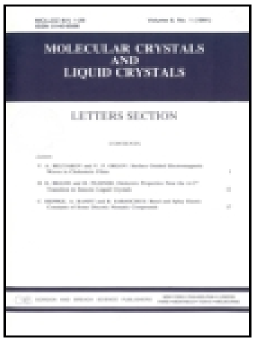

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Synthesis, Characterization and Crystal Structure of Ethyl 2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate

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Ethyl 2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate was synthesized from ethyl 6-(4-bromophenyl)-4-(4-fluorophenyl)-2-oxocyclohex-3-ene-1-carboxylate and ammonium acetate in glacial acetic acid. The synthesized compound was characterized by elemental analysis, FT-IR, thermogravimetric analysis (TGA), differential thermal analysis (DTA), UV-Visible, and single-crystal X-ray diffraction. The title compound, ethyl 2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate, $C_{21}H_{2}OFNO_{2}$, crystallizes in the orthorhombic space group Pbca with the following unit-cell parameters: $a = 17.417(2)$, $b = 9.7287(9)$, $c = 21.014(2)$ Å, *and* $Z = 8$. *The crystal structure was 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 0.0644 for 1616 observed reflections. An intramolecular N–H… O hydrogen bond generates an S(6) graph-set motif. In the crystal, molecules are linked by N–H… O hydrogen bonds, forming a two-dimensional network.*

Keywords Crystal structure; direct methods; hydrogen bonding

1. Introduction

Cyclohexenones are efficient intermediates in the synthesis of various functionalized derivatives such as benzisoxazoles, indazoles, dibenzodiazepines, terphenyls, aminated derivatives, etc. [1–3]. The amination of cyclohexenone derivative of 1-(4-fluorophenyl)-3-phenylprop-2-en-1-one with ammonium acetate afforded the title compound (I). The crystal structure of similar aminated products viz., ethyl 2-amino-4,6-bis(4-fluoro phenyl)cyclohexa-1,3-diene-1-carboxylate and ethyl 2-amino-6-(4-bromophenyl)-4-(4-fluorophenyl)cyclohexa-1,3-diene-1-carboxylate have been reported [4,5]. The crystal structure of the cyclohexenone derivatives viz., ethyl 6-(4-bromophenyl)-4-(4-fluorophenyl)-2-oxocyclohex-3-ene-1-carboxylate and ethyl 4,6-bis(4-fluorophenyl)-2-oxocyclohex-3-ene-1-carboxylate have been reported [6,7]. In continuation of our work

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on synthesis of cyclohexenone derivatives [2], the title compound (I) is prepared and characterized by elemental analysis, FT-IR, thermogravimetric analysis (TGA), differential thermal analysis (DTA), UV-Visible, and single-crystal X-ray diffraction.

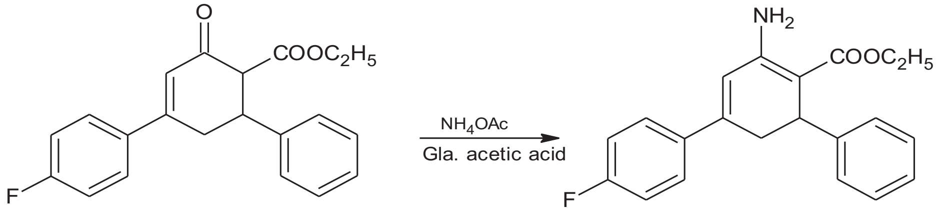
2. Experimental

2.1. Materials and Methods

All chemicals were purchased commercially and used without prior purification. Melting points were taken in open capillary tubes and were uncorrected. The purity of the compounds was confirmed by thin layer chromatography using Merck silica gel 60 F_{254}-coated aluminum plates using ethyl acetate: n-hexane (1:3, v/v) as solvent system. IR spectra were recorded on Shimadzu-FTIR Infrared spectrometer in KBr (λ_{max} in cm^{-1}). A Shimadzu DTG-60 (Japan) thermogravimetric analyzer was used to obtain TGA and DTA curve under nitrogen atmosphere with a heating rate of 10°C 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).

