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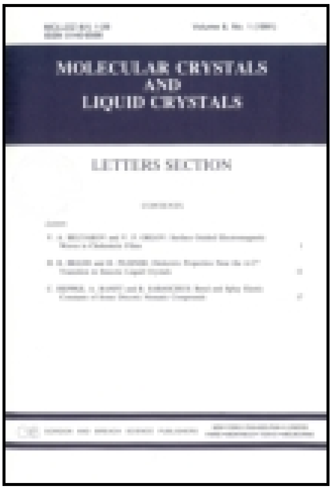

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Synthesis, Characterization, Crystal Structure, and Thermal Analysis of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic Acid

Prakash S. Nayak[a], Badiadka Narayana[a], Sumati Anthal[b], Vivek K. Gupta[b], Rajni Kant[b] & H. S. Yathirajan[c]

[a] Department of Studies in Chemistry, Mangalore University, Mangalagangotri, Karnataka, India

[b] Post-Graduate Department of Physics & Electronics, University of Jammu, Jammu Tawi, India

[c] Department of Studies in Chemistry, University of Mysore, Manasangotri, Mysore, India

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Synthesis, Characterization, Crystal Structure, and Thermal Analysis of 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic Acid

PRAKASH S. NAYAK,[1] BADIADKA NARAYANA,[1,*]
SUMATI ANTHAL,[2] VIVEK K. GUPTA,[2] RAJNI KANT,[2]
AND H. S. YATHIRAJAN[3]

[1]Department of Studies in Chemistry, Mangalore University, Mangalagangotri, Karnataka, India
[2]Post-Graduate Department of Physics & Electronics, University of Jammu, Jammu Tawi, India
[3]Department of Studies in Chemistry, University of Mysore, Manasangotri, Mysore, India

*4-[(3-Acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid (**1**) is synthesized by a ring opening reaction of itaconic anhydride with 3-aminoacetophenone and characterized by FT-IR, ^1H NMR, UV-Vis, TGA, DTA, and single crystal X-ray diffraction. The crystal of **1** belongs to triclinic unit cell in the P-1 space group with the unit cell dimensions $a = 4.9485(3)$, $b = 5.3614(6)$, $c = 22.457(2)$ Å, $\alpha = 88.295(8)$, $\beta = 89.379(7)$, $\gamma = 84.495(7)$, and $Z = 2$ The crystal structure is solved by direct methods using single-crystal X-ray diffraction data collected at room temperature and refined by full-matrix least-squares procedures to a final R-value of 0.0467 for 1623 observed reflections. Intermolecular N—H ... O and O—H ... O hydrogen bonds links the molecules into chains along [010] direction. In addition the thermal stability of the **1** is determined by using DTA, TGA analysis, and wavelength absorption at $\lambda_{max} = 297$ nm is determined by UV-Vis spectrophotometer.*

Keywords Crystal structure; FTIR; intermolecular interactions; itaconic anhydride; NMR spectrum; thermal property

1. Introduction

Itaconic anhydride (ITA) is an unsaturated dicarbonic organic anhydride with one carbonyl group conjugated to the methylene group. It can be regarded as a substituted acrylic or methacrylic derivatives. In addition, it can be obtained from renewable resources [1, 2]. ITA is produced from the pyrolysis of citric acid or through the fermentation of carbohydrates forming itaconic acid followed by its dehydration to form the anhydride [3]. ITA can be polymerized [4] or copolymerized with various other monomers [5, 6] by free radical

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[*] Address correspondence to Badiadka Narayana, Department of Studies in Chemistry, Mangalore University, Mangalagangotri 574-199, Karnataka, India. E-mail: bnarayana@mangaloreuniversity.ac.in

