Synthesis, Structural and Spectroscopic Analysis, Thermodynamic and Micro Hardness Testing of a Chalcone Molecule

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A novel chalcone derivative, (2E)-3-(3, 4 dimethoxy phenyl)-1-(1-hydroxy-2 naphthyl)prop-2-en-1-one (DHNP), $C_{21}H_{18}O_4$, has been synthesized from the mixture of 4-hydroxy acetophenone (0.05mol) and 4-hydroxy-3-ethoxybenzaldehyde (0.05mol) by Claisen-Schmidt reaction mechanism. The structural features of the grown crystal were elucidated by single X-ray diffraction (XRD) studies which confirm the title compound, belongs to the monoclinic system with the $P2_1/n$ space group. Functional groups, the number of unique proton and carbon environments were identified using FT-IR, ^1H, and ^{13}C NMR spectral investigation. The optical behavior of the crystal was analyzed by UV-Vis absorption studies, and the value of the optical band gap energy (Eg) of the crystal is found to be 3.386eV. The Photoluminescence (PL) spectrum of the compound indicates the green to yellow light emission in the visible region. By employing thermogravimetric analysis (TGA), the thermal stability of crystal and the dehydration and decomposition nature were found. The Coats and Redfern relation was applied to evaluate the kinetic and thermodynamic parameters. Mechanical properties such as the Hardness (H_V), Meyer's index (n), Newtonian resistance pressure (W), load independent constant (b), and elastic stiffness constant (C_{ij}) were calculated by performing a Vickers hardness test on the compound and found to exhibits an excellent mechanical power.

Introduction

Aromatic compounds having an unsaturated side chain is commonly known as chalcones [1,2]. Chalcones are widely distributed as secondary metabolites in plant kingdom and are important intermediate in the biosynthesis of flavonoids and isoflavonoids [3]. Claisen-Schmidt condensation reaction method was one of the most favoured methods used in the synthesis of chalcone derivatives. Researches on both synthetic and naturally available chalcones have gained momentum in the past three decades because of easy synthesis procedure, low cost, and plentifulness. Chalcones as bio molecules restrain the role of β (1,3)‑glucan and chitin synthases, enzymes, in the biosynthesis of (1,3)‑glucan and chitin polymers of the fungal cell wall, respectively [4,5]. The highly reactive α, β-unsaturated propenone group in chalcones is believed to be useful for the conversion of chalcones to various classes of heterocyclic compounds, which makes chalcones, a favored pharmacophore in medicinal chemistry [6]. Journal reports on chalcones disclosed that chalcones with phenyl rings at the ends showed excellent biological profiles [7,8]. In the recent past, attention has been given to organic NLO materials for applications in field of photonics and optoelectronics [9] because of their attributes including nonlinearity, optical limiting, fast switching time, and effortless boosting methods [10]. Chalcone and their derivatives are exhibiting high NLO behaviour and crystallinity [11]. There is a quite large number of chalcone compounds are reported to crystallize in non-centrosymmetric system which is the preferred configuration for NLO property [12,13], mostly second order nonlinear efficiency [14,15].

The structure-activity relationship of a material can be easily quantified via structural, optical, thermal, mechanical, and biological characterization. In this work, the title material DHNP has been prepared and studied for its structural and physical properties and the outcomes are reported in this communication.

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Methods and materials

Synthesis and growth of the compound DHNP

The title molecule was synthesized by following the published procedure [16a,b]. During the synthesis, the mixture of 2-acetyl-1-naphthol and 3, 4-dimethoxybenzaldehyde (1:1), was added with 120mL of absolute alcohol and agitated for 5 minutes using magnetic stirrer at constant temperature. Intermixture was then supplemented with 20mL (10%) of sodium hydroxide solution and whirled for 8h. After adding enough amount of cold dilute hydrochloric acid, the resultant product was filtered and washed with distilled water. The title material was obtained via recrystallization of the crude product from absolute alcohol. The estimated yield and the melting point using melting point apparatus were 90% and 110°C, respectively. The reaction scheme is given in **Fig. 1**.
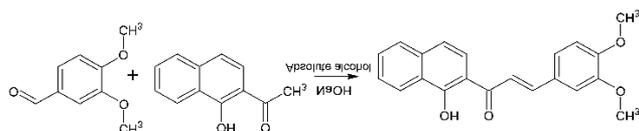
Fig. 1. Reaction scheme of DHNP.

