Synthesis, Crystal Structure and Hirshfeld Study of 3,3'-dinitrobenzophenone

N.Latha Rani[1], C.S.Karthik[2], P.Mallu[2], L.Mallesha[3] and M.A.Sridhar[1*]

1. Department of Studies in Physics, Manasagangotri, University of Mysore, Mysuru-570 006, **INDIA**
2. Department of Chemistry, S.J. College of Engineering, Mysuru-570 006, **INDIA**
3. PG Department of Chemistry, JSS College of Arts, Commerce and Science, Ooty Road, Mysuru-570 025, **INDIA**

Email: mas@physics.uni-mysore.ac.in

ABSTRACT

The compound 3, 3'-dinitrobenzophenone is prepared by nitrating benzophenone. The structure was confirmed by ^{1}H NMR, FT-IR, Differential Scanning Calorimetry (DSC), X-ray diffraction. X-ray diffraction study reveals that the compound crystallizes in the triclinic crystal system, in space group $P\bar{1}$. The unit cell parameters are a=7.6180(5) Å, b=8.0341(6) Å, c=10.8056(8) Å, α=74.358(4)°, β= 82.516(4)°, γ= 68.607(5)°, Z=2, and V=592.60(8) Å[3]. The compound exhibits intermolecular interaction of the type C–H...O with symmetry code 1+x, y, 1+ z.

INTRODUCTION

Benzophenones were chosen as the Allergen of the year 2014 by the American Contact Dermatitis Society to raise the awareness of both allergy and photoallergy of this ubiquitous compound [1]. Recently it has been shown that a bifunctional benzophenone derivative, bis-BP, can be used to pattern cross links into polymer thin films [2]. Nitro compounds are also the promising candidates for battery cathodes. It has been found that 2-nitrophenylpyruvic acid is found to be an efficient cathode material for primary batteries [3, 4]. Nitro benzophenone derivatives show strong cytotoxic activity [5].

With this background herein we report the synthesis of 3, 3'-dinitrobenzophenone. The structure of the title compound was elucidated using ^{1}H NMR, FT-IR, X-ray diffraction. Thermal analysis was done using DSC. The study of Hirshfeld surface and the fingerprint plot of the title compound also provide the essential information about the intermolecular interactions.

MATERIALS AND METHODS

Chemicals were purchased from Sigma Aldrich Chemical Corporation. Infrared spectra were recorded on KBr discs on Jasco FT-IR 4100 spectrophotometer in the wavelength range 400-4000 cm^{-1}. ^{1}H NMR spectra were recorded on Bruker DRX - 500 spectrometer at 400 MHz using $CDCl_3$ as a solvent and TMS

as an internal standard. DSC study was performed on DSC Q200 V.24.11 instrument, temperature ranging from 50–240°C at a heating rate of 20°C min^{-1}.

Synthesis of 3,3'-dinitrobenzophenone: 3,3'-Dinitrobenzophenone was prepared by nitrating benzo phenone (1.0 g). The resulting product is a mixture of various isomers. In order to isolate the desired 3,3'-dinitro compound, large amount of solvents were used. The purification was done according to the procedure reported earlier [6]. Suitable crystals for single crystal X-ray diffraction were obtained by slow evaporation using ethanol as a solvent. The melting range was found to be 154-156°C (Scheme-1).
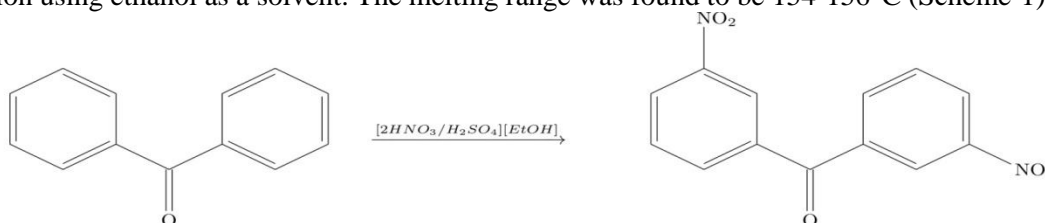
Scheme 1: Schematic diagram of the 3,3'-dinitrobenzophenone.

