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Introduction

Over the past two decades, there has been growing interest in the elaboration of π -conjugated organic compounds due to their applications in various fields such as molecular wires, liquid crystals, electronic and optoelectronic devices, non-linear optical (NLO) and two photon absorption material.^{1–4}

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Synthesis, growth and characterization of 4-bromo-4'-nitrobenzylidene aniline (BNBA): a novel nonlinear optical material with a (3+1)-dimensional incommensurately modulated structure[†]

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The organic nonlinear optical material of 4-bromo-4'-nitrobenzylidene aniline (BNBA, $C_{13}H_9BrN_2O_2$), a new derivative of benzylideneaniline family, was synthesized and purified by repeated recrystallization. Single crystals of BNBA were grown in acetone solvent by slow evaporation at room temperature. Its (3+1)-dimensional incommensurately modulated structure was elucidated from single crystal X-ray diffraction data obtained at 173 K. The non-centrosymmetric structure was solved and refined in the monoclinic superspace group $A2(\alpha 0\gamma)0$; the unit cell parameters are a = 10.5217(10) Å, b = 16.2535(16) Å, c = 7.4403(7) Å, $\beta = 110.709(7)^{\circ}$, modulation vector $q = 0.0658(1)a^{*}-0.2658(1)c^{*}$. At 290 K, the structure is partially disordered, however, the local structure of domains is identical to that at 173 K. The ¹H and ¹³C NMR and Fourier Transform Infrared and FT-Raman spectroscopic studies confirmed the molecular structure. The Kurtz powder second-harmonic generation (SHG) test reveals that the SHG efficiency of BNBA is about 9.4 times higher than that of potassium dihydrogen phosphate. According to the thermogravimetric, differential thermal and differential scanning calorimetric analyses, BNBA is a stable phase starting from room temperature and up to the melting point, 436 K. The optical nonlinearity of BNBA was investigated at 532 nm using 5 ns laser pulses, employing the open aperture Z-scan technique.

Second-order nonlinear optical materials find excellent applications in laser frequency conversion, optical parameter oscillator (OPO), signal communication,^{5,6} high-speed information processing and optical data storage.^{7–11} In the case of third order nonlinearities, two photon absorber (TPA) materials find applications in upconversion lasing,¹² information technology,¹³ three dimension fluorescence imaging,^{14,15}

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[†] Electronic supplementary information (ESI) available: Refinement details of the (3+1) dimensional structure at 173 K. Discussion of the C-H...O and C-H...Br interactions. Details of the room temperature single crystal XRD analysis. Table S1, details of XRD experiments and structure refinements at 173 and 290 K. Tables S2 and S3, positional and ADP parameters of atoms in the rigid BNBA molecule at 173 K. Table S4, modulations of the rotation and displacement parameters of the rigid molecule at 173 K. Tables S5 and S6, interatomic distances and angles. Table S7, candidates for the C-H...O and C-H...Br interactions aperiodically appear between molecules. Tables S8 and S9, positional and ADP parameters of atoms in the rigid BNBA molecule at 290 K. Fig. S1, the hol and h2l experimental patterns of the reciprocal space at 173 K. Fig. S2, the most probable C-H...O and C-H...Br interactions in the incommensurately modulated BNBA structure. Fig. S3, split BNBA molecule at 290 K. Fig. S4, the calculated and experimental powder X-ray diffraction patterns of BNBA at room temperature. CCDC 900429 and 900430. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3ce26663j

microfabrication,¹⁶ optical power limiting, optical pulse shaping and processing and laser mode locking.¹⁷ Benzylideneanilines are Schiff bases, which have been widely used in coordination, medicinal and biological chemistry. Further, benzylideneanilines show significant anticancer and anti-inflammatory activities and in stereo selective organic synthesis they may serve as reagents.

