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Theoretical Study of Urea. I. Monomers and Dimers

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Ab initio (HF, MP2, and B3PW91 with basis sets up to D95++**) and semiempirical (AM1, PM3, and SAM1) molecular-orbital calculations are presented for urea and four different general classes of urea dimeric structures that correspond to interactions between nearest-neighbor molecular pairs in the crystal structures of urea and thiourea. While the urea monomers have nonplanar minima on all ab initio surfaces, on the HF and MP2/6-311+G(3df,2p) surfaces they are planar after vibrational and thermal corrections. Urea chain and ribbon dimers are calculated to be planar after counterpoise and thermal corrections for all HF calculations and nonplanar for MP2 calculations (D95** and D95++**). The DFT calculations predict planar chain but nonplanar ribbon dimers. The ribbon dimer is the most stable, as it uses both H-bond acceptors, while the chain dimer uses only one and the herringbone dimer has one H bond. Stacking interaction is much less stabilizing. The PM3 method fails in both predicting molecular conformations and H bonds, while AM1 gives reasonable results.

Urea and thiourea provide interesting and contrasting examples of how small changes in molecular structures can have large influences upon crystal structures. Investigating the bases for these effects can be of singular importance for understanding and designing the intermolecular interactions that dictate crystal packing. These will eventually play important roles in crystal engineering.

We have previously studied the intermolecular interactions that lead to crystallization for several other organic compounds, including acetic acid,[1] cyclohexane-1,3-dione,[2] and both *m*- and *p*-nitroaniline.[3] In this and subsequent papers, we shall apply similar molecular-orbital techniques to urea and thiourea. This paper concentrates upon the particular problems posed by the monomeric and dimeric structures of urea itself.

Most chemists assume that urea is a planar symmetrical molecule. Indeed, the crystal structures that have been published reinforce this assumption.[4] Recently, Bowen,[5] Coussens,[6] Frenking,[7] and Dixon[8] published theoretical studies of urea using ab initio and DFT calculations up to MP4/6-311G**//MP2/6-31G*. These studies showed the parent molecule to be nonplanar. The planar structure was reported to be a second-order saddle point connecting the two pairs of equivalent nonplanar minima. In fact, the nonplanarity of urea had previously been reported as part of an early vibrational analysis in an argon matrix.[9] Although several groups were aware of the reported nonplanarity of urea, other vibrational and microwave analyses have assumed planarity for simplicity. These studies posed serious complications to our initially planned project, which assumed the planar urea structure to be correct. The work reported here concentrates on the relative energies and structures of the various monomeric and dimeric forms. In particular, we evaluate the problems involved in assuming a planar structure for larger aggregates leading to microcrystals.

Methods

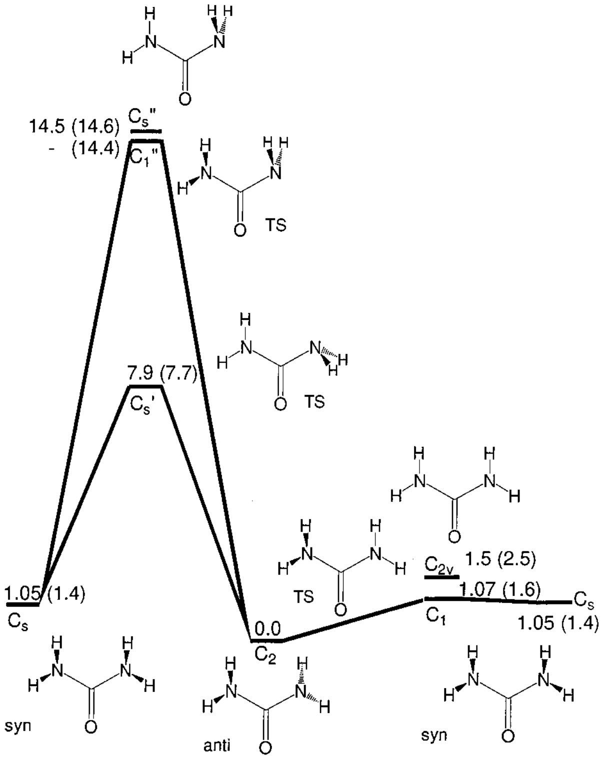

Figure 1. Various stationary points on the monomeric urea potential surface. B3PW91/D95** relative energies before vibrational corrections are presented with MP2/D95** values in parentheses.

