Spherical and Aspherical Intermolecular Force Fields for Sulfur Allotropes

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Elemental sulfur exists in many crystalline forms, with many of these forms being composed of discrete S_n cyclic molecules. Eleven experimentally determined S_n crystal structures are used to define a new spherical S···S intermolecular force field of the (exp-6) type. Evidence is presented that the bonded sulfur atom in these structures is not spherical. The asphericity was modeled by placing repulsion bumps at optimized locations on the sulfur atoms to represent lone pair electron repulsion. The bump locations deviate from perfect tetrahedral geometry, being located more perpendicular to the S−S−S plane. A new aspherical sulfur intermolecular force field was derived from eleven S_n crystal structures. The aspherical force field gives an improved prediction of the S_n crystal structures.

Introduction

Elemental sulfur readily forms many ring molecules S_n; the crystal structures of several of these cyclic allotropic forms of sulfur have been determined. Some examples are S_6,[1] γ-S_7,[2] δ-S_7,[2] α-S_8,[3] γ-S_8,[4] S_{10},[5] S_{11},[6] S_{12},[7] S_{13},[6] α-S_{18},[8] β-S_{18},[9] and S_{20}.[8] Quantitative knowledge of the details of S···S nonbonded interaction is needed in order to understand the structures of these crystals,[10−12] molecular distortion in the crystal,[16] crystal lattice vibrations,[17,18] lattice dynamics,[19] effects of hydrostatic pressure,[20] and molecular dynamics simulation.[21]

Most previous efforts toward development of an intermolecular force field for sulfur utilized only the α-S_8 crystal structure. Early efforts to describe nonbonded interaction in crystalline α-S_8 were made by Giglio, Liquori, and Mazzarella,[11] who used an Ar−Ar nonbonded potential function to describe nonbonded interaction in this structure. Rinaldi and Pawley[12] fitted an (exp-6) type nonbonded potential function to the crystal structure. Their report predicted lattice constant shifts when the intermolecular energy was minimized. We were not able to reproduce their results, perhaps because we used a larger number of terms in the lattice sums (made possible by improvements in computer performance), along with the use of the accelerated convergence[13,14] to further increase accuracy.

Kurittu and Pawley[16] proposed new values for S···S nonbonded potential parameters and used them to predict molecular distortion in α-S_8. Predicted lattice constants were not reported; using their potential we obtained unit cell edge shifts of 0.17, −0.99, and 0.13 Å and a molecular rotation of 5.2° when the lattice energy was minimized (Table 2). Rinaldi and Pawley[18] obtained an S···S nonbonded potential function from the lattice vibrational frequencies of α-S_8. Again, predicted lattice constants were not reported; we obtained energy-relaxed cell edge shifts of 0.34, −0.59, and 0.44 Å and a molecular rotation of 3.3°. Gramaccioli and Filippini[19] used this potential in lattice-dynamical calculations for α-S_8 using a nonrigid molecular model.

A different approach was used by Filippini and Gavezzotti,[22] who report new (exp-6) parameters for several atoms, of which sulfur is one. Their potential parameters were optimized using distributions of nonbonded atom−atom distances in the crystal and heats of sublimation. With their force field we obtained energy-relaxed cell edge shifts of 0.16, −1.02, and 0.09 Å and a molecular rotation of 3.3° for α-S_8. It is apparent that a better force field is needed, which will more accurately predict S_n crystal structures.

