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Theoretical Study of Urea and Thiourea. 2. Chains and Ribbons

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One-dimensional hydrogen-bonding aggregates of urea and thiourea corresponding to the two patterns, chains and ribbons, which are found in crystal structures of these molecules have been studied using *ab initio* and semiempirical molecular orbital theory. In accord with experimental evidence, long chains are found to be more stable than comparably sized ribbons for urea, although ribbons are favored for dimers and small aggregates. Thiourea ribbons are favored over chains for all aggregates, large and small, again in agreement with the experimental crystal structure. Thus, cooperative interactions dictate the hydrogen-bonding structure for urea, but not thiourea, crystals. Various *ab initio* (HF, MP2, and B3PW91 all the with the D95** basis set) and semiempirical (AM1 and SAM1) molecular orbital calculations were used for this study.

This is the second paper in the series dealing with the differences in molecular aggregation of urea and thiourea.¹ We have previously studied the molecular cluster formation preceding crystallization for several other organic compounds, including acetic acid,² cyclohexane-1,3-dione,³ and both *m*- and *p*-nitroaniline.⁴ In this paper, we shall apply similar molecular orbital techniques to urea and thiourea. Despite the close similarity in the molecular structure, urea and thiourea form different crystal structures. As was discussed in the first paper of the series, urea molecules linked in the crystal by H-bonds in head-to-tail manner, whereas thiourea molecules linked by centrosymmetric cyclic H-bonds.⁵ Understanding the reasons for these differences is both interesting and important to the theoretical analysis of intermolecular interactions in general and for crystal engineering in particular.

In the first paper of this series we have shown that equilibrium geometry of the urea molecule is not planar in all levels of theory, in accord with other theoretical calculations.^{6–11} However, the barrier to planarization is systematically lowered by H-bond formation and application of external electric fields.¹² Moreover, zero-point vibrational energy (ZPVE) and thermal energy corrections make the planar structure of the isolated molecule preferable at the Hartree–Fock (HF) and density functional theory (DFT) levels using both large (6-311+G(3df,2p)) and medium-sized (D95**) basis sets. At the MP2/6-311+G(3df,2p) level (the highest level considered) ZPVE correction makes the planar structure the most stable; however, the nonplanar structure remains more stable with the smaller (D95**) basis set at the second-order Møller–Plesset (MP2) level. These results agree with the recent microwave spectroscopic investigation of a urea molecule in the gas phase.¹⁰ The experiment shows the zero-point vibration to be above the planarization barrier. The nuclear wave function is symmetric, with the planar conformation as the average. On the basis of these results, we considered the urea molecule to be planar for all aggregates considered. The thiourea molecule, which is even more easily planarized (see below), was also held planar in the aggregates calculated.

Methods

Theoretical calculations were performed using the GAUSSIAN 94, and GAUSSIAN 98¹³ programs for both *ab initio* and semiempirical molecular orbital (MO) methods. Single-point HF calculations on infinite chains and ribbons were performed using the CRYSTAL 92/95¹⁴ programs. Unless otherwise noted, all geometries were optimized with the following constraints: (a) all molecules are assumed to have C_{2v} symmetry; (b) inter- and intramolecular geometrical parameters were kept equivalent for molecules within a given aggregate. These constraints are meant to simulate translational symmetry within the crystal. Full optimization was performed in some cases for comparison.

Since the result of partial optimization is not a stationary point, vibrational frequencies were calculated for fully optimized oligomers only. These were used to estimate ZPVE corrections for other oligomers. We performed HF, DFT, and MP2 (frozen core) calculations using the D95** basis set, as well as AM1¹⁵ semiempirical calculations. For the DFT calculations, we used the hybrid B3PW91 method, for reasons described previously.¹ This method combines Becke's three-parameter functional¹⁶ with the nonlocal correlation provided by the Perdew–Wang expression.¹⁷ Correction for BSSE was performed using the somewhat controversial¹⁸ counterpoise (CP) method of Boys and Bernardi,¹⁹ taking into account the distortion of the reagents as described elsewhere.²⁰

