

Spring-Loading at the Molecular Level: Relaxation of Guest-Induced Strain in Channel Inclusion Compounds

Mark D. Hollingsworth,^{*,†,‡} Ulrike Werner-Zwanziger,[‡]
Michael E. Brown,[‡] Jason D. Chaney,[‡] John C. Huffman,[‡]
Kenneth D. M. Harris,[‡] and Sharon P. Smart[‡]

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

Department of Chemistry, University of St. Andrews
St. Andrews, Fife KY16 9ST, U.K.

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Although urea inclusion compounds (UICs) are typically nonstoichiometric (incommensurate) solids, a number of UICs form commensurate structures in which guest molecules adopt well-defined orientations that distort the honeycomb channel of urea away from its usual hexagonal symmetry.¹ By virtue of this distortion, many of these inclusion compounds are ferroelastic, that is, they undergo domain switching under application of external anisotropic stress. In optimal cases, single crystal to single crystal transformations occur in which the external stress reorients macroscopic domains by approximately 60°. To probe the cooperative processes that control domain switching, we have synthesized over 20 distorted UICs that differ in the extent of distortion away from hexagonal symmetry and in the topology of their H-bonding networks. Here we focus on three commensurate, nonferroelastic UICs of the general formula X(CH₂)₆Y/urea, and show through a combination of X-ray diffraction and solid state ²H NMR how specific motions of guest molecules relax the distortion of the urea channel and shift the cell toward hexagonal symmetry. This work helps provide a molecular basis for understanding the mechanism of domain switching in ferroelastic UICs and shows how a coiled guest can induce an unusual “spring-loaded” phase transition to an undistorted phase.

Although commensurate UICs with stoichiometric host–guest ratios have been known for many years,³ early attempts to solve their crystal structures yielded coordinates only for the hosts, in part because guest molecules undergo dynamic averaging.^{4,5} Here we report crystal structures of the UICs of 1,6-dibromohexane (**1**), 1-bromo-6-chlorohexane (**2**), and 1,6-dichlorohexane (**3**), all of which have host–guest stoichiometries of 6:1. Although subtle differences exist in unit cell parameters, these monoclinic (*P*2₁/*n*) structures⁶ are nearly isomorphous near 100 K; all exhibit similar distortions of approximately 10% away from hexagonal metric symmetry. Unlike their longer chain counterparts, which exist predominantly in their extended conformations in their

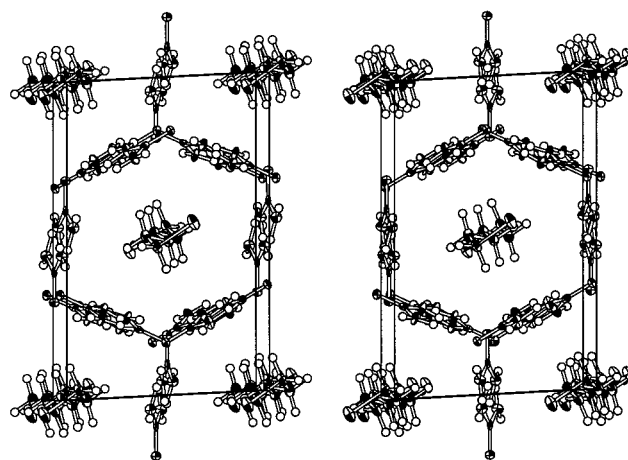


Figure 1. ORTEP view down the channel (*b* axis) of **1**/urea at $-164\text{ }^{\circ}\text{C}$ (50% ellipsoids, *a* horizontal). Absolute values of torsional angles ($\text{Br}(\text{Cl})-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma$) are $66.3\text{--}66.7^\circ$ for **1–3**/urea.