Theoretical calculations were performed using the GAUSSIAN 92, GAUSSIAN 94,[10] GAMESS,[11] and AMPAC 5.0[12] programs for ab initio and semiempirical molecular-orbital (MO) methods, respectively. Unless otherwise noted, all geometries were completely optimized at the level of calculation noted. Vibrational frequencies were calculated to verify the nature of the stationary points found on the potential surface. We performed HF, DFT, and MP2 calculations using the D95** and D95++** basis sets. For the DFT calculations, we used the hybrid B3PW91 method. This method combines Becke's

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TABLE 1: Results of Semiempirical and ab Initio Calculations for Urea Conformers[a]

method	sym	I.F.	m_D	ΔH	E	ΔE	$\Delta\Delta H_0$	$\Delta\Delta H_{298}$
AM1	C_{2v}	1	4.13	−44.08				0.87
	C_2	0	3.59	−44.95				0.00
SAM1	C_{2v}	1	4.23	−44.07				0.04
	C_2	0	4.13	−44.11				0.00
PM3	C_{2v}	2	4.07	−40.96				6.05
	C_2	0	3.02	−47.01				0.00
	C_s	0	3.82	−45.82				1.19
HF/6-31G*	C_{2v}	2	4.6		−223.982192	1.57	0.08	0.00
	C_2	0	3.85		−223.984692	0.00	0.00	0.17
	C_s	1	4.6		−223.982603	1.31	0.32	0.44
HF/D95**	C_{2v}	2	4.7		−224.046152	1.29	0.00	0.00
	C_2	0	4.01		−224.048215	0.00	0.14	0.37
	C_s	0	4.69		−224.046551	1.04	0.35	1.05
HF/6-311+G(3df,2p)	C_{2v}	2	4.59		−224.080708	0.58	0.00	0.00
	C_2	0	4.06		−224.082071	0.00	0.26	0.47
	C_s	1	4.56		−224.080919	0.49	0.17	0.35
MP2/D95**	C_{2v}	2	4.85		−224.681770	2.49	1.04	0.84
	C_2	0	3.92		−224.685742	0.00	0.00	0.00
	C_s	0	4.82		−224.683453	1.44	1.01	1.20
MP2/6-311G+(3df,2p)	C_{2v}	op[b]	4.72		−224.887657	1.19	0.00	0.00
	C_2	op[b]	3.91		−224.889549	0.00	0.51	0.64
	C_s	op[b]	4.68		−224.888181	0.86	1.06	1.33
DFT/D95**	C_{2v}	2	4.43		−225.234852	1.46	0.10	0.00
	C_2	0	3.74		−225.237182	0.00	0.00	0.15
	C_s	0	4.43		−225.235506	1.05	0.43	0.91
DFT/6-311+G(3df,2p)	C_{2v}	2	4.38		−225.274381	0.59	0.00	0.00
	C_2	0	3.86		−225.275759	0.00	0.21	0.43
	C_s	1	4.35		−225.274654	0.47	0.15	0.31
experiment (gas)[c]			3.83					
experiment (solution)[d]			4.2					

[a] I.F. = number of imaginary frequencies; ΔH_0 = heat of formation (kcal/mol); E = total electronic energy (au); ΔE = relative energy (kcal); $\Delta\Delta H_0$ = relative energy with zero-point vibration correction (kcal/mol); $\Delta\Delta H_{298}$ = relative energy corrected for thermal vibrations at 298 K (kcal); μ_D = dipole moment (debye). [b] Optimization only, vibrational energies calculated at MP2/6-311++G** level. [c] Reference 23. [d] Reference 24.

three-parameter functional[13] with the nonlocal correlation provided by the Perdew−Wang expression.[14] According to recent reports,[15] only hybrid functionals can provide an accurate description for the systems with hydrogen bonds. MP2(full)/6-31G* was also used for comparison with Frenking's work.[6] Unless otherwise noted, all MP2 calculations were performed using the frozen-core (FC) option. We prefer the D95 to the 6-31G series of basis sets as they tend to give smaller basis-set superposition errors (BSSE) when intermolecular interaction are considered.[16] We performed semiempirical calculations using the AM1,[17] PM3,[18] and SAM1[19] approximations of MO theory.

Vibrational corrections using the habitual harmonic approximation were performed to obtain the zero-point vibrational energies (ZPVE) and heats of formation at 298 K. Correction for BSSE was performed using the somewhat controversial[20] counterpoise (CP) method of Boys and Bernardi,[21] taking into account the distortion of the reagents as described elsewhere.[22]

Optimizations of urea molecules in uniform electric fields were performed using the GAMESS program, as GAUSSIAN 94 does not allow this procedure. Since GAMESS does not perform DFT calculations, these optimizations were restricted to HF and MP2 calculations.

Results and Discussion

Monomers. The results for urea monomer are summarized in Tables 1 and 2. Figure 1 depicts the various possible structures for urea monomer. The energetic data of Table 1 (and Table 1a in the Supporting Information) show that none of the methods used found a planar minimum for the monomeric urea molecule. Most ab initio methods (before vibrational correction) and PM3 found two negative vibrational frequencies for planar urea, while HF/6-31G*, AM1, and SAM1 each found only one.

Ab initio methods using large basis sets and PM3 predict two minima on the potential energy surface: (a) an anti-conformation of C_2 symmetry with the H's of the NH_2 groups pyramidalized on opposite sides of the molecule and (b) a less stable syn-conformation C_s with the H's of the NH_2 groups pyramidalized on the same side. The conversion between these two conformations could occur either by inversion (via transition-state C_1) or rotation (via transitions states C_s', C_1'').