The solution of recrystallized product was prepared at 30°C using the dissolvent ethylmethylketone. The beaker containing the solution was covered and housed in a constant temperature bath (0.1°C) and continuously stirred using Teflon coated immiscible magnetic stirrer. The temperature was lowered at a rate of 0.5°C/day and after a fortnight, large size crystals were obtained (**Fig. 2**).

Fig. 2. A grown crystal of DHNP.

Characterization techniques

The chemicals used for experimental were of analytical grade (Sigma-Aldrich) purchased from common commercial suppliers and used it without further purification.

The intensity data for structural characterization were collected using Bruker AXS SMART APEXII single crystal X-ray diffractometer equipped with graphite monochromated MoKα (λ = 0.7103Å) radiation and CCD detector up to $\theta_{max} = 28.39°$. Crystal structure was solved and analyzed using the computer programs: Data Reduction- SAINT [17]; Structure solution & Refinement-SHELXS-97 and SHELXL-08 [18,19]; Molecular graphics- ORTEP 3 [20]; Plane calculation, puckering & asymmetry parameters-PARST [21]; Geometrical calculation, molecular interactions and unit cell packing-PLATON [22].

The grown single crystals of DHNP were subjected to optical (FTIR, UV-Vis-NIR, ^{1}H and ^{13}C NMR and PL), thermal (TG/DTA), mechanical (Vickers hardness test), Pharmacological (antimicrobial and antioxidant) characterization using the instruments at Sophisticated Analytical Instrumentation Facility (SAIF), IIT-M, Chennai, Tamilnadu and LifeTeck Research Centre, Arumbakkam, Chennai, Tamil Nadu, India.

Calculation of kinetic and thermodynamic parameters

Thermogravimetric analysis (TGA) of drug materials is often used to measure the solubility of drug materials in solvents. The collected data were assessed using the Coats-Redfern expression to obtain the kinetic parameters and thermodynamic properties [23,24]. The above said relation is

$$\log_{10}\left[\left(\frac{\left\{1-(1-\alpha)^{1-n}\right\}}{T^2(1-n)}\right)\right] = \log_{10}\left\{\left(\frac{AR}{\alpha E}\right)\left(1-\frac{2RT}{E}\right)-\left(\frac{E}{2.303RT}\right)\right\}$$

where, β- rate of heating, T-temperature and α- is the fraction of original substance decomposed at time t. α.is given by

$$\alpha = \frac{m_o - m_t}{m_o - m_f}$$

here, m_t, m_o and m_f are masses of the sample estimated using TGA thermal data, and R denotes gas constant.

Mechanical properties of the synthesized compound were studied by Vickers hardness test and the averaged diagonal lengths of the square based indentation was used in $H_V = 1.854P/d^2$ Kg/mm^2, where P is the load employed in grams and d is the averaged diagonal length in millimetre.

Results and discussion

Single crystal X-ray diffraction (XRD)

The data collected by XRD technique for the title compound DHNP reveals its monoclinic crystal system and space group P2$_1$/n with unit cell parameters a = 9.8784, b = 15.4108, c = 11.2288 (Å); β = 92.674°; V = 1707.5 (Å^3). A multipurpose Crystallographic software program PLATON was utilized to derive number of parameters associated with the title crystal [18,25-26]. Physical and geometrical features of the compound DHNP is listed in **Table 1.** **Fig. 3** and **Fig. 4** illustrate the molecular plot and the pattern of packing of molecules in the unit cell [26].

