scheme 1) were filtered, washed with water and dried *in vacuo*.

*5-(4-Chloro-benzylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione (**2**)*

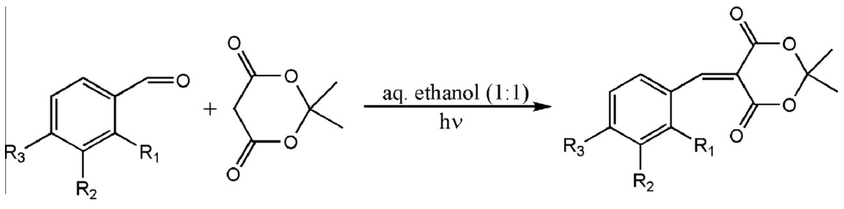
Colorless solid; yield 90%; mp 156(1) °C; IR (KBr) ν_{max}/cm^{-1}: 3010, 2988, 2864, 1770, 1738, 1732, 1694, 1682, 1622; ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}) 8.37 (s, 1H), 8.03 (d, *J* 8.2 Hz, 2H), 7.46 (d, *J* 8.3 Hz, 2H), 1.81 (s, 6H); elemental analysis: found C 58.70, H 4.25%, calculated for $C_{13}H_{11}O_4Cl$; C 58.64, H 4.13%.

*5-(3-Hydroxy-benzylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione (**3**)*

Light green solid; yield 79%; mp 166(1) °C; IR (KBr) ν_{max}/cm^{-1}: 3421, 3006, 2990, 1765, 1713, 1608, 1591; ^{1}H NMR (300 MHz, $CDCl_3$, δ_{ppm}) 8.36 (s, 1H), 7.80 (s, 1H), 7.46 (d, *J* 7.7 Hz, 1H), 7.36 (t, *J* 7.9 Hz, 1H), 7.08 (dd, *J* 7.9 Hz, 1.9 Hz, 1H), 5.70 (s, 1H), 1.80 (s, 6H); elemental analysis: found C 62.80, H 4.75%, calculated for $C_{13}H_{12}O_5$; C 62.90, H 4.84%.

*5-(3,4-Dimethoxy-benzylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione (**4**)*

Light yellow solid; yield 88%; mp 171(1) °C; IR (KBr) ν_{max}/cm^{-1}: 3014, 2984, 2942, 1747, 1714, 1602, 1578, 1557; ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}) 8.36 (s, 1H), 8.29 (d, *J* 2.0 Hz, 1H), 7.64 (dd, *J* 8.5 Hz, 2.0 Hz, 1H), 6.94 (d, *J* 8.5 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 1.79(s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ_{ppm}) 164.3, 160.8, 158.4, 154.9, 149.0, 132.8, 125.3, 115.9, 110.9, 110.7, 104.3, 56.4, 56.2, 27.6; elemental analysis: found C 61.70, H 5.60%, calculated for $C_{15}H_{16}O_6$; C 61.64, H 5.48%.



2a-5a 1 2-5

2: $R_1 = H, R_2 = H, R_3 = Cl$
3: $R_1 = H, R_2 = OH, R_3 = H$
4: $R_1 = H, R_2 = OMe, R_3 = OMe$
5: $R_1 = OMe, R_2 = H, R_3 = OMe$

Scheme 1.