

Characterization of Intermolecular Interactions in a Disordered Solid via a One-Dimensional Patterson Synthesis

Mao-Hsun Chao, Kenneth D. M. Harris,* Benson M. Kariuki, Clare L. Bauer, and Bruce M. Foxman†

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

Received: November 27, 2001; In Final Form: February 4, 2002

We report the application of a one-dimensional Patterson analysis of diffuse X-ray scattering from the 1,8-diiodooctane/urea inclusion compound to obtain information on the intermolecular interaction between the iodine end groups of adjacent 1,8-diiodooctane guest molecules within the urea tunnel host structure in this inclusion compound. One aspect of the X-ray scattering from the guest component in this incommensurate inclusion compound comprises diffuse sheets perpendicular to the host tunnel axis, and we consider measurements of the intensity, $I(l_g)$, obtained from one-dimensional scans perpendicular to the diffuse sheets in reciprocal space (each diffuse sheet is specified by integer l_g). The one-dimensional Patterson map constructed from $I(l_g)$ has a dominant peak at ca. 3.94 Å, which is interpreted as the projection, on to the tunnel axis, of the intermolecular I...I distance. This value of $D_z(\text{I}\cdots\text{I})$ is shown to be consistent with a model in which the iodine end groups are in van der Waals contact with the I → I vector lying essentially parallel to the tunnel axis. We emphasize that this well-defined structural information has been obtained despite the substantial disorder in this system.

Introduction

Urea inclusion compounds, which have received considerable attention in recent years,^{1–4} exhibit a broad range of fundamental physicochemical phenomena, including incommensurate structural properties,^{5–10} order–disorder phase transitions,^{11–15} molecular motion,^{16–21} properties relating to one-dimensional confinement,^{22–24} and ferroelastic properties.²⁵ In these solid inclusion compounds, the *host* structure^{1,5} comprises a hydrogen-bonded arrangement of urea molecules and contains one-dimensional, continuous, parallel tunnels. These tunnels are filled with a dense packing of *guest* molecules. The “conventional” urea inclusion compounds are characterized by the following: (i) a hexagonal host tunnel structure ($P6_122$ or $P6_522$), (ii) an incommensurate relationship²⁶ between the periodicities of the host and guest substructures along the tunnel, and (iii) substantial dynamic disorder (reorientation about the tunnel axis) of the guest molecules at ambient temperature. In most cases, order–disorder phase transitions occur below ambient temperature and are associated with a distortion of the host tunnel and a concomitant decrease in the reorientational motion of the guest molecules.

An important local structural property of urea inclusion compounds is the interaction between adjacent guest molecules within the tunnel, and clearly many properties are influenced by the nature of this interaction. However, for a number of reasons, including the dynamic disorder of the guest molecules, a conventional structure determination of the guest structure from diffraction data has not so far been possible for a conventional urea inclusion compound, and thus, no detailed structural information on the nature of the guest–guest interac-

tions has been obtained. Nevertheless, a number of local structural probes have been used to investigate this issue, on the basis that well-defined local guest–guest interactions may exist despite the disorder of the guest molecules with respect to the host structure. However, bromine K-edge extended X-ray absorption fine structure (EXAFS) experiments²⁷ on $\text{Br}(\text{CH}_2)_n\text{Br}$ /urea inclusion compounds ($n = 7–11$) were unable to establish the $\text{Br}\cdots\text{Br}$ distance at any temperature within the range from ambient temperature to 9 K. In another approach, high-resolution solid-state ^{19}F NMR studies²⁸ were carried out on $\text{F}(\text{CH}_2)_{10}\text{F}$ /urea to probe the $^{19}\text{F}\cdots^{19}\text{F}$ dipole–dipole interaction and hence to estimate the $^{19}\text{F}\cdots^{19}\text{F}$ distance. However, the analysis was complicated both by conformational disorder (the ^{19}F end group may be in *gauche* or *trans* positions with respect to the alkane chain, leading to *trans*–*trans*, *trans*–*gauche*, and *gauche*–*gauche* situations between adjacent end groups) and by the need to consider disorder of the guest molecules with respect to reorientation about the tunnel axis.

