

Article

Subscriber access provided by READING UNIV

Concomitance, reversibility and switching ability of centrosymmetric and non-centrosymmetric crystal forms: Polymorphism in an organic NLO material

Kunal K. Jha, Sanjay Dutta, and Parthapratim Munshi

Cryst. Growth Des., Just Accepted Manuscript • DOI: 10.1021/acs.cgd.7b01560 • Publication Date (Web): 20 Dec 2017

Downloaded from http://pubs.acs.org on December 23, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Crystal Growth & Design is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Concomitance, reversibility and switching ability of centrosymmetric and non-centrosymmetric crystal forms: Polymorphism in an organic NLO material

Kunal K. Jha, Sanjay Dutta and Parthapratim Munshi*

Chemical and Biological Crystallography Laboratory, Department of Chemistry, School of Natural Science, Shiv Nadar University, Tehsil Dadri, Uttar Pradesh- 201314, India.

E-mail: parthapratim.munshi@snu.edu.in

ABSTRACT

Reversibility between two concomitant polymorphs and their switching ability is demonstrated for the novel organic NLO material, Z-3-(3-methoxyphynyl)-2-(4-nitrophenyl)acrylonitrile. The appearances of their concomitant as well as exclusive polymorphic forms were discovered upon systematic crystallization experiments using various solvents. Determination of X-ray crystal structures confirmed that the polymorphs crystalize in centrosymmetric ($P2_1/n$) and noncentrosymmetric (Fdd2) space groups. A search using the Cambridge Structural Database revealed that there exist only 10 such polymorphic pairs. A reversible phase transitions and the switching ability between the polymorphs can be achieved *via* both heat and solvents as stimuli. Structural analysis confirmed that the polymorphs have 2D similarity. Further, quantitative and

qualitative analysis of interaction energies based on the UNI force field and energy frameworks indicate that they possess very similar energies, although the centrosymmetric form is slightly lower in energy. A comparably high value of SHG activity and the NLO properties as estimated based on gas-phase and in-crystal calculations suggest that the non-centrosymmetric form could be a potential NLO material. To the best of our knowledge, this study is the rarest of its kind to show the reversibility and switching ability between centrosymmetric and non-centrosymmetric polymorphic phases in an organic material, induced *via* both thermal and solvent stimuli.

INTRODUCTION

Focus on materials science research is slowly but steadily shifting from inorganic and organometallic systems to organic materials.¹⁻⁷ Interest in organic materials has been increasing gradually due to their design flexibility, low molecular weight, low cost and eco-friendly nature.⁸⁻⁹ Certain classes of organic compounds in their solid-state respond to external stimuli and find myriad of applications in optoelectronics, non-linear optics (NLO), ferroelectrics, semiconductors etc.^{10–13} However, most of these properties demand not only the presence of noncentrosymmetric phases but also the existence of polar phases of the materials in their crystalline form. But controlling the non-centrosymmetric phase remains a key challenge for designing such materials.^{14–17} While crystal symmetry is mainly governed by the molecular packing in the crystal lattice the external parameters such as crystallizing solvents, pressure, thermal stimuli etc. play crucial role in controlling the desired phases of the materials. In the presence of such stimuli, the materials may even undergo changes between different polymorphic modifications existence of at least two different crystal structures of the same material.¹⁸ While the phenomenon of polymorphism is not uncommon in molecular crystals and it is predominantly discovered in pharmaceutical compounds, its existence in organic materials with responsive

Crystal Growth & Design

characteristics is scarce.^{19–21} Moreover, the ability of appearance of two polymorphs simultaneously in a given condition, i.e. *concomitant polymorphs*²² and their reversible switching between centrosymmetric and non-centrosymmetric forms in such responsive organic materials are extremely rare.^{23,24}

Switching ability in organic materials is employed for various applications in material industries, in the field of fluorescence, live cell imaging microscopy, environmental interface cutter, optoelectronics, photonic devices, etc.²⁵⁻²⁸ The common approaches for attaining switching materials include introduction of conformational modifications in the π -conjugated donor-acceptor system, photochemical reactions under UV-Vis light and probing samples under thermal stimulus etc.^{29,30} Switching of centrosymmetric to non-centrosymmetric or polar to nonpolar form can occur in their solid state or in crystals. Although there are some reports on such switching upon UV light irradiation^{31,32} but reports either induced via solvent^{33,34} or temperature³⁵ are very rare. To the best of our knowledge, centrosymmetric to noncentrosymmetric switching and their reversibility, induced by both solvent and temperature as stimuli and in a single organic material has not been reported before. Moreover, interconversion between polymorphic forms are uncommon.³⁶ Formation of co-crystals and organic-inorganic hybrid structures were also investigated to achieve better switching ability and reversibility in NLO materials.³⁷ Recently, single component plastic crystals have been investigated and found to display record high on/off contrast.³⁸ Considering only organic structures, search using CSD (version 5.38, update May 2017)^{39,40} revealed 115,443 (~13%, total number of reported structures is 892,156) structures belong to the non-centrosymmetric space groups, out of which only 4167 (~0.46%) structures exist in polymorphic form. Further, occurrences of concomitant

polymorphs in organic systems are limited²² and the existence of centrosymmetric and noncentrosymmetric forms as *concomitant polymorphs* is also rare.^{41,42}

The π -conjugated organic scaffolds such as stilbene and chalcone are known to exhibit polymorphic behavior and occasionally exist in non-centrosymmetric forms, which give rise to SHG effect.^{43–45} Careful and intuitive substitution of donor and acceptor group in a π -conjugated organic scaffolds such as MMONS and CMONS led to highly NLO active materials with different morphology and structures when crystallized using different solvents.^{43,44}

Here we report the systematic investigations of (i) two concomitant polymorphs of *Z*-3-(3-methoxyphynyl)-2-(4-nitrophenyl)acrylonitrile (**Scheme I**) and discovered their existence in centrosymmetric and non-centrosymmetric space groups, (ii) their reversible phase transitions in the presence of both solvents and heat as stimuli, (iii) the differences and degree of similarities between the two polymorphic crystal structures (iv) quantitative and qualitative pictures of their interaction energies and (v) NLO properties of the non-centrosymmetric polymorph.