Crystal Structures of S_n

Previously proposed spherical nonbonded potentials for α-S_8 sulfur (with the exception of the early work reported in ref 12) were obtained from crystal lattice vibrational frequencies or nonbonded distance distributions. Generally these potentials were not checked by minimization of the energy of the crystal by allowing changes in cell constants and molecular orientation. We have carried out these lattice energy minimizations not only for α-S_8 but also for 10 additional S_n crystal structures. S_{10} was not included because there are inconsistencies between the published crystal structure and nonbonded contact distances.[5]

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Table 1. Crystal Data for S_n Crystals

structure	S_6	γ-S_7	δ-S_7	α-S_8	γ-S_8	S_{11}	S_{12}	S_{13}	α-S_{18}	β-S_{18}	S_{20}
space group	$R\bar{3}$	$P2_1/c$	$P2_1/n$	$Fddd$	$P2/c$	$Pca2_1$	$Pnnm$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$Pbcn$
temp (K)	183	163	163	298	294	163	298	173	298	163	298
Z	1	4	8	16	4	8	2	8	4	8	4
Z'	1	1	2	$^1/_2$	$^1/_2$[a]	2	$^1/_4$	2	1	2	$^1/_2$
mol symmetry	1	1	1	2	2	1	$2/m$	1	1	1	2
packing group	$R\bar{3}$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$Pca2_1$	$P2_1$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
no. of forces	2	10	16	5	9	14	4	16	9	7	5

[a] Two half-molecules in the asymmetric unit.

Each of the included crystal structures has several degrees of freedom, as allowed by space group symmetry. For instance, in α-S_8, which crystallizes in space group *Fddd*, the crystallographic asymmetric unit is a half-molecule ($Z' = {}^1/_2$). The remainder of the molecule is generated by a crystallographic 2-fold axis. Thus the S_8 molecule can only rotate about and translate along the crystallographic 2-fold axis; any other rotation or translation would contradict the space group symmetry. In addition the space group requires that all cell angles be 90°. Thus the symmetry-allowed degrees of freedom in α-S_8 are 5 in number: 3 cell edge lengths, 1 rotation, and 1 translation of the molecule may vary in this crystal structure.

Table 1 lists salient characteristics of 11 S_n crystal structures. It is seen that there is quite a variety of molecular packing arrangements; the asymmetric unit can be as small as one-quarter of the molecule, or as large as two molecules. The molecular packing group symmetry[25,26] can be $R\bar{3}$, $P2_1/c$, $C2/c$, $P\bar{1}$, $Pca2_1$, $P2_1$, or $P2_12_12_1$. This multitude of molecular packing arrangements might enhance the definition of the S···S nonbonded potential, as compared to dealing with a single crystal structure. The molecular structures in the two forms of both S_7 and S_8 are essentially identical; however, the molecules in α-S_{18} and β-S_{18} have different conformations. The molecular structures are shown in Figure 1. Steudel, Steidel, and Reinhardt[5] classify S_n molecules into two types: highly symmetrical species with equal (or almost equal) bond distances within the molecule (S_6, S_8, S_{12}, α-S_{18}) and less symmetrical species with unequal and usually alternating long and short bonds within the molecule (S_7, S_{11}, S_{13}, β-S_{18}, S_{20}).

Force Fields Using Spherical Sulfur Atoms

Each degree of freedom in a crystal structure corresponds to a force (or torque in the case of rotation) which must be zero at equilibrium. Each force is the negative of the first derivative of the lattice energy with respect to that degree of freedom. A completely accurate nonbonded potential will show zero forces at the observed structure. In practice a given nonbonded potential will show nonzero forces at the observed structure. When the lattice energy is minimized, the structure is allowed to shift along the symmetry-allowed degrees of freedom to give a relaxed structure with zero forces. Obviously, a completely accurate potential will show zero shifts; the size of the shifts in going from the observed to the relaxed structure may be used as an indicator of the quality of the nonbonded potential.