A literature survey shows that many researchers have reported on the synthesis and growth of crystals of some of the benzylideneaniline derivatives and on their structural and other properties. For example, 4-nitro-4'-methylbenzylidene aniline (NMBA),¹⁸ 4-nitro-4'-methoxybenzylidene aniline (NMOBA)¹⁹ and 4-methoxy-4'-dimethylaminobenzylidene aniline (MDMABA)²⁰ crystallize in the monoclinic crystal system. The powdered second harmonic generation efficiency of NMBA is 16 times larger than that of urea¹⁸ and NMOBA is 1.3 times than that of potassium dihydrogen orthophosphate (KDP).¹⁹ Employing the Z-scan technique, third order nonlinear optical properties were studied for centrosymmetric compounds such as 4-chloro-4'-dimethylaminobenzylidene aniline [CDMABA]²¹ and 4-bromo-4'-chlorobenzylidene aniline [BCBA]²² and centrosymmetric MDMABA²³ compound. In the present work, we report on the synthesis, growth and characterization of one such derivative, 4-bromo-4'-nitrobenzylidene aniline (BNBA, C13H9BrN2O2), for the first time. The structure of BNBA appears as incommensurately modulated at 173 K. The structure solution has been obtained using the superspace concept based on consideration of higher dimensional periodicity of a crystal lattice.^{24,25} The recent review on organic molecular compounds with modulated crystal structures shows that structures with higher dimensional periodicity are quite common in the field of organic materials.²⁶

Experimental section

Synthesis and growth of BNBA

BNBA was synthesized by reacting *p*-bromoaniline (*p*-BA) and *p*-nitrobenzaldehyde (*p*-NB) in a molar ratio of 1:1. A calculated amount of *p*-BA was dissolved in ethanol containing the appropriate amount of *p*-NB. The solution was refluxed for 6 h and then cooled to ambient temperature, yielding BNBA as a yellow solid. The reaction mechanism is depicted in Scheme 1.

The yellow solid was dissolved in acetone and a successive recrystallization process was adopted to improve the purity of the salt. Single crystals of BNBA were grown by slow evaporation at room temperature from an acetone solution in a beaker covered by parafilm. A transparent crystal of dimension $4 \times 2 \times 1 \text{ mm}^3$ was grown in a period of 20 days and is shown in Fig. 1a. The morphology of the grown crystal is given in Fig. 1b and the different crystallographic planes of the crystal were identified from single crystal X-ray diffraction study.



NMR spectroscopy

The ¹H NMR and ¹³C NMR spectral analyses were made on the BNBA sample in chloroform-D (CDCl₃) using a Bruker AC 200-NMR spectrometer.

FTIR and FT-Raman spectroscopy

The Fourier transform infrared (FTIR) and Fourier transform Raman (FT-Raman) spectra were recorded in the wavelength range 400–4000 cm⁻¹. FTIR spectrum was recorded using a Perkin-Elmer-Paragon 500 spectrometer using a potassium bromide (KBr) pellet, and the FT-Raman spectrum was recorded using a Varian FT-Raman spectrometer.

Single crystal and powder XRD

The single crystal X-ray diffraction data were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System equipped with a two-circle goniometer and using Mo K α graphite



Fig. 1 Harvested crystal of BNBA

monochromated radiation ($\lambda = 0.71073$ Å). Image plate distance 130 mm, ω rotation scans 0–180° at φ 0°, and 0– 123° at $\varphi = 90^{\circ}$, step $\Delta \omega = 1.0^{\circ}$, exposures of 2 minutes per image, 2θ range 1.76–52.59°, $d_{\min}-d_{\max} = 23.107-0.802$ Å. The images showed clearly satellite reflections indicating an incommensurately modulated structure. A unit cell was obtained for the strong non-satellite reflections and the average structure was solved by direct methods with SHELXS.27 Least-squares refinement was attempted with SHELXL²⁷ but the solution was of course not satisfactory. The description and refinement of the solution of this incommensurately modulated structure is described later. The room temperature (290 K) data set was collected on the Swiss-Norwegian Beamline BM01A at the ESRF, Grenoble. Diffraction patterns were collected using a MAR Research MAR345 image plate detector with a rotation angle of 2° per image. A focussed beam with a wavelength of 0.7000 Å was selected with a Si(111) monochromator. Integration of the images and indexation of the diffraction reflections were performed with the CrysAlis software package from Agilent. All structure analysis calculations were performed using the program JANA 2006.²⁸ The main crystallographic and refinement details are given in Table S1 of the ESI.†

X-ray powder diffraction pattern was obtained with Cu K α (λ = 1.54060 Å) radiation from the crushed powder of a BNBA crystal. The sample was scanned over the 10–80° 2 θ range at a scan rate of 2° min⁻¹.