To properly compare the energies obtained from ab initio calculations (which give ΔE's) with those obtained from semiempirical calculations (which give ΔH's), thermal and vibrational corrections must be applied to the ab initio results. After application of the vibrational corrections at 298 K, all HF and DFT ab initio methods predict planar, C_{2v} to be very slightly more stable than C_2 (by 0−0.4 kcal/mol). The MP2 calculations all find the anti, C_2, urea molecule to be the most stable. The highest level within the D95 hierarchy (MP2/D95++**) predicts the C_2 structure to be 1.2 kcal/mol more stable than C_{2v}. At the MP2/6-311+G(3df,2p) level (which has a lower total energy than MP2/D95++**) with thermal correction from MP2/6-311++G**, C_2 is 0.6 kcal/mol less stable than the planar structure. AM1 predicts the C_2 structure to be more stable than the C_{2v} one by 0.9 kcal/mol, in agreement with the MP2 calculations in the medium basis sets. SAM1 favors C_{2v} by less than 0.1 kcal/mol. PM3, on the other hand, favors the C_2 structure by over 6 kcal/mol, in clear disagreement with all the others. The largest energy range among the three structures among the ab initio results is 1.45 kcal/mol for MP2-(full)/6-31G*.

While the best calculations predict planar urea at 298 K, one should note that the calculated dipole moments of the C_2 structure are consistently in better agreement with the reported

TABLE 2: Bond Lengths and H Bonds for Planar Urea Monomers and Dimers (Å)[a]

method		C═O	C−N	C−N′	N−H	N−H″	N′−H″	N′−H‴	H···O	H″···O
AM1	monomer	1.258	1.390		0.984	0.988				
	CF dimer, d	1.262	1.388		0.988	0.986			2.206	
	CF dimer, a	1.262	1.387		0.985	0.988				
	RF dimer	1.268	1.382	1.391	0.988	0.996	0.985	0.987		1.988
PM3	monomer	1.232	1.405		0.990	0.990				
	CF dimer, d	1.236	1.402		0.991	0.990			2.597	
	CF dimer, a	1.236	1.402		0.990	0.990				
	RF dimer	1.245	1.391	1.403	0.989	1.011	0.990	0.990		1.792
HF/6-31G*	monomer	1.202	1.360		0.990	0.991				
HF/D95**	monomer	1.205	1.364		0.991	0.992				
	CF dimer, d	1.210	1.362		0.994	0.991			2.222	
	CF dimer, a	1.213	1.357		0.992	0.993				
	RF dimer	1.217	1.349	1.363	0.991	1.004	0.991	0.992		1.966
HF/D95++**	monomer	1.204	1.364		0.992	0.993				
	CF dimer, d	1.209	1.361		0.994	0.992			2.242	
	CF dimer, a	1.213	1.357		0.992	0.993				
	RF dimer	1.217	1.349	1.363	0.992	1.004	0.992	0.993		1.980
HF/6-311G**	monomer	1.196	1.361		0.990	0.991				
MP2/6-31G*	monomer	1.228	1.374		1.007	1.007				
MP2/D95**	monomer	1.232	1.381		1.005	1.005				
	CF dimer, d	1.237	1.379		1.009	1.005			2.104	
	CF dimer, a	1.240	1.372		1.005	1.006				
	RF dimer	1.247	1.362	1.379	1.006	1.024	1.005	1.005		1.836
MP2/D95++**	monomer	1.233	1.381		1.006	1.006				
	CF dimer, d	1.237	1.378		1.010	1.006			2.121	
	CF dimer, a	1.241	1.372		1.006	1.007				
	RF dimer	1.247	1.362	1.379	1.006	1.024	1.006	1.006		1.841
MP2/6-311G**	monomer	1.221	1.377		1.004	1.005				
MP2/6-311G(3df,2p)	monomer	1.219	1.370		1.002	1.002				
DFT/D95**	monomer	1.226	1.378		1.006	1.006				
	CF dimer, d	1.231	1.376		1.011	1.005			2.122	
	CF dimer, a	1.234	1.370		1.007	1.007				
	RF dimer	1.243	1.357	1.376	1.007	1.032	1.006	1.006		1.779
DFT/D95++**	monomer	1.226	1.377		1.007	1.007				
	CF dimer, d	1.231	1.374		1.011	1.006			2.153	
	CF dimer, a	1.234	1.369		1.007	1.007				
	RF dimer	1.242	1.356	1.375	1.007	1.031	1.007	1.007		1.795
neutron diffraction[b]	crystal	1.261	1.345		1.005	1.009			2.058	

[a] For chain dimers, d and a refer to the H donor and H acceptor, respectively. [b] Reference 4.

gas-phase experimental value of 3.83 D[23] and the calculated dipole moments of the planar C_{2v} structure are in better agreement with solution experimental value of 4.2 D.[24] However, HF calculations generally overestimate dipole moments. MP2 calculations, while usually significantly better than HF, still often overestimate dipoles.[25]

The rotational transitions of the urea molecule were the subjects of previous theoretical studies. Rotational barriers of about 8−9 kcal/mol have been reported for the lower barrier[5,7,8] and 13.5−14.3 kcal/mol for the higher barrier.[8] We have calculated similar rotational barriers of 8.5 and 13.7 (HF/D95**) and 7.3 and 13.4 kcal/mol (DFT/D95**) after thermal correction.

