



S=o...s=o Interactions as a Driving Force for Low-Temperature Conformational Rearrangement of Stable H-Bonding {S(O)-CH₂-CH₂-OH...}₂ Synthons in two Modifications of Diastereomeric Pinanyl Sulfoxides Co-Crystal

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S=O . . . S=O INTERACTIONS AS A DRIVING FORCE FOR LOW-TEMPERATURE CONFORMATIONAL REARRANGEMENT OF STABLE H-BONDING {S(O)-CH₂-CH₂-OH . . . }₂ SYNTHON IN TWO MODIFICATIONS OF DIASTEREOMERIC PINANYL SULFOXIDES CO-CRYSTAL

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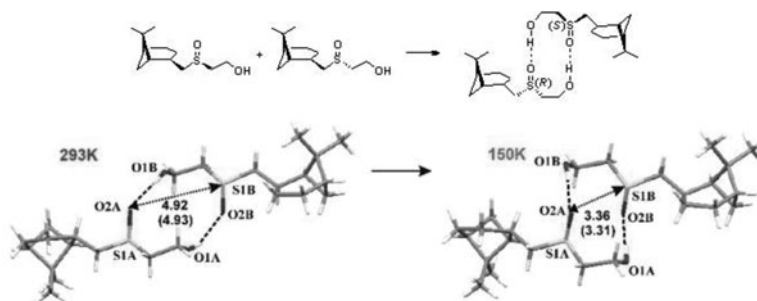
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GRAPHICAL ABSTRACT



For the triclinic and monoclinic modifications of diastereomeric pinanyl sulfoxides co-crystal, remarkable alterations in unit cell parameters by transition from 293 to 150 K were ascertained. Such alterations are accompanied by conformational restructuring of a stable hydrogen-bonded synthon from an “unfolded” to a “folded” form. The driving force of this restructuring is the tendency to form S=O . . . S=O interactions, which show up

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Dedicated to the memory of Dr. Z. A. Starikova, our colleague.

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in the low-temperature phases of both polymorphs. These are well-supported by the methods of quantum chemistry (DFT, B97-D/6-31G(d,p), AIM All).

Keywords β -Hydroxy sulfoxide; (–)- β -pinene; “racemic compound-like” crystallization; hydrogen-bonded cyclic dimers; polymorphic modifications; low-temperature X-ray structural analysis

INTRODUCTION

The conformation of a molecule is one of its most fundamental characteristics, often responsible for the physical and chemical properties of a substance or its biological activity. A molecular conformation can be modified by its crystallographic environment, which is observed for crystals with $Z' > 1$ or polymorphic structures.^{1–3}

In certain cases the crystals may undergo thermodynamic phase transitions, which involve conformational changes of molecules. Several types of conformational phase transitions are known.⁴ For example, in the crystal of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate, a functional group attached to the phenyl ring rotates around the C-C_{ar} bond during phase transition.⁵ A similar phenomenon was observed for 4-methylbenzyl alcohol⁶ and 4-chlorobenzyl alcohol, and 4-bromobenzyl alcohol,⁷ in which the phase transition is accompanied by a remarkable change in molecular conformations around the C(H₂)-C_{ar} bond. Conformational transformations are not only limited to acyclic moieties but are also observed for cyclic molecules, which assume different conformations due to ring inversion,⁸ or are partially dynamically or statically disordered.

It is worth noting that here there are two possibilities: the conformational transformations proceed continuously within one phase, or are coupled with phase transitions. In turn, the phase transition can have a clearly defined character and be accompanied by a change of space group and (or) the number of independent molecules,^{9,10} or can occur within the same space group, accompanied by a discontinuous change in any parameter of the unit cell.^{7,11}

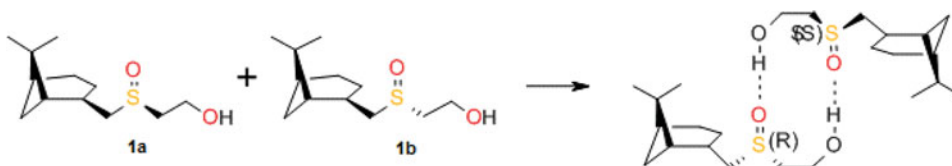
In any case, temperature-dependent conformational change is a hot topic in crystal engineering. It is extremely interesting in this context to compare temperature-dependent phenomenon in different polymorphic modifications. Comparison of behavior of different polymorphs of the same substance under external influences may contribute to the understanding of intermolecular interactions and structural forming factors.^{12–16}

In this article we present the unexpected results of low-temperature (150 K) X-ray structural analysis of two polymorphic modifications of diastereomeric pinanyl sulfoxides co-crystal in comparison with those obtained earlier at room temperature.

