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Selective Growth of Polymorphs: An Investigation of the Organic Nonlinear Optical Crystal 5-Nitro-2-thiophenecarboxaldehyde-4-methylphenylhydrazone

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An organic nonlinear optical crystal, 5-nitro-2-thiophenecarboxaldehyde-4-methylphenylhydrazone (NTMPH), has been prepared and investigated with regard to polymorphism, growth, and characterization of the structural and physical properties. Recrystallization of NTMPH in various solvents under different conditions showed the existence of three crystalline phases, red greenish plates (NTMPH−I) in space group $P2_1/n$, red orange prisms (NTMPH−II) in space group $Pna2_1$, and black needle (NTMPH−III) in space group $P2_1/n$. The crystal structures of NTMPH showed that three different intermolecular forces dominate the stabilization of one- or two-dimensional structures (called secondary structures in this work) of the three phases of the NTMPH crystals, namely the hydrogen bonding, dipole−dipole interactions, and the van der Waals forces for NTMPH−I, −II, and −III crystals, respectively. The thermal analysis showed that within the trimorphs the NTMPH−I crystal has the lowest thermodynamic stability with the lowest melting point and enthalpy, but NTMPH−II and −III crystals possess a higher thermodynamic stability and are called thermodynamic phases. The NTMPH−I crystal is easily crystallized in most conditions and is called a kinetic phase, whereas NTMPH−II and −III are crystallized with a higher supercooling (equal to a higher chemical potential), which also means that higher energy barriers for the nucleation of NTMPH−II and −III must be overcome. Since crystal structures cannot be designed precisely based on the molecular properties, especially for flexible molecules, the finding and selective growth of interesting polymorphic crystals is an essential step for the development of highly active nonlinear optical materials.

1. Introduction

Novel organic materials with large second-order nonlinear optical (NLO) susceptibilities are interesting because of their potential applications in optical signal processing and frequency conversion.[1−3] Among the various classes of materials presently investigated, organic crystals are of special interest since a stable orientation of NLO chromophores in the lattice can be imposed. The optimization of these organic crystals needs to combine two key steps. One is to design and synthesize stable chromophoric molecules with large molecular hyperpolarizabilities, called NLO molecular engineering. The second one is to grow these chromophores into crystals with optimized orientation to maximize large macroscopic NLO effects, called NLO crystal engineering. However, the development of optimized NLO organic crystals still presents severe challenges. For example, optimized NLO chromophores normally show poor crystallinity, which limits the growth of high-quality crystals for practical applications. Additionally there is no reliable approach for crystal engineering to control the molecular packing, mainly due to the multiplicity of possible orientations of molecules in crystals and the entanglement of thermodynamic and kinetic contributions to the crystal growth.[4]

Recently, an efficient class of NLO crystalline materials based on push−pull hydrazone derivatives was developed in our laboratory.[5,6] Among them, the benzaldehyde phenylhydrazone and thiophenecarboxaldehyde phenylhydrazone derivatives with electron-donor and -acceptor groups showed two significant features, a large first-order hyperpolarizability and good crystallinity. Another feature, polymorphism (the occurrence of more than one crystalline structure for one molecule), was also found on further investigation of the crystallization and crystal growth of these derivatives.[5,7] Although polymorphism is in principle undesired in

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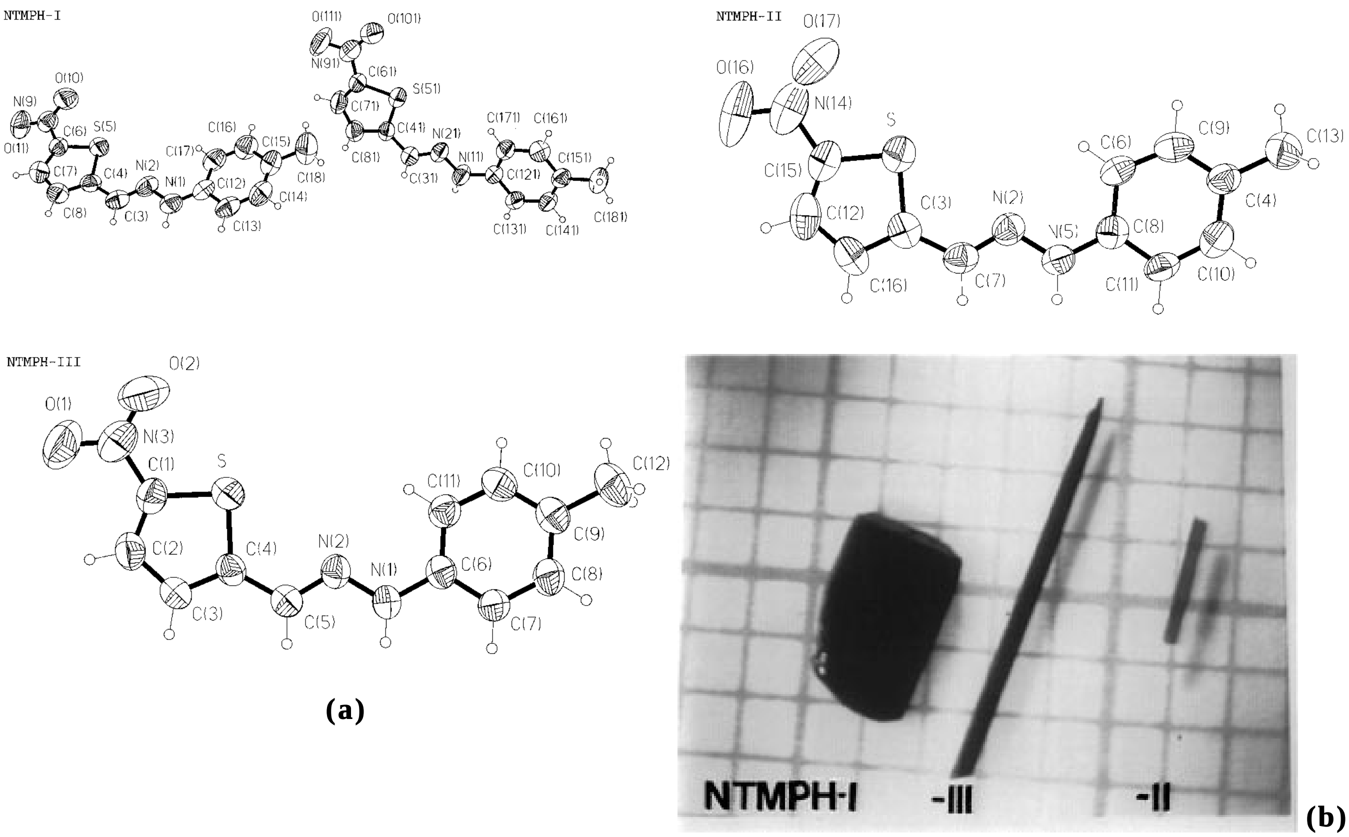