Fluorescence study

The emission spectrum for BNBA was recorded using a Perkin-Elmer LS55 Luminescence spectrometer in the range 400–600 nm.

Kurtz powder test

The second harmonic generation (SHG) conversion efficiency of BNBA was determined by the powder technique developed by Kurtz and Perry.²⁹ The crystal was powdered and the fine powdered sample was inserted in a microcapillary tube and then subjected to a Q-switched Nd:YAG laser emitting 1064 nm radiation at the pulse energy of 4.0 mJ. The frequency doubling was confirmed by the emission of green radiation of wavelength 532 nm collected by a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A detector connected to a power meter was used to detect the second harmonic intensity. A powdered sample of potassium dihydrogen phosphate (KDP) crystal of the same size was used as a reference material.

Z-Scan

In order to study the third order optical nonlinearity, the nonlinear optical absorption of BNBA dissolved in chloroform was measured using 532 nm, 5 ns laser pulses from a frequency doubled Nd:YAG laser (Continuum Minilite), employing the open aperture *Z*-scan technique. The laser beam was focused using a convex lens and the sample was translated along the beam axis (*z*-axis) through the focal region. The focal point is taken as z = 0. As the sample is translated along the *z*-axis, it sees different laser intensity at each position. The position (and hence the intensity) dependent transmission is measured using an energy meter placed after the sample. For this study the sample was placed in a 1 mm path length glass cuvette (Helma GmBH) which was mounted on a stepper motor controlled linear translation stage. The optical density of the prepared solution is low at 532 nm, and its linear transmission is high (82%). The laser pulse energy reaching the sample is 90 μ J. The sample was translated in the Z direction in steps of 200 µm, and the transmitted energy was measured for each position, using a pyroelectric energy meter (RiP 735 Laser Probe Inc.). The experiment was automated using the program LabVIEW. The interval between two successive laser pulses was always kept sufficiently large (typically more than 2 s), to enable the complete thermal relaxation of the sample before the arrival of the following pulse. The open aperture transmission normalized to the linear transmission of the sample (normalized transmittance) was then plotted against the sample position measured relative to the beam focus. Nonlinear absorption was indicated by a smooth valley shaped curve, which is symmetric about the focal (Z = 0) position. The Z-scan of pure chloroform was run separately to ensure that the solvent shows no nonlinearity under identical excitation conditions.

Thermal analyses

Thermogravimetric (TG) and differential thermal (DT) analyses were recorded using an S. T. A – 1500 Simultaneous Thermo Analytical system in the temperature region 40–940 °C at a heating rate of 10 K min⁻¹ under nitrogen atmosphere. 13.79 mg of the BNBA material was taken for TG-DTA measurements. The differential scanning calorimetry (DSC) experiment was performed using a TA instrument, Model Q20 V24.2 Build 107 differential scanning calorimeter. 5.02 mg of BNBA sample was taken in a sealed aluminium pan with a perforated lid and subjected to DSC analysis under an inert nitrogen atmosphere (50 ml min⁻¹). BNBA crystalline powder was heated from 5 °C to 165 °C at a rate of 5 °C min⁻¹.