RESULTS AND DISCUSSION

Previously we have ascertained a stable “racemic compound-like” behavior of diastereomeric mixture of sulfoxides **1a+1b** obtained by the oxidation of enantio-pure sulfide derivative of (–)- β -pinene.¹⁷ We have shown that these compounds, in both solution and crystal, are in the form of hydrogen-bonded dimers. The dimer of diastereomeric sulfoxides **1a** and **1b** (Scheme 1) is the building block of both crystal modifications – triclinic and monoclinic. We have examined their structures previously at room temperature (293 K).

We have got the possibility to resolve the crystal structure of monoclinic (**polymorph 1**) and triclinic (**polymorph 2**) modification co-crystal **1a+1b** at 150 K and obtained



Scheme 1 Structural formulas of diastereomeric sulfoxides **1a** and **1b**, and schematic representation of their dimer.

unexpected results. Thus, transition from room to low temperature has caused an essential increase in the mosaicity of both crystals, which in turn was accompanied by loss of quality of X-ray data. Visually, the turbidity and cracking of both crystals occurred after freezing, which can be considered as evidence that a phase transition had occurred. However, we were able to collect low temperature datasets for both monoclinic and triclinic crystals, which were suitable for solving and refinement.

Structures of polymorphs at 150 K were solved in space groups $P2_1$ and $P1$, similar to appropriate experiments at room temperature. Essentially, the unit cell angles differ. We examine the intra- and inter-molecular structural alterations that are associated with essential cell parameter changes.

Crystal Structure of Room- and Low-Temperature Phases According to X-ray Diffraction Analysis Data

We started by examining the molecular geometry. The geometry of molecules A (diastereomer **1a**) and B (diastereomer **1b**) does not essentially change at lower temperatures, so the lengths of corresponding bonds and the values of valence angles are equal within experimental error, and discrepancies in torsion angles do not exceed $6\text{--}7^\circ$ (see Table 1). However, there is an essential difference in molecule geometry at different temperatures; this is in the position of the hydrogen atom of hydroxyl group. The conformation of $\text{C}^{11}\text{C}^{12}\text{O}^1\text{H}^1$ fragment is similar to a *trans* conformation at room temperature, but at low temperature it is similar to a *gauche* formation (appropriate torsion angles are close to 180° or 60°).

As crystal structure analysis shows, the hydrogen atom of hydroxyl group participates in the formation of classic hydrogen bonds, in both room- and low-temperature phases (Table 2). Thus, the basic supramolecular associate in the low-temperature phases of triclinic and monoclinic polymorphs is the same dimer as that of diastereomeric molecules **1a+1b**, formed by $\text{S}=\text{O}\cdots\text{H}-\text{O}$ hydrogen bonds (Scheme 1, Figure 1). Still, in spite of the preservation of classical H-bonds motive, the conformation of central H-bonded $\{-\text{SO}(\text{CH}_2)_2\text{-OH}\cdots\}_2$ synthon does undergo an essential change, which occurs through the shift of molecules within the dimer relative to each other. So if the conformation of the H-bonded synthon at room temperature for both polymorphs can be determined as “unfolded,” then by transition to low temperature it becomes “folded” in both cases as well. Differences in the conformation of supramolecular synthon cause a different location of the hydrogen atom of hydroxyl group in room- and low-temperature phases.

