

Melting Behavior of Crown Thioethers: Correlation of Entropy Changes with Conformational Disorder

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We have examined the following crown thioethers by differential scanning calorimetry from $-90\text{ }^{\circ}\text{C}$, or lower, up to their melting points: 1,4,7-trithiacyclononane (9S3); 1,5,9-trithiacyclododecane (12S3); 1,4,7,10-tetrathiacyclododecane (12S4); 1,4,8,11-tetrathiacyclotetradecane (14S4); 1,4,7,10,13-pentathiacyclopentadecane (15S5); and 1,5,9,13-tetrathiacyclohexadecane (16S4). We have identified new solid–solid phase transitions above room temperature in 12S3, in the α -phase of 14S4, in 15S5, and in both the α -phase and β -phase of 16S4. Of those crown thioethers examined, only 9S3 and 12S4 do not show any solid–solid phase transitions. From an analysis of the entropy of fusion, we find that only the high-temperature solid phase of 16S4 is orientationally disordered. Analysis of the entropy changes associated with the solid–solid phase transitions and with fusion indicate that all except 12S4 have considerably more conformational freedom in the melt than in the room-temperature solid. Insight into these conformational changes is of considerable importance for understanding complexation of thioethers to metals.

I. Introduction

For several years there has been growing awareness of the role that conformation of multidentate ligands plays in the formation, stability, and properties of their metal complexes, from small molecules to naturally occurring metalloproteins. Crown thioethers are particularly interesting because, as free molecules, most prefer to adopt conformations that have their sulfur atoms exodentate, i.e., in the wrong orientation for binding.^{1,2} Although acyclic thioethers are not very good binders,³ crown thioethers are important ligands, especially for late transition metals. The unusual properties of crown thioethers have been attributed to assumed conformational preferences, largely based on X-ray studies of the ligands and their complexes in the solid state.^{1,2,4–14} In recent molecular modeling studies of crown thioethers, we have been investigating relative stabilities and structures of conformers of crown thioethers to advance understanding of the relationship between binding properties and conformational stability,¹⁵ as have others.^{16–18}

The purpose of the present investigation was to use thermal analysis to look for solid–solid phase changes in crown thioethers, and to determine both their entropy changes and the entropy changes associated with melting. One of our main aims was to see how the entropy changes compare with our understanding of conformational populations. Another aim was to make links between conformations in the solid state and those in the melt and in solution. Six cyclic thioethers were investigated (see Figure 1): 1,4,7-trithiacyclononane (9S3); 1,5,9-trithiacyclododecane (12S3); 1,4,7,10-tetrathiacyclododecane (12S4); 1,4,8,11-tetrathiacyclotetradecane (14S4); 1,4,7,10,13-pentathiacyclopentadecane (15S5); and 1,5,9,13-tetrathiacyclohexadecane (16S4).

II. Experimental Methods

Thioethers 9S3, 12S4, 14S4, 15S5, and 16S4 were obtained commercially (Aldrich). 16S4 was recrystallized by diffusion

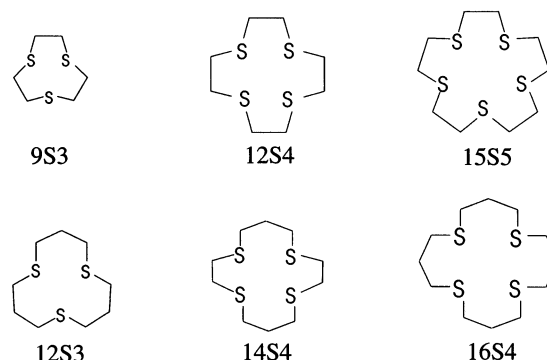


Figure 1. Molecular structures of crown thioethers investigated and their abbreviated designations.

of hexane into CH_2Cl_2 solutions, and the α -form (needles) and β -form (plates)¹⁹ were separated by hand for thermal analysis studies. 12S3 was generously supplied by Professor R. D. Adams of the University of South Carolina.

Preliminary differential scanning calorimetry experiments were performed on a DuPont DSC-2910 system. Further experiments for all samples were carried out on a Perkin-Elmer Pyris-1 DSC. In both sets of DSC experiments, samples (mass $\approx 1\text{ mg}$ to $\approx 10\text{ mg}$) were loaded in air into aluminum pans. Typical sample heating rates were 10 K min^{-1} . Melting of indium²⁰ was used to calibrate the DSC for temperature and enthalpy change. At least two samples of each material were examined; thermal events for most samples were not reproducible after melting, and replications were carried out with new samples. The reproducibility of a phase transformation or other thermal event for a fresh sample on a given instrument was generally within $\pm 1\text{ K}$ in temperature and $\pm 10\%$ in enthalpy change (ΔH). The enthalpy changes from one instrument to the other also fell within $\pm 10\%$, but the temperatures sometimes differed by as much as 2 K (with the Pyris-1 results at higher temperature). This difference is likely due to slightly different configurations of the two DSCs and the fact that the thermal

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TABLE 1: Thermodynamic Data for Cyclic Thioethers^a

compound	lowest $T/^\circ\text{C}$	$T_{\text{trs}}/^\circ\text{C}$	$\Delta H_{\text{trs}}/^\circ\text{C}$	$\Delta S_{\text{trs}}/J K^{-1} \text{ mol}^{-1}$	$\Delta S_{\text{tot}}/J K^{-1} \text{ mol}^{-1}$
9S3	−175	81	29	82	82
12S3	−100	76	12	35	87
		100	100	52	
12S4	−100	226	31	62	62
14S4(α)	−100	72	2.7	8.0	91
		120	33	83	
15S5	−100	45 ^b	11	34	89
		67 ^b	4.2	12	
		118	17	43	
16S4(α)	−90	55 ^b	32	99	115
		60	5.2	16	
16S4(β)	−90	55 ^b	27	83	99
		60	5.2	16	

^a Lowest temperature refers to the lowest temperature examined in the DSC experiment. Of the transition temperatures, labeled T_{trs} , the highest temperature transition is fusion; any lower-temperature transitions are from one solid phase to another. Where more than one polymorph is known, the polymorph examined is indicated. ΔH_{trs} , ΔS_{trs} , and ΔS_{tot} are the enthalpy change due to the transition, the entropy change due to the transition, and the total entropy change (solid–solid transitions plus fusion), respectively. Uncertainties are ± 1.5 K in temperature, $\pm 10\%$ in ΔH_{trs} and ΔS_{trs} . ^b Shape indicates possibly more than one transition.

link between the sample and the temperature sensor is not very strong in poor thermal conductors such as these materials. Furthermore, no attempt was made to sort samples according to morphology or particle size. Therefore, thermal results can be considered to be accurate to ± 1.5 K in temperature and $\pm 10\%$ in ΔH and ΔS (entropy change). ΔS_{trs} was determined as $\Delta H_{\text{trs}}/T_{\text{trs}}$ for the transitions studied here (i.e., transitions were assumed to be first-order), which gives a lower bound on ΔS and ΔH because nonisothermal contributions are omitted in DSC experiments.^{21–24}

III. Results

The thermal analysis results for the cyclic thioethers examined are summarized in Table 1. (All values in the table are weighted averages from the two DSC instruments.) All materials were examined from far below room temperature (lowest temperature is given in Table 1) to just above the melting point. Temperatures quoted are onset temperatures, i.e., the intersection of the baseline and the tangent to the steepest slope of the DSC peak, as this, not the peak temperature, is the characteristic temperature associated with a thermal process.²⁴

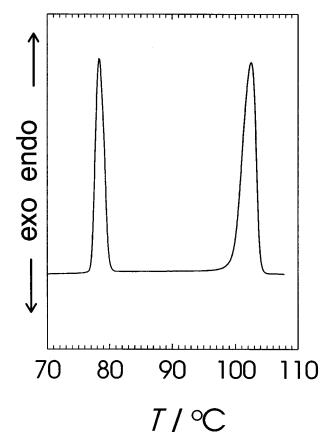
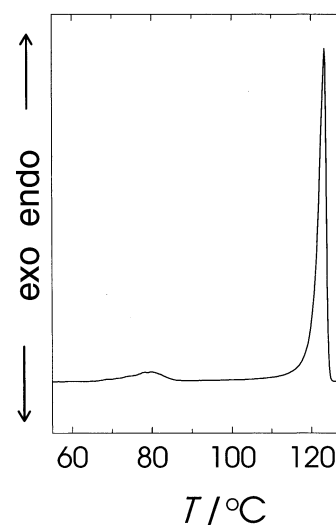
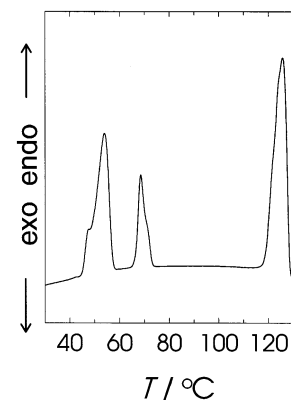
DSC results for compounds that showed solid–solid transitions, viz. 12S3, 14S4, 15S5, and 16S4 (α – and β –forms), are shown in Figures 2–5. (All DSC diagrams shown are from the results with the Pyris-1 DSC.)

All compounds were examined during heating on a hot-stage microscope. In addition to melting, the solid–solid transition in 12S3 was observable as a change in reflectivity at 76 $^\circ\text{C}$; the other noticeable change was marked increase in transparency in 12S4 from about 100 $^\circ\text{C}$ to its melting point.

IV. Discussion

A. Solid–Solid Transitions. Of the six cyclic thioethers investigated, four showed solid–solid phase transitions in the temperature region examined. None of these transitions has been reported previously.

A recent vibrational spectroscopic investigation of 9S3 suggested that it has a structural phase transition near 225 K,²⁵ but we find no thermal evidence for this or any other solid–

**Figure 2.** DSC scan for 12S3.**Figure 3.** DSC scan for 14S4.**Figure 4.** DSC scan for 15S5.

solid transition in the temperature range from 98 K to the melting point of 9S3 (see Figure 6). (The limit of detection in the DSC experiment is ΔH of 0.1 kJ mol^{−1}.) It should be noted that sometimes the sharpening and shifting of vibrational lines, which could by themselves be taken as an indication of a phase transition, can be attributable to anisotropic thermal expansion and resulting temperature-dependent polarization effects in the vibrational spectroscopy experiment.²⁶

Timmermans categorized what we now call orientationally disordered crystals as those with entropies of fusion less than $2.5R$ (R is the gas constant, so the Timmermans' limit is $\Delta S_{\text{fus}} < 21 \text{ J K}^{-1} \text{ mol}^{-1}$).²⁷ On this basis, from the results in Table 1, only 16S4 is likely to exist as an orientationally disordered solid

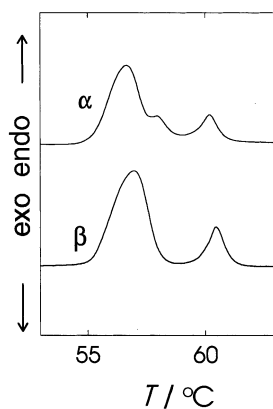


Figure 5. DCS scan for 16S4 in both its α -form and β -form.

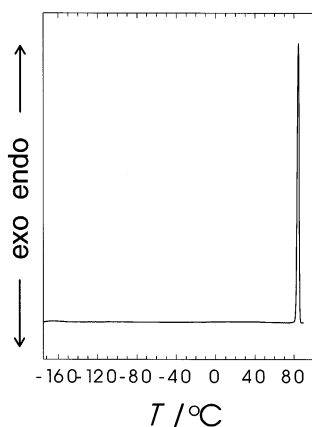


Figure 6. DSC scan for 9S3.

(i.e., with the molecules on fixed lattice positions but dynamically disordered with respect to their orientations), in the phase just below its melting point. The onset of dynamical disorder is almost certainly the driving force for the high-entropy solid–solid transition at 55 °C in 16S4. On the basis of their larger ΔS_{fus} values, the increases in disorder that set in at solid–solid transitions in 12S3, 14S4, and 15S5 are likely due to extended conformational populations and/or structural rearrangements. Understanding the origins of these solid–solid transitions requires further experiments using other methods (e.g., vibrational spectroscopy or solid-state NMR); the present results indicate the important temperature regions for investigation of solid–solid transitions in these compounds and the expected magnitude of the transition.

B. Entropy of Fusion: General Considerations. Unlike the near constancy of the entropy change associated with vaporization, generalized by Trouton,²⁸ there is no such simple rule for the entropy change on fusion (melting). Nevertheless, many rigid organic molecules obey Walden's generalization:²⁹ $\Delta S_{\text{fus}} = 54 \text{ J K}^{-1} \text{ mol}^{-1}$. This has been confirmed by Gilson³¹ in his examination of CRC data for 358 compounds which show an average ΔS_{fus} of about $50 \text{ J K}^{-1} \text{ mol}^{-1}$. Gavezzotti¹ similarly found a value of ΔS_{fus} of $54 \text{ J K}^{-1} \text{ mol}^{-1}$ for substituted benzenes. We have analyzed assessed thermodynamic data for 767 organic compounds^{32,33} and, except for extreme outliers, found a reasonably Gaussian distribution of values of ΔS_{fus} with a mean of $64 \text{ J K}^{-1} \text{ mol}^{-1}$, median of $58 \text{ J K}^{-1} \text{ mol}^{-1}$, mode of $59 \text{ J K}^{-1} \text{ mol}^{-1}$, and Gaussian standard deviation of $19 \text{ J K}^{-1} \text{ mol}^{-1}$. Gilson³⁰ found that most low values of ΔS_{fus} were associated with dynamical orientational disorder in the solid state and $\Delta S_{\text{tot}} (= \Delta S_{\text{fus}} + \Delta S_{\text{trs}}$ for all known solid–solid transitions) showed about the same average value of ΔS_{fus} as for “normal” solids. Others^{34–36} also have shown the importance of dealing

with ΔS_{tot} in attributing entropy changes to differences in degrees of freedom of the (low-temperature) solid compared with the melt.

For molecular materials ΔS_{fus} (or ΔS_{tot} in the case of one or more solid–solid transition) can be expressed as:

$$\Delta S_{\text{fus}} = \Delta S_{\text{transl}} + \Delta S_{\text{rot}} + \Delta S_{\text{vol}} + \Delta S_{\text{conf}} \quad (1)$$

where ΔS_{transl} , ΔS_{rot} , and ΔS_{conf} are, respectively, the increases in entropy due to increases in translational, rotational, and conformational degrees of freedom in the liquid compared with the solid. ΔS_{vol} is associated with the molar volume change on melting, and this has been shown³⁰ to range widely for typical organic compounds; a general absence of experimental data makes ΔS_{vol} the largest unknown in the delineation of entropy changes associated with melting.

On the basis of eq 1, ΔS_{tot} for most rigid organic molecules will be expected to be approximately constant (i.e., ΔS_{transl} , ΔS_{rot} , and ΔS_{vol} are approximately independent of the composition and $\Delta S_{\text{conf}} \approx 0$): the assessments of experimental data discussed earlier indicate a probable value of $60 \pm 20 \text{ J K}^{-1} \text{ mol}^{-1}$ for a “normal” ΔS_{tot} in a rigid organic solid. On the other hand, molecules that have significant increases in their conformational degrees of freedom on melting (or in their solid–solid phase transitions) will be expected to have increased values of ΔS_{tot} because of the contribution of ΔS_{conf} . An example is the cycloalkanes: those with 14 or fewer carbons in the ring have normal values of ΔS_{tot} but for larger rings, where new conformers are expected on melting, ΔS_{tot} is exceptionally large, and larger with larger rings.³⁷ We now consider what is known about the structures and conformers of each of the thioethers examined here, especially to look for correlations between ΔS_{tot} and conformational disorder. We begin by mentioning that 1,4-dithiane (6S2 in our designation) has a “normal” value of ΔS_{fus} ($56 \text{ J K}^{-1} \text{ mol}^{-1}$),³⁸ which indicates that it does not adopt more conformations in the liquid state than in the solid.

C. Melting of 9S3. For 9S3, we find no solid–solid transitions above -175 °C (as discussed above), and melting at 81 °C which compares well with a literature value³⁹ of $81 - 82 \text{ °C}$.

The crystal structure of 9S3 has been determined satisfactorily ($R = 2.2\%$, $R_w = 2.9\%$); the compound is found to crystallize in the space group $R3c$ with six molecules per hexagonal unit cell.⁴⁰ 9S3 is found to be in the C_3 conformation in the solid state with its sulfur atoms endodentate.

On the basis of the rather large ΔS_{fus} for 9S3 ($\approx 20 \text{ J K}^{-1} \text{ mol}^{-1}$ more than usual for a rigid organic molecule), it would appear that melting leads to more conformational disorder than is exhibited in the solid.

From spectroscopic studies,⁴¹ it is known that 9S3 has a different dominant conformer in the solid compared to the melt or solution. (These findings contradict earlier conclusions that the C_3 conformer is most populated in solution, and we discuss this in detail elsewhere.¹⁵) Infrared and Raman studies of 9S3 show that the C_3 conformer of the solid is not appreciably present in the melt or in CCl_4 solution.⁴¹ Our recent infrared investigations using CS_2 as the solvent and by ^{13}C NMR spectroscopy confirm that the dominant conformation in solution is different from that in the solid.¹⁵

Single-molecule conformational calculations,¹⁵ which we take to be representative of the conformational freedom in the liquid state, were carried out at the temperature of the melting point (stochastic search routine in MM3(94) with Boltzmann weighting factors); they show that one conformer (C_1) dominates (74%), but enough other conformers contribute to make ΔS_{conf}

have a value of $7.7 \text{ J K}^{-1} \text{ mol}^{-1}$, where ΔS_{conf} is defined as

$$\Delta S_{\text{conf}} = -R \sum_i n_i \ln n_i \quad (2)$$

where n_i is the mole fraction of conformer i . A value of $7.7 \text{ J K}^{-1} \text{ mol}^{-1}$ is not a sufficient addition to a normal (rigid molecule) value of ΔS_{fus} to match the observed ΔS_{fus} . The extra contribution is likely associated with a rather large volume change on melting. This conclusion is based on the very large dipole moment of the C_3 conformation (calculated to be $> 4 \text{ D}$,¹⁵ in good agreement with other calculations^{16,18}) and concomitant favorable packing in the solid state; the change in conformation on melting would be expected to lead to a large increase in volume and substantial ΔS_{vol} . Recent studies of 9S3 in the gas phase by photoelectron spectroscopy at $60 \pm 2 \text{ }^\circ\text{C}$ and by microwave spectroscopy at $70\text{--}90 \text{ }^\circ\text{C}$ also conclude that the C_1 conformer is most populated with contributions from other undetermined conformers.¹⁸

D. Phase Transitions in 12S3. 12S3 shows a solid–solid phase transition at $76 \text{ }^\circ\text{C}$ prior to melting at $100 \text{ }^\circ\text{C}$; the latter is in good agreement with a $97\text{--}98 \text{ }^\circ\text{C}$ melting point observed previously.⁴² X-ray diffraction indicates that 12S3 crystallizes in the monoclinic space group $P2_1/a$ with four molecules per unit cell, each with a square conformation (close to C_2 symmetry); final values of R and R' were 3.4% and 5.2%, respectively.⁴² This same conformation was found for the ligands in a number of complexes.^{5,9–14,42–44}

Infrared studies show virtually identical room-temperature spectra for the solid and CS_2 solution of 12S3, and ^{13}C NMR results also are consistent with the same conformer in solution as in the solid state.¹⁵ If the same conformation existed in the melt, the value of ΔS_{tot} would be expected to be $\approx 60 \text{ J K}^{-1} \text{ mol}^{-1}$, which is less than observed (Table 1). If the difference is not associated with an unusually high value of ΔS_{vol} , then conformational changes at higher temperatures (the melting point) likely play a role.

Our recent molecular modeling results show¹⁵ that the C_2 conformer observed in the crystal structure⁴⁰ is most stable at room temperature. When extended to the temperature of the solid–solid transition, the C_2 conformer still dominates (79%), but two other conformers contributing more than 5% each, giving a calculated ΔS_{conf} of $7.7 \text{ J K}^{-1} \text{ mol}^{-1}$ relative to an ordered solid.¹⁵ Calculations at the melting point of 12S3 show that the C_2 conformer contributes still less (62%); one other conformer contributes about 8%, three others contribute about 2% each.¹⁵ The total calculated ΔS_{conf} at the melting point is $15.8 \text{ J K}^{-1} \text{ mol}^{-1}$ relative to a rigid molecule. On the basis of the ease of thermal population of new conformers and the rather large experimentally determined ΔS_{tot} , it seems that at the solid–solid phase transition and/or on melting there are conformational changes in 12S3 which increase ΔS_{tot} beyond that normally expected for a rigid organic solid.

E. Melting in 12S4. We find no solid–solid transitions in 12S4 in the temperature range examined ($-100 \text{ }^\circ\text{C}$ to the melting point), and we find a melting point ($226 \text{ }^\circ\text{C}$) in good agreement with the literature value of $224\text{--}225 \text{ }^\circ\text{C}$.⁴⁵

The room-temperature infrared spectra of 12S4 in the solid state and CS_2 solution are virtually identical, and ^{13}C NMR results are consistent with the presence of one conformer in the solid.¹⁵ By room-temperature X-ray diffraction, 12S4 has been found to crystallize in the Cc space group, with eight molecules per unit cell, $R \approx 3\%$.^{46,47} The conformation of 12S4 in the solid state was found to be square (approximately D_4) with the sulfur atoms at the corners (two distinct but similar molecules in the crystal structure),^{46,47} and our molecular modeling

calculations show that the D_4 conformer also is dominant in the gas phase at room temperature,¹⁵ in agreement with other calculations.^{16,17} We find ΔS_{fus} to be within the normal range for rigid molecules, which indicates virtually no conformational change on melting in 12S4.

F. Phase Transitions in 14S4. 14S4 occurs in two forms⁸ and, from X-ray diffraction, we have determined that our thermal analysis experiments were performed on the α -form. We find a solid–solid transition at $72 \text{ }^\circ\text{C}$ prior to melting at $120 \text{ }^\circ\text{C}$; the latter is in good agreement with the literature value of $121\text{--}122.5 \text{ }^\circ\text{C}$.⁴⁵ From the X-ray crystal structure, α -14S4 crystallizes in a monoclinic unit cell, space group $P2_1/n$, with two molecules per unit cell, $R = 2.7\%$.⁸ The 14S4 molecules are square, with sulfurs at the corners, C_i conformation (C_{2h} slightly distorted).⁸ The main distinction between the α - and β -forms is disorder in the ethano bridges in the latter.⁸ Since the α - and β -polymorphs are reported to melt at the same temperature,⁸ it is possible that the solid–solid transition that we observe at $72 \text{ }^\circ\text{C}$ is the transformation from the α -form to the β -form. This conclusion is consistent with the small value of ΔS_{trs} .

Our IR and NMR investigations indicate significant conformational differences between the 14S4 molecule in the solid state and in solutions at room temperature.¹⁵ From our conformational calculations¹⁵ at room temperature, a C_{2h} conformer is lowest in energy, in agreement with other calculations;¹⁷ at the melting point, we calculate that many conformers contribute, with C_{2h} at 5%, C_i at 12%, two C_1 conformers at 12% and 9%, and nine other conformers each contributing a least 2%.¹⁵ The calculated value of ΔS_{conf} at the melting point (starting from a solid of only one conformer) is $30.2 \text{ J K}^{-1} \text{ mol}^{-1}$. It seems likely, based on the present experimental data (especially the large value of ΔS_{fus}), that conformational disorder is enhanced considerably on melting in 14S4.

G. Phase Transitions in 15S5. We find two solid–solid transitions ($45 \text{ }^\circ\text{C}$ and $67 \text{ }^\circ\text{C}$, each broadened and possibly involving more than one step) in 15S5 prior to melting at $118 \text{ }^\circ\text{C}$. We are puzzled by the lack of agreement with the literature⁴⁵ melting point of $97.5\text{--}99 \text{ }^\circ\text{C}$, but note that our melting point value was essentially the same in three different methods (two DSCs and hot-stage microscope), and ours is the same melting point as quoted by Aldrich. We confirmed that the compound measured was indeed 15S5 by mass spectrometry (prominent M^+ peak and no higher mass peaks).

In the $23 \text{ }^\circ\text{C}$ X-ray diffraction investigation,⁴⁶ 15S5 was found to crystallize in the monoclinic space group $P2_1/n$, four molecules per unit cell, $R = R_w = 4.6\%$; the conformation observed for 15S5 is of C_1 symmetry. From our room-temperature ^{13}C NMR studies, we find that the solid-state conformation is changed to a mixture of conformations in solution and the solid-state conformation is no longer dominant.¹⁵

The total entropy change for the solid–solid transitions and melting, ΔS_{tot} , is $89 \text{ J K}^{-1} \text{ mol}^{-1}$, which indicates that more conformational degrees of freedom likely are active in the melt than in the room-temperature solid. Molecular modeling calculations for the melting point temperature indicate no dominant conformer: a C_1 conformer has the highest probability at 8%, with 16 conformers contributing at least 2% each.¹⁵ The value of ΔS_{conf} relative to a rigid molecular solid is calculated¹⁵ to be $34.4 \text{ J K}^{-1} \text{ mol}^{-1}$ which, with a “normal” ΔS_{fus} of $60 \text{ J K}^{-1} \text{ mol}^{-1}$, provides a good match for the experimentally determined value of ΔS_{tot} . Given the rather low value of ΔS_{fus} for 15S5, it is likely that the two solid–solid transitions are associated with

increasing conformational degrees of freedom and possibly some orientational disorder.

H. Phase Transitions in 16S4. 16S4 has three distinct polymorphs: the morphologies are acicular (α), lamellar, (β) and columnar (γ).¹⁹ The α - and β -forms can be obtained by the diffusion of hexane into CH_2Cl_2 at room temperature, and the γ -form is obtained at lower temperature.¹⁹ We carried out thermal analysis of both the α - and β -forms here and found that they are very similar (Table 1 and Figure 5). (The sample examined with the DSC-2910, which was somewhat larger [8 mg compared with 1 mg] and possibly not a pure polymorph, gave less separation of the two observed transitions.) The melting points (Table 1) are very close to previous observations (59.5–60.2 °C for α and 57.8–59.0 °C for β)¹⁹ and not very much different for mixed polymorphs.¹⁹ Although it has been concluded¹⁹ that α , β , and γ are distinct crystalline forms, we find it surprising that both the solid–solid transition and the melting points of α and β should be so similar if they are distinct. In any case, X-ray crystallography shows that the conformation of the 16S4 molecule is very similar in both the α and β structures, approximately rectangular with sulfur atoms in two corners (approximately C_2 symmetry).¹⁹

As discussed already, the low value of ΔS_{fus} for 16S4 is consistent with an orientationally disordered phase just below the melting point. Considering the large value of ΔS_{tot} (ca. 105 J K⁻¹ mol⁻¹), the melt likely is considerably more disordered conformationally than is the room-temperature solid. Molecular modeling calculations at the melting temperature indicate no dominant conformer (major contributor is C_1 at 16% probability; 10 conformers contribute 3% or more each), and the calculated value of ΔS_{conf} relative to an ordered solid is 30 J K⁻¹ mol⁻¹.¹⁵ On the basis of a “normal” ΔS_{fus} and this value of ΔS_{conf} , ΔS_{tot} would be expected to be ≈ 90 J K⁻¹ mol⁻¹, which is still somewhat less than that observed, possibly indicating a large contribution from ΔS_{vol} .

I. Melting Points. From the present data, two melting points look somewhat unusual: the melting point of 12S4 is anomalously high and that of 16S4 is anomalously low. Kitaigorodsky¹ has pointed out the relationship between melting point and packing coefficient (defined as the ratio of volume occupied by the molecule to available volume). Whereas most molecular crystals have packing coefficients in the range 0.65 to 0.77, the packing coefficients calculated from the X-ray diffraction data for the crown thioethers studied here all have packing coefficients in the range 0.59 ± 0.03 . These values are low and closer to that expected for a liquid,³⁹ so it is somewhat surprising that these materials are solids at room temperature. Nevertheless, the packing coefficients for the compounds with anomalous melting points (12S4 and 16S4) are not out of line with the others, and an explanation for the unusual melting points must be sought elsewhere.

It was observed some time ago that symmetric molecules form solids with higher melting points than less symmetric molecules.^{49,50} This conclusion fits with Timmermans' finding that solids exhibiting orientational disorder (which is prevalent in symmetric molecules) have higher melting points (i.e., reduced liquidus ranges) compared with more ordered materials.²⁷ Therefore, we could understand the unusual melting points if 12S4 formed a disordered solid (but it does not) and if 16S4 remained ordered up to the melting point (but it has an order–disorder transition), and the anomalous melting points must have other origins.

Considerations of packing fractions and molecular symmetry in controlling the melting point ignore the important role of

the stability of the liquid phase. If, for example, the liquid were highly disordered due to conformational degrees of freedom unavailable in the solid, this could stabilize the liquid relative to the solid and lower the melting point, as for 16S4. The converse also would be true: if the liquid had no more conformational disorder than the solid, the melting point would be expected to be higher, as in 12S4. Detailed thermodynamic studies of the solid and liquid phases of crown thioethers would be useful to investigate this matter further.

V. Conclusions

From our thermoanalytical studies of a series of crown thioethers, we find that several undergo solid–solid transformations prior to melting, and, in all cases examined except 12S4, experimental entropy changes indicate that the melt has considerably more conformational freedom than the room-temperature solid.

To assess the role of preorganizational conformation on the ability of crown thioethers to complex with transition metals, our investigations indicate directions for possible further investigation. For example, in 12S4 the solid, melt, and solution conformations are all the same, whereas in 9S3 and 15S5 the solid-state conformation is significantly different from that in solution or the melt.

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