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ISSN: 2278-1862

Journal of Applicable Chemistry

2020, 9 (5): 684-690

(International Peer Reviewed Journal)

Synthesis and Crystal Structure Analysis of propyl 3-(4-acetoxyphenyl) Acrylate

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Accepted on 5th August, 2020

ABSTRACT

The title compound propyl 3-(4-acetoxyphenyl) acrylate is synthesized and the structure was confirmed by X-ray diffraction. X-ray diffraction study reveals that the compound crystallizes in the triclinic crystal system in space group P-1 with cell parameters a= 7.798 (10) Å, b= 8.800 (11) Å, c= 10.731 (13) Å, α = 92.001 (19)°, β= 91.45 (3)°, γ= 107.52 (2)°, Z=2 and V=701.3 (15) Å^3. The molecule exhibits intramolecular hydrogen bonds of the type C–H...O which can account for the stability of the molecule.

Graphical Abstract

Keywords: p-hydroxy cinnamic acid, Hirshfeld surface analysis, Fingerprint plot.

INTRODUCTION

The para-hydroxycinnamic acid is a natural product which is found in many plants. This naturally occurring phenolic acid falls into flavonoids class of compounds. This p-cinnamic acid derivative compounds are found immense applications in fragrances, fluorescence, optical materials and mainly medicinal applications, such as age-dependent chronic neurodegenerative disease like Alzheimer's disease, anti-infective agent, contraceptive agents, free radical scavengers, and anti-oxidant and etc [**1, 2**]. Further, this cinnamic acid analogues may also used in polymer synthesis and their applications [**3**]. Since we are working on liquid crystal and single crystal structural studies of various heteroaromatic cores like coumarin, phenylene, naphthalene and other cores derived molecules [**4, 5**]. In continuation of our research in different class of single crystallographic studies, here we report medicinally potent Propyl 3-(4-acetoxyphenyl) acrylate molecule.

MATERIALS AND METHODS

The title compound Propyl 3-(4-acetoxyphenyl) acrylate was synthesized using the procedure reported elsewhere [**6-8**]. The (E)-3-(4-acetoxyphenyl) acrylic acid was alkylated with propylbromide in the presence of potassium carbonate as a base in dry Dimethylformamide under reflux condition for 2 h. After completion of reaction, the solvent was removed under vaccumme. The crude product obtained was purified by column chromatography with pure ethylacetate as an eluent. The chemical formula $C_{14}H_{16}O_4$ is having molecular weight: 248.27. The micro elemental analysis calculated is C, 67.73; H, 6.50; O, 25.78 % and practically found values are C, 67.81; H, 6.55%. The pure single crystals are grown by slow evaporation of ethyl-alcohol at room temperature and it shows melting point 90-91°C.

Crystal structure determination: A transparent single crystal of the synthesized compound with approximate dimensions of 0.25 x 0.24 x 0.23 mm was used for X-ray diffraction study. The title compound Propyl 3-(4-acetoxyphenyl) acrylate is synthesized and the structure was confirmed by X-ray diffraction. X-ray diffraction study reveals that the compound crystallizes in the triclinic crystal system in space group *P*-1 with cell parameters a=7.798 (10) Å, b=8.800 (11) Å, c = 10.73 (13) Å, α=92.001(19)°, β=91.45 (3)°, γ= 107.52 (2)°, Z=2 and V=701.3 (15) Å^3. Data were collected on a Bruker CCD diffractometer equipped with MoKα radiation. Data reduction and applying absorption correction were carried out using the APEX 2 package [**7**]. Crystal structure was solved by direct methods using *SHELXS-97* [**8**] and was refined by full matrix least squares refinement against F^2 using *SHELXL-97*. Geometry Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles. Refinement on F^2 for all reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors w*R* and all goodness's of fit S are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on all data will be even larger. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at chemically acceptable positions. A total of 168 parameters were refined with 3088 which converged the residual to *R*=0.068.

Table 1. Crystal data and structure refinement details.

