Theoretical Study of the Thermochemistry of Sulfur Molecular Crystals. I. Method and Application to α- and 1D-Polymerized Sulfurs

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The combination of two semiempirical methods, the "extended Hückel theory" for repulsive energy and a method derived from classical perturbation expansions for the dispersion energy, is used to evaluate the weak interaction energy between covalent rings or chains of sulfur compounds. In this paper, the parametrization method of both parts of the energy is set up. The volume of the elementary cell and the heat of sublimation of α-sulfur are in correct agreement with experimental values. As a test for the study of polymerized *ω*-sulfur, a simple 1D-example shows correct behavior for interchain distance and cohesive energy. In each case, a detailed analysis of the contribution of each term involved in the total intermolecular potential function is given. In particular, we show the importance of three-body terms in the energetics of such structures.

1. Introduction

The purpose of this paper is to describe a method of calculation suitable for the study of *ω*-sulfur, whose structure is characterized by large unit cells resulting from the assemblage of covalent moieties through weak bonds. Sulfur appears under several allotropic forms in the solid state where building blocks are rings (S_6 or S_8) or chains (infinite helixes). The α-sulfur is a well-known molecular crystal made of S_8 crown-shape rings. The *ω*-sulfur is not the most common variety, but it presents industrial interests; it is used in agriculture and in the vulcanization process. Its building blocks are infinite helixes. There are two different allotropes whose complicated elementary units cells are not completely resolved. Our final goal is to investigate the low-energy structures, to compute from there a reaction path leading from this solid to S_8 molecules, and thus to study the sublimation process. The complexity of the structure requires our strategy to be a combination of two semiempirical methods. A careful parametrization is necessary to obtain sufficient accurate energies.

The sulfur crystalline structures involve both intra- and intermolecular interactions; the potential associated with the intermolecular forces is usually partitioned into a repulsive part and a negative part. In our systems, the size of the unit cell and the great number of calculations required to explore the hypersurface of potential energy rule out the use of ab initio methods. For the intramolecular and the repulsive parts of the intermolecular interactions, we have used a crystalline extension of the extended Hückel method (EHT). The theoretical treatment of weak intermolecular forces necessitates going beyond the EHT approximation: the EHT method only accounts for the repulsive part, whereas the attractive part corresponding to the dispersion energy may also be reached from semiempirical approximations. The combination of the two methods did allow a successful treatment of the alkane adsorption on graphite.[1] Here, we propose the same type of approach but with more refinements of the dispersive part as recently introduced in the determination of the intermolecular potential function for the simulation of the physical adsorption of rare gases in silicalite zeolite.[2]

In this first paper (sections 2 and 3), we will briefly recall the methods and develop the adequate parametrization for the sulfur compounds. The parametrization of the attractive part is unambiguously derived from the dispersion equations. For the repulsive part, we will discuss the influence of the parameters already published. In section 4, we will test the method on S_8 molecular rings and on a known structure, the α-sulfur. Finally, in section 5, we will apply the method to a model structure made of two infinite helixes. This is a preliminary calculation in a complete study of the *ω*-sulfur that will be fully developed in part II.

2. Theoretical Methods

As outlined in the Introduction, the quantum mechanical ab initio approaches for calculating the energy between two molecular systems in weak interaction are quite complex.[3] Even at the SCF level of approximation,[4] which is insufficient to correctly involve the dispersion, since electronic correlation is required, this algorithm is too complicated and time-consuming to treat atomic systems such as α- or polymerized sulfurs. Indeed, both the number of atoms in the elementary cell and the number of calculations to optimize the geometry are large. Therefore, a simplified formulation for the interaction potential between the two systems is needed. For weakly polar or nonpolar systems only a short-range repulsive part and a long-range dispersion part are involved. For a supermolecule calculation, the first one is essentially obtained from an SCF

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calculation, since at this level of approximation (Hartree−Fock) the energy curve either is repulsive (as in our cases in this paper) or may have a very weak minimum (in some other cases).[5,6] The second one would appear with the introduction of electronic correlation.

Repulsive Energy. The extended Hückel theory[7] (EHT) implemented on crystalline structures[8] has proved to give a correct repulsive energy in describing the physisorption of alkanes on graphite.[1] In nonzero temperature simulations, adjusted potentials are currently used. For example, in the adsorption of argon in silicalite zeolite ZSM-5, very accurate potentials for both the dispersion and repulsive parts (referred as the PN1 model) were elaborated and used in Monte Carlo simulations.[2,9] In a recent study, it has been shown that replacing the adjusted Born−Mayer type repulsive potential, part of the PN1 potential, by EHT potential curves led to accurate energy profiles too.[10] Therefore, it looks quite legitimate to use EHT in the calculation of the repulsive energy of molecular crystals.

The repulsive energy of the whole system is deduced from the difference between the total EHT energy of the solid and n times the EHT energy of one covalent molecule or infinite helix where n is the number of such covalent entities in the unit cell. The EHT calculation leads to a repulsive interaction that originates from the repulsion between the valence electrons of each covalent part. Indeed, each molecule (or chain) individually appears as a saturated compound with a bandgap between the occupied and unoccupied electronic levels. The interaction of two similar molecules, therefore, concerns the pair combinations of degenerate levels, an occupied orbital of one molecule interacting with the equivalent occupied orbital on the other molecule. The antibonding combination being populated, one gets a four-electron repulsion. At the distances considered, the repulsion between the core levels is negligible; a fortiori, the nuclear repulsion is screened and is not the origin of the sulfur−sulfur repulsion. Equations of periodic EHT have been widely developed and discussed in the literature. For physisorbed systems, a detailed discussion of the repulsive character can be found elsewhere[1] with references therein. For the sake of clarity, we briefly recall main formulas and notations for periodic EHT. A set of valence Slater type orbitals (STO) and translation vectors applied to a unit cell define the periodic system. Then a set of atomic Bloch functions $\phi_j(\mathbf{k})$, where $\mathbf{k}$ is a vector in the reciprocal space, is constructed. These functions form a basis for a linear combination expansion of crystal orbitals $\psi_j(\mathbf{k})$. The application of the variational theorem for each $\mathbf{k}$-point leads to the secular determinant

$$|H_{\mu\nu}(\mathbf{k}) - e(\mathbf{k})S_{\mu\nu}(\mathbf{k})| = 0 \qquad (1)$$

where the energy integral $H_{\mu\nu}(\mathbf{k})$, the overlap integral $S_{\mu\nu}(\mathbf{k})$, and energies $e(\mathbf{k})$ are defined in terms of Bloch functions. The overlap integral $S_{\mu\nu}(\mathbf{k})$ is directly expanded in terms of basic overlap integrals between atomic orbitals $S_{\mu\nu}$; it is modulated by a phase-dependent term. The energy integrals are expressed in terms of overlap integrals and the atomic energy levels $H_{\mu\mu}$ and $H_{\nu\nu}$ according to the weighted formula[11]

$$H_{\mu\mu}(\mathbf{k}) = H_{\mu\mu}[1.75S_{\mu\nu}(\mathbf{k}) - 0.75] \qquad (2)$$

$$H_{\mu\nu}(\mathbf{k}) = [K/2](H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}(\mathbf{k}) \qquad (3)$$