2.2. Synthesis

A mixture of ethyl 4-(4-fluorophenyl)-2-oxo-6-phenylcyclohex-3-ene-1-carboxylate (3.38 g, 0.01 mol) and ammonium acetate (1.54 g, 0.02 mol) in glacial acetic acid (30 ml) was refluxed for 6 hr (Scheme 1). The reaction mixture was cooled and poured into 50 ml ice-cold water. The precipitate was collected by filtration and purified by recrystallization from ethanol. The single crystal was grown from ethanol by slow evaporation method (m.p. 377–379 K).



Scheme 1. Synthesis of ethyl 2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate (I).

3. Results and Discussion

3.1. Elemental Analysis

The chemical composition of the synthesized compound was determined by using CHN elemental analysis. The results of elemental analysis of the title compound are given in Table 1 below.

3.2. FT-IR Spectral Analysis

The IR spectrum of the title compound (I) showed absorption bands at 3402 and 3296 cm^{-1} corresponding to the asymmetric and symmetric stretching of the NH_2 group. An absorption

Table 1. Elemental analysis data of the compound (I)

Element	Found (%)	Calculated (%)
C	74.73	74.76
H	5.99	5.97
N	4.13	4.15

band at 1649 cm^{-1} indicats the presence of a carbonyl group. Furthermore, absorption bands at 2983 and 2939 cm^{-1} are due to the aromatic and aliphatic C–H stretching respectively (Fig. 1).

3.3. Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermal analyses were carried out under nitrogen flow. TG and DTA curves obtained for the compound (I) is shown in Fig. 2. These curves show the thermal behavior of the title compound. The compound decomposes on heating between 30°C to 300°C. The TG curve shows that, there was no weight loss observed up to 241°C shows the absence of moisture in the crystal. The compound decomposes from 241°C to 276°C and is associated with the weight loss of 40%. The DTA curve for ethyl-2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate displays an endothermic peak at 170°C.

3.4. UV-Visible Spectral Analysis

Like IR spectroscopy, UV spectroscopy is useful in the evaluation of the compounds. In UV electronic spectrum, compounds are analyzed based on the characteristic frequencies

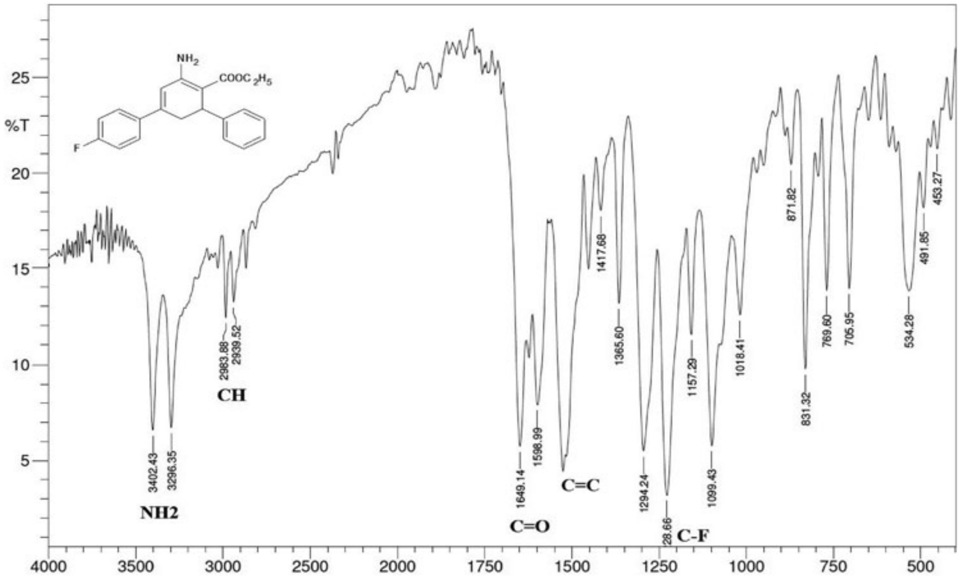


Figure 1. FTIR spectrum of the crystal.

