

Entry of chiral phthalimides with significant second order nonlinear optical and piezoelectric properties†

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Anil K. Singh,^a Ram Kishan,^b N. Vijayan,^c V. Balachandran,^d Taruna Singh,^b Hemandra K. Tiwari,^a Brajendra K. Singh^a and Brijesh Rath^{†*a}

Three new chiral phthalimides have been synthesized and characterized. Phthalimides (**1–3**) possess an acentric structure as revealed by structural investigation. Compounds **1** and **2** crystallize in an orthorhombic system with the space group $P2_12_12_1$, however the monoclinic system with the chiral space group $P2_1$ is observed for **3**. The presence of C–H $\cdots$ O hydrogen bonds in **1–3** facilitates the construction of several supramolecular structures. Helical structural motifs are also observed. The maximum value of hyperpolarizability (β), 159.9446×10^{-30} esu calculated for compound **3** is several times greater than that of urea. On the other hand **1** and **2** have hyperpolarizabilities of 10.8063×10^{-30} and 121.9519×10^{-30} esu, respectively. The polycrystalline samples of **1–3** were assessed for a second-harmonic generation response, which was found to be 8.8, 10.2 and 9.7 mV respectively. Further, compounds **1–3** showed d_{33} values of 0.93, 1.97 and 1.88 pC N $^{-1}$ respectively. The present investigation demonstrates chiral phthalimides as effective contenders for nonlinear optical and piezoelectric properties.

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Introduction

The search for a new generation of materials with greater technological applications, especially nonlinear optical properties is being addressed successfully with the aid of crystal packing arrangements.^{1,2} Extensive research on organic and metal–organic frameworks has led to numerous classes of second harmonic generation (SHG) and also synthons for supramolecular assemblies.^{1,3,4} Specifically, the designing and construction of organic molecules with nonlinear optical and piezoelectric properties possessing better transparency is a rapidly growing field. Organic materials are of interest owing to their easy tailoring, high solubility and informal biocompatibility over pure inorganic materials. Nonlinear optical efficacy of organic materials is governed by their acentric nature, high hyperpolarizability (β) and their helical structural motifs.⁵ The fabrication of acentric organic crystals has attracted enough consideration from scientists because of their wide application

in the area of information technology, optical storage and information processing among other areas.⁶ Hence, the discovery of new organic molecules with acentric structures is the most crucial component in advancing technology.

Even in recent years the rational design and preparation of organic crystals with an acentric structure has been a most challenging and laborious task. However, the problem has been tackled by employing several approaches, mainly the use of functionalized chiral molecules to generate new acentric crystals.^{1b,7,8} Not enough reports are available on organic acentric crystals possessing high nonlinear optical potential.^{5b} The presence of one or more chiral centers in a molecule helps in developing the acentric structure and this strategy is employed to obtain novel acentric materials.⁹ We have been interested in extending the concept of chirality in phthalimides with the aim of exploring their structural aspects and solid state properties. The presence of C–H $\cdots$ O hydrogen bonding in several phthalimides supported their great significance in crystal engineering and allowed the building of supramolecular-structures.¹⁰ In this paper, we report the synthesis, spectroscopic characterization and structural investigation of functionalized chiral phthalimides (**1–3**). An economic and convenient synthesis is reported and shown in Scheme 1. The strategy of introducing chirality enables us to obtain acentric organic crystals.

We also report polarizability and hyperpolarizability (β) calculations, which are further substantiated by the second order NLO response of newly prepared molecules. The significant properties of hyperpolarizability, second order NLO response and piezoelectric properties measured for **1–3**

^aBio-organic Research Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India. E-mail: brathi@svc.ac.in; Fax: +91-11-24118535