Our nonbonded potential function (intermolecular force field) is a pairwise additive atom−atom function of the (exp-6) type. The first part of this function is exponential and models the exchange repulsion energy, which results from prohibition of orbital overlap between filled orbitals dictated by the Pauli principle. The second part is dispersion attraction, which arises from instantaneous dipole−dipole polarization of the interacting nonbonded atoms *j* and *k*. In this model there are three adjustable parameters: *A*, *B*, and *C*.

$$E(r_{jk}) = B\exp(-Cr_{jk}) - Ar_{jk}^{-6}$$

$$E_t = \frac{1}{2}\sum\sum E(r_{jk}) = \frac{B}{2}\sum\sum \exp(-Cr_{jk}) - \frac{A}{2}\sum\sum r_{jk}^{-6}$$

The total crystal energy E_t is obtained by summation over nonbonded contacts of the reference molecule(s) with surrounding molecules in the lattice. The factor of $^1/_2$ avoids duplicate counting of atom−atom interactions.

Our goal is to find *A*, *B*, and *C* values which will result in zero forces for all observed crystal structures under consideration. It is quickly seen that there is a trivial solution $A = B = 0$ which will make all forces zero. At least one side condition is needed to normalize E_t to the negatives of the energies of sublimation, $\Delta E_{\text{sublimation}}$, of the crystals. At very low pressure $\Delta E \sim \Delta H$, so we can add as side conditions $\Delta E_t = -\Delta H_{\text{sublimation}}$ for crystals with known measured heats of sublimation. A residual function is defined which, when minimized, finds optimum lowest values for the magnitudes of the forces and also best fits to heats of sublimation:

$$R = \sum_i \sum_{m,n} w_{imn} F_m F_n + \sum_i w_i'(E_t + \Delta H_{\text{sublimation}})^2 = R_F + R_E$$

where *i* runs over crystal structures and *m* and *n* run over forces. There are weight matrices w_{mn} for each structure and a weight w_i' for each heat of sublimation. The summation over forces includes weighted cross terms F_mF_n, which can make an important contribution, since the forces are not completely independent. The second summation is a penalty function requiring a best least-squares fit to the heats of sublimation. If there is only one heat of sublimation, it will be fitted exactly. In the latter case the penalty function can optionally be replaced with a Lagrangian multiplier condition. It is probably not a good idea to require exact fits to several heats of sublimation because of possible errors in the heat of sublimation data and inadequacies of the intermolecular energy model. The weights w' are set so as to achieve the desired goodness of fit to the heats of sublimation. The method for assigning the weight matrices w_{mn} has been described previously.[27]

Very high correlation between *B* and *C* makes it difficult to determine these nonbonded parameters independently from crystal data, where significant dispersion energy is present. We obtained a value of *C* by making Hartree−Fock (HF) ab initio quantum mechanical calculations of the intermolecular energy of the α-S_8 dimer at various separations. The HF method does not include dispersion energy, so that intermolecular energies can be fitted using only exponential atom−atom repulsion terms.