Table 1. Crystal data for **1**

CCDC No.	949575
Crystal description	Block-shaped
Crystal color	Light-orange
Crystal size	0.3 × 0.2 × 0.2 mm
Empirical formula	$C_{13}\ H_{13}\ N\ O_4$
Formula weight	247.24
Radiation, Wavelength	MoKα, 0.71073 Å
Unit cell dimensions	$a = 4.9485(3)$, $b = 5.3614(6)$, $c = 22.457(2)$Å, $\alpha = 88.295(8)$, $\beta = 89.379(7)$, $\gamma = 84.495(7)$ º
Crystal system	Triclinic
Space group	P-1
Unit cell volume	592.77(9) Å^3
No. of molecules per unit cell, Z	2
Temperature	293(2)
Absorption coefficient	0.104 mm^{-1}
F(000)	260
Scan mode	ω scan
θ range for entire data collection	$3.82 < \theta < 26.00$º
Range of indices	$h = -5$ to 6, $k = -6$ to 6, $l = -26$ to 27
Reflections collected/unique	3867/2328
Reflections observed ($I > 2\sigma$ (I))	1623
R_{int}	0.0201
R_{sigma}	0.0440
Structure determination	Direct methods
Refinement	Full-matrix least-squares on F^2
No. of parameters refined	172
Final R	0.0467
$wR(F^2)$	0.1129
Weight	$1/[\sigma^2(F_o{}^2) + (0.0593P)^2 + 0.0000P]$ where $P = [F_o{}^2 + 2F_c{}^2]/3$
Goodness-of-fit	1.029
$(\Delta/\sigma)_{\max}$	0.001 (for y C1)
Final residual electron density	$-0.162 < \Delta\rho < 0.182$ Å^{-3}
Measurement	*X'calibur system – Oxford diffraction make, U.K.*
Software for structure solution:	SHELXS97 (Sheldrick, 2008)
Software for refinement:	SHELXL97 (Sheldrick, 2008)
Software for molecular plotting:	ORTEP-3 (Farrugia, 2012) PLATON (Spek, 2009)
Software for geometrical calculation	PLATON (Spek, 2009) PARST (Nardelli, 1995)

Table 2. Elemental analysis for $C_{13}H_{13}NO_4$

Element	Experimental (%)	Calculated (%)
Carbon	63.12	63.15
Nitrogen	5.64	5.67
Hydrogen	5.32	5.30

reactions. Because it forms highly reactive tertiary radicals [7, 8], ITA is more reactive than maleic anhydride and is an alternative monomer for introducing polar functionality into polymers. It can be also useful for the synthesis of various biodynamic derivatives such as imides [9], pyridazine [10], oxazepine [11], and oxobutanoic acid [12] derivatives. In view of above importance we have synthesized 4-[(3-Acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid (**1**) and reported the crystal structure, UV-Vis spectroscopy, thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) results.

2. Experimental

2.1 Materials and Methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. Melting point was taken in open capillary tube and