However, the apparent planarity of the vibrationally corrected molecule argues that the barrier for inversion should be zero or very close to zero. A TS with one pyramidal and one planar NH_2 group was studied for the first time. Its uncorrected energy is intermediate between C_2 and C_{2v}, lying below C_s after ZPVE and thermal correction for all ab initio methods. The C_{2v} structure becomes most stable after vibrational corrections at the MP2/6-311G+(3df,2p) level. Therefore, one can effectively consider the urea molecule as being planar. Further details are furnished in the Supporting Information.

Selected geometrical information of the monomers is collected in Table 2 (a more complete table is included in the Supporting Information). The semiempirical calculations tend to have longer C−N and shorter C═O distances than the best (MP2 and DFT) calculations, while the HF calculations tend to have shorter C−N and longer C═O distances.

Dimers. The results of the calculations on the dimers are collected in Tables 2 and 3. The geometric analysis for the dimers becomes somewhat complex due to (a) the possible combinations of monomer conformations that can statistically occur in the dimer and (b) the different possibilities of intermolecular interactions. We located four general classes of dimeric interactions: chain dimers, **C**, ribbon dimers, **R**, herringbone dimers, **H**, and stacked dimers, **S** (Figure 2). The first three of these structure types (**C**, **R**, and **H**) correspond to minima on the potential surface, while the last (**S**) corresponds to a saddle point. All four of these kinds of interactions play important roles in the crystal structures of urea and thiourea. The **C** interactions are similar to those in the linear chains found in urea crystals, while the **T** interactions are representative of the interchain interactions in these crystals. The **R** interactions form the ribbon-like structure of the thiourea crystals, while the **C** interactions link the ribbons together. **S** interactions are typical for many crystals with planar molecules. The fragments of urea and thiourea crystal structures are shown in Figure 3.

To better compare the MO-optimized geometries with experimental crystal structures, we imposed geometrical constraints in some (but not all) calculations. For the chains, we optimized the geometries with (a) both molecules constrained to be planar and geometrically equivalent, **CE**; (b) planar but geometrically different, **CF**; (c) collinear C═O bond, but not planar, **CL**; and (d) no constraints, **CB**. The **CE** structure mimics the translational symmetry of the urea crystal. In the **CB** structure, one urea is turned to form an additional H bond

TABLE 3: Dimers of Urea[a]