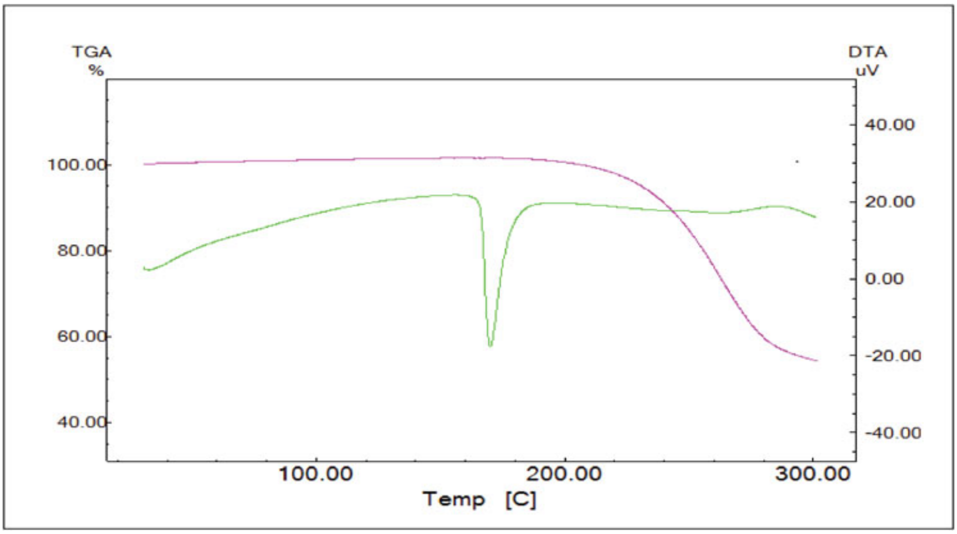


Figure 2. TGA and DTA curves of the crystal.

(or λ_{max}) corresponding to definite groups. In unsaturated compounds like (I), π to π^* transition is common with λ_{max} 365 nm (Fig. 3).

3.5. Single Crystal X-Ray Diffraction

X-ray intensity data of 9143 reflections (of which 3480 unique) were collected on *X'calibur* CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The crystal used for data collection was of dimensions 0.30 × 0.20 × 0.20 mm. The cell dimensions were determined by least-squares fit of angular settings of 2241 reflections in the θ range 3.54 to 27.84°. The intensities were measured by ω scan

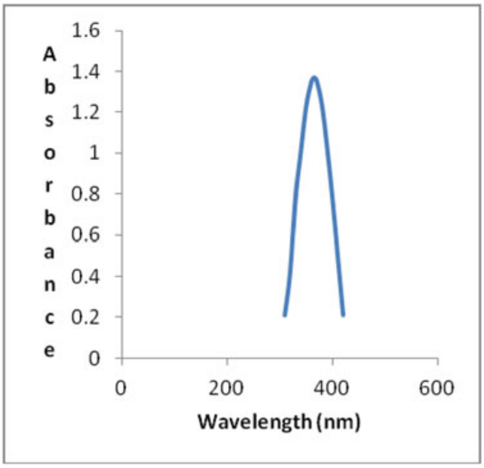


Figure 3. UV-visible spectrum of the crystal.

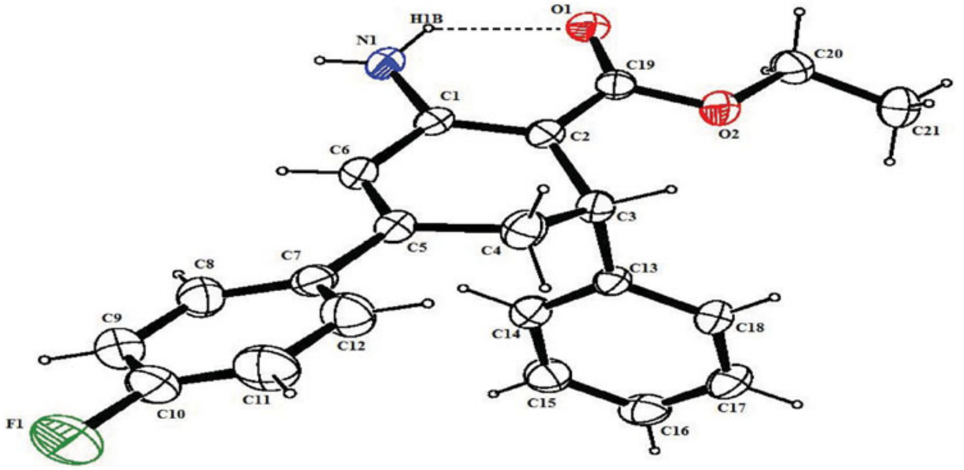


Figure 4. *ORTEP* view of the molecule with displacement ellipsoids drawn at 40%. H atoms are shown as small spheres of arbitrary radii.

mode for θ ranges 3.69 to 26.00°. 1616 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 [8]. All nonhydrogen atoms of the molecule were located in the best E-map. All the hydrogen atoms (except N1 H atoms) were geometrically fixed and allowed to ride on their parent C atoms with C–H = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) except for the methyl groups where U_{iso}(H) = 1.5U_{eq}(C). Full-matrix least-squares refinement was carried out using SHELXL97 [8]. The final refinement cycles converged to an $R = 0.0644$ and wR (F^2) = 0.1360 for the observed data. Residual electron densities ranged from −0.192 to 0.268 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 2.