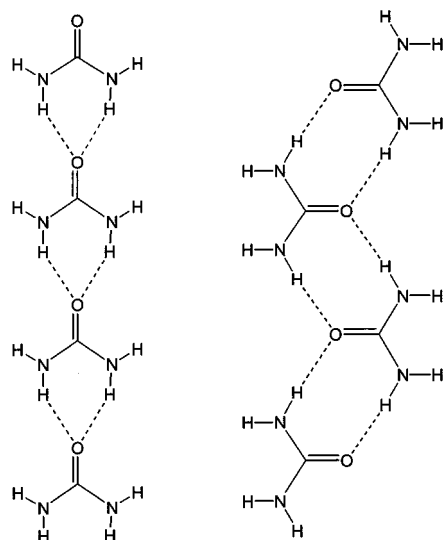
Results and Discussion

Thiourea Monomer. The results for thiourea monomer are summarized in Table 1. At the HF/D95** level, the planar conformation is the only critical point on the surface. Using DFT and/or MP2 with the same basis set resulted in minima representing trans and cis conformers, as in the case of urea.¹ However, the planar barrier for thiourea is about half that of urea. Like urea, thiourea becomes planar after the thermal corrections are applied.

Aggregates. Urea. We have considered two types of planar, one-dimensional oligomers: chains and ribbons (Figure 1). The energies obtained for these oligomers at the HF/D95** level are presented in Tables 2 and 3. The geometrical parameters

TABLE 1: Energetic Results of ab Initio Calculation on Thiourea Monomer^a

method	sym	total energy	ΔE , kcal/mol	ΔH_0 , kcal/mol	ΔH_{293} , kcal/mol
HF/D95**	C_{2v}	-546.652508			
DFT/D95**	C_{2v}	-548.143869	0.73	0.00	0.00
DFT/D95**	C_2	-548.145032	0.00	0.49	0.82
DFT/D95**	C_s	-548.143977	0.66	0.30	0.58
MP2/D95**	C_{2v}	-547.238024	1.50	0.15	0.00
MP2/D95**	C_2	-547.240409	0.00	0.00	0.10
MP2/D95**	C_s	-547.238691	1.08	0.52	0.91

^a Total energies in hartree, others in kcal/mol.**Figure 1.** Hydrogen-bonding patterns in chains (left) and ribbons (right) of urea. The structures for thiourea are analogous.**TABLE 2: Ab Initio Results for Urea Ribbons, HF/D95**^a**

n	ΔE	ΔE_n	ΔE_n				
			CP	ZPVE	CP	ZPVE	CP + ZPVE
2	-12.44	-12.44 (-12.75)	0.95	(1.92)	-11.49	-10.52	-9.57
3	-23.62	-11.18 (-11.37)	2.03	(3.63)	-10.10	-9.48	-8.40
4	-35.18	-11.56 (-11.65)	3.02	(5.37)	-10.57	-9.82	-8.38
5	-46.67	-11.49	4.04	7.08	-10.46	-9.78	-8.75
6	-58.23	-11.56	5.06	8.85	-10.54	-9.79	-8.77
7	-69.76	-11.54	6.08	10.62	-10.52	-9.77	-8.75
8	-81.32	-11.56	7.10	12.39	-10.54	-9.79	-8.77
9	-92.88	-11.55	8.13	14.16	-10.53	-9.78	-8.76
10	-104.44	-11.56	9.14	15.93	-10.55	-9.79	-8.78
∞		-11.58			-10.65	-9.81	-8.91

^a All values are given in kcal/mol. Total stabilization energy ΔE is uncorrected; last H-bond energy $\Delta E_n = \Delta E(n) - \Delta E(n-1)$ is given before and after counterpoise (CP) and zero-point vibrational (ZPVE) correction is applied. Values in parentheses correspond to completely optimized oligomers; ZPVE correction values for $n = 5-10$ are estimated, asymptotic values obtained by extrapolation using formula $E_n = E_2 + a(\exp(b(2-n)) - 1)$.

are summarized in Table 4. As one can see from comparison of Tables 2 and 3, the net stabilization energy, ΔE , is greater for ribbons than for chains when the oligomers are small. The difference is most significant for the dimers, decreasing as the oligomer grows. For the decamer (the largest oligomer considered) the order of stability reverses. Extrapolating this trend, we can expect infinite chain to be more stable than the infinite ribbon.