Results and discussion

Confirmation of the BNBA molecule formation

NMR spectra. The ¹H NMR spectrum provides information about the number of different types of protons and also regarding the nature of the immediate environment of each of them. ¹H NMR spectrum of BNBA shows five important absorption peaks named A, B, C, D and E in Fig. 2. They point to the different hydrogen atoms present in five different chemical environments in the BNBA molecule. The chemical shift values of protons in different environments corresponding to peaks A, B, C, D and E, respectively are: a one proton singlet (C-H) at δ 8.88 ppm, a two proton doublet at δ 8.44 ppm, a two proton doublet at δ 8.24 ppm, a two proton doublet at δ 7.70 ppm and a two proton doublet at δ 7.38 ppm. The singlet signal A at δ 8.88 ppm corresponds to the proton of imine group,³⁰ which confirms the formation of Schiff base compounds. The other adjacent four doublet protons are due to aromatic ring protons. In the NMR spectrum of BNBA, the ratio of steps obtained are A: B: C: D: E = 1:2:2:2:2.



Thus, the number of protons associated with the signals is A – 1H and B, C, D, E – 2H.

The ¹³C NMR is an important tool in chemical structure elucidation in organic chemistry.³¹ The ¹³C NMR spectrum of BNBA, presented in Fig. 3, contains nine signals. The signal at A is attributed to the carbon of imine group, which confirms the formation of Schiff base compounds. The presence of the signals at B, C, D and I are attributed to the singlet carbons of the aromatic ring. The doublet signals at E, F, G and H are due to the aromatic ring carbon. The three-line signal at J from the solvent corresponds to the single carbon atom of deutero-chloroform, CDCl₃; it appears as a triplet because of the interaction with the deuterium atom. Molecular structure of BNBA is thus confirmed from the NMR spectra.

FTIR and FT-Raman spectra. The functional groups present in the BNBA sample were analysed by FTIR and FT-Raman spectral analyses and are shown in Fig. 4.

Aromatic nitro compounds can be recognized from two strong bands in the region 1570–1500 cm⁻¹ and 1370–1300 cm⁻¹.¹⁹ In the FTIR spectrum the peak at ~1516 cm⁻¹ and at ~1353 cm⁻¹ represents the asymmetric and symmetric modes of vibration of the nitro group (-NO₂), respectively.



Fig. 3 ¹³C-NMR spectrum of BNBA.



Fig. 4 FTIR and FT-Raman spectra of BNBA

Similarly in the FT-Raman spectrum asymmetric stretching vibrations of the nitro group occurs at 1516 cm⁻¹ and symmetric stretching vibrations of the nitro group occurs at 1339 cm⁻¹. Benzylidene anilines display their C=N stretching as a band at 1600 cm⁻¹.³² Thus the band obtained at ~1594 cm⁻¹ and ~1595 cm⁻¹ in the FTIR and FT-Raman spectrum, respectively, of BNBA is due to the formation of imine group (C=N) as a result of the condensation reaction between aldehyde and amine. *Para*-di- substituted benzenes show C–H deformation vibration in the region 840–800 cm⁻¹ and in FTIR the C-H deformation vibration appears at ~838 cm⁻¹. In the FTIR spectrum the band at ~532 cm⁻¹ is due to aromatic C–Br stretching. Thus the FTIR and FT-Raman spectral analyses confirm the formation of BNBA.

Crystal structure of BNBA

Crystal structure at 173 K. The diffraction patterns contain strong satellite reflections, which cannot be indexed using three indexes *hkl* (Fig. 5 and S1, ESI[†]).

The presence of satellites points to an incommensurately modulated structure, which has been solved in the noncentrosymmetric monoclinic (3+1)-dimensional superspace group $A2(\alpha 0\gamma)0$, (crystallographic data,‡ lattice parameters and the *q*-vector are given in Table S1, ESI[†]). A reliable solution of this structure (twinned by a mirror plane normal to the *c* axis) has been reached with twin components 0.504(3) and 0.496(3); the Flack-parameter is equal to 0.01(1). A single molecule has been considered as a rigid unit. The structural modulations appear as a result of relative shifts and tilts of the molecules. Details of the structure refinement are given in Table S1, ESI,[†] Positional and anisotropic displacement parameters of atoms in the BNBA molecule and information