Scheme I. Chemical diagram of Z-3-(3-methoxyphenyl)-2-(4-nitrophenyl)acrylonitrile.

EXPERIMENTAL SECTION

Synthesis. All the reagents used for the synthesis of Z-3-(3-methoxyphynyl)-2-(4nitrophenyl)acrylonitrile (**3-OMe-CNS**) were procured from Sigma-Aldrich. The reagents were used without further purifications. **3-OMe-CNS** was prepared by Knoevenagel condensation of

Crystal Growth & Design

4-nitrophenylacetonitrile and 3-methoxybenzaldehyde using piperidine as basic catalyst in ethanol at 70°C for three hours as reported earlier (**Scheme SI**).^{46,47} Compound thus formed was purified by column chromatography and characterized *via* FT-IR, ¹H, ¹³C NMR and HRMS (**Figs. S1-S3**).

Crystallization. A range of HPLC grade solvents were employed for growing the crystals of **3**-**OMe-CNS** using slow evaporation method at room temperature (22-25°C) and low temperature (3-6°C). A systematic crystallization experiment of **3-OMe-CNS** at both low temperature (LT) and room temperature (RT) using the solvents as listed in **Table 1** provided crystals with two morphologies; needles and plates. Crystallizations using chloroform and tetrahydrofuran (THF) as solvents resulted in the appearance of both morphologies together, *i.e.* concomitantly. However, at RT and using THF only the plate form was obtained. Further, optimization of crystallization conditions afforded the growth of the individual forms. High quality single-crystals grown using chloroform were used for the X-ray diffraction experiment. The crystal morphologies as captured using Olympus SC30 polarizing microscope are shown in **Figure 1**.

Table 1.	Details	of crystal	lization	experiments.
I able I.	Dottunio	or or your	inZation	experiments.

Solvent(s)	Temperature	Crystal morphology
Chloroform	LT	plate/needle ^{<i>a</i>}
	RT	plate/needle ^a
Acetone	LT	Needle
	RT	Needle
Dichloromethane	LT	plate
	RT	۰۵
1,4-Dioxane	LT	"

58	
59	
60	

	RT	"
Toluene	LT	"
	RT	"
Ethyl-acetate	LT	"
	RT	"
Tetrahydrofuran	LT	plate/needle ^{<i>a</i>}
	RT	plate
Dimethyl Sulfoxide	RT	plate
Acetonitrile	LT	Needle
	RT	Needle
2-Propanol	RT	plate

^aconcomitant polymorphs



Figure 1. Optical images of needle (left), concomitant (middle) and plate (right) form crystals.

X-ray Crystallography. Single-crystal X-ray diffraction data on both polymorphs were collected using D8 Venture Bruker diffractometer equipped with a PHOTON 100 CMOS detector. Crystals were cooled to 100K under liquid nitrogen flow using an Oxford Cryosystems nitrogen gas flow-cooling device. *Mo* K_{α} radiation (λ =0.71073 Å) was used for data collection using phi (ϕ) and omega (ω) scan strategy. The crystal to detector distance was set to 50 mm.

Cell measurement, data collection, integration and scaling were done using the APEX3 software.⁴⁸ The data was processed using SAINT⁴⁹ and absorption correction was done using SADABS⁵⁰ program integrated in APEX3. The structure was solved using SHELXT program and refined within the XSHELL graphic interface.⁵¹ The non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. All H-atoms were placed at the calculated positions and refined using a riding model with appropriate HFIX commands.

Powder X-ray Diffraction (PXRD) patterns for each polymorphic form were recorded on a Rigaku Miniflex 600 diffractometer using parallel beam geometry and $Cu K_{\alpha}$ radiation. The powder samples were prepared after grinding the respective polymorphic crystal forms.

Thermal Characterizations and NLO Measurement. Differential Scanning Calorimetry (DSC) measurements on each polymorphic crystal were carried out using Mettler Toledo DSC3 instrument under nitrogen gas atmosphere. Hot Stage Microscopy (HSM) studies on each crystal form were carried out using Nikon polarizing microscope CFI60 infinity, equipped with heating stage LTS420. Linksys software was used for image grabbing and monitoring the sample temperatures.

NLO activity measurement was carried out using Spectre Physics instrument equipped with INDI LASER (Nd:Yag Laser 1064 nm) at repetition rate of 10 Hz and pulse width of 8 ns.

THEORETICAL SECTION

NLO property calculations

The molecular gas-phase dipole moment (μ), linear polarizability (α) and static first hyperpolarizability (β) values were estimated based on crystal geometry using *Gaussian 09*.⁵² The keyword 'Polar = Enonly' was used for α and β calculation. The hybrid functional, M05-2X⁵³ which is widely used^{54,55} for such calculations in conjugated systems, was also used here with 6-31+G* basis set. The β tensor components as obtained from above calculation was used to determine β_{total} as given by the following expression,

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

The program CRYSTAL14⁵⁶ was used to perform a single-point periodic theoretical calculations at the B3LYP⁵⁷ level and 6-31G** basis set based on the experimental geometry of the non-centric polymorph of 3-OMe-CNS. Grimme's dispersion function (D2)⁵⁸ was also taken in to account for this calculation. Given the nonstandard space group Fdd2 and the need to accommodate all 16 molecules in the unit cell, the conventional supercell was generated using the keyword SUPERCON. The keywords CPKS (Couple Perturbed Kohn-Sham) along with THIRD (energy derivatives up to the third order) and both ANDERSON and BROYDEN (for mixing of KS matrix derivatives) were used to perform the in-crystal α , β and second order nonlinear susceptibility (χ^2). For smooth convergence, the TOLALPHA was set to 4. The shrinking factors were set at 4. The accuracy of the calculation of the bielectronic Coulomb and exchange series were controlled by using the keyword ITOLINTEG with ITOL1 = ITOL2 = ITOL3 = ITOL4 = 6 and ITOL5 = 14. For faster convergence, the level shifter value was set equal to 0.6 Hartree. The periodic wavefunction obtained upon convergence (10^{-8}) of energy was used to calculate the in-crystal properties (α , β and χ^2). The computed properties were compared with that of urea.

