Crystal structure of dimethyl ammonium 5-(2,4-dinitrophenyl)-1,3-dimethyl barbiturate

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The titled molecular salt dimethyl ammonium 5-(2,4-dinitrophenyl)-1,3-dimethyl barbiturate has been prepared from the ethanolic solution of 1-chloro-2,4-dinitrobenzene, 1,3-dimethylbarbituric acid and dimethyl amine. FT-IR, ^{1}H-NMR, ^{13}C-NMR, and single crystal diffraction results support the proposed structure of the compound. The crystal structure of the titled complex [monoclinic, space group p21/n, a=11.5729 (15)Å, b=8.6857(11) Å, c=16.701(2) Å, Z=4] are analyzed by single-crystal X-ray diffraction. In this crystal, intermolecular N-H…O and C-H…O hydrogen bonds forming a three dimensional network and small red spot in Hirshfeld surfaces indicates the presence of C-H...π interactions.

Barbiturates are pyrimidine derivatives and most of them have anticonvulsant activity[1-4]. Different types of anionic sigma complexes such as carbon-bonded, nitrogen-bonded, and oxygen-bonded and Spiro-Meisenheimer complexes have been reported by different groups of scientists[5-7]. Derivatives of 1,3-dimethyl barbituric acid including pyrimidine-2,4,6-trione heterocycles play an important role in the pharmaceutical chemistry[8,9]. 1-chloro-2, 4-dinitrobenzene is a unique functional group used in medicinal chemistry. Nitro group is associated with mutagenicity and genotoxicity and therefore is often used in the drug discovery process[10]. The nitroaromatic compound is also used to synthesize dyes and high energy materials. These compounds are very common environmental pollutants that are used as pesticides and explosives[3].

A recurring theme in recent publications was devoted to intermolecular interactions in solids. To consider two or more structures i.e., similar or dissimilar, two are involved in these interactions, a) Identification of the core structural features b) evaluation of the extent of their resemblance. Hirshfeld surfaces encircle the molecules surrounded by the crystals[11]. The locus of points in Hirshfeld surfaces are those for which the ratio of electron density contributions computed from a sum of atoms in a test molecule with spherical scattering factors to the electron density contribution determined from all of the atoms. Hirshfeld surfaces are typically plotted at a ratio of 0.5, that place where the contribution to the electron density from a molecule is equal to the contribution from all the other molecules. As such, Hirshfeld surfaces are reactive to intermolecular interactions and can be elaborated by plotting on them any scalar function that can be devised from the crystal structure or the surface itself. Predominantly informative are Hirshfeld surfaces on which are plotted the distance to the nearest atom within the surface or external to it.

Experimental Details

All the reagents used for the synthesis and analysis were commercially available and used as received without further purification. The UV-visible spectra were obtained by using Shimadzu UV/Vis 1800 spectrometer. The FT-IR spectra were recorded using Perkin-Elmer RXI infrared spectrometer as KBr pellets. The ^{1}H NMR and ^{13}C NMR spectral data were obtained using Bruker DRX 600 MHz spectrophotometers. DMSO d_6 is used as a solvent and tetra methyl silane as internal reference.

Preparation of dimethyl ammonium 5-(2, 4-dinitrophenyl)-1,3-dimethyl barbiturate

1-chloro-2,4-dinitrobenzene (0.01 mol) is dissolved in absolute ethanol and mixed with 1,3-dimethyl barbituric acid (0.01 mol) in ethanol. Then added N, N-dimethyl amine (0.05 mol) and the mixture was

shaken well for 5-6 h. On standing, orange coloured crystals come out from the solution after 15 days. The crystals were filtered and washed with distilled ether and dried. These crystals were recrystallized from distilled ethanol. Good quality single crystals of the titled compound were obtained from ethanolic solution at room temperature by slow evaporation (m.p. 491 K, yield 75%).

Thin layer chromatographic (TLC) studies

The study was carried out to check the purity of the isolated molecules. Silica gel was used as an adsorbent. The slurry of silica gel was made with chloroform and coated uniformly on a TLC plate. The complex solution was prepared in pure absolute ethanol and spotted on the plate. The eluent used was the mixture of tertiary butyl alcohol and ethyl acetate in the ratio (3:1).