RESULTS AND DISCUSSION

FT-IR Spectral Analysis: The FT-IR spectrum of the crystal structure is shown in **figure 1**. The peak at 3070 cm^{-1} corresponds to the C–H stretching of the aromatic protons. The peaks at 1636 cm^{-1}, 1536 cm^{-1}, 1428 cm^{-1} and 1360 cm^{-1} correspond to the stretching vibrations of the C=O, NO$_2$, C=C and C–N respectively.
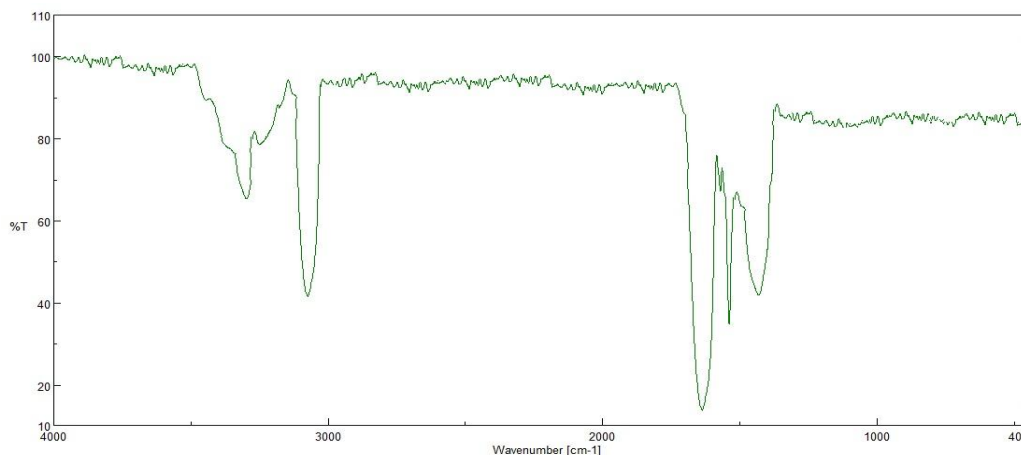

Figure 1. FT-IR spectrum of the 3,3'-dinitrobenzophenone.

^{1}H NMR Spectral Analysis: The spectrum of ^{1}H NMR of the title compound is shown in the **figure 2**. The NMR peak appearing as singlet at δ = 8.79 ppm (2H, s, Ar-H) corresponds to aromatic hydrogen. The peaks appearing as doublets at δ = 8.49 and 7.65 ppm (4H, d, Ar-H) correspond to the aromatic protons.
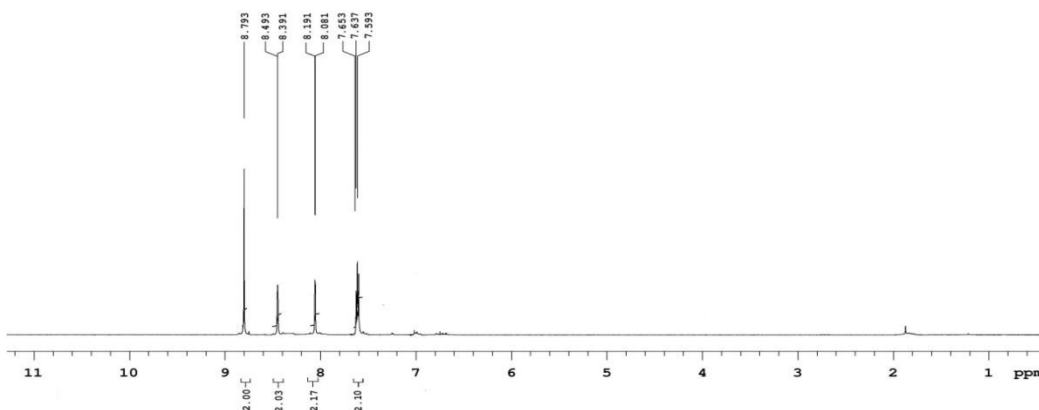
Figure 2. ^{1}H NMR spectra of the 3,3'-dinitrobenzophenone

The peak appearing as a triplet at δ = 8.19 ppm (2H, t, Ar-H) is attributed to the aromatic protons..