	type	sym	I.F.	mon		$\Delta\Delta H_{298}$	H···O	H···O	O···H	N···H
MP2/D95++**	CF	C_{2v}	op	C_{2v}	C_{2v}	−3.78(−4.57)	2.12	2.12		
MP2/D95**	CF	C_{2v}	op	C_{2v}	C_{2v}	−4.73(−5.05)	2.10	2.10		
DF/D95**	CF	C_{2v}	5	C_{2v}	C_{2v}	−6.17(−5.87)	2.12	2.12		
HF/D95++**	CF	C_{2v}	5	C_{2v}	C_{2v}	−7.23(−6.43)	2.24	2.24		
HF/D95**	CF	C_{2v}	5	C_{2v}	C_{2v}	−7.26(−6.52)	2.22	2.22		
AM1	CF	C_{2v}	4	C_{2v}	C_{2v}	−4.41(−6.15)	2.21	2.21		
PM3	CF	C_{2v}	4	C_{2v}	C_{2v}	8.99(−3.11)	2.60	2.60		
SAM1	CF	C_{2v}	2	C_{2v}	C_{2v}	−3.92(−4.00)	1.99	1.99		
MP2/D95++**	CL	C_2	op	C_2	C_2	−6.12	2.16	2.16		
MP2/D95**	CL	C_2	op	C_2	C_2	−5.41	2.15	2.15		
DF/D95**	CL	C_2	1	C_2	C_2	−4.03	2.15	2.15		
HF/D95++**	CL	C_2	1	C_2	C_2	−5.50	2.27	2.27		
HF/D95**	CL	C_2	1	C_2	C_2	−5.30	2.28	2.28		
AM1	CL	C_2	1	C_2	C_2	−5.62	2.22	2.22		
PM3	CL	C_2	1	C_2	C_2	−1.83	2.68	2.68		
SAM1	CL	C_2	1	C_{2v}	C_{2v}*	−4.05	1.99	1.99		
MP2/D95++**	CB1	C_1	0	C_2*	C_2*	−6.75	1.97	2.77		2.10
MP2/D95**	CB1	C_1	0	C_2*	C_2*	−6.73	1.96	2.71		2.08
DF/D95**	CB0	C_1	0	C_2*	C_2*	−7.05	1.91	2.93		2.07
DF/D95**	CB1	C_1	0	C_2*	C_2*	−6.94	1.91	2.86		2.07
HF/D95++**	CB1	C_1	0	C_2*	C_2*	−5.80	2.16	2.59		2.44
HF/D95**	CB0	C_1	0	C_2*	C_2*	−5.98	2.12	2.66		2.39
HF/D95**	CB1	C_1	0	C_2*	C_2*	−6.17	2.13	2.61		2.41
AM1	CB0	C_1	0	C_2*	C_2*	−6.55	2.20	2.24		2.65
AM1	CB1	C_1	0	C_2*	C_2*	−6.57	2.18	2.26		2.62
AM1	CB2	C_1	0	C_s*	C_2*	−6.68	2.18	2.18		2.72
SAM1	CB2	C_s*	0	C_s*	C_{2v}*	−4.19	1.99	2.00		3.84
SAM1	CB3	C_1	0	C_{2v}*	C_{2v}*	−4.42	1.87	3.10		3.45
PM3	CB0	C_1	0	C_2*	C_2*	−2.59	1.84	3.71		2.70
MP2/D95++**	RF	C_{2h}	op	C_{2v}*	C_{2v}*	−6.18(−8.88)		1.84	1.84	
MP2/D95**	RF	C_{2h}	op	C_{2v}*	C_{2v}*	−7.38(−9.47)		1.84	1.84	
DF/D95**	RF	C_{2h}	5	C_{2v}*	C_{2v}*	−11.82(−11.52)		1.78	1.78	
HF/D95++**	RF	C_{2h}	5	C_{2v}*	C_{2v}*	−10.07(−9.27)		1.98	1.98	
HF/D95**	RF	C_{2h}	5	C_{2v}*	C_{2v}*	−10.13(−8.03)		1.97	1.97	
AM1	RF	C_{2h}	3	C_{2v}*	C_{2v}*	−6.90(−8.64)		2.04	2.04	
PM3	RF	C_{2h}	4	C_{2v}*	C_{2v}*	4.07(−8.03)		1.79	1.79	
SAM1	RF	C_{2h}	0	C_{2v}*	C_{2v}*	−8.34(−8.42)		1.80	1.80	
MP2/D95++**	RP	C_i	0	C_2*	C_2*	−8.56		1.87	1.87	
MP2/D95**	RP	C_i	0	C_2*	C_2*	−8.46		1.87	1.87	
DF/D95**	RP	C_i	0	C_2*	C_2*	−10.22		1.80	1.80	
HF/D95++**	RP	C_i	0	C_2*	C_2*	−8.30		2.01	2.01	
HF/D95**	RP	C_i	0	C_2*	C_2*	−8.41		1.99	1.99	
AM1	RP	C_i	0	C_2*	C_2*	−8.56		2.07	2.07	
PM3	RP	C_i	0	C_2*	C_2*	−5.75		1.81	1.81	
MP2/D95++**	RT	C_2	0	C_2*	C_2*	−8.55		1.87	1.87	
MP2/D95**	RT	C_2	0	C_2*	C_2*	−8.47		1.87	1.87	
DF/D95**	RT	C_2	0	C_2*	C_2*	−10.24		1.80	1.80	
HF/D95++**	RT	C_2	0	C_2*	C_2*	−8.31		1.99	1.99	
HF/D95**	RT	C_2	0	C_2*	C_2*	−8.41		1.99	1.99	
AM1	RT	C_2	0	C_2*	C_2*	−8.86		2.09	2.09	
PM3	RT	C_2	0	C_2*	C_2*	−4.66		1.85	1.85	
DF/D95**	HB	C_1	0	C_s*	C_2*	−3.34	2.96	3.47	1.92	
HF/D95**	HB	C_1	0	C_s*	C_2*	−3.77	3.22	3.31	2.09	
AM1	HB	C_1	0	C_s*	C_2*	−6.71	2.58	2.62	2.14	
SAM1	HB	C_1	0	C_s*	C_2*	−3.67	2.93	2.95	1.86	
PM3	HB	C_1	1	C_s*	C_2*	−3.06	3.25	3.27	2.54	
DF/D95**	ST	C_{2h}	2	C_s	C_s	−1.75	3.18	3.18	3.18	
DF/D95**	SC	C_i	1	C_2*	C_2*	−3.32	2.67		2.67	
HF/D95**	ST	C_{2h}	2	C_s	C_s	−1.88	3.18	3.18	3.18	
HF/D95**	SC	C_i	1	C_2*	C_2*	−3.36	2.85		2.85	
AM1	ST	C_{2h}	2	C_s	C_s	−1.98	3.11	3.11	3.11	
SAM1	ST	C_{2h}	3	C_s	C_s	−1.60	4.01	4.01	4.01	
PM3	ST	C_{2h}	2	C_s	C_s	−1.67	3.72	3.72	3.72	