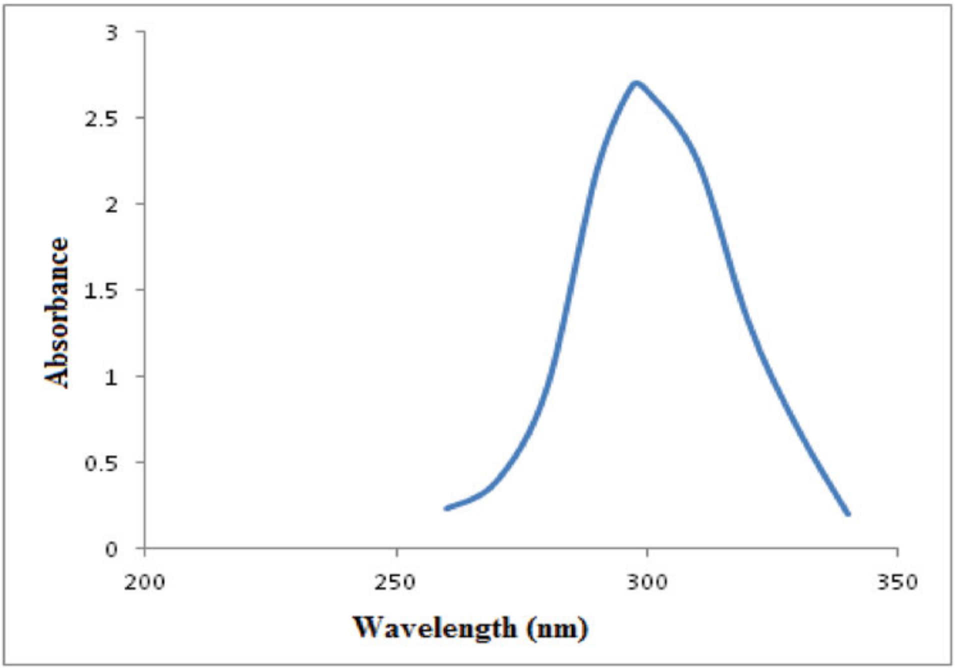


Figure 1. UV-Vis spectrum of compound **1**.

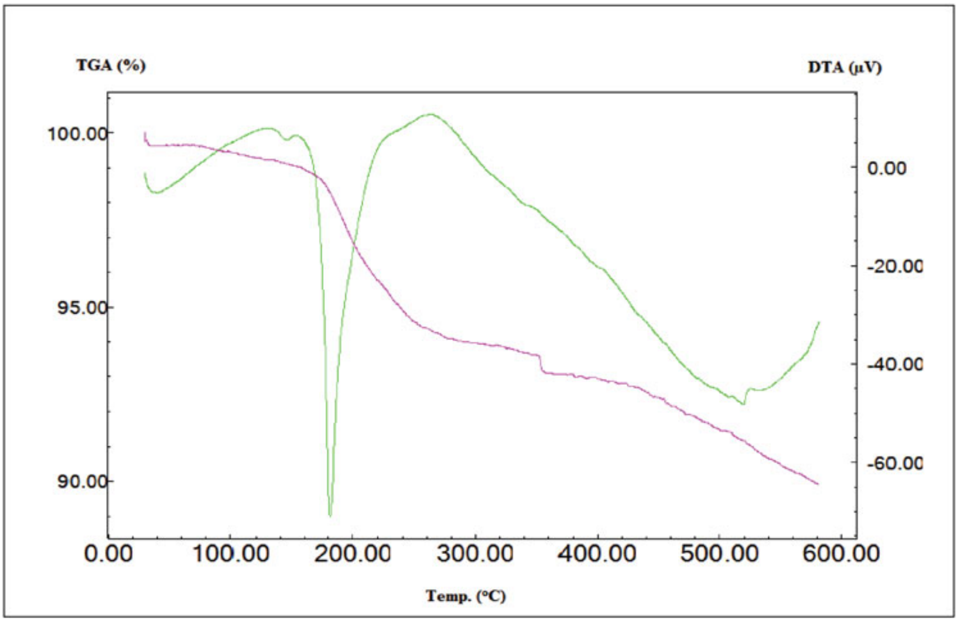


Figure 2. TGA and DTA curves of **1** at the heating rate of 10 °C min^{-1}.

was uncorrected. The purity of the compound was confirmed by thin-layer chromatography using Merck silica gel 60 F_{254} coated aluminum plates. IR spectrum was recorded on Shimadzu-FTIR Infrared spectrometer in KBr (ν_{max} in cm^{-1}) and ^{1}H-NMR (400 MHz) spectrum was recorded on a Varian 400 spectrometer, with 5 mm PABBO BB-1H TUBES. A Shimadzu DTG-60 thermogravimetric analyzer was used to obtain TGA and DTA curve under nitrogen atmosphere with a heating rate of 10åC min^{-1}. The UV-Vis spectrum was recorded in Shimadzu UV-2550 UV-Visible spectrophotometer. Elemental analysis was carried out by using VARIO EL-III (Elementar 10 Analysensysteme GmBH). Crystallographic data were collected on a Bruker SMART APEXII CCD area-detector diffractometer with a graphite monochromated MoKα radiation ($k = 0.71073$ A°) equipped with an *X'calibur* CCD area-detector diffractometer. The geometry of the molecule was calculated using the PLATON [13] and PARST [14] software. The structure was solved by direct method and refined by least-squares using the SHELX97 [15] software package.