In this weighted formulation, the parameter K in eq 3, instead of being equal to 1.75 as in the Wolfsberg−Helmoltz formula, is an expression that is dependent on the atomic energy levels. The atomic energy levels are often approximated by the experimental ionization potentials of the corresponding orbitals. Sometimes it is more appropriate to parametrize from ab initio values, for example, from Herman and Skillman tables.[12] Some fluctuations around these values can also be allowed according to the charges on atoms in complex systems. Parametrization for the sulfur atom is discussed in section 3. Calculations are carried out for a set of representative points in a reduced part of the Brillouin zone, and energy is averaged over these points.

Dispersion Energy. Application of time-dependent perturbation theory leads to a dispersion multipole expansion, which in the case of two-body terms, is expressed as

$$u_{\mathrm{d}}^{\mathrm{AB}}(R) = -[C_6^{\mathrm{AB}}R^{-6} + C_8^{\mathrm{AB}}R^{-8} + C_{10}^{\mathrm{AB}}R^{-10} + ...] \qquad (4)$$

where the coefficients C's describe the interaction between two instantaneous dipoles (C_6), a quadrupole and a dipole (C_8), an octopole and a dipole, and two quadrupoles (C_{10}). Little algebra is needed to link these coefficients to 2^l-pole dynamic polarizabilities $\alpha_l(\omega)$ at frequency ω. They are expressed as an infinite sum whose terms are functions of the n-pole energy transition between the ground state and an excited state, of its oscillator strength, and of the frequency. A straightforward relation between $\alpha_l(\omega)$ and $\alpha_l(0)$, the static lth pole polarizability (at $\omega = 0$), leads to a general formulation for the two-body coefficients in atomic units:[2]

$$C^{\mathrm{AB}}(l_1l_2) = \frac{(2l_1 + 2l_2)!}{4(2l_1)!(2l_2)!}\frac{\eta_{l_1}^{\mathrm{A}}\,\eta_{l_2}^{\mathrm{B}}}{\eta_{l_1}^{\mathrm{A}} + \eta_{l_2}^{\mathrm{B}}}\alpha_{l_1}^{\mathrm{A}}(0)\alpha_{l_2}^{\mathrm{B}}(0) \qquad (5)$$

where l_1 and l_2 equal 1, 2, ... for a dipole, a quadrupole, etc., α_l is the lth pole polarizability, and η_l is an average lth-pole transition energy for each interacting species. The connection between the notations of eqs 4 and 5 is ensured for the first terms by[13]

$$\begin{aligned} C_6^{\mathrm{AB}} &= C^{\mathrm{AB}}(1,1) \\ C_8^{\mathrm{AB}} &= C^{\mathrm{AB}}(1,2) + C^{\mathrm{AB}}(2,1) \qquad (6) \\ C_{10}^{\mathrm{AB}} &= C^{\mathrm{AB}}(2,2) + C^{\mathrm{AB}}(1,3) + C^{\mathrm{AB}}(3,1) \end{aligned}$$

The parameters η_l can be approximated by[13]

$$\eta_l = [S_l(0)/\alpha_l(0)]^{1/2} \qquad (7)$$

where $S_l(0)$ is known as the lth-order sum rule. It has been shown that a good approximation for the parameter η_1 is given by[13]

$$\eta_1^{\mathrm{A}} = [N_{\mathrm{eff}}^{\mathrm{A}}/\alpha_1^{\mathrm{A}}(0)]^{1/2} \qquad (8)$$

where $N_{\mathrm{eff}}^{\mathrm{A}}$ is the effective number of electrons for A. A detailed discussion of this approximation is given in earlier papers.[2] This is sufficient to entirely define C_6 parameters. For C_8 we need η_2 expressed from the $S_2(0)$ function (second-order sum rule) and $\alpha_2(0)$ already defined. Unfortunately, these quantities are only known for few species. Kiselev et al.[14] proposed an approximate equation for the quadrupole−dipole dispersion coefficient C_8^{AB}, which involves only known and previously defined quantities η_1 and α_1

$$C_8^{\mathrm{AB}} = \frac{45}{8}\alpha_1^{\mathrm{A}}\,\alpha_1^{\mathrm{B}}\left[\frac{\eta_1^{\mathrm{A}}}{2\eta_1^{\mathrm{A}} + \eta_1^{\mathrm{B}}} + \frac{\eta_1^{\mathrm{B}}}{2\eta_1^{\mathrm{B}} + \eta_1^{\mathrm{A}}}\right] \qquad (9)$$

For pairs of like atoms, this expression underestimates the values found from correlated ab initio calculations for neutral atoms.[15] Let us denote K_8 the ratio between the "exact" and the approximated value for C_8^{AA}. Combining eqs 6, 5, 8, and 9 and introducing this K_8 factor lead to a quadratic equation in $(\alpha_2^{\mathrm{A}})^{1/2}$ for pairs of like atoms:

$$2\left[\frac{S_1^{\mathrm{A}}\,S_2^{\mathrm{A}}}{\alpha_1^{\mathrm{A}}}\right]^{1/2}\alpha_2^{\mathrm{A}} - K_8[\alpha_1^{\mathrm{A}}\,S_1^{\mathrm{A}}\,\alpha_2^{\mathrm{A}}]^{1/2} - K_8[S_2^{\mathrm{A}}(\alpha_1^{\mathrm{A}})^2]^{1/2} = 0 \qquad (10)$$

where the $\omega = 0$ value is understood. An approximate expression for S_2^{A} has been given:[16]

$$S_2^{\mathrm{A}} = [9S_1^{\mathrm{A}}\,\alpha_1^{\mathrm{A}}]^{1/2} \qquad (11)$$

Substitution of (11) in (10) leads to the final form of the equation:[2]

$$2[9(N_{\mathrm{eff}}^{\mathrm{A}})^3/\alpha_1^{\mathrm{A}}]^{1/4}\alpha_2^{\mathrm{A}} - K_8[N_{\mathrm{eff}}^{\mathrm{A}}\,\alpha_1^{\mathrm{A}}]^{1/2}(\alpha_2^{\mathrm{A}})^{1/2} - K_8[9N_{\mathrm{eff}}^{\mathrm{A}}(\alpha_1^{\mathrm{A}})^5]^{1/4} = 0 \qquad (12)$$

The resolution of eqs 12 and 11 are sufficient to get η_2 and therefore C_8^{AB}. Similar, but more complex, derivations are available elsewhere[2] for C_{10}^{AB}.

