Articles

Conformational Properties of Guest Molecules in Constrained Solid-State Environments: Bromine K-Edge X-ray Absorption Spectroscopy of 2-Bromoalkane/Urea Inclusion Compounds

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Urea inclusion compounds containing 2-bromoalkane guest molecules are of considerable interest as they provide an opportunity to investigate host−guest chiral recognition between the chiral 2-bromoalkanes and the chiral urea tunnel structure. To understand the conformational properties of the guest molecules in these solids, this paper reports bromine K-edge X-ray absorption (EXAFS) studies of the 2-bromotridecane/urea and 2-bromotetradecane/urea inclusion compounds. There are two plausible conformations for a 2-bromoalkane guest molecule within the urea tunnel structure: in one conformation (denoted G), the bromine atom attached to the chiral center is gauche and the methyl group attached to the chiral center is trans with respect to the alkane chain, whereas in the other conformation (denoted T), the bromine atom is trans and the methyl group is gauche. The distance between the bromine atom and the third carbon shell from the bromine atom is ca. 3.2 Å for the G conformation and ca. 4.3 Å for the T conformation, allowing these conformations to be distinguished directly by bromine K-edge EXAFS spectroscopy. As a consequence of the incommensurate relationship between the host and guest substructures in the 2-bromoalkane/urea inclusion compounds, no well-defined distances between the bromine atom and atoms of the host substructure are observed; the EXAFS data therefore provide a selective probe of the local structural properties of the guest molecules. Analysis of the bromine K-edge EXAFS spectra indicates that both G and T conformations of the 2-bromoalkane guest molecules are present within the urea tunnel structure, with an excess of the T conformation. Considering both inclusion compounds over the range of temperatures (80−200 K) investigated, the proportion of guest molecules in the T conformation is in the range 0.54−0.68. For an isolated 2-bromoalkane molecule, the G conformation is lower in energy than the T conformation, and thus inclusion of the 2-bromoalkane within the urea tunnel structure promotes a relative stabilization of the conformation that is less favored in the isolated state. The more favorable host−guest interaction in the case of the T conformation provides a basis to rationalize the preference for this conformation within the urea tunnel structure.

1. Introduction

In recent years, significant progress has been made in understanding aspects of the structural and dynamic properties of solid one-dimensional inclusion compounds, typified by the urea inclusion compounds.[1−3] In these solids, the urea molecules form an extensively hydrogen-bonded "host" structure,[4,5] which contains parallel one-dimensional tunnels; these tunnels are densely packed with guest molecules. The effective diameter of the urea tunnel is ca. 5.5−5.8 Å,[6] and only

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guest molecules based on a sufficiently long *n*-alkane chain (with only a limited degree of substitution) can be accommodated within these tunnels. The guest molecules in such inclusion compounds are often disordered (frequently this disorder is dynamic), limiting the ability of diffraction-based techniques to elucidate information on the structural properties of the guest molecules. However, even when the guest substructure is substantially disordered in the sense that it lacks long-range periodicity, the local structural properties of the guest molecules may still be well defined, and techniques that specifically probe these local properties can provide significant insights into the structural characteristics of the guest molecules.

In this regard, we have previously used bromine K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate conformational properties of the guest molecules in urea inclusion compounds containing α,ω-dibromoalkane guest molecules[7] and thiourea inclusion compounds containing bromocyclohexane and *trans*-1-bromo-2-chlorocyclohexane guest molecules.[8] In both cases, these experiments led to unambiguous information on the intramolecular geometry in the vicinity of the bromine atoms of the guest molecules, and demonstrated that bromine K-edge EXAFS spectroscopy can be a powerful technique for probing the conformational properties of brominated guest molecules inside solid host structures.

In this paper, we consider a new direction within our interest in the properties of bromoalkane guest molecules inside solid host structures. The urea tunnel is constructed from a spiral arrangement of urea molecules, and a single crystal contains either *only* right-handed spirals (space group $P6_122$) or *only* left-handed spirals (space group $P6_522$). Thus, the host tunnel structure in urea inclusion compounds is chiral (with this chirality generated spontaneously during crystal growth), and there is clearly considerable potential for exploiting this chirality in the properties and applications of these solids. However, exploiting the chirality of urea inclusion compounds is limited by the difficulty of accommodating guest molecules containing a side group on the *n*-alkane chain within the confined space available in the tunnel (a side group on the *n*-alkane chain is required for the guest molecule to be chiral). Apart from the early work of Schlenk[9-11] (which demonstrated experimentally that urea inclusion compounds containing chiral guest molecules can indeed exhibit some degree of chiral recognition), virtually all reported studies of urea inclusion compounds have focused on achiral guest molecules. Thus, the potential for exploiting the chiral nature of urea inclusion compounds is still largely unexplored. We note, however, that an alternative method for understanding chiral recognition in urea inclusion compounds has been presented recently by Brown et al.[12]

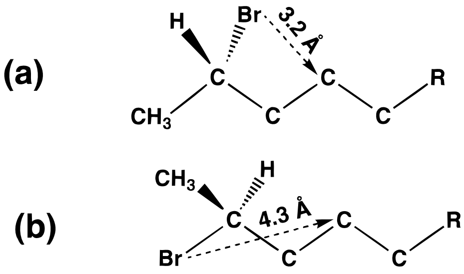

Figure 1. Diagram showing a 2-bromoalkane molecule in (a) the G conformation (bromine gauche/methyl trans) and (b) the T conformation (bromine trans/methyl gauche). In the G conformation, the distance between the bromine atom and the third carbon shell is ca. 3.2 Å. In the T conformation, the distance between the bromine atom and the third carbon shell is ca. 4.3 Å. These distances have been estimated on the basis of standard molecular geometries.

Recently, we have successfully prepared urea inclusion compounds containing the chiral guest molecules 2-bromotridecane and 2-bromotetradecane, and we are now engaged in a comprehensive program of experimental and computational research[13-15] to investigate and understand the structural and dynamic properties of these solids. Before an understanding of the chiral recognition between the host and guest components can be developed, it is important to understand the conformational properties of the guest molecules. The objective of the present paper is to address this issue for the 2-bromotridecane/urea and 2-bromotetradecane/urea inclusion compounds. As shown in Figure 1, there are two plausible conformations that a given enantiomer of a 2-bromoalkane guest molecule may adopt within the urea tunnel structure. In one conformation (denoted G; Figure 1a) the bromine atom attached to the chiral center is gauche and the methyl group attached to the chiral center is trans with respect to the alkane chain, whereas in the other conformation (denoted T; Figure 1b) the bromine atom is trans and the methyl group is gauche. These conformations differ in the distance between the bromine atom and the third carbon shell from the bromine atom (ca. 3.2 Å for the G conformation and ca. 4.3 Å for the T conformation). As demonstrated previously,[7,8] the distance between the bromine atom and the third carbon shell in bromoalkanes can be determined directly by bromine K-edge EXAFS spectroscopy.

We note that a third conformation may be considered, in which the hydrogen atom attached to the chiral center is in the trans position with respect to the alkane chain and both the bromine atom and the methyl group are in gauche positions with respect to the alkane chain. However, in view of the steric nature of this conformation and the geometric features of the urea tunnel structure, no significant amounts of this conformation are expected to exist within the 2-bromoalkane/urea inclusion compounds (furthermore, even for the isolated molecule, this conformation is higher in energy than the

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T and G conformations discussed above). It is important to note, however, that the bromine EXAFS spectrum for this third conformation would be identical to that for the G conformation discussed above. Thus, even if small amounts of the conformation with hydrogen in the trans position do indeed exist within the urea inclusion compounds, our data analysis will subsume their existence within the contributions assigned to the G conformation.

In the experiments reported here, bromine K-edge X-ray absorption spectra were recorded for 2-bromotridecane/urea and 2-bromotetradecane/urea as a function of temperature (200 to 80 K) to investigate the relative amounts of the T and G conformations within the urea tunnel structure. It is known[15] that (as for most urea inclusion compounds) 2-bromotridecane/urea and 2-bromotetradecane/urea have an incommensurate relationship[16,17] between the periodicities of the host and guest substructures along the tunnel axis. As a consequence, the radial distribution function for bromine··· host atom distances represents a broad, featureless continuum, and no significant features are expected to arise in the bromine X-ray absorption spectra due to backscattering by atoms of the host structure. This simplifies considerably the X-ray absorption spectra, and allows the intramolecular Br···C distances in the guest molecule to be determined directly and unambiguously from such spectra.

We note that single-crystal X-ray diffraction studies[15] suggest that the 2-bromotridecane/urea and 2-bromotetradecane/urea inclusion compounds undergo structural phase transitions between ambient temperature and liquid nitrogen temperature. Detailed single-crystal X-ray diffraction studies to establish the structural nature of these transitions are in progress,[15] but it is clear that they involve a change in the symmetry of the urea tunnel structure through a minor structural distortion. The range of temperatures spanned by the EXAFS studies reported here allows us to assess whether these distortions of the host structure at low-temperature exert any significant influence on the conformational properties of the 2-bromoalkane guest molecules.

2. Experimental Section

2.1. Sample Preparation. The 2-bromotridecane/urea and 2-bromotetradecane/urea inclusion compounds were prepared from commercially available compounds using the following method. An excess amount of the 2-bromoalkane (excess with respect to the expected guest/host molar ratio in the inclusion compound) was added to a saturated solution of urea in methanol in a conical flask under ultrasonic agitation at ca. 55 °C. A sufficient amount of 2-methyl-2-butanol was then added to render the liquid 2-bromoalkane completely miscible with the methanol. At this stage, crystals of the 2-bromoalkane/urea inclusion compound precipitated immediately; these crystals were then dissolved by addition of a sufficient amount of methanol to establish a homogeneous solution. The flask was then transferred to an incubator, in which it was cooled systematically from 55 to 15 °C over a period of 24 h. When sufficiently large crystals (hexagonal needles) had grown (generally after a few days) they were collected and washed with 2,2,4-trimethylpentane. Powder X-ray diffraction indicated that the crystals had the conventional hexagonal urea tunnel structure at ambient temperature and confirmed that the samples did not contain any significant amounts of the "pure" crystalline phase of urea (the crystal structure of which differs substantially from the urea host structure in urea inclusion compounds).

2.2. X-ray Absorption Experiments. Bromine K-edge X-ray absorption spectra were recorded in transmission mode on Station 9.2 at the Synchrotron Radiation Source, Daresbury Laboratory (which operates at 2 GeV with typical current in the range 150−250 mA). A Si(220) double-crystal monochromator was used to select the X-ray energy, and ion chambers filled with Ar/He gas mixtures were used to record incident and transmitted X-ray intensities. The sample was ground to a powder, pressed into a self-supporting wafer and loaded into an Oxford Instruments cryostat. About 0.15 g of sample was used (chosen to correspond to an edge jump of ca. 1). The sample chamber within the cryostat was initially evacuated (to avoid condensation in subsequent low-temperature experiments), followed by the introduction of dry nitrogen. Powder X-ray diffraction analysis of the samples recovered following the X-ray absorption experiments indicated that no decomposition of the inclusion compounds occurred either during the evacuation stage or as a consequence of X-ray beam damage.

Bromine K-edge X-ray absorption spectra were recorded for 2-bromotridecane/urea at 200 and 80 K and for 2-bromotetradecane/urea at 200, 175, 130, and 80 K. Two spectra were recorded (data collection time ca. 40 min) for each sample at each temperature, and the two spectra were subsequently combined in order to improve the signal/noise ratio.

3. Data Analysis

The X-ray absorption data were analyzed using the following programs (available at Daresbury Laboratory): EXCALIB (to convert the raw data to absorption coefficient), EXBROOK (for preedge and postedge background subtraction), and EXCURV92 (for extracting structural information by fitting theoretical spectra to experimental spectra). The data were processed without Fourier filtering and k^3 weighting was used. In all cases, the k range used for data analysis was 4.1−14.2 Å^{-1}. Theoretically derived phase shifts were generated within the EXCURV92 program using von-Barth ground states and Hedin−Lundqvist exchange potentials. Further details of specific aspects of the data analysis are given in Section 4.

4. Results and Discussion

As discussed in section 1, we consider that 2-bromoalkane guest molecules within the urea tunnel structure may exist in the G conformation or the T conformation (see Figure 1). The first two shells are identical in each conformation and comprise one carbon atom at ca. 1.97 Å and two carbon atoms at ca. 2.90 Å. The G and T conformations differ with regard to the third shell; for the G conformation the Br···C distance is ca. 3.2 Å, whereas for the T conformation the Br···C distance is ca. 4.3 Å. Thus, analysis of the bromine K-edge EXAFS data (up to at least 4.5 Å in the bromine radial distribution function) should allow the relative amounts of the G and T conformations to be determined.

Before extracting structural information, it is necessary to establish the value of the amplitude reduction factor AFAC. Normally this parameter is evaluated using a suitable model compound, but in the present case the structural properties of the first two shells are known and can therefore be regarded as an internal standard, allowing AFAC to be determined by fitting these shells. However, analysis in the present case is complicated by the fact that the data are affected by a low-frequency oscillation in $\chi(k)$, which appears in the

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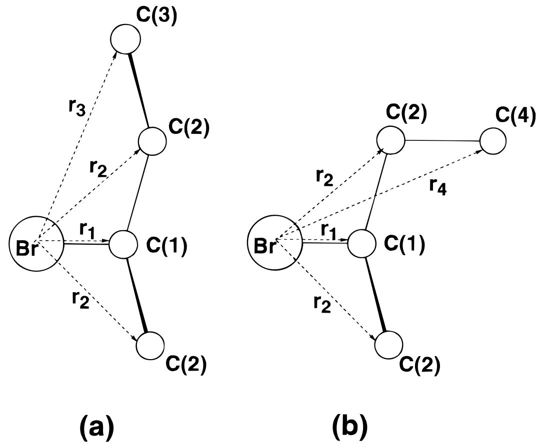

Figure 2. Specification of the model considered for analysis of the bromine K-edge EXAFS spectra: (a) structural unit representing the G conformation, (b) structural unit representing the T conformation.

region of low *r* in the Fourier transform of the EXAFS spectrum and overlaps considerably with the first shell at ca. 1.97 Å. This low-frequency oscillation in $\chi(k)$ (and the corresponding feature at low *r* in the Fourier transform) has been noted in many other bromine K-edge EXAFS studies and has been attributed to so-called "atomic EXAFS".[18–21] One complication arising from atomic EXAFS is that a unique value for AFAC could not be obtained by fitting the first two shells with known structural parameters. Thus, consideration of the correlation map (generated from such fits) between AFAC and the Debye–Waller factor for the first shell led to an AFAC value of 1.09, whereas consideration of the correlation map between AFAC and the Debye–Waller factor for the second shell (which is not affected significantly by the atomic EXAFS) led to an AFAC value of 0.94. As a compromise between these results, the AFAC value was taken as 1.0 for all subsequent analysis.

Addition of shells comprising carbon atoms at ca. 3.2 and 4.3 Å (with coordination numbers assumed initially to be 0.5) improved the fit significantly, although satisfactory results could not be achieved using the simple single-scattering, curved-wave theory. For this reason, our detailed analysis of the EXAFS spectra considered multiple scattering, together with a restrained refinement procedure (as discussed below, this approach decreases the number of independent parameters, particularly with regard to the occupancies of shells). In this analysis, a three-dimensional model (Figure 2) comprising two structural units was considered. One unit represents the environment around the bromine atom in the G conformation, and the other unit represents the environment around the bromine atom in the T conformation. On the assumption that each 2-bromoalkane guest molecule is either in the G conformation or the T conformation, the local environment around each bromine atom is defined by one or other of these units. In each unit, there are three shells of carbon atoms around the bromine atom. The two units have identical first shells [comprising one carbon atom denoted C(1)] and identical second shells [comprising two carbon atoms denoted C(2)], and the two units differ only in the third shell [in each case, the third shell comprises one carbon atom, denoted C(3) for the unit representing the G conformation and C(4) for the unit representing the T conformation]. The Br···C distance (denoted *r*) and Debye–Waller factor (denoted $2\sigma^2$) were constrained to be the same for the first shell in both units and for the second shell in both units. The Debye–Waller factors for C(3) and C(4) were also constrained to be equal.

The occupancies of the G and T conformations are denoted N_G and N_T respectively, and N_G and N_T represent the only two occupancy variables in the refinement calculations. For the model defined above, the occupancy of C(1) is $N_G + N_T$ (ideally equal to 1) and the occupancy of C(2) is $2(N_G + N_T)$ (ideally equal to 2). As the C(1) shell is affected significantly by the atomic EXAFS, it was considered best to fix the occupancy of this shell as 1, rather than to allow its occupancy to refine (as $N_G + N_T$) through the variables N_G and N_T. Thus, in the refinement calculations, the occupancies (denoted *N*) of each shell were as follows: N(C(1)) = 1 (fixed); N(C(2)) = $2(N_G + N_T)$; N(C(3)) = N_G; N(C(4)) = N_T. Clearly the refined value of $N_G + N_T$ is dictated principally by fitting the C(2) shell, whereas the relative values of N_G and N_T are dictated by fitting the shells for C(3) and C(4). The relative proportion of guest molecules in the T conformation is given by $P_T = N_T/(N_G + N_T)$.

In the refinement calculations, the Debye–Waller factors and the occupancies were never refined together, and an iterative approach was adopted whereby, in a given set of refinement cycles, the Debye–Waller factors were refined with the occupancies fixed whereas in the next set of refinement cycles the occupancies were refined with the Debye–Waller factors fixed. Initially, the spectrum recorded for 2-bromotetradecane/urea at 80 K was considered, with the Debye–Waller factors fixed at standard values and the occupancies refined from the following different sets of starting values: $N_G = 0.5$, $N_T = 0.5$; $N_G = 0.7$, $N_T = 0.3$; $N_G = 0.3$, $N_T = 0.7$. In each case, the occupancies refined to similar values ($N_G \approx 0.4$, $N_T \approx 0.6$). Then, with the occupancies fixed at these values, the Debye–Waller factors were refined. This process was repeated, with the Debye–Waller factors and occupancies refined and fixed in successive calculations, until the values of all parameters had converged. The same strategy was followed for 2-bromotetradecane/urea at all other temperatures and for 2-bromotridecane/urea at all temperatures, except that, in the initial refinement calculation, N_G and N_T were set to the final values determined for 2-bromotetradecane/urea at 80 K and the Debye–Waller factors were refined.

We now consider the refinement of geometrical parameters, with particular reference to the definition of the multiple scattering calculation. Because the C(1) shell is significantly affected by the atomic EXAFS, this shell was excluded from the multiple scattering calculation and was treated as an isolated shell [in any case, as the Br–C(1)–C(*n*) angles for $n = 2$, 3, and 4 are all

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Table 1. Results of Refinement Calculations for the Bromine K-Edge EXAFS Data for 2-Bromotetradecane/Urea and 2-Bromotridecane/Urea at Different Temperatures (for the *k* Range 4.1–14.2 Å^{-1} in Each Case)[a]

inclusion compound	T/K	shell	N	r/Å	$2\sigma^2$/Å^2	P_T
2-bromotetradecane/urea	200	C(1)	1	1.98	0.007	0.60
		C(2)	2.20	2.86	0.014	
		C(3)	0.44	3.33	0.018	
		C(4)	0.66	4.34	0.018	
2-bromotetradecane/urea	175	C(1)	1	1.99	0.007	0.55
		C(2)	2.06	2.86	0.011	
		C(3)	0.46	3.35	0.015	
		C(4)	0.57	4.34	0.015	
2-bromotetradecane/urea	130	C(1)	1	1.98	0.006	0.68
		C(2)	2.14	2.86	0.012	
		C(3)	0.34	3.33	0.014	
		C(4)	0.73	4.34	0.014	
2-bromotetradecane/urea	80	C(1)	1	1.98	0.0055	0.68
		C(2)	2.08	2.85	0.012	
		C(3)	0.33	3.33	0.014	
		C(4)	0.71	4.34	0.014	
2-bromotridecane/urea	200	C(1)	1	1.98	0.005	0.54
		C(2)	2.02	2.85	0.011	
		C(3)	0.46	3.35	0.013	
		C(4)	0.55	4.33	0.013	
2-bromotridecane/urea	80	C(1)	1	1.98	0.005	0.56
		C(2)	1.82	2.86	0.009	
		C(3)	0.40	3.35	0.009	
		C(4)	0.51	4.35	0.009	

[a] Estimated errors in the refined parameters are ±0.02 Å for r, 10% for $2\sigma^2$, and 15% for N (the corresponding absolute error in P_T is ca. ± 0.1). Note: $N_G = N(C(3))$; $N_T = N(C(4))$.

far from linear, C(1) is not expected to play a significant part in multiple scattering processes]. Thus, the multiple scattering calculation considered the C(2), C(3), and C(4) shells, with the geometry of the multiple scattering unit defined by the angles α_3 (which defines Br–C(2)–C(3)) and α_4 (which defines Br–C(2)–C(4)) and the C(2)···C(3) and C(2)···C(4) distances. In the initial geometry, standard bond lengths, bond angles and torsion angles were used.[22] The geometric parameters considered as variables in the refinements were the Br···C(1), Br···C(2), Br···C(3), and Br···C(4) distances and the angles α_3 and α_4. Restraints were applied to the C(2)···C(3) and C(2)···C(4) distances (corresponding to the normal C–C bond length of ca. 1.55 Å) in order to preserve plausible molecular geometry. The major contribution to multiple scattering is expected to involve the Br, C(2), and C(4) atoms, as the angle α_4 (ca. 160°) is significantly closer to linear than any of the other angles that define the geometry of the system. Indeed, test calculations demonstrated that inclusion of multiple scattering made a significant improvement in the ability to fit parameters representing C(4).

In summary, the following parameters were considered as variables in fitting models to the experimental spectra: the energy zero parameter E_0, the Br···C(1), Br···C(2), Br···C(3), Br···C(4) distances, the Debye–Waller factors for C(1), C(2), C(3) and C(4) [with Debye–Waller factors for C(3) and C(4) constrained to be the same], the occupancies N_G and N_T, and the angles α_3 and α_4.

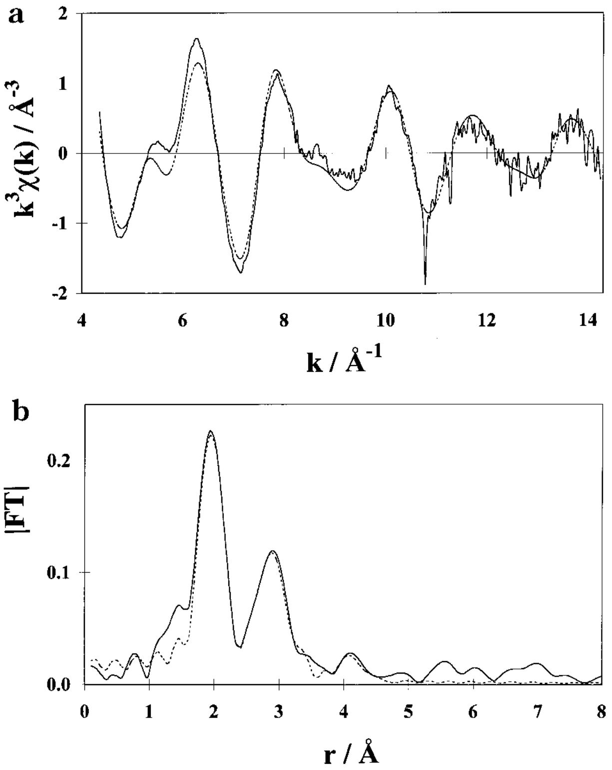

Figure 3. (a) Bromine K-edge EXAFS spectrum (solid line) and (b) its Fourier transform (solid line) for 2-bromotetradecane/urea at 80 K with data analysis carried out over the k range 4.1–14.2 Å^{-1}. Relevant parameters for the theoretical fits (dotted lines) are specified in Table 1.

Structural parameters determined in the final refinement calculations are summarized in Table 1, and the fits to the spectra recorded at 80 K for 2-bromotetradecane/urea and 2-bromotridecane/urea are shown in Figures 3 and 4, respectively. The refined Br···C distances are within experimental error of the values expected for standard geometries of the G and T conformations, and these distances do not vary significantly with temperature. The refined Debye–Waller factors are also consistent with expectations, with $2\sigma^2$ increasing as the Br···C distance increases; in general, the Debye–Waller factor for a given shell increases as temperature increases, although the changes with temperature are not substantial.

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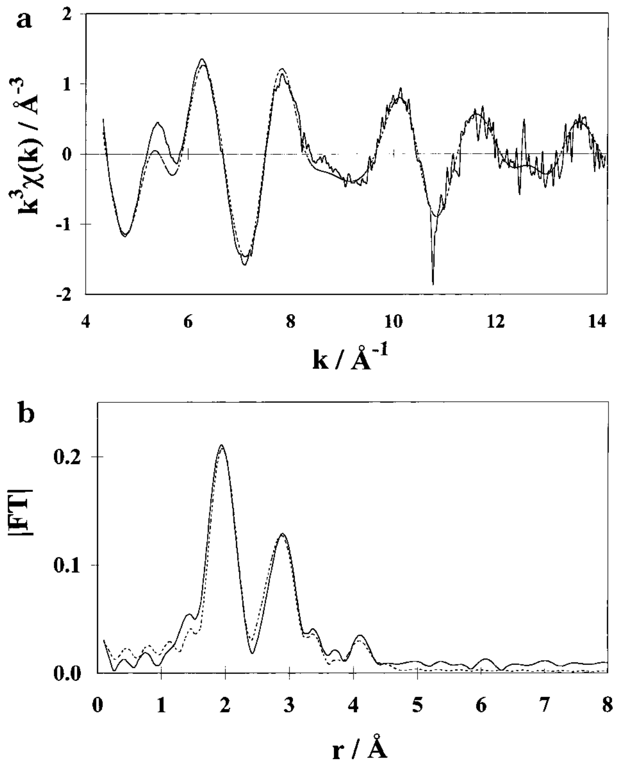

Figure 4. (a) Bromine K-edge EXAFS spectrum (solid line) and (b) its Fourier transform (solid line) for 2-bromotridecane/urea at 80 K with data analysis carried out over the k range 4.1−14.2 Å^{-1}. Relevant parameters for the theoretical fits (dotted lines) are specified in Table 1.

We now consider the occupancies of the T and G conformations. As required, the value of $N_G + N_T$ for the refined occupancies N_G and N_T is always close to 1, confirming the validity of the approach in which $N_G + N_T$ is essentially determined by fitting the C(2) shell. The relative values of N_G and N_T, on the other hand, are established from fitting the C(3) and C(4) shells. For the different temperatures investigated, the proportion (P_T) of guest molecules in the T conformation (see Table 1) ranges from 0.54 to 0.56 for 2-bromotridecane/urea (average 0.55) and from 0.55 to 0.68 for 2-bromotetradecane/urea (average 0.63). Thus, both the G and T conformations of the 2-bromoalkane guest molecules are present within the urea tunnel structure, and for both inclusion compounds at all temperatures investigated there is an excess of the T conformation. The absolute error in the derived values of P_T is estimated to be ca. ±0.1, and we may conclude, with due caution, that the observed excess of the T conformation for both inclusion compounds at all temperatures probably represents a statistically significant preference for the T conformation of 2-bromoalkane guest molecules within the urea tunnel structure. It is clear that this conclusion may be reached with rather more confidence for 2-bromotetradecane/urea than for 2-bromotridecane/urea. However, the amount of information presently available does not allow us to establish if there is a dependence on the chain length and/or the odd/even character of the alkane part of the 2-bromoalkane guest molecules—a wider range of different 2-bromoalkane/urea inclusion compounds would need to be studied to establish any trends in this regard.

For 2-bromotetradecane/urea (which was studied at several temperatures) there is no well-defined trend in the proportions of the G and T conformations with temperature, and for 2-bromotridecane/urea (which was studied only at 80 and 200 K) there is no significant variation of P_T with temperature (suggesting, inter alia, that the structural phase transitions (see section 1) in these inclusion compounds are not associated with any significant changes in the conformational properties of the 2-bromoalkane guest molecules). At both 80 and 200 K, P_T is slightly higher for 2-bromotetradecane/urea than for 2-bromotridecane/urea. However, with the limited data available at the present stage, we make no attempt to derive any conclusions regarding the dependence of P_T on temperature nor the dependence of P_T on the chain length of the 2-bromoalkane guest molecule. It is interesting to note that no significant variation in the relative amounts of trans and gauche bromine end groups with temperature for α,ω-dibromoalkanes within the urea tunnel structure were found from a detailed study using Raman spectroscopy.[23]

5. Concluding Remarks

The results reported here have shown that, for 2-bromoalkane guest molecules within the urea tunnel structure, the bromine trans/methyl gauche conformation (T) is preferred over the bromine gauche/methyl trans conformation (G). It is interesting to note that the preferred conformation of the 2-bromoalkane guest molecules within the urea tunnel structure contrasts significantly with the preference for the G conformation in the isolated molecule—ab initio quantum mechanical calculations[24] with 3-21G* basis set (following local geometry optimization) for 2-bromohexane in the type of linear conformation required to fit within the urea tunnel structure suggest that the isolated molecule in the G conformation is lower in energy by ca. 0.65 kcal mol^{-1} than the isolated molecule in the T conformation). The reversal of this preference when the 2-bromoalkane molecule is included as a guest within the confined space of the urea tunnel is probably due to the fact that the C−Br bond for the G conformation protrudes toward the tunnel wall, entailing a repulsive local interaction. Indeed, calculations[12,13] of host−guest interaction energies for 2-bromoalkane guest molecules in the urea tunnel structure indicate that the host−guest interaction energy is more negative for the T conformation than the G conformation (typically by an amount in the range ca. 4−7 kcal mol^{-1}). Thus, the host−guest interaction provides a relative stabilization of the T conformation relative to the G conformation, in support of the conclusions from the EXAFS analysis discussed above. In addition, we note that the host−guest interaction energy is more negative for the T conformation than the G conformation at all positions of the guest molecules along the tunnel (recalling that, for an incommensurate inclusion compound, it is necessary to consider properties of host−guest interaction as a function of the position of the guest molecule along the host tunnel).

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(24) Johnston, R. L. Harris, K. D. M. Unpublished results.

The energetic properties of urea inclusion compounds can be considered in terms of four contributions: the energy of the host structure (which may be perturbed to some extent depending on the guest molecules), the energy of host−guest interaction, the energy of guest−guest interaction, and the intramolecular potential energy of the guest molecules. In principle, all of these contributions will vary for different conformations of the guest molecule. In the present case, diffraction data suggest that the host structure in 2-bromoalkane/urea inclusion compounds at ambient temperature is the conventional urea tunnel structure, and therefore the periodic properties of the host structure are not affected significantly by the presence of the bromine substituent in the 2-position of the alkane chain (however, the possibility that there is some local distortion of the host structure, depending on whether the guest molecule is in the G conformation or the T conformation, cannot be ruled out). So far, there have been no attempts to assess the question of guest−guest interaction for 2-bromoalkane guest molecules within the urea tunnel structure. Clearly a detailed (quantitative) rationalization of the conformational properties of 2-bromoalkane guest molecules within the urea tunnel structure requires full consideration of all four energy contributions discussed above. However, at a qualitative level, it is clear from the above discussion that the intramolecular potential energy favors the G conformation whereas host−guest interaction favors the T conformation. The overall excess of the T conformation observed from the experimental EXAFS results reported here suggests (although does not prove, since guest−guest interaction has not been considered in this discussion) that host−guest interaction is an important determinant of the preferred conformational behavior of the guest molecules in the 2-bromoalkane/urea inclusion compounds.

Knowledge of the conformational properties of the 2-bromoalkane guest molecules reported here is an important prerequisite before the chiral recognition properties of 2-bromoalkane/urea inclusion compounds can be understood in depth. Significant future progress in addressing the question of chiral recognition properties of these materials is forecast with confidence. In addition, the work reported here has demonstrated that the conformational properties of 2-bromoalkanes can be utilized as a means of probing the geometric constraints imposed by solid host structures and that bromine K-edge X-ray absorption spectroscopy provides a viable means of probing these properties. We are now exploiting this approach to study a wide range of other solid host materials that have tunnel structures appropriate for inclusion of 2-bromoalkane guest molecules.

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