UICs,⁷ **1–3** all contain gauche carbon–halogen bonds (Figure 1). The metric properties of longer chain α,ω -dibromoalkanes in urea^{4c} provide the most likely explanation for the unexpected conformations: a plot of channel axis guest repeat length (c_g) versus *n* for $\text{Br}(\text{CH}_2)_n\text{Br}$ is a fairly straight line for $n = 7\text{--}10$, but the extrapolated value for $n = 6$ is 12.8 \AA , not the 11.0 \AA expected for a commensurate structure with host–guest stoichiometry of 6:1. To form commensurate structures with urea, **1–3** coil into gauche conformations and tilt away from the channel axis by $12\text{--}14^\circ$ (primarily toward the *a* axis). In all three structures, the planes defined by the methylene chains of the guest ($\text{C}_1\text{--}\text{C}_6$) lie $21.6\text{--}22.1^\circ$ away from the (001) plane (horizontal in Figure 1), and the C–X bonds point toward the vertices of the channels. The net result is a guest structure that imposes an internal stress on the urea host; this stress generates a lattice strain in which *a* ([100]) is elongated and *c* ([001]) is compressed relative to an ideal hexagonal structure. The *n*-glide also generates a nonhelical topology⁸ of H-bonds in which certain rows of urea molecules lying closest to the (001) face are translated along the channel relative to their counterparts in helical structures.

Single-crystal XRD measurements from 100 to 300 K show that **1–3**/urea gradually shift toward hexagonal metric symmetry as the temperature is raised (Figure 2). In each case the thermal expansion is first manifested as an elongation along *a*, but concomitant expansion along *c* (and a decrease in β) yields a net shift toward hexagonal metric symmetry as the temperature is raised. The approach toward hexagonal symmetry occurs most gradually for the largest guest (**1**) and least gradually for the smallest (**3**), as expected for an order–disorder process in which the guest becomes progressively more mobile as the temperature is raised. (The smaller **3** is freer to move than **1**.) Remarkably, however, **1**/urea undergoes a first-order phase transition to an undistorted structure at a lower temperature (onset at $63\text{ }^{\circ}\text{C}$) than analogous transitions in **2**/urea ($70\text{ }^{\circ}\text{C}$) and **3**/urea (approximately

* To whom correspondence should be addressed at Kansas State University. Phone: 785-532-2727. Fax: 785-532-6666. E-mail: mdholl@ksu.edu.

[†] Kansas State University.

[‡] Indiana University.

[‡] University of St. Andrews.

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(6) Crystal data for **1–3**/urea: **1**/urea: $a = 8.561(8)\text{ \AA}$, $b = 10.889(6)\text{ \AA}$, $c = 13.381(7)\text{ \AA}$, $\beta = 92.82(6)^\circ$, $V = 1245(1)\text{ \AA}^3$ at 109 K; $R = 0.032$, $R_w = 0.027$, $\text{GOF} = 1.31$, 1426 obsd $w/I \geq 3.00\sigma(I)$, 146 parameters. **2**/urea: $a = 8.542(2)\text{ \AA}$, $b = 10.875(1)\text{ \AA}$, $c = 13.418(2)\text{ \AA}$, $\beta = 92.44(2)^\circ$, $V = 1245.3(3)\text{ \AA}^3$ at 102 K; $R = 0.038$, $R_w = 0.030$, $\text{GOF} = 1.58$, 1615 obsd $w/I \geq 3.00\sigma(I)$, 148 parameters. **3**/urea: $a = 8.509(1)\text{ \AA}$, $b = 10.860(7)\text{ \AA}$, $c = 13.435(9)\text{ \AA}$, $\beta = 92.02(7)^\circ$, $V = 1240(1)\text{ \AA}^3$ at 99 K; $R = 0.041$, $R_w = 0.036$, $\text{GOF} = 1.70$ for 1881 obsd $w/I \geq 3.00\sigma(I)$ and 146 parameters.

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(8) Although they are potentially ferroelastic, the nonhelical topologies and large distortions from hexagonal metric symmetry present significant kinetic barriers to domain switching in **1–3**/urea. We have observed ferroelastic domain switching in $\text{Cl}(\text{CH}_2)_6\text{CN/urea}$, which has a much smaller distortion.¹

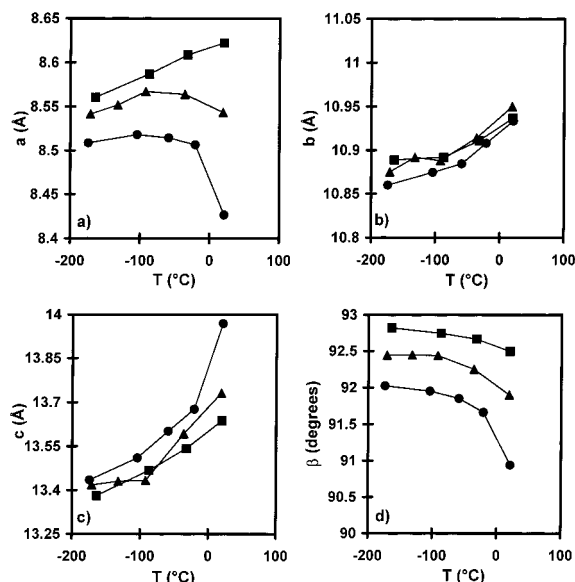


Figure 2. Temperature dependence of cell parameters for 1/urea (squares), 2/urea (triangles), and 3/urea (circles) from 100 to 300 K. At room temperature, an unstrained, orthorhombic cell would be: $a = 8.22 \text{ \AA}$, $b = 11.01 \text{ \AA}$, $c = 14.24 \text{ \AA}$ ($= (8.22 \text{ \AA})(\sqrt{3})$), $\beta = 90^\circ$.¹

72 °C, overlapped with decomposition).⁹ We attribute this inverted behavior to a stress-induced process in which dynamic averaging of guests requires them to break free from the confines of the 11.0 Å unit cell to form helical channel structures with longer guest repeats.¹⁰ Although we are unaware of direct precedents, such a stress-induced process may be expected for a system in which a flexible guest is coiled like a spring within a rigid, tubular host. This is related to solid-state reactions in which irreversible motions occur so as to accommodate reaction-induced stress.¹¹

In conjunction with crystallographic results, ²H NMR provides a detailed mechanistic view of the guest motions responsible for relaxation of the urea tunnel toward the undistorted structure as the temperature is raised to 300 K. When motions are in the fast time limit for ²H NMR, it is impossible to independently determine the relative populations of sites and the jump angle between them from the lineshape of the ²H quadrupolar Pake pattern. However, by comparing the ²H NMR spectra of α , β , and γ deuterated 1,6-dibromohexane in urea between 172 and 300 K, and by recognizing characteristic features in the spectra, we could show that the guests undergo motions closely related to torsional jumps between major and minor gauche conformers.¹² One critical feature is that the positions of the “shoulders” of the Pake doublets do not change appreciably as a function of temperature for any of the isotopomers studied. This restricts the motional models to ones in which the α , β , and γ CD₂ groups jump between two or more sites within planes defined by the respective CD₂ groups. (Unlike α CD₂ groups, the β and γ CD₂

(9) For the high-temperature phase of 1/urea, least-squares refinement of 10 reflections in the powder X-ray diffraction pattern (rotating Cu anode, Siemens Hi-Star detector) gave an orthorhombic cell with $a = 8.23(1) \text{ \AA}$, $b = 14.22(2) \text{ \AA}$, $c = 11.02(1) \text{ \AA}$ at 20 °C (c.f. Figure 2 for undistorted cell).

(10) Single-crystal XRD studies of 1/urea during the phase transition (rotating Cu anode, Siemens Hi-Star detector with the crystal sealed in liquid Br(CH₂)₆Br) reveal that the guest elongates to 12.8 Å and conforms to a monoclinic supercell in which a and c are doubled and $6c'_g = 7c'_h$. See ref 5 and: Yeo, L.; Harris, K. D. M.; Guillaume, F. *J. Solid State Chem.* **1997**, *128*, 273–281. Because it contains contributions from torsional strain and cooperative host–guest interactions, an exact calculation of the load on the spring is not feasible. However, for a “compression energy” of 0.5 kcal mol⁻¹ and an end-on guest diameter of 4.5 Å, contraction of 1.8 Å requires a stress of 1.2 kbar. See: McBride, J. M.; Segmuller, B. E.; Hollingsworth, M. D.; Mills, D. E.; Weber, B. A. *Science* **1986**, *234*, 830–835.

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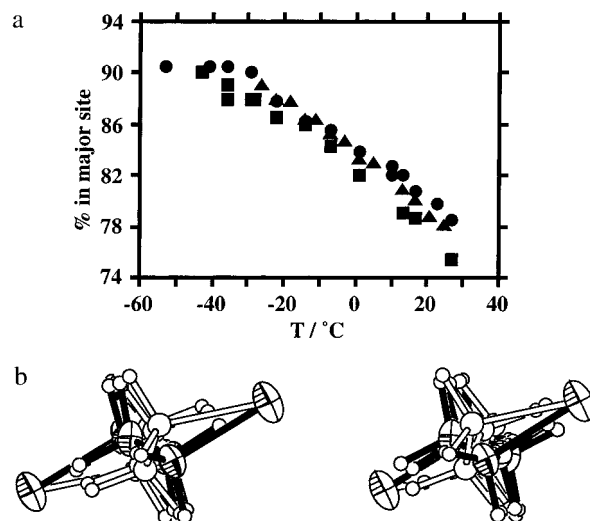


Figure 3. (a) Temperature dependence of the population of the major conformer, as determined by ²H NMR of 1/urea labeled with ²H in α (circles), β (squares), and γ (triangles) positions (for approximate gauche–gauche jumps). (b) ORTEP channel axis view of 1/urea at –60 °C showing conformers of major (solid bonds, sectored atoms) and minor (open bonds, open atoms) guests (30% ellipsoids, a horizontal).

groups jump within roughly parallel planes defined initially by the 109 K crystal structure.) In addition, the motions of the deuterons within each CD₂ group are equivalent (giving a single Pake pattern in each case), and the bromines refine to a single position in each crystal structure of 1/urea (see below). For a two-site gauche–gauche jump model¹³ (which matches these constraints) the ²H NMR spectra of α , β , and γ deuterium labeled 1 in urea can be fit independently to give a single, temperature-dependent population for the major conformer (within error limits, Figure 3a).¹⁴ Such constraints on geometry and population were critical in our development and refinement of disordered structural models for the guest from X-ray diffraction data at –60 °C and 25 °C for 1/urea (Figure 3b). At –60 °C, the final refinement of the X-ray data¹⁵ matches the NMR model quite well, whereas at 25 °C the structural model for the guest is less well determined. Between –60 and 25 °C, the increased population of the minor conformer tends to equalize the anisotropic stress on the channel walls and shifts the inclusion compound toward the undistorted structure. Similar reorientational processes should control domain switching in a number of ferroelastic UICs.

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Supporting Information Available: Sample preparation and characterization, DSC traces, and tables giving crystallographic data for five structures of 1–3/urea (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) This is also confirmed by low-temperature ²H NMR, in which the spectra are in the intermediate time scale regime. See: Greenfield, M. S.; Ronemus, A. D.; Vold, R. L.; Vold, R. R.; Ellis, P. D.; Raidy, T. E. *J. Magn. Reson.* **1987**, *72*, 89–107.

(14) van't Hoff plots for α ($\Delta H^\circ = 2.0 \text{ kcal mol}^{-1}$, $R^2 = 0.987$, $n = 13$), β ($\Delta H^\circ = 2.0 \text{ kcal mol}^{-1}$, $R^2 = 0.978$, $n = 12$), and γ ($\Delta H^\circ = 2.3 \text{ kcal mol}^{-1}$, $R^2 = 0.995$, $n = 13$), from spectral fits for jump angles of 62° (α), 109° (β), and 109° (γ), predict a 94:6 conformer ratio at –60 °C. The crystal structure at –60 °C¹⁵ gives jumps of 65.5° (α), 100.6° (β), and 93.8° (γ).

(15) Crystal data for 1/urea (both are monoclinic, space group $P2_1/n$): At –60 °C, $a = 8.6102(5) \text{ \AA}$, $b = 10.9148(7) \text{ \AA}$, $c = 13.5102(8) \text{ \AA}$, $\beta = 92.752(1)^\circ$, $V = 1268.2(1) \text{ \AA}^3$; $R1(\text{on } F_o^2) = 0.033$, $wR2(\text{on } F_o^2) = 0.0657$, $\text{GOF}(\text{on } F_o^2) = 2.017$, 3034 obsd $wI \geq 2.00\sigma(I)$, 155 parameters when the population of the major guest conformer is fixed at 94%. At 25 °C, $a = 8.6235(8) \text{ \AA}$, $b = 10.9426(11) \text{ \AA}$, $c = 13.6622(14) \text{ \AA}$, $\beta = 92.549(2)^\circ$, $V = 1287.9(2) \text{ \AA}^3$; $R1(F^2) = 0.0691$, $wR2(\text{on } F_o^2) = 0.0793$, $\text{GOF}(\text{on } F_o^2) = 1.929$, 2110 obsd $wI \geq 2.00\sigma(I)$, 156 parameters.