The repulsive part of the energy, proportional to the square of the overlap integral between the valence orbitals of the two interacting species, is well represented by an atom–atom Born–Mayer type expansion:

$$u_{\mathrm{r}} \approx \sum_{i \neq j} A_{\mathrm{r}} \exp(-b_{\mathrm{r}} R_{ij}) \qquad (13)$$

where A_{r} and b_{r} are fitted parameters obtained from EHT energy vs distance curves. To take into account the fact that overlap of electron clouds cannot be neglected in the short-range region of distances, i.e., around the equilibrium separation, a *damped* multipole expansion was introduced.[17] The dispersion multipole expansion is now written as

$$u_{\mathrm{d}} = -\sum_{n>2} f_{2n}(C_{2n}/R^{2n}) \qquad (14)$$

where

$$f_{2n} = 1 - \left(\sum_{k=0}^{2n} \frac{(b_{\mathrm{r}}R)^k}{k!}\right)\exp(-b_{\mathrm{r}}R) \qquad (15)$$

In the last equation, b_{r} is the Born–Mayer parameter of eq 13. The damping functions f_{2n} are positive and tend to unity at sufficiently large distances where long-range intermolecular forces prevail. On the other hand, it is clear from eq 14 that terms with large n are unimportant at separations that occur in condensed phases.

Perturbation theory up to third and fourth order is necessary to obtain three-body dispersion terms involving triplets of species A, B, and C. The sign of these three-body terms depends on the geometrical configuration, since such triplets are both distance- and angle-dependent. Therefore, it is customary to write the dispersion three-body term as[18]

$$u_{\mathrm{d}}^{\mathrm{ABC}}(l_1,l_2,l_3) = \sum_{l_1}\sum_{l_2}\sum_{l_3} Z^{\mathrm{ABC}}(l_1,l_2,l_3)W^{\mathrm{ABC}}(l_1,l_2,l_3) \qquad (16)$$

with the notations already used for two-body terms and where W^{ABC} is a geometrical factor and Z^{ABC} is an electronic factor. The function Z^{ABC} is a direct extension of the two-body formula, connected to the η_{l_i}'s and the $\alpha_{l_i}(0)$'s that can be found elsewhere.[2,19] The geometrical factors W^{ABC} are functions of the three l_i's, the three interatomic distances, and the three interior angles of the triangle in which the triplet of atoms are vertexes.[2,13] These terms have to be damped just like two-body interactions. Two or three different interatomic distances are present in each W term. Therefore, we propose in this work to introduce a damping factor for three-body interactions that is a product of two or three f_{2n}—such as expressions given in eq 15.

3. Parametrization

Dispersion Expressions. The two key parameters are N_{eff} and α_1, which are sufficient to determine C_6. Then eqs 11 and 12 give S_2 and α_2—provided that K_8 is known—and consequently η_2 and C_8. Here, the development of the series has been considered up to C_8, after checking numerically that higher contributions were of the same order of errors compared with those brought by other approximations elsewhere in the method. This will be shown in the discussion of one of the examples at the end of the paper. We shall successively discuss the main steps necessary to determine α_1, N_{eff}, and K_8 for in-framework sulfur atoms. The parameter b_{r} necessary to determine the damping factors in eq 15 can only be found once the repulsive part has been parametrized. We delay this discussion at the end of the next section.

A new method, combining general relaxation theory with Moretti's electrostatic model, was designed to determine in-framework dipole polarizabilities from the evaluation of extra-atomic relaxation energy during the two-electron Auger process.[20] Although this method was primarily set up for ionic and semi-ionic solids, it has been shown for silicon, aluminum, and magnesium compounds[20] that the model can be applied whatever the target environment (ionic, covalent, or ionocovalent).

Auger electron spectroscopy (AES) relies on a two-electron process. When X-ray radiation of a chosen frequency hits a target atom in a compound, one electron of its inner shell is ejected. This allows an electronic transition for a second electron from an upper shell to the hole left in the inner shell. In doing so, this second electron does not give rise to a radiation but gives its energy to another electron of the same level, which is in turn ejected. Therefore, the transition energy is converted into kinetic energy. The generalized Auger parameter is defined as the sum of this kinetic energy plus the binding energies of the two electrons originally in the upper levels minus that for electrons in the inner shell at the beginning of the Auger process. If one considers two compounds containing the same atomic target, the variation of the Auger parameter is equal to

$$\Delta\xi = 2\Delta R_{\mathrm{D}}^{\mathrm{ea}} \qquad (17)$$

where $R_{\mathrm{D}}^{\mathrm{ea}}$ is the dynamic extra-atomic relaxation energy associated with the Auger process in each of the two species considered. The dynamic extra-atomic relaxation energy can be obtained from ligand polarization energy, as proposed by Moretti.[21] The second electron ejected during the Auger process is used as a probe of the ligand electrostatic energy associated with the emission of the first electron from the atomic target.

Classical formulas developed elsewhere[20] for N identical ligands lead to an expression for the polarization energy

$$U_{pol} = -\frac{N\alpha}{2\gamma}E^2 \tag{18}$$

where $\vec{E}$ is the electrostatic field experienced by any ligand at distance R from the atomic target, N is the coordination number, and $\gamma = 1 + D\alpha R^{-3}$. D is a dimensionless factor that depends only upon the site symmetry. By identifying the polarization energy with the extra-atomic dynamic relaxation energy, one can derive the following expression for the variation of the generalized Auger parameter (between two compounds containing the same atomic target):

$$\Delta\xi = 14.4\Delta\left(\frac{N\alpha}{R^4\gamma}\right) \tag{19}$$

The factor 14.4 arises when transforming energy units from au to eV and distance units from au to Å. For two compounds A and B *having the same atomic target,* eq 19 is more clearly rewritten as

$$\xi_A - \xi_B = 14.4\left[\frac{N_A\alpha_A}{R_A{}^4 + D_A\alpha_A R_A} - \frac{N_B\alpha_B}{R_B{}^4 + D_B\alpha_B R_B}\right] \tag{20}$$

Knowing the ligand dipole polarizability and the extra-atomic relaxation energy for a given compound is sufficient to get these pieces of information for the second compound. Unfortunately, these values are not known unambiguously for a large number of compounds. An idea was to scale eq 20 by considering an ideal unpolarizable compound[20] (UP) with a refractive index equal to unity. It was shown[22] that a linear behavior can be expected when the generalized Auger parameter vs $(1 - \epsilon_0{}^{-1})$ was plotted. This provides a means of calculating ξ_{UP}. Then the dipole polarizability for the ligands linked to the atomic target (S in our case) is given by

$$\alpha_s^{comp} = \frac{\Delta\xi R_{S-L}{}^4}{14.4N_S - D_S R_{S-L}\Delta\xi} \tag{21}$$

where $\Delta\xi$ is the variation of the generalized Auger parameter between a given sulfur compound and the ideal UP-sulfur compound and R_{S-L} is the sulfur−ligand distance.