CCDC Number	
Empirical Formula	C_{14} H_{16} O_4
Formula Weight	248.27
Temperature	293
Wavelength	0.71073
Reflections for cell determination	3987
Crystal System	triclinic
Space Group	P-1 (No. 2)
Cell Dimensions	a=7.798(10) Å, b=8.800(11) Å, c=10.731(13) Å α=92.001(19)˚ , β=91.45(3)˚, γ=107.52(2)˚
Volume	701.3(15) Å^3
Z	2
Density (Calculated)	1.176 g/cm^3
Absorption Coefficient	0.086 mm^{-1}
F_{000}	264
Crystal Size	0.25 x 0.24 x 0.23 mm
θ range for data collection	3.0° to 27.5°
Index ranges	-10 ≤ h ≤ 6, -7 ≤ k ≤ 11,-13 ≤ l ≤ 13
Reflection Collected	3987
Independent Reflections	3088
Refinement Method	Full matrix least-squares on F^2
Data/ Restraints/Parameters	3088 / 0 / 168
Goodness-of-fit on F^2	1.05
Final [I>2σ(I)]	R=0.0686, wR^2=0.14152, S=1.05
Largest diff. peak and hole	-0.36 and 0.37 e Å^{-3}

The geometrical calculations were carried out using the program PLATON [9]. The molecular and packing diagrams were generated using the software MERCURY [10]. The details of the crystal structure and data refinement are given in table 1. The list of selected bond lengths and bond angles are given in table 2 and table 3. A list of hydrogen-bond geometry is given in the table 4. The *ORTEP* diagram of the title compound with thermal ellipsoids drawn at 50% probability is shown in the figure 1-4 show the packing diagrams viewed down *a, b* and *c* axes respectively.

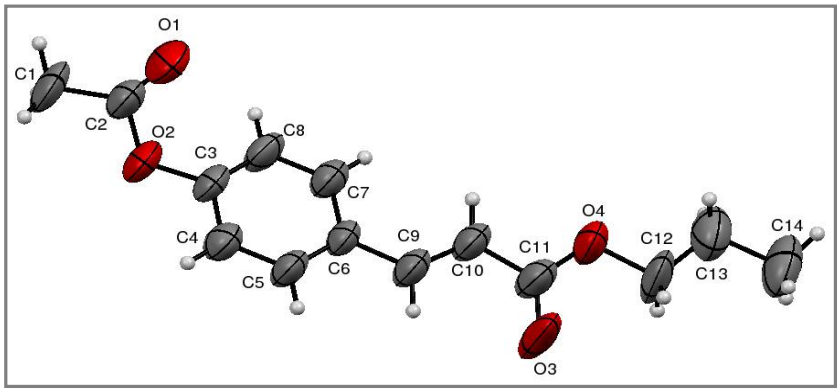

Figure 1. The *ORTEP* diagram of the propyl 3-(4-acetoxyphenyl) acrylate with 50% probability ellipsoids.

Table 2. Selected Bond Lengths (Å)

Atoms	Length	Atoms	Length
O(1) - C(2)	1.195(10)	C(6) - C(7)	1.419(8)
O(2) - C(2)	1.381(9)	C(6) - C(9)	1.467(8)
O(4) - C(12)	1.473(9)	C(1) - C(2)	1.507(10)
O(3) - C(11)	1.208(9)	C(13) - C(14)	1.540(12)

Table 3. Selected Bond Angles (deg)

Atoms	Angle	Atoms	Angle
C(12)-C(13)-C(14)	113.5(7)	C(11)-O(4)-C(12)	116.2(5)
O(2)-C(2)- C(1)	110.6(6)	C(5)-C(6) - C(7)	118.1(5)
O(4)-C(12)-C(13)	111.2(7)	C(6) -C(9) -C(10)	128.8(5)

In the title compound, the acrylate group makes an angle of 56.08° with benzene ring. Benzene ring is deviated by an angle of 25.16° with the atoms (C9-C14). The bond distance between C2 and O2 is 1.38 Å a small deviation compared to the standard value. The bond distance between C13-C14 is slightly larger than the standard value. The molecule is stabilized by intramolecular hydrogen bond of the type C-H...O with the symmetry code -x, 1-y,2-z . No classic hydrogen bonds found here.

Table 4. Hydrogen-bond geometry (Å, deg)

D-H...A	D - H	H...A	D...A	D-H...A	Symmetry code
C(9)-H(9)...O(3)	0.93	2.53	3.410 (9)	2.61	-x,1-y,2-z

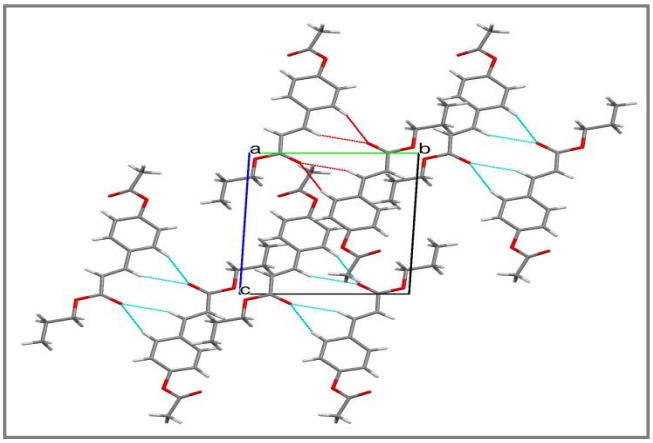

Figure 2. Packing diagram of the molecule, viewed along the crystallographic ***a*** axis.