[‡] Crystallographic data of BNBA, C₁₃H₉BrN₂O₂ at 173 K: the (3+1)D group of symmetry is $A2(\alpha 0\gamma)0$; the modulation vector $\boldsymbol{q} = 0.0658(1)\boldsymbol{a}^* - 0.2658(1)\boldsymbol{c}^*$; a = 10.5217(10), b = 16.2535(16), c = 7.4403(7) Å, $\beta = 110.709(7)$; V = 1190.2(2) Å³; Z = 4; $d_x = 1.7024$ g cm⁻¹. Crystallographic data of BNBA, C₁₃H₉BrN₂O₂ at 290 K: space group A2; a = 10.6408(09), b = 16.2706(10), c = 7.5669(7) Å, $\beta = 110.783(8)$; V = 1224.8(2) Å³; Z = 4; $d_x = 1.6542$ g cm⁻¹.

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1

Fig. 5 Satellite reflections (indicated by red circles) in the h0l section of the reciprocal space. The satellite reflections are split owing to the twin mirror plane normal to the *c* axis.

on the molecule modulation are presented in the ESI† (Tables S2–S4) and in the CIF file. The nine crystallographically independent H atoms (Table S2, ESI†) are in perfect agreement with the NMR spectra of BNBA.

The crystal packing of BNBA is illustrated in Fig. 6, along with the details of a single molecule in Fig. 7, which confirm the expected molecular connectivity (Scheme 1). For refinement purposes, each BNBA molecule has been constrained as two flat units, $(=)N-C_6H_4-Br$ (BB) and $NO_2-C_6H_4-CH(=)$ (NB). The angle between the units was refined to $18.1(8)^{\circ}$. No restrictions were applied in the final refinement. However, H atoms were constrained at 0.96 Å from the respective parent C-atoms. A complete listing of bond distances and angles are available in the ESI† (Tables S5 and S6) and CIF file. The following distances characterize the NB moiety: C-C = 1.39(3) \pm 0.03 Å in the phenyl rings, C_{ar}-C(=N) = 1.47(2) Å, C_{ar}-NO₂ = 1.47(2) Å, N–O = 1.23(2) \pm 0.02 Å in NO₂. The following distances characterize the BB moiety: C–C = $1.39(3) \pm 0.03$ Å in the phenyl rings, C_{ar} -N = 1.43(2) Å, Br- C_{ar} = 1.89(1) Å. The C=N distance is equal to $1.25(2) \pm 0.02$ Å. In BNBA, all angles between closest atoms have been refined as $120(1) \pm 5^{\circ}$ (Table S6 in ESI[†]). According to the high-dimensional symmetry, the molecules tilt and shift following the structure modulation (Table S4 in ESI[†]).

The displacements and rotations are imposed by C–H···O and C–H···Br interactions occurring between molecules (Fig. 6, 8 and S2 in the ESI†). These interactions do not satisfy periodicity in the 3-dimensional bulk, only the [010] direction remains periodic (Fig. 6 and 8).

The H···O (H···Br) average distances vary from 2.47(5) to 2.63(5) Å (from 2.88(5) to 3.82(3) Å) and C-H···O (C-H···Br) average angles vary from 148(4) to $165(2)^{\circ}$ (from 132(3) to $165(2)^{\circ}$). Full details are given in Table S7, ESI.[†]

Crystal structure at 290 K. No satellite reflections were observed in the diffraction patterns obtained at room



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Fig. 6 *ac* projection of a portion of the structure and a representative layer of the incommensurately modulated structure of BNBA. In the layer, the dashed lines indicate H···A bonds with the distances H···Br \leq 3.6 Å, H···O \leq 2.6 Å and angles C–H···A \leq 140°.

temperature, however, diffuse scattering pointed to a partially disordered crystal structure. This 290 K structure was successfully refined using the average structural model obtained for the incommensurately modulated structure at 173 K. This model corresponds to split molecules (Table S8 and Fig. S3 in the ESI†) and implies that the local domain structure at room temperature is identical to that at 173 K, whereas a long-range order of the domains is missing at room temperature. The main difference between the molecule at 290 and 173 K relates to the atomic displacement parameters (ADP), which are unusually large for all atoms at 290 K (Table S9 in the ESI†). Splitting of the molecules and the large ADP atomic



Fig. 7 A single molecule of BNBA with displacement ellipsoids drawn at the 50% probability level.



Fig. 8 View along the [010] direction and perspective view of the typical connection of the BNBA molecules by C–H···O and C–H···Br interactions (dashed lines). Brown, blue, red, black and pink colours correspond to Br, N, O, C and H atoms, respectively.

parameters confirmed the molecule modulations in local domains. Absence of satellite reflections on the diffraction patterns indicates an absence of coherency of the modulations between the domains. Despite the almost identical molecular structure at both temperatures, the correct structure solution is available only for the lower temperature structure owing to the presence of the satellite reflections.

The recorded powder X-ray diffraction pattern of BNBA is shown in Fig. 9, and is compatible to that calculated using the room temperature single crystal CIF file (see Fig. S4 in the ESI†). CCDC 900430 and 900429 contain the crystallographic data for the BNBA structure at 173 K and 290 K, respectively.

Fluorescence of BNBA

Fluorescence finds wide applications in the branches of biochemical, medical and chemical research fields for analyzing organic compounds.³³ Fluorescence generally occurs in compounds containing aromatic functional groups with lowenergy $\pi \rightarrow \pi^*$ transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double-bond structures exhibit fluorescence, but the number of such compounds is small compared with the number of aromatic systems.³⁴



Fig. 9 Powder XRD pattern of BNBA.

The BNBA sample was excited at 325 nm and the fluorescence emissions were observed at \sim 469 nm (Fig. 10) which are due to the presence of aromatic rings in the BNBA compound. The broad fluorescence maxima is probably due to the modulated nature of BNBA.

BNBA as a nonlinear optical material

The Kurtz Powder Test showed that the reference KDP powdered crystal produced 6.4 mV as output beam voltage, while the BNBA powdered crystal of the same size has produced about 60 mV. Hence, the BNBA material has an NLO efficiency of about 9.4 times higher than that of KDP.

The open-aperture *Z*-scan curve obtained for BNBA is shown in Fig. 11.

An increase in absorption is observed as the laser intensity is increased, indicating nonlinear optical absorption. Since the linear transmission of the sample at the excitation wavelength is high at 82%, the observed nonlinear absorption might have contributions from genuine two-photon (2PA) or three-photon



Fig. 10 Fluorescence spectrum of BNBA



Fig. 11 The open aperture Z-scan curve measured for BNBA dissolved in chloroform. Open circles are experimental data points while the solid curve is the numerical fit for a two-photon absorption process, calculated using the non-linear transmission equation.³⁵ T_{norm} is the normalized transmittance.

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600

. 900

Fig. 12 The TG (blue) and DTA (black) diagrams of BNBA.

300

163.24

(3PA) absorption, as well as from excited state absorption (ESA). We tried to fit the data to both two-photon and three-photon absorption equations, and the best fit was obtained for a two-photon process described by the non-linear transmission equation:³⁵

$$T = \left(\frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi q_0}}\right) \int_{-\infty}^{\infty} \ln\sqrt{1+q_0 \exp(-t^2)} dt$$

where *T* is the intensity dependent transmittance of the sample; *L* is the length of the sample; *R* is its surface reflectivity; α is the linear absorption coefficient; q_0 is given by $\beta(1 - R)I_0L_{\text{eff}}$, where β is the two-photon absorption coefficient and I_0 is the peak intensity, L_{eff} is given by $[1 - \exp(-\alpha L)]/\alpha$.

In the present case, the quantity β is the effective 2PA coefficient, which has contributions from both resonant and non-resonant nonlinear processes (ESA and 2PA, respectively).³⁶ The resonant term is given by the expression $\beta_{\text{ESA}}I = \sigma N$, where σ is the ESA cross-section and N(I) is the intensity-dependent excited state population density. By determining the best-fit curve for the *Z*-scan data, the effective two-photon absorption coefficient β is calculated to be 5.95 $\times 10^{-11}$ m W⁻¹.