Results and Discussion

Crystal Growth & Design

3-OMe-CNS - a cyano substituted nitro stilbene derivative, belongs to the family of donoracceptor π -conjugated systems. The compound as shown in **Scheme I** has a π -conjugated stilbene core and one end, which contains one $-NO_2$ group as an acceptor. At the other end at the *meta* position it has one -OMe group as a donor. There is also one moderate acceptor -CN group attached next to the C=C bond. These specific arrangements make **3-OMe-CNS** a 'push-pull' chromophore.

Characterizations of polymorphs

Single-crystal X-ray diffraction experiment on crystals with plate morphology confirmed that these crystals belong to orthorhombic system with non-centrosymmetric space group, Fdd2 and the crystals with needle morphology belong to a monoclinic system with centrosymmetric space group, $P2_1/n$. Here after we identify form Fdd2 as **non-centric** and form $P2_1/n$ as **centric**. Detailed crystallographic data of these two concomitant polymorphs are summarized in **Table 2**. Search using CSD (version 5.38, update May 2017, **Table S1, ESI**) revealed that there are only 1172 (0.13%) organic structures reported in Fdd2 space group, out of which only 54 unique structures exist in polymorphic forms. The search further shows that only 10 of these polymorphs exist as polymorphic pairs together with space group $P2_1/n$. The same atomic numbering scheme is followed for both crystal forms as depicted in **Figure 2**. In both polymorphs the molecule is found to adopt a planar geometry. Further, no conformational changes were noticed between the molecules in these two polymorphic forms (**Figure 2**).

Table 2:	Single c	rystal X-ray	diffraction	data and	refinement	parameters
		/ /				

Compound	Centric	Non-centric
Morphology	Needle	Plate
Chemical Formula	$C_{16}H_{12}N_2O_3$	$C_{16}H_{12}N_2O_3$

ACS Paragon Plus Environment

Formula Weight	280.28	280.28
Crystal Size (mm)	0.026 x 0.057 x 0.283	0.049 x 0.160 x 0.243
Space Group	$P2_l/n$	Fdd2
Temperature/K	100(2)	100(2)
a(Å)	6.8818(3)	12.6352(7)
$b(\text{\AA})$	30.0658(11)	59.580(3)
$c(\text{\AA})$	7.0543(3)	6.8942(4)
$\beta(^{\circ})$	116.826(1)	90
Volume/ Å ³ ; Z	1302.50(9); 4	5190.00(5); 16
Density/g cm ⁻³	1.429	1.435
<i>F</i> (000)	584	2336
Absorption Coefficient /mm ⁻¹	0.101	0.101
T_{\min}, T_{\max}	0.972, 0.997	0.927, 0.988
<i>R</i> (merge)	0.0626	0.0438
Measured Reflections	22315	16786
Independent Reflections	2655	2624
No. of parameters	191	191
$R(F^2), R_{\rm w}(F^2)$	0.0419, 0.0897	0.0371, 0.0749
Goodness of fit (S)	1.067	1.101
$\Delta \rho_{max}/e \text{ Å}^{-3}, \Delta \rho_{min}/e \text{ Å}^{-3}$	0.284, -0.302	0.155, -0.265



Figure 2: Overlay of **centric** and **non-centric** forms drawn with respect to plane containing N2, C7 and C9 atoms.

Both polymorphic forms were further characterized using various techniques such as solid state FT-IR, powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC) and hot stage microscopy (HSM). In order to check the purity, and for accurate identification of phase differences the single-crystals of the two forms were carefully separated upon checking their unit cell parameters.

The crystals were then crushed before performing the FT-IR and UV experiments. The recorded FT-IR spectra (**Figure S1, ESI**) on the two forms displayed an identical pattern. The absorption maximum (λ_{max}) as recorded from the UV-Vis spectra are almost identical; 342.89 nm and 342.13 nm for the **centric** and **non-centric** forms, respectively (**Figure S4, ESI**). This suggests that the two polymorphs possess the same absorptions in solution. The λ_{max} values suggest that these polymorphs belong to the family of 'yellow material'.^{59,60}

PXRD experiments were performed on pure phases of crystalline samples at room temperature. The scan rates used for this experiments were 1°/min with 0.02° step in 2 θ . The comparison of experimental PXRD patterns clearly indicates the phase differences (e.g. peaks at

 $2\theta = \sim 16^{\circ}$ for the **non-centric** form and $2\theta = \sim 18.5^{\circ}$ for **centric** form) between the **centric** and the **non-centric** polymorphs (**Figure 3**). The PXRD patterns were also compared with their corresponding simulated PXRD patterns as generated from the respective single-crystal structures determined at room temperature. The comparison displayed good agreement between the observed and the predicted patterns of each form (**Figure S5, ESI**).