In the present work, we propose (and demonstrate the success of) a different approach for determining information directly on the guest–guest interactions in urea inclusion compounds, based on analysis of the intensity distribution of diffuse sheets in the X-ray diffraction pattern. First, we consider salient features of the X-ray diffraction patterns of conventional urea inclusion compounds, details of which are discussed elsewhere.⁵ The incommensurate relationship between the host and guest substructures in urea inclusion compounds gives rise to two distinguishable diffraction patterns (denoted “h” and “g”). The “h” diffraction pattern arises from diffraction by the basic host structure (and by the incommensurate modulation within the guest substructure), and the “g” diffraction pattern arises from diffraction by the basic guest structure (and by the incommensurate modulation within the host substructure). For conventional urea inclusion compounds, the “h” diffraction pattern comprises intense Bragg diffraction maxima, whereas the “g”

* To whom correspondence should be addressed. Telephone: +44-121-414-7474. FAX: +44-121-414-7473. E-mail: K.D.M.Harris@bham.ac.uk.

† Permanent Address: Department of Chemistry, Brandeis University, Mail Stop 015, P.O. Box 549110, Waltham, MA 02454-9110.

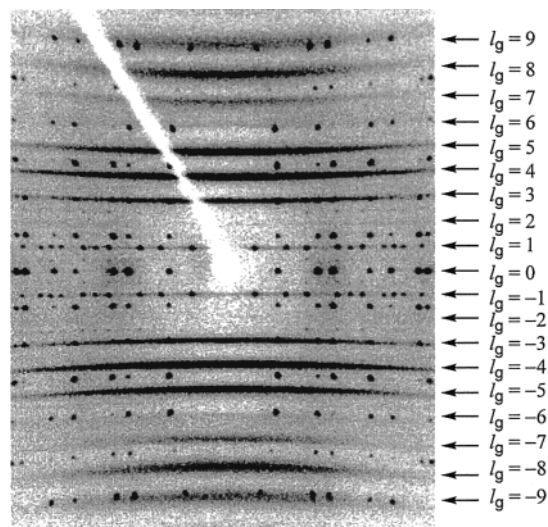


Figure 1. Single-crystal X-ray diffraction photograph recorded at ambient temperature for the 1,8-diiodooctane/urea inclusion compound rotating about the tunnel axis (Rigaku R-Axis II; Mo K α radiation; image plate detector). Layer lines of the “g” diffraction pattern comprise diffuse sheets labeled by integer l_g . For low l_g values, weak Bragg maxima are superimposed on these diffuse sheets. The layer lines of the “h” diffraction pattern (comprising intense Bragg maxima) occur between these layer lines of the “g” diffraction pattern.

diffraction pattern generally comprises both weak Bragg diffraction maxima and diffuse scattering (see Figure 1). In this paper, we focus on the diffuse scattering in the “g” diffraction pattern, which takes the form of two-dimensional sheets perpendicular to the tunnel axis (in direct space).²⁹ Such diffuse scattering arises from a one-dimensional diffraction grating, corresponding in the present case to ordering of the guest molecules only in one dimension (along the tunnel axis). Thus, analysis of the diffuse sheets provides information on the structural properties of the periodic linear array of guest molecules along an individual tunnel. For example,⁵ the periodic repeat distance, c_g , of the guest molecules along the tunnel may be determined from the periodic spacing of the diffuse sheets in reciprocal space. The value $c_g = 16.30 \text{ \AA}$ in the present case²⁶ corresponds to one 1,8-diiodooctane molecule within the repeat unit of the linear array of guest molecules along the tunnel axis.

Methodology

In this paper, we focus on analysis of the intensity distribution of the diffuse scattering, specifically by considering the intensity $I(l_g)$ as a function of l_g for fixed h and k , where l_g specifies the direction perpendicular to the sheets (and takes an integer value for each diffuse sheet) and h and k (which may take any value) specify position *within* the sheet. Within the approximation of a one-dimensional diffraction grating for the guest substructure, $I(l_g)$ depends on the structural properties of the one-dimensional array of guest molecules projected on to the tunnel axis (z -axis) in direct space. Thus, in a one-dimensional Patterson map,

$$P_z(w) = \frac{1}{c_g} \sum_{l_g} I(l_g) \exp(2\pi i l_g w) \quad (1)$$

constructed from experimental values of $I(l_g)$, the peaks correspond to the projections, onto the tunnel axis, of the interatomic distances within one repeat unit of the linear array of guest molecules.