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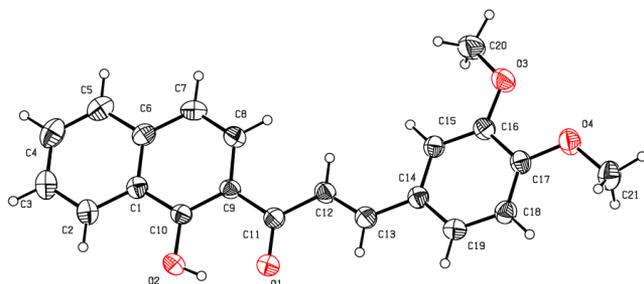
Fig. 3. Molecular structure with numbering scheme.
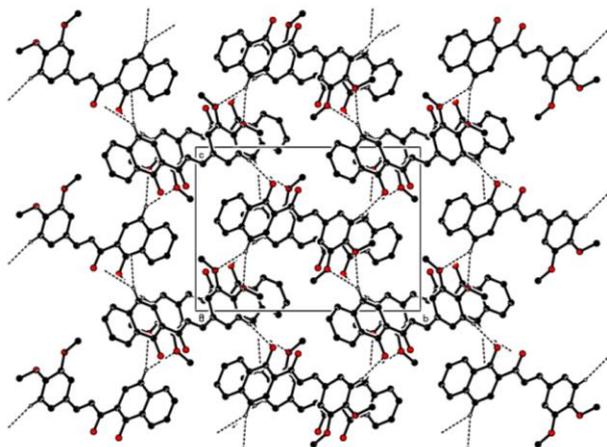
Fig. 4. Hydrogen bonded molecules in the unit cell of the crystal structure.

Table 1. Physical and geometrical features of the compound DHNP.

Molecular formula	$C_{21}H_{18}O_4$
Chemical diagram	
Crystal system	Monoclinic
space group	$P2_1/n$
S-value on F^2	1.065
Residual index	$R_1 = 0.075$
C-C distance of naphthalene and phenyl ring	1.348(4) - 1.423(4)Å; 1.373(4)-1.4080(4)Å
The C-O bond lengths	1.336(3) -1.417(4) Å
The C=O bond length	1.254(3) Å,
Angle of orientation between aromatic hydrocarbon and benzene rings	2.65 (1)°
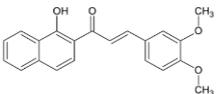
In the title compound, the molecular and crystal stability are ensured by O-H…O and C-H...O intra and intermolecular hydrogen bonds, respectively. The atom C7 is bifurcated and generating C7-H7...O3 and C7-H7...O4 hydrogen bonds described by a ring motif $R^2_1(6)$.

Proton and carbon NMR spectral studies

For the compound DHNP, Yield 90%; reddish-purple; mp 110°C; 1H NMR (DMSO, 500 MHz, δppm (**Fig. 5(a)**) 3.85 & 3.90 (s, -CH₃, 6H), 15.3 (s, -OH, 1H), 7.08 (dd, H$_\alpha$, 1H), 7.48 (d, H$_\beta$, 1H), 7.60- 8.39 (medium, Aromatic-H, 9H).

Proton decoupled ¹³C NMR (DMSO, 125 MHz, δppm, (**Fig. 5(b)**)): 40.32(-CH₃), 162.33(α, β-unsaturated carbon), 111.50.-161.47 (aromatic carbon), 205.99 (carbonyl carbon). In this work, the observed chemical shift values of protons of different chemical species and the assigned values of carbons of different environment are in absolute conformity with the published values [27,28].

(a)

