Analytical, Spectroscopic and Crystallographic Characterization of 3-[(2E)-3-Phenylprop-2-en-1-ylidene]pentane-2,4-dione

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The structure of 3-[(2E)-3-phenylprop-2-en-1-ylidene]pentane-2,4-dione was determined by X-ray crystallography. The crystallographic data analysis reveals that the title compound crystallizes in monoclinic system and space group $P2_1/a$ with the cell parameters $a = 12.7006(4)\text{Å}$, $b = 10.0271(5)\text{Å}$, $c = 20.1044(10)$ and $\beta = 106.525(3)^\circ$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.083$ and $wR2 = 0.257$. Some spectroscopic data were also reported.

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Knoevenagel condensation is widely the main method to obtain a carbon-carbon double-bond reacting aldehyde or ketone with organic acid compounds. The condensation between formaldehyde and diethyl malonate, in the presence of diethylamine, appears to be the 1st example of this reaction.¹ Doebner modification, for instance, is used to synthesize α -, β -unsaturated compounds with advantage since the reaction can be performed at room temperature, tolerate a variety of functional groups, and avoid unnecessary reactions.² Another modification of the Knoevenagel reaction is known as the Weiss-Cook reaction, which is an extremely versatile reaction used for the synthesis of a high number of natural products.^{3,4} The title compound (Fig. 1) was obtained by following the literature.³ Briefly, about 10.3 mL (0.1 mol) of acetylacetone was mixed with 13.3 mL of cinnamaldehyde (0.1 mol), and the mixture was stirred under an ice bath. After 2 h, only one drop of pyrrolidine was added to the reaction solution, and stirring at room temperature (25°C) continued for 10 min. The solution was washed 3 times with a mixture of 10 mL of a HCl aqueous solution (1.0 mol L⁻¹) and 10 mL of CH₂Cl₂. The organic layer

was concentrated, yielding a residue which was purified by column chromatography using n-hexane and ethyl-acetate as an eluent (95:5) to afford the product in solution. Light-yellow crystals were obtained by slow evaporation of the solvent. The yield was 72%, m.p.: 105 – 107°C. *Anal.* Calcd (%) for C₁₄H₁₄O₂: C, 78.5; H, 6.59; Found (%): C, 78.3; H, 6.61. IR bands: $\nu_{\text{C=O}}$, 1700 cm⁻¹; $\nu_{\text{C=C}}$ + $\nu_{\text{C=C aromatic}}$ at 1607, 1541 and 1345 cm⁻¹; $\nu_{\text{C-O}}$ at 1198 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm): 2.34 (s, 3H, CH₃) and 2.40 (s, 3H, CH₃); 7.035 (dd, 1H, $J = 13.5$ Hz, $-\text{HC}=\text{CH}-\text{CH}=\text{}$); 7.49 ($J = 11.4$ Hz, 1H, $-\text{HC}=\text{CH}-\text{CH}=\text{}$) and 7.32 ($J = 15.4$ Hz, 1H, $-\text{HC}=\text{CH}-\text{CH}=\text{}$); 7.61 (d, 2H, $J = 7.2$, H_{aromatic}); 7.42 (m, 3H, H_{aromatic}). ¹³C (125 MHz, DMSO-*d*₆) δ (ppm) 203 and 198 (C=O); 145, 142.6 and 124 ($-\text{HC}=\text{CH}-\text{CH}=\text{}$); 142, 135, 128.3, 129.5 and 130.3 (C_{aromatic} and C_{non-hydrogenated}). UV-Vis: 332 nm ($\pi-\pi^*$ transition). The X-ray measurements were performed on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073\text{Å}$) radiation. Diffraction data were collected (φ and ω scans with κ -offsets) with COLLECT.⁵ Integration, scaling and reduction of the diffraction intensities were performed with HKL DENZO-SCALEPACK⁶ suite of programs. The data were corrected empirically for absorption effects with the multi-scan method.⁷ The unit cell parameters were obtained by least-squares refinement based on the angular settings for all collected reflections using HKL SCALEPACK.⁸ The structure was solved by direct methods with SHELXS-97⁹ and the molecular model refined by the full-matrix least-squares procedure on F2 with SHELXL-97.¹⁰ The compound belongs to the monoclinic system. The a , b and c axes are: 12.7006(4)Å, 10.0271(5)Å and 20.1044(10)Å, respectively, and the β angle is 106.525(3)°. Crystallographic data are reported in Table 1 and the some torsion angles are described in Table 2. There is no solvent molecule in this structure, and there are two independent asymmetric units in the unit cell ($Z = 8$). The slight difference between two asymmetric units could only be observed in the torsion angles of the ketone groups. The C12-C11-C111-C112 angle is -121.3° while in a similar asymmetric unit is -122.2° (C22-C21-C213-C214). Also, the C12-C11-C113-C114 angle is 13.6° , while C22-C21-C211-C212 is 9.4° . An ORTEP 3 representation of only one molecule is represented in Fig. 2.

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal data and structure refinement for the title compound

Empirical formula	C ₁₄ H ₁₄ O ₂
Formula weight	214.25
Temperature	296(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>
Unit cell dimensions	<i>a</i> = 12.7006(4) Å <i>b</i> = 10.0271(5) Å <i>c</i> = 20.1044(10) Å β = 106.525(3)°
Volume	2454.55(19) Å ³
Z	8
Density (calculated)	1.160 g/cm ³
Absorption coefficient	0.077 mm ⁻¹
<i>F</i> (0 0 0)	912
Crystal size	0.295 × 0.182 × 0.163 mm ³
θ range for data collection	2.63 to 25.99°
Index ranges	−14 ≤ <i>h</i> ≤ 15, −12 ≤ <i>k</i> ≤ 11, −23 ≤ <i>l</i> ≤ 24
Reflections collected	24070
Independent reflections	4711 [<i>R</i> _{int}] = 0.1136]
<i>R</i> 1 and <i>wR</i> 2	0.0831 and 0.2565
Completeness to θ = 25.99°	97.9%
Absorption correction	None
CCDC number	999316

Table 2 Torsion angle of the *keto* groups and H interactions

Atom	Torsion angle/°
C12–C11–C111–C112	−121.3(4)
C22–C21–C213–C214	−122.2(4)
C12–C11–C113–C114	13.6(6)
C22–C21–C211–C212	9.4(6)
Atom	Interaction/Å
O11–H12C12	2.519
O11–H11FC114	2.612
O22–H22C22	2.521
O22–H21BC212	2.659
O12–H110C110	2.526

However, the same features were observed for both molecules. Intermolecular interactions between O11...HC12, O11...HC114, O12...HC110 and O22...HC22 and O22...HC212 are present and they are also described in Table 2. NMR and IR spectra are available as supporting materials.

Fig. 2 ORTEP structure of both independent asymmetric units of the title compound. All atoms were labeled. All atoms show 30% probability ellipsoids.

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Supporting Information

This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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