Crystal structure determination

A single-crystal X-ray diffraction unit has the dimensions of 0.15 mm x 0.26 mm x 0.28 mm used for determination of the structure. The frames have been integrated with Bruker SAINT software package by using a narrow-frame algorithm.

Results and Discussion

Mechanism

As shown below, in step-1, as carbon basicity i.e., the affinity of a nucleophile to attack an electron-deficient carbon atom of aromatic nucleus) of carbanion is greater than negatively charged nitrogen or oxygen atom[12], carbanion **a** readily attacks the aromatic carbon atom bearing chlorine atom resulting in the formation of intermediate complex.
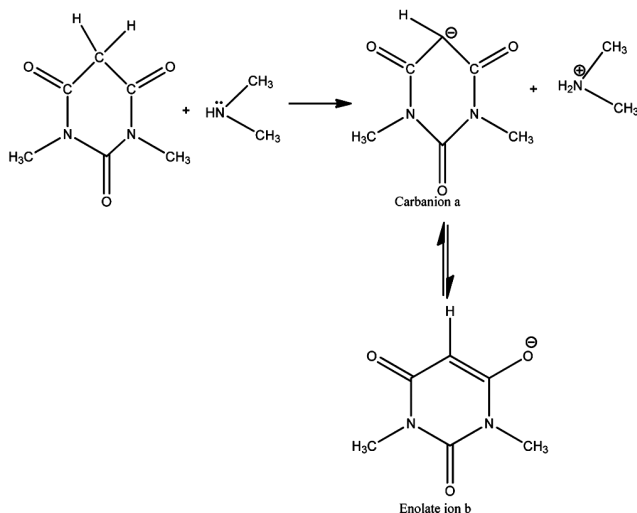
Then as shown in step-2 followed step-3, chloride ion has good leaving ability, so, it gives the substitution product.

The final structure of the product is shown after step-4 in Fig. 1.

The common name of the final product is Dimethylammonium 5-(2,4-dinitrophenyl)-1,3-dimethyl barbiturate and IUPAC name is Dimethylammonium-5-(2,4-dinitrophenyl)-1,3-dimet-hyl-2,6-dioxo-1,2,3,6 -tetrahydropyrimidin-4-olate.

In the present investigation, a new carbanionic sigma complex containing two dinitrophenyl moieties is formed on adding dimethyl amine to the ethanolic