Accordingly, all the “intra-dimeric” torsion angles have changed (see Table S1; available online in Supplemental Materials). Overall, the “unfolded” conformation of the H-bonded fragment is similar to a stable cyclodecane conformation and can be

Table 1 Crystallographic data and parameters of X-ray diffraction experiments by 293 K and 150 K

	Polymorph 1		Polymorph 2	
	293	150	293	150
Chemical formula	2(C ₁₂ H ₂₂ O ₂ S)			
Formula mass	460.72			
Temperature, K	293	150	293	150
Crystal system	Monoclinic		Triclinic	
Space group	P2 ₁		P1	
No. of formula units per unit cell, Z	2		1	
a (Å)	6.648(2)	6.466(7)	6.622(4)	6.438(2)
b (Å)	28.381(8)	28.38(3)	7.137(4)	6.709(2)
c (Å)	7.148(2)	6.709(7)	14.777(9)	14.322(5)
α (°)	90	90	96.339(6)	87.473(4)
β (°)	104.106(4)	95.76(2)	102.573(6)	80.918(4)
γ (°)	90	90	104.397(6)	85.121(4)
Unit cell volume, Å ³	1307.9(6)	1225(2)	650.1(7)	608.4(4)
d _{calc} , g/cm ³	1.170	1.249	1.177	1.258
Absorption coefficient, mm ⁻¹	0.229	0.244	0.230	0.246
No. of reflections measured	9616	9843	10417	6489
No. of independent reflections	5322	4573	5595	4685
R _{int}	0.116	0.099	0.0267	0.0380
Final R _I values (I > 2σ(I))	0.0791	0.0969	0.0497	0.0800
wR ₂ (I > 2σ(I))	0.1422	0.2175	0.1052	0.2151
Final R _I values (all data)	0.2226	0.1468	0.0901	0.0887
Final wR(F ²) values (all data)	0.1917	0.2488	0.1275	0.2246
Flack parameter	0.0(1)	0.1(2)	0.03(9)	0.1(1)
CCDC No.	817380	1010129	817381	1010130

defined as “boat–chair–boat,”¹⁸ while the “folded” conformation corresponds to the “twist–boat–chair–twist–boat” conformation.

Most clearly, the difference in the conformation of central fragment is associated with distances between the sulfinyl groups of molecules A and B (see Figure 1).

Thus, in the room-temperature phases, the S . . . O distances were about 5 Å, which implies minimal interactions between molecules; in low-temperature phases, these distances reduce markedly and have values of about 3.3 Å in both polymorphs. The sulfoxide bond has been described as a single bond with ionic character, with the sulfur bearing a formal

Table 2 Hydrogen bonds in monoclinic and triclinic crystals by X-ray data

Crystal modification	Monoclinic				Triclinic			
	293		150		293		150	
H-bond*	1	2	1	2	1	2	1	2
D–H (Å)	0.71(9)	0.70(8)	0.9(2)	0.85(8)	0.78(4)	1.08(5)	0.80(7)	0.75(8)
H . . . A (Å)	2.01(8)	1.96(8)	1.82(19)	1.82(7)	1.91(3)	1.57(5)	1.91(7)	1.91(8)
D . . . A (Å)	2.667(8)	2.658(8)	2.670(8)	2.673(8)	2.682(5)	2.643(5)	2.700(6)	2.659(6)
∠D–H . . . A (°)	154(11)	173(11)	171(11)	176(11)	171(3)	173(6)	170(7)	174(9)

* 1: denotes a bond O^{1A}–H^{1A} . . . O^{2B}; 2: denotes a bond O^{1B}–H^{1B} . . . O^{2A}.

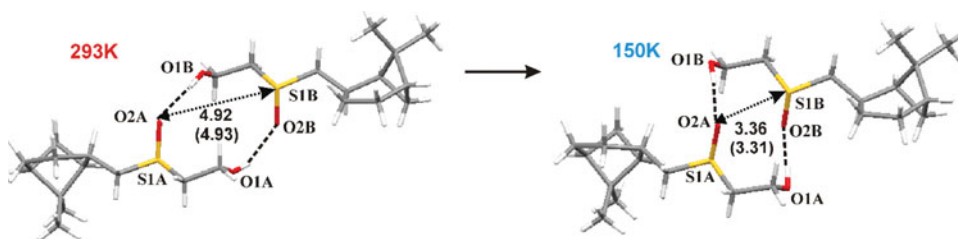


Figure 1 Conformation of dimer **1a+1b** at different temperatures for monoclinic polymorph (situation with triclinic polymorph is analogous); distances $S^{1B} \dots O^{2A}$ in Å are marked (corresponding distances for triclinic polymorph are given in parentheses).

positive charge and the oxygen bearing a formal negative charge.^{18,19} The large dipole moments in these bonds allow unique intermolecular interactions in the packing of these molecules, namely $S=O \dots S=O$ dipole–dipole interactions.^{20,21}

Thus, the main difference in the crystal structure of low-temperature phases comprises additional, secondary “cross-linking” of a stable hydrogen-bonded synthon by means of $S=O \dots S=O$ interactions. Apparently, the tendency to achieve this interaction can serve as a main driving force for the observed low-temperature phase transition.

