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Structural Rationalization of the Phase Transition Behavior in a Solid Organic Inclusion Compound: Bromocyclohexane/Thiourea

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S *Supporting Information*

ABSTRACT: Structural properties of the bromocyclohexane/thiourea inclusion compound have been determined using both single-crystal and powder X-ray diffraction over a range of temperatures above and below a first-order phase transition at 233 K in this material. The results demonstrate marked contrasts to the phase transition behavior in the prototypical cyclohexane/thiourea inclusion compound, demonstrating that relatively small changes in molecular geometry (in this case bromine substitution) can have a profound influence on the structural properties of the low-temperature phase in such materials.
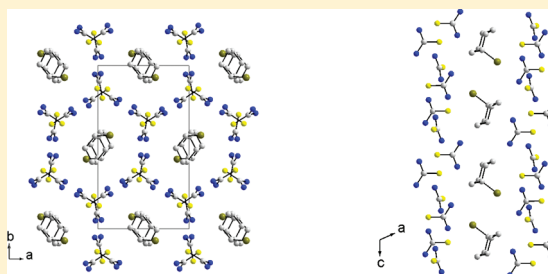
Solid organic inclusion compounds[1−3] of the type that comprise one-dimensional tunnel host structures loaded with a dense packing of guest molecules are well-known to exhibit a range of important physicochemical properties that can serve as models of wider relevance to other types of organic solids. Among these materials, urea inclusion compounds[1,2] have been explored extensively with regard to structural and dynamic properties, including detailed characterization of the changes in these properties that occur at low-temperature phase transitions. To date, the corresponding family of thiourea inclusion compounds[1] has received much less attention, although it is important to note that thiourea inclusion compounds offer potentially greater scope than urea inclusion compounds with regard to materials applications,[4] as the thiourea host tunnel can include a range of bulkier guest molecules possessing a much wider diversity of chemical functionality.

In thiourea inclusion compounds, a crystalline hydrogen-bonded network of thiourea molecules forms a tunnel host structure. This tunnel structure is stable only when it is filled with guest molecules. Examples of suitable guest molecules for inclusion inside the thiourea tunnel structure are cyclohexane and adamantane and several of their derivatives, branched hydrocarbons and small organometallics (e.g., ferrocene). The "conventional" thiourea inclusion compounds are characterized, at ambient temperature, by a rhombohedral crystal structure,[5] in which the guest molecules exhibit extensive orientational disorder and the structural relationship between the host and guest substructures is commensurate[6] (with the exception of one case of an incommensurate system discovered recently[7]). In contrast, most urea inclusion compounds have an incommensurate relationship between the periodicities of the host and guest substructures along the tunnel axis. In general, there are two guest molecules per unit repeat distance along the tunnel of the thiourea host structure and the guest/thiourea molar ratio is 1/3. The thiourea tunnel structure has prominent bulges (diameter ≈7.1 Å) and constrictions (diameter ≈5.8 Å)

at different positions along the tunnel,[8] and in many respects, it behaves more like a cage-type than a tunnel-type host structure.

The thiourea inclusion compound containing cyclohexane (CH) guest molecules is the prototypical member of this family, and has been studied widely.[5a,9] CH/thiourea has three distinct phases, with phase transition temperatures (on cooling) at 148 and 127 K. The structural[9d,e] and dynamic[9d] properties of each phase have been characterized in detail.[10]

In the present paper, we investigate the effects of bromine substitution of the guest molecule on the structural aspects of the phase transition behavior, by comparing the structural properties of the low-temperature phases of the thiourea inclusion compounds containing bromocyclohexane (BrCH) and cyclohexane (CH) guest molecules. In previous studies,[11] it has been shown that, at ambient temperature, the BrCH/thiourea inclusion compound has the conventional thiourea tunnel structure ($R\overline{3}c$; $a \approx 16.0$ Å, $c \approx 12.5$ Å), with substantial orientational disorder of the BrCH guest molecules at this temperature. Previous studies[12] have also demonstrated that BrCH/thiourea undergoes a first-order phase transition at *ca.* 237 K. However, the structural properties of the low-temperature (LT) phase (i.e., at temperatures below the phase transition at *ca.* 237 K) have not been reported previously. We focus here on analysis of the structural properties of the LT phase of BrCH/thiourea.