Thermal stability of BNBA

TG-DTA of BNBA is shown in Fig. 12. In TGA a single stage weight loss was observed and the major weight loss starts at 200 °C due to decomposition of BNBA. The decomposition of BNBA leads to zero residue. The shape of the TGA curve indicates that the melting is immediately followed by decomposition with the formation of the volatile reaction products of the sample.³⁷ A sharp endothermic peak at ~163 °C (436 K) corresponds to the melting point of the material in DTA.

In DSC a sharp endothermic peak was observed at ~ 163 °C, which represents the melting point of the BNBA material and there is no phase transformation before the melting point. The melting point of the BNBA is in good agreement with the DTA result. The BNBA material is stable up to its melting point. The

sharpness of the peak reveals the good crystallinity of the synthesized compound.

Temperature (°C)

Conclusions

-1600

-2000

-2400

Heat Flow (mW/g)

Single crystals of the Schiff base 4-bromo-4'-nitrobenzylideneaniline (BNBA) have been grown from acetone solution by the slow evaporation technique at room temperature. BNBA is a new novel nonlinear optical material. Its relative powder SHG efficiency was measured to be 9.4 times higher than that of KDP. The effective two-photon absorption coefficient β is estimated to be 5.95 × 10⁻¹¹ m W⁻¹.

The molecular structure and the functional groups are confirmed by NMR, FTIR and FT-Raman spectra.

The noncentrosymmetric structure of the grown crystal is incommensurately modulated ($A2(\alpha 0\gamma)0$ superspace group) at 173 K. The C-H···O and C-H···Br interactions occurring between molecules in structural layers force the structure modulations. The C-H···A_{cceptor} interactions do not exhibit periodicity in the 3-dimentional bulk of the crystal, only the [010] direction is periodic. The layers subject to interactions are at the origin of a strong preferred orientation in a powder sample using to record powder XRD pattern. At room temperature, the structure is partially disordered, however, the local structure of domains is identical to that at 173 K. The model obtained for the incommensurately modulated structure at 173 K is necessary to solve the room temperature structure.

The fluorescence emissions of BNBA observed at \sim 469 nm is due to the presence of aromatic rings in its structure.

The melting point of the BNBA material was found to be \sim 436 K and no phase transformation has been observed before melting.

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References

- 1 C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897.
- 2 Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, 109, 5868.
- 3 H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs and H. von Lohneysen, *Chem. Phys.*, 2002, **281**, 113.
- 4 S. Achelle, N. Ple and A. Turck, RSC Adv., 2011, 1, 364.
- 5 B. H. T. Chai, Optical crystals, in *CRC Handbook of Laser Science and Technology Supplement 2: Optical Materials*, ed. M. J. Weber, CRC Press, Boca Raton, FL, 1995.
- 6 V. G. Dmitriev, G. G. Gurzadyan and D. N. Nicogosyan, *Handbook of Nonlinear Optical Crystals*, Springer-Verlag, New York, 1999.
- 7 C. Razzetti, M. Ardoino, L. Zanotti, M. Zha and C. Paorici, *Cryst. Res. Technol.*, 2002, **37**, 456.
- 8 M. S. Wong, C. Bosshar, F. Pan and P. Gunter, *Adv. Mater.*, 1996, **8**, 677.
- 9 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers*, Wiley, New York, 1991.
- Y. Duorong, Z. Zhenwu, L. Mingguo, X. Dong, Q. Fang, B. Yonghong, S. Suoying and M. Jiang, *J. Cryst. Growth*, 1998, **186**, 240.
- S. Oliveira, D. Correa, L. Misoguti, C. Constantino, R. Aroca, S. Zilio and C. Mendonca, *Adv. Mater.*, 2005, 17, 1890.
- 12 S. Kawata and Y. Kawata, Chem. Rev., 2000, 100, 1777.
- 13 W. Denk, J. Strickler and W. Webb, Science, 1990, 248, 73.
- 14 L. Ventelon, S. Charier, L. Moreaux, J. Mertz and M. Blanchard-Desce, Angew. Chem., 2001, 113, 2098.
- 15 B. Curnpston, S. Ananthavel, S. Barlow, D. Dyer, J. Ehrlich, L. Erskine, A. Heikal, S. Kuebler, I. Lee, D. McCord-