Quantum-Chemical Calculations

In order to confirm the existence of dipole–dipole $S=O \dots S=O$ interaction and its contribution to additional stabilization of the dimer of diastereomeric molecules, we

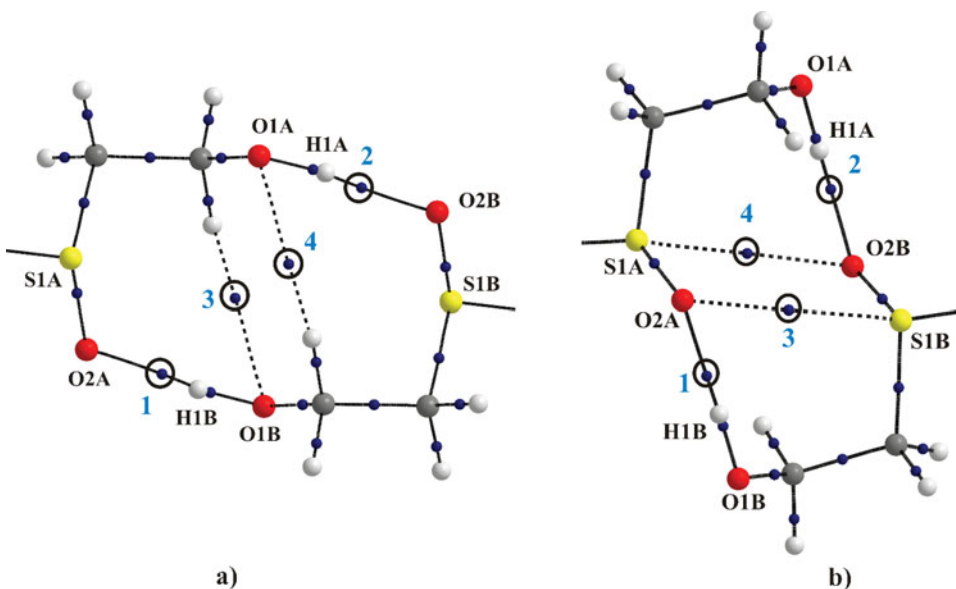


Figure 2 Hydrogen bonds and secondary intermolecular interactions in H-bonded synthons in (a) “unfolded opt,” and (b) “folded opt” conformations according to quantum-topological analysis. Numbers 1–4 refer to intermolecular interactions; their quantum-topological characteristics are shown in Table 3.

Table 3 Topological characteristics of intermolecular interaction critical points (3,-1) according to quantum-chemical calculations

(a) "Unfolded" conformation					
Interaction	Number in Figure 2a	$\rho(r)$ (e·Bh ⁻³)	$\nabla^2\rho(r)$ (e·Bh ⁻⁵)	$V(r)$ (au)	E_{int} (kcal mol ⁻¹)
O-H...O	1	0.0406	0.1255	-0.0313	9.83
	2	0.0406	0.1249	-0.0324	10.15
C-H...O	3	0.0075	0.0260	-0.0048	1.51
	4	0.0073	0.0253	-0.0046	1.45
ΣE^*					22.94
(b) "Folded" conformation					
Interaction	Number in Figure 2b	$\rho(r)$ (e·Bh ⁻³)	$\nabla^2\rho(r)$ (e·Bh ⁻⁵)	$V(r)$ (au)	E_{int} (kcal mol ⁻¹)
O-H...O	1	0.0409	0.1210	-0.0314	9.84
	2	0.0432	0.1309	-0.0340	10.66
S=O...S =O	3	0.0080	0.0277	-0.0052	1.64
	4	0.0081	0.0276	-0.0052	1.64
ΣE^*					23.78