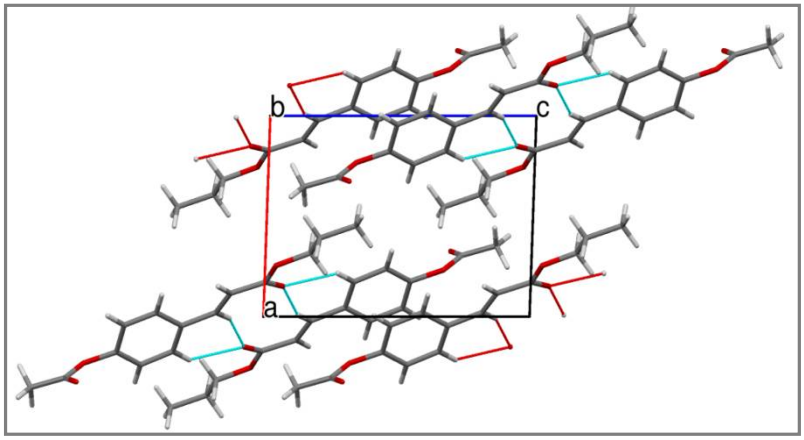

Figure 3. Packing diagram of the molecule, viewed along the crystallographic ***b*** axis.

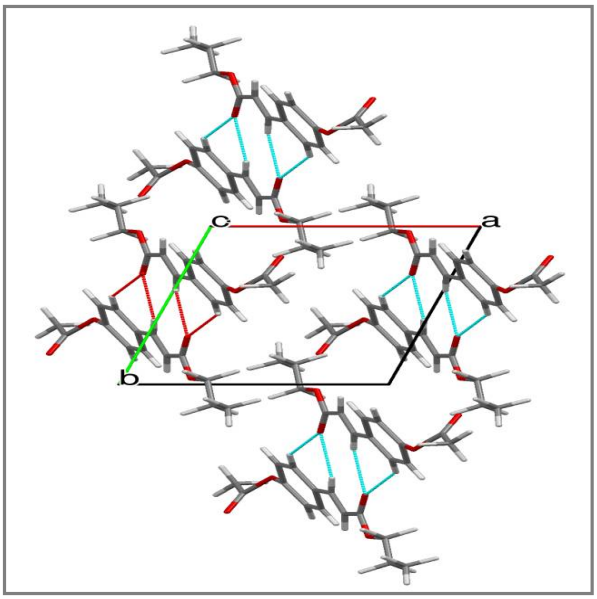

Figure 4. Packing diagram of the molecule, viewed along the crystallographic ***c*** axis.

RESULTS AND DISCUSSION

Hirshfeld surface and electrostatic potential surface analysis: Hirshfeld surfaces, electrostatic potential and the associated 2D-fingerprint plots were calculated using Crystal Explorer 3.1, [**11**] which accepts a structure input file in CIF format. The fingerprint plot provides a summary of intermolecular contacts in the crystal, which is a combination of d_i and d_e. For each point on the Hirshfeld iso surface, two distances d_e, the distance from the point to the nearest nucleus external to the surface, and d_i, the distance to the nearest nucleus internal to the surface, are defined [**12**]. The parameter d_{norm} displays a surface with a red-white-blue colour scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are de void of close contacts. The 3D d_{norm} surface of the title compound was shown in figure 5. The molecular electrostatic potential is a physical property of a molecule can be defined in terms of total charge distribution of the molecule. A portion of a molecule that has a negative electrostatic potential is susceptible to an electrophilic attack-the more negative the better. It provides a medium to understand the electron density which is useful for determining the electrophilic reactivity and nucleophilic reactivity as well as hydrogen-bonding interactions. The different values of the electrostatic potential at the surface are represented by different colours; red and blue areas refer to the regions of negative and positive potentials and corresponding to the electron–rich and electron–poor regions [**13**]. The electrostatic potential is mapped on Hirshfeld surfaces using DFT theory over the range of –7.184 a.u to –7.184 a.u. as shown in figure 6 [**14**].