Maughon, J. Qin, H. Rockel, M. Rumi, X. Wu, S. Marder and J. Perry, *Nature*, 1999, **398**, 51.

- 16 J. E. Ehrlich, X. L. Wu, I.-Y. S. Lee, Z.-H. Hu, H. Rockel, S. R. Murder and J. W. Perry, *Opt. Lett.*, 1997, 22, 1843.
- 17 C.-K. Wang, P. Zhao, Q. Miao, Y.-P. Sun and Y. Zhou, J. Phys. B: At., Mol. Opt. Phys., 2010, 43, 105601.
- 18 R. T. Bailey, G. Bourhill, F. R. Cruickshank, D. Pug, J. N. Sherwood and G. S. Simpson, *J. Appl. Phys.*, 1993, 73(4), 1591.
- 19 A. N. Azariah, A. S. H. Hameed, T. Thennappan, M. Noel and G. Ravi, *Mater. Chem. Phys.*, 2002, **88**, 90.
- 20 S. Leela, R. Hema, K. Ramamurthi and H. Stoeckli-Evans, *Acta Crystallogr.*, 2009, E65, 0477.
- 21 S. Leela, K. Ramamurthi and G. Bhagavannarayana, *Spectrochim. Acta*, 2009, **74A**, 78.
- 22 A. Subashini, R. Kumaravel, S. Leela, H. Stoeckli-Evans, D. Sastikumar and K. Ramamurthi, *Spectrochim. Acta*, 2011, 78A, 935.
- 23 S. Leela, R. Hema, H. Stoeckli-Evans, K. Ramamurthi and G. Bhagavannarayana, *Spectrochim. Acta*, 2010, 77A, 927.
- 24 T. Janssen, G. Chapuis and M. de Boissieu, *Aperiodic Crystal: from Modulated Phases to Quasicrystals*, Oxford University Press, Oxford, 2007.
- 25 S. van Smaalen, *Incommensurate Crystallography*, Oxford University Press, Oxford, 2007.
- 26 A. Schonleber, Z. Kristallogr., 2011, 226, 499.
- 27 G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.
- 28 V. Petricek, M. Dusek and L. Palatinus, *Jana 2006, Structure determination software*, Institute of Physics, Praha, Czech Republic, 2006.
- 29 S. K. Kurtz and T. T. Perry, J. Appl. Phys., 1968, 39, 3798.
- 30 S. S. Clerc, Tables of Structure Determination of Organic Compounds, Springer-Verlag, Berlin, Heiderberg, New York, 2nd edn, 1989.
- 31 J. Mohan, Organic Spectroscopy, Principles and Applications, Narosa Publishing House, New Delhi, 2nd edn, 2008.
- 32 J. C. Pouchert, *Aldrich Library of FTIR Spectra*, Aldrich Chemical Co. Inc, Milwaukee, 3rd edn, 1984.
- 33 H. H. Willard, L. L. Merritt Jr, J. A. Dean and F. A. Settle Jr, *Instrumental Methods of Analysis*, Wadsworth Publishing Company, USA, 6th edn, 1986.
- 34 D. A. Skoog, *Principles of Instrumental Analysis*, Holt, Rinehart & Winston, New York, 1st edn, 1971.
- 35 R. L. Sutherland, *Handbook of Nonlinear Optics*, Marcel Dekker, New York, 1996.
- 36 M. Rumi and J. W. Perry, Adv. Opt. Photonics, 2010, 2, 451.
- 37 Principles and Applications of Thermal Analysis, ed. P. Gabbott, Blackwell, 2008.