$\rho(r)$ is the electron density; $\nabla^2\rho(r)$ is the Laplacian (the sum of eigenvalues of the second derivative matrix); $V(r)$ is the potential energy density; E_{int} is the interaction energy. *Total energy of interactions.

carried out a number of quantum-chemical calculations. Thus, the calculation of two dimer conformations (B97-D/6-31G(*d,p*)), which are observed in the crystals of room- and low-temperature phases, carried out at non-optimized geometry (taken directly from X-ray diffraction analysis data for **polymorph 1**) has shown a significantly larger (by 7.00 kcal/mol) energy efficiency of the "folded" conformation (we designate it as "folded *cryst*") compared with the "unfolded" one (we designate it as "unfolded *cryst*"). At the same time, attempts to optimize two dimer conformations have brought an interesting result. The "unfolded" conformation undergoes some conformational changes, and, in addition, stabilizes by means of pair C-H...O interactions, which are not observed in crystals (we designate these two optimized dimer geometries as "folded *opt*" and "unfolded *opt*").

At the optimized geometry of both dimer conformations, we involved the quantum-topological approach "Atoms in Molecules"²² implemented in the AIMAll program.

The search for non-covalent interactions based on the topological analysis of electron density distribution for the "unfolded *opt*" conformation allowed us to see two nonequivalent C-H...O bonds in addition to two nonequivalent hydrogen bonds. The critical points (3, -1) and the corresponding bonding path to them were found for each interaction (Figure 2a). Analysis of the topological characteristics of electron density at critical points (3, -1) corresponding to interactions showed that both classical and nonclassical hydrogen bonds were formed by the closed shell-type ($h_e(r) > 0$, $\nabla^2(r) > 0$). This allowed us to evaluate their energies in terms of the published approach (Table 3 (a)).²³

Regarding the "folded *opt*" conformation, two S=O...S=O (dipole-dipole) interactions, in addition to two classical O-H...O hydrogen bonds, were found (Figure 2b). Analogous to the method described above, we calculated their energy (Table 3(b)).

Table 4 Temperature-corrected energy characteristics of “folded opt” conformation versus “unfolded opt” conformation of diastereomeric sulfoxide **1a+1b** dimer

Energy*/temperature	293 K	150 K
$\Delta Z^0 = Z^0_{\text{folded opt}} - Z^0_{\text{unfolded opt}}$ (kcal/mol)	-2.71	-2.71
$\Delta H = H_{\text{folded opt}} - H_{\text{unfolded opt}}$ (kcal/mol)	-2.86	-2.84
$\Delta G = G_{\text{folded opt}} - G_{\text{unfolded opt}}$ (kcal/mol)	-1.60	-2.24

* Z^0 : zero-point energy, H : enthalpy, G : Gibbs free energy.

Thus, different types of secondary interactions stabilize the robust H-bonded dimers in first and second cases. The total energy of interactions is higher for the “folded opt” conformation by the value of 1 kcal/mol.

We have calculated (B97-D/6-31G(*d,p*)) the basic energy characteristics of two conformations. Two temperature-corrected values of energy have been calculated for both conformations ($T = 293$ K and 150 K, corresponding to the temperatures of X-ray structural analysis; Table 4). According to this data, the zero-point energy (E_0), enthalpy (H), and Gibbs energy (G) have somewhat more negative values for the “folded opt” conformation at both room (293 K) and low (150 K) temperatures. This fact indicates that the “folded opt” conformation is more stable than the “unfolded opt” conformation. It should be noted that the relative stability of the “folded opt” conformation compared with the “unfolded opt” conformation is greater at low temperature than at room temperature.

By generalizing the results of quantum-chemical calculations, we can point at the following conclusions:

1. The H-bonded $\{\text{S(O)-CH}_2\text{-CH}_2\text{-OH}\cdots\}_2$ synthon is stable because it is implemented in the crystals of room- and low-temperature phases of both polymorphs and is reproducible by means of quantum chemistry.
2. For this synthon, there are two possibilities of additional stabilization by means of secondary interactions – for the “unfolded” conformation these are C-H...O interactions, for the “folded” these are dipole–dipole S=O...S=O interactions. The first variant, however, is registered only in the gas phase according to the calculation data and is not ascertained in crystals; the energetically preferred second variant is implemented in both gas phase and crystals of **polymorphs 1** and **2** low-temperature phases (calculation data and X-ray diffraction analysis, respectively).