A mean linear curve, plotted from the available data, is shown in Figure 1. When $n = 1$, we obtain $\xi_{UPS} = -38.7 \pm 1.1$ eV, which leads to $\Delta\xi = 7.9 \pm 1.1$ eV, which should be used in eq 21. In fact, we decided to consider $\Delta\xi$ as a parameter, of course with a rational value, but directly connected to the parametrization of the repulsive part in order to have the simplest parametrization for the whole. We shall discuss this point in more detail later on. We finally chose $\Delta\xi = 6.8$ eV, which can be considered as issued from the lower bound for ξ_{UPS}.

Sulfur is divalent ($N_S = 2$), and in eq 21, the factor D_S remains to be determined. Its expression has been derived elsewhere,[20]

$$D_S = \frac{1 + \cos^2\theta_j}{8\cos^3\theta_j} \tag{22}$$

where $\theta_j = (180 - \alpha_j)/2 = 36.1°$, $\alpha_j = 107.8°$ being the angle between two adjacent S−S bonds. Then $D_S = 0.39$. The

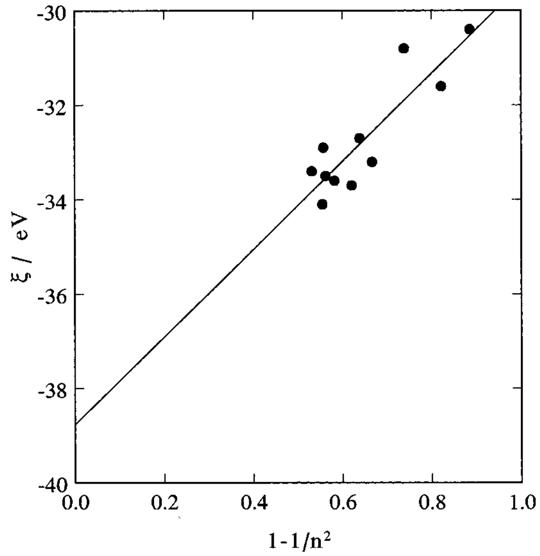

Figure 1. Scaling line for sulfur compounds. Generalized Auger parameters[23,24] (ξ in eV) and refractive indices[25] (n), respectively, are 31.6 and 2.367 for ZnS, 33.7 and 1.625 for NaSCN, 33.5 and 1.511 for $Na_2S_2O_3{\cdot}5H_2O$, 34.1 and 1.499 for $Na_2SO_4{\cdot}2H_2O$, 32.7 and 1.665 for $ZnSO_4{\cdot}nH_2O$, 32.9 and 1.503 for $NiSO_4{\cdot}nH_2O$, 33.2 and 1.732 for $CuSO_4{\cdot}nH_2O$, 33.4 and 1.460 for $NaHSO_4{\cdot}H_2O$, 33.6 and 1.548 for Na_2SO_3, and 30.4 and 2.967 for HgS.

covalent distance has been taken to be $R_{S-S} = 2.07$ Å. From eq 21, we obtain $\alpha_1 \equiv \alpha_S = 5.4$ Å^3 (from the upper bound for ξ_{UPS} we would have obtained $\alpha_1 = 7.7$ Å^3). The fact that the value of the dipole polarizability of sulfur atoms in α-sulfur rings is actually roughly twice that for the neutral and isolated sulfur species reflects the covalent character of the S−S bond. The view provided by the Auger model considers atomic sites; the polarizability is attributed to ligands of a given X-ray target. Another equivalent view is brought about by introducing the concept of bond polarizability originally derived for covalent bonding. This model leads us to consider bonds rather than atoms as centers of interactions.

The parameters for the fit of N_{eff} vs the electronic structure have been previously determined.[2] For neutral sulfur atoms the appropriate formula is

$$N_{eff}^S = -0.0293N^2 + 0.9966N + 0.0062 \tag{23}$$

where N is the total number of (s, p) electrons in the outer shell. Straightforwardly, we obtain $N_{eff}^S = 4.931$. In the first paper of a previous study,[2] the correction factor K_8 is drawn vs the effective number of electrons (Figure 2). For S atoms, using the N_{eff}^S value determined above, we obtain $K_8 = 2.968$. Now all remaining parameters can be computed; they are all listed in Table 1.

Repulsive Interaction. Four parameters are necessary to compute terms in eqs 2 and 3: the matrix elements $H_{\mu\mu}$ for each atomic orbital (s and p electrons) and the Slater exponents ζ_s and ζ_p entering in the algebraic development of overlap integrals. Many techniques, more or less empirical, and approximations have been proposed. Diagonal terms of the Hamiltonian are usually identified with ionization potentials of the valence subshell considered, i.e., with the corresponding orbital energies assuming Koopman's theorem to be valid. The Slater exponents may thus be determined from ab initio atomic calculations. They also can be derived from empirical rules. Some of the main parametrizations proposed are listed in Table 2. The exponent parameters for STO's have been determined

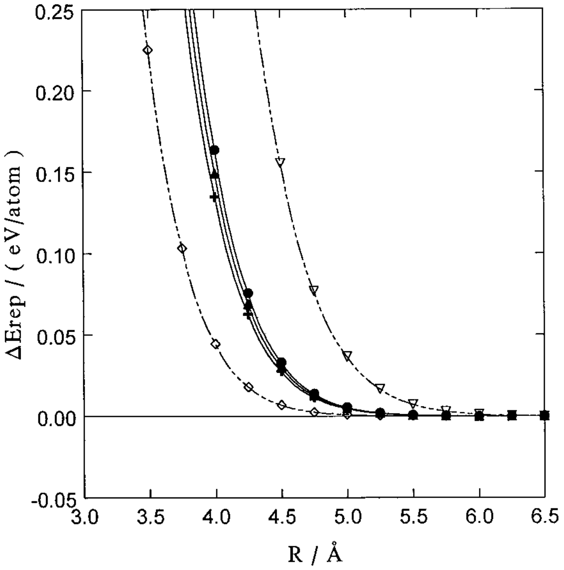

Figure 2. Repulsive interaction energy between two infinite 1D helixes (three atoms per cell) of sulfur atoms. *R* is the distance between centers of helixes. Curves are for the following values of, respectively, $\zeta_s = \zeta_p$, H_{ss} (in eV), and H_{pp} (in eV): (+) 1.817, −16, −13 and 1.817, −20, −11; (▲) 1.817, −20, −13; (●) 1.817, −24, −13 and 1.817, −20, −15; (▽) 1.6, −20, −13; (◇) 2.0, −20, −13.