Figure 1. (a) ORTEP plot of the NTMPH molecule in the crystal structures of NTMPH−I, −II, and −III; (b) NTMPH crystals grown as red greenish plates (NTMPH−I), red orange prisms (NTMPH−II), and black needles (NTMPH−III).

crystal growth, the existence of polymorphic forms also provides an opportunity to obtain NLO-active forms and also to investigate the molecular orientation—property relationship and the growth kinetics—packing thermodynamic relationship.[8,9] For example, one of the benzaldehyde phenylhydrazone derivatives, (dimethylamino)-benzaldehyde-4-nitrophenylhydrazone (DANPH) showed the existence of three crystalline phases in various solvents under different conditions, a cocrystal (form I) of DANPH with benzene in a ratio 4 to 1 in space group $P2_12_12$, red greenish prisms (form II) in space group Cc, and red orange plates (form III) in space group $P2_1/c$.[5,7] Only DANPH of form II showed large second harmonic generation (SHG) efficiencies[5] (comparable to that of 4′-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST)[10]) in the powder test at 1.3 μm. Furthermore large second-order nonlinear optical coefficients of DANPH (form (II)) were measured, e.g., $d_{12} = 270 \pm 50$ pm/V at $\lambda = 1.542$ μm.[11]

In this work, we investigated one thiophenecarboxaldehydephenylhydrazone derivative, 5-nitro-2-thiophenecarboxaldehyde-4-methylphenylhydrazone (NTMPH, see Figure 1a) with regard to its growth, polymorphism, structure, and physical properties. The motivation of investigating NTMPH was based on the following considerations. First, to develop new organic NLO crystals since one of its forms showed large SHG efficiencies (comparable to that of DANPH in the powder test at 1.3 μm[5]). In addition it contains a thiophene ring, a five-membered heteroaromatic which is a better π-conjugated bridge than a phenyl ring to enhance the molecular nonlinearity.[6,12,13] Second, to exemplify an important step for the development of NLO-active molecular crystals based on selective growth of polymorphs since the molecular orientation in polymorphic structures can be modified by the conditions and the environment of crystallization. Third, to investigate the important intermolecular forces such as hydrogen bonding, dipole−dipole interaction, and van der Waals forces in crystal engineering by comparing the polymorphic structures obtained in alternative crystallization conditions and environment.[14]

2. NTMPH Crystal Growth and Polymorphism

NTMPH was synthesized by condensation of the 5-nitro-2-thiophenecarboxaldehyde with 4-methylbenzaldehydes according to a known procedure[15] and then was purified by recrystallization from methanol and acetonitrile to reduce the total impurity level to below 1%. Recrystallization of NTMPH in various solvents with different conditions showed the existence of three crystalline phases (see Tables 1 and 2), red greenish

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Table 1. Crystallization Habit of NTMPH in Different Solvents

solvent	dipole moment in the gas phase (D)	crystallization method	crystal form
toluene	0.375	rapid cooling	NTMPH−II
		slow evaporation	NTMPH−I
chloroform	1.04	rapid cooling	NTMPH−II
		slow evaporation	NTMPH−I
methanol	1.7	rapid cooling	NTMPH−III (−II)
		slow evaporation	NTMPH−I
ethanol	1.69	rapid cooling	NTMPH−III (−II)
		slow evaporation	NTMPH−I
ethyl formate	1.98	rapid cooling	NTMPH−II
		slow evaporation	NTMPH−I
acetone	2.88	rapid cooling	NTMPH−II
		slow evaporation	NTMPH−I
acetonitrile	3.92	rapid cooling	NTMPH−II
		slow evaporation	NTMPH−I

