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A Study on the Crystal Structure of Ethyl 2-(2, 4-difluoro phenyl) acetate

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Abstract: The title compound $C_{10}H_{10}F_2O_2$ was synthesized by esterification of 2- (2, 4-difluoro phenyl) acetic acid. The synthesized compound was recrystallized by slow Evaporation of the saturated solution of ethanol and single crystal was selected for X-ray Diffraction study. The compound was characterized by ^{1}H NMR. A monoclinic unit cell of $C_{10}H_{10}F_2O_2$ was diffracted for X-ray beam of wavelength 0.71073 Å, from which we got maximum angle of reflection 24.75° (0.85 Å resolution), with R value 0.067 and the dihedral angle between the acetyl group and phenyl ring as 113.4º.
Key words: Crystallization, Crystal Structure, Refinement, SHELXTL, Monoclinic.

Introduction:

Ethyl 2-(2, 4-difluoro phenyl) acetate is a fluorinated phenyl group containing ethyl ester on side chain, is a important chemical and pharmaceutical intermediate, for synthetic molecules[1-2]. In the background of the present study, the supra molecular synthons were reported by Thalladi[3], the similar related compounds, such as Phenyl acetic acid, 2-(2,4-Dichloro phenyl) acetic acid[5], 2-(2-Bromo phenyl) acetic acid[6] and their crystal structure were reported in literature. The main aim of the study is to, solve the crystal structure of the Ethyl 2-(2, 4-difluoro phenyl) acetate.

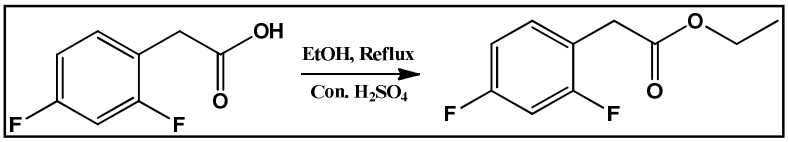
Experimental Section:

Materials and Methods:

Reaction was performed in two necked 100 mL round bottom flask. The glasswares were previously rinsed with acetone and dried in hot air oven. The monitoring of reaction was carried out by Thin Layer Chromatography (TLC), using aluminium plate, coated with silica (Merck), by using appropriate solvent mixtures. The melting point (mp) was determined by open capillary method and was uncorrected. The product was confirmed by LCMS and ^{1}H NMR spectral studies. NMR spectrum was recorded by an Agilent 500 MHz instrument and LCMS was recorded by positive mode, using solvent 0.1 % formic acid in Acetonitrile. The crystal was diffracted with the Bruker SAINT Software package using a narrow-frame algorithm. The structure was solved and refined using the Bruker SHELXTL Software Package[7].

Synthesis and crystallization:

The title compound was synthesized from esterification of 2- (2, 4-difluoro phenyl) acetic acid. Here, 2-(2, 4-difluoro phenyl) acetic acid was refluxed with ethanol in the presence of catalytic amount of Con. H_2SO_4. After completion of the reaction (confirmed by TLC), the reaction mixture was evaporated, quenched with water and extracted with ethyl acetate[8]. The organic layer was evaporated and the solid material was dissolved in minimum quantity of ethanol. On slow evaporation, colorless crystals were formed.



Melting point: 44-45° C

^{1}H NMR spectrum: ($CDCl_3$, 500 MHz), δ 7.39-7.34 (m, 1H), 6.99-6.93 (m, 2H), 4.32-4.278 (q, 2H), 1.40-1.37 (t, *J* = 7.0, 14.0 Hz, 3H). LCMS found: *m/z* 201.01 for [M^++1] peak and calculated for $C_{10}H_{10}F_2O_2$ 200.06

Results and Discussion:

Single Crystal X-Ray Diffraction:

Single crystal of the suitable size of the title compound was selected for the data collection. X-ray intensity were collected on Oxford Xcalibur Eos (Nova) CCD diffractometer with x-ray generating operation at 50 kV and 1mA, using MoKα radiation (λ = 0.7107 Å) Here a specimen of $C_{10}H_{10}F_2O_2$ was used for the X-ray crystallographic analysis. The total exposure time was 2.01 hrs. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 4382 reflections to a maximum θ angle of 24.75° (0.85 Å resolution), of which 1502 were independent (average redundancy 2.917, completeness = 92.2%, R_{sig} = 11.56 %) and 727 (48.40 %) was greater than 2σ(F^2). The final cell constants of a = 13.226(6) Å, b = 5.285(2) Å, c = 15.056(6) Å, β = 115.151(6)°, volume = 952.6(7) Å^3, are based upon the refinement of the XYZ-centroids of 691 reflections above 20 σ(I) with 5.978° < 2θ < 44.49°. Data was corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.819.

