for the greater strength of the C–O bond in CO than in CO_2 or SCO, since σ charge, being concentrated along the molecular axis, exerts a greater attractive force upon the two nuclei. Nevertheless, the near-equality of the total internuclear valence electronic charges emphasizes the artificiality of the characterization of these C–O bonds as "double" or "triple" bonds.

It has been suggested that the electronic structure of a bond C–Z in a triatomic molecule X–C–Z is relatively little affected by the nature of the atom X.[6,29] Some support for this idea, at least in the case of CO_2 and SCO, is provided by the fact that the quantities of σ and π electronic charge in the CO portions of these two molecules are so very similar. There are, of course, certain differences in detail between the electronic structures of the C–O bonds in CO_2 and SCO.[28]

It has been noted[28] that there is no localized buildup of electronic charge to the outside of the sulfur atom in SCO; apparently the sulfur has nothing resembling a "lone pair," in marked contrast to the oxygen atoms in CO, CO_2, and SCO.[28] Another indication of this fact can now be obtained by computing the positions of the centers of the electronic charges associated with the sulfur and oxygen atoms in these molecules. It has been shown that the centers of charge of the covalently bonded atoms in a series of diatomic molecules are generally to the *outsides* of the atoms, rather than in the internuclear regions.[2,30] These results can, in most cases, be attributed to the effects of fairly localized molecular orbitals representing what may loosely be termed "lone pairs." The center of electronic charge of the sulfur atom in SCO, however, is only 0.01 au to the outside of the S–C internuclear region; the corresponding figures for the oxygen atoms in CO, SCO, and CO_2, on the other hand, are 0.06, 0.07, and 0.17 au, respectively. These indications that there is not associated with the sulfur in SCO any buildup of electronic charge which could be described as a lone pair are consistent with Bird and Townes' conclusion, based on the measured ^{33}S quadrupole coupling constant, that this sulfur atom is in an essentially unhybridized state.[31]

Acknowledgment. The authors greatly appreciate several very helpful discussions with Dr. Ieva Ruks Politzer. They are grateful to the Kayser–Roth Foundation for its support of this work, and they also thank the LSU—NO Computer Research Center for its financial assistance.

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Molecular Orbital Studies on Hexagonal Ice

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Abstract: Molecular orbital calculations, based on the CNDO (complete neglect of differential overlap) approximation, are reported for hexagonal ice. The theoretical structural data are found to agree well with experiment. The difference between the bond angles for gas-phase and crystalline water molecules is interpreted in terms of the crystal polarization energy.

Although the most important manifestations of hydrogen bonding, such as the anomalous properties of certain solids and liquids, the conformation of proteins and solvation effects in some chemical reactions, involve semiinfinite aggregates of interacting molecules, theoretical investigations[1–6] of this effect have heretofore been largely limited to the study of dimers or trimers. These studies are clearly useful only in so far as the hydrogen-bonding interactions within these systems can be represented by the sum of pairwise potentials, and the long-range crystal or solvent interactions are negligible. In the present paper we consider these questions by departing from the traditional dimer approach to the study of hydrogen bonding, and consider instead the interactions within an infinite lattice of hydrogen-bonded molecules.

Hexagonal ice, the stable form of ice under ordinary conditions, was chosen as the subject for this study since it provides an intermediate step to the understanding of the properties of liquid water and its solutions. Thus, if the present investigation shows that molecular orbital theory adequately describes the intermolecular hydrogen-bonding interaction within the ice lattice, it would suggest that the present treatment could be usefully extended to the study of solvation in aqueous solution. Such a study would aid the understanding of, for example, the role of solvation molecules in organic chemical reactions.

The structure of hexagonal ice (ice-1h) has, of course, an intrinsic interest of its own. Although the main features of the lattice structure are fairly well understood, several questions concerning the observed small asymmetry of the oxygen sublattice (see below) remain to be resolved.[7,8] The structure of the water molecule

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in the ice-Ih lattice is also of interest. Neutron diffraction[9] and broad line nmr[10] studies have revealed an increase, over gas-phase values, of about 5° in the HOH bond angle and about 0.01 Å in OH bond length.

Theoretical Section

The LCAO-MO calculations reported here for the ice-Ih crystal are based on the CNDO/2[11] (complete neglect of differential overlap) approximate molecular orbital scheme. The basis set for these calculations consists of the conventional valence shell set of 1s orbitals centered on the protons and Slater 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals, referred to as the *a*, *b′*, and *c* crystal axes, centered on the oxygen atoms of the lattice.