Table 2. Crystal Data for NTMPH−I, −II, and −III

	NTMPH−I	NTMPH−II	NTMPH−III
empirical formula	$C_{12}H_{11}N_3O_2S$	$C_{12}H_{11}N_3O_2S$	$C_{12}H_{11}N_3O_2S$
molecular weight	261.3	261.3	261.3
color and habit:	green red plate	red orange prisms	black needle
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pna2_1$	$P2_1/n$
point group	$2/m$	$mm2$	$2/m$
unit-cell dimensions	$a = 16.136(3)$ Å	$a = 7.475(4)$ Å	$a = 4.49(3)$ Å
	$b = 7.760(2)$ Å	$b = 29.409(9)$ Å	$b = 16.962(16)$ Å
	$c = 20.723(4)$ Å	$c = 5.795(3)$ Å	$c = 16.489(13)$ Å
	$\beta = 104.53(3)°$		$\beta = 96.59(6)°$
volume	2511.8(9) Å^3	1273.9(10) Å^3	1249(2) Å^3
Z	4 × 2	4	4
density	1.382 g/cm^3	1.362 g/cm^3	1.389 g/cm^3

plates (NTMPH−I), red orange prisms (NTMPH−II) and black needles (NTMPH−III, see Figure 1b). Slow growth of the crystals by solvent evaporation or by controlled lowering of the temperature mostly resulted in NTMPH−I crystals in all solvents. In contrast, on rapid recrystallization from highly supersaturation solutions by lowering the temperature, NTMPH−II and NTMPH−III crystals were obtained mainly, NTMPH−II in nonprotic solvents and NTMPH−III in protic solvents. Note that both NTMPH−II and NTMPH−III crystals were sometimes generated together in proton solvents according to the above recrystallizing process. Additionally the NTMPH synthesis yielded the NTMPH−II phase.

In the second-harmonic powder test at 1.3 μm, NTMPH−II crystals showed an efficiency comparable to that of the well-known DAST.[10] NTMPH−I and NTMPH−III crystals, however, showed no SHG signal. Thermal analysis by using DSC showed that NTMPH−II and −III crystals had a higher thermodynamic stability than the NTMPH−I crystals. All crystals performed no phase change for temperatures up to the melting point (see Figure 2). Isothermal decomposition experiments using the pure material showed that at a temperature around the melting point (±2 °C), the impurity level caused by decomposition and polymerization increased significantly. Hence, the phase transformation of NTMPH at these temperatures was not investigated.

3. Polymorphic Structures of NTMPH Crystals

We noted that there exist distinct differences among the NTMPH crystals of phase I, II and III with regard to crystal growth, phase stability, and SHG activities.

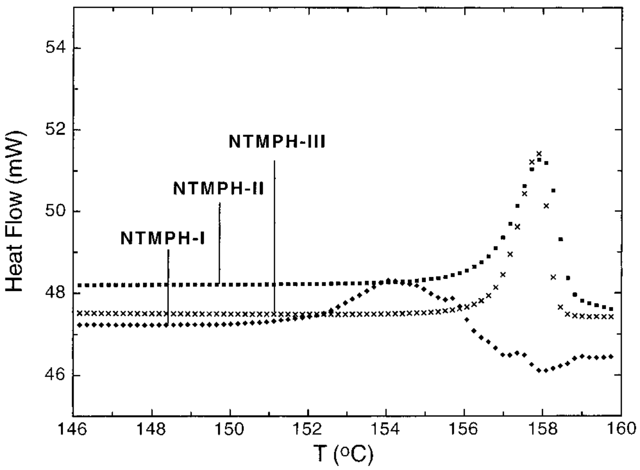

Figure 2. Thermal analysis of NTMPH−I, −II, and −III crystals by using DSC. Their melting points (T_{mp}) and melting enthalpies (ΔH) are $T_{mp} = 152 \pm 1$ °C and $\Delta H = 20$ J/g for NTMPH−I, $T_{mp} = 157 \pm 1$ °C and $\Delta H = 97$ J/g for NTMPH−II, and $T_{mp} = 156 \pm 1$ °C and $\Delta H = 58$ J/g for NTMPH−III.