TABLE 1: Parameters Used in the Calculation of the Dispersion Energy of Sulfur[a]

	Basic Parameters
K_8	2.97
$N_{eff} \equiv S_1$	4.93
α_1	36.36
S_2	40.17
α_2	292.09
	Two- and Three-Body Parameters[b]
C_6	365.11
C_8	14716.50
DDD	3318.83
DDQ	26723.17
QQD	2151.763×10^2
QQQ	1732.623×10^3
$DDD_{(4)}$	-4525.219×10^2

[a] All values are in a.u., apart the dimensionless numbers N_{eff} and K_8. [b] D stands for "dipole interaction" and Q for "quadrupole interaction". The last term is a fourth-order term. They are coefficients in the *W* factor in eq 16.

TABLE 2: Parametrization of Integrals and Exponents for EHT for Sulfur Atoms

authors	ζ_s	ζ_p	$-H_{ss}$[a]	$-H_{pp}$[a]
Slater[26]	1.817	1.817		
Burns[27]	1.967	1.517		
Clementi & Raimondi[28]	2.122	1.827		
Pyykkö & Lehr, Jr.[29]	2.042	1.689	24.145	11.555
Herman & Skillman[12]			20.8	10.3
EHT standard parameters	1.817	1.817	20.0	13.3
Chen & Hoffmann[30]			20.0	11.0

[a] In eV.

a long time ago by Slater[26] from the so-called Slater rules and by Burns[27] who distinguished between s and p electrons. Derivations from ab initio SCF calculations were also used.[28] Values obtained from Slater rules look roughly as mean values. For $H_{\mu\mu}$, all values are close together except the H_{ss} value of Pyykkö and Lehr, Jr.,[29] which is large.

It is important to evaluate the influence of these parameters on the energy of our atomic systems. For a simple system sufficient to give a trend, we considered the interaction energy of two infinite 1D helixes of sulfur atoms built from three-atom elementary cells whose geometry will be described later. In Figure 2 are plotted the results arising from changes both in ζ and $H_{\mu\mu}$. Clearly, even large changes in H_{ss} or H_{pp} do not affect significantly the interaction energy. Conversely, the Slater exponents are the sensitive parameters. This is not completely surprising. Indeed, the main terms in the EHT-matrix elements are overlap integrals whose magnitudes are directly determined from the values of Slater exponents. The $H_{\mu\mu}$ terms are less important. As it was explained in the last section, the $\Delta\xi$ value was chosen in order to use the simplest parametrization of the repulsive part—the standard one—i.e., mean values for ζ exponents and no d functions. Polarization functions (d functions here) may also be introduced in these semiempirical calculations. It is worth noting that these are needed to correctly describe the ab initio electronic structure in some highly coordinated sulfur compounds. Since we consider here low-coordinated sulfur compounds and since we have to calculate repulsive intermolecular interactions, it is safe not to take into account d functions. We checked on typical cases, indicating that these choices were reasonable. For example, for all the sulfur compounds studied in our work, it has been proved that it was not worth using a value of ζ_s very different from that of ζ_p.

As outlined in section 2, we need a Born−Mayer expression of the repulsive energy (eq 13) to get the parameter b_r needed to parametrize the damping function (eq 15). First, it is important to stress that the total energy is reached from two independent contributions. This means that dispersion parameters (C_6, C_8, ...) are determined as shown above and that for the repulsive part EHT results are directly introduced in the calculation. Therefore, A_r and b_r are not required for the calculation of the repulsive part of the energy. Only b_r is needed in the damping function (eq 15) for the dispersion energy. Moreover, close to the interhelix distances corresponding to the energy minima encountered in these weakly bounded molecular crystals, this damping contribution is weak and, thus, so is the influence of the b_r value. The simple exponential form is in fact too simple to reproduce the repulsive energy of intermolecular systems in a large range of intersystem distances. Therefore, since in this paper we are mainly interested in obtaining information close to the energy minimum, and not in obtaining a general potential, we decided to fit only a small part of the repulsive curves, the one close to intermolecular system distances. In Figure 2, for the retained set of atomic parameters, the fitted values thus are $A_r = 33.3$ eV and $b_r = 1.7$ Å^{-1}.

4. α-Sulfur Structure

At room temperature, sulfur is an orthorhombic molecular crystal made of S_8 crown-shaped rings. The structure is well-known.[31−33] The unit cell ($a = 10.465$ Å, $b = 12.866$ Å, $c = 24.486$ Å) includes 16 S_8 rings organized in a nontrivial noncoaxial stacking. The rings are slightly distorted owing to crystal field effects. Enthalpies of sublimation H_{sub}(298 K, 1 atm) of α-sulfur have been obtained in a mass spectrometer coupled to a Knudsen effusion cell.[34] These experiments investigate the stability of the gaseous clusters in equilibrium with the solid. Taking S_8 as the reference, they obtained an enthalpy of sublimation H_{sub}(298 K, 1 atm) = 100 ± 5 kJ mol^{-1}. From our 0 K calculations, one can determine E_{sub}(0 K) and then ΔH_{sub} by adding the integral of ΔC_p, the molar heat capacity from low-temperature adiabatic calorimetry experiments.[35] To check the validity of our method, we will determine the minimum energy structure, i.e., the value of the crystalline parameters, and then the energy of sublimation connected to experiments. We are mainly concerned by the weak interaction energies between covalent clusters (molecular rings here). Starting from the experimental positions of atoms, we shall vary the crystalline parameters, keeping the covalent bonds and angles at their original values. Therefore, the treatment of the covalent rings by the EHT method (only a semiempirical method!) is not of crucial importance, since we are concerned with finding the intermolecular interaction energy from a difference energy calculation. However, to check the validity of the EHT method in determining the minimum energy structure of this type of covalently bonded systems, we first perform calculations on the isolated S_8 molecule.