An ORTEP view of the title compound with atomic labeling is shown in Fig. 4 [9]. The geometry of the molecule was calculated using the PLATON [10] and PARST [11] software.

The title molecule comprises of three six membered rings named as ring A, ring B and ring C (Fig. 4).

Bond lengths and angles of the title molecules are within normal ranges [12]. The dihedral angle between the mean planes of the two phenyl rings (ring A and B) is 85.7(1)°. Ring C has adopts half chair conformation with best two fold axis bisecting the bonds C1–C6 and C3–C4 with asymmetry parameters [ΔC_2(C1 – C6) = 2.62] [13]. The double bonds C19 = O1 is confirmed by its respective distance of 1.233(4) Å. The length of the double bond C19C19 = O1 is larger than the standard value for carbonyl group (1.192 Å) and lengthening of the C19C19 = O1 double bond is due to strong intramolecular hydrogen bonding between N1 and O1. This intramolecular interaction leads to the formation of a virtual six-membered ring comprising atoms N1, C1, C2, C19, O1, and H1B. Bond distances and bond angles for nonhydrogen atoms are listed in Table 3.

Packing view of the molecules in the unit cell viewed down the *b* axis is shown in (Fig. 5).

Table 2. Salient crystallographic data and structure refinement parameters of compound (I)

CCDC No	952587
Crystal description	Block-shaped
Crystal colour	Light-yellow
Crystal size	0.3 × 0.2 × 0.2 mm
Empirical formula	$C_{21}\ H_{20}\ F\ N\ O_2$
Formula weight	337.38
Radiation, Wavelength	Mo $K\alpha$, 0.71073 Å
Unit cell dimensions	$a = 17.417(2)$, $b = 9.7287(9)$, $c = 21.014(2)$ Å
Crystal system	Orthorhombic
Space group	*P b c a*
Unit cell volume	3560.7(7) Å^3
No. of molecules per unit cell, Z	8
Temperature	293(2)
Absorption coefficient	0.088 mm^{-1}
$F(000)$	1424
Scan mode	ω scan
θ range for entire data collection	$3.69 < \theta < 26.00°$
Range of indices	$h = -21$ to 16, $k = -12$ to 11, $l = -25$ to 14
Reflections collected/unique	9143/3480
Reflections observed ($I > 2\sigma(I)$)	1616
R_{int}	0.0630
R_{sigma}	0.0972
Structure determination	Direct methods
Refinement	Full-matrix least-squares on F^2
No. of parameters refined	236
Final R	0.0644
wR(F^2)	0.1360
Weight	$1/[\sigma^2(F_o{}^2)+(\ 0.0612\ P)^2+\ 0.0000P]$ where $P = [F_o{}^2 + 2F_c{}^2]/3$
Goodness-of-fit	0.963
$(\Delta\ /\sigma)_{\max}$	0.001 (for U11 H2A)
Final residual electron density	$-0.192 < \Delta\rho < 0.268$ 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 3. Bond lengths (Å) and bond angles (°) for nonhydrogen atoms (e.s.d.'s) are given in parentheses

Bond Lengths (Å)			
F1–C10	1.371(4)	N1–C1	1.352(4)
O1–C19	1.233(4)	O2–C19	1.345(3)
O2–C20	1.443(3)	C1–C2	1.361(4)
C1—C6	1.459(4)	C2–C19	1.433(4)
C2–C3	1.525(4)	C3–C13	1.524(4)
C3–C4	1.539(4)	C4–C5	1.504(4)
C5–C6	1.345(4)	C5–C7	1.479(4)
C7–C8	1.378(4)	C7–C12	1.396(4)
C8–C9	1.373(5)	C9–C10	1.364(5)
C10–C11	1.349(5)	C11–C12	1.387(5)
C13–C14	1.379(4)	C13–C18	1.379(4)
C14–C15	1.375(4)	C15–C16	1.364(4)
C16–C17	1.380(5)	C17–C18	1.384(4)
C20–C21	1.495(4)		
Bond Angles (°)			
C19–O2–C20	118.4 (2)	N1–C1–C2	123.9 (3)
N1–C1–C6	115.4 (3)	C2–C1–C6	120.6 (3)
C1–C2–C19	121.3 (3)	C1–C2–C3	119.7 (3)
C19–C2–C3	118.9 (3)	C13–C3–C2	113.3 (3)
C13–C3–C4	111.9 (2)	C2–C3–C4	110.6 (2)
C5–C4–C3	114.6 (3)	C6–C5–C7	122.9 (3)
C6–C5–C4	118.1 (3)	C7–C5–C4	118.8 (3)
C5–C6–C1	122.5 (3)	C8–C7–C12	116.8 (3)
C8–C7–C5	122.5 (3)	C12–C7–C5	120.7 (3)
C9–C8–C7	122.3 (4)	C10–C9–C8	118.0 (4)
C11–C10–C9	123.2 (4)	C11–C10–F1	117.6 (4)
C9–C10–F1	119.2 (4)	C10–C11–C12	117.8 (4)
C11–C12–C7	121.8 (3)	C14–C13–C18	117.4 (3)
C14–C13–C3	123.1 (3)	C18–C13–C3	119.6 (3)
C15–C14–C13	121.8 (3)	C16–C15–C14	120.3 (3)
C15–C16–C17	119.2 (3)	C16–C17–C18	120.0 (3)
C13–C18–C17	121.2 (3)	O1–C19–O2	120.5 (3)
O1–C19–C2	126.2 (3)	O2–C19–C2	113.3 (3)
O2–C20–C21	106.8 (3)		

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–H2A... O1	0.90(4)	2.695(4)	2.02(4)	131 (3)
N1–H1A... O1^{i}	0.81(3)	2.995(4)	2.20(3)	170 (3)

Symmetry: i $-x + 1/2$, $+y-1/2$, $+z$.

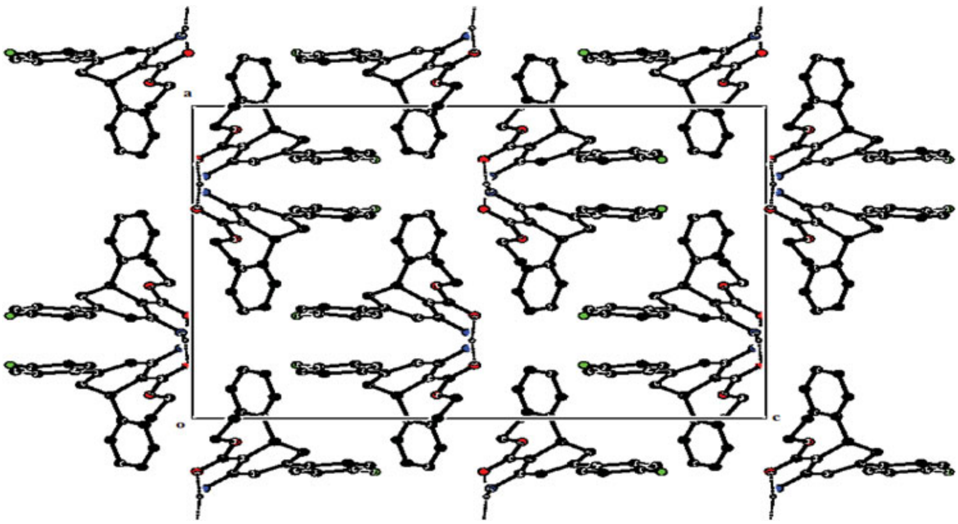


Figure 5. The packing arrangement of molecules viewed down the *b*-axis.

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

Conclusion

The compound ethyl 2-amino-4-(4-fluorophenyl)-6-phenylcyclohexa-1,3-diene-1-carboxylate was synthesized and characterized by spectral data. The elemental analysis confirms the formation of the compound in a stoichiometric ratio. TGA and DTA were carried out to study the thermal behaviour of the crystal. The FTIR spectrum characterizes the presence of various functional groups. The single crystal X-ray diffraction study indicates that the compound crystallizes in orthorhombic space group.

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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- *952587* 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.

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