Table 3. Final Fractional Coordinates for NTMPH−I

atom	x/a	y/b	z/c	U(eq)
N(1)	0.33370	0.35247	0.54959	81 (1)
N(2)	0.39122	0.32745	0.51302	73 (1)
C(3)	0.37201	0.39051	0.45412	74 (2)
C(4)	0.43046	0.36969	0.41100	67 (1)
S(5)	0.52357	0.25590	0.43670	71 (1)
C(6)	0.54683	0.29933	0.36187	62 (1)
C(7)	0.48707	0.39720	0.32081	81 (2)
C(8)	0.42019	0.43849	0.34929	81 (2)
N(9)	0.62448	0.24084	0.34939	76 (1)
O(10)	0.67800	0.17930	0.39571	104 (1)
O(11)	0.63388	0.25905	0.29309	106 (1)
C(12)	0.35189	0.29862	0.61490	70 (1)
C(13)	0.29405	0.34587	0.65346	86 (2)
C(14)	0.31155	0.29611	0.71902	89 (2)
C(15)	0.38345	0.20514	0.75092	85 (2)
C(16)	0.43884	0.16042	0.71160	90 (2)
C(17)	0.42374	0.20714	0.64663	82 (2)
C(18)	0.40178	0.15428	0.82265	126 (3)
N(11)	0.27605	0.49893	0.02080	72 (1)
N(21)	0.34357	0.58017	0.00747	63 (1)
C(31)	0.35125	0.57265	−0.05239	65 (1)
C(41)	0.42549	0.65486	−0.06669	59 (1)
S(51)	0.49827	0.75588	−0.00623	63 (1)
C(61)	0.55698	0.80175	−0.06312	64 (1)
C(71)	0.52363	0.74092	−0.12288	82 (2)
C(81)	0.44564	0.65436	−0.12732	79 (2)
N(91)	0.63541	0.89303	−0.03975	83 (1)
O(101)	0.66155	0.92851	0.01899	94 (1)
O(111)	0.67414	0.93292	−0.08196	127 (1)
C(121)	0.25889	0.52049	0.08336	63 (1)
C(131)	0.18376	0.44725	0.09332	71 (1)
C(141)	0.16255	0.47409	0.15343	71 (1)
C(151)	0.21232	0.57008	0.20309	63 (1)
C(161)	0.28787	0.63677	0.19259	69 (1)
C(171)	0.31052	0.61279	0.13255	66 (1)
C(181)	0.18651	0.60679	0.26735	82 (2)

The crystalline structures of phase I−III (in Tables 2−5) were determined by X-ray diffraction (see our previous work in ref 5). To find out structural details of each of these polymorphs, the investigation of the NTMPH structures is herein carried out in three levels by analogy with biomolecules,[14] which are the primary, secondary, and tertiary structures. In this work we define the primary structure as the molecular structure (conformations of molecules), the secondary structure as the one-dimensional (e.g., chains or tapes) network or two-dimensional (e.g., layers) network, and the tertiary structure as the three-dimensional structure

Table 4. Final Fractional Coordinates for NTMPH−II

atom	x/a	y/b	z/c	U(eq)
S	0.75775	0.33530	0.18251	69 (1)
N(2)	0.67986	0.42398	0.42987	59 (2)
C(3)	0.64299	0.34388	0.43894	58 (2)
C(4)	0.82803	0.58781	0.24699	65 (3)
N(5)	0.64819	0.46423	0.52971	63 (2)
C(6)	0.80363	0.50535	0.22446	58 (2)
C(7)	0.61656	0.38885	0.52694	60 (2)
C(8)	0.71036	0.50444	0.43390	56 (2)
C(9)	0.86059	0.54747	0.14218	66 (2)
C(10)	0.73660	0.58571	0.45394	73 (3)
C(11)	0.67508	0.54477	0.55045	61 (2)
C(12)	0.64407	0.26592	0.40795	81 (3)
C(13)	0.88438	0.63234	0.14300	86 (3)
N(14)	0.80788	0.24751	0.04558	97 (3)
C(15)	0.73093	0.27817	0.21620	69 (3)
O(16)	0.78851	0.20640	0.07258	131 (4)
O(17)	0.88885	0.26535	−0.11619	114 (3)
C(18)	0.59117	0.30380	0.53290	75 (3)

Table 5. Final Fractional Coordinates for NTMPH−III

atom	x/a	y/b	z/c	U(eq)
S1	1.14809	0.51773	0.23773	62 (1)
C(2)	1.39639	0.55493	0.10971	68 (2)
N(1)	0.70728	0.70845	0.34760	60 (1)
C(10)	0.31147	0.59678	0.49380	63 (1)
N(2)	0.82853	0.65178	0.30564	55 (1)
C(6)	0.54452	0.68915	0.41198	52 (1)
C(3)	1.26987	0.62333	0.13615	65 (1)
C(9)	0.21584	0.65616	0.54250	61 (1)
C(11)	0.47298	0.61229	0.42950	59 (1)
C(7)	0.44584	0.74968	0.45881	61 (1)
C(4)	1.12789	0.61344	0.20439	52 (1)
C(1)	1.34625	0.49395	0.15847	59 (1)
C(8)	0.28526	0.73296	0.52249	65 (1)
C(5)	0.98278	0.67245	0.24831	58 (1)
O(1)	1.60146	0.40033	0.09586	116 (2)
N(3)	1.45240	0.41534	0.15196	84 (2)
O(2)	1.39503	0.36716	0.20268	113 (2)
C(12)	0.04673	0.63810	0.61368	83 (2)

Table 6. Molecular Structures of the NTMPH Polymorphs

	planar angles (deg) (phenyl vs thiophene rings)	torsion angles (deg)[a] (1−2−3−4 atoms)	torsion angles (deg)[a] (1′−2′−3′−4 atoms)
NTMPH-Ia	7.9	178	174
NTMPH-Ib	8.6	176	−172
NTMPH-II	3	176	179
NTMPH-III	16	171	174

[a] The atoms defining the torsion angles are marked in Figure 2.

with a packing of the secondary motifs to build up the entire crystal.