In our preliminary work to demonstrate the application of this approach, we have focused on the 1,8-diiodooctane guest

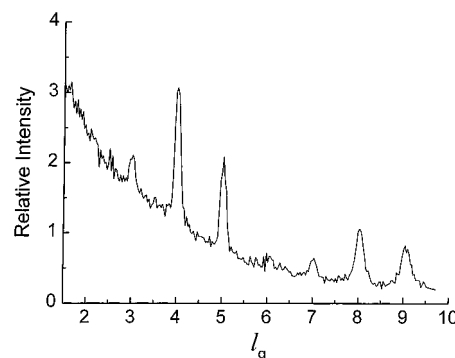


Figure 2. $(0.2, 0.2, l_g)$ scan recorded for 1,8-diiodooctane/urea at 150 K. The peaks representing the diffuse sheets of the “g” diffraction pattern occur at integer values of l_g .

molecule for two reasons: (i) the Patterson map will be dominated by the peak due to the $I\cdots I$ interaction, and (ii) previous Raman studies³⁴ have shown that 1,8-diiodooctane/urea has a negligible amount of conformational disorder (ca. 99% trans end groups), leading to a dominant trans–trans situation for adjacent end groups. For 1,8-diiodooctane/urea, the Patterson map, $P_z(w)$, should be dominated by the projection on the tunnel axis [denoted $D_z(I\cdots I)$] of the intermolecular $I\cdots I$ distance [denoted $D(I\cdots I)$].

Experimental Section

The 1,8-diiodooctane/urea inclusion compound was prepared by slowly cooling a solution containing 1,8-diiodooctane and urea in methanol. Powder and single-crystal X-ray diffraction indicated that the crystals have the conventional urea tunnel structure. The diffuse sheets in the “g” diffraction pattern are evident in the single-crystal rotation photograph shown in Figure 1. To measure $I(l_g)$, single-crystal X-ray diffraction experiments were performed (with $\lambda = 1.000 \text{ \AA}$) on Station 16.3³⁵ at the Synchrotron Radiation Source, Daresbury Laboratory. Station 16.3 is a high-resolution, high-energy facility based on a six-circle diffractometer equipped with a solid-state detector. A standard Oxford Cryostream was used for temperature control below ambient temperature. Measurements of $I(l_g)$ involved continuous one-dimensional scans through reciprocal space as a function of l_g for fixed h and k . We note that some scans of this type [e.g., $(0, 0, l_g)$] are complicated by the fact that Bragg diffraction maxima from the “h” or “g” diffraction patterns or both occur for certain values of l_g (noninteger values in the case of Bragg peaks of the “h” diffraction pattern), and we have focused on two specific scans $(0.2, 0.2, l_g)$ and $(1.2, 0.2, l_g)$ for which it is known that no Bragg peaks are encountered. The range of l_g scanned was 0 to 9.75, with a total scan time of ca. 40 min. The $I(l_g)$ data were obtained by integration of the peaks in the scan (Figure 2), and the one-dimensional Patterson map was calculated using eq 1. In general, values of $I(l_g)$ could be extracted reliably from these scans for $l_g = 3$ –9 (reliable information on $l_g = 1$ and 2 could not be obtained due to the high background at low l_g evident from Figure 2).

Results and Discussion

Figure 3 shows the one-dimensional Patterson maps calculated from the $(0.2, 0.2, l_g)$ and $(1.2, 0.2, l_g)$ scans at 150 K. In each case, there is a dominant peak at ca. 3.91 \AA , which is interpreted as $D_z(I\cdots I)$. Similar $(0.2, 0.2, l_g)$ and $(1.2, 0.2, l_g)$ scans were recorded at several temperatures in the ranges 293–100 K and 170–100 K, respectively. In all cases, the dominant peak lies