(b)
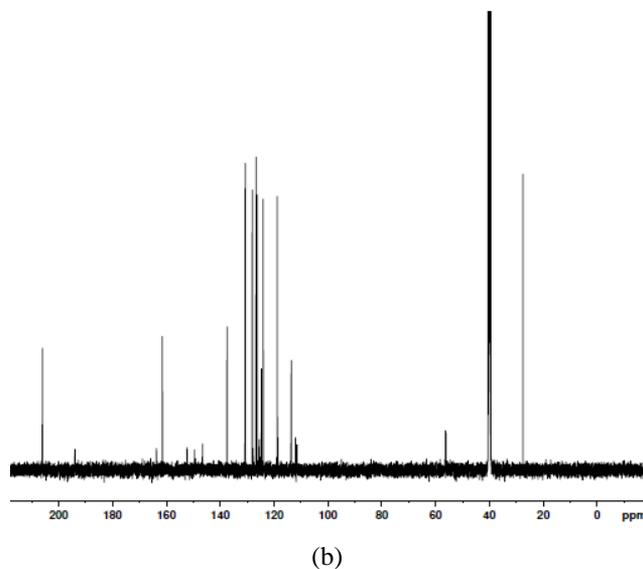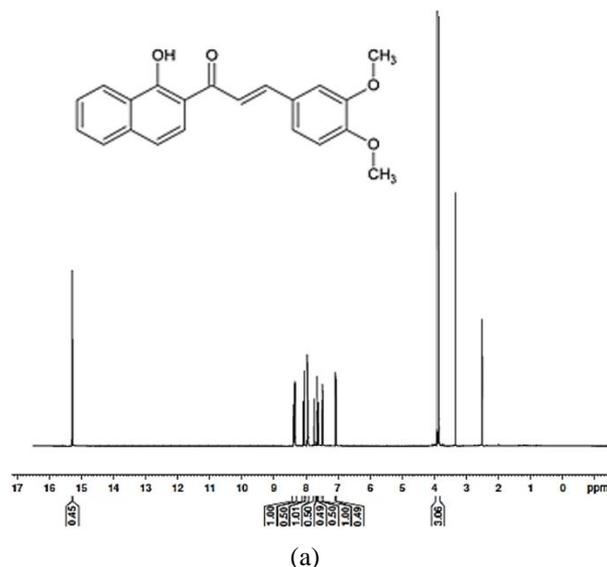
Fig. 5. [a] Proton and [b] Carbon NMR spectra of DHNP.

FTIR- spectral analysis

The absorbance signals in the recorded FT-IR spectrum of the compound DHNP (**Fig. 6**) have been assigned with wave numbers as follows :[(str./bending, intensity of the peak and wave number cm⁻¹]: -OH(stretching.,s,3423), aromatic C-H (stretching, m, 3030-2917), -CH₃ (stretching, w, 2496 -2042), carbon=O (stretching, s, 1666 & 1609), carbon-carbon aromatic (stretching, m, 1591), carbon =

carbon aromatic (stretching, s, 1511), C-O (stretching, s, 1368), asymmetric C-O-C (stretching, s, 1228-1258), symmetric C-O-C (stretching, m,993). The absorbance bands associated with the functional groups present in DHNP are found to be within the expected range and the assigned wave number values are similar to that of the accepted data [29,30].
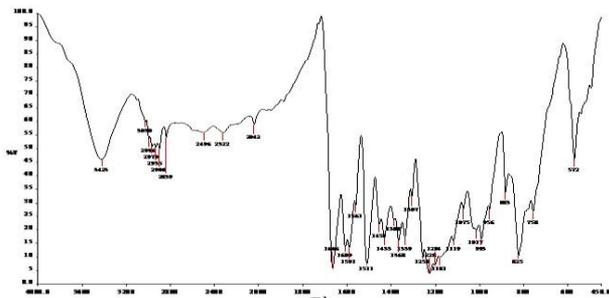
Fig. 6. FT-IR spectrum of DHNP.

UV-VIS-NIR spectral studies

In case of chemical compounds with double/unsaturated system, absorption bands are due to the electronic changeover across the nonbonding orbital to pi star orbital and pi to pi star orbital in the 200-700nm region. The title compound exhibits prominent excitation peaks at 256 and 367nm (**Fig. 7**) and the existence of two eminent signals is the characteristic feature of flavanoids. The absorbance bands in the range 211-256nm is ascribed to the pi to pi star orbital conversion in the aromatic ring and the one at 367nm is due to the π electron delocalization across ethylenic and the carbonyl groups of the molecule [31]. The red shift of bonding to anti-bonding orbital and nonbonding to anti-bonding orbital electronic transfiguration (longer wavelength) might be due to the association of donor groups like-OH(at ortho) and -OMe with the aromatic rings. The band gap energy which measure the reactivity of the compound was calculated using λ_{max} = 367nm in the formula $E_g = [12.4237/\lambda c]$ eV, and is found to be 3.386eV. This small band gap energy accounts the effortless excitation and longer absorption wavelength. The absence of any prominent signals in the visible region illustrates the material's transparent nature and thus finds applications in optoelectronic devices.
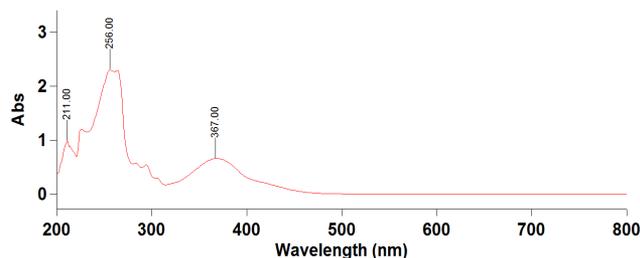
Fig. 7. UV-VIS-NIR spectrum of DHNP.