Figure 3. Overlay of experimental PXRD patterns of centric and non-centric polymorphs

Thermally induced phase reversal

Further, both crystal forms were subjected to thermal characterization *via* a DSC experiment. The pure single crystal samples were heated at the rate of 5°C/min from 25-250°C and cooled down to room temperature in two successive cycles. The sharp melting and crystallization peaks as appeared during the heating and cooling cycles clearly indicate that the polymorphs exist in their pure crystalline forms (**Figure 4**). The **non-centric** form displayed slightly higher melting

point (195.04°C) compared to that of **centric** form (194.23°C). Interestingly, during the second heating cycle, the melting peak (194.04°C) of the **non-centric** form is found to be very close to the melting peak of **centric** form recorded during the first heating cycle. This observation suggests that the **non-centric** form transforms to the **centric** form upon melting and recrystallization.



Figure 4. DSC traces for centric and non-centric polymorphs.

Further, these phase changes were monitored and visualized *via* complementary HSM technique on the pure single-crystals of the two polymorphs. The change in the morphology of the **centric** form was first noticed at around 195°C and finally melted at around 200°C (**Figure 5**). Whereas for the **non-centric** form the first change was observed at around 190°C. It finally melted also at around 200°C. During the cooling cycle for the **centric** form the compound appeared to crystallize at around 172°C, the corresponding temperature for the **non-centric** form

Crystal Growth & Design

was at around 180°C. The melting and cooling steps as observed in HSM correlate well with the results obtained from the DSC experiment. In order to confirm their phases, crystals obtained at the end of HSM experiments were subjected to unit-cell determination by X-ray diffraction. Interestingly, the cell-parameters of both the crystals were found to match those of the **non-centric** form (**Table S2**). This confirms that in case of HSM the **centric** form converts to its **non-centric** form.



Figure 5. HSM images of centric and non-centric forms.

Furthermore, we performed *in-situ* crystallization experiment. For this purpose, we chose single-crystals of the **centric** form and subjected to heating and cooling under the cryo-stream while mounted in a capillary and placed on the goniometer. The unit-cell determination using X-ray diffraction on the recrystallized sample from its melt confirmed that the crystal belonged to the **non-centric** form, which is in accordance with the HSM experiment as discussed above. Unfortunately, we could not confirm the reverse process by performing the same experiment on a **non-centric** crystal. However, the results from DSC experiment as discussed earlier demonstrates the occurrence of a reverse process.

Solvent mediated phase reversal

Crystal Growth & Design

Additionally, the reversible transformation of the polymorphic forms was investigated *via* systematic solvent exchange experiments. For this purpose, the crystals with needle morphology (centric form) were dissolved and recrystallized from the solvents in which the crystals with plate morphologies (non-centric form) were obtained and *vice versa*. The outcomes of the recrystallization experiments are summarized in Table 4. From visual inspection as well as upon determining their cell parameters it was confirmed that the two forms also undergo reversible phase transitions in the presence of appropriate solvent as stimulus. To the best of our knowledge, this experiment is the first of its kind to demonstrate solvent mediated phase reversal of polymorphic forms.

Collating all these results from DSC, HSM, *in-situ* recrystallization *via* heating and cooling and the solvent exchange experiments we conclude that the compound **3-OMe-CNS** undergoes reversible polymorphic phase transitions. The phase reversal process under various stimuli as discussed above is summarized in **Figure 6**.

Table 4. Re-crystallization of polymorphic forms using solvent exchange experiments.

First crystallization solvent	Morphology	Polymorph	Second crystallization solvent	Morphology	Polymorph
Ethyl-acetate	***	Non-centric	Acetone	A. M.	Centric
2-Propanol		Non-centric	Acetone		Centric
Ethyl-acetate	214. 902' 3	Non-centric	Acetonitrile	X	Centric
Acetonitrile		Centric	2-propanol		Non-centric
Acetonitrile		Centric	1,4-Dioxane		Non-centric



Figure 6. Summary of phase changes using both heat and solvent as stimuli.

Molecular packing and intermolecular interactions

Molecular packing diagrams as displayed in **Figure 7** show that the molecules in both **centric** and **non-centric** forms arrange in a similar brick stacking like pattern. The molecules are essentially held together in their crystal lattice *via* π ··· π and C-H···O interactions. The interplanar distance were found to be 3.28 Å and 3.27 Å for **centric** and **non-centric** form, respectively. Further, close inspection of the monolayer packing in the two forms indicate that there is a similarity of molecular orientation but overall the interactions differ significantly (**Figure 8**). The similarity of orientation of the molecule in the two forms within their unit-cell is also shown in **Figure S6**. In case of **centric** form two adjacent molecules within the monolayer are arranged in such way along the *b*-axis that the -CN groups are facing opposite to each other. Whereas in the case of **non-centric** form the -CN groups of the corresponding molecules are oriented in the same direction. In both forms the molecules are held together *via* C(*Ar*)-H···O, C(*sp3*)-H···O, C(*Ar*)-H···N and C(*sp2*)-H···N interactions. However, subtle differences in their interaction patterns between the two forms are evident from **Figure 8**.



Figure 7. Packing diagrams of **centric** form, viewed down the *a*-axis (above) and **non-centric** form, viewed down the *c*-axis (bellow). The color codes for different atom types are also given. The shaded boxes highlights the similarity of stacking of molecules in (**a**) and (**b**).



Figure 8. Monolayer packing diagram of (a) centric form viewed down *c*-axis, (b) non-centric form viewed down *a*-axis. The shaded boxes highlights the similarity of molecular orientation in (a) and (b).

Additionally, in order to visualize and quantify the subtle differences in intermolecular contacts between the two polymorphs, Hirshfeld surface analysis⁶¹ was performed based on their crystal geometries using *CrystalExplorer 3.1.*⁶² The Hirshfeld surface based on d_{norm} as drawn on

a molecule in the **centric** form displays a greater number of contact points compared to that of the **non-centric** form (**Figure 9**). The subtle differences in the surface contact area (red and white regions) in both forms are also highlighted. Red surfaces are the indication of deeper interpenetrations of the molecular surfaces and white ones are due to the lighter interpenetrations.