2.2 Synthesis of 4-[(3-Acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid (1)

ITA (0.112 g, 1 mmol) dissolved in a 30 mL acetone and it was stirred at ambient temperature and 3-aminoacetophenone (0.135 g, 1 mmol) was added portion wise over 30 mins. The mixture turned into pale yellow slurry. After stirring 1.5 hr, the slurry was filtered. The solid was washed with acetone and dried to give title compound **1**. Single crystals were grown from methanol by the slow evaporation method. Yield: Light orange powder (85%), mp 180–182°C.

2.3 Preparation of the Single Crystal for Structure Determination

Light orange Colored block-shaped single crystals of **1** suitable for X-ray diffraction study were obtained from CH_3OH solution by slow evaporation at room temperature after several

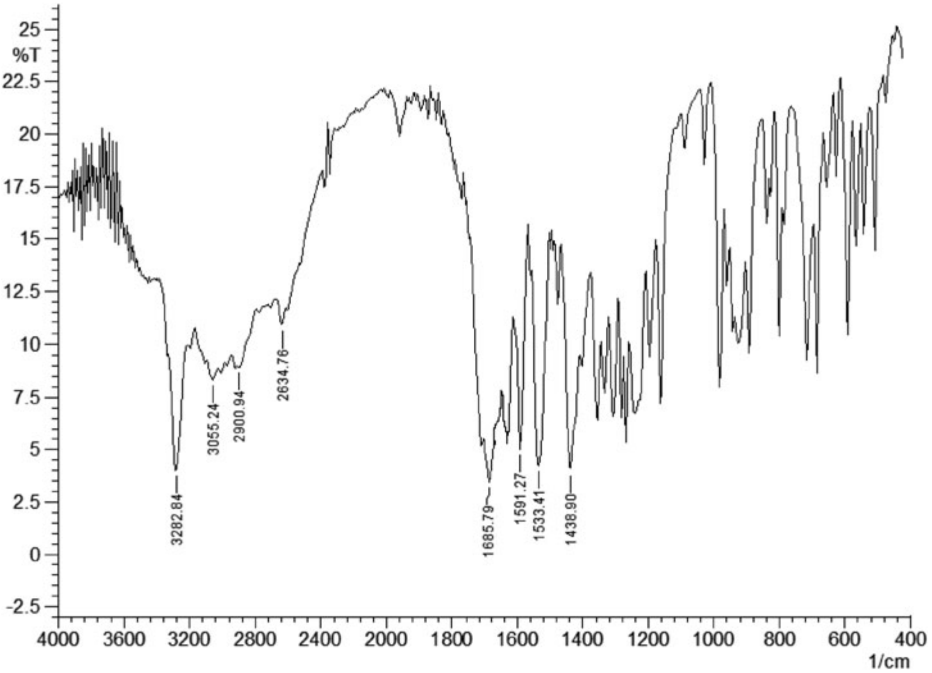


Figure 3. FTIR spectrum of the compound (**1**).

days. A single crystal of dimensions 0.3 mm × 0.2 mm × 0.2 mm was selected optically for the diffraction study. X-ray intensity data of 3867 reflections (of which 2328 unique) were collected on *X'calibur* CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The cell dimensions were determined