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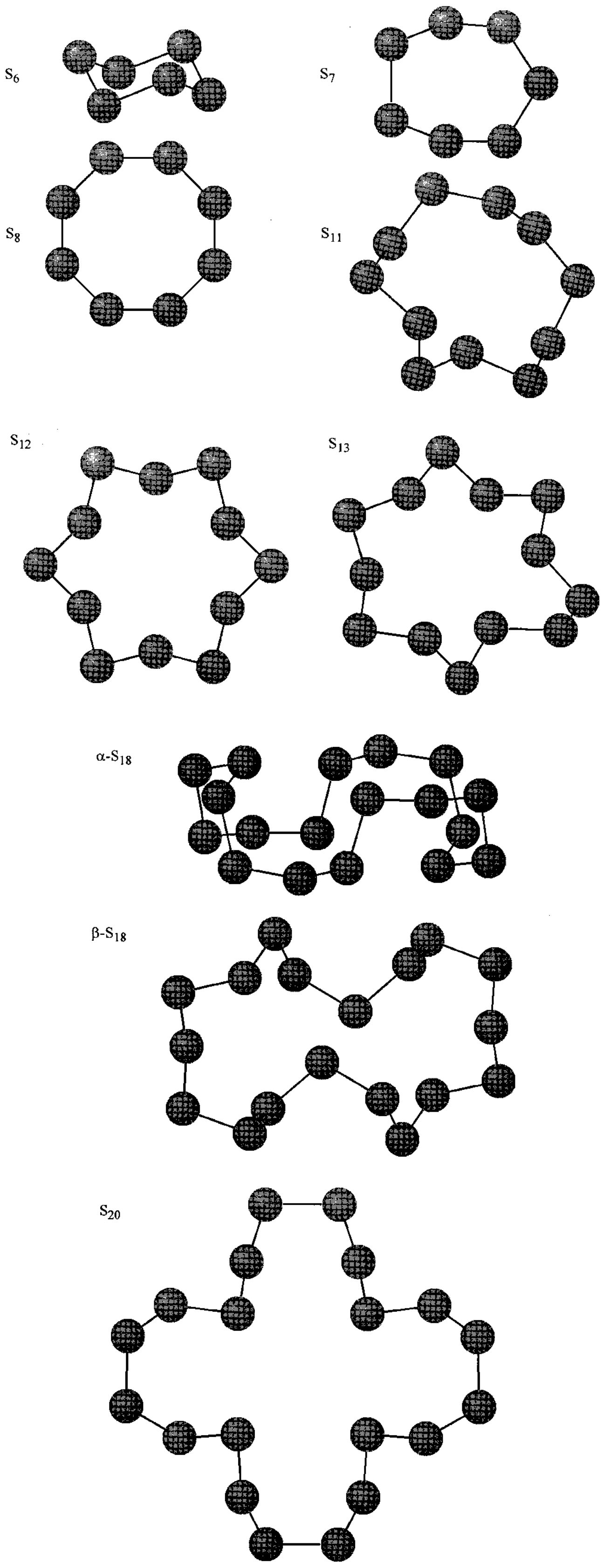

Figure 1. Molecular structures of S_n.

A value of $C = 2.83$ Å^{-1} was found; since this value is very close to the value $C = 2.9$ Å^{-1} previously used by Rinaldi and Pawley,[15] we adopted the latter value.

Using the above-described procedures, we optimized A and B of a spherical sulfur nonbonded potential to 11 S_n crystal structures, using the computer program nbp.[28] The heat of sublimation of α-S_8 has been measured experimentally;[29−31] we adopt the value of 104.4 kJ mol^{-1} reported by Chastel and Ezzine.[31] Since α-S_8 was the only structure for which heat of sublimation data was available, the energy side condition was fitted exactly.

The quality of the resulting spherical S···S potential was tested by subjecting each of the 11 S_n crystal structures to lattice energy minimization using the program mpa.[32] Table 2 shows shifts in cell edge lengths and molecular rotation and translation for the force-relaxed structures. The results are compared with similar calculations using three previously published spherical S···S nonbonded potentials.

Aspherical Sulfur Atom in α-S_8

Williams and Gao[23] recently confirmed that in the dichlorine crystal chlorine atoms are not spherical; they exhibit what has been called "polar flattening". The experimental charge distribution[24] in α-S_8 also shows that sulfur atoms are not spherical; there is a charge extension 0.6 Å above and below the S−S−S plane. Just as in the case of dichlorine, it seems likely that asphericity of the bonded sulfur atom will have consequences with regard to the S···S nonbonded potential.

The accuracy of a force field can be checked with mpa by calculating lattice constant shifts of the structure from observed values. With the spherical force field, shifts of cell edge lengths of α-S_8 were 0.33, −0.60, and 0.43 Å. For all 11 S_n structures the root-mean-square (the square root of the mean of the sum of squared shifts in a, b, and c) cell edge change was 0.47 Å with the spherical model. These results suggested that perhaps we could define an improved nonbonded potential if additional lone pair repulsion sites ("bumps") were placed on the sulfur atoms. After the locations of the bump sites are fixed, this aspherical model for the bonded sulfur atom has three adjustable parameters: the A parameter at the sulfur site, a B parameter at the sulfur site, and a B_{bump} parameter at the bump site. As with the spherical model, the C value was set to 2.9 Å^{-1}; the position of the bump site was set as described below.