Figure 9. *d_{norm}* mapped on the Hirshfeld surface of centric (left) and non-centric (right) forms.

Further, the interaction lengths are highlighted *via* 2D fingerprint plots as shown in **Figure 10**. The fingerprint plots reveal slightly shorter H...H (2.2 Å *vs* 2.5 Å) and O...H (2.3 Å *vs* 2.5 Å) contacts in the case of the **non-centric** form in compared to the **centric** forms. The overall intermolecular interactions in these two forms are further quantified based on the percentage contribution of intermolecular interactions extracted from the corresponding fingerprint plots and displayed in a form of pie-chart (**Figure 11**). The H...H and O...H contacts together contribute nearly 56% of the total interactions present in their crystal structures. About 1% contribution differences of C...H and C...C interactions are noticed between the **centric** and **non-centric** forms. Overall, the percentage contributions to the Hirshfeld surface area due to the different types of intermolecular interactions are found to be almost similar in both forms.



Figure 10. Hirshfeld surface associated fingerprints for centric and non-centric polymorphs.



Figure 11. Percentage contribution to the Hirshfeld surface area due to the various intermolecular interactions in the **centric** and **non-centric** forms.

Structural similarity relationship

Further, in order to quantify the similarity relationship between these two reversible concomitant polymorphic structures, an XPac⁶³ analysis was performed based on the "supramolecular construct" concept, which implies spatial arrangement of molecules in crystals. Although the structural similarities using XPac are traditionally deduced for whole 3D structures, they are also interpreted for 2D molecular layers of the crystal structures.^{64,65} In this case, the analysis revealed that these two polymorphs possess 2D similarity with a dissimilarity index of

1. The values of the stretch parameter (0.06), the change in angles ($\Delta a = 0.6^{\circ}$) and a change in plane angles (0.9°) obtained by comparison between the two polymorphs are well within the similarity limits as reported earlier.^{64, 65} This analysis suggests that spatial arrangements of the molecules forming the monolayers are identical in both polymorphic forms. This is in accordance with the molecular packing analysis as discussed above (**Figures 7 and 8**). The relevant plots from XPac analysis are given in **Figure S7** in **ESI**.

Intermolecular interaction energies

Energetic stability of these two polymorphic forms was determined by performing interaction energy calculations based on both energy frameworks⁶⁶ as constructed using the program *CrystalExplorer 3.1* (details are given in **ESI**) and also using the UNI force field as implemented in the program *Mercury*.⁶⁷

The color coded cluster of the molecules and the energy profiles along with the values of interaction energies as calculated between the molecular pairs in each polymorphic crystal form are given in **Figure S8** and **Table S3** in the **ESI**, respectively. For this purpose, all the hydrogen bond distances were normalized to 1.083 Å and scale factor value was set to the default value of $1.0.^{68}$ The energy frameworks for the **centric** and the **non-centric** forms appeared to be similar when viewed down the *c*-axis and *a*-axis, respectively (**Figure 12**). The corresponding views in other directions for both forms are given in **Figure S9**. The energy frameworks clearly show that the molecules in the respective crystal forms are held *via* strings (represent weaker interaction energy), rods (represent moderate interaction energy) and cross bars (represent strong interaction energy), forming triangular or quadrilateral frameworks. The distinct energy frameworks are noticed at the bottom area of the respective forms; the **centric** form displays a triangular framework while the **non-centric** form displayed a quadrilateral framework (**Figure 12**). While

Crystal Growth & Design

the **non-centric** form has slightly higher electrostatic interaction energy, the **centric** form is having a higher dispersion energy. Overall, the **centric** form has slightly lower interaction energy (-146.6 kJ mol⁻¹) compared to that of the **non-centric** form (-144.8 kJ mol⁻¹).



Crystal Growth & Design

Figure 12: Energy frameworks corresponding to different energy components and total interaction energy of the centric (above) and the **non-centric** (below) forms. Red, green and blue color codes represent electrostatic (E_{ele}), dispersion (E_{dis}) and the total (E_{tot}) interaction energies, respectively.

Further, the intermolecular interaction energies as calculated based on the UNI force field are found to follow a similar trend as those observed from the energy framework analysis. Once again the **centric** form is found to have a slightly lower interaction energy (-172.3 kJ mol⁻¹) than that of the **non-centric** form (-170.6 kJ mol⁻¹).

The comparable interaction energies explain the occurrence of concomitant polymorphs with nearly equal melting points. These results further suggest that the polymorphs with concomitance characteristics and have almost equal energies can easily alter their phases in the presence of thermal and solvent stimuli as depicted in **Figure 6**.

NLO properties of non-centric form

In order to explore the potentiality of the **non-centric** form as an NLO material, we measured SHG activity on a crushed homogeneous powder sample of **3-OMe-CNS** crystals using Perry-Kurtz method.⁶⁹ The SHG activity results were then compared with the standard samples urea and KDP. The experimental SHG activity of the **non-centric** form of **3-OMe-CNS** was found to be of about three times and 1.4 times higher than that of KDP and urea, respectively (**Table 5**).

 Table 5. Comparison of powder SHG activities

Sample	Signal (mv)	SHG x Urea	SHG x KDP
KDP	55	0.45	1.00
Urea	122	1.00	2.21

3-OMe-CNS (non-centric)	168	1.37	3.05

Further, molecular gas-phase dipole moment (μ), the linear polarizability (α) and the static first hyperpolarizability (β) values as estimated based on crystal geometry and using *Gaussian* $09^{[52]}$ are listed in **Table 6**. Compared to urea, **3-OMe-CNS** is estimated to have about 1.5 times higher dipole moment. Linear polarizability (α) and static first hyperpolarizability (β) values were estimated to be about seven times and 175 times higher than those of urea, respectively.

The in-crystal NLO property values of α_{total} , β_{total} , and χ^2 tensor components as estimated based on periodic calculations using *CRYSTAL14*⁵⁶ are listed in **Table 7**. The promising values clearly suggest that the **non-centric** form of **3-OMe-CNS** is indeed a potential NLO material.

 Table 6. Gas-phase linear and non-linear properties.

Compound		Gas phase (M05-2X/6-31+G*)								
- F										
	Dipole moment (µ)	Polarizability (<i>a</i>)	Hyper-polarizability (β) *E ⁻³⁰							
	(Debye)	(au)	(esu)							
Urea	5.03	30.22	0.19							
3-OMe-CNS	7.42	222.19	33.40							

Table 7. In-crystal linear and non-linear properties.

Compound	In-crystal (B3LYP/6-31G**)											
	α _{total} (au)	β_{total} (esu)	χ^2 xxx (au)	χ^2 xxy (au)	χ^2 xxz (au)	χ^2 xyy (au)	χ^2 xyz (au)	χ^2 xzz (au)	χ ² ууу (au)	χ^2 yyz (au)	χ^2 xzz (au)	χ^2 zzz (au)
Urea	55.57	0.99	0	0	0	0	- 0.74	0	0	0	0	0
3-OMe- CNS	2359.95	55.15	0	0	0.15	0	0	0	0	3.05	0	- 2.06

Conclusion

As part of this study we discovered two concomitant polymorphs of a novel organic material, Z-3-(3-methoxyphynyl)-2-(4-nitrophenyl)acrylonitrile performed and systematic characterizations to investigate their important properties. Careful crystallization experiments using a variety of solvents resulted in obtaining their exclusive forms as well. Single-crystal Xray diffraction experiments revealed that the polymorphs crystallize in centrosymmetric space group $P2_1/n$ and the non-centrosymmetric space group Fdd2. The PXRD patterns recorded on the respective forms also confirmed their phase differences. FT-IR and UV-Vis spectra of these two concomitant polymorphs appeared to be almost indistinguishable. The sharp melting points as recorded using DSC experiment suggested that the polymorphic forms exist as pure phases. Collating the results from DSC, complementary HSM, *in-situ* recrystallization via heating and cooling and solvent exchange experiments we conclude that the compound 3-OMe-CNS has switching ability between its **centric** and **non-centric** forms and they undergo reversible phase transitions. To the best of our knowledge, this is the first report on a solvent-exchange experiment for reversibility controlling between polymorphic forms. Detailed structural analyses based on both molecular packing and the 'supramolecular construct' confirmed that the polymorphs possess 2D similarity. The quantitative and qualitative analyses of interaction energies based on the UNI force field and the energy frameworks, respectively, indicated that the concomitant polymorphs exist with almost equal energies. However, centric form is found to have a slightly higher interaction energy than the **non-centric** form. The high value of SHG activity and the NLO properties as estimated based on the gas-phase and in-crystal calculations clearly suggests that the **non-centric** form is a highly NLO active material may find potential

applications. The compound **3-OMe-CNS** can also be used as a switching organic material. To the best of our knowledge, this study is first of its kind to show the reversibility and switching ability of polymorphic phases in an organic material, induced *via* both thermal and solvent stimuli.

Supplementary Information

The Supporting Information is available free of charge on the ACS Publications website. The information contains the general experimental procedures for characterization of compound by FT-IR, NMR, UV-Vis and HRMS experimental techniques and the corresponding spectra, synthesis scheme, the details of CSD search, PXRD patterns, Unit-cell parameters from HSM, Molecular orientation in the unit-cells, XPac analysis and interaction energy calculations.

Corresponding Author

Parthapratim Munshi, E-mail: parthapratim.munshi@snu.edu.in

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgements

We thank Shiv Nadar University for research facilities, infrastructure and funding and for research fellowships to KKJ and SD. We are grateful to Prof. Rupamanjari Ghosh for her encouragements and kind supports. We are thankful to Prof. A. Ramanan and Mr. Vineet for their help with the PXRD experiments.

References

2 3	(1)	Matulková I · Cihelka I · Pojarová M · Feifarová K · Dušek M · Vaněk P · Krouna I ·
4 5	(1)	mataikova, i., emeika, s., i ojaiova, m., i ejiaiova, ik., Dušek, m., vanek, i ., ikioupa, s.,
6 7		Krupková, R.; Fábry, J.; Němec, I. CrystEngComm 2012, 14, 4625–4636.
8	(2)	Liang E: Kang I: Zhang X: Lee M-H: Lin Z: Wu V Crust Growth Des 2017 17
9 10	(2)	Liang, T., Kang, L., Zhang, A., Ecc, Wi-11., Lin, Z., Wu, T. Cryst. Orowin Des. 2017, 17,
11 12		4015-4020
13		
14 15	(3)	Halasyamani, P. S.; Zhang, W. Inorg. Chem. 2017, 56, 12077-12085.
16		
17 18	(4)	Garcia, M. H.; Mendes, P. J.; Florindo, P.; Silva, T. In AIP Conference Proceedings;
19 20		2015; Vol. 1642, pp 514–517.
21		
22 23	(5)	Nayar, C. R.; Ravikumar, R. J. Coord. Chem. 2014, 67, 1–16.
24		
25 26	(6)	Maury, O.; Le Bozec, H. In Molecular Materials; Bruce, D. W., O'Hare, D., Walton, R. I.,
27		
29		Eds.; John Wiley & Sons, Ltd. 2010, Chapter 1, pp 1-53.
30 31	(7)	Henry have M. C. C. C. Conter M. D. Conter M. Le Malandar Operation of the Material
32	(/)	Humphrey, M. G.; Chuentes, M. P.; Samoc, M. In Molecular Organometallic Materials
33 34		for Optics; Springer, 2010; pp 57–73.
35		
36 37	(8)	Williams, D. J. Angew. Chemie Int. Ed. English 1984, 23, 690-703.
38 39		
40	(9)	Shirota, Y. J. Mater. Chem. 2000, 10, 1–25.
41 42		
43	(10)	Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. J. Am. Chem. Soc. 2010, 132, 2160-2162.
44 45		
46 47	(11)	Shi, C.; Guo, Z.; Yan, Y.; Zhu, S.; Xie, Y.; Zhao, Y. S.; Zhu, W.; Tian, H. ACS Appl.
48		Mater Interfaces 2012 5 192–198
49 50		
51	(12)	Mutai, T.: Satou, H.: Araki, K. Nat. Mater. 2005, 4, 685–687.
52 53		
54 55	(13)	Horiuchi, S.: Tokunaga, Y.: Giovannetti, G.: Picozzi, S.: Itoh, H.: Shimano, R.: Kumai,
56		
57 58		
59		ACS Paragon Plus Environment
60		

R.; Tokura, Y. Nature 2010, 463, 789–792.

- (14) Delaire, J. a; Nakatani, K. Chem. Rev. 2000, 100, 1817–1846.
- (15) Lu, H.; Gautier, R.; Donakowski, M. D.; Tran, T. T.; Edwards, B. W.; Nino, J. C.; Halasyamani, P. S.; Liu, Z.; Poeppelmeier, K. R. J. Am. Chem. Soc. 2013, 135, 11942–11950.
- (16) Davis, D.; Sreekumar, K.; Sajeev, Y.; Pal, S. J. Phys. Chem. B 2005, 109, 14093–14101.
- Badan, J.; Hierle, R.; Perigaud, A.; Zyss, J. In Nonlinear Organic Crystals: Theoretical Concepts, Materials, and Optical Properties, ACS Symposium Series, 1983; Vol. 233 Chapter 4, pp 81–107.
- (18) McCrone, W. C.; Fox, D.; Labes, M. M. In *Physics and Chemistry of the Organic Solid State*, New York: Wiley Interscience 1965; Vol 2.
- (19) He, Z.; Zhang, L.; Mei, J.; Zhang, T.; Lam, J. W. Y.; Shuai, Z.; Dong, Y. Q.; Tang, B. Z.
 Chem. Mater. 2015, *27*, 6601–6607.
- (20) Zhang, Y.; Song, Q.; Wang, K.; Mao, W.; Cao, F.; Sun, J.; Zhan, L.; Lv, Y.; Ma, Y.; Zou, B.; others. *J. Mater. Chem. C* 2015, *3*, 3049–3054.
- (21) Hariharan, P. S.; Mariyatra, M. B.; Mothi, E. M.; Neels, A.; Rosair, G.; Anthony, S. P.
 New J. Chem. 2017, 41, 4592–4598.
- (22) Bernstein, J.; Davey, R. J.; Henck, J. O. Angew. Chemie Int. Ed. 1999, 38, 3440-3461.
- (23) Schulze, M.; Utecht, M.; Hebert, A.; Rück-Braun, K.; Saalfrank, P.; Tegeder, P. J. Phys. Chem. Lett. 2015, 6, 505–509.

- (24) Braga, D.; Cojazzi, G.; Paolucci, D.; Grepioni, F. CrystEngComm 2001, 3, 159-161.
 - (25) Hovhannisyan, V. A.; Su, P.-J.; Dong, C.-Y. In European Conference on Biomedical Optics; 2011; p 808710.
 - (26) Priimagi, A.; Ogawa, K.; Virkki, M.; Mamiya, J.; Kauranen, M.; Shishido, A. *Adv. Mater.* **2012**, *24*, 6410–6415.
- (27) Berkovic, G.; Krongauz, V.; Weiss, V. Chem. Rev. 2000, 100, 1741-1754.
- (28) Iliopoulos, K.; Krupka, O.; Gindre, D.; Sallé, M. J. Am. Chem. Soc. 2010, 132, 14343– 14345.
- (29) Sergeeva, E. V.; Puntus, L. N.; Kajzar, F.; Rau, I.; Sahraoui, B.; Pekareva, I. S.;
 Suponitsky, K. Y.; Bushmarinov, I. S.; Lyssenko, K. A. Opt. Mater. (Amst). 2013, 36, 47–52.
- (30) Skakle, J. M. S.; Low, J. N.; Wardell, J. L.; Glidewell, C. Acta Crystallogr. Sect. B Struct.
 Sci. 2005, 61, 321–328.
- (31) Chaudhary, A.; Mohammad, A.; Mobin, S. M. Cryst. Growth Des. 2017, 17, 2893–2910.
- (32) Huang, S. L.; Hor, T. S. A.; Jin, G. X. Coord. Chem. Rev. 2017, 346, 112–122.
- (33) Choudhury, A. R.; Nagarajan, K.; Guru Row, T. N. CrystEngComm 2006, 8, 482-488.
- (34) Zhang, L.; Dang, L.; Luo, F.; Feng, X. J. Mol. Struct. 2016, 1106, 114–120.
- (35) Oliver, S. N.; Pantelis, P.; Dunn, P. L. Appl. Phys. Lett. 1990, 56, 307–309.
- (36) Reddy, J. P.; Swain, D.; Pedireddi, V. R. Cryst. Growth Des. 2014, 14, 5064–5071.