To analyze individual H-bonds, we used the last H-bond energy, ΔE_n , defined as the difference between stabilization for oligomers with n and $(n-1)$ molecules. This value converges

TABLE 3: Energetic (kcal/mol) Results of ab Initio Calculation on Urea Chains Using HF/D95**

n	ΔE	ΔE_n	CP	ZPVE	ΔE_n		
					CP	ZPVE	CP + ZPVE
2	-8.64	-8.64 (-8.78)	0.69	(1.06)	-7.96	-7.58	-6.90
3	-19.54	-10.89 (-11.01)	1.45	(2.08)	-10.13	-9.74	-8.97
4	-31.23	-11.69 (-11.79)	2.15	(3.36)	-11.00	-10.41	-9.71
5	-43.27	-12.04	3.06	4.80	-11.13	-10.60	-9.69
6	-55.49	-12.22	3.88	6.00	-11.41	-11.02	-10.21
7	-67.82	-12.33	4.69	7.20	-11.52	-11.13	-10.32
8	-80.22	-12.40	5.52	8.40	-11.57	-11.20	-10.37
9	-92.66	-12.44	6.34	9.60	-11.62	-11.24	-10.42
10	-105.14	-12.47	7.17	10.80	-11.65	-11.27	-10.45
∞		-12.49			-11.77	-11.38	-10.70

to the same asymptotic limit as the average H-bond energy. However, the convergence is faster, thus, easier to extrapolate. Comparison of Tables 2 and 3 indicates the last H-bond to be stronger for chains than for ribbons starting with tetramer. Application of CP and especially ZPVE corrections favors the chains, moving the crossover point to the trimers. For the chains the increase in the magnitude of ΔE_n is monotonic with growth of the cluster. This behavior is consistent with the chain structure, which has only one repeating unit (Figure 1). However, the magnitude of ΔE_n oscillates for ribbons: decreasing with n for odd oligomers, constant for even oligomers. Ribbons have a repeating unit that contains two molecules (Figure 1) where 1-3 interactions should be destabilizing (see below). Thus, aggregation is progressively stabilizing H-bonding for chains, but not for ribbons. We extrapolated last H-bond energy using the same relationship

$$\Delta E_n = \Delta E_2 + a(\exp(b(2-n)) - 1)$$

as in previous work² (for ribbons, only even oligomers were used). The asymptotic value of ΔE_n for chains is about 1 kcal/mol more stable than the corresponding value for ribbons, which is comparable to H-bonding energy for the ribbon dimer. CP and ZPVE corrections increase the energetic preference for the chain (see Figure 2).

The extrapolated value of ΔE_n is 46% greater than that of the dimer for the chain. For ribbons the extrapolated value of ΔE_n is 8% less than that of the dimer but very similar to the ΔE_n for the trimer and higher aggregates. The apparent anticooperative behavior of the ribbon is due to the repulsive nature of the 1-3 interactions that do not exist in the dimer. To illustrate this point, we calculated the pairwise components of the stabilization energies of the oligomers. To this end, we performed single point, CP-corrected calculations for all possible molecular pairs within the structure of the cluster. The CP-corrected interaction for the 1-3 pair is 1.37 kcal/mol (HF/D95**). The ratio of 1-2 to 1-3 interactions decreases from 2 (for the trimer) to 1 (for an infinite chain) as the aggregate grows.

The behavior of the dipole moments of the aggregates as a function of size (Table 4) is consistent with the energetic analysis. For the urea chain, the dipole moment/molecule increases from the monomeric value of 4.70 to 6.57 D in the decamer, an increase of 40%. Thus, the molecules become increasingly polarized as the chain grows. Since the dipole moment of an aggregate of classical dipoles is the vector sum of their individual dipole moments, this behavior is consistent with a significant component of nonadditive cooperativity. For the ribbon, the situation is quite different. All aggregates that contain even quantities of monomers have zero dipole moments

TABLE 4: Dipole Moments, μ (D), and the Bond Lengths (Å) for the Ribbons and Chains of Urea, from *ab Initio* Calculations (HF/D95**)^a

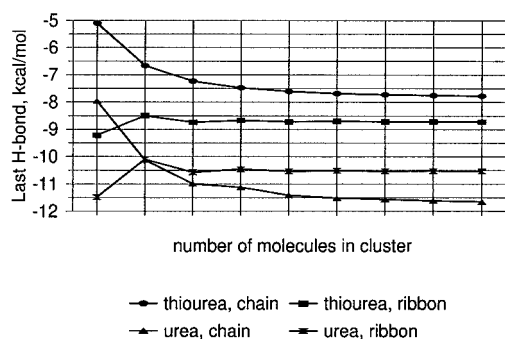
	ribbon						chain					
	μ	C=O	C—N	N—Hs	N—Ha	O···H	μ/n	C=O	C—N	N—Hs	N—Ha	O···H
1	4.70	1.2047	1.3644	0.9911	0.9923		4.70	1.2047	1.3644	0.9911	0.9923	
2	0.00	1.2164	1.3563	0.9997	0.9912	1.9856	5.42	1.2110	1.3595	0.9927	0.9919	2.2405
3	4.78	1.2199	1.3543	0.9989	0.9912	1.9948	5.82	1.2146	1.3568	0.9938	0.9917	2.1894
4	0.00	1.2218	1.3531	0.9998	0.9912	1.9943	6.06	1.2169	1.3551	0.9946	0.9915	2.1614
5	4.81	1.2230	1.3525	1.0003	0.9912	1.9960	6.22	1.2184	1.3541	0.9952	0.9914	2.1440
6	0.00	1.2238	1.3520	1.0007	0.9912	1.9958	6.33	1.2195	1.3533	0.9956	0.9914	2.1323
7	4.82	1.2243	1.3517	1.0009	0.9912	1.9956	6.41	1.2204	1.3527	0.9959	0.9913	2.1239
8	0.00	1.2248	1.3514	1.0011	0.9912	1.9954	6.48	1.2210	1.3523	0.9961	0.9914	2.1174
9	4.83	1.2251	1.3512	1.0013	0.9912	1.9951	6.53	1.2215	1.3519	0.9963	0.9913	2.1126
10	0.00	1.2254	1.3511	1.0014	0.9912	1.9951	6.57	1.2220	1.3516	0.9964	0.9912	2.1087
∞		1.2259	1.3507	1.0018	0.9912	1.9919		1.2233	1.3507	0.9967	0.9911	2.1002
ex								1.2580	1.3440	1.0220	1.0040	2.001

^a Experimental values for the chain are taken from neutron diffraction results⁵ of the crystal structure.**TABLE 5:** Energetic (kcal/mol) Results of *ab Initio* Calculations (MP2/D95**) for Urea Ribbons and Chains^a

<i>n</i>	ribbon						chain					
	ΔE	ΔE_n	CP	ΔE_n			ΔE	ΔE_n	CP	ΔE_n		
				CP	ZPVE	CP + ZPVE				CP	ZPVE	CP + ZPVE
2	-15.86	-15.86	3.87	-12.00	-14.23	-10.36	-10.41	-10.41	2.59	-7.81	-9.32	-6.73
3	-30.95	-15.08	7.62	-11.33	-13.64	-9.89	-23.41	-13.00	5.31	-10.28	-11.95	-9.24
4	-46.41	-15.46	11.44	-11.64	-13.99	-10.16	-37.36	-13.95	8.14	-11.12	-12.64	-9.81
5	-61.85	-15.44	15.28	-11.60	-13.99	-10.15	-51.75	-14.39	11.04	-11.50	-12.92	-10.03
∞		-15.48		-11.66	-13.99	-10.17		-14.50		-11.55	-13.00	-10.05

^a For ZPVE corrections HF/D95** values were used.**TABLE 6:** Energetic (kcal/mol) Results of *ab Initio* Calculations (DFT/D95**) for Urea Ribbons and Chains

<i>n</i>	ribbon						chain					
	μ	ΔE	ΔE_n	ΔE_n			μ/n	ΔE	ΔE_n	ΔE_n		
				CP	ZPVE	CP + ZPVE				CP	ZPVE	CP + ZPVE
1	4.43						4.43					
2	0.00	-14.38	-14.38	-12.83	-12.46	-10.91	5.31	-8.51	-8.51	-7.23	-7.59	-6.31
3	4.53	-27.60	-13.22	-11.64	-11.52	-9.94	5.83	-19.69	-11.18	-9.74	-10.03	-8.59
4	0.00	-41.24	-13.64	-12.03	-11.90	-10.29	6.15	-31.90	-12.21	-10.71	-10.93	-9.43
5	4.56	-54.85	-13.60	-11.99	-11.89	-10.28	6.37	-44.59	-12.69	-11.16	-11.25	-9.72
6	0.00	-68.53	-13.69	-12.08	-11.92	-10.31	6.54	-57.53	-12.94	-11.39	-11.74	-10.19
7	4.58	-82.21	-13.68	-12.06	-11.91	-10.29	6.66	-70.63	-13.10	-11.53	-11.90	-10.33
8	0.00	-95.92	-13.71	-12.09	-11.94	-10.32	6.76	-83.82	-13.19	-11.63	-11.99	-10.43
9	4.59	-109.63	-13.71	-12.09	-11.94	-10.32	6.84	-97.08	-13.26	-11.67	-12.06	-10.47
10	0.00	-123.35	-13.72	-12.10	-11.95	-10.33	6.89	-110.38	-13.30	-11.75	-12.10	-10.55
∞	4.61		-13.73	-12.11	-11.96	-10.34	7.07		-13.34	-11.77	-12.12	-10.57

**Figure 2.** Comparison of last H-bond interaction energies, ΔE_n , for urea and thiourea chain and ribbon aggregates.

because they are centrosymmetric. The dipole moments of the aggregates that contain odd quantities of monomers increase only modestly from 4.70 to 4.83 D upon increasing the aggregate from monomer to nonamer. This behavior is consistent with a negligible level of nonadditive cooperativity.

The results of the MP2, DFT, and semiempirical calculations are qualitatively similar to the HF calculations discussed above.

Table 5 indicates that the chain dimer is 4% less stable, while the ribbon dimer is 4% more stable at the MP2/D95** level than at the HF/D95** level (after all corrections). Consequently, ΔE_n for the chain tetramer does not exceed that for the ribbon tetramer (as it did for HF). However, the extrapolated values suggest that ΔE_n for the chain will exceed that for the ribbons at some later point in the growth of the aggregates. The DFT results reported in Table 6 are very similar to MP2 results. Although the stabilization energy and CP-corrected ΔE_n for the ribbon are more negative than for the chain even for the decamer, this is not true after ZPVE correction. This result must be qualified since ZPVE correction is extrapolated from the HF results for the tetramers. The AM1 and SAM1 semiempirical calculations results are presented in Table 7. These are close to the DFT results prior to ZPVE correction, which predict ribbons to be more stable.

Thiourea. The results of similar calculations of ribbons and chains formed by thiourea are presented in Tables 8 and 9. Ribbons are predicted to be more stable than chains for all aggregates (independent of size) at both HF and DFT levels. No MP2 calculations were performed for the thiourea aggre-

TABLE 7: Results of Semiempirical Calculations for Urea Ribbons and Chains (Energies in kcal/mol)

n	ribbon			chain		
	μ	ΔE	ΔE_n	μ/n	ΔE	ΔE_n
AM1						
1	4.14			4.14		
2	0.00	-8.80	-8.80	4.60	-6.13	-6.13
3	4.13	-17.02	-8.22	4.85	-13.54	-7.40
4	0.00	-25.41	-8.39	4.99	-21.38	-7.84
5	4.14	-33.75	-8.34	5.08	-29.40	-8.03
6	0.00	-42.13	-8.38	5.15	-37.53	-8.12
7	4.14	-50.49	-8.36	5.20	-45.70	-8.18
8	0.00	-58.87	-8.38	5.24	-53.91	-8.21
9	4.15	-67.24	-8.37	5.27	-62.15	-8.23
10	0.00	-75.61	-8.37	5.29	-70.39	-8.25
∞	4.15		-8.37	5.35		-8.27
SAM1						
1	4.23			4.23		
2	0.00	-8.04	-8.04	4.79	-3.85	-3.85
3	4.25	-15.41	-7.37	5.10	-9.33	-5.48
4	0.00	-23.10	-7.69	5.28	-15.40	-6.06
5	4.27	-30.72	-7.62	5.40	-21.72	-6.33
6	0.00	-38.40	-7.68	5.49	-28.18	-6.46
7	4.28	-46.07	-7.66	5.56	-34.72	-6.54
8	0.00	-53.76	-7.69	5.61	-41.31	-6.59
9	4.29	-61.43	-7.68	5.65	-47.93	-6.62
10	0.00	-69.11	-7.68	5.68	-54.57	-6.64
∞	4.32		-7.68	5.71		-6.67

TABLE 8: Energetic (kcal/mol) Results of ab Initio Calculations (HF/D95) for Thiourea Ribbons and Chains**

n	ribbon				chain			
	μ	ΔE	ΔE_n	ΔE_n , CP	μ/n	ΔE	ΔE_n	ΔE_n , CP
1	5.95				5.95			
2	0.00	-10.67	-10.67	-9.22	6.73	-5.42	-5.42	-5.10
3	6.08	-20.59	-9.92	-8.50	7.15	-12.45	-7.03	-6.66
4	0.00	-30.76	-10.17	-8.74	7.41	-20.05	-7.61	-7.23
5	6.11	-40.87	-10.11	-8.67	7.58	-27.92	-7.86	-7.47
6	0.00	-51.04	-10.16	-8.72	7.70	-35.91	-8.00	-7.60
7	6.12	-61.18	-10.15	-8.70	7.79	-43.99	-8.07	-7.68
8	0.00	-71.35	-10.17	-8.72	7.86	-52.11	-8.12	-7.72
9	6.13	-81.51	-10.16	-8.72	7.92	-60.26	-8.15	-7.75
10	0.00	-91.67	-10.17	-8.73	7.96	-68.43	-8.17	-7.77
∞	6.14		-10.17	-8.73	8.11		-8.19	-7.79

TABLE 9: Energetic (kcal/mol) Results of ab Initio Calculations (DFT/D95) for Thiourea Ribbons and Chains**

n	ribbon				chain			
	μ	ΔE	ΔE_n	ΔE_n , CP	μ/n	ΔE	ΔE_n	ΔE_n , CP
1	5.43				5.43			
2	0.00	-11.91	-11.91	-10.38	6.38	-5.19	-5.19	-4.78
3	5.60	-23.08	-11.17	-9.66	6.92	-12.25	-7.06	-6.59
4	0.00	-34.53	-11.45	-9.91	7.27	-20.05	-7.79	-7.28
5	5.63	-45.94	-11.41	-9.87	7.50	-28.17	-8.13	-7.61
6	0.00	-57.22	-11.48	-9.95	7.68	-36.48	-8.30	-7.76
7	5.64	-68.86	-11.46	-9.91	7.80	-44.89	-8.41	-7.81
8	0.00	-80.34	-11.48	-9.94	7.90	-53.36	-8.47	-7.92
9	5.65	-91.81	-11.47	-9.93	7.97	-61.87	-8.51	-7.97
10	0.00	-103.29	-11.48	-9.94	8.04	-70.42	-8.54	-7.98
∞	5.64		-11.48	-9.94	8.10		-8.61	-8.14

gates due to the limitations of our computational resources. The interaction energies between thiourea molecules is significantly less than between urea molecules. Furthermore, the ratio of the interaction energies of the chain vs ribbon dimers is 0.55 for thiourea compared to 0.72 for urea (HF/D95**). While the cooperative effect upon the extrapolated value of the thiourea chain for the infinite chain is comparable to that for urea, 53% vs 55% (HF/D95**), it is insufficient to overcome the more favorable interaction energy of the chain com-

pared to the ribbon dimer. Figure 2 presents a comparison of urea and thiourea CP-corrected ΔE_n 's in chains and ribbons.

The dipole moments of the thiourea chain increase from the monomeric value of 5.95 to 7.96 D in the decamer, an increase of 36% (similar to the 40% increase for urea). For the ribbon, the nonamer has a dipole moment of 6.13, only slightly more than the monomeric value of 5.96 D.

Conclusions

The observed differences in the hydrogen-bonding patterns within the crystal structures of urea (which forms chains) and thiourea (which forms ribbons) are primarily due to the relative quantitative strengths of the H-bonds in the relevant dimers. For both urea and thiourea, the ribbon dimer (which contains two H-bonds with each O or S acting as an acceptor) is more stable than the chain dimer (where one O or S is the acceptor for both H-bonds). The comparable interactions are weaker in thiourea than in urea. Furthermore, the relative strength of the ribbon vs chain is greater in thiourea. The cooperative interactions for the urea and thiourea chains are similar. The cooperative interactions for both ribbons are negligible. The result is that, as the chains grow, the cooperative interaction of the urea chain (but not the thiourea chain) becomes sufficient to overcome the disparity between the H-bonding energies of the chain and ribbon dimers.

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References and Notes

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