The geometrical characteristics of the S_8 molecule are well-known. The covalent interatomic distance, the covalent angle, and the dihedral angle, respectively, are[36] 2.060 ± 0.005 Å, 108.0 ± 0.8°, and 98.3 ± 2.1°. More recent determinations[37] propose a smaller value for the distance (~2.050 Å) but quite comparable values for the angles. Most of the recent ab initio calculations fall in each range of errors when the minimum energy structure[38] is determined. From our set of EHT parameters, defined in section 3, we find $d = 2.106$ Å, $\alpha = 112.6°$, and $\beta = 92.5°$. When they are compared with the experimental values, the error is roughly 2%, 4%, and 6% for d, α, and β, respectively. This molecule has been already studied by EHT with other parametrizations,[39] including in some cases an electrostatic correction.[40] These authors found comparable results as ours. The introduction of d functions give worse results, and the introduction of electrostatic corrections does not bring significant improvements. In conclusion, we see that in such types of element and molecules, EHT calculations restricted to s and p orbitals lead to correct results even for strongly covalent bonds (i.e., for short values of interatomic distances). For difference energies between the solid and the constituting molecules, only EHT terms corresponding to weak intermolecular bonds (i.e., for large values of interatomic distances) will effectively contribute. Therefore, we may legitimately use EHT calculations for determining the repulsive interaction energies of our sulfur systems.

Coming back to orthorhombic sulfur, we started from the geometry, taking the slight distortions of rings into account.[41] Then we varied the crystalline parameters, keeping fixed the geometry of the rings. Let us first discuss the choice of the number of **k**-points, sampling the (reduced) Brillouin zone, on which the total EHT energy is averaged. It is well-known that the larger the size of the elementary cell the lower the number of necessary **k**-points required for good accuracy of the total energy. Indeed, for large unit cells, the band dispersion is weak; it corresponds to taking into account phase relationships at distances equal to or larger than the norm of translation vectors, and the calculations can be performed at a single point of the Brillouin zone when the cell vectors exceed 10−15 Å. Then it has been checked that we can use the origin of the Brillouin zone, the Γ point, since this high symmetry point is the most obvious one. In the case of the two-helixes example given in section 5, we will see later that we have to introduce six **k**-points, the zone-center point alone being quite insufficient in this (1D) small elementary cell case. Adding the dispersion part of the energy, as described earlier with parameters given in Table 2 and taking into account that all ring environments are not the same, we show in Figure 3 the variations of the components of the interaction energy vs the crystalline parameter b; the two other crystalline parameters a and c are kept constant (experimental values). Under these assumptions, we are very close to the absolute minimum (see results below). The role of the three-body terms is important because some triplets involving two bonded atoms are taken into account. Removing these terms would lead to a very weak cohesion. The complete minimization of the energy with respect to all three crystalline parameters leads to $a = 10.9$ Å, $b = 13.7$ Å, $c = 24.5$ Å, and $\Delta E_{\mathrm{tot}} = -0.80$ eV/mol(S_8).

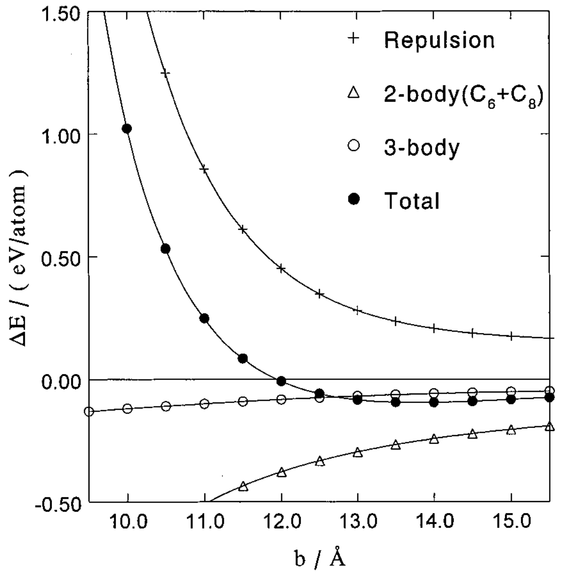

Figure 3. Partitioning of the interaction energy between rings in α-sulfur along the *b*-axis.

Comparing the experimental values given at the beginning of the section, we see that the calculated values for a and b are, respectively, 4% and 6% larger than their experimental counterparts. The experimental value for c is found from our calculations. The volume of the calculated elementary cell is about 11% higher than the experimental volume. The enthalpy of sublimation is reached by adding the integral of the ΔC_p term between $T = 0$ and $T = 298$ K, equal to 27 kJ mol^{-1},[35] to the interaction energy. We obtain $\Delta H_{\mathrm{sub}}(298\ \mathrm{K}) = 104$ kJ mol^{-1}. The difference in the experimental value falls within the error range of the mass spectrometer measurement, the error on ΔC_p being negligible.[35] Therefore, the model of intermolecular potential function and its parametrization is able to predict structural and thermodynamic properties of α-sulfur in agreement with experimental results. Theoretical calculations on α-sulfur have been published some years ago, but the driving idea of these studies was different from ours. They use the so-called "6-exp" potential function (the r^{-6} term as the attractive part and the exponential function for the repulsive one), but the parameters C_6, A_r, and b_r (in our notations) are adjusted in order to have the right geometrical structure and sublimation energy. Then they use the ad hoc potential in a dynamic calculation to study intermolecular vibrational modes,[42−44] internal ones in a nonrigid body model,[44] and Raman frequencies.[42] As a first remark, let us stress on the parameters values. As explained at the end of section 3, our values for A_r and b_r (and for C_6 too) are fitted to a few points close to the minimum energy structure only and cannot be compared to those of Rinaldi and Pawley. However, from the retained set of atomic parameters (central curves in Figure 2), we can get another fit, better at short distances than the previous one but worse close to the interhelix distances. These new values are $A_r = 2303$ eV and $b_r = 2.9$ Å^{-1}. A straightforward

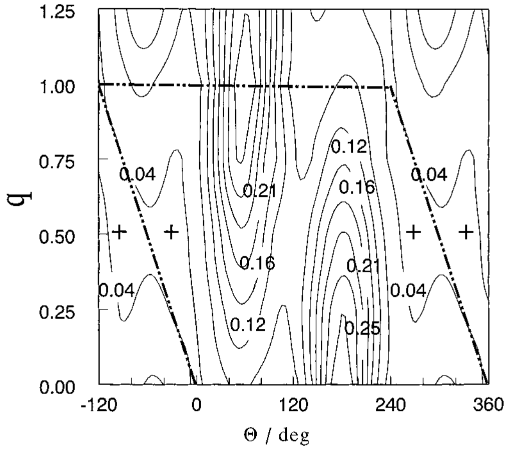

Figure 4. Repulsive interaction energy contour maps as a function of the shift and the rotation of the second helix relative to the first. Energies are in eV/atom. Minima are indicated by crosses.