The contribution of various intermolecular contacts to the Hirshfeld surface is given by in the table 5. The major contribution is from H...H (49.7%) contacts. The minor contribution is from O...O (0.5%). figure 7 shows the percentage contributions of H...H (49.7%), O...H (15.8%), H...O (13.7%) and C...H (9.0%) contributed to total Hirshfeld surface area of the molecules. The other contributions are O...C (1.0%), C...O (1.2%), C...C (2.0%) and H...C (7.1%). These contacts are highlighted by a conventional mapping of d_{norm} on the molecular Hirshfeld surface as shown in figure 5.

Table 5. Percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts of molecules in the crystal.

Inter-contacts	Contributions (%)	Inter-contacts	Contributions (%)	Inter-contacts	Contributions (%)
O...H	15.8	C...O	1.2	H...O	13.7
O...C	1.0	C...C	2.0	H...C	7.1
O...O	0.5	C...H	9.0	H...H	49.7

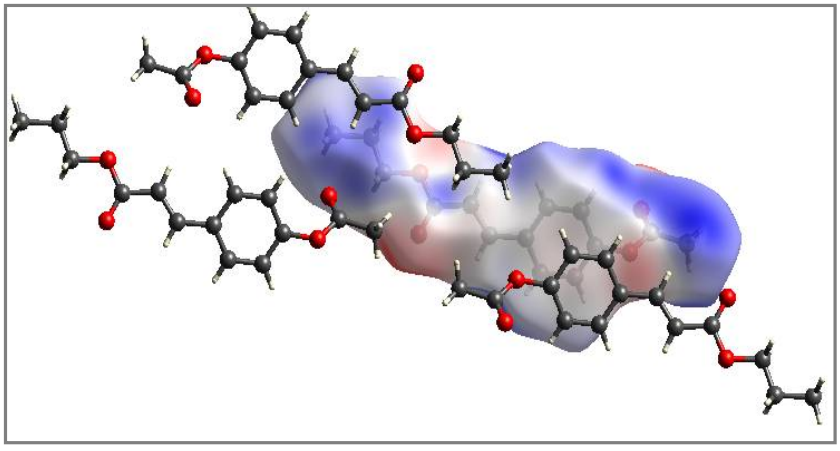

Figure 5. d_{norm} mapped on Hirshfeld surface for the visualization of intermolecular contacts of the title compound.

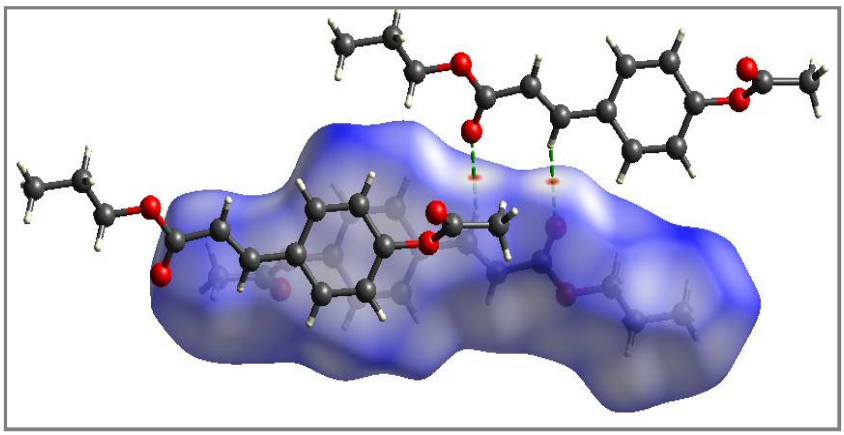

Figure 6. The electrostatic potential is mapped on Hirshfeld surfaces of the title compound.

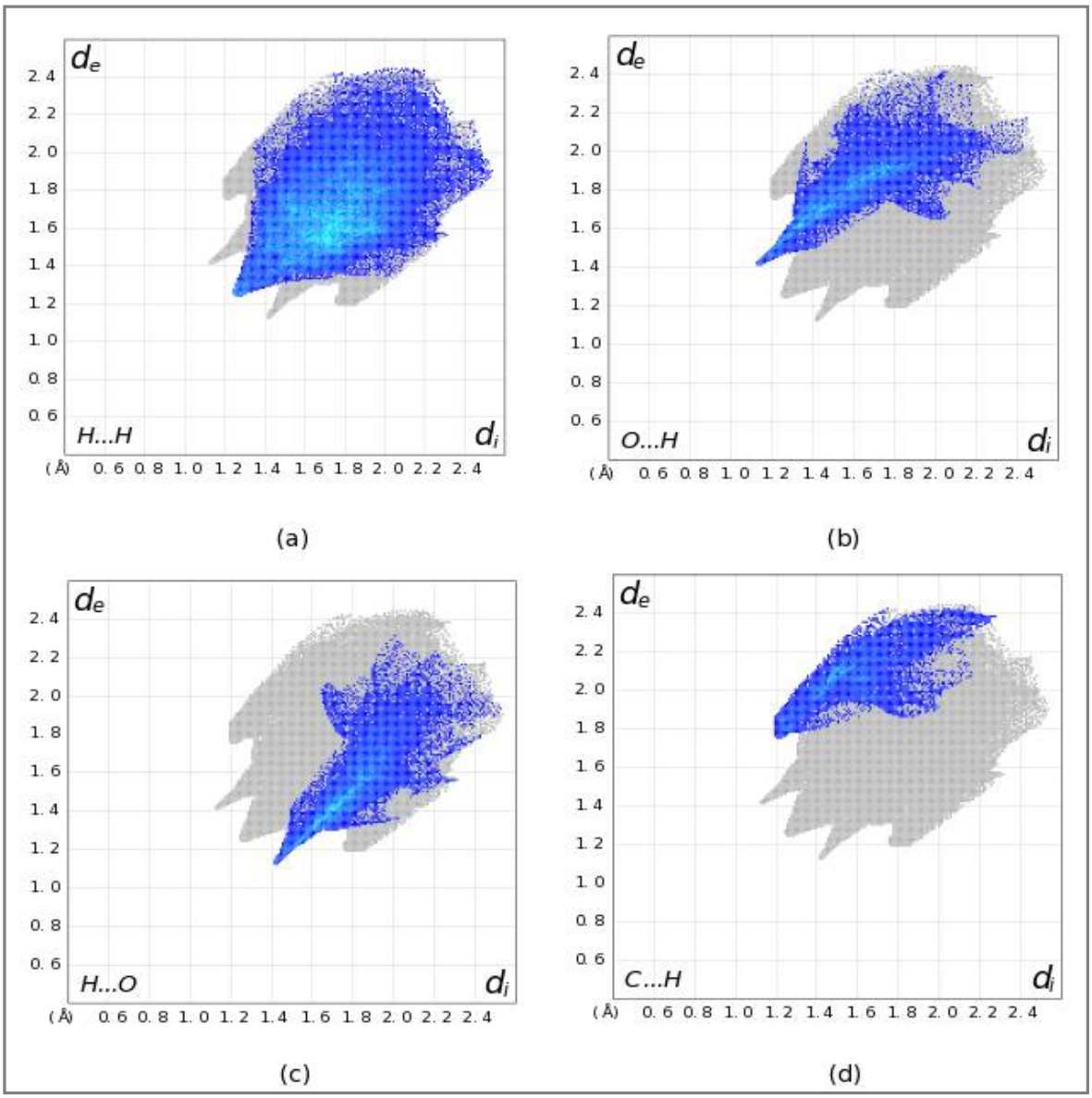

Figure 7. Fingerprint plot of the title compound resolved into H...H (a), O...H (b), H...O (c) and C...H (d) contacts showing the percentage of contacts contributed to the total Hirshfeld surface area for the molecule.

APPLICATION

Propyl 3-(4-acetoxyphenyl) acrylate are found immense applications in fragrances, fluorescence, optical materials and mainly medicinal applications, such as age-dependent chronic neuro degenerative disease like Alzheimer's disease, anti-infective agent, contraceptive agents, free radical scavengers, and anti-oxidant and etc [**1, 2**]. Further, this cinnamic acid analogues may also used in polymer synthesis and their applications.

CONCLUSION

The para-hydroxycinnamic acid is a natural product which is found in many plants. In order to understand the structural activity, the title component is synthesized and the structure was confirmed by X-ray diffraction. X-ray diffraction study reveals that the compound crystallizes in the triclinic crystal system in space group *P*-1. The Hirshfeld surface analysis shows that the major contributions are from H...H (49.7%) of various intermolecular contacts the Hirshfeld surface.

ACKNOWLEDGEMENT

The author would like to thank Mr. Mahesh a research student, University of Mysore for experimental help.

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