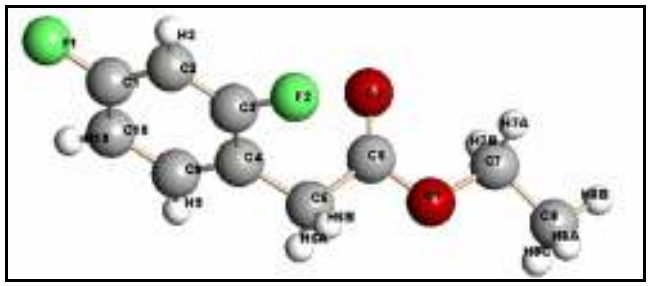


Fig 1. The molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 30 % probability level.

Table 1. Sample and Crystal data

Chemical formula	$C_{10}H_{10}F_2O_2$	
Formula weight	200.18	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.226(6) Å	α = 90°
	b = 5.285(2) Å	β = 115.151(6)°
	c = 15.056(6) Å	γ = 90°
Volume	952.6(7) Å^3	
Z	4	

Density (calculated)	1.396 Mg/cm^3	
Absorption coefficient	0.121 mm-1	
F(000)	416	

Refinement

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{10}H_{10}F_2O_2$. Crystal data, data collection and structure refinement details are summarized in Table 2. The C-H bound atoms were placed in calculated positions and allowed to ride on their carrier atom C-H = 0.93–0.97 A°, with Uiso(H) = 1.5Ueq(C) for methyl H atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 128 variables converged at R_1 = 6.71%, for the observed data and wR_2 = 23.37% for all data. The goodness-of-fit was 0.926. The largest peak in the final difference electron density synthesis was 0.219 $e^-/Å^3$ and the largest hole was -0.261 $e^-/Å^3$ with an RMS deviation of 0.075 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.396 g/cm^3 and F(000), 416 e^-.

Table 2. Data collection and structure refinement

Theta range for data collection	1.70 to 24.75°	
Index ranges	-15<=h<=15, -6<=k<=6, -17<=l<=17	
Reflections collected	4382	
Coverage of independent reflections	92.2 %	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1502 / 0 / 128	
Goodness-of-fit on F2	0.926	
Δ/σmax	0.012	
Final R indices	727 data; I>2σ(I)	R_1 = 0.0671, wR_2 = 0.1719
	all data	R_1 = 0.1320, wR_2 = 0.2337
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1229P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.219 and -0.261 eÅ-3	
R.M.S. deviation from mean	0.075 eÅ-3	

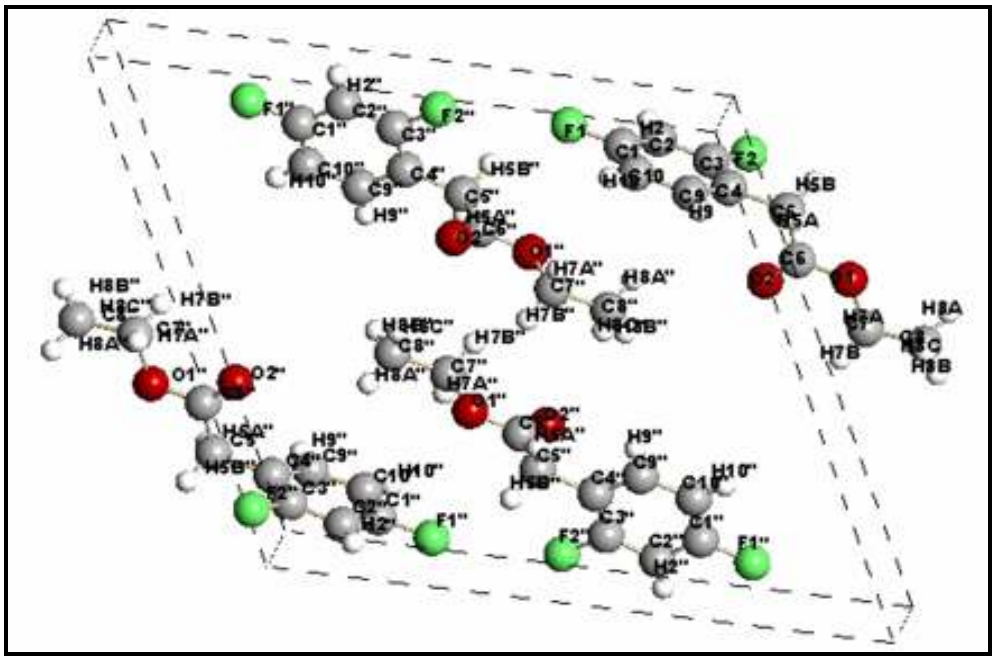


Fig 2. Partial packing diagram for the title compound, viewed along the c axis.

The acetyl group forms a dihedral angle of 113.4º on the phenyl ring corresponding to the axial position. However, phenyl ring C1/C2/C3/C4/C9/C10 are in equatorial position with respect to acetyl group C5/C6/O1/C7/C8 as confirmed by the similar compound 2-(2,4-Dichloro phenyl) acetic acid[5].

Conclusion:

Single crystal was grown by the slow evaporation method and by NMR analysis confirms the formation of title compound. The single crystal X-ray Diffraction study reveals that, the compound crystallizes in the monoclinic crystal system.

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