change of units shows that these last parameters are of the same order of magnitude than those of Rinaldi and Pawley.[42] In Rinaldi and Pawley's potential, (i) there is no C_8 or three-body terms and (ii) the numerical values of repulsive parameters are not extracted from an independent quantum mechanical calculation. With their adjusted "6-exp" potential all the cited authors[42−44] were able to find a correct agreement between their calculated lattice frequencies and the experimental ones. We have shown in our examples how the C_8 and three-body terms may be important quantities for determining the right cohesive energy. We may conclude that for lattice frequencies these terms, rather connected to the structure (which is correctly described by two-body terms as shown in our second example in the next section), are likely less important than in the calculation of cohesive energies. However, the remaining slight discrepancies compared with experimental values might be, at least partly, canceled out by the introduction of higher order terms in the dispersive perturbation expansion, as in our calculations.

5. Interaction of Two 1D Helixes of Polymerized Sulfur

For this example, we study the interaction of two 1D helixes in a simple case for their respective geometry. Let us consider two parallel conrotatory helixes, with a three-atoms per helix elementary cell. All parameters have been determined in the preceding sections, apart from the distances and the angles between covalent bonds we have considered $r_{\mathrm{S-S}} = 2.07$ Å, $\alpha_{\mathrm{SSS}} = 108.5°$, and $h = 4.58$ Å, where h is the height of each elementary cell. This choice is connected to the real 3D case of ω-sulfur, which will be studied and discussed in part II. Without carrying out the complete optimization of structures, let us first see on this example the behavior of the repulsive energy when two of the geometrical parameters are varied. Let us define the parameter q as a measure of the shift of the second helix relative to the first. It is defined as the percentage of the height Q between two successive atoms (here, $Q = h/3 = 1.53$ Å). Shifts larger than 1 ($1 + x$) are analogous to shifts for x ($0 \le x < 1$). The parameter θ represents the angle between the projection of the position of the first atom of the second helix and the y-axis. For the first helix the choice of reference axes is such that $q = 0$ and $\theta = 0°$. In Figure 4, we plot the interaction repulsive energy contour map as a function of q and θ. In this 1D calculation six **k**-points are sufficient to obtain the convergence of the average energy. Starting from [$q = 0$, $\theta = 0°$], a shift followed by a rotation [$q = 1$, $\theta = -120°$] leads to an equivalent geometry. The periodicity is indicated in the figure by the double-pointed dashed-line cell. For this structure, a low-energy region ($\Delta E_{\mathrm{rep}} < 0.04$ eV/atom) exists and the positions of two minima (~0.026 eV/atom) are indicated by crosses. They lie in the flat region at the coordinates $q = 1/2$ and $\theta = 260°$ and 340°. Let us examine why we have the minima at such values of q and θ. Some typical interactions are schematized in Figure 5. Three atoms (the elementary cell) of each helix are represented, and the black, full circles correspond to the atoms in the middle with respect to the height. For $q = 0$, the repulsion is maximum for $\theta = 180°$, while the most stable configuration must be reached for $\theta = 0°$. This is effectively what is observed from Figure 4. Now, for $q = 1/2$, where minima occur, it is useful to consider four values of θ for the discussion. In all our plots, the helix on the left is kept fixed. The helix on the right is shifted and rotated (in the clockwise direction) appropriately. Let us first consider the angles $\theta = 60°$ and $\theta = 180°$. Clearly, they correspond to the greatest repulsions. The lowest energy configurations might be the ones when the atom at height zero in the helix on the left has no atoms just in front of it in the helix on the right, as was the case for the structure [$q = 0$; $\theta = 0°$]. These angles, whose corresponding configurations are $\theta = 0°$ and $\theta = 240°$, are shown in Figure 5. In these two cases the repulsions are not identical. Only the greatest repulsions are indicated and taken into account in our reasoning. Repulsions of other atoms must have a smaller but not negligible influence. To minimize the repulsions between other atoms, the helixes on the right have to be rotated by an additional small angle θ_{S} in a sense indicated by the arrow in Figure 5. If we admit a small variation of $\theta_{\mathrm{S}} = 20°$, we exactly find the two minima, in Figure 4, at $\theta = 340°$ ($0° - 20°$) and $\theta = 260°$ ($240° + 20°$). Now, by addition of the dispersion part of the energy, the same type of plot is shown in Figure 6. The similarity between the two figures is evident. A large part of the map corresponds to cohesive energy, the lowest energy region has the same shape and, as previously, is very flat. A small difference appears in the localization of energy minima. We have only one minimum of the energy, still for $q = 1/2$ but for $\theta = 300°$. A simple scheme as the one proposed in Figure 5 for repulsions cannot be applied here, since the dispersion, introduced by pertubations, has complicated the energy equations. However, this small

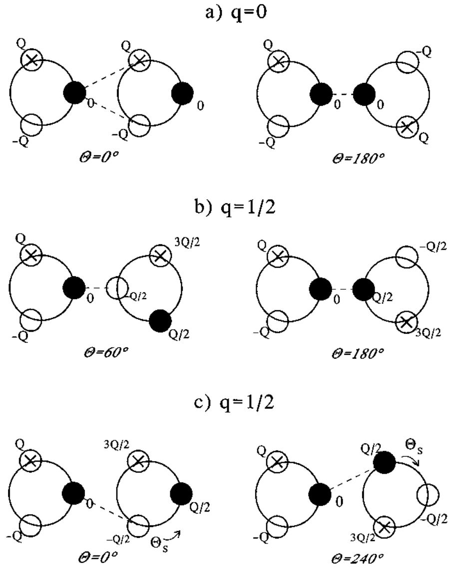

Figure 5. Simple schemes emphasizing the main interactions (dashed lines) responsible of the minima locations in Figure 4. The height of each atom is indicated. See text for other definitions.