3.1. Primary Structures of NTMPH Polymorphs.

There are two kinds of polymorphism, the conformational and the orientational one.[16] The former describes the formation of crystals in which a molecule adopts different conformations, and the latter describes the formation of different crystals from the same conformation of the molecule. Table 6 shows that the molecular conformations in the NTMPH polymorphs are different, so that we deal with the conformational polymorphism. In one unit cell, only one conformation is included in the case of NTMPH−II and −III crystals, but two conformations are present in NTMPH−I. By analysis of their torsion angles (see Table 6), it can be found that the thiophene and phenyl rings in NTMPH−Ia (see Figure 3), −II and −III are bent toward the same side with regard to the hydrazone (−C=N−NH−) plane while in NTMPH−Ib they are twisted toward opposite sides with regard to the hydrazone plane with a negative torsion angle between the 1′, 2′, 3′, and 4 atoms. The NTMPH molecule is a type **II** hydrazone in which the conjugation extends over the entire NTMPH molecule.[5] The molecule in NTMPH−II shows a good coplanarity with a very small planar twist angle (3°) between the thiophene and phenyl rings. However, the coplanarity becomes a little bit worse in NTMPH−Ia and −Ib with the planar twist angle of 8°, and even worse more in NTMPH−III with the planar twist angle of 16°.

3.2. Secondary Structures of NTMPH Polymorphs.

In the NTMPH−I crystal (point group $2/m$, space group $P2_1/n$), a hydrogen-bonding network exists as shown in Figure 3, in which two types of hydrogen bonds (N−H···O) with different bonding lengths and directions are involved. One is assembled by the central amino group of the NTMPH−Ia molecule and an oxygen atom of the nitro group of the NTMPH−Ib molecule with a short hydrogen bond ($d_{\mathrm{H-O}} = 2.0$ Å, $d_{\mathrm{N-O}} = 3.01$ Å, $\angle\mathrm{NHO} = 161°$). The second one is assembled by the central amino group of the NTMPH−Ib molecule and an oxygen atom of the nitro group of the NTMPH−Ia molecule with a longer hydrogen bond ($d_{\mathrm{H-O}} = 2.3$ Å, $d_{\mathrm{N-O}} = 3.18$ Å, $\angle\mathrm{NHO} = 160°$). This hydrogen-bonding network with coplanar molecules forms a planar sheet in NTMPH−I (see also Figure 6).

In the NTMPH−II crystal (point group $mm2$, space group $Pna2_1$), there is no hydrogen-bonding interaction. The polar axis of the crystal is the crystallographic c axis. A herringbone motif for the planar NTMPH−II molecules can be found as shown in Figure 4, in which neighboring molecules are arranged with 2-fold symmetry along the crystallographic c axis, so that the dipole moments of neighboring molecules projected onto the $a-c$ plane are antiparallel. Hence the dipole−dipole interaction is the dominant intermolecular force to control this kind of packing. These herringbone structures extend along the crystallographic a axis and form a corrugated sheet.

In the NTMPH−III crystal (point group $2/m$, space group $P2_1/n$), a chain along the crystallographic b axis can be found as shown in Figure 5, in which an assembly occurs between the central amino group of one NTMPH−III molecule and a oxygen atom of the nitro group of another NTMPH−III molecule with a geometry such as $d_{\mathrm{H-O}} = 2.60$, $d_{\mathrm{N-O}} = 3.387$, $\angle\mathrm{NHO} = 146°$. From the point of view of the geometry of the normal hydrogen bond in N−H···O with $d_{\mathrm{H-O}} = 1.8-2.0$ Å and $d_{\mathrm{N-O}} = 2.8-3.0$ Å, the interaction between the amino group and the oxygen atom of the nitro group in NTMPH−III is not a typical hydrogen bond.[14] However the distance between H and O atoms ($d_{\mathrm{H-O}} = 2.60$ Å) is smaller than that of the van der Waals distance ($d_{\mathrm{H-O}}$ about 2.8 Å). From the viewpoint of the graphic set of hydrogen bonding,[17] this interaction within the chain in the NTMPH−III crystal is therefore still a hydrogen bond. We believe that the electrostatic nature of the N−H···O interaction plays an important role in the molecular assembly for the chain in the NTMPH−III crystal. A

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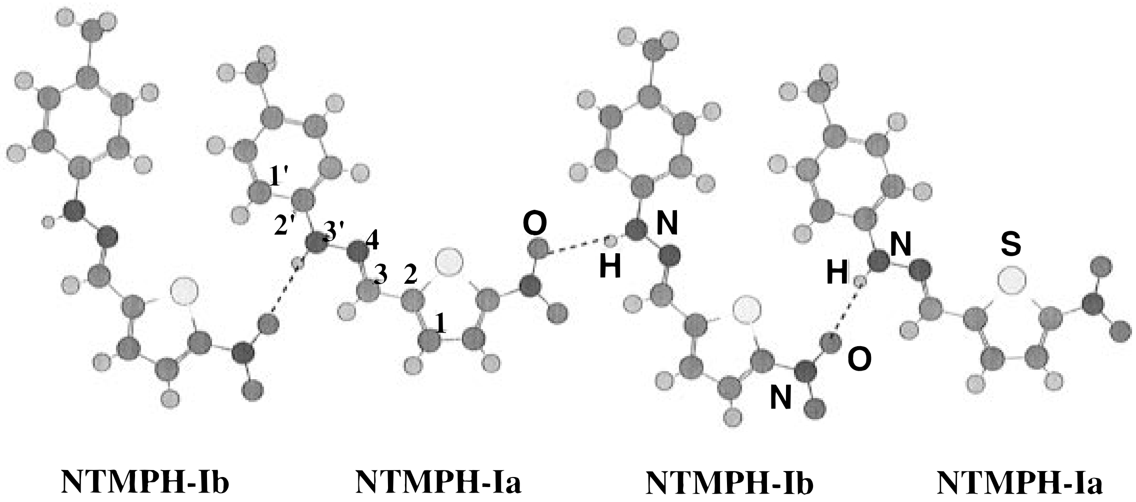

Figure 3. Hydrogen-bonding network as a secondary structure in the NTMPH−I crystals.