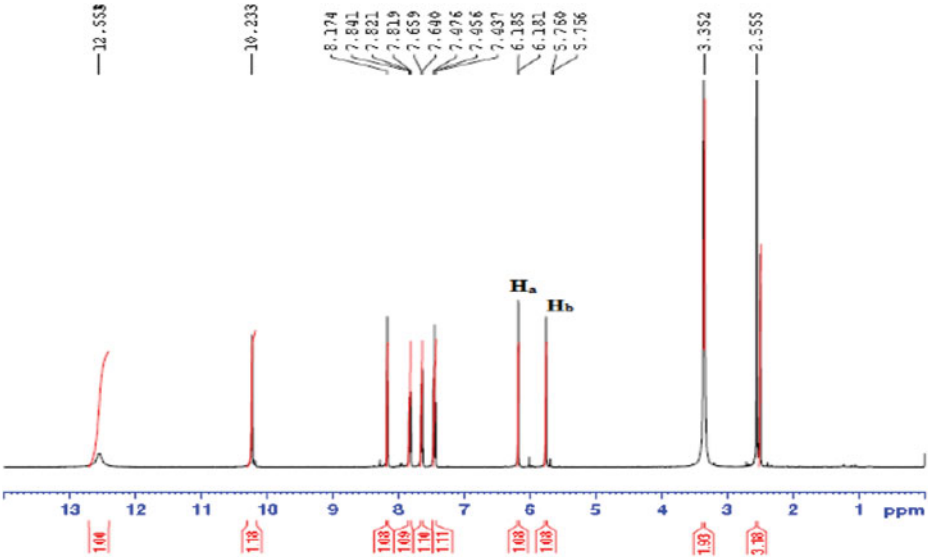


Figure 4. ^{1}H NMR spectrum of the compound (**1**).

Table 3. Bond lengths (Å) and bond angles (^{O}) for nonhydrogen atoms (e.s.d.'s are given in parentheses)

Bond lengths (Å)			
N1-C5	1.336(2)	N1-C6	1.420(2)
O1-C1	1.262(2)	O2-C1	1.259(2)
O3-C5	1.220(2)	O4-C12	1.211(2)
C1-C2	1.479(3)	C2-C3	1.311(3)
C2-C4	1.497(2)	C4-C5	1.508(3)
C6-C7	1.382(2)	C6-C11	1.386(2)
C7-C8	1.380(3)	C8-C9	1.390(2)
C8-C12	1.489(3)	C9-C10	1.366(3)
C10-C11	1.375(3)	C12-C13	1.497(3)
Bond angles (°)			
C5-N1-C6	125.2(1)	O2-C1-O1	123.2(2)
O2-C1-C2	117.3(2)	O1-C1-C2	119.4(2)
C3-C2-C1	119.7(2)	C3-C2-C4	123.9(2)
C1-C2-C4	116.4(2)	C2-C4-C5	112.8(1)
O3-C5-N1	123.2(2)	O3-C5-C4	121.1(2)
N1-C5-C4	115.6(1)	C7-C6-C11	119.3(2)
C7-C6-N1	121.3(2)	C11-C6-N1	119.4(2)
C8-C7-C6	121.0(2)	C7-C8-C9	118.9(2)
C7-C8-C12	118.5(2)	C9-C8-C12	122.5(2)
C10-C9-C8	120.1(2)	C9-C10-C11	120.9(2)
C10-C11-C6	119.8(2)	O4-C12-C8	120.4(2)
O4-C12-C13	120.7(2)	C8-C12-C13	118.9(2)