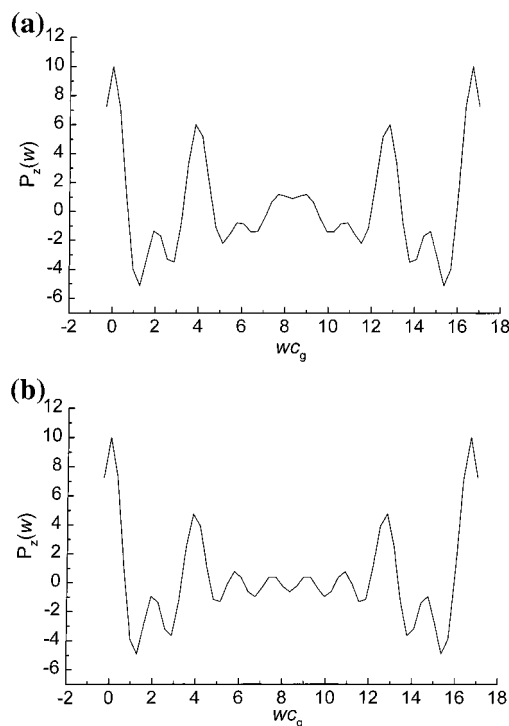


Figure 3. One-dimensional Patterson maps, $P_z(w)$, for 1,8-diiodooctane/urea calculated (a) from the (0.2, 0.2, l_g) scan at 150 K and (b) from the (1.2, 0.2, l_g) scan at 150 K.

within the range 3.86–4.02 Å.³⁶ The results do not reveal any systematic variation in $D_z(\text{I}\cdots\text{I})$ as a function of temperature, although we note that the experimental uncertainty in the determination of $D_z(\text{I}\cdots\text{I})$ is probably comparable to the variation that may be expected as a function of temperature. In the high-temperature phase ($T > 133$ K for 1,8-diiodooctane/urea), there is rapid reorientation of the guest molecules about the tunnel axis, and it is clear from the one-dimensional Patterson map that a well-defined intermolecular $\text{I}\cdots\text{I}$ distance is maintained despite this dynamic disorder. Thus, while there is considerable disorder within the guest substructure in a three-dimensional sense, the one-dimensional projection onto the tunnel axis of the linear array of guest molecules within a given tunnel is sufficiently well-ordered to give the well-defined value of $D_z(\text{I}\cdots\text{I})$ observed.

We now consider in more detail the values of $D_z(\text{I}\cdots\text{I}) \approx 3.94$ Å (median value) obtained experimentally, noting first that they are consistent with the interaction between adjacent iodine end groups being in van der Waals contact (the widely accepted value for the van der Waals radius of iodine is 1.98 Å³⁷). However, we emphasize that the value of $D_z(\text{I}\cdots\text{I})$ depends both on the distance $D(\text{I}\cdots\text{I})$ and on the angle between the $\text{I} \rightarrow \text{I}$ vector and the tunnel axis. Considering that the iodine end groups are indeed in van der Waals contact, we obtain two extreme situations shown in Figure 4, in which two spheres (representing the iodine atoms) of radius R are located within a rigid cylinder (representing the urea tunnel) of diameter D_c . The distance between the centers of the spheres is denoted D_s , and the projection on the cylinder axis is denoted D_{sz} . For the two spheres in contact, $D_s = 2R$. The maximum value of D_{sz} is $D_{sz}^{\text{max}} = D_s = 2R$ and corresponds to a situation (Figure 4a) in which the $\text{I} \rightarrow \text{I}$ vector is parallel to the tunnel axis. The minimum value of D_{sz} (obtained when the spheres are in contact with “opposite” walls of the cylinder, Figure 4b) is $D_{sz}^{\text{min}} = \sqrt{(2R)^2 - (D_c - 2R)^2}$. Taking $R = 1.98$ Å as the van der

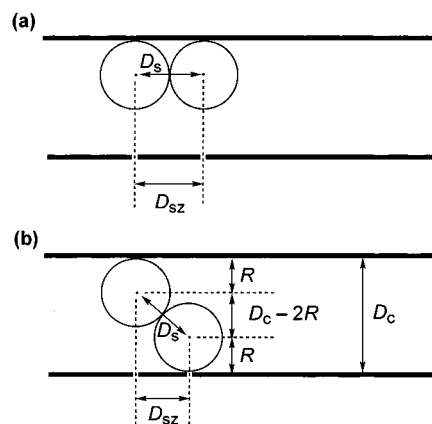


Figure 4. Models representing two iodine end groups in van der Waals contact within the host tunnel structure, with (a) the maximum value of D_{sz} ($\text{I} \rightarrow \text{I}$ vector essentially parallel to the tunnel axis) and (b) the minimum value of D_{sz} . The thick horizontal lines represent (schematically) the walls of the urea host tunnel, and the two circles represent the iodine end groups of adjacent 1,8-diiodooctane guest molecules. The tunnel diameter is denoted D_c , and the van der Waals radius of iodine is denoted R . The distance between the centers of the iodine atoms on adjacent guest molecules is denoted D_s , and the projection of this distance on to the tunnel axis is denoted D_{sz} .