The conventional method[12] for molecular orbital calculations for crystals is based on the use of lattice translational symmetry to factorize the infinite dimension SCF matrix equation in much the same way as point group symmetry is used to simplify molecular calculations. The first step in this procedure involves the construction of *delocalized* crystal orbitals from translationally equivalent localized atomic orbital basis functions. With these new basis functions, the infinite dimension Fock matrix for the crystal breaks down into an infinite number of coupled finite matrix equations. As only a finite number of these equations can be solved, the infinite aspect of the crystal is simulated by averaging over the solutions of the chosen equations by means of numerical interpolation.

While the above approach is suitable for molecular orbital calculations for metals, it is wasteful when applied to molecular crystals where the electrons are localized. Such a molecular crystal calculation would consume a considerable amount of computer time first constructing *delocalized* crystal orbitals and then more time *localizing* them again through the solution of the SCF submatrix equations. Clearly, an alternative theoretical approach that takes advantage of the special properties of molecular (and valence) crystals is required.

An alternative method for molecular orbital calculations for molecular crystals was recently proposed by Bacon and Santry.[13,14] This method starts with molecular orbitals localized on the constituent lattice molecules and treats the delocalization over surrounding lattice molecules by a technique based on third-order SCF perturbation theory. The serious disadvantages of the crystal orbital (Bloch) method are avoided by working with the crystal bond order matrix throughout and by using the crystal symmetry in a simple and direct manner. The use of perturbation theory of course raises the question of accuracy. However, in the present application, *three-dimensional* crystals, the error[13,14] resulting from the neglect of fourth and higher order terms in the perturbation expansion probably compares favorably with that inherent in the numerical interpolation necessary in the crystal orbital approach.[12]

As the SCF perturbation method has been described in detail elsewhere, we shall limit the present discussion to the salient features of the first-order theory. We start with the infinite SCF matrix equation for the crystal

$$FC = CE \tag{1}$$

where *F*, *C*, and *E* are respectively the crystal Fock, molecular orbital, and orbital energy matrices, referred to a basis set of atomic orbitals centered on the atoms of the constituent lattice molecules. For convenience of exposition, it will be assumed that this basis set is organized so all atomic orbitals associated with a given molecule are collected together in a group. Intuitively following the molecular character of molecular crystals, the molecular orbitals of hypothetically noninteracting lattice molecules are taken to be zero-order approximate solutions to eq 1. These zero-order solutions satisfy the zero-order SCF equation[13,14]

$$F^{(0)}C^{(0)} = C^{(0)}E^{(0)} \tag{2}$$

where, because of the basis set convention, $F^{(0)}$ will be a block diagonal matrix, with each diagonal submatrix, ${}^{RR}F^{(0)}$, being the Fock matrix for a hypothetically isolated lattice molecule, R. Similarly, $C^{(0)}$ can be *assumed* to be a block diagonal matrix, with each diagonal submatrix, ${}^{RR}C^{(0)}$, containing the molecular orbitals, both occupied and vacant, of a particular lattice molecule.

All interactions between all molecules in the crystal are now included as a *single* perturbation. Their inclusion is effected through the solution of the first- (and higher) order SCF perturbation equation[13,14] for the crystal

$$F^{(0)}C^{(1)} + F^{(1)}C^{(0)} = C^{(0)}E^{(1)} + C^{(1)}E^{(0)} \tag{3}$$

where $F^{(1)}$, $C^{(1)}$, and $E^{(1)}$ are the first-order Fock, molecular orbital, and orbital energy matrices, respectively, for the crystal. The first step in the solution of this equation is the partitioning of all matrices into inter- and intramolecular submatrices using the special ordering of the basis set. The following notation is introduced for the elements of these submatrices.

$${}^{RS}F^{(1)} = ({}^{RS}F_{\mu\nu}{}^{(1)}) \tag{4}$$

$${}^{RS}C^{(1)} = ({}^{RS}C_{\mu i}{}^{(1)}) \tag{5}$$

and for the crystal bond order matrix *P*

$${}^{RS}P^{(1)} = ({}^{RS}P_{\mu\nu}{}^{(1)}) \tag{6}$$

where μ and ν label atomic orbitals associated with the Rth and Sth lattice molecule, respectively, and *i* labels a molecular orbital localized on the Sth molecule to the zeroth order. Explicit expressions for the various ${}^{RS}F^{(1)}$ are given in ref 14. Equation 3 can now be partially multiplied out in terms of these submatrices. Noting the block diagonal form of $F^{(0)}$ and $C^{(0)}$ we find

$${}^{RR}F^{(0)RR}C^{(1)} + {}^{RR}F^{(1)RR}C^{(0)} = {}^{RR}C^{(1)RR}E^{(0)} + {}^{RR}C^{(0)RR}E^{(1)} \tag{7}$$

and

$${}^{RR}F^{(0)RS}C^{(1)} + {}^{RS}F^{(1)SS}C^{(0)} = {}^{RS}C^{(1)SS}E^{(0)} \tag{8}$$
$$R \neq S$$