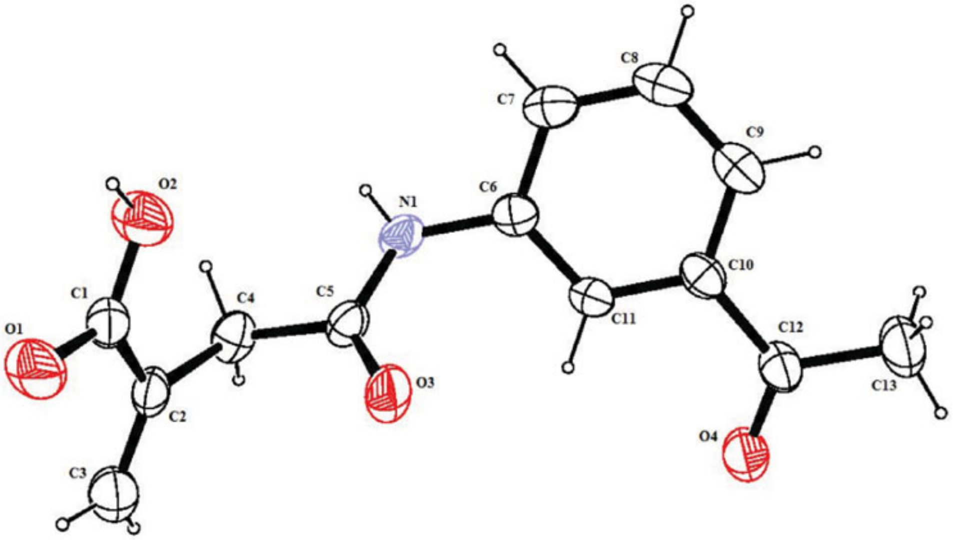


Figure 5. *ORTEP* view of the molecule with displacement ellipsoids drawn at 40%. H atoms are shown as small spheres of arbitrary radii.

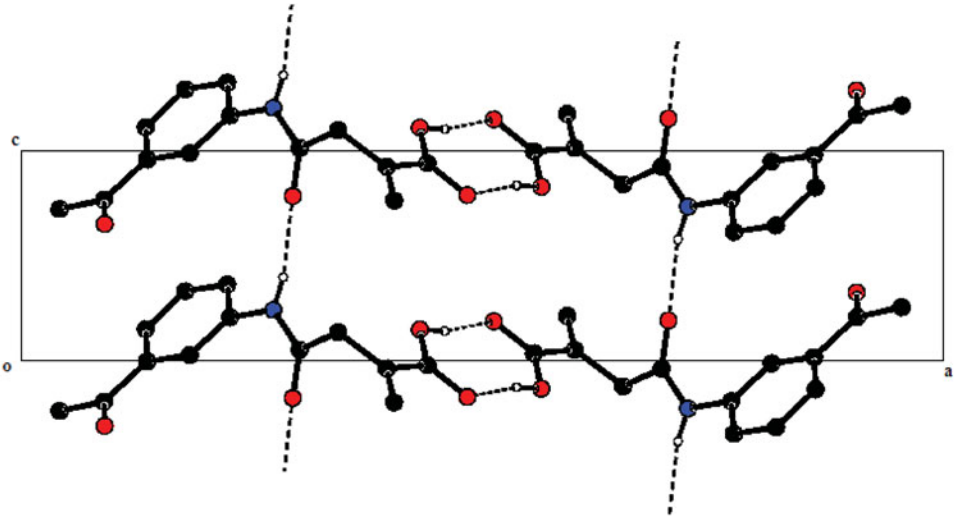


Figure 6. The packing arrangement of molecules viewed down the *b*-axis.

by least-squares fit of angular settings of 1277 reflections in the θ range 3.96–27.28°. The intensities were measured by ω scan mode for θ ranges 3.82–26.00°. 1623 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz, polarization and absorption factors. The structure was solved by direct methods using SHELXS97 [15]. All nonhydrogen atoms of the molecule were located in the best E-map. All the hydrogen atoms (except C3 H atoms) were geometrically fixed and allowed to ride on their parent C/N atoms with C-H = 0.93–0.97 Å and N-H distance of 0.86 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$. Full-matrix least-squares refinement was carried out using SHELXL97 [15]. The final refinement cycles converged to an $R = 0.0467$ and $wR(F^2) = 0.1129$ for the observed data. Residual electron densities ranged from –0.162 to 0.182 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. The supplementary crystallographic data for this structure has been deposited (CCDC-949575)

3. Results and Discussion

3.1 Elemental Analysis

In order to confirm the chemical composition of the synthesized compound CHN analysis was carried out. The experimental and calculated percentages of C, H, and N were given in Table 2. The differences between experimental and calculated percentages of C, H, and N were very close to each other and within the experimental errors. This confirms the formation of the product in the stoichiometric proportion.

3.2 UV-Vis Spectral Analysis

Like IR and ^{1}H NMR spectroscopy, UV-Vis spectroscopy also useful in the evaluation of compounds. In the UV electronic spectrum, compounds are analyzed based on the characteristic frequencies (or λ_{max}) corresponding to definite groups. In unsaturated compounds

Table 4. Hydrogen-bonding geometry (e.s.d.'s in parentheses)

D–H... A	D–H(Å)	H... A(Å)	D... A(Å)	D–H... A(°)
N1-H1 ... O3^{i}	0.86	2.00	2.850(2)	169
O2-H2... O1^{ii}	0.82	1.83	2.636(2)	168

Symmetry code: (i) $x+1, +y, +z$ (ii) $-x, -y+1, -z+1$

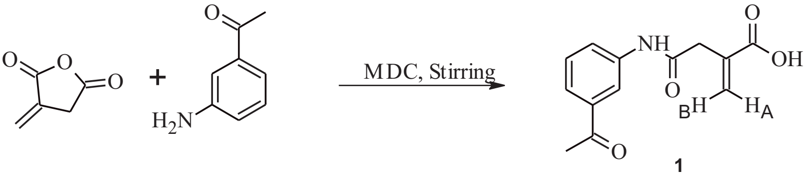
like (**1**) π–π^* transition is common with λ_{max} 297 nm (Fig. 1). There was no absorption peak between 360 nm and 900 nm in the entire visible region. Hence, the material may be useful for optoelectronic applications.

3.3 Thermal Property

The TGA and DTA data of **1** was collected in the temperature range from 30 to 600 °C, with a heating rate of 10 °C min^{-1}. The TGA and DTA curve of **1** was presented in Fig. 2 showing that there is no decomposition and weight loss before 181 °C indicating the absence of moisture in the crystal. Compound **1** exhibits two stages of thermal decomposition. Here, the corresponding weight ratio in the TGA curve is approximately 4.48 wt% and 1.947 wt% which is assigned to the content of solvent and CO in the compound **1**. In the DTA curve, the endothermal peak at 181.4 °C is corresponding to the melting point of the compound **1**. It is good fit with the value (180–182 °C) measured by a capillary method.

3.4 FTIR and ^{1}H NMR Spectral Analysis

As shown in Scheme 1, compound **1** was obtained from ring opening reaction of an ITA with the 3-aminoacetophenone in the presence of acetone as a solvent. Its spectroscopic data are in good agreement with the crystallographic data. The FT-IR spectrum (Fig 3) of **1** revealed the stretching vibration of amide NH was observed at 3282 cm^{-1} and C=O stretching vibration was observed at 1685 cm^{-1} confirms the amide link. The appearance of OH peak at 3055 cm^{-1} indicates the ring opening of ITA. The strong peak of C=C stretching vibration in aromatic ring was observed at 1591 cm^{-1}.



1

Scheme 1.

The ^{1}H NMR spectrum (Fig 4) of compound **1**, showed singlet at δ 3.35 ppm indicated the two protons of O = C-CH$_2$ of amide moiety. Two doublets appeared at δ 5.75 ppm (J_{AB} = 1.6 Hz) and δ 6.18 ppm (J_{AB} = 1.6 Hz) were due to germinal coupling between H_A and H_B with respect to carboxylic acid group. Beside these signals, two singlets appeared at δ 10.23 ppm and 12.55 ppm were due to amide NH and carboxylic acid OH proton. The singlet peak at δ 6.18 ppm represents the acetophenone CH$_3$ proton.