- (37) Bi, W.; Louvain, N.; Mercier, N.; Luc, J.; Rau, I.; Kajzar, F.; Sahraoui, B. Adv. Mater.
 2008, 20, 1013–1017.
- (38) Sun, Z.; Chen, T.; Liu, X.; Hong, M.; Luo, J. J. Am. Chem. Soc. 2015, 137, 15660–15663.
- (39) Allen, F. H. Acta Crystallogr. Sect. B Struct. Sci. 2002, 58, 380–388.
- (40) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater. 2016, 72, 171–179.
- (41) Timofeeva, T. V.; Nesterov, V. N.; Dolgushin, F. M.; Zubavichus, Y. V.; Goldshtein, J. T.; Sammeth, D. M.; Clark, R. D.; Penn, B.; Antipin, M. Y. *Cryst. Eng.* 2000, *3*, 263–288.
- (42) Timofeeva, T. V.; Nesterov, V. N.; Clark, R. D.; Penn, B.; Frazier, D.; Antipin, M. Y. J.
 Mol. Struct. 2003, 647, 181–202.
- (43) Munshi, P.; Skelton, B. W.; McKinnon, J. J.; Spackman, M. A. CrystEngComm 2008, 10, 197–206.
- (44) Vrcelj, R. M.; Shepherd, E. E. A.; Yoon, C. S.; Sherwood, J. N.; Kennedy, A. R. *Cryst. Growth Des.* 2002, *2*, 609–617.
- (45) Gleixner, A.; Ulm, U. 1998, 213, 411-415.
- (46) Asiri, A. M.; Khan, S. A.; Tan, K. W.; Ng, S. W. Acta Crystallogr. Sect. E Struct. Reports Online 2010, 66, 606–617.
- (47) Jha, K. K.; Dutta, S.; Kumar, V.; Munshi, P. CrystEngComm 2016, 18, 8497–8505.
- (48) Bruker (2016). APEX3, SAINT, and SADABS. Bruker AXS Inc., Madison, Wisconsin,

2	
3	
4	
5	
6	
7	
/	
8	
9	
10	
11	
11	
12	
13	
14	
15	
16	
10	
17	
18	
19	
20	
עב 1	
21	
22	
23	
24	
25	
25	
20	
27	
28	
29	
30	
21	
27	
32	
33	
34	
35	
36	
27	
57	
38	
39	
40	
41	
42	
12	
43	
44	
45	
46	
47	
48	
10	
77	
50	
51	
52	
53	
54	
57	
22	
56	
57	
58	
59	

60

USA.

- (49) Sheldrick, G. M. Acta Crystallogr., Sect. A Found. Crystallogr 1990, 46, 467-473.
- (50) Sheldrick, G. M. Acta Crystallogr. Sect. A Found. Crystallogr. 2007, 64, 112–122.
- (51) Sheldrick, G. M. Acta Crystallogr. Sect. C Struct. Chem. 2015, 71, 3-8.
- (52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; others. *Inc. Wallingford, CT, USA* 2009.
- (53) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. J. Chem. Theory Comput. 2006, 2, 364–382.
- (54) Capobianco, A.; Centore, R.; Noce, C.; Peluso, A. Chem. Phys. 2013, 411, 11-16.
- (55) Suponitsky, K. Y.; Masunov, A. E.; Antipin, M. Y. *Mendeleev Commun.* 2009, *19*, 311–313.
- (56) Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalleri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D'Arco, P.; others. *Int. J. Quantum Chem.* 2014, *114*, 1287–1317.
- (57) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.
- (58) Grimme, S. J. Comput. Chem. 2006, 27, 1787–1799.
- (59) Brédas, J. L.; Chance, R. R. In Conjugated polymeric materials: opportunities in electronics, optoelectronics, and molecular electronics; Springer Science & Business Media, 2012; Vol. 182.

1		
2 3 4	(60)	Chemla, D. S.; Zyss, J. In Nonlinear Optical Properties of Organic Molecules and
5 6 7		Crystals; Materials Science and Technology Series; Academic Press, 1987. Vol. 1.
7 8 9 10	(61)	Spackman, M. A.; Jayatilaka, D. CrystEngComm 2009, 11, 19-32.
11 12 13	(62)	Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman,
13 14 15		M. A. The University of Western Australia Perth, Australia 2012.
16 17 18	(63)	Gelbrich, T.; Hursthouse, M. B. CrystEngComm. 2005, 7, 324-336.
19 20 21 22	(64)	Jha, K. K.; Dutta, S.; Kumar, V.; Munshi, P. CrystEngComm 2016, 18, 8497-8505.
23 24 25	(65)	Coles, S. J.; Threlfall, T. L.; Tizzard, G. J. Cryst. Growth Des. 2014, 14, 1623–1628.
26 27 28	(66)	Turner, M. J.; Thomas, S. P.; Shi, M. W.; Jayatilaka, D.; Spackman, M. A. Chem.
28 29 30		<i>Commun.</i> 2015 , <i>51</i> , 3735–3738.
31 32 33	(67)	Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.;
34 35		Towler, M.; Streek, J. van de. J. Appl. Crystallogr. 2006, 39, 453-457.
36 37 38	(68)	Turner, M. J.; Grabowsky, S.; Jayatilaka, D.; Spackman, M. A. J. Phys. Chem. Lett. 2014,
39 40		5, 4249–4255.
41 42 43 44	(69)	Kurtz, S. K.; Perry, T. T. J. Appl. Phys. 1968, 39, 3798-3813.
45 46		
47 48 49		
50 51		
52		
54 55		
55 56		
57 58		
59 60		ACS Paragon Plus Environment

For Table of Contents Use Only

Concomitance, reversibility and switching ability of centrosymmetric and noncentrosymmetric crystal forms: Polymorphism in an organic NLO material

Kunal K. Jha, Sanjay Dutta and Parthapratim Munshi*



Reversibility between two concomitant polymorphs (**centric** and **non-centric**) and their switching ability is demonstrated in case of a novel organic NLO material, *Z*-3-(3-methoxyphynyl)-2-(4-nitrophenyl)acrylonitrile. To the best of our knowledge, this study is first of its kind to show the reversibility and switching ability of polymorphic phases in an organic material, induced by both thermal and solvent stimuli.