[a] I.F. = number of imaginary frequencies; approximate symmetry marked with an asterisk (*); $\Delta\Delta H_{298}$ (interaction energy) is defined as the difference between ΔH_{298} for the dimer and monomers in C_2 conformation.

between the H_s atom of one monomer and one of N atoms of the other. For the ribbons we (a) enforced both a 2-fold axis and a plane of symmetry, **RE**; (b) enforced only a plane of symmetry, **RF**; (c) kept the heavy atoms of each monomer in parallel planes, **RP**; and (d) used no constraints, **RT**. The **RE** mimics the crystal structure reported for thiourea. For herringbone dimers we (a) used no constraints, **HB**; (b) enforced a plane of symmetry, **HF**; and (c) constrained molecules to be geometrically equivalent, have antiparallel C═O bonds, and be planar with molecular planes perpendicular to each other, **HE**. For the stacking dimers we imposed C_{2h} (**ST**) or centrosymmetric (**SC**) structures. Without these constraints, the optimiza-

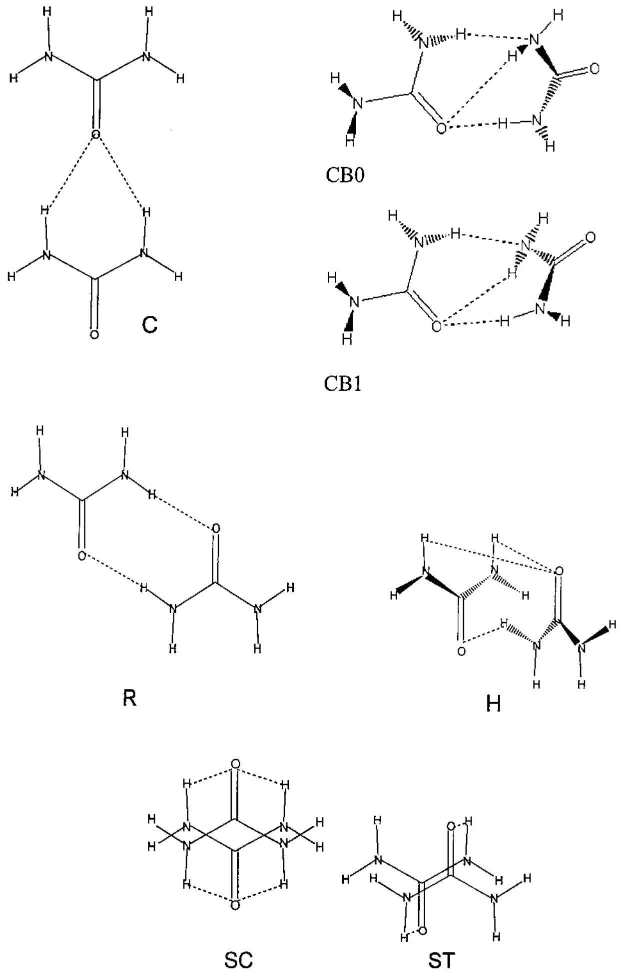

Figure 2. Structures of urea dimers (see text for explanation).

tions of the stacked dimers converged to the chain or ribbon dimers. The energetic data for the dimers are presented in Table 3. For the PM3 calculations, the planarization energy more than canceled the stabilization due to H-bond formation, resulting in net repulsion. For this reason we list H-bonding stabilization (the difference between ΔH_f's for planar dimers and monomers) in brackets.

Only **CB**, **RP**, **RT**, and **HB** are true minima on the potential surface as only they have no imaginary vibrational frequencies. The ab initio and AM1 calculations (Table 3, and Supporting Information Table 3a) agree reasonably well both for geometries and interaction enthalpies. Since the **CE**, **RE**, and **HE** dimers are not stationary points on the potential surface, we approximated the zero-point vibrational and thermal corrections using the corresponding results for **CF** and **RF**. Due to computational limitations, frequency calculations were not possible at the MP2/D95++** level. We used the MP2/D95** calculations to estimate the vibrational corrections. Despite the fact that the planar dimers can have as many as five imaginary frequencies, all thermally corrected HF calculations predict the relaxed planar dimers (**CF** and **RF**) to be the most stable of each type (chain or ribbon). The corresponding thermally corrected MP2 structures remain pyramidal about the nitrogens. However, the enthalpies required to planarize the dimers are much less than those required to planarize two monomers (except for the **CB** type structures which have an additional H bond that is not possible in the crystal). Together with our earlier conclusion that the monomer is effectively planar (see above), this suggests that a growing aggregate would likewise tend to be planar, in accord with the crystal structure. The corrected DFT calculations predict planar dimers (once again except for **CB** dimers). However, the enthalpy required for planarization of the **CB** dimers is quite small (0.9 kcal/mol). All ab initio methods predict the uncorrected planarization energies of the **CL**, **RP**, and **RT** dimers to be similar to that of the monomer. Thus, the H bond overcomes the planarization barrier of the second molecule. To illustrate this point, we optimized the transition state for NH_2-group inversion in a ribbon dimer, **RTP** (a saddle point between **RP** and **RT** conformers). The uncorrected inversion barrier is significantly lower than that of the monomer (0.7 vs 1.0 kcal/mol in both HF/D95** and DFT/D95**).