In a first attempt, bump sites were placed at tetrahedral sp^3 positions, varying only the distance of the sites from the sulfur nucleus. Better results were obtained if the angle between the bump sites and the S−S−S plane was also varied, with local C_{2v} symmetry. A systematic exploration for the location of the bump sites was made using the α-S_8 crystal structure as data. In a first step, the nbp program was used to find optimum force-field parameters for assumed locations of the bump sites. In a second step, the crystal structure was relaxed with the resulting force field, using the mpa program. The optimum position found for the bump site was 0.7 Å from sulfur at an angle of 80° to the S−S−S plane. This position is consistent with electron distribution studies.[24]

Using these positions for the bump sites, optimum values for A, B, and B_{bump} were found from the S_n crystal structures. Eleven S_n structures and the heat of sublimation of α-S_8 were used to find optimum values for the force field using the program nbp

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Table 2. Structural Shifts Predicted by Three Published S⋯S Spherical Potentials, a New Spherical Potential Optimized to 11 S_n Crystal Structures, and a New Aspherical Potential Optimized to 11 S_n Crystal Structures[a]

structure	shift	ref 16	ref 18	ref 22	this work[b]	this work[c]
A. Highly Symmetrical Species with Equal or Nearly Equal Bond Distances						
s_6	Δa	0.31	0.49	0.30	0.48	0.42
	Δb	0.31	0.49	0.30	0.48	0.42
	Δc	−0.28	−0.12	−0.30	−0.13	−0.02
α-S_8	Δa	0.17	0.34	0.16	0.33	0.16
	Δb	−0.99	−0.59	−1.02	−0.60	−0.41
	Δc	0.13	0.44	0.09	0.43	0.08
	$\Delta\theta$	5.2	3.3	5,4	3.3	2.8
	Δt	0.88	0.60	0.91	0.61	0.39
γ-S_8	Δa	−0.39	−0.15	−0.41	−0.15	−0.20
	Δb	0.06	0.16	0.05	0.15	0.01
	Δc	−0.58	−0.28	−0.61	−0.29	−0.12
	$\Delta\beta$	−0.5	−0.2	−0.6	−0.2	−0.3
	$\Delta\theta$	1.5, 3.6	1.4, 2.4	1.5, 3.7	1.4, 2.5	0.4, 1.2
	Δt	0.15, 0.18	0.09, 0.22	0.15, 0.18	0.09, 0.22	0.08, 0.10
S_{12}	Δa	−0.01	0.15	−0.02	0.14	−0.07
	Δb	0.09	0.18	0.08	0.10	0.04
	Δc	−0.58	−0.41	−0.60	−0.41	0.00
	$\Delta\theta$	0.1	0.2	0.1	0.2	0.2
α-S_{18}	Δa	−0.27	−0.04	−0.29	−0.05	−0.03
	Δb	−0.15	0.09	−0.17	0.08	0.09
	Δc	−0.11	0.05	−0.12	0.05	0.05
	$\Delta\theta$	0.9	1.1	0.9	1.1	0.8
	Δt	0.20	0.05	0.22	0.05	0.02
B. Less Symmetrical Species with Unequal and Usually Alternating Long and Short Bonds						
γ-S_7	Δa	0.21	0.54	0.19	0.54	0.26
	Δb	−0.20	−0.04	−0.21	−0.03	−0.17
	Δc	−0.09	0.00	−0.10	−0.01	0.32
	$\Delta\beta$	2.4	1.9	2.4	1.9	2.1
	$\Delta\theta$	2.3	4.6	2.2	4.6	1.8
	Δt	0.07	0.30	0.07	0.29	0.17
δ-S_7	Δa	−0.11	0.20	−0.14	0.19	0.14
	Δb	−0.11	0.06	−0.12	0.06	0.04
	Δc	−0.03	0.75	−0.06	0.75	0.39
	$\Delta\beta$	3.6	13.3	3.5	13.4	2.1
	$\Delta\theta$	1.7, 6.9	20.0, 15.0	1.7, 6.7	20.1, 15.1	3.6, 8.4
	Δt	0.53, 0.62	1.76, 1.29	0.53, 0.63	1.78, 1.30	0.32, 0.44
S_{11}	Δa	−0.22	0.01	−0.24	0.01	0.07
	Δb	0.02	0.15	0.01	0.15	0.09
	Δc	−0.48	−0.03	−0.52	−0.05	−0.01
	$\Delta\theta$	2.9, 4.7	2.8, 4.2	2.9, 4.7	2.8, 4.2	1.1, 2.2
	Δt	0.12, 0.29	0.15, 0.27	0.13, 0.30	0.14, 0.27	0.10, 0.17
S_{13}	Δa	0.02	0.23	0.01	0.22	0.20
	Δb	−0.27	−0.07	−0.28	−0.07	−0.15
	Δc	0.02	0.30	0.0	0.29	0.34
	$\Delta\beta$	1.0	0.5	1.1	0.5	0.5
	$\Delta\theta$	1.1, 2.2	1.6, 2.3	1.0, 2.1	1.6, 2.3	1.9, 3.0
	Δt	0.31, 0.20	0.33, 0.04	0.32, 0.21	0.32, 0.05	0.30, 0.09
β-S_{18}	Δa	−0.28	−0.11	−0.29	−0.12	−0.20
	Δb	−0.08	0.04	−0.09	0.04	0.08
	Δc	−0.47	−0.22	−0.49	−0.22	−0.19
	$\Delta\beta$	−2.0	−1.7	−2.1	−1.7	−1.8
	$\Delta\theta$	3.1	2.7	3.2	2.7	2.6
	Δt	0.14	0.06	0.15	0.06	0.09
S_{20}	Δa	−0.10	0.07	−0.11	0.07	0.01
	Δb	−0.19	−0.08	−0.20	−0.08	−0.03
	Δc	−0.31	−0.10	−0.33	−0.11	−0.17
	$\Delta\theta$	1.2	0.9	1.2	1.0	0.9
	Δt	0.25	0.09	0.27	0.09	0.13