Waals radius of iodine and taking D_c to range from 5.5 to 5.8 Å, corresponding to the minimum and maximum diameter of the urea tunnel,³⁸ we obtain $D_{sz}^{\text{max}} = 3.96$ Å and $D_{sz}^{\text{min}} = 3.51 - 3.65$ Å. Clearly, our measured values of $D_z(\text{I}\cdots\text{I})$ suggest that the actual experimental situation lies closer to the extreme shown in Figure 4a. We note that if the iodine end groups distort the tunnel wall slightly (to give locally a slightly larger value of D_c), the value of D_{sz}^{min} should be decreased further, whereas the value of D_{sz}^{max} should be unaffected.

Concluding Remarks

In summary, our one-dimensional Patterson analysis of the diffuse scattering from the 1,8-diiodooctane/urea inclusion compound is consistent with the existence of a well-defined intermolecular interaction between the iodine end groups, and the value of $D_z(\text{I}\cdots\text{I})$ obtained is consistent with a model in which the iodine end groups are in van der Waals contact. Further, on the assumption of van der Waals contact, our experimental results suggest that the $\text{I} \rightarrow \text{I}$ vector lies essentially parallel to the tunnel axis. We emphasize that this well-defined structural information [i.e., $D_z(\text{I}\cdots\text{I})$] has been obtained despite the substantial disorder in this system, which has hitherto precluded a conventional structure determination of the guest component in conventional urea inclusion compounds. Indeed, the fact that a well-defined $\text{I}\cdots\text{I}$ distance is observed has important implications concerning the extent to which the motions of adjacent guest molecules within the urea tunnel structure are correlated with one another. This aspect and other issues relating to the results obtained from such one-dimensional Patterson analysis of the diffuse X-ray scattering from urea inclusion compounds will be discussed in more detail elsewhere.³⁹ Clearly, there is considerable scope to apply similar methodology to characterize intermolecular interactions in other disordered systems.

Acknowledgment. We are grateful to EPSRC (grant to K.D.M.H.) for financial support, including the award of beamtime on Station 16.3 at Daresbury Laboratory, to Drs. Steve

Collins and Bridget Murphy for assistance in the use of this facility, and to the National Science Foundation (Grant No. DMR-0089257 to B.M.F.) for partial support of this research.