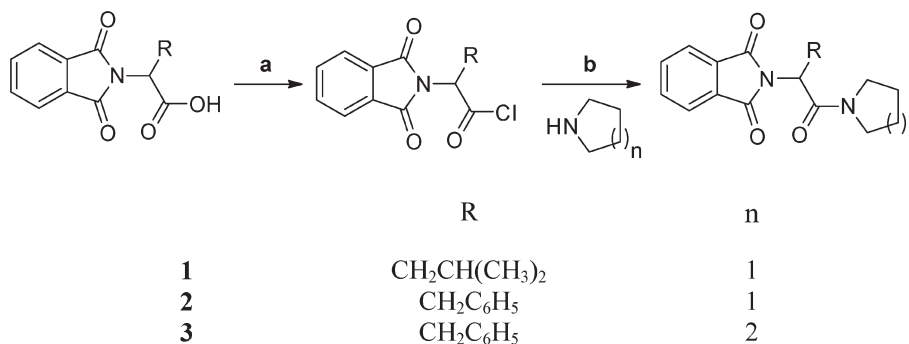
^bDepartment of Chemistry, University of Delhi, Delhi-110 007, India

^cCSIR-National Physical Laboratory, Dr K. S. Krishnan Road, New Delhi-110 012, India

^dPG & Research Department of Physics, Aringer Anna Government Arts College, Musiri-621 211, India

† Electronic supplementary information (ESI) available: General consideration, TGA plots, NMR spectra and X-ray crystallographic details for compounds **1–3** having CCDC No. 895512-14. For ESI and crystallographic details and additional data in CIF See DOI: 10.1039/c3ra41089g

‡ Current address: Department of Chemistry, Sri Venkateswara College, University of Delhi, New Delhi-110021, India.



Scheme 1 Reagents and conditions: a) SOCl₂, DMF, 90 °C, 2 h; b) EtOAc, TEA, RT, 2 h.

advocate their entry as important agents for technological applications.

Computational details

The first hyperpolarizability (β_{tot}) and related properties like electric dipole moment (μ_{tot}), and mean polarizability (α_{tot}) of 1–3 are calculated based on a finite field approach. The computed results by density functional quantum chemical method with a 6-311++G(d,p) basis set are summarized in Table 1. To calculate all the electric dipole moments and the first hyperpolarizabilities for the isolated molecules, the origin of the Cartesian coordinate system (x,y,z) = (0,0,0) was chosen at the centre of mass of 1–3. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman

symmetry.¹¹ It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrix is a tetrahedral. The components of β_{tot} are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_x F_x - 1/2 \alpha_{x\beta} F_x F_\beta - 1/6 \beta_{x\beta\gamma} F_x F_\beta F_\gamma + \dots$$

Where E^0 is the energy of the unperturbed molecules, F_x is the field at the origin μ_x , $\alpha_{x\beta}$ and $\beta_{x\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizability, respectively. The total static dipole moment μ , the mean polarizability α_{tot} , and the mean first hyperpolarizability β_{tot} , using the x,y,z components are defined as:

$$\mu_{\text{tot}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_{\text{tot}} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

Table 1 The electric dipole moment μ (D), the average polarizability α_{tot} and the first hyperpolarizability β_{tot} of compounds 1–3

Parameters	1	2	3
μ_x	−0.4772	1.1073	−1.7334
μ_y	3.5577	0.9830	−1.0093
μ_z	−2.3447	−2.6007	−2.6580
μ_{tot}	4.2782	2.9927	3.3299
α_{xx}	−107.5749	−108.2113	−113.4885
α_{xy}	6.3287	−6.4977	−3.585
α_{yy}	−130.637	−152.2904	−164.0771
α_{xz}	−4.5720	2.0965	−1.2792
α_{yz}	3.0273	−3.7465	1.3812
α_{zz}	−140.0213	−151.8510	−162.1268
α_{tot} (esu)	126.0777×10^{-24}	$−137.4509 \times 10^{-24}$	$−146.5641 \times 10^{-24}$
β_{xxx}	−18.4676	152.3067	−199.6724
β_{xxy}	−35.1465	2.9313	1.1339
β_{xyy}	−5.6707	−18.6060	18.6896
β_{yyy}	22.2701	44.6063	−39.3774
β_{xxz}	−0.4911	11.3165	15.9238
β_{xyz}	2.5461	6.0577	0.3823
β_{yyz}	4.2231	21.0832	23.4222
β_{xzz}	14.0224	−22.1001	27.0008
β_{yzz}	11.2541	−3.4872	5.9294
β_{zzz}	−7.1690	−10.5563	−10.5778
β_{tot} (esu)	10.8063×10^{-30}	121.9519×10^{-30}	159.9446×10^{-30}

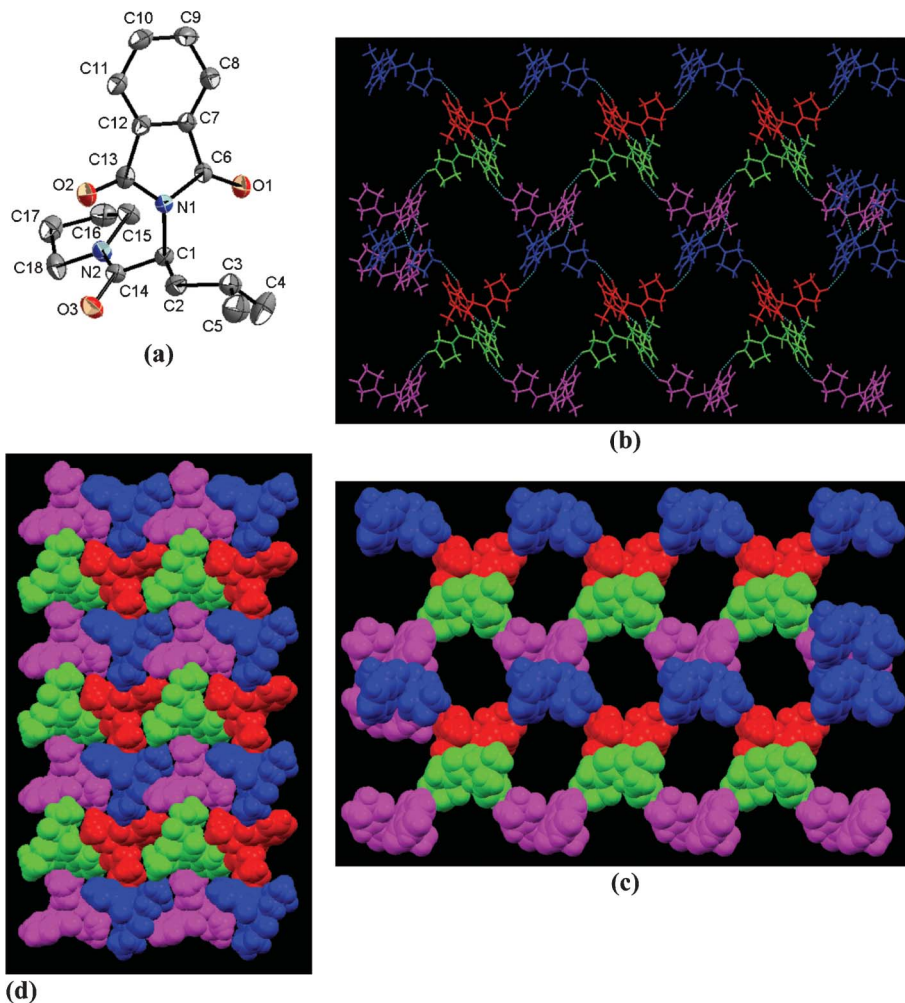


Fig. 1 (a) Molecular structure of **1** at 40% probability level. (b) A view of the hydrogen bonded network stabilized by C–H···O hydrogen bonds. (c) Space filling model of the packing diagram forming the supramolecular architecture (viewed along the *b*-axis). (d) Space filling model of the packing diagram (viewed along the *a*-axis).

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Results and discussion

Synthesis and spectroscopic characterization

We have designed phthalimides possessing chirality and functionalized them with heterocyclic amines with the expectation of their acentric structure. Compounds (**1–3**) were prepared from the reaction of *N*-phthaloyl-L-amino acids with corresponding cyclic amines in the presence of triethylamine.

The reaction afforded **1–3** as colorless solids in good yield. The composition of new compounds **1–3** was confirmed by analytical and spectroscopic techniques. The presence of functional groups and their vibrational mode was studied by FTIR spectroscopy. The two characteristic bands at 1712 and 1648 cm^{-1} in compound **1**, 1718 and 1647 cm^{-1} in compound **2** and 1718 and 1645 cm^{-1} in compound **3** correspond to two types of carbonyl stretching frequencies. Bands at higher frequencies are stronger and correspond to carbonyl groups present in the isoindoline ring. Bands at lower frequencies correspond to the carbonyl group attached to the cyclic amine. In the ^1H NMR spectrum, the peak of the chiral proton was obtained as a double doublet at δ values ranging from 4.99 to 5.30 with *J* values of 4.4 and 11.72 Hz for **1**, 6.60 and 9.56 Hz for **2** and 5.80 and 10.24 Hz for **3**. Peaks for protons corresponding to the heterocyclic ring (pyrrolidine and piperidine) were observed as two bunches. Four N–C protons were assigned as multiplets ranging from δ 3.67 to 3.42 and the remaining protons were assigned upfield as multiplets ranging from δ 1.93 to 1.39. Methylene protons adjacent to the chiral carbon of compounds **1**, **2** and **3** were found in the range

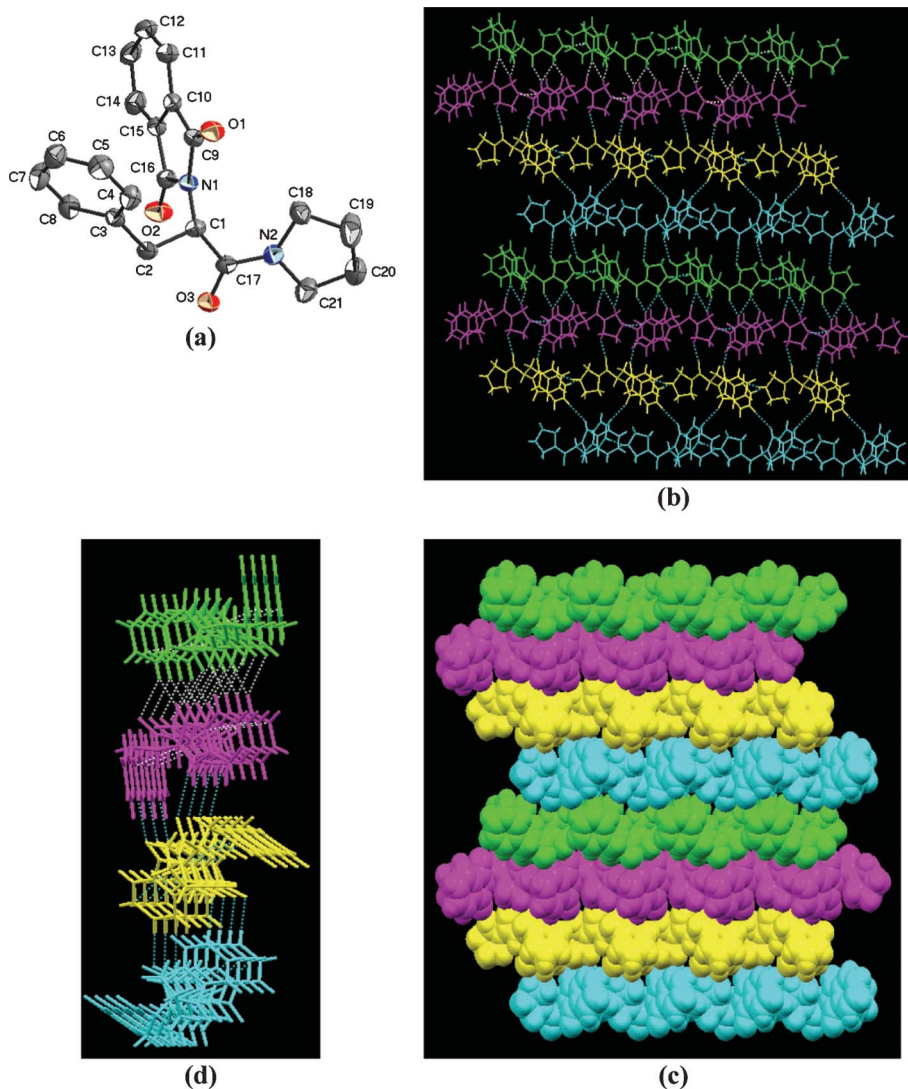


Fig. 2 (a) Molecular structure of **2** at 40% probability level. (b) A view of hydrogen bonded network. (c) Space filling model of the packing diagram (viewed along the *b*-axis). (d) A view of the hydrogen bonded network (viewed along the *a*-axis).

from δ 2.55 to 1.75. Peaks of aromatic protons of the isoindoline ring were found from δ 7.81 to 7.64. All the protons of the benzylic nucleus ranged from δ 7.18 to 7.11. The peaks were assigned with the aid of 2D NMR spectra of all three compounds (see ESI†). The solid-state UV-Visible spectra of **1–3** showed λ_{max} at ~ 240 nm indicating their transparency in the visible region.

Crystal structure investigation

Suitable colorless crystals of **1–3** were grown from acetonitrile and subjected to single crystal X-ray diffractometry to explore their solid-state features. Compound **1** crystallized in the acentric orthorhombic system with a $P2_12_12_1$ space group. The molecular structure and self-assemblies of **1** are depicted in Fig. 1. The chiral central carbon C1 is surrounded by four different substituents, a phthalimide molecule, an isobutyl molecule, and a carbonyl group, which is further attached to a puckered pyrrolidine unit and a hydrogen atom. The geometry

around the central carbon atom is tetrahedral but not a regular one. The O1 of the phthalimide ring is involved in bifurcated intermolecular hydrogen bonding with H17B and H2B of two different adjacent molecules. The angles between C17–H17B $\cdots$ O1 and C2–H2B $\cdots$ O1 are 144.4° and 175.2° , respectively which suggests the former one has moderate and the latter one has very strong intermolecular hydrogen bonding. The oxygen atom, O3 of **1** is involved in very weak intermolecular hydrogen bonding with H10 of the neighboring molecule with a bond angle 129.3° . In compound **1** each building block is involved in intermolecular hydrogen bonding with three neighboring building blocks, and the extension of such interactions generated a zig-zag 2D sheet when viewed along the *b*-axis (Fig. 1b and c). Each tetrahedral unit combined to form a closed layer type sheet when viewed along the *a*-axis.

Compound **2** crystallized in the orthorhombic system with a $P2_12_12_1$ space group. The molecular structure and self-assemblies of **2** are shown in Fig. 2. The geometry of the

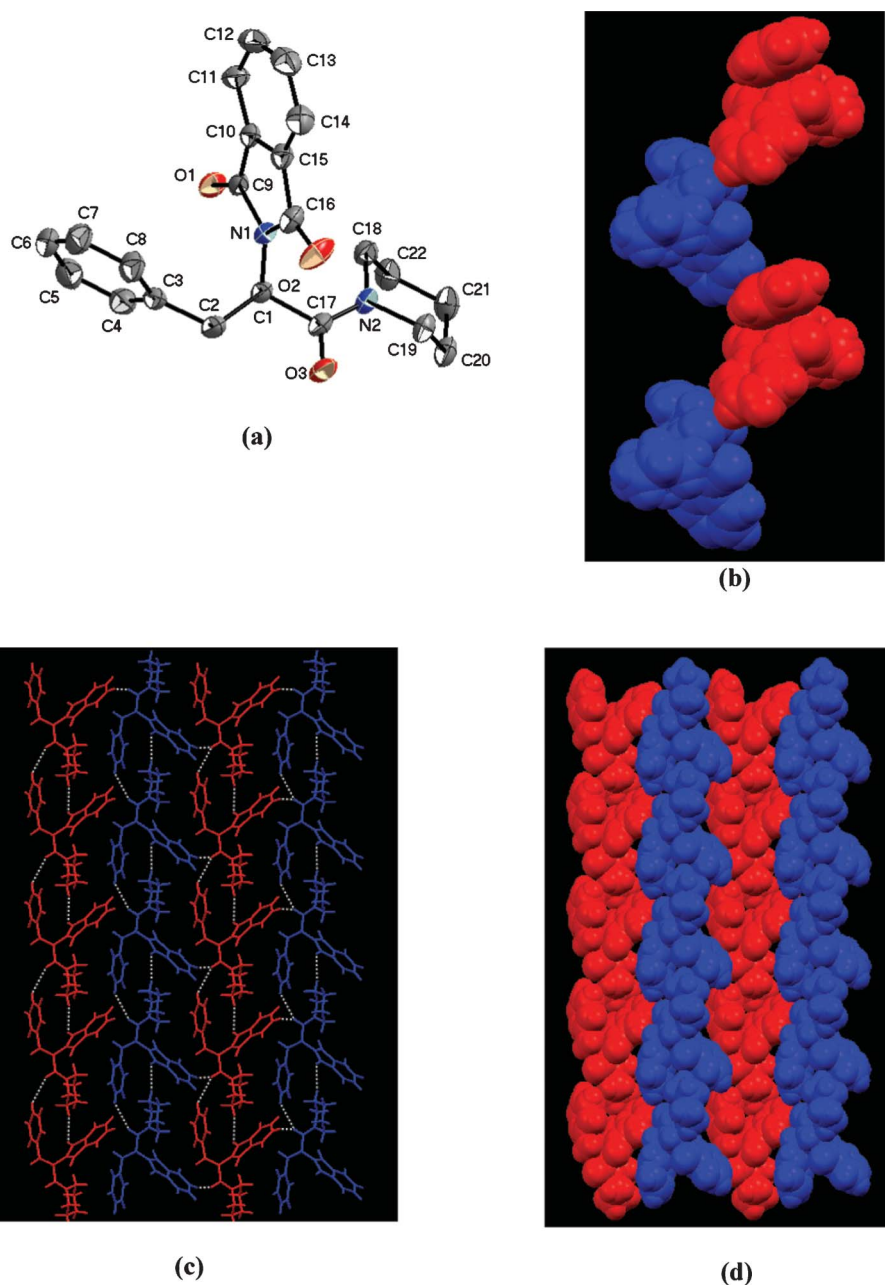


Fig. 3 (a) Molecular structure of **3** at 40% probability level. (b) Space filling model of the packing diagram showing the helical motifs (viewed along the *c*-axis). (c) A view of the hydrogen bonded network. (d) Space filling model of the packing diagram (viewed along the *a*-axis).

chiral central carbon C1 was found to be similar to compound **1**. Three imide oxygen atoms are involved in intermolecular hydrogen bonding with neighboring molecules. Atom O1 of **2** is involved in intermolecular hydrogen bonding with H12 of the neighboring molecule and the bond angle between C12–H12···O1, 174.9° , suggests very strong intermolecular hydrogen bonding between them. Bifurcated C–H···O intermolecular hydrogen bonding was observed between O2 and H6/H21A of two different neighboring molecules. The bond angle values of C6–H6···O2 (137.9°) and C21–H21A···O2 (155.9°) suggest the former has moderate and the latter has strong intermolecular

hydrogen bonding. Atom O3 of compound **2** is also involved in bifurcated hydrogen bonding with H14 and H18A of two different neighboring molecules. The bond angle between C14–H14···O3 and C18–H18A···O3 was found to be 142.2 and 144.5° respectively. Both the values suggest the presence of strong intermolecular hydrogen bonding. The extension of the above hydrogen bonding in 2 dimensions leads to the formation of a 2D sheet like structure when viewed along the *b*-axis (Fig. 2b and c).

Compound **3** crystallized in the monoclinic system with a $P2_1$ space group. The molecular structure and self-assemblies

Table 2 Second Order NLO and d_{33} response

	SHG Response (mV)	KDP (mV)	d_{33} (pC N ⁻¹)
1	8.8	13.6	0.93
2	10.2	13.6	1.97
3	9.7 ^a	21 ^a	1.88

^a Input beam energy: 1.3 mJ per pulse.

of **3** are depicted in Fig. 3. Compound **3** has a planar six membered nitrogen containing piperidine moiety. The geometry around the central carbon atom is the same as in compound **1** and **2**. Three imide oxygen atoms are involved in intermolecular hydrogen bonding with neighboring molecules. The O1 of **3** is involved in intermolecular hydrogen bonding with H20B of the neighboring molecule and their angle value 166.5° between C20–H20B...O1 suggests very strong intermolecular hydrogen bonding. Atom O2 of **3** is involved in intermolecular hydrogen bonding with H18B of the piperidine moiety of a different neighboring unit. The bond angle value, 126.8° for C18–H18B...O2 suggests weak intermolecular hydrogen bonding. Atom O3 of **3** is also involved in bifurcated hydrogen bonding with H6 and H13 of two different neighboring molecules. The bond angle between C6–H6...O3 and C13–H13...O3 are 140.9 and 158.3° respectively, which indicates the presence of strong intermolecular hydrogen bonding. The extension of the above hydrogen bonding in 2 dimensions leads to the formation of a 2D sheet like structure when viewed along the *a*-axis (Fig. 3c and d).

Hyperpolarizability calculations

The DFT/6-311++G(d,p) calculated first hyperpolarizability of compounds **1**, **2** and **3** are 10.8063×10^{-30} , 121.9519×10^{-30} and 159.9446×10^{-30} esu, respectively. The calculated values of μ_{tot} , (4.2782, 2.9927 D, 3.3299 D), α_{tot} values are 126.0777×10^{-24} , $-137.4509 \times 10^{-24}$ and $-146.5641 \times 10^{-24}$ esu and β_{tot} values are 10.8063×10^{-30} , 121.9519×10^{-30} and 159.9446×10^{-30} esu for compounds **1**, **2** and **3**, respectively. From these results, the hyperpolarizability value of compound **3** is higher than the other molecules, which is 428.9 times greater than that of urea (the μ_{tot} , α_{tot} and β_{tot} of urea are 1.373 D, 3.8312×10^{-24} esu and 0.37289×10^{-30} esu obtained by the B3LYP/6-31G(d) method.¹² The results indicate that compound **3** is a good candidate as a NLO material. As can be seen from the β_{tot} value for this molecule, the larger value of first hyperpolarizability corresponds to the lower HOMO–LUMO gap. This correlation is reported in the literature.¹³ In addition, the maximum β_{tot} value may be due to π -electron cloud movement from donor to acceptor which makes the molecule highly polarized and the intramolecular charge transfer (ICT) possible. The presence of ICT is confirmed with vibrational spectral analysis.

Optical and piezoelectric properties

In order to validate our computational results, the crystalline forms of **1–3** were evaluated for SHG response by a modified Kurtz–Perry powder method and the results are shown in Table 2. For compounds **1–3** the measured SHG values are 8.8,

10.2 and 9.7 mV respectively. A significant value of SHG of 10.2 mV was recorded for compound **2** and is comparable with the 13.6 mV observed for KDP. Further, phthalimides (**1–3**) were also evaluated for piezoelectric response and d_{33} values are 0.93, 1.97 and 1.88 pC N⁻¹ respectively.

Thermal stability analysis

In order to determine the thermal stability, thermogravimetric analysis (TGA) of **1–3** was conducted and the plots are given in the ESI.† The onset of the decomposition of compound **1** starts at 200 °C after that drastic weight loss is observed up to 300 °C. Compound **2** is relatively stable up to 210 °C, a sharp weight loss is observed up to 360 °C. Compound **3** is most stable, the onset of the decomposition starts at 230 °C and after that weight loss is observed up to 360 °C. Out of these observations we can conclude that the compounds are fairly stable.

Conclusions

In summary, we have discovered chiral phthalimides as new acentric organic crystals with substantial second order NLO activity. The incorporation of chirality into the phthalimides facilitated the production of acentric crystals. Our structural investigations indicated that these phthalimides are robust and encouraging synthons for the formation of hydrogen-bonded frameworks with helicity. Compound **2** exemplifies a promising candidate for future study in the field of second order nonlinear optics and piezoelectricity. The present study establishes a simple and suitable route for the production of new chiral organic materials enriched with technological applications.

General procedure for synthesis of **1–3**

N-Phthaloyl-L-amino acids were prepared following the literature procedure.¹⁴ To *N*-phthaloyl-L-amino acid (3.83 mmol) two drops of DMF were added and heated up to 40–50 °C followed by the slow addition of freshly distilled thionyl chloride (0.5 mL). The contents were heated at 90 °C for 2 h. The reaction mixture was cooled to room temperature and kept in an ice bath. Cyclic amine (4.59 mmol, dissolved in 20 mL of ethyl acetate) and triethylamine (1.0 mL) were added subsequently to the reaction mixture and the contents were stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and extracted into ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue thus obtained was purified by silica gel chromatography (9 : 1–1 : 1 petroleum ether/ethyl acetate gradient) to afford the title compounds as white solids.

2-(4-Methyl-1-oxo-1-(pyrrolidin-1-yl)pentan-2-yl)isoindoline-1,3-dione (1). Yield = 78%; Melting point: 115 °C (DSC); $[\alpha]_{\text{D}}^{20}$ –47.2; FTIR (KBr) ν_{max} (cm⁻¹): 2962, 2949, 2866, 1712, 1648, 1466, 1425, 1380, 1057, 719, 530, 498; ¹H NMR (400 MHz, CDCl₃): δ 7.82 (2H, m), 7.70 (2H, m), 5.00 (1H, dd, *J* = 11.72, 4.4 Hz), 3.47 (4H, m), 2.58 (1H, m), 1.93 (2H, m), 1.84 (2H, m), 1.76 (1H, m), 1.55 (1H, m), 0.94 (6H, t, *J* = 5.88 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 168.0, 167.6, 134.0, 131.6, 123.3, 51.5,

46.4, 46.3, 36.7, 26.3, 25.0, 23.2, 23.1, 21.2 ppm; HRMS calculated for $C_{18}H_{23}N_2O_3^+$ ($M + H$)⁺: 315.1703 found: 315.1508.

2-(1-Oxo-3-phenyl-1-(pyrrolidin-1-yl)propan-2-yl)isoindoline-1,3-dione (2). Yield = 83%; Melting point 145 °C (DSC); $[\alpha]_D^{18.2}$ –136.9; FTIR (KBr) ν_{max} (cm^{–1}) 3062, 3029, 2936, 2867, 1718, 1646, 1467, 1432, 1381, 1331, 1167, 1099, 723, 497; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (2H, m), 7.67 (2H, m), 7.18 (5H, m), 5.13 (1H, dd, J = 9.56, 6.6 Hz), 3.58 (4H, m), 1.82 (4H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 167.6, 166.6, 137.1, 134.0, 131.3, 129.1, 128.4, 126.6, 123.3, 54.3, 46.5, 46.0, 34.7, 26.2, 23.7 ppm; HRMS calculated for $C_{21}H_{21}N_2O_3^+$ ($M + H$)⁺: 349.1547 found: 349.1266.

2-(1-Oxo-3-phenyl-1-(piperidin-1-yl)propan-2-yl)isoindoline-1,3-dione (3). Yield = 80%; Melting point 150 °C (DSC); $[\alpha]_D^{19.4}$ –174.5; FTIR (KBr) ν_{max} (cm^{–1}) 3030, 2934, 2922, 2858, 1718, 1645, 1453, 1440, 1381, 1080, 717, 528, 489; ¹H NMR (400 MHz, CDCl₃): δ 7.75 (2H, m), 7.67 (2H, m), 7.18 (5H, m), 5.30 (1H, dd, J = 10.24, 5.88 Hz), 3.7 (1H, dd, J = 14.3, 11.0 Hz), 3.60 (2H, m), 3.43 (1H, dd, J = 14.64, 5.16 Hz), 3.32 (m, 2H), 1.57 (2H, m), 1.53 (4H, m) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 167.7, 166.5, 137.2, 134.0, 131.4, 129.0, 128.4, 126.7, 123.3, 52.7, 46.6, 43.6, 35.0, 26.2, 25.4, 24.3 ppm; HRMS calculated for $C_{22}H_{23}N_2O_3^+$ ($M + H$)⁺: 363.1703 found: 363.1400.

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