Representing and understanding geometric features of one-dimensional tunnel structures in solid inclusion compounds

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A computational method is presented for probing geometric, topological, and structural characteristics of one-dimensional tunnel structures in solid inclusion compounds. The method is illustrated for the urea and thiourea inclusion compounds, highlighting important structural differences between the urea and thiourea tunnel structures, and potential areas of application of the methodology are discussed.

INTRODUCTION

Considerable attention has been devoted to studies of those solid inclusion compounds in which the "host" solid contains one-dimensional tunnels; materials in this category include certain zeolites as well as several crystalline organic inclusion compounds such as those containing urea or thiourea as the host.[1-3] There is currently considerable interest in the chemistry and physics of these materials, motivated, in part, by the desire to understand the structural, dynamic, and chemical properties of organic "guest" molecules constrained within solid state environments. In this article we present a straightforward computational method for representing and understanding geometric features of those solid inclusion compounds in which the "host" structure contains one-dimensional tunnels. The application of this method is illustrated for the tunnel structures in the urea and thiourea inclusion compounds.
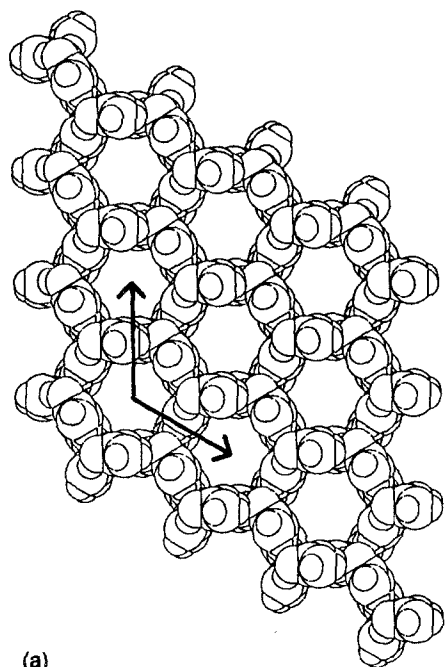
In conventional urea inclusion compounds,[4,5] the urea molecules form an extensively hydrogen-bonded arrangement (Figure 1) that contains linear, parallel tunnels running the length of the crystal. This host tunnel structure is stable only if guest molecules are densely packed along the tunnels. Urea crystallizes in this tunnel structure only in the presence of appropriate guest molecules, and the guest molecules therefore serve as a template for construction of the urea tunnel structure. Structural compatibility between host and guest components is a fundamental requirement for the formation of most inclusion systems, and urea will only form inclusion compounds with guest molecules that are based on a sufficiently long n-alkane chain, with a further requirement that the degree of substitution of this chain must be small. Appropriate guest molecules include n-alkanes and certain derivatives such as α,ω-dihalogenoalkanes, diacyl peroxides, carboxylic acids, and carboxylic acid anhydrides. The urea tunnel structure is unstable[6-8] if the guest molecules are removed from the inclusion compound (the urea then transforms to its "pure" crystalline phase, which does not contain empty tunnels). Thus, appropriate guest molecules are required as an essential template for the construction of the host structure and as an essential buttress in maintaining the existence of the host structure.

Thiourea also crystallizes in a tunnel structure in the presence of appropriate guest molecules, and these tunnels have a larger cross-section than those in urea inclusion compounds. As a consequence of this fact, and other structural differences between these tunnels (vide infra), the urea and thiourea host structures preferentially accommodate different types of guest molecule. The thiourea tunnel structure, for example, can include guest molecules such as cyclohexane, certain derivatives of cyclohexane, ferrocene and other organometallics, and certain compounds containing a ben-

(a)
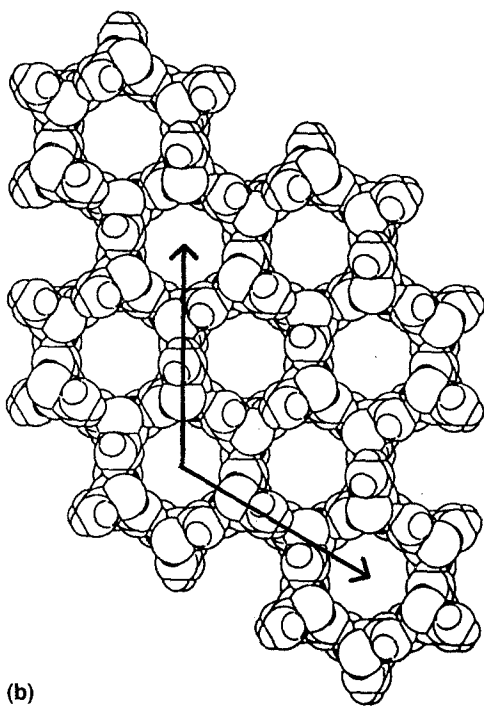
(b)

Figure 1. (a) Representation with van der Waals radii showing nine complete tunnels of the host structure in conventional urea inclusion compounds, viewed along the tunnel axis (c_h). The vectors shown define a_h and b_h. Note: $|a_h| = |b_h| \approx 8.23$ Å; $|c_h| \approx 11.02$ Å (space group $P6_122$). (b) Representation with van der Waals radii showing nine complete tunnels of the host structure in conventional thiourea inclusion compounds, viewed along the tunnel axis (c_h). The vectors shown define a_h and b_h. Note: $|a_h| = |b_h| \approx 15.97$ Å; $|c_h| \approx 12.48$ Å (hexagonal setting of space group $R\bar{3}c$). Note that, in the real inclusion compounds, the tunnels of these host structures are filled with a dense packing of guest molecules (not shown).

zene ring—such guest molecules do not generally form inclusion compounds with urea.

Detailed information, established from empirical observations, on the characteristic features of the guest molecules that form inclusion compounds with urea and thiourea have been elucidated previously.[1,9–12]

Even though the three-dimensional host structure of a solid inclusion compound is known from diffraction data, there are considerable difficulties in representing the inclusion topology adequately in a two-dimensional representation (as on a conventional printed page). For example, simply viewing the structure projected down the tunnel axis (as in Figure 1) will not reveal depressions, grooves, or crevices that may exist in the surface of the tunnel. It is important to note that such features may have an important bearing on the ability of the tunnel structure to accommodate particular types of guest molecule and on the structural and dynamic properties of these guest molecules. Similarly, a "cut-away" view of the tunnel structure (i.e., a view perpendicular to the tunnel axis in which, say, the front wall of the tunnel has been removed) is unsatisfactory in several respects, not least because it provides only a partial description of the structure. In this article we present a computational method for representing and understanding geometric features of those solid inclusion compounds in which the host structure contains one-dimensional tunnels, and the application of this method is illustrated for the tunnel structures in the urea and thiourea inclusion compounds.

METHODOLOGY

To describe geometric features of the host structures in one-dimensional inclusion compounds in a manner that is simple and readily interpreted, we represent the van der Waals surface of the tunnel in terms of cylindrical polar coordinates r, θ, and z, where θ represents rotation angle about the tunnel axis (θ defined in the range 0–360°), z represents position along the tunnel axis, and r represents the "radius" of the tunnel (i.e., the distance between the center of the tunnel and the van der Waals surface of the tunnel) (Figure 2). An understanding of geometric characteristics of the host tunnel structure is obtained from a contour plot in which r is represented as a function of θ and z. As illustrated below, the symmetry of such a contour plot arises directly from the crystallographic symmetry of the host tunnel structure. From this contour plot, the geometric and topological
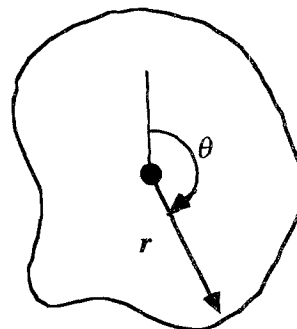

Figure 2. Diagram defining r and θ for a particular value of z.

characteristics of the tunnel structure can be interpreted readily.

In some applications, it may be more convenient to consider the diameter (d) of the tunnel as a function of θ and z (with θ now defined in the range 0–180°). Thus,

$$d(\theta, z) = r(\theta, z) + r(\theta + 180°, z) \qquad (1)$$

Consideration of the diameter of the tunnel gives particular emphasis to the steric nature of the tunnel structure. Thus, for example, a sinusoidal tunnel with a given cross-sectional shape (which may vary as a function of z) will give the same contour plot as a straight tunnel possessing the same cross-sectional shape (as a function of z). Thus, while some information concerning the overall topology of the tunnel structure is lost in considering the diameter of the tunnel, this approach may in some cases provide a more direct insight into the space available for guest molecules within the tunnel.

Further structural properties may be derived from the $r(\theta, z)$ data, including the maximum and minimum tunnel diameters, as a function of z, as defined by

$$d_{max}(z) = \overset{max}{\underset{\theta}{}} \{d(\theta, z)\} \qquad (2)$$

$$d_{min}(z) = \overset{min}{\underset{\theta}{}} \{d(\theta, z)\} \qquad (3)$$

However, the fact that the van der Waals surface of a tunnel will generally contain "holes" leads to values of $d(\theta, z)$ that are essentially infinite for certain combinations of θ and z, and, as a consequence, $d_{max}(z)$ is not straightforward to consider. Alternative approaches of mapping the structural features of the tunnel are essential for a physically meaningful interpretation of a "maximum tunnel diameter." Such an approach, not pursued here, could consider the space available to a probe sphere within the host tunnel structure. The function $d_{min}(z)$, on the other hand, has a well-defined interpretation, as illustrated below in the discussion of structural properties of the urea and thiourea tunnel structures.

APPLICATION OF THE METHODOLOGY

To illustrate the application of the methods described above, we consider the host tunnel structures in the conventional urea and thiourea inclusion compounds. The published crystal structures for the urea substructure in the hexadecane/urea inclusion compound[5] and the thiourea substructure in the chlorocyclohexane/thiourea inclusion compound[13] were used in this work. The van der Waals surfaces of the tunnels in these structures were computed using the following van der Waals radii: $r_{vdw}(C) = 1.55$ Å; $r_{vdw}(N) = 1.40$ Å; $r_{vdw}(H) = 1.10$ Å; $r_{vdw}(O) = 1.32$ Å; $r_{vdw}(S) = 1.81$ Å.

For each tunnel structure, the tunnel "radius" r was determined as a function of θ and z for θ in the range 0–360° and with z in the range 0–11.1 Å (urea) and 0–12.5 Å (thiourea). In each case, the range of z corresponds to translation by just over one lattice vector of the host structure along the tunnel axis. In all calculations, θ and z were sampled in increments of $\Delta\theta = 2°$ and $\Delta z = 0.1$ Å. Contour plots representing r as a function of θ and z are shown in Color Plate 1a and b for the urea and thiourea tunnel structures, respectively. Contour plots representing d as a

function of θ and z are shown in Color Plate 2a and b for the urea and thiourea tunnel structures, respectively.

We focus first on the $r(\theta, z)$ contour plot for the urea tunnel structure (Color Plate 1a). The plot clearly reflects the $P6_122$ symmetry of the urea tunnel structure. The 6_1 screw axis is apparent from the fact that equivalent points on the contour plot are obtained for 60° rotation in θ combined with translation by $|c_h|/6$ ($|c_h| = 11.017$ Å) along the tunnel axis [i.e., $r(\theta, z) = r(\theta + 60°, z + |c_h|/6)$]. It is clear from the $r(\theta, z)$ contour plot that the screw is right handed. Twofold symmetry axes perpendicular to the tunnel axis are represented on the contour plot by points at those positions at which the twofold axis intersects the surface of the tunnel, and, for example, the point at $\theta = 240°$ and $z = 4.59$ Å ($z = 5/12$ in fractional coordinates) represents a twofold axis. We consider now the $d(\theta, z)$ contour plot for the urea tunnel structure (Color Plate 2a). We note first that the procedure for calculating d [Eq. (1)] essentially adds symmetry to the contour plot, as a consequence of which we consider only values of θ in the range 0–180°. It can be seen that the range of tunnel diameters represented on this contour plot is comparatively small, consistent with the notion that the urea tunnel is actually rather "smooth," with no major bulges or constrictions. This is also seen readily from Figure 3, which shows a plot of $d_{min}(z)$ versus z for the urea tunnel structure. From this plot, the minimum tunnel diameter fluctuates only between ca. 5.5 and 5.8 Å on moving along the tunnel.

We now consider the $r(\theta, z)$ contour plot for the thiourea tunnel structure (Color Plate 1b). For the $R\bar{3}c$ symmetry of this structure, the origin is defined by a center of symmetry lying on the tunnel axis (z axis), and there is also a center of symmetry on the tunnel axis at $(0, 0, \frac{1}{2})$. In general, if a center of symmetry lies on the tunnel axis at $(0, 0, z_c)$, then the $r(\theta, z)$ contour plot is such that $r(\theta, z_c + \Delta) = r(\theta + 180°, z_c - \Delta)$ for any Δ. This is seen clearly in the plot for the thiourea tunnel structure for $z_c = 0$ and $z_c = \frac{1}{2}$. In addition, the threefold rotation axis lying along the tunnel axis manifests itself as the relationship $r(\theta, z) = r(\theta + 120°, z) = r(\theta + 240°, z)$, for any value of z. Again, this symmetry is observed directly in the $r(\theta, z)$ contour plot. It is clear from the $d(\theta, z)$ contour plot for the thiourea tunnel structure (Color Plate 2b) that a considerably wider range of d values is represented for the thiourea tunnel structure than for the urea tunnel structure. There are prominent constrictions in the tunnel at $z \approx 0$ and $z \approx \frac{1}{2}$, whereas between these values there are bulges corresponding to significantly larger values of d. This is readily apparent from the plot of $d_{min}(z)$ versus z (Figure 3), with d_{min} ranging from ca. 5.8 Å at the constrictions to ca 7.1 Å (at maximum) at the bulges. This large fluctuation in the tunnel diameter on moving along the thiourea tunnel suggests that, in some respects, the thiourea tunnel structure may be better considered as a "cage" type host rather than a "tunnel" type host.

CONCLUDING REMARKS

The structural representation developed in this article provides a convenient and straightforward means of assessing the potential for a given type of guest molecule to fit within a host tunnel for which the crystal structure is known. At the level presented here, the method provides a visual assess-
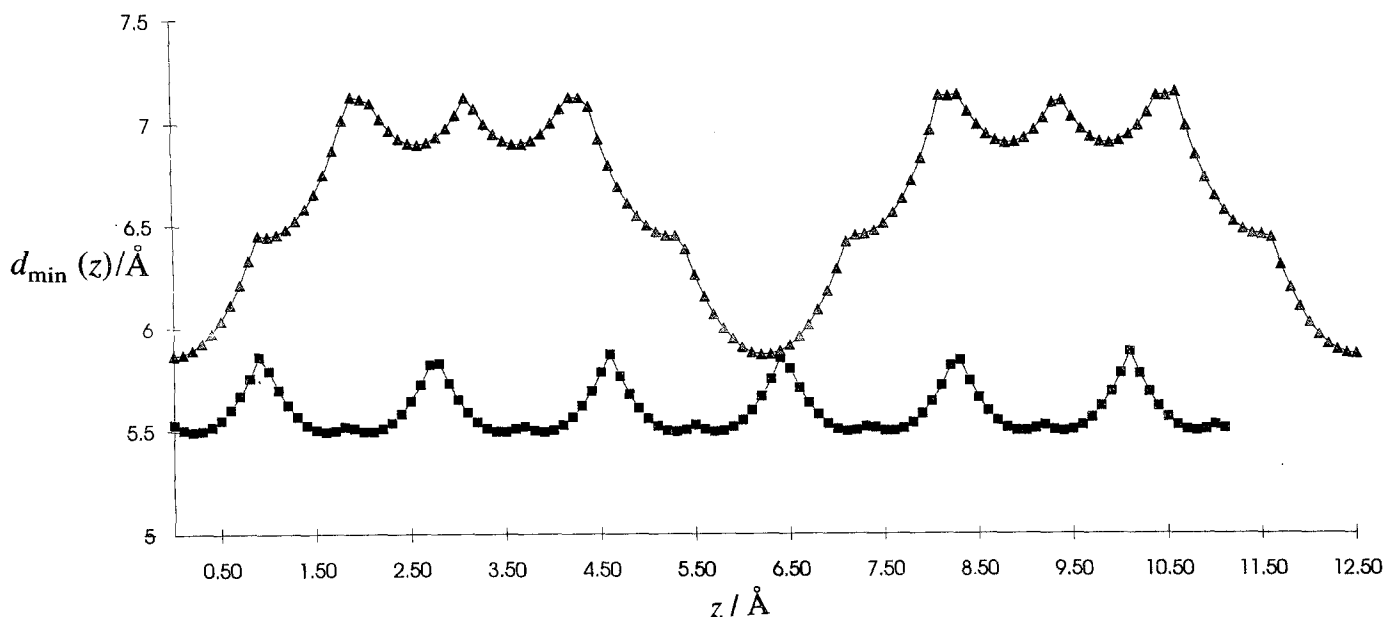
Figure 3. The minimum tunnel diameter, d_{min}, as a function of z, for (■) the urea tunnel structure and (▲) the thiourea tunnel structure. In both cases, the range of z considered in the graph corresponds to just over one lattice period of the host structure along the tunnel axis.

ment of structural and topological features of the host tunnel structures in a manner that can be readily interpreted. Clearly the method could be extended to encompass more sophisticated approaches for assessing the match between the van der Waals surface of the tunnel and the van der Waals surface of the guest molecule in order to assess the optimum positional and orientational characteristics of the guest molecule inside the tunnel. However, we emphasize here that such an approach would provide, at best, only a crude assessment of these structural characteristics, as other factors (such as electrostatic interaction between host and guest, and guest–guest interaction) must be considered in a rigorous assessment of the optimum positional and orientational characteristics of the guest molecules. Thus, for many solid inclusion compounds, consideration of only a single guest molecule within the host tunnel structure is often not a valid approach for predicting structural properties of the guest molecules in the inclusion compound.

The method reported here for representing the host tunnel structures of solid inclusion compounds has considerable potential as a means of representing structural perturbations of host tunnel structures that can occur when guest molecules are included inside the tunnels. We aim to exploit the technique in this way in our future research in this area.

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