References and Notes

- (1) Smith, A. E. *Acta Crystallogr.* **1952**, 5, 224.
- (2) Fetterly, L. C. In *Nonstoichiometric Compounds*; Mandelcorn, L., Ed.; Academic Press: New York, 1964; p 491.
- (3) Hollingsworth, M. D.; Harris, K. D. M. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon Press: New York, 1996; Vol. 6, p 177.
- (4) Guillaume, F. *J. Chim. Phys. (Paris)* **1999**, 96, 1295.
- (5) Harris, K. D. M.; Thomas, J. M. *J. Chem. Soc., Faraday Trans.* **1990**, 86, 2985.
- (6) Rennie, A. J. O.; Harris, K. D. M. *Proc. R. Soc. London, Ser. A* **1990**, 430, 615.
- (7) Harris, K. D. M.; Hollingsworth, M. D. *Proc. R. Soc. London, Ser. A* **1990**, 431, 245.
- (8) van Smaalen, S.; Harris, K. D. M. *Proc. R. Soc. London, Ser. A* **1996**, 452, 677.
- (9) Lefort, R.; Etrillard, J.; Toudic, B.; Guillaume, F.; Breczewski, T.; Bourges, P. *Phys. Rev. Lett.* **1996**, 77, 4027.
- (10) Weber, T.; Boysen, H.; Frey, F.; Neder, R. B. *Acta Crystallogr., Sect. B* **1997**, 53, 544.
- (11) Parsonage, N. G.; Pemberton, R. C. *Trans. Faraday Soc.* **1967**, 63, 311.
- (12) Fukao, K. *J. Chem. Phys.* **1990**, 92, 6867.
- (13) Lynden-Bell, R. M. *Mol. Phys.* **1993**, 79, 313.
- (14) Yeo, L.; Kariuki, B. M.; Serrano-González, H.; Harris, K. D. M. *J. Phys. Chem. B* **1997**, 101, 9926.
- (15) Le Lann, H.; Odin, C.; Toudic, B.; Ameline, J. C.; Gallier, J.; Guillaume, F.; Breczewski, T. *Phys. Rev. B* **2000**, 62, 5442.
- (16) Casal, H. L.; Cameron, D. G.; Kelusky, E. C. *J. Chem. Phys.* **1984**, 80, 1407.
- (17) Harris, K. D. M.; Jonsen, P. *Chem. Phys. Lett.* **1989**, 154, 593.
- (18) El Baghdadi, A.; Dufour, E. J.; Guillaume, F. *J. Phys. Chem.* **1996**, 100, 1746.
- (19) Guillaume, F.; Sourisseau, C.; Dianoux, A.-J. *J. Chim. Phys. (Paris)* **1991**, 88, 1721.
- (20) Smart, S. P.; Guillaume, F.; Harris, K. D. M.; Dianoux, A.-J. *J. Phys.: Condens. Matter* **1994**, 6, 2169.
- (21) Girard, P.; Aliev, A. E.; Guillaume, F.; Harris, K. D. M.; Hollingsworth, M. D.; Dianoux, A.-J.; Jonsen, P. *J. Chem. Phys.* **1998**, 109, 4078.
- (22) Hollingsworth, M. D.; Cyr, N. *Mol. Cryst. Liq. Cryst.* **1990**, 187, 135.
- (23) Harris, K. D. M.; Jupp, P. E.; Lee, S.-O. *J. Chem. Phys.* **1999**, 111, 9784.
- (24) Khan, A. A.; Bramwell, S. T.; Harris, K. D. M.; Kariuki, B. M.; Truter, M. R. *Chem. Phys. Lett.* **1999**, 307, 320.
- (25) Brown, M. E.; Hollingsworth, M. D. *Nature* **1995**, 376, 323.
- (26) The relationship between the periodicity (denoted c_h) of the host structure along the tunnel and the periodicity (denoted c_g) of the guest molecules along the tunnel is incommensurate if there are no sufficiently small integers m and n that satisfy the relationship: $mc_g = nc_h$. Thus, c_g/c_h is not equal to a rational number with sufficiently small denominator. The nature of incommensurate versus commensurate behavior in tunnel inclusion compounds is discussed in refs 6 and 8. For 1,8-diiodooctane/urea at ambient temperature, $c_h = 11.02$ Å and $c_g = 16.30$ Å.
- (27) Shannon, I. J.; Harris, K. D. M.; Mahdyarfar, A.; Johnston, P.; Joyner, R. W. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 3099.
- (28) Nordon, A.; Hughes, E.; Harris, R. K.; Yeo, L.; Harris, K. D. M. *Chem. Phys. Lett.* **1998**, 289, 25.
- (29) Additional forms of diffuse scattering (which are generally weaker than the diffuse sheets discussed above) have also been reported [refs 30–33].
- (30) Forst, R.; Jagodzinski, H.; Boysen, H.; Frey, F. *Acta Crystallogr., Sect. B* **1987**, 43, 187.
- (31) Fukao, K. *J. Chem. Phys.* **1994**, 101, 7882.
- (32) Fukao, K. *J. Chem. Phys.* **1994**, 101, 7893.
- (33) Welberry, T. R.; Mayo, S. C. *J. Appl. Crystallogr.* **1996**, 29, 353.
- (34) Smart, S. P.; El Baghdadi, A.; Guillaume, F.; Harris, K. D. M. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 1313.
- (35) Collins, S. P.; Murphy, B. M.; Tang, C. C.; Miller, M. C.; Oszlanyi, G. *J. Phys. D* **1999**, 32, A81.
- (36) A similar result was also obtained from $(0, 0, l_g)$ scans, although in this case only $l_g = 4, 5, 7$, and 8 were used to calculate the one-dimensional Patterson map. All other peaks due to the diffuse sheets overlap with a Bragg peak in the “h” ($l_g \approx 3n/2$) or “g” ($l_g = 3n$) diffraction pattern ($n = \text{integer}$).
- (37) Bondi, A. *J. Phys. Chem.* **1964**, 68, 441.
- (38) George, A. R.; Harris, K. D. M. *J. Mol. Graphics* **1995**, 13, 138.
- (39) Chao, M.-H.; Kariuki, B. M.; Harris, K. D. M.; Foxman, B. M., manuscript in preparation.