[a] $\Delta\theta$ and Δt refer to molecular rotation and translation; molecular translation includes the effect of cell changes. Δa, Δb, Δc, and Δt are in Å; $\Delta\beta$ and $\Delta\theta$ are in deg. [b] $E_{jk} = 173320 \exp(-2.9r_{jk}) - 11667.0{r_{jk}}^{-6}$ (spherical potential). [c] $E_{jk} = 91606 \exp(-2.9r_{jk}) - 11268.98{r_{jk}}^{-6}$ (nuclear potential); and $E_{jk} = 719 \exp(-2.9r_{jk})$ (bump site potential, see text for site locations).

Table 3. Rms Cell Edge Shifts (Å) for the Relaxed Crystal Structures

structure	ref 16	ref 18	ref 22	this work[a]	this work[b]
A. Highly Symmetrical Species with Equal or Nearly Equal Bond Distances					
S_6	0.30	0.41	0.30	0.39	0.34
α-S_8	0.58	0.47	0.60	0.47	0.26
γ-S_8	0.41	0.21	0.43	0.21	0.14
S_{12}	0.34	0.27	0.35	0.26	0.04
α-S_{18}	0.22	0.06	0.21	0.06	0.06
B. Less Symmetrical Species with Unequal and Usually Alternating Long and Short Bonds					
γ-S_7	0.30	0.31	0.21	0.31	0.26
δ-S_7	0.09	0.45	0.11	0.45	0.09
S_{11}	0.31	0.09	0.33	0.09	0.07
S_{13}	0.16	0.22	0.16	0.21	0.24
β-S_{18}	0.32	0.14	0.33	0.15	0.17
S_{20}	0.22	0.08	0.23	0.09	0.10

[a] Spherical potential. [b] Aspherical potential.