Initially formed anionic sigma complex intermediate

Step — 2

Step — 3

Step — 1
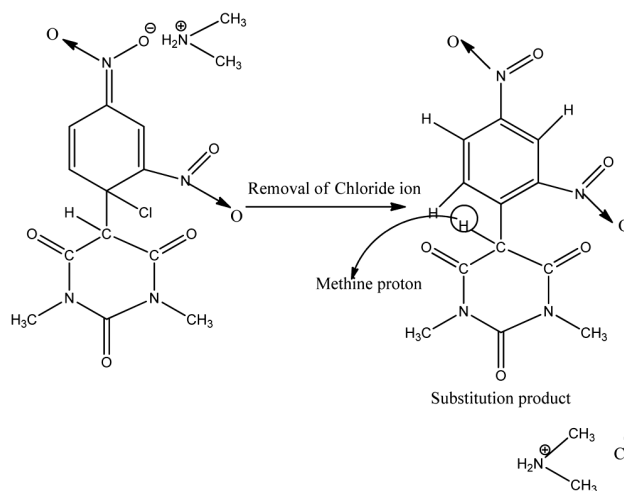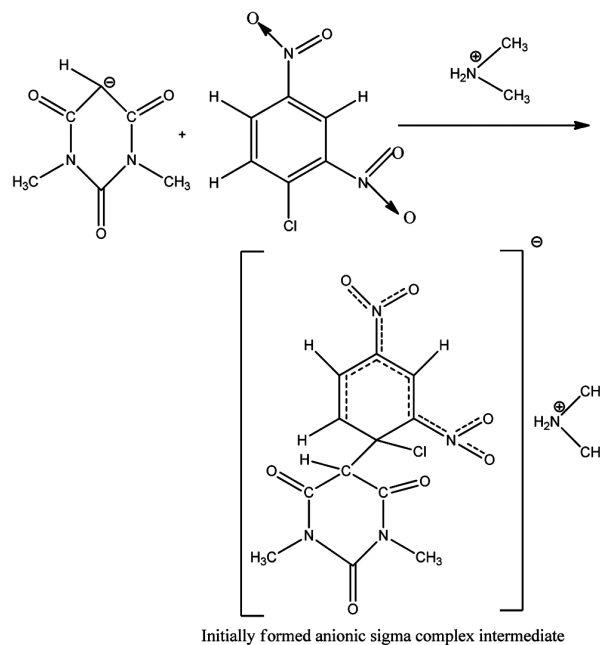
solution containing DNCB (an electron deficient nitro aromatic compound) and 1,3-dimethyl barbituric acid. The titled molecules probably have formed through the carbanionic sigma complex (ORTEP).
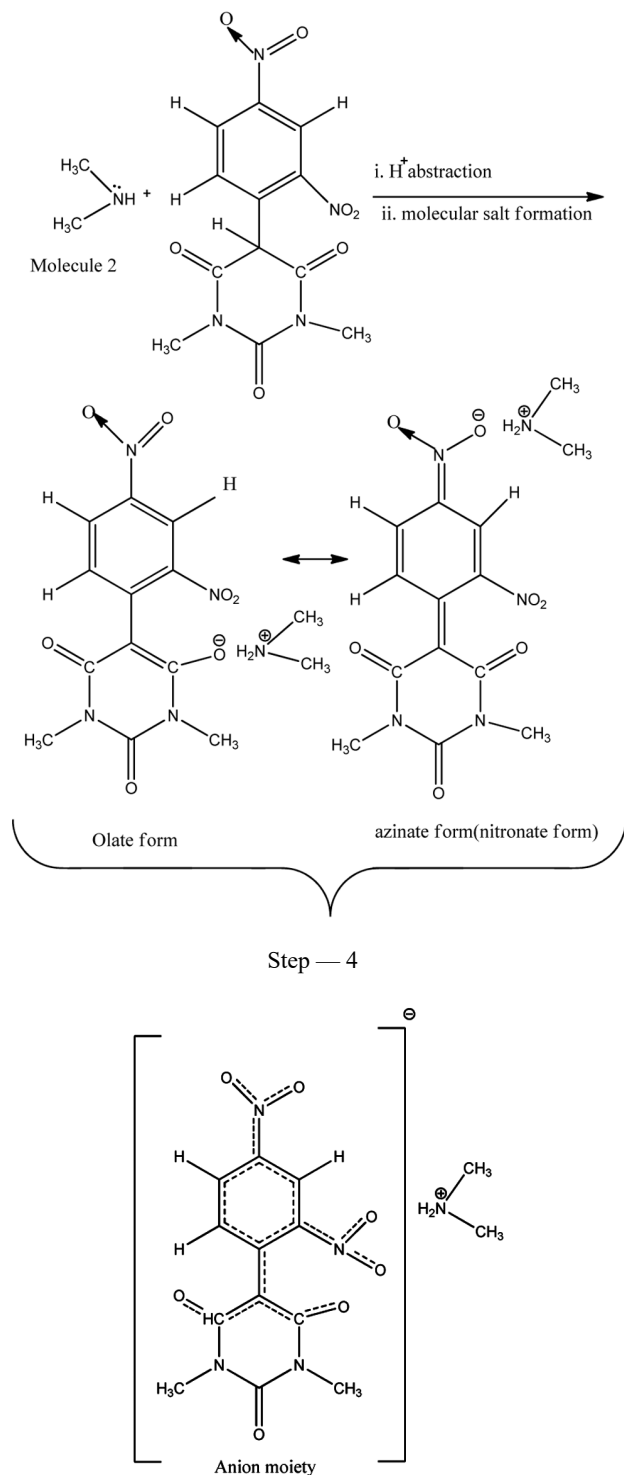

Fig. 1 — Structure of Dimethyl ammonium 5-(2,4-dinitrophenyl) -1,3-dimethyl barbiturate

Spectral analysis

In the reactant DNCB, a strong sharp absorption bond characteristic of C-Cl stretching mode has been observed at 732 cm^{-1}, which is absent in the isolated product. This shows the formation of the product (Fig. 2). –NO$_2$ asymmetric and symmetric stretching mode of the titled molecule exhibit bands at 1522 cm^{-1} and 1330 cm^{-1}, respectively. The broad band at 2900-3500 cm^{-1} is characteristic of amine salt[13].