Thus, the calculation data are in good agreement with X-ray diffraction analysis data: in the low-temperature phases of both polymorphs, the energetically preferred conformation of the H-bonded synthon with the strongest interactions is realized. In turn, the key dimer crystallization at room temperature as an “unfolded cryst” conformation can be explained by slightly stronger inter-dimer interactions in room-temperature phases (see Table S2; available online in Supplemental Materials).

CCDC Search

In order to answer the question whether the low-temperature rearrangement of H-bonded synthon is typical only for our compounds or is a general feature of the $\{\text{S(O)-CH}_2\text{-CH}_2\text{-OH}\cdots\}_2$ synthon, we carried out search in the Cambridge Crystallographic Data Centre

(CCDC),²⁴ and found only two crystal structures containing it: JAYVAG and VENMEG. For the first structure, the X-ray structural experiments were carried out at two temperatures: 150 K and 183 K, and no temperature-dependent changes were revealed.²⁵ In both first and second cases, the conformation of the synthon is “unfolded” similar to the one we have observed at room temperature. Possibly, the absence of conformational transition in this case is associated with the presence of three-dimensional system of hydrogen bonds which stabilize the crystal structure.

Unfortunately, we cannot answer the question about phase transition temperature. As we have mentioned above, the fast cooling of crystals is accompanied by pronounced increase in the grade of their mosaicity. Attempts of slow cooling of both monoclinic and triclinic crystals for the purpose of detection of the point of assumed phase transition have caused the total destruction of crystals, and accordingly we could not obtain correct diffraction pattern in the key temperature range.

CONCLUSIONS

Crystals of both modifications of diastereomeric pinanyl sulfoxides co-crystal undergo the conformational rearrangement of stable hydrogen-bonded synthon generated via S=O...H-O interactions, from “unfolded” to “folded” form by transition from 293 K to 150 K. There is a conformational rearrangement of stable hydrogen-bonded synthon generated via S=O...H-O interactions from “unfolded” to “folded” form. The driving force for this rearrangement is the tendency to realization of S=O...S=O interactions, which show up in the low-temperature phases of both polymorphs and are verified using the methods of quantum chemistry (DFT, B97-D/6-31G(*d,p*), AIM All).

EXPERIMENTAL

Experimental procedures and spectral characterization of synthesized sulfoxides **1a** and **1b** were described in our previous article.¹⁷

Single-Crystal X-ray

The X-ray diffraction data for the crystals of **polymorphs 1** and **2** were collected on a Smart Apex II automatic diffractometer using graphite monochromated radiation MoK α ($\lambda = 0.71073$ Å). Details of crystal data, data collection, and refinement are given in Table 1. The structures were solved by direct method using the SHELXS²⁶ program and refined by full-matrix least-squares using SHELXL97²⁶ program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H(C) atoms were constrained as riding atoms, with C-H set to 0.95 Å. The H(O) atoms were located from a difference Fourier map and refined isotropically in the final stages of refinement with O-H set to 0.85 Å. All calculations were performed using WinGX²⁷ and APEX²⁸ programs. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the CCDC as supplementary publication, the corresponding CCDC numbers are given in Table 1. These data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations

Quantum-chemical calculations were performed at a basic DFT level using the Gaussian 09 software.²⁹ Single-point calculations were performed for “unfolded cryst” and “folded cryst” conformations. The optimization of geometries was carried out without limitations on the symmetry for both “unfolded opt” and “folded opt” conformations; only the positive values of frequency were obtained. A Grimme’s standalone functional B97-D³⁰ and a standard basis set 6-31G(*d,p*) were used. Topological analysis of electron density distributions was performed using the AIMAll program.³¹

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SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher’s website at <http://dx.doi.org/10.1080/10426507.2015.1072185>

Also, X-ray crystallographic information files (CIF) and corresponding data table are available for **polymorphs 1** and **2** (see Table S1). This material is available free of charge via Internet at <http://pubs.acs.org>. CIFs are also available from CCDC upon request (<http://www.ccdc.cam.ac.uk>, CCDC deposition numbers 817380, 817381, 1010129, and 1010130).

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