Thermal Studies: DSC spectrum of the title compound is as shown in the **figure 3**. The curve in the figure shows that a relatively small endothermic process occurred, which evidenced by a sharp peak at 153.66°C. This is assigned to the melting of the specimen. The sharpness of the endothermic peak indicates the good crystallinity of the specimen.
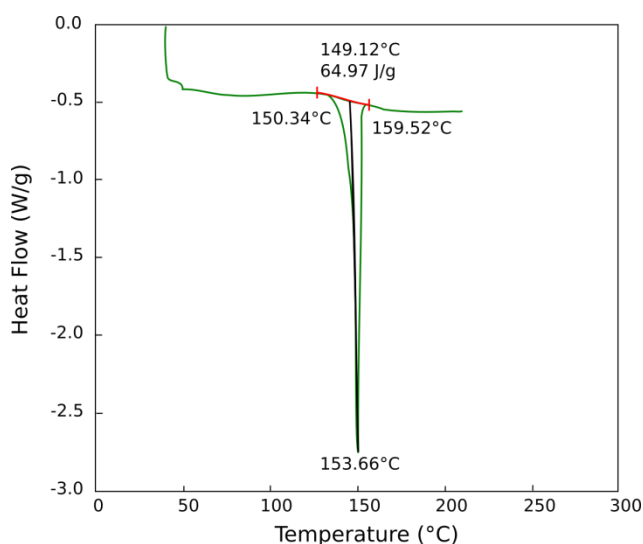

Figure 3. DSC spectrum of the 3,3'-dinitrobenzophenone.

Crystal Structure Determination: A yellow colored, prismatic single crystal of the synthesized compound with approximate dimensions of 0.23 x 0.22 x 0.21 mm was used for X-ray diffraction study. The title compound $C_{13}H_8N_2O_5$ crystallizes in triclinic crystal system, with space group $P\bar{1}$. The unit cell parameters are a=7.6180(5) Å, b=8.0341(6) Å, c=10.8056(8) Å, α=74.358(4)°, β=82.516(4)°,γ= 68.607(5)°, Z=2, and V= 592.60(8) Å^3. Data were collected on a Bruker CCD diffractometer equipped with Cu K_α radiation. Data reduction and applying of absorption corrections were carried out using the *APEX 2* package [7]. Crystal structure was solved by direct methods using *SHELXS-97* and was refined by full-matrix least squares refinement against F^2 using *SHELXL-97* [8]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at chemically acceptable positions. A total of 181

233

parameters were refined with 1959 unique reflections which converged the residual to R=0.0364. The bond lengths and bond angles values are within the expected range.

Table.1. Crystal data and structure refinement details.

CCDC Deposit Number	1062088
Empirical formula	$C_{13}H_8N_2O_5$
Formula weight	272.21
Temperature	293 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell dimensions	a = 7.6180(5) Å, b = 8.0341(6) Å, c = 10.8056(8) Å, α = 74.358(4)°, β = 82.516(4)°, γ = 68.607(5)°
Volume	592.60(8) Å^3
Z	2
Density(calculated)	1.526 Mgm^{-3}
Absorption coefficient	1.026 mm^{-1}
F_{000}	280
Crystal size	$0.21 \times 0.21 \times 0.21$ mm
θ range for data collection	4.25° to 64.66°
Index ranges	$-8 \leq h \leq 8$ $-9 \leq k \leq 9$ $-12 \leq l \leq 12$
Reflections collected	7196
Independent reflections	1959 [R_{int} = 0.0372]
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	1959 / 0 / 181
Goodness-of-fit on F²	1.051
Final [I > 2σ(I)]	R1 = 0.0364, $wR2$ = 0.0969
Largest diff. peak and hole	0.482 and −0.911 eÅ^{-3}

The crystal data and the refinement details are given in table 1. The *ORTEP* diagram of the title compound is shown in the Figure 4. Figures 5 and 6 show the packing diagrams viewed down *a* and *b* axes respectively. The bond distances and angles are listed in the table 2. Torsion angles are listed in the table 3. Hydrogen-bond geometry is given in the table 4. The geometrical calculations were carried out using the program *PLATON* [9]. The molecular and packing diagrams were generated using *Mercury* [10].
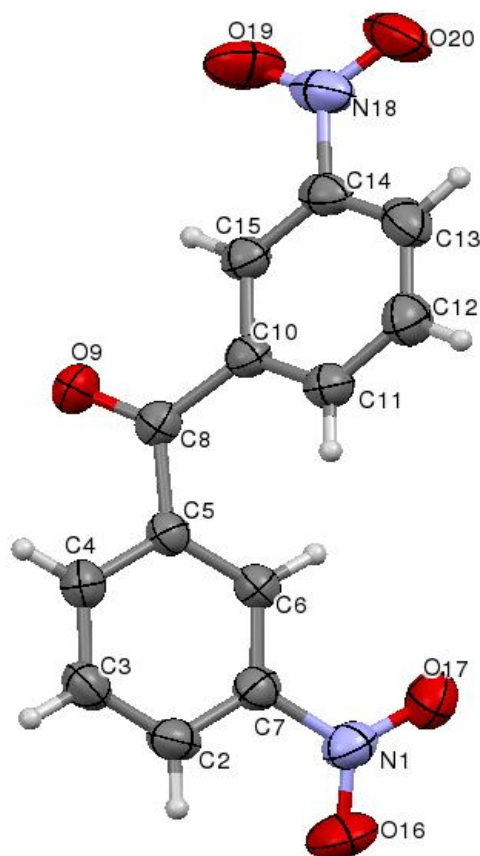
234

Figure 4. The *ORTEP* diagram of the 3,3'-dinitrobenzophenone.

Table 2. Selected bond lengths and bond angles (Å, deg.)

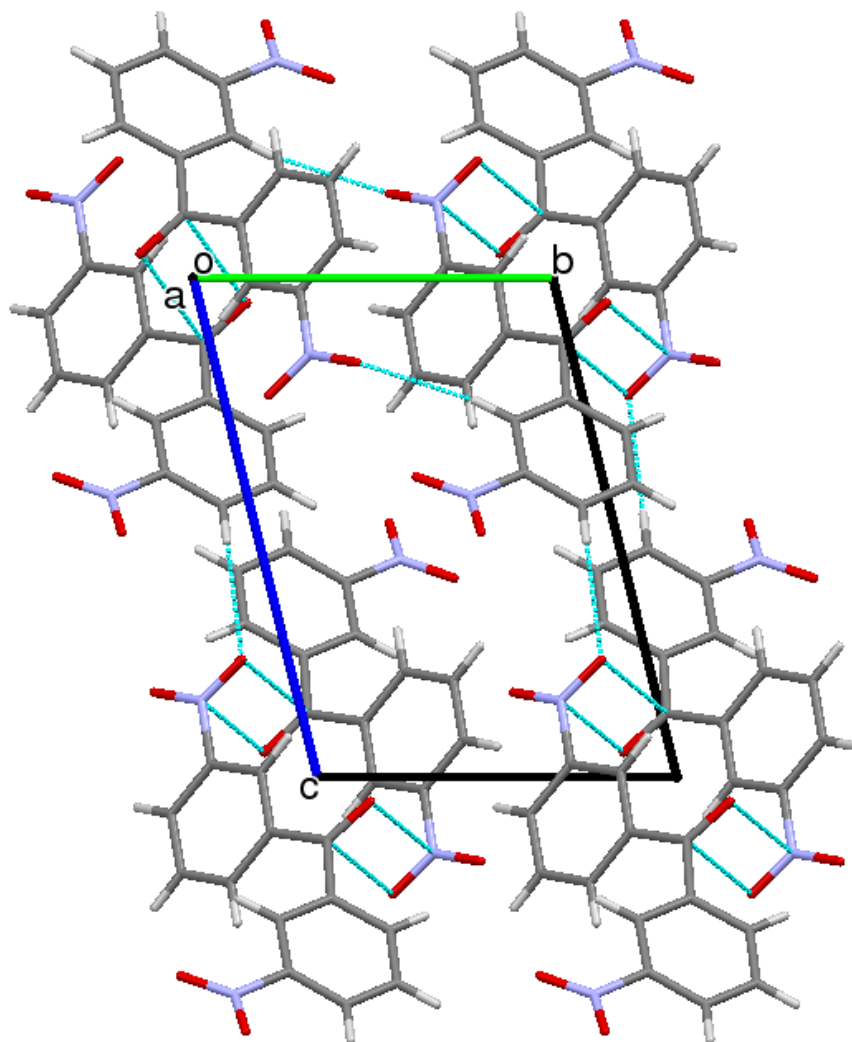| Atoms	Bond Lengths/Angles	Atoms	Bond Lengths/Angles
O9-C8	1.2166(17)	O16-N1	1.221(2)
C14-C15	1.380(2)	C4-C5	1.398(2)
N18-C14	1.471(2)	C3-C4	1.375(2)
C10-C11	1.387(2)	C10-C15	1.394(2)
O19-N18	1.222(2)	C11-C12	1.383(2)
O16-N1-O17	123.32(15)	C10-C15-C14	118.63(13)
O16-N1-C7	118.33(14)	C13-C14-C15	122.83(14)
O19-N18-O20	124.00(17)	C11-C12-C13	120.73(15)
O20-N18-C14	118.16(15)	C8-C10-C15	118.01(12)
C3-C2-C7	118.10(14)	C2-C7-C6	123.23(14)

Figure 5. The molecular packing view of the 3,3'-dinitrobenzophenone down the *a* axis.

Table 3. Selected torsion angles (deg.)

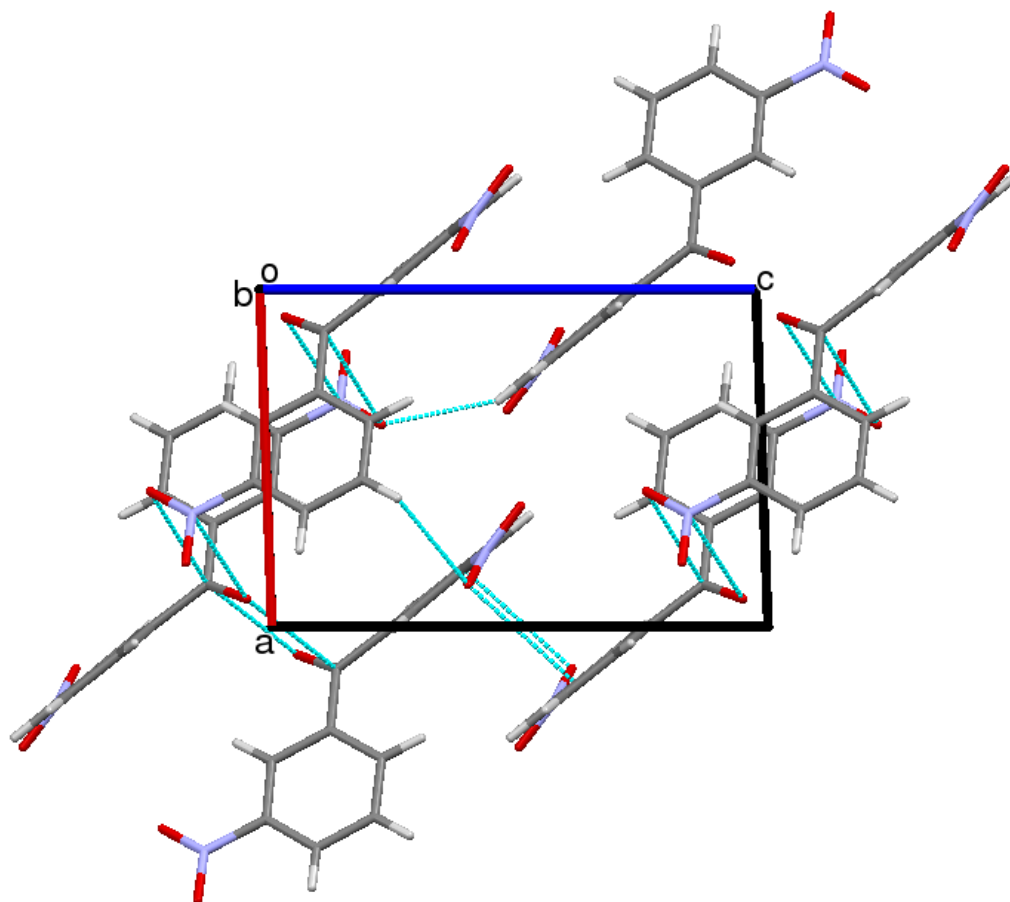| Atoms	Torsion Angles	Atoms	Torsion Angles
C5-C8-C10-C11	−18.3(2)	C6-C5-C8-O9	135.94(15)
O16-N1-C7-C2	15.8(2)	C12-C13-C14-N18	179.85(15)
O17-N1-C7-C2	−163.91(14)	N18-C14-C15-C10	179.65(14)
O19-N18-C14-C13	−171.69(16)	C15-C10-C11-C12	−0.6(2)
O20-N18-C14-C15	−173.65(16)	C5-C8-C10-C15	166.01(14)
C3-C2-C7-C6	1.1(2)	O9-C8-C10-C11	159.34(15)

Figure 6. The molecular packing view of the 3,3'-dinitrobenzophenone down the *b* axis.

The phenyl rings are highly planar. The maximum deviation from the mean plane in the rings C2—C7 and C10—C15 are for atoms C7 (0.009(1) Å) and C15 (0.004(2) Å) respectively. The dihedral angle between the least-square planes of the two phenyl rings is -18.3(2)° (C5-C8-C10-C11).

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

D—H...A	D—H	H...A	D...A	D—H...A	Symmetry code
C(2)—H(2)...O(19)	0.93	2.52	3.3565(19)	150	*1+x, y, 1+z*

The phenyl rings C2—C7 and C10—C15 are *sp2* hybridized. They are well described by the torsion angles 1.07° and 0.43° respectively indicating +*syn-periplanar* conformation. The bond lengths and angles agree well with those of previously reported benzophenone derivatives.

The double bond character of C8-O9 is confirmed by the bond length 1.2166(17) Å. The torsion angle between the phenyl ring and the carbonyl group (C6-C5-C8-O9) is 135.94(15)° which is lesser than 151.5(2)° observed for (C6-C1-C7-O1) the molecule ethyl 2-(4-benzoyl-2,5-dimethylphenoxy)acetate [11].

237

The molecules are connected by intermolecular interaction of the type C—H…O. The crystal structure is also stabilized by short contacts of the type: N18—O19…*Cg1* with the O…*Cg* distance of 3.6172(17) Å, the angle of the N—O…*Cg* is 126.86(12)°, whose symmetry code is *-x,-y,-z;* N18—O20…*Cg2* with the O…*Cg* distance of 3.7341(18) Å, the angle of the N—O…*Cg* is 87.57(11)°, whose symmetry code is 1-*x,-*1-*y,-z.* Here *Cg1* is the centroid of the C2—C7 ring and *Cg2* is the centroid of the C10—C15 ring.

Hirshfeld Surface Analysis: Hirschfield surface analysis was carried out using the program *Crystal Explorer* [12]. The 2D fingerprint plot provides a summary of intermolecular contacts in the crystal, which is a combination of d_i and d_e [13]; here d_i and d_e are the distances from the Hirschfield surface to the nearest nuclei inside and outside the surface respectively [14].

The contribution of various intermolecular contacts to the Hirschfield surface is given in the table 5. The major contribution is from O...H (43.6%) contacts. The minor contribution is from N...H (1.6%). Figure 8 shows the percentage contributions of O...H (43.6%), C...H (15.5%), H...H (14.9%), O...C (12.7%) contributed to total Hirschfield surface area of the molecules. The other contributions are N...C (1.9%), O...N (2.9%), C...C (3.0%), O...O (3.9%). These contacts are highlighted by a conventional mapping of d_{norm} on the molecular Hirschfield surface (figure 7). The red coloured regions on the d_{norm} surface represent the intermolecular contacts closer than the sum of the vanDer Waal's radii; the blue region shows the longer contacts [14].
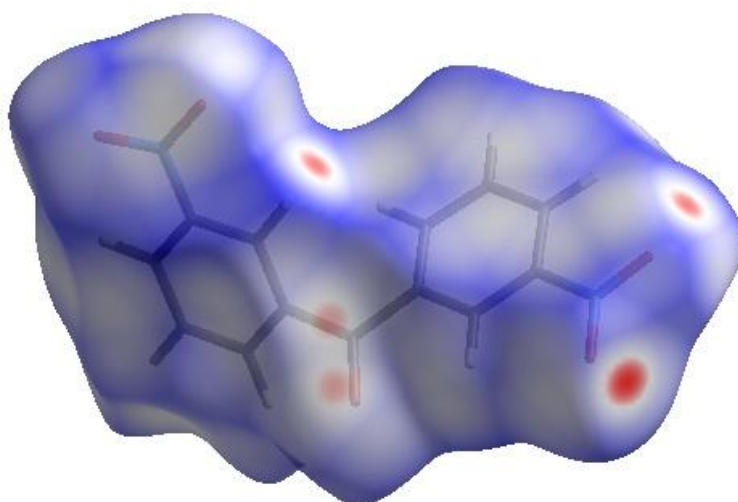

Figure 7. d_{norm} mapped on Hirschfield surface for the visualization of intermolecular contacts of the title compound.

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

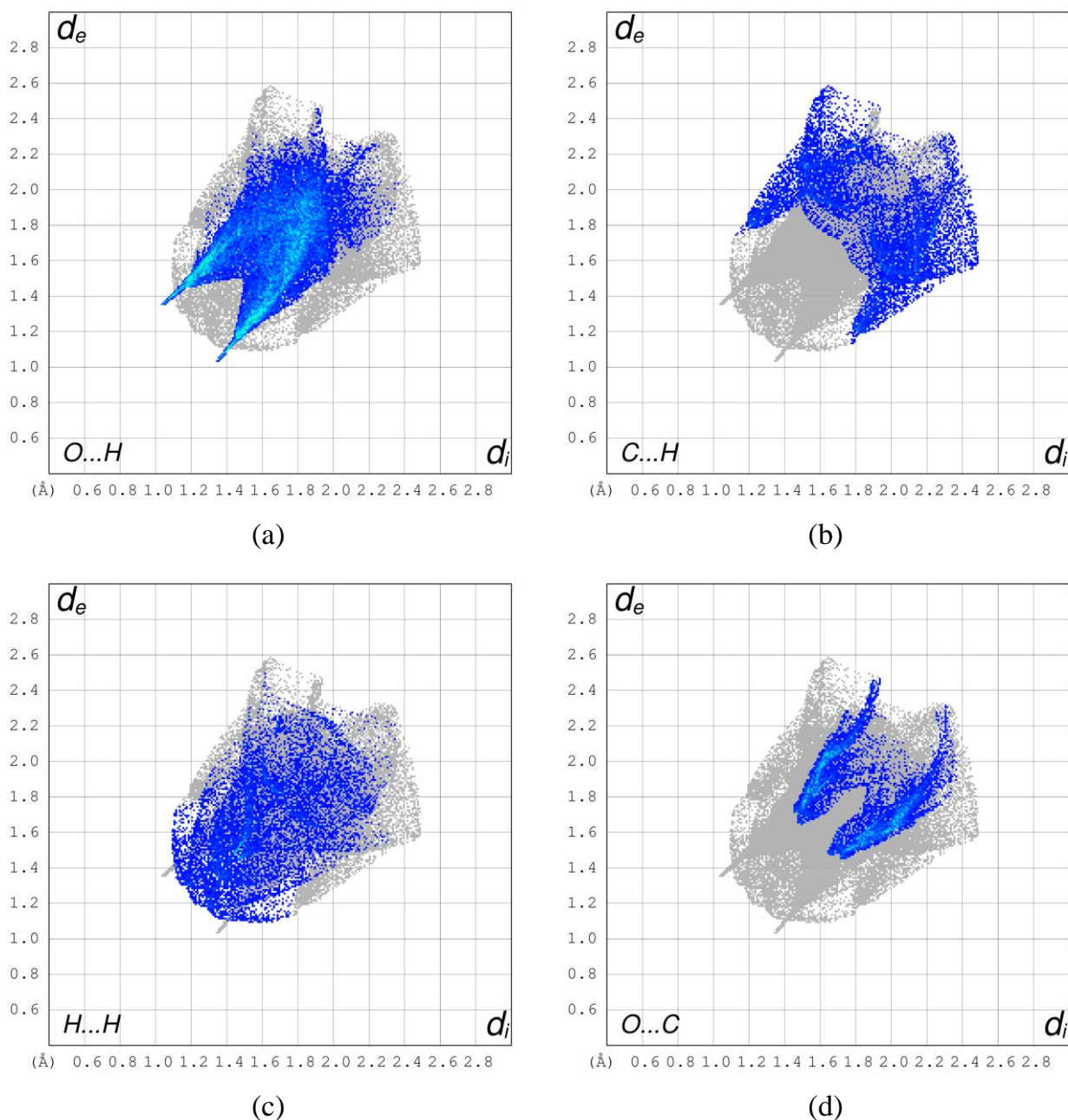| Inter-contacts	Contributions (%)	Inter-contacts	Contributions (%)
O - H	43.6	O - O	3.9
C - H	15.5	C - C	3.0
H - H	14.9	O - N	2.9
O - C	12.7	N - C	1.9

(a)

(b)

(c)

(d)

Figure 8. Fingerprint plot of the title compound resolved into O...H, C...H, H...H, O...C contacts showing the percentage of contacts contributed to the total Hirshfeld surface area for the molecules.

APPLICATIONS

Literature shows that the benzophenone derivatives are pharmacologically active when the nitro group is in the meta- position. The current work helps us to understand their behaviour better and synthesise more efficient materials.

CONCLUSIONS

In view of the importance of benzophenone and nitro compounds the title compound was synthesized; the structure was confirmed by ^{1}H NMR, FT-IR, DSC. Further, X-ray diffraction study reveals that the compound crystallizes in the triclinic crystal system in the space group $P\bar{1}$. The Hirschfield surface analysis shows that the major contribution is from O...H (43.6%) of various intermolecular contacts to the Hirschfield surface.

ACKNOWLEDGMENT

REFERENCES

[1]   Ashley R. Heurung, Srihari I. Raju, Erin M. Warshaw, Benzophenones, *Dermatitis*, **2014,** *25*, 3–10.

[2]   T.C. Gregory, J.T. Nicholas, T.K. Jeffrey, Patterning dewetting in thin polymer films by spatially directed photocrosslinking, *J. Colloid and Interface Science*, **2010,** *351*, 556–560.

[3]   R. Renuka, 2-Mitrophenylpyruvic acid as a cathode material in a magnesium/zinc-based primary battery, *J. Appl. Electrochem,* **2000**, *30*, 483–490.

[4]   R. Renuka, V. John Fredrick, S. Saravanan, P.C. Srinivasan, 3-3'-dinitrobenzophenone as a cathode material in a magnesium/zinc based primary battery, *Indian J. Chem,* **2001**, *40A*, 175–181.

[5]   E. Kumazawa, K. Hirotani, S.C. Burford, K. Kawagoe, T. Miwa, I. Mitsul, A. Ejima, Synthesis and antitumor activity of novel benzophenone derivatives, *Chem. Pharm. Bull,* **1997,** *45*, 1470–1474.

[6]   E. Barmatt, *J. Chem. Soc,* **1924**, *125,* 767.

[7]   Bruker, *APEX2, SAINT*, *SADABS*, **2009**, Bruker AXS Inc, Madison, Wisconsin, USA.

[8]   G.M. Sheldrick, *SHELXS 97*, *A program for crystal structure determination,* Univ. of Göttingen, **2008**, Germany.

[9]   A.L. Spek, *Acta Cryst,* **1990,** *A46*, 34.

[10] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van de Streek, P.A. Wood, *J. Appl. Cryst,* **2008**, *41*, 466.

[11] H.C. Devarajegowda, A.K. Shaukath, S. Jeyaseelan, A.E. Waleed, J. Shylajakumari, Ethyl 2-(4-benzoyl-2,5-dimethyl-phenoxy)acetate, *Acta Crsytallogr,* **2009**, *E65,* o2854–o2855.

[12] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, *CrystalExplorer* (Version 3.1), **2012**, University of Western Australia.

[13] S. Saikat Kumar, M. Gopal Chandra, K. Tanusree, Hirshfeld surface analysis and quantum mechanical study of para-nitro benzylidene methyl arjunolate, *J. Mol. Str,* **2011**, *1000*, 120–126.

[14] Mark A. Spackman, Dylan Jayatilaka, Hirscfeld surface analysis, *Cryst. Eng. Comm,* **2009**, *11,* 19–32.

AUTHORS' ADDRESSES

1. **Dr. M.A. Sridhar**
       Professor, Department of Studies in Physics, University of Mysore,
       Manasagangotri, Mysuru 570 006, India
       E-mail: mas@physics.uni-mysore.ac.in, Phone: 0821-2419333
2. **Dr. P. Mallu**
       Professor, Department of Chemistry,
       S.J. College of Engineering, Mysuru 570 006, India
       E-mail: drmallu66@gmail.com, Phone: 0821-2548285

3. **Dr. L. Mallesha**
    Asst. Professor, PG Department of Chemistry,
    JSS College of Arts, Commerce and Science, Ooty Road, Mysuru, 570 025, India
    E-mail: mallesha83@gmail.com, Phone: 0821-2548252
4. **Ms. Latha Rani**
    Research Scholar, Department of Studies in Physics, University of Mysore,
    Manasagangotri, Mysuru 570 006, India
    E-mail: lathascxrd@gmail.com, Phone: 0821-2419333
5. **Mr. C. S. Karthik**
    Research Scholar, Department of Chemistry,
    S.J. College of Engineering, Mysuru 570 006, India,
    E-mail: karthikkumarcrs@gmail.com, Phone: 0821-2548285