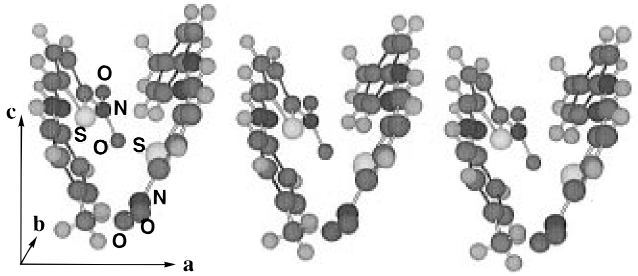

Figure 4. Herringbone motif built by planar NTMPH−II molecules as a secondary structure in the NTMPH−II crystals.

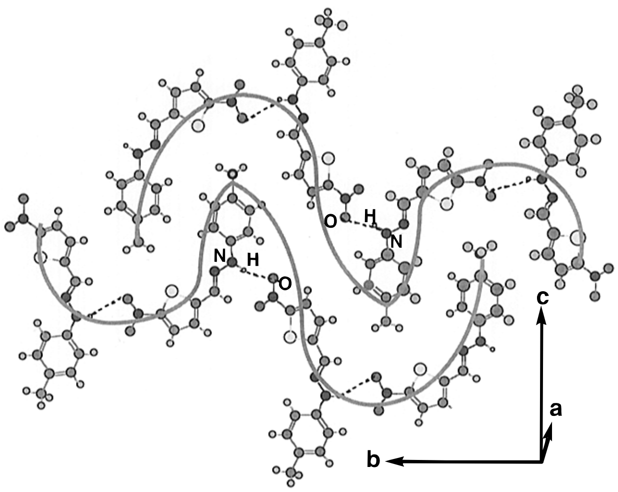

Figure 5. Layer built within the neighboring chains packs with one molecule dovetailing into the hollows of its neighbors in another chain. Molecules in a chain are linked with very weak hydrogen bonds with $d_{H-O} = 2.60$, $d_{N-O} = 3.387$.

more important point for the secondary structure of NTMPH−III, however, is that the neighboring chains, which are in antiparallel orientation along the *b* axis, pack with one molecule of one chain dovetailing into the hollows of its neighbors in another chain (see Figure 5), leading to the close van der Waals contact between chains. These chains are aggregated along the *c* axis into a two-dimensional layer.

3.3. Tertiary Structures of NTMPH Polymorphs. The crystal structure of NTMPH−I is constituted in a way that the planar sheets pack parallel to each other in the same layer but cross each other between neighboring layers with an angle between the planes (according to the phenyl ring of each molecule) of about 68° (see Figure 6). Differently, the crystal structure of NTMPH−II is constituted of a stack of corrugated sheets (see Figure 7), and that of NTMPH−III by a stack of layers aggregated by chains (see Figure 8). Comparing the thermodynamic stability of the trimorphic crystals (see Figure 2), the NTMPH−I, −II, and −III crystals with the melting enthalpies, $\Delta H = 20$ J/g, $\Delta H = 97$ J/g, and $\Delta H = 58$ J/g, respectively, show a large difference. Especially the NTMPH−I crystal with a hydrogen-bonding network in the secondary structure showed the lowest thermodynamic stability among the trimorphs. Hence the thermodynamic stability of polymorphic crystals, which depend on the contribution of the sum of all the intermolecular interactions but not

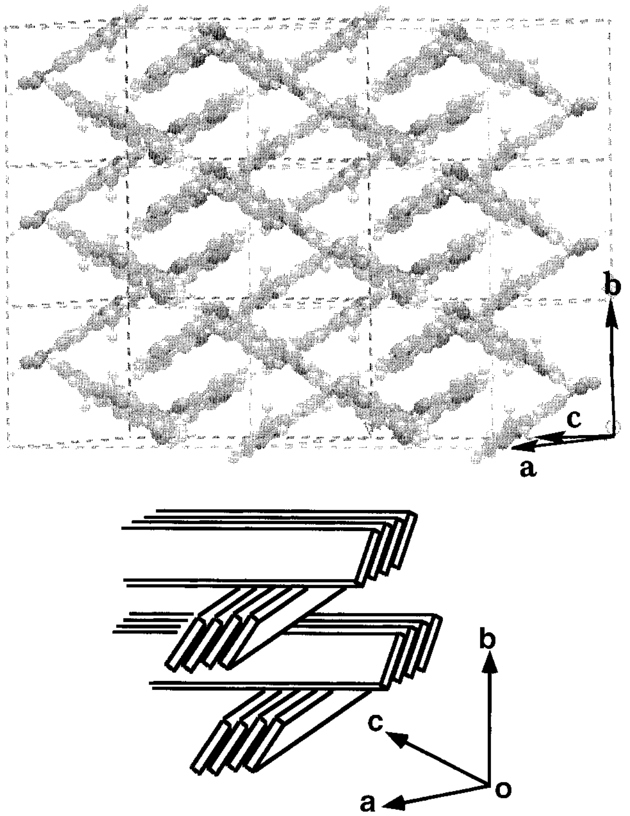

Figure 6. (a) Three-dimensional structure of the NTMPH−I crystals with the insulating planar sheet; (b) schematic drawing of (a).