A variety of spectroscopic techniques, including Raman,[13] solid-state ^{13}C NMR,[14,15] and Br K-edge EXAFS[16] have been used to probe the relative amounts of axial and equatorial conformations of BrCH guest molecules in the thiourea tunnel structure, indicating a strong preference for the guest molecules to adopt the axial conformation. Thus, from ^{13}C NMR studies,[15] the proportion of BrCH guest molecules with the axial conformation at 208 K has been determined to be *ca.* 95%.

The dynamic properties of the BrCH guest molecules in the BrCH/thiourea inclusion compound have been investigated by solid-state ^{13}C NMR and ^{2}H NMR techniques[12,17,18] between 100 and 350 K. The results suggest that rapid ring inversion occurs in the high-temperature (HT) phase, together with essentially unrestricted reorientation of the whole guest molecule relative to the host tunnel. In the higher temperature region of the LT phase, restricted but rapid motion of the BrCH guest molecules still occurs. However, at *ca.* 110 K and lower temperatures, rigid-limit spectra are observed, indicating that the reorientational motions of the guest molecules are frozen in this temperature regime.

In the present work (see Experimental Section), DSC studies indicate that BrCH/thiourea undergoes an exothermic transition at 233 K on cooling and an endothermic transition at 233 K on heating, in close agreement with the phase transition temperature reported previously.[12,18] From our single-crystal XRD study, the rhombohedral structure of the HT phase transforms to a monoclinic structure in the LT phase.[19] In the LT phase, the thiourea molecules have the same topology of hydrogen-bond connectivity as in the HT phase, and a tunnel host structure is retained. However, the host tunnels are distorted significantly from the higher (rhombohedral) symmetry of the HT phase (Figure 1a). Thus, the host tunnel cross section, when projected onto the plane perpendicular to the tunnel axis (c_m-axis; subscript "m" denotes monoclinic), is a distorted hexagon (Figure 1b). In the projection on the plane perpendicular to the c_m-axis shown in Figure 1b, the repeat vectors in this plane are the b_m-axis and the projection of the a_m-axis [denoted proj(a_m)].

From our analysis of the single-crystal XRD data, there is considerable orientational disorder of the BrCH guest molecules in the HT phase, in agreement with a previous report[11] of the structure of BrCH/thiourea at ambient temperature. Furthermore, our results suggest that, in the temperature region of the LT phase just below the phase transition temperature, there is no significant increase in the ordering of the BrCH guest molecules and the extent of disorder remains similar to that in the HT phase. This observation is consistent with conclusions from previous solid-state NMR studies[12,18] discussed above. It is only at sufficiently low temperature within the LT phase that the orientational properties of the BrCH guest molecules become more localized, with evidence from our single-crystal XRD analysis that the guest substructure in this temperature regime (below *ca.* 180 K) is characterized by two well-defined guest orientations at each guest site within the host tunnel.

At the lowest temperature (110 K) studied, the guest substructure is described by a model comprising two distinct orientations of the BrCH guest molecule (with total occupancy of unity), centered at the same site in the host tunnel. For each guest orientation, the cyclohexane ring has the chair conformation with the Br substituent in the *axial* position (Figure 1c,d), in agreement with conclusions from spectroscopic studies (see above) that the axial conformation predominates for BrCH guest molecules in the thiourea host structure. At 110 K, the occupancies of the two guest orientations are *ca.* 80% (major component) and 20% (minor component), confirmed from independent studies of two different crystals. The shape of the "structural envelope" (van der Waals surface) occupied by the two guest orientations is roughly prolate spheroidal, with the principal axis oriented
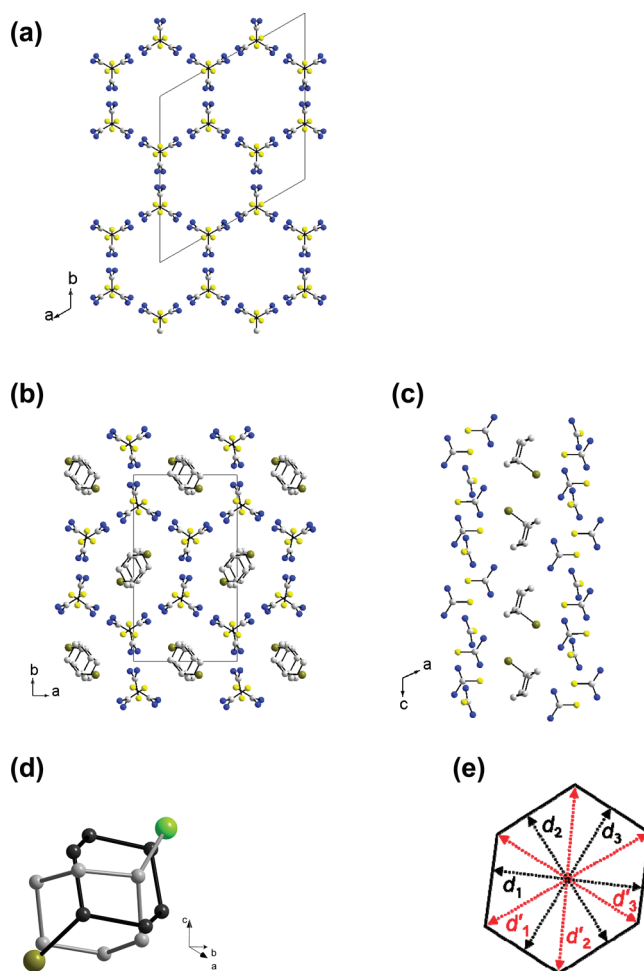

Figure 1. (a) The "conventional" rhombohedral thiourea host structure, as observed in the HT phase of BrCH/thiourea, viewed along the tunnel axis. (b) Crystal structure of BrCH/thiourea viewed parallel to the tunnel axis of the thiourea host structure at 110 K, showing only the major orientation of the BrCH guest molecule. (c) Crystal structure of BrCH/thiourea at 110 K, viewed perpendicular to the tunnel axis, showing only the major orientation of the BrCH guest molecule. (d) The two distinct orientations of the BrCH guest molecule at 110 K, viewed perpendicular to the tunnel, with the tunnel axis vertical. (e) Definition of the distances used to describe the distorted cross-sectional shape of the thiourea host tunnel, projected onto the plane perpendicular to the tunnel axis. In parts a–d, hydrogen atoms are omitted for clarity.

at *ca.* 86°, 54°, and 45° with respect to the a_m, b_m, and c_m axes, respectively. The C–Br bonds in the major and minor components of the guest are tilted from the tunnel axis (+c-axis) by 52.5° and 126.3°, respectively, and the angle between the orientations of the C–Br bond in the two components is *ca.* 98°. For the major component, the projection of the C–Br bond on to the plane perpendicular to the tunnel (c_m) axis forms an angle of 3.5° with the proj(a_m) axis and an angle of 86.5° with the b_m-axis. The two guest orientations occupy essentially the same volume of space (see Figure 1d), and it is reasonable to infer that the difference in host–guest interaction energy between the two orientations must be comparatively small, such that both orientations have significant populations at low temperature.

To further explore the extent of ordering of the BrCH guest molecules in the higher temperature region of the LT phase,

the structure determined at 110 K was used as the starting model for refinements at higher temperatures, in which the occupancies of the two guest orientations were allowed to refine. On increasing the temperature from 110 to 220 K, the relative occupancies (*ca.* 4:1 at 110 K) of the two guest orientations converge to similar values. However, the precision of the refined guest substructure decreases significantly as temperature is increased, reflecting an increased degree of disorder such that the model comprising two well-defined orientations of the guest molecule becomes inadequate, even with refinement of large anisotropic displacement parameters to subsume the effects of molecular motion. From single-crystal XRD data recorded with temperature cycling in the LT phase, the relative occupancies of the two guest orientations are found to vary reversibly as a function of temperature, suggesting that a process of dynamic interconversion between the two guest orientations occurs inside the host tunnel.

To explore the temperature dependence of the lattice parameters in more detail, we carried out a powder XRD study (Figure 2) to determine the unit cell at a significantly
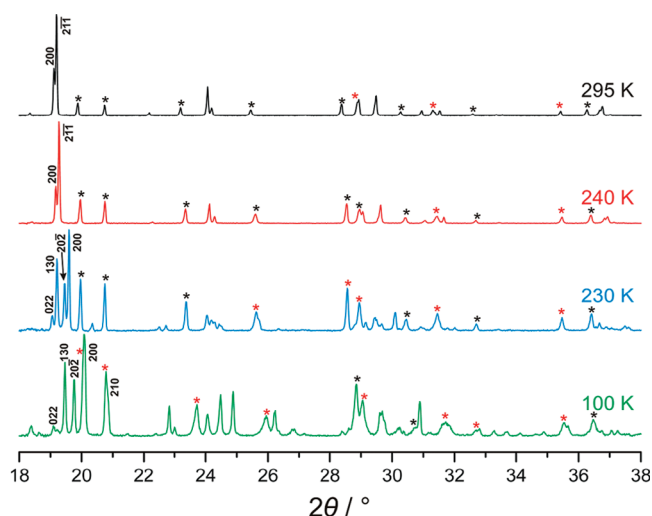
Figure 2. Powder XRD patterns for BrCH/thiourea recorded at selected temperatures above and below the phase transition at 233 K. The lowering of symmetry in the LT phase is evident from the peak splittings observed. Additional peaks due to pure thiourea (see Experimental Section) are marked with asterisks (black, peaks due to pure thiourea only; red, peaks due to pure thiourea overlapping with peaks due to BrCH/thiourea).

greater number of temperatures and covering a wider temperature range (down to 30 K) than our single-crystal XRD study. In order to follow the lattice distortion at the phase transition, we use a common definition of lattice parameters for both the HT and LT phases, corresponding to the monoclinic unit cell $\{a_m, b_m, c_m, \beta_m\}$ (see ref 9d). The temperature-dependence of the lattice parameters on cooling from 295 to 30 K, shown in Figure 3, exhibits good quantitative agreement with our single-crystal XRD results (assessed for the specific temperatures studied by both techniques). The periodic repeat distance along the tunnel (c_m) decreases only slightly as temperature is decreased across the full temperature range studied, and it does not change significantly at the phase transition. In contrast, the phase transition is associated with abrupt changes in a_m, b_m, and β_m (corresponding to a significant

distortion of the tunnel cross section, as evident from the projection on the plane perpendicular to the c_m-axis in Figure 1b) and a small (but significant) discontinuity in unit cell volume (V_m). In the LT phase, a_m, b_m, and β_m have contrasting temperature dependences; in particular, b_m and β_m evolve in a nonmonotonic (but continuous) manner as a function of temperature, passing through a maximum and a minimum, respectively, in the region *ca.* 210−220 K. These rather complicated changes in the nature of the distortion of the host tunnel as a function of temperature in the region just below the phase transition may be associated with the fact that, in the same temperature regime, there are significant changes in the degree of ordering (and dynamics) of the guest molecules, as noted above.

The distortion of the thiourea tunnel structure in the LT phase may be quantified using the function D (eq 1), which indicates the extent to which the projection of the structure on the plane perpendicular to the tunnel (c_m) axis deviates from the hexagonal metric symmetry of the HT phase [the repeat unit in this two-dimensional projection is a rectangular unit cell with cell edges of lengths b_m and $proj(a_m)$]:

$$D = b_m/[\sqrt{3}a_m \cos(\beta_m - 90°)] \tag{1}$$

When the projection of the monoclinic unit cell has hexagonal metric symmetry (as in the HT phase), $b_m = \sqrt{3}a_m \cos(\beta_m - 90°)$, and hence, $D = 1$. Thus, deviations from $D = 1$ are interpreted as a measure of the degree of distortion from hexagonal metric symmetry, with $D > 1$ and $D < 1$ corresponding to different modes of distortion, as discussed in more detail below. Importantly, the distortion of the thiourea tunnel in the LT phase for BrCH/thiourea (Figure 4) corresponds to $D > 1$, whereas the distortion in the LT phase for CH/thiourea (Figure 4) corresponds to $D < 1$.

Further details of the mode of distortion of the host tunnel in the LT phase may be established by considering the shape of the distorted tunnel cross section observed in the projection of the structure shown in Figure 1b. Thus, to define the distorted hexagonal shape of the tunnel cross section, we consider the relative values of the three corner-to-corner distances (denoted d'_1, d'_2, and d'_3; defined in Figure 1e) and the three perpendicular face-to-face distances between opposite faces (denoted d_1, d_2, and d_3; defined in Figure 1e). For BrCH/thiourea (Figure 1b), the distortion is such that one face-to-face distance (d_3) becomes <u>longer</u> than the other two face-to-face distances [values relative to the longest distance (d_3): $d_1/d_3 = 0.90$, $d_2/d_3 = 0.91$, $d_3/d_3 = 1$], while one corner-to-corner distance (d'_3) becomes <u>shorter</u> than the other two corner-to-corner distances [values relative to the longest distance (d'_1): $d'_1/d'_1 = 1$, $d'_2/d'_1 = 0.99$, $d'_3/d'_1 = 0.88$]. This mode of distortion corresponds to compressing one corner-to-corner distance and stretching one face-to-face distance perpendicular to it (note from Figure 1e that d_3 and d'_3 are essentially perpendicular to each other).

Significantly, the mode of distortion of the host tunnel in the LT phase of CH/thiourea (Figure 5) is completely different. In this case, the distortion is such that one face-to-face distance (d_2) becomes <u>shorter</u> than the other two face-to-face distances [values relative to the longest distance (d_3): $d_1/d_3 = 0.99$, $d_2/d_3 = 0.92$, $d_3/d_3 = 1$], while one corner-to-corner distance (d'_1) becomes <u>longer</u> than the other two corner-to-corner distances [values relative to the longest distance (d'_1): $d'_1/d'_1 = 1$, $d'_2/d'_1 = 0.88$, $d'_3/d'_1 = 0.85$]. This mode of distortion corresponds
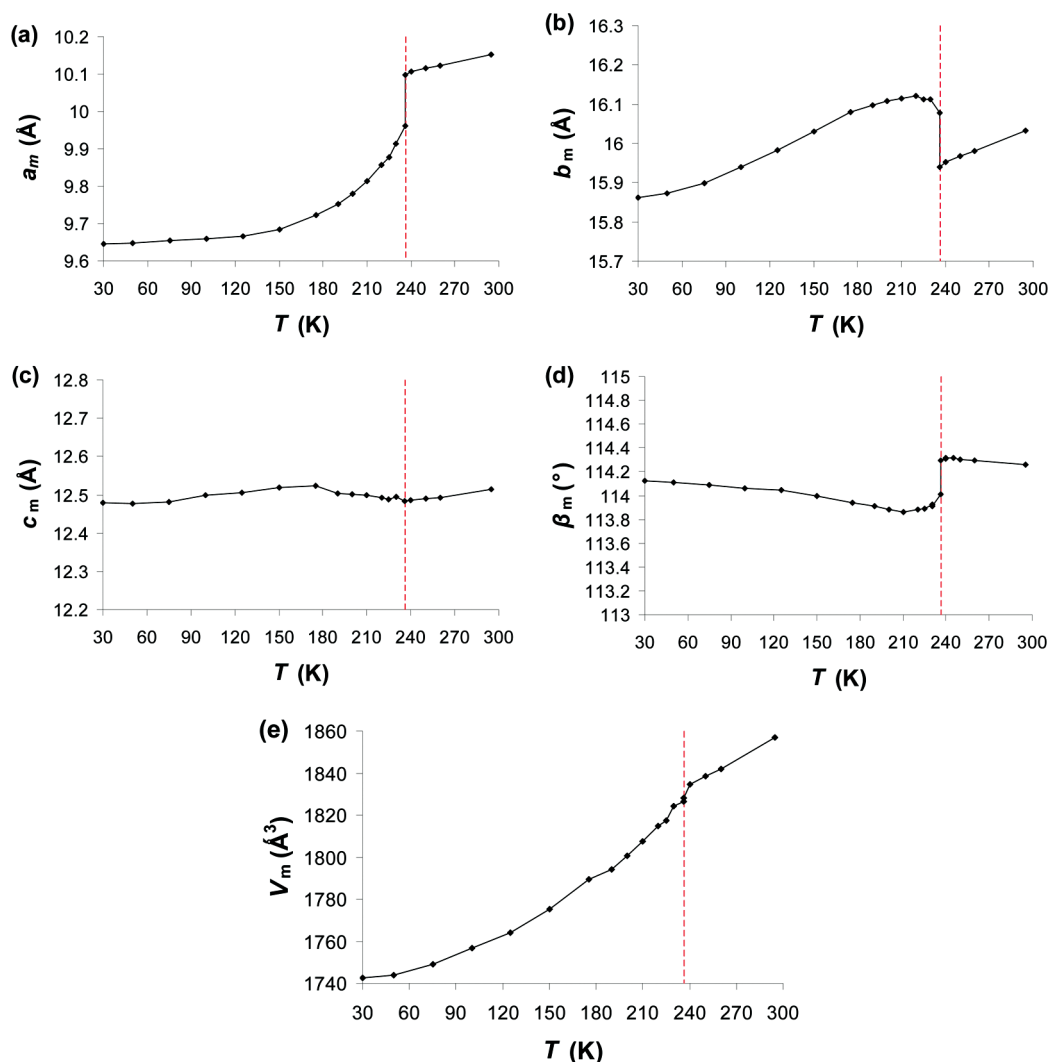
Figure 3. Temperature-dependence of the lattice parameters and unit cell volume (referred to the monoclinic unit cell discussed in the text) for BrCH/thiourea, determined from our powder XRD data. The red dashed line indicates the phase transition temperature.
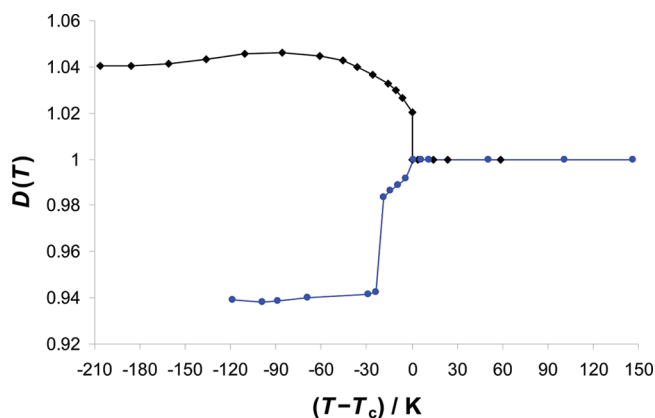
Figure 4. Temperature-dependence of the "distortion parameter" D, defined in the text, for CH/thiourea (blue; data from ref 9d) and BrCH/thiourea (black). The temperature scale is plotted as $T - T_c$, where T_c denotes the temperature of the phase transition at which the structure changes from rhombohedral to monoclinic ($T_c = 233$ K for BrCH/thiourea; $T_c = 148$ K for CH/thiourea). Note that the second phase transition for CH/thiourea [at 127 K, corresponding to $(T - T_c) = -21$ K] is associated with a significant discontinuity in the value of D.
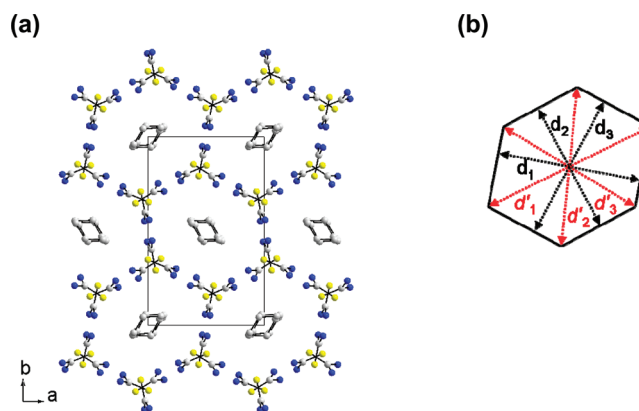
Figure 5. (a) Crystal structure of CH/thiourea viewed parallel to the tunnel axis of the thiourea host structure at 100 K (data from ref 9e). (b) Definition of the distances used to describe the distorted cross-sectional shape of the thiourea host tunnel, projected onto the plane perpendicular to the tunnel axis.

to stretching one corner-to-corner distance and compressing one face-to-face distance perpendicular to it (note from Figure 1e that d_2 and d'_1 are essentially perpendicular to each other).

Given these differing modes of distortion of the hexagonal tunnel cross section in the LT phases of CH/thiourea and BrCH/thiourea, the contrasting behavior of the "distortion parameter" D within the LT phases of these inclusion compounds can be readily understood. Thus, in the plane perpendicular to the tunnel axis in the LT phase (for both CH/thiourea and BrCH/thiourea), the b_m-axis is nearly parallel to the corner-to-corner distance d'_2, whereas the $\text{proj}(a_m)$ axis is nearly parallel to the face-to-face distance d_1. For BrCH/thiourea, the distortion in the LT phase involves a relative lengthening of d'_2 and shortening of d_1, whereas for CH/thiourea, the distortion involves a relative shortening of d'_2 and lengthening of d_1. As a consequence, $D > 1$ for BrCH/thiourea and $D < 1$ for CH/thiourea. Although the structural properties of the chlorocyclohexane/thiourea inclusion compound have not been studied at the same level of detail as BrCH/thiourea and CH/thiourea, the results from a previous low-temperature powder XRD study[20] suggest that the distortion in the LT phase of this material corresponds to $D > 1$.

In conclusion, comparison of the structural properties of the LT phase of the BrCH/thiourea inclusion compound reported here with those of the CH/thiourea inclusion compound reported previously[9d,e] reveals the subtle yet important changes that can occur in phase transition behavior simply by substitution of a single atom in the guest molecule (in this case bromine substitution). This observation reflects the fine energetic balances that pertain in such materials and the role of small and subtle changes in intermolecular interactions involving the host and guest components.

■ EXPERIMENTAL SECTION

The BrCH/thiourea inclusion compound was prepared by cooling a solution of thiourea and BrCH (ca. 3:1 molar ratio) in methanol from 55 to 20 °C over ca. 29 h. Needle-shaped crystals were obtained (width ca. 0.25−2 mm, length ca. 5−10 mm), with cross-sectional shape corresponding to a distorted hexagon (i.e., with angles of 120° between adjacent sides, but with sides of unequal length). Powder XRD confirmed that the product was a monophasic sample of a conventional thiourea inclusion compound.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments heat flux Q100 DSC instrument. The ground sample of BrCH/thiourea was subjected to a cycle of cooling and heating between 298 and 203 K, at cooling/heating rates of 10 K min^{-1}. After cooling, the sample was held at 203 K for 1 min before commencing the heating cycle.

Single-crystal XRD was carried out on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems cryostat. Data were recorded at several temperatures on cooling from ambient temperature to 110 K and on heating back to ambient temperature. The same crystal was used to record data over the entire temperature range. The transition from the HT phase to the LT phase is accompanied by crystal twinning, associated with the reduction in symmetry from rhombohedral to monoclinic, as evident from splitting of diffraction maxima. On heating the crystal from the LT phase across the phase transition temperature, each set of split diffraction maxima coalesces into a single maximum, and thus the twinning/detwinning process is reversible. Structure determination in the LT phase involved analysis of the data from a single twin component. Structure determination was carried out using SHELXS-97.[21] The non-H atoms that were not located in the structure solution were found by difference Fourier methods. For the LT phase, inspection of difference Fourier maps following initial refinement of the thiourea host structure revealed two relatively large peaks inside the host tunnel, interpreted as the locations of two Br atoms with fractional occupancies and suggesting that the BrCH guest molecule is disordered between two well-defined orientations. At the lower temperatures studied in the LT

phase (ca. 110 K), it was possible to locate the other non-H atoms of the BrCH molecule from difference Fourier maps. In the final stages of refinement, geometrical restraints were applied to both orientations of the BrCH molecule, and the fractional occupancies were refined. For non-H atoms, anisotropic displacement parameters were refined. H atoms were inserted at calculated positions and refined using a riding model. The isotropic displacement parameter of each H atom was 1.2 times the equivalent isotropic displacement parameter of the atom to which it is bonded.

Powder XRD data were recorded at several temperatures between 295 and 30 K on a Bruker D8 diffractometer (reflection mode; Ge monochromated Cu $K\alpha 1$ radiation; data range, $15° \leq 2\theta \leq 41°$; step size, 0.01607°; time per step, 6 s). Temperature was controlled using an Oxford Cryosystems Phenix cryostat (accuracy ca. 0.1 K). However, under the conditions of our powder XRD measurement, the inclusion compound undergoes partial decomposition (as a result of subjecting the sample to reduced pressure in the cryostat), leading to the presence of some amount of pure thiourea[22,23] in the sample. Thus, peaks due to pure thiourea (marked with asterisks in Figure 2) are observed in the powder XRD patterns. Lattice parameters for BrCH/thiourea were determined by profile fitting using the Le Bail method[24] in the GSAS program package.[25,26] A two-phase refinement was employed, with simultaneous profile-fitting for both the BrCH/thiourea inclusion compound and pure thiourea. Good quality fits were obtained in all cases.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Crystallographic information (cif file) for the crystal structure of the bromocyclohexane/thiourea inclusion compound in the LT phase at 110 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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(10) For CH/thiourea, the phase transition at 148 K is a second-order transition and is associated with a change in symmetry from rhombohedral (above 148 K) to monoclinic (below 148 K). The phase transition at 127 K is a first-order transition and is associated with a significant discontinuity in the lattice parameters, although there is no change in the crystal symmetry at this transition (the space group remains $P2_1/a$ on crossing the phase transition at 127 K). The phase transitions at 148 and 127 K are each associated with well-defined changes in the dynamic properties of the CH guest molecules.

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