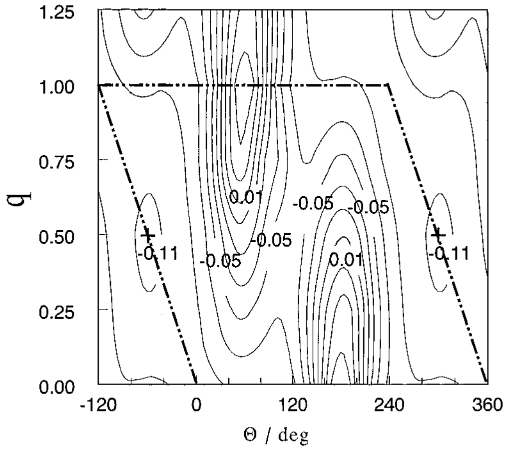

Figure 6. Total interaction energy contour maps as a function of the shift and the rotation of the second helix relative to the first. Energies are in eV/atom. Minima are indicated by crosses.

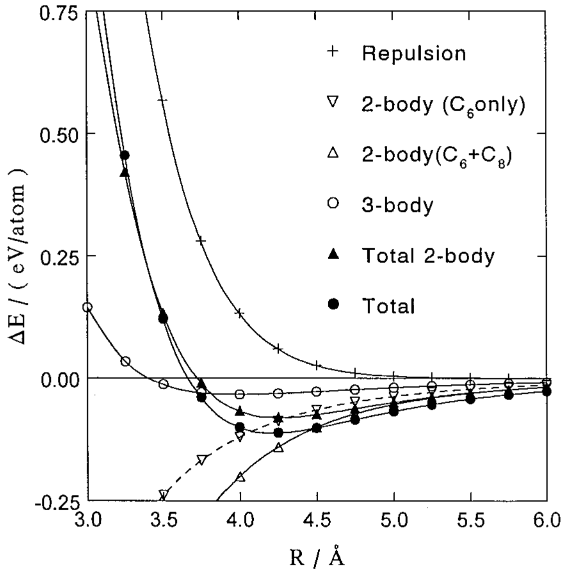

Figure 7. Partitioning of the interaction energy between two infinite conrotatory 1D helixes (three atoms per cell) of sulfur atoms. R is the distance between centers of helixes.

difference is not very important; we are in the flat region, and we are only running semiempirical calculations and cannot claim we are as accurate as in the case of very elaborate ab initio calculations (which are not feasible in our case anyway!). What is important is the *complete similarity* between the general shapes of the contours, which may allow us for all subsequent calculations (in part II) to start from q and θ-values determined from the repulsive part only, at least in the case of the most complicated structures for which a complete optimization of q and θ with equations including dispersion terms is not possible. This is a non-negligible simplification concerning the computing time point of view.

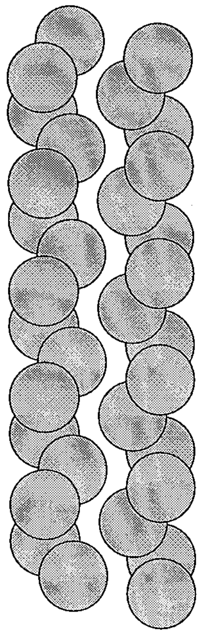

Figure 8. View of the most stable structure of two 1D helixes with three atoms per elementary helical chain.

TABLE 3: Coordinates of Atoms in Two Helixes with Three Atoms per Elementary Cell and Parameters Equal to q = 1/2, θ = 300°, R = 4.25 Å[a]

atom	x	y	z
A_1	0.0	0.80709	0.0
A_2	1.52667	−0.40355	0.69897
A_3	3.05334	−0.40355	−0.69897
A_4	4.58	0.80709	0.0
B_1	0.76330	4.65355	0.69897
B_2	2.29	3.44290	0.0
B_3	3.81660	4.65355	−0.69897
B_4	5.34330	4.65355	0.69897

[a] In Å.

Now at this minimum in q and θ, the interhelix distance R is varied. Results are shown in Figure 7 where each contribution to the total energy is clearly indicated. The coordinates of all atoms, including the fourth in each helix that is deduced from the first by translation symmetry, are given in Table 3 for a value of R very close to the minimum: R = 4.25 Å. The introduction of the C_8 term has lowered the energy, and the relative contributions of C_6 and C_8 are such that we may expect a smaller contribution of C_{10}. Three-body interactions are not negligible because we consider some triplets of atoms in which two are chemically bound and are therefore at very short separation. The final total interaction energy is lowered by about 40%. However, the equilibrium interchain distance is approximately the same with or without three-body terms. The damping of three-body terms is small and may be neglected as the C_{10} terms contributions. The numerical values for the equilibrium point are $R_{\min}$ = 4.24 Å and $\Delta E_{\min} = -0.111$ eV/atom. Let us note from Figure 7 that the consideration of C_6 terms only, without C_8 and the three-body terms, would lead to a very weak minimum and cohesion. Although concerning a nonrealistic structure, these results *look quite satisfactory*. Indeed, the interchain distance is roughly of the order of a/2 and b/2 for ω_1 and of the order of a and b for ω_2 (the real 3D interchain distances), a and b being the crystalline parameters (a = 9.02 Å, b = 8.33 Å, c = 4.58 Å for $S_{\omega 1}$, and $a = b$ = 4.58 Å, c = 16.32 Å for $S_{\omega 2}$, from Tuinstra[45]). The depth of the potential curve is about 10 kJ/atom. This is a reasonable value that should increase when considering more realistic 3D systems, since more interactions are taken into account. In Figure 8, a view of the space arrangement for the most stable structure of the above example is shown. The value of q (1/2) is mainly responsible for the strong interpenetration of the two helixes. The shortest distance between atoms in different helixes is equal to 3.45 Å. Then the value of the van der Waals radius of sulfur in this system is equal to 1.73 Å. This is in excellent agreement with the experimental value[46] (1.74 Å for S_α).

6. Conclusion

We have presented in this paper a calculation method aimed at the study of ω-sulfur. This method is based on semiempirical methods; it combines the periodic version of EHT that allows the description of crystals with large unit cells and a perturbation theory for the dispersion interactions. The first correctly describes the covalent bonds and the repulsive part of the intermolecular potential; we have checked that EHT calculations on a crown-shaped S_8 ring led to a correct minimized structure. The second part generates the attractive part of the intermolecular interactions. The parametrization has been tested and validated on the known structure of the α-sulfur. The new intermolecular potential function predicts values in agreement with experimental values for the unit cell parameters and for the sublimation energy. The polarizability $\alpha_S = 5.4$ Å^3 that we have obtained for the sulfur atom seems satisfactory and could be compared with the value $\alpha_S = 6.14$ Å^3 in SCN^- where the sulfur atom is poorly and negatively charged, $-0.19e$.[47] We have also calculated the equilibrium geometry for a system made of two infinite sulfur chains (polymerized sulfur). The energetics and structural parameters are also in good agreement with experimental results. This is an encouragement to use our method on less known structures and in particular that of ω-sulfur. This is the goal of our part II.

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