Table 4. Calculated Energies (kJ mol^{-1}) of Relaxed Structures of Highly Symmetrical Species with Equal or Nearly Equal Bond Distances Using Various Force Fields

structure	ref 16	ref 18	ref 22	this work[a]	this work[b]
S_6	−89.37	−84.49	−108.94	−85.65	−78.68
γ-S_7	−98.08	−93.24	−119.51	−94.52	−93.00
δ-S_7	−98.80	−94.23	−120.39	−95.53	−90.23
α-S_8	−108.97	−104.55	−132.71	−105.99	−105.26
γ-S_8	−111.68	−105.61	−136.13	−107.07	−102.19
S_{11}	−135.79	−131.29	−165.29	−133.08	−127.78
S_{12}	−138.88	−134.94	−168.99	−136.79	−140.53
S_{13}	−151.82	−147.92	−184.74	−149.93	−145.42
α-S_{18}	−203.46	−196.17	−247.76	−198.87	−191.56
β-S_{18}	−209.96	−202.06	−255.67	−204.82	−198.46
S_{20}	−228.17	−225.90	−277.35	−228.96	−223.17

[a] Spherical potential. [b] Aspherical potential.

with full weight matrices. The aspherical model assumes that all of the attractive forces originate at the nucleus, but repulsion originates both from nuclear sites and from the bump sites. The optimized force field for the aspherical model was found to be (units are kJ mol^{-1} and Å)

$$E_{jk} = 91606 \exp(-2.9r_{jk}) - 11268.98{r_{jk}}^{-6}$$

for the nuclear atom and

$$E_{jk} = 719 \exp(-2.9r_{jk})$$

for the bump sites.

Discussion

As we have mentioned before, the success of an intermolecular force field may be measured by how well it can reproduce observed cell parameters. The symmetrically bonded structure which was used to calibrate the location of the bump sites, α-S_8, showed a considerably better fit with the aspherical force field. In the force-field relaxed structure the rms cell constant change was reduced to 0.26 Å using the aspherical force field, as compared to 0.47 Å using the spherical force field. Table 3 shows that rms fits for the symmetrical species S_6, γ-S_8, and S_{12} were also improved. The α-S_{18} structure was already well fitted by the spherical force field, so not much improvement was possible.

As for the asymmetrical structures, Table 3 shows that the predicted relaxed crystal structures of S_{11}, β-S_{18}, and S_{20} are satisfactory using either force field. The δ-S_7 structure shows a dramatic improvement from 0.45 Å rms error with the spherical force field to 0.09 Å with the aspherical force field. The fit to γ-S_7 was also slightly improved from 0.31 to 0.26 Å.

The calculated energies of the relaxed crystal structures are given in Table 4. Because of relaxation shifts, the energy of α-S_8 decreases from the assumed value of -104.4 kJ mol^{-1} at the observed structure to -105.99 kJ mol^{-1} using the spherical force field and -105.26 kJ mol^{-1} using the aspherical force field. We have also compared crystal energies of the 11 relaxed structures calculated with the other force fields. The table shows considerable scatter in values obtained with the various force fields.

Crystal energies should be rather similar for polymorphs. For S_7, our spherical force field predicts 1.01 kJ mol^{-1} lower energy for the δ polymorph, while the aspherical force field predicts 2.77 kJ mol^{-1} lower energy for the γ form. A similar reversal occurs with S_8, with the spherical force field favoring the γ polymorph by 2.08 kJ mol^{-1}, with the aspherical field favoring the α form by 3.07 kJ mol^{-1}. These differences are consistent with the existence of polymorphism, since the energies are in a thermally available range. The specific polymorph which is obtained is sensitive to crystallization conditions.[33] The β form of S_{18} is favored by both force fields, but in this case the molecular conformations are different.

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