3.5 Crystal Structure of 1

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes with a triclinic unit cell in the P-1space group. An ORTEP view of the title compound **1** with atomic labeling is shown in Fig. 5 [16]. The geometry of the molecule was calculated using the PLATON [13] and PARST [14] software. Bond lengths and angles of the title molecules are within normal ranges [17]. Phenyl ring (C6-C11) is perfectly planar with a maximum deviation of 0.010(2) Å for C11. The double bonds C12 = O4 [1.211(2) Å], C5 = O3 [1.220(2) Å], and C1 = O1 [1.262(2) Å] are confirmed by their respective distances. The dihedral angle between the phenyl ring (C6-C7) and chain of oxabutanoic acid is 55.55(8)^o. Bond distances and bond angles for nonhydrogen atoms are listed in Table 3.

The Packing view of the molecules in the unit cell viewed down the *b*-axis is shown in (Figure 6).

In the crystal, molecules are held together by strong N-H . . . O and O-H . . . O intermolecular interactions. Details of intra and intermolecular hydrogen bonding are given in Table 4.

Conclusions

A novel compound 4-[(3-acetylphenyl)amino]-2-methylidene-4-oxobutanoic acid (**1**) is synthesized and well-characterized by spectral data. The structure of the compound was determined by single crystal X-ray diffraction method. The crystal structure analysis shows that the compound forms a block shaped structure with the triclinic crystal system and P-1 space group. In addition, molecules are held together by strong N-H . . . O and O-H . . . O intermolecular interactions with different bond lengths sustains the stability of three-dimensional structure. Thermal analysis showed high thermal stability up to 181°C implying that compound **1** requires high activation energy for the reaction.

Acknowledgments

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Supplementary Material

The original compound and spectra are available with the authors and can be provided free of cost for reference purposes. CCDC-949575 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] Wallach, J. A. (2000). *Biodegradable Polymers Derived from Renewable Resources: Highly Branched Copolymers of Itaconic Anhydride in Polymer Science*. Storrs, CT: University of Connecticut.

[2] Meier, M. A. R., Metzger, J. O., & Schubert U. S. (2007). *Chem. Soc. Rev.*, *36*, 1788–1802.

[3] Kinoshita, K. (1929). *J. Chem. Soc. Japan*, *50*, 583–593

[4] Ishida, S., Saito, S. (1967). *J. Polym. Sci. Part A-1: Polym. Chem.*, *5*, 689–705.

[5] Garrett, E. R., & Guile, R. L. (1951). *J. Am. Chem. Soc.*, *73*, 4533–4535.

[6] Wallach, J. A., & Huang, S. J. (2000). *Biomacromolecules*, *1*, 174–179.

[7] Sharabash, M. M., & Guile, R. L. (1976). *J. Macromol. Sci. Chem.*, *A10*, 1033–1048.

[8] Miles, A. F., Cowie, J. M. G., Bennett, R. H., & Brambley, D. R., (1991). *Polymer*, *32*, 484–488.

[9] Shetgiri, N. P., & Nayak, B. K. (2005). *Indian J. Chem.*, *44B*, 1933–1936.

[10] Katla, S., Pothana, P., Gubba, B., & Manda, S. (2011). *Der Chemica Sinica*, *2*, 47–53.

[11] Hanoon, H. D. (2011). *Nat. J. Chem.*, *41*, 7–89.

[12] Nayak, P. S., Narayana, B., Yathirajan, H. S., Gerber, T., Van Brecht, B., & Betz, R. (2013). *Acta Cryst.*, *E69*, o83.

[13] Spek, A. L. (2009). *Acta Cryst.*, *D65*, 148–155.

[14] Nardelli, M. J. (1995). *Appl. Cryst.*, *28*, 659.

[15] Sheldrick, G. M. (2008). *Acta Cryst.*, *A64*, 112.

[16] Farrugia, L. J. (2012). *J. Appl. Cryst.*, *45*, 849–854.

[17] Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G., & Taylor, R. (1987). *J. Chem. Soc., Perkin Trans-II*, S1.