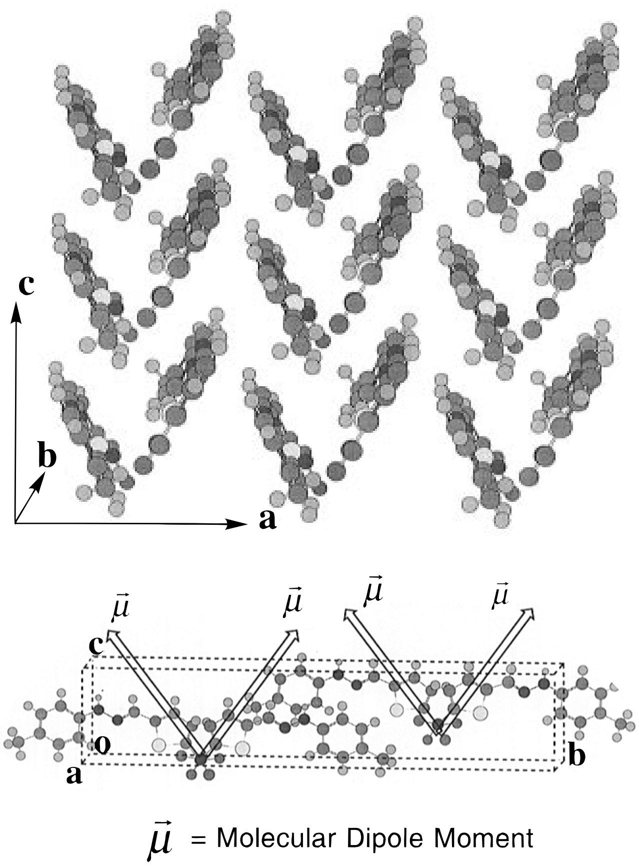

Figure 7. Three-dimensional structure of the NTMPH−II crystals with a stack of corrugated sheets.

just on the one- or two-dimensional assembly, can be largely different due to the kinetic process of their crystallization.

4. Discussion

4.1. Structure and Nonlinear Optical Properties. In a previous work, a high value of the molecular hyperpolarizability of NTMPH was measured in solution by electric field induced SHG (EFISH) ($\beta = 140 \times 10^{-40}$ m^4/V at $\lambda = 1.907$ μm, $\lambda_{\max} = 420$ nm in 1,4-dioxane).[5] NTMPH−I and −III crystallize in the centrosymmetric point group 2/*m*, so that there is no SHG effect in both crystals. NTMPH−II crystals crystallize in the noncentrosymmetric point group *mm*2 with a large SHG activity. Furthermore we found from its crystal structure that the polar axes (if assuming dipole and charge-transfer (CT) axes along the same directions) of the molecules are oriented with an angle of 51.4° with regard to the *c* axis (the polar axis in the crystal), which is very close to the optimized orientation (55°) for phase-matched second harmonic generation with optimized projection factors of the molecular hyperpolarizabilities along the polar crystal direction (*c* axis).

4.2. Polymorphism and Selective Growth. The purpose of molecular crystal engineering is to design and build crystals with a rational molecular orientation. The occurrence of polymorphism means that not just one single result is generated by crystal engineering based on the properties of a molecule. Therefore, polymorphism is a distinct problem for crystal engineering.[14] From the point of view of the thermodynamics of the crystals, polymorphism in a system is caused by the minimal free energy differences between the various forms. When these differences become more blurred, the probability of obtaining polymorphic structures increases. Hence the crystal structure cannot be designed with absolute certainty. On the other hand, the crystallization is a kind of supermolecular synthesis, like molecular synthesis in chemical reaction, yielding alternative products under various physical or/and chemical conditions.[18] As observed in this work, several polymorphs of a compound may exist but each of them may be governed by certain conditions of temperature, pressure, impurity, or solvent. These polymorphic structures may be controlled not by the minimal free energy of crystals but by kinetic processes of nucleation and growth of crystals. As an example, the melting enthalpies of the NTMPH−I ($\Delta H = 20$ J/g), which is one of the most easily crystallized phases, is about 5 times lower than that of the NTMPH−II ($\Delta H = 97$ J/g). Hence we here propose a practical way for the development of highly active nonlinear optical molecular crystals with the following steps: (1) searching polymorphic structures by crystallization under various physical or/and chemical conditions, (2) investigating their properties (such as powder SHG) and further comparing the crystal structures, and (3) growing the selected crystal under defined conditions.

On the basis of the polymorphic structures, conditions of crystallization and thermal analysis of the NTMPH crystals, some interesting points will be discussed in the following.