Thus, the infinite dimension perturbation equation, (3), has been broken down into a infinite number of finite dimension equations. These equations are

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(13) J. Bacon and D. P. Santry, *ibid.*, 55, 3743 (1971).
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termed intramolecular if they are of the same type as (7) and intermolecular if the same type as (8). There is one intramolecular equation for each lattice molecule in the crystal and two intermolecular (RS and SR) equations for each pair of molecules. These equations cannot be solved independently since to set up and solve the intramolecular equation for a given molecule[14] one requires the charge distributions, or solutions to the intramolecular equations, for all other molecules in the lattice.

At this point the new theory appears no less complicated than the one it is intended to replace. However, no use has, as yet, been made of the crystal symmetry. If it is assumed, to simplify the discussion, that all molecules in the crystal are related by one or more elements of the space group, then the intramolecular Fock and bond-order submatrices for all lattice molecules are related. If two molecules are translationally equivalent, their Fock and bond-order submatrices will be equal. If, on the other hand, the two molecules are related by an element of rotational symmetry, their submatrices will be related by a similarity transformation. This fact can be used to decouple the above equations since the solution of the equation for a given molecule can be used to calculate the charge distributions for all other lattice molecules. Furthermore, since all molecules in the lattice are equivalent, it is necessary to solve only one representative intramolecular equation and only one set of intermolecular equations involving a chosen reference molecule with all remaining lattice molecules. In practice (see later), it is usually sufficient to solve only equations involving molecules up to the next nearest neighbor. Thus, a solution to eq 1 can be achieved through the solution of a *few* matrix equations, (7) and (8), of the *same dimensionality* as the SCF equation for the constituent lattice molecules. In the present treatment, the perturbation expansion is taken up to and including the third order.

In the case of CNDO/2 theory, the coupling of the intramolecular equations is particularly simple since it involves only the total atomic electron populations for the lattice molecules.[14] Thus, the equations are decoupled by simply noting that the total electron population for a given atom is the same for all molecules.

A detailed description of the solution of the perturbation equations is given in ref 13 and 14. Although the equations must be solved iteratively, since $F^{(1)}$ depends on $C^{(1)}$ through $P^{(1)}$, the computing time required is relatively short since the method of solution depends on multiple matrix multiplication rather than matrix diagonalization. The higher order perturbation equations are solved in an analogous manner. Iteration of the higher order equations is of course necessary since an nth order change in C effects a corresponding change in P and hence in F.

The computational efficiency of the method is such that the time required for a calculation for a three-dimensional crystal is about the same as that required for a direct calculation on the corresponding dimer. Thus, the perturbation approach enables calculations on extremely large and complex systems to be carried through on relatively modest computational facilities.

The Crystal Energy

In practice the perturbation equations are solved for the bond-order matrices ${}^{\mathrm{RS}}P^{(n)}$ in preference to the molecular orbital matrices ${}^{\mathrm{RS}}C^{(n)}$. These bond-order matrices are then used to calculate the crystal energy by means of eq 9, where H and F are respectively the total

$$W = \tfrac{1}{2}\sum_{\mu}^{\mathrm{Xstal}}\sum_{\nu}^{\mathrm{Xstal}} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \text{nuclear repulsion} \quad (9)$$

Hamiltonian and Fock matrices for the crystal.[14] The summations over μ and ν include all the atomic orbitals in the crystal basis set. When the crystal P, H, and F matrices are expanded in the perturbation series[13,14] and expressed in terms of the corresponding submatrices, it is found that the crystal energy (per molecule), W_{Xstal}, can be most conveniently written as the sum of five contributions.[14]

$$W_{\mathrm{Xstal}} = W_{\mathrm{molecule}} + W_{\mathrm{electrostatic}} + W_{\mathrm{polarization}} + W_{\mathrm{intermolecular}} + W_{\mathrm{intramolecular}} \quad (10)$$