Methyl protons of N-CH$_3$ groups appear as a single at δ3.11 (6H). The ring protons flanked ring protons of nitro groups at δ8.39. Adjacent ring protons of nitro aromatic moiety appear at δ8.18 as shown in Fig. 3. The ^{13}C NMR spectrum (Fig. 4) indicates ten different carbon environments in the molecule. The peak at 87.16 represents the formation of new C=C bonds.

Description of the crystal structure

Details of crystal data, refinement, and data collection are tabulated in Table 1. The nearly similar bond lengths of various C-C bonds of dinitroaromatic rings imply that there is charge delocalization of cyclic π -electron cloud inside the phenyl ring. ORTEP view of the titled compound is shown in Fig. 5. The presence of leaving group (i.e., chlorine atom) para with respect to the nitro group of the 1-chloro-2, 4-dinitrobenzene (starting material) facilitates the formation of the titled compound in presence of 1,3-dimethyl barbituric acid and dimethyl amine. Absence of chlorine atom, as indicated by the qualitative test on the synthesized barbiturate has been supported by the crystallographic data. The titled molecule is red in colour and it has been attributed to the delocalization of negative charge (Kalaivani et al.,) which has been substantiated by the bond angles and bond lengths of single-crystal X-ray data of 2,4-dinitrophenyl and 1,3-dimethyl barbiturate rings. The bond angles and bond lengths of dimethyl barbiturate residue of the titled molecule are compatible with that of barbiturate ion (Craven, 1964)[14] evidencing the delocalization of negative charge in the barbiturate ring.

Presence of delocalized double bond between C6 and C7 atoms fixes the configuration of the molecule as depicted in Fig. 5. The N5-H5….O6 hydrogen bond between the asymmetric units is the main driving force for the orientation of the dimethyl ammonium cation Fig. 6 and Table 2.

Hirshfeld surface calculations

Hirshfeld surface analysis is a progressive technique used for measuring intermolecular interactions by
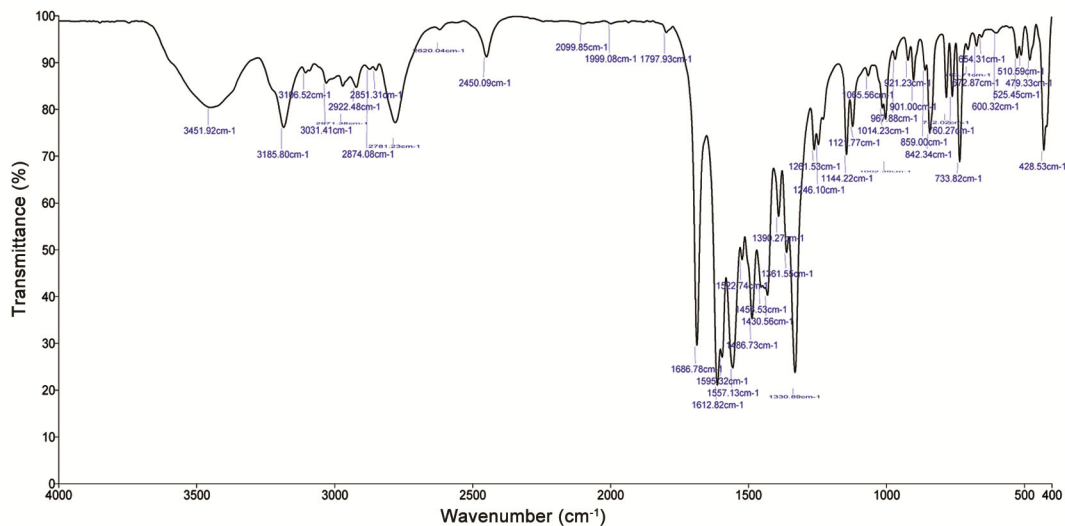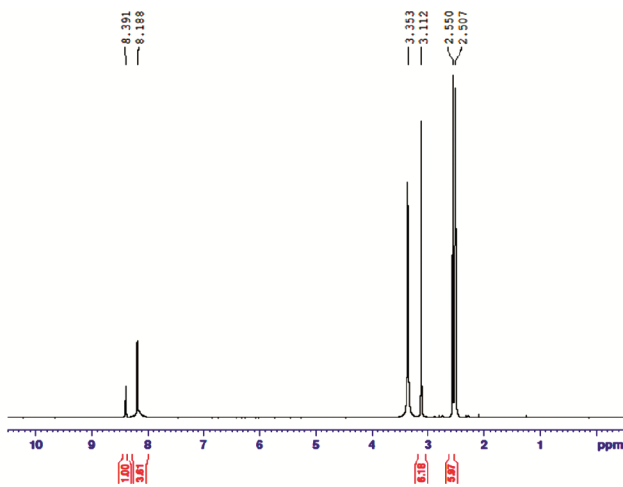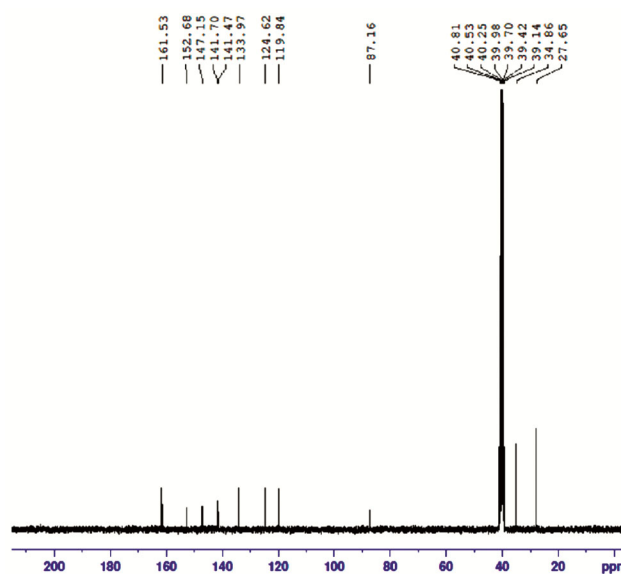
Fig. 2 — IR Spectrum of the complex

Fig. 3 — ¹H NMR spectrum of the complex

Fig. 4 — ¹³C NMR Spectrum of the complex

consideration of the interactions throughout the whole molecule. The Hirshfeld surface has been mapped over d_{norm}, di, de, shape index, curvedness (Mckinnon et al., 2004). Molecular Hirshfeld surface calculations[15-17] have been performed by using the crystal explorer 3.1 programs. When CIF files are entered into the Crystal Explorer Program, all bond lengths to hydrogen are automatically modified to typical standard neutron values [17] i.e., C-H=1.083Å, N-H=1.009 Å and O-H= 0.983Å. For comparison of intermolecular interactions in the crystal structures, the Hirshfeld surfaces have been mapped with normalized contact distances (d $_{norm}$).

The d_{norm} parameter is based on di. di is the distance from the surface to the nearest atom in the molecule itself, de is the distance from the

surface to the nearest atom in another molecule, and van der Waals radii of the corresponding atoms (r_i^{Vdw} and r_e^{Vdw}).

The d_{norm} values are employing a red-blue-white colour scheme, where red regions represent closer contacts and negative d_{norm} value; blue regions represent longer contacts and a positive d_{norm} value and white regions represent the distance of contacts exactly corresponding to the van der Waals separation with d $_{norm}$ value of zero[16-18]. The negative d_{norm} value indicates the sum of di and de is shorter than the sum of the relevant van der Waals radii, which is considered to be the closest contact and is visualized

as red colour in the Hirshfeld surfaces. Hirshfeld surfaces also enabling rapid computation of molecular volume (V_H), surface area (S_H) and two other descriptors of global shape also have been calculated (i) globularity and (ii) asphericity. Globularity[19] is a measure of the degree to which the surface area differs from that of a sphere of the same value volume. Globularity will be 1.0 for a sphere, and progressively less than one becomes more structured. Asphericity[20,21] is a measure of anisotropy,

when applied to the positions of atoms in the molecules.

Hirshfeld surface of synthesized complex

The large and red spot on the 3D Hirshfeld surfaces shows those close-contact interactions, responsible for corresponding hydrogen bond contacts. Fig. 6 represents Hirshfeld surfaces in various forms. The small red spots on surfaces indicate that C-H...π interactions. The Hirshfeld surface of the complex shows percentage of contributions i.e., the number of molecular interactions for a variety of contacts. The de and di combination provides a summary of intermolecular interactions. The molecular volume and surface area are calculated to be 411.96 Å^3 and

Table 1 — Crystal Data and Structure Refinement

|	
Identification code	shelx
Empirical formula	$C_{14} H_{17} N_5 O_7$
Formula weight	367.32
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 11.5729(15) Å α= 90°
	b =8.6857(11) Å β= 94.475(5)°
	c = 16.701(2) Å γ = 90°
Volume	1673.7(4) Å^3
Z, Calculated density	4, 1.458 Mg/m^3
Absorption coefficient	1.019 mm^{-1}
F(000)	768
Crystal size	0.200 x 0.180 x 0.150 mm
Volume	1673.7(4) A^3
Theta range for data collection	4.489 to 69.999 deg.
Limiting indices	-14<=h<=14, -10<=k<=10, -19<=l<=20
Reflections collected / unique	26212 / 3173 [R(int) = 0.0688]
Completeness to theta	67.679 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.3709
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3173 / 0 / 244
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1590
R indices (all data)	R1 = 0.0664, wR2 = 0.1758
Extinction coefficient	0.0054(9)
Largest diff. peak and hole	0.247 and -0.232 e.A^-
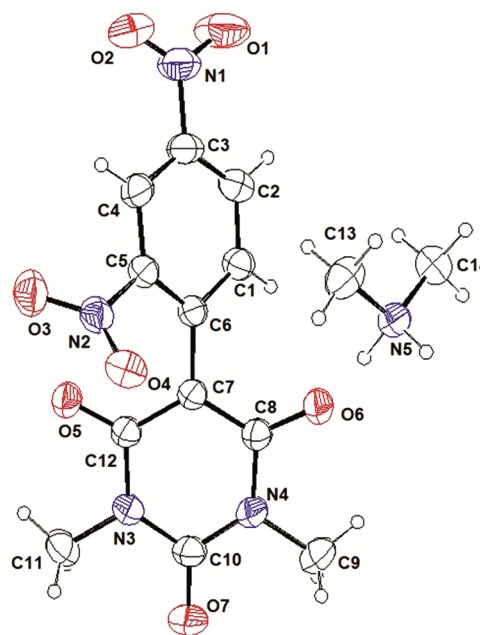
Fig. 5 — ORTEP View
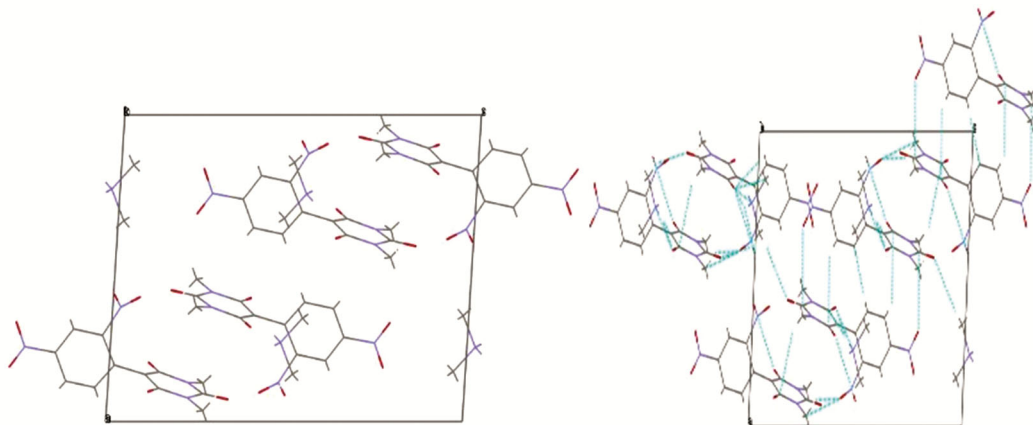
Fig. 6 — Packing View
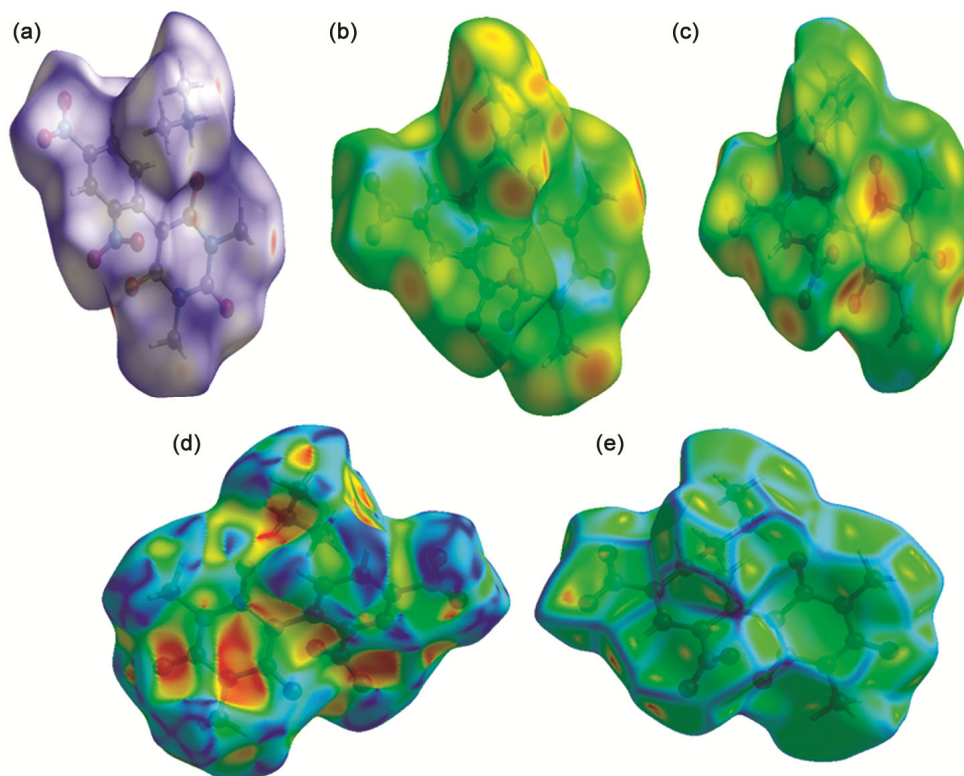
Fig. 7 — 3D Hirshfeld surfaces of compound (a) d_{norm} ranging from -0460 to 1.434 (b) di (c) de (d) shape index (e) curvedness

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Table 2 — Hydrogen bonds (Å and °)				
C(9)-H(9B)...O(4)#1	0.96	2.45	3.220(3)	136.8
C(13)-H(13A)...O(3)#2	0.96	2.61	3.264(4)	125.7
C(13)H(13A)...O(7)#1	0.96	2.59	3.258(3)	126.6
N(5)H(5A)...O(5)#3	0.87(3)	2.12(3)	2.832(3)	139(3)
N(5)-H(5B)...O(6)	1.02(3)	1.74(3)	2.746(3)	168(2)

Table 3 — Surface property statistics of synthesized complex

Property	Min	Max	Mean	Mean+	Mean-	Pi	Sigma+	Sigma-	SigmaT	nu
dnorm	-0.4597	1.4339	0.4599	0.4599	0.4734	0.2141	0.065237	0.065237	0.015405	0.1545
di (Å)	0.8402	2.6584	1.6633	1.6633	nan	0.2055	0.067567	nan	nan	nan
de (Å)	0.8407	2.6558	1.6469	1.6767	nan	0.2047	0.065304	nan	nan	nan
Shape index	-0.9954	0.9987	0.2173	0.5462	-0.4747	0.4599	0.047257	0.058038	0.105295	0.2474
Curvedness	-3.8064	0.6121	-0.9685	0.0866	-0.9820	0.4394	0.007103	0.293098	0.300201	0.0231

360.49 Å², respectively. Globularity and Asphericity values are calculated to be 0.743 and 0.098, respectively. The surface property statistics are listed Table 3. Globularity value is less than one as the molecular surface becomes more structured and the value is 0.685.

cost materials. It has monoclinic crystal system with p21/n space group. The complex showed intermolecular N-H…O and C-H…O hydrogen bonds. Various kinds of interactions are seen in Hirshfeld surface analysis and visualized by intermolecular interactions.

Conclusion

The titled molecule was obtained in good yield with high purity through one-pot synthesis from low-

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