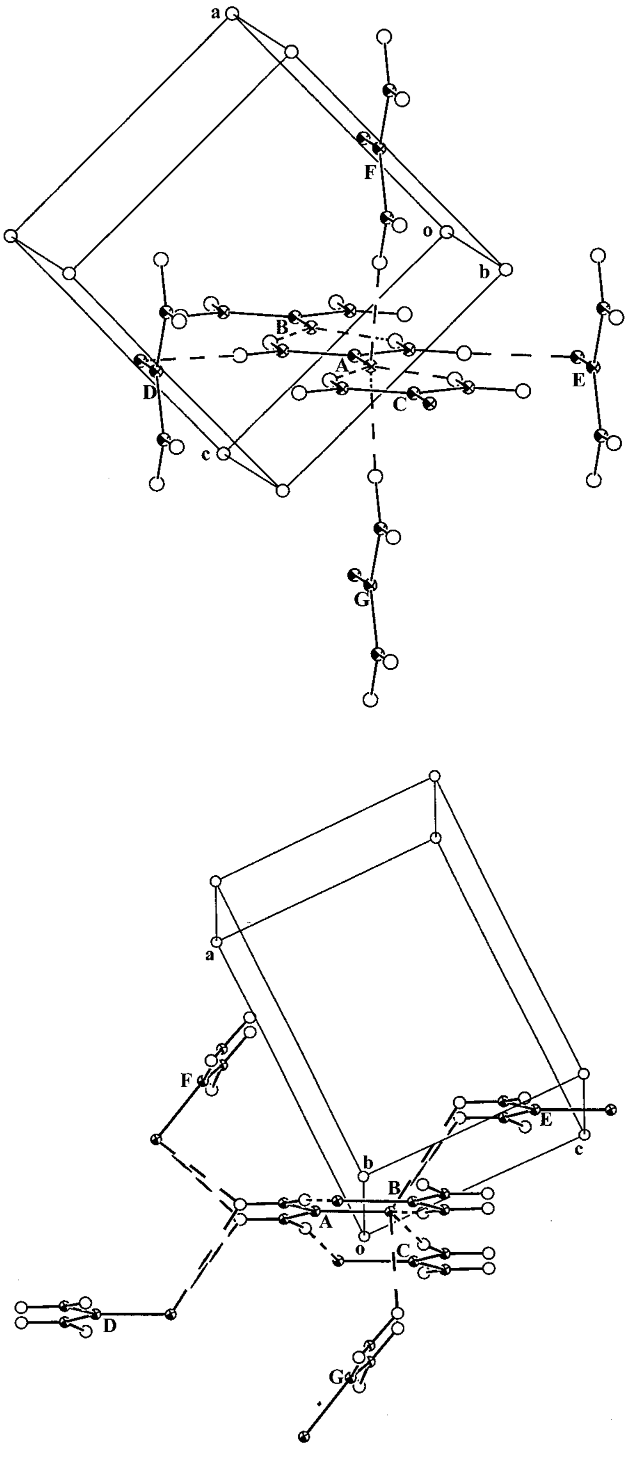

Figure 3. Depiction of H-bonding interactions taken from the crystal structures of (a) urea and (b) thiourea.

TABLE 4: Urea Planarization in Uniform Electric Field[a]

method	F	ΔE_{pl}	OCNH	OCNH′	$\mu_D(C_2)$	$\mu_D(C_{2v})$	ΔE	$\mu_D F$
HF/D95**	0.00	1.29	12.6	151.0	4.01	4.70	0.00	−0.00
HF/D95**	0.01	0.21	12.0	164.3	5.39	5.61	−12.73	−13.86
HF/D95**	0.02	0.00	0.0	180.0	6.52	6.52	−27.70	−32.22
HF/D95**	0.04	0.00	0.0	180.0	8.35	8.35	−64.41	−82.54
HF/D95**	0.06	0.00	0.0	180.0	10.24	10.24	−110.27	−151.72
MP2/D95**	0.00	2.50	14.7	146.5	3.46	4.38	0.00	−0.00
MP2/D95**	0.01	0.87	17.1	158.4	4.44	5.37	−12.03	−13.26
MP2/D95**	0.02	0.24	16.8	169.1	6.24	6.36	−26.50	−31.43
MP2/D95**	0.04	0.07	15.9	178.3	8.39	8.38	−62.87	−82.80
MP2/D95**	0.06	0.24	22.4	178.3	10.54	10.47	−109.37	−155.27

[a] F = field strength, au; ΔE_{pl} = planarization energy, kcal; μ_D = molecular dipole moment, debye; OCNH, OCNH′ = dihedrals, degrees; ΔE = stabilization energy in the field (the difference in total energy with and without the field), kcal; classical value $\mu_D F$ is given for comparison, kcal.

From the above discussion, one sees that HF calculations favor planar monomers and dimers while MP2 favors nonplanarity. The DFT calculations tend to favor planar structures except for the **R** dimers. If one considers the interaction energies between planar monomers to form planar dimers, all the ab initio methods agree reasonably well, as does AM1. However, the interaction energy between optimized monomers and dimers includes a destabilizing contribution from the energy of planarization. One might reasonably expect the monomers to planarize upon polarization. This might lead to the conclusion that the MP2 optimized structures have lower polarizabilties.

To test this hypothesis, we optimized the urea monomers in increasing uniform electric fields up to 0.06 au (e/Bohr) using the HF and MP2/D95** models. The results are presented in Table 4. The HF urea molecules planarize at a field of 0.02 au and remain planar at higher fields. The MP2 urea molecules become almost planar at 0.04 au (the planarization energy is $<$0.1 kcal/mol) but become more pyramidal at 0.06 au (planarization energy is 0.24 kcal/mol). Surprisingly, the MP2 method predicts a more polarizable urea than HF, despite the higher energy of planarization.

The relative stabilities of the dimers are calculated to be the same: **R** > **C** > **HB** > **SC** > **ST** by all ab initio methods used. Since urea normally crystallizes in a structure containing **C**, not **R**, interactions, the dimeric interactions are insufficient to explain the observed crystal structures. Rather, the crystal structure must be dictated by cooperative interactions involving several molecules. We have previously shown that the favored form of H-bonding chains of 1,3-cyclohexanedione (enolic form) predominated only upon aggregation of 5−7 molecules.[2b] We anticipate a similar situation here.

Among the semiempirical methods, AM1 produces the closest agreement to the ab initio calculations. SAM1 does reasonably well (however, it finds neither **RP** nor **RT** minima), while PM3 is erratic both for energies and geometries, appearing to be unreliable, as we have previously noted.[3a,26] For example, PM3 predicts unreasonably large enthalpies for planarizations of the NH_2 groups in both monomers and dimers. Furthermore, PM3 predicts two minima each for **CF** and **RF** dimers, which differ only in H-bond lengths. These multiple minima were not found by any other method. The data of Table 3 report only the most stable dimer of each category for PM3. We see that AM1 predicts multiple minima in only one case (**CB**). Two minima (denoted **CB0** and **CB1** in Table 3) differ in the relative lengths of the H···O and H···N interactions (see Figure 2). HF and DFT methods also predict these minima (we did not attempt to find them using MP2). The third minimum (**CB2**) contains one *syn*-urea, which is unstable as an isolated molecule using this method. Only SAM1 found a similar minimum.

Geometrical information on the dimers is collected in Table 2. All methods predict C═O bond lengthening upon dimerization by about 0.004 Å for the H-bond donor and 0.008 Å for the H-bond acceptor in the chain dimer and 0.014 Å for the ribbon dimer. This correlates with shortening of the H bond. The N−H bonds involved in H-bonding formation elongates by 0.005 (**CF**) or 0.025 Å (**RF**); other N−H bonds change insignificantly. The C−N bonds shorten (by 0.01 Å for **CF** and 0.02 Å for **RF**) for the NH_2 groups involved in the H bonds. The effects are larger for the **RF** than the **CF** dimers. Effects similar to those observed for **RF** were reported for acetic acid dimers[1a] (which have a similar cyclic H-bonding structure), in agreement with experimental[27] observations. No similar experimental reports exist for urea dimers in the gas phase. These trends are consistent with reinforced polarization (opposite charge developing on alternate atoms) in O═C−N−H···O in the ribbon dimer. They are also consistent with the resonance-assisted H bonds proposed by Gilli.[28]

Conclusions

The present calculations confirm the previous reports that the minima on the urea potential surface correspond to a nonplanar structure. However, inclusion of vibrational and thermal corrections suggests that the molecule might be effectively planar. HF and DFT calculations at the D95** level predict planar urea at 298 K. The corresponding MP2 calculations predict the transition structure which connects the C_2 and C_s structures to be below the zero-point vibration. The more extensive basis set 6-311+G(3df,2p) predicts a planar structure after both ZPVE and thermal corrections at the MP2 level.

The multiple minima found for the urea monomers complicate the calculations of urea dimers. Here again, the HF and DFT calculations suggest that the dimers are planar or planarize with little distortion. The MP2 calculations predict the dimers are be nonplanar. However, the planarization energy for the dimers is similar to that of one monomer (not two). Thus, it seems likely that urea chains and ribbons are effectively planar.

Supporting Information Available: Tables of results of semiempirical and ab initio calculations (8 pages). Ordering information is given on any current masthead page.

Note Added in Proof: A recent experimental report (Godfrey, P. D.; Brown, R. D.; Hunter, A. N. *J. Mol. Struct.* **1997**, *413−414*, 405) suggests that the zero-point energy of urea is well above a small barrier at the planar geometry.

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