W_{molecule} in eq 10 corresponds to the zero-order energy and is the energy of the reference molecule, including nuclear repulsion, calculated at the molecular geometry appropriate for the crystal. As this geometry will usually differ slightly from that for a free molecule, W_{molecule} will not, in general, equal the free molecule energy $W^{\mathrm{f}}{}_{\mathrm{molecule}}$. This difference reflects the fact that the crystal molecule is usually in a state of some internal strain. We allow for this by defining the crystal binding energy as

$$W_{\mathrm{binding}} = W_{\mathrm{Xstal}} - W^{\mathrm{f}}{}_{\mathrm{molecule}} \quad (11)$$

where W_{binding} will be negative for stable crystals. The strain energy for a molecule in the lattice, which may be of some interest, is given by

$$W_{\mathrm{strain}} = W_{\mathrm{molecule}} + W_{\mathrm{intramolecular}} - W^{\mathrm{f}}{}_{\mathrm{molecule}} \quad (12)$$

$W_{\mathrm{electrostatic}}$ is given by

$$W_{\mathrm{electrostatic}} = \tfrac{1}{2}\sum_{\alpha}^{\text{any molecule}}\sum_{\beta}(Q_{\alpha}{}^{(0)}Q_{\beta}{}^{(0)} - 2Q_{\alpha}{}^{(0)}Z_{\beta})\Gamma_{\alpha\beta} + \tfrac{1}{2}\sum_{\alpha\beta}\sum Z_{\alpha}Z_{\beta}\sum_{\mathrm{S}}{}' 1/R_{\alpha\mathrm{S}\beta\mathrm{R}} \quad (13)$$

where $Q_{\beta}{}^{(0)}$ is the total zero-order electron density on the βth atom of, say, the reference molecule R, and Z_{β} the effective nuclear charge of the same atom. $\Gamma_{\alpha\beta}$ is a lattice sum of CNDO Coulomb integrals

$$\Gamma_{\alpha\beta} = \sum_{\mathrm{S}}^{\mathrm{Xstal}}{}'\gamma_{\alpha\beta}{}^{\mathrm{RS}} \quad (14)$$

where $\gamma_{\alpha\beta}{}^{\mathrm{RS}}$ is the average Coulomb integral between the αth atom of the reference molecule R, and the βth atom of the Sth molecule in the lattice. The summation over S excludes the origin or reference molecule R. Both contributions to $W_{\mathrm{electrostatic}}$ in eq 6 are strongly divergent, but their combined sum is reasonably convergent for a three-dimensional crystal.

While the various terms in eq 13 clearly represent an electrostatic interaction between the unperturbed charges centered on the atoms of the lattice molecules, the neglect of penetration[15] in the CNDO/2 method leads to a positive value for this contribution for all the hydrogen-bonded molecular crystals studied so far (HF, H_2O, HCN, HCOOH, $HCONH_2$, $(NH_2)_2CO$, and

[15] J. Pople and D. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1971.

α-$(COOH)_2$).[14,16] As this neglect of penetration supposedly partially compensates for the neglect of the overlap, $W_{\mathrm{electrostatic}}$ may be considered to include part of the overlap dependent repulsive energy for the crystal. $W_{\mathrm{polarization}}$ is given by

$$W_{\mathrm{polarization}} = {}^1/_2\sum_{\alpha\beta}\sum(Q_\alpha{}^{(0)}Q_\beta{}^{(1)} + Q_\alpha{}^{(1)}Q_\beta{}^{(1)} + Q_\alpha{}^{(0)}Q_\beta{}^{(2)} + Q_\alpha{}^{(1)}Q_\beta{}^{(2)} + Q_\alpha{}^{(2)}Q_\beta{}^{(1)} + Q_\alpha{}^{(0)}Q_\beta{}^{(3)})\Gamma_{\alpha\beta} + {}^1/_2\sum_{\alpha\beta}\sum(Q_\alpha{}^{(1)} + Q_\alpha{}^{(2)}) \times (Q_\beta{}^{(0)} - 2Z_\beta)\Gamma_{\alpha\beta} \quad (15)$$

and includes all remaining terms in the crystal energy explicitly dependent on the Coulomb lattice sums $\Gamma_{\alpha\beta}$. At the simplest level this contribution gives the electrostatic interaction between the perturbed charge densities of the lattice molecules. The neglect of penetration, however, complicates this interpretation.

The intermolecular energy, $W_{\mathrm{intermolecular}}$, includes all terