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Unanticipated Guest Motion during a Phase Transition in a Ferroelastic Inclusion Compound

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When designing solid-state reactions,[1] adherence to the precept that reactions proceed with either the least amount of motion or a minimal distortion of the reaction cavity[2] (the topochemical postulate) is usually required for success. Nevertheless, there is ample precedent for solid-state reactions that violate the topochemical postulate, especially for those under the influence of reaction-induced stress[3] or those occurring at defects.[4] Here we show how inclusion compounds of urea containing $X(CH_2)_6CN$ ($X = Cl, Br$) undergo reversible single crystal to single crystal (topotactic) phase transitions in which small conformational changes of guests give rise to guest translations of approximately 5.5 Å. In closely related materials, we have observed analogous conformational processes *without* concomitant translation, so this large guest motion was unanticipated. Thus, although adherence to the topochemical postulate is not required for phase transitions, the present case serves as a cautionary example that helps delimit the utility of "least-motion" ideas. Recognition of the nature of this process was the key to understanding discrimination between guests during crystal growth.

There are several classes of urea inclusion compounds (UICs), which differ in the topology of their H-bonded networks, the metric relationships of host and guest substructures, and the distortion of the urea honeycomb from high symmetry. Most UICs are best treated as incommensurate (nonstoichiometric), high symmetry (uniaxial) systems in which ureas are tethered in helical H-bonded networks to generate linear, nonintersecting channels.[5] Nevertheless, many UICs form commensurate structures that have either high or low symmetry, depending upon the relative orientations of guests within the channels. The low symmetry (biaxial) crystals may be separated into two major classes: ones in which ureas adopt helical H-bonded topologies and those in which ureas form nonhelical H-bonded networks. Our continued interest in UICs arises because almost all of the biaxial crystals with helical topologies exhibit macroscopic domain reorientation under external anisotropic stress (ferroelasticity).[6] In these crystals, small forces may be used to reorient the guests by approximately 60° about the channel axis. This domain reorientation is facilitated by the helical H-bonded topology of the host, since rotation of the guest is coupled to a translational progression of the guest along the urea helix.

We have identified several biaxial UICs in which host molecules adopt nonhelical H-bonding topologies that are best described as stacked loops of urea hexamers (Figure 1).[7] This alternative $P2_1/n$ packing mode is routinely adopted for guests with the formula $X(CH_2)_6Y$ ($X, Y = Br, Cl, CN, NC$). Although these crystals are distorted from hexagonal metric symmetry, most are not ferroelastic because a simple rotation−translation of the guest would produce an inequivalent structure. Ferroelastic (degenerate) domain reorientation would require reorientation of the *n*-glide symmetry plane by approximately 60° and necessitate a large-scale reorganization of the urea framework and rupture of numerous H-bonds.

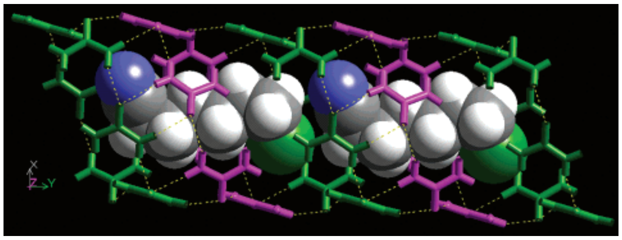

Figure 1. Stacked loop structure (viewed along [001]) of $Cl(CH_2)_6CN$/urea at −90 °C showing undulation in the channel walls. The magenta and green colors highlight the (identical) stacked loops of urea molecules. End group orientation is arbitrary.

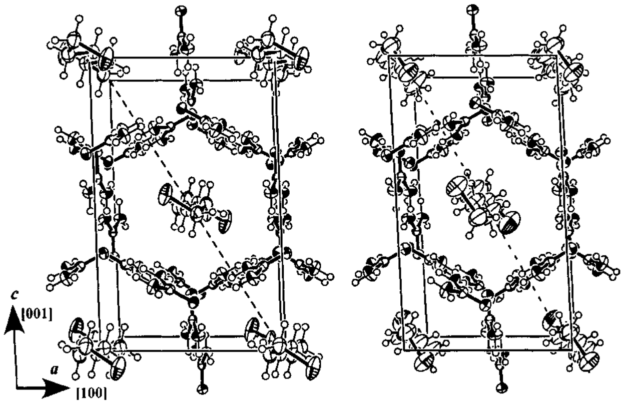

Figure 2. ORTEP views (50% ellipsoids) down the channel of $Cl(CH_2)_6$-CN/urea at −90 (left) and −64 °C (right). The dashed line is (101). Note the distortions from hexagonal symmetry along [100] and [001] in the low- and high-temperature forms.

The stacked loop structures may be separated again into two classes, those distorted along [100] and those distorted along [001] (Figure 2). Because of the preferred orientation of guests in the channels, UICs of $Br(CH_2)_6Br$, $Br(CH_2)_6Cl$, and $Cl(CH_2)_6Cl$ are distorted from hexagonal symmetry by as much as 10% along [100].[7] Earlier work showed that temperature-dependent variation in the populations of guests in two gauche conformers accounts for the relaxation of strain as the crystals are warmed.[7,8] In all three crystals, planes defined by the guest methylenes lie 21.6−22.1° from [100] in the major conformers, which widen the channel along [100]. In contrast to the halogen derivatives, $NC(CH_2)_6CN$/urea exhibits a distortion of only 2% along [001]. This distortion is produced in part by the significant population of a conformer in which the mean plane of the alkyl chain lies 4° from [001].[5] Although they are potentially ferroelastic, distortions of 2−10% in the stacked loop systems are apparently too great for observation of this phenomenon.

Because the terminal functional groups in the guests appear to control the direction and magnitude of the host distortion, one

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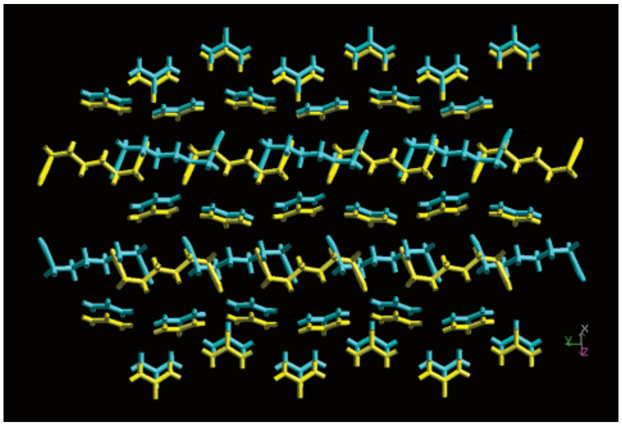

Figure 3. View normal to (101) (*b* horizontal) in $Cl(CH_2)_6CN$/urea at −90 (blue) and −64 °C (yellow). An alternative mechanism requiring large-scale host reorganization is shown in an analogous image in the Supporting Information.

strategy for preparing ferroelastic crystals would be to tailor that distortion by forming solid solutions containing mixtures of guests from the two different classes. This ordinarily fails, however, because solid solution formation of the stacked loop form is usually possible within a series (e.g. with $Cl(CH_2)_6Cl$ and $Br(CH_2)_6Br$), but not between series (e.g. $Cl(CH_2)_6Cl$ and $NC(CH_2)_6CN$). Crystals of $Cl(CH_2)_6CN$/urea, however, produce the desired effect. At 298 K, these crystals are distorted along [001] by only 0.5% from hexagonal symmetry[10] and exhibit ferroelastic domain reorientation at relatively high forces. The "sense" of this distortion (along [001]) was surprising, however, since the larger distortions observed for chlorine-containing guests should have resulted in a structure distorted along [100].

At −64 °C, the chain orientation of the guest in $Cl(CH_2)_6CN$/urea corresponds closely to those of the minor guest conformers in $Br(CH_2)_6Br$/urea and $NC(CH_2)_6CN$/urea (Figure 2).[11,12] This guest orientation distorts the host along [001]. Upon cooling to −66 °C, $Cl(CH_2)_6CN$/urea undergoes a first-order phase transition in which the crystal morphology elongates along [100] and contracts along [001]. The structure of this low-temperature phase (Figure 2) is isomorphous with $Cl(CH_2)_6Cl$/urea and its congeners,[7] and confirms our prediction that the chlorine should bias the distortion toward [100].

This transition involves much more than a simple conformational change and concomitant reorientation of strain. Superposition of ureas from the structures at −64 and −90 °C shows that the guests translate along the channel by 5.5 Å (*b*/2) during this process (Figure 3)! Alternative models involving reorganization of host H-bonds are untenable. Longitudinal motion of guests is consistent with the relatively weak host−guest interactions and with lower amplitude guest motions in other UICs.[13] It has also been implicated as a critical surface roughening step in the crystal growth of UICs.[14] Nevertheless, the present case is striking[15] because analogous gauche to gauche jumps are well established in $NC(CH_2)_6CN$/urea and $Br(CH_2)_6Br$/urea, which adopt high- and low-temperature forms, respectively.

Although there are no short contacts between host and guest in the high- or low-temperature structures, the nontopochemical process described here is most readily understood in terms of host−guest steric interactions. In these structures, ureas tilt in and out of the channels to make H-bonds with urea carbonyls from adjacent walls. This tilting produces an undulation in the channel, whose constrictions dictate the position and orientation of the conformer that predominates in a given phase.[16] In Figure 3, the alkyl chain of the low-temperature guest (blue) zigzags in and out of a plane parallel to (101) in a channel section that is constricted in that same plane. In the high-temperature form (yellow), the CH_2 chain lies approximately parallel to the (101) plane, so this conformer is not accommodated in the section of channel that is constricted in (101). Instead, translation by *b*/2 moves the guest to a section of the channel in which the orientation of the chain better matches the confines of the surrounding host.

In all of the low-temperature forms, terminal guest substituents point toward the vertices of the channels, whereas in the high-temperature forms, they lie close to (101) and point to the channel walls. Crystals of $Br(CH_2)_6CN$/urea undergo an analogous transition at a much higher temperature (22 °C), suggesting that the bromine favors the channel vertex. UICs containing mixtures of $Br(CH_2)_6CN$ and $Cl(CH_2)_6CN$ exhibit a systematic variation in transition temperature with guest composition, allowing us to tailor the temperature range over which these materials are ferroelastic.

The large guest displacement explains our inability to prepare solid solutions of the $P2_1/n$ form with guests from the two series (e.g. $Cl(CH_2)_6Cl$ and $NC(CH_2)_6CN$). This failure arises *not* from the different orientations of guest-induced strain, but from preferential occupation of sites along the channel by the two types of guests. The subtlety of the interactions involved highlights the difficulty in using simple considerations of isomorphism to design new materials.

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Supporting Information Available: Preparation of materials, DSC and crystal data for $Cl(CH_2)_6CN$/urea at −120, −90, −75, and −64 °C, as well as a figure analogous to Figure 3 showing an alternative process in which the guest does not translate down the channel (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) At 298 K, a = 8.246(3) Å, b = 10.955(6) Å, c = 14.366(7) Å, β = 92.71(3)°, V = 1296.2(8) Å^3 for $Cl(CH_2)_6CN$/urea.

(11) $Cl(CH_2)_6CN$/urea (1:6) at −90 °C: ($P2_1/n$), a = 8.550(2) Å, b = 10.848(2) Å, c = 13.489(3) Å, β = 92.658(3)°, V = 1249.7(4) Å^3; $R1$ = 0.038, S = 1.26. At −64 °C, ($P2_1/n$): a = 8.1604(14) Å, b = 10.891(2) Å, c = 14.304(3) Å, β = 93.542(3)°, V = 1268.8 (4) Å^3; $R1$ = 0.046, S = 1.14. For these two structures, the differences in the Eulerian angles are Δa = 3.24°, Δb = 0.055°, and Δc = 0.55°, indicating a topotactic process.

(12) At −64 °C, C_3 of the guest exhibits disorder. The DSC warming curve gives $\Delta H°$ =730 cal mol^{-1} and $\Delta S°$ =3.5 cal mol^{-1} K^{-1} at −65.6 °C.

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(16) The H-bonding to adjacent walls gives rise to the undulation, so it is not feasible to "phase-shift" the undulation by half a unit cell via small disrotatory motions of ureas about their C_2 axes. This mechanism would disrupt the H-bonds to adjacent channel walls.

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