(1) *Molecular conformation and flexibility*: The trimorphic NTMPH contains four molecular structures in which single bonds between the hydrazone and the thiophene ring and between the hydrazone and phenyl ring are quite flexible and allow torsions. Generally the conformational changes in the molecular structure occur frequently for a flexible molecule since the intermolecular forces (about 4−20 kJ/mol) responsible for the stabilization of secondary and tertiary structures of crystals easily bring about these torsional changes.

(2) *Secondary structures and kinetic control of polymorphic crystallization*: The NTMPH−I crystal was always obtained from most solvents under the slow crystallization conditions (typically by slow evaporation). An analysis of the crystal structure showed that only the NTMPH−I crystals have strong hydrogen-bonding networks between the H−N group of the hydrazone and the nitro group of NTMPH−I. This secondary structure may be assembled in solution under supersaturation, which causes an lowering of the energy barrier of nucleation of the form of NTMPH−I, leading to an easy crystallization. However the thermal analysis showed that the NTMPH−I form has the lowest thermodynamic stability within the trimorphs with the lowest melting point and enthalpy. Thus the NTMPH−I crystal is a kinetic phase controlled by an assembly of the hydrogen bonding.

(3) *Thermodynamic control and stability of crystal structures*: Compared with NTMPH−I crystals, NTMPH−II and −III crystals possess lower free energies with higher thermodynamic stability (called thermodynamic phases) but without strong hydrogen bonding.

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(18) Desiraju, G. R. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327.

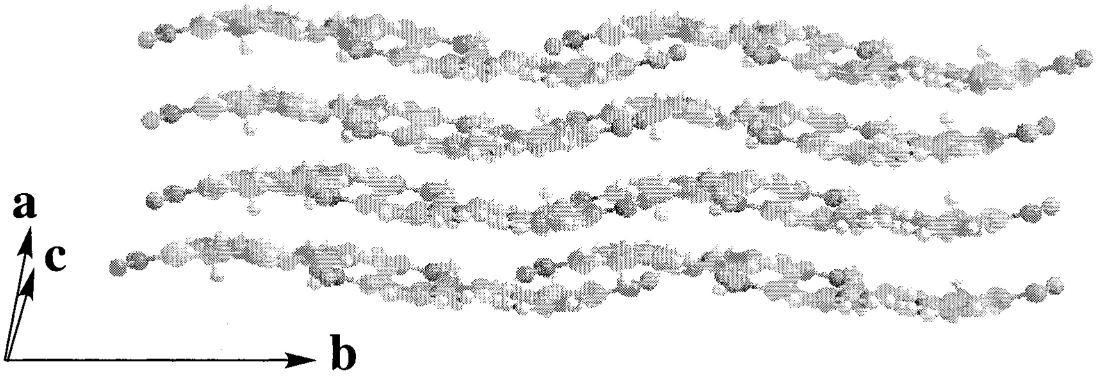

Figure 8. Three-dimensional structure of the NTMPH−III crystals with a stack of layers aggregated by chains.

However, a higher supercooling (equal to a higher chemical potential) in the crystallization process is needed for obtaining the two thermodynamic phases, which also means that higher energy barriers for the nucleation of NTMPH−II and −III must be overcome. Since the crystallization is a kinetic process with a typical chemical environment and carried on by physical forces, a higher chemical potential may be necessary for the nucleation and growth of crystals with the higher thermodynamic stability structures. Hence polymorphism controlled by thermodynamics can be found in these cases.

5. Conclusions

By investigating the polymorphic crystallization of NTMPH in different solvents and under different conditions and by examining the crystal structures and their stability, we found that the NTMPH−I crystal with the hydrogen-bonding network is easily crystallized with a low energy barrier for nucleation and growth. Its growth is mainly under kinetic control. In contrast, growth of NTMPH−II and −III crystals without the strong hydrogen bonding but with high thermodynamic stability only grew under high supersaturation (corresponding to a high chemical potential) since the crystallization may need to break down the assembly of the NTMPH hydrogen bonding in solution and to overtake the high energy barrier for nucleation and growth.

Investigation of the structure−property relationship showed that the polar axes of the molecules in the NTMPH−II crystals are oriented with an optimized orientation for phase-matched SHG, making it an interesting second-order NLO crystal. It should be noted, however, that phase-matching is possible only with an appropriate dispersion of the refractive indexes.

The crystal structures of the trimorphic NTMPH showed that three different intermolecular forces dominate the stabilization of the one- or two-dimensional structures (the secondary structure), e.g., the hydrogen bonding between the H−N group of the hydrazone backbone and the O atom of the nitro group for NTMPH−I crystals, dipole−dipole interactions between the molecules in the NTMPH−II crystals, and the van der Waals forces in the intermolecular close packing in the NTMPH−III crystal. Although the secondary structure may be expected according to the strong intermolecular interaction, such as the hydrogen bonding, crystal structures cannot be designed with absolute certainty based on the molecular properties, especially for flexible molecules. Thus we propose that the finding and selective growth of interesting crystals from their polymorphs is an essential step for the development of highly active nonlinear optical materials.

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Supporting Information Available: Structure determination summary (8 pages). Ordering information is given on any current masthead page.

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