Photoluminescence studies (PL)

PL spectrum of the title material (**Fig. 8**) reveals a broad peak of medium intensity at 509nm and a relatively strong and sharp emission peak at 587nm. α, β unsaturated carbonyl compounds commonly emit less quantum of photons but the emission efficiency can be improved by extended conjugation, high coplanar conformation, and introduction of OMe donor groups. In this study, the molecule is with extended conjugation (C=C, C=O), highly coplanar defined by the angular orientation of the ring systems (2.65(1)°) of the molecule, and OMe groups substituted phenyl ring brought about π-electron redistribution across the crystal [32-34].
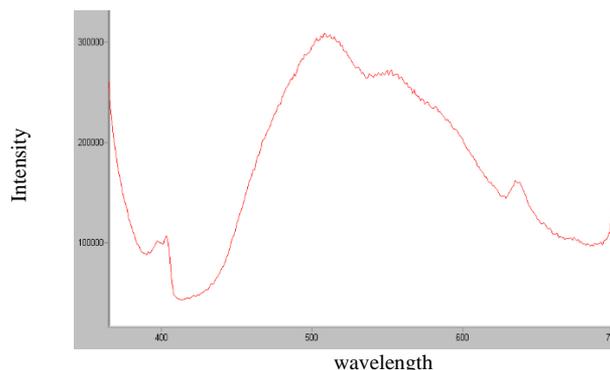
Fig. 8. Photoluminescence spectrum of DHNP.

Thermal analysis

Themogravimetric/DTA thermographs of DHNP (**Fig. 9(a)**) in which differential thermal analysis thermogram exhibits both exothermic and endothermic thermal processes and the small endothermic peak around the temperature 92°C in DTA graph indicates the release of water molecules and the broad endothermic signal centered on 149°C provides the melting point of the compound, respectively. Presence of two strong endothermic changes approximately between 225-300°C and 350-450°C are ascribed to the substituent loss and its fragmentation and the Chalcone fragmentations, respectively, yielding a ring containing ionic carbonyl group (C≡O+) and a substituent free ring system is derived by the elimination of carbon monoxide [35]. Chalcones in combination with an OH substituted ring in the vicinity of the propen-one bridge is converted to flavanones due to number of chemical processes which causes the exothermic change observed as intermediate at first minimum in the DTA curve [36].

The degree of decomposition is measured as the mass loss which is noted from the corresponding TG curve (**Fig. 9(a)**). A major mass reduction of about 67.49 % is observed between the temperatures 190 - 270°C, followed by further mass loss of 13.86% between the temperatures 270 - 375°C. Stability of the title crystal is extended up to 150°C and undergoes decomposition in two stages leaving a residual mass of about 19.80% at 499.7°C. These thermal changes

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demonstrated that the synthesized material can be of great use for thermal applications up to 150ºC.

[a]

[b]
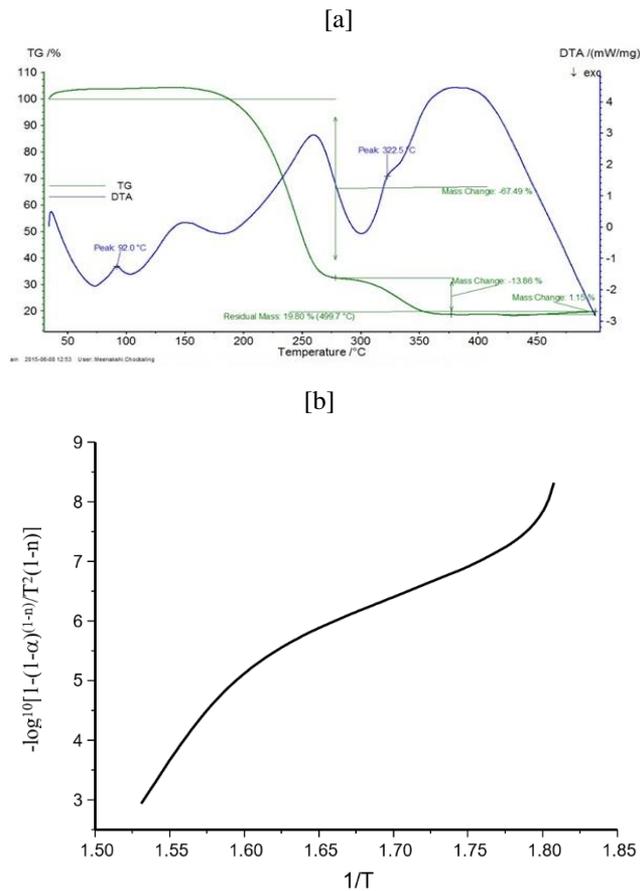
Fig. 9. [a] TG/DTA curves and [b] Plot of Coats-Redfern relation of DHNP.

Calculation of kinetic and thermodynamic parameters

From the TGA/DTA thermocurves, Coats-Redfern plot is drawn [**Fig. 9(b)**] and the straight-line fits due to different 'n' values help estimating E and A in $k = Ae^{-E/RT}$. In this work, the calculated n, E and A values were 4, 294.10 kJmol^{-1} and 1.294×10^{-2} S^{-1} respectively.

Using kinetic parameters, Arrhenius equation can be written as $k = Ae^{-E/RT}$. The frequency factor can be further used in the calculations of different thermodynamic properties such as entropy $\Delta S = 2.303 \times R \times$ Ah K_B T, enthalpy $\Delta H = E - 2 R T$, Gibbs free energy $\Delta G = \Delta H - T\Delta S$ and whose values are -282.23, -46.55, and 103.40 (kJ/mol), respectively. Negative value of ΔH and ΔS is indicative that the thermal process is exothermic and manipulated; while the undeniable value of ΔG mean the material is thermodynamically stable.

Vickers microhardness test

Microhardness indentations were made on the grown crystals by Vickers testing procedure for about 10s. Increasing the applied load in steps of 5g(P), the mean diagonal lengths (d) of the impressions were estimated and listed in **Table 4**. Vickers Hardness Number (VHN) was calculated using P and d in $H_V = 1.854P/d^2$ Kg/mm^2. The load versus VHN is plotted for the grown compound (**Fig. 10**).

(a)

(b)

(c)
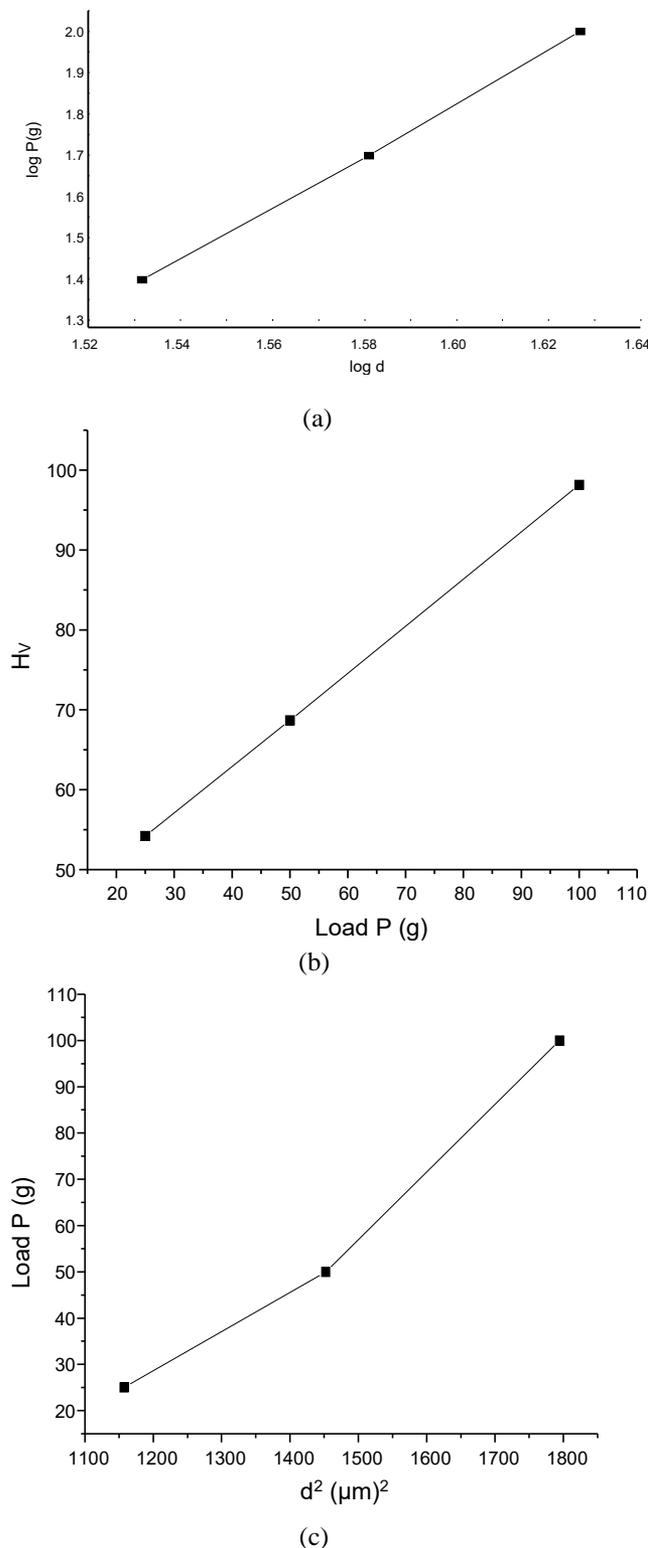
Fig. 10. Plots relating various microhardness parameters of DHNP.

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Table 4. Parameters defining the Mechanical properties of the compound.

Compound	Load P (g)	d (mm)	H_V (Kg/mm^2)	C_{ij} (Kg/mm^2)	Work hardening coefficient (n)	Newtonian resistance pressure W (g)
DHNP	25	34.02	54.2	1082.6766	6.32	0.1184
	50	38.11	68.7	1639.359833		
	100	42.36	98.15	3060.610275		
	50	38.11	68.7	1639.359833		
	100	42.36	98.15	3060.610275		

A graph is plotted between log d and log P (**Fig. 10(a)**) whose slope is the measure of Meyer's index 'n'. For strong materials 'n' is in the range of 1-1.6 and greater than 1.6 for susceptible materials. In this study, 'n' is found to be 6.32 which show that the compound goes with soft materials. Another graph is also drawn between load P and d^2 (Fig.10c), whose slope and intercept accord W (**Table 4**) and the load independent invariable 'b' [**37**]. The calculated C_{ij} using $C_{ij} = (H_V)^{7/4}$, for i= j and i ≠ j are listed in **Table 4**, that are indicative of mechanical goodness of the title material.

Conclusion

The title derivative DHNP has been consolidated and studied for crystallographic features. The Centro-symmetric crystal was equilibrated by C-H…O and O-H…O type inter and intramolecular hydrogen bonds. The title material has been studied for its optical and thermal properties via FTIR, $_1$H^1 and ^{13}C NMR and UV-Vis-NIR spectra and TGA/DTA thermograms, respectively. From the TG/DTA thermograms, the thermodynamic properties like the melting point, activation energy, frequency factor, enthalpy, entropy and Gibb's free energy of the grown compound were calculated. The values of thermodynamic parameters suggest that the chemical process is exothermic, non-spontaneous and the compound is thermodynamically unstable. From the Vickers microhardness test of the compound, the Hardness number (H_V), Meyer's index (n), Newtonian resistance pressure (W), load independent constant (b) and elastic stiffness constant (Cij) were calculated which characterizes its mechanical behaviour.

Conflicts of Interest
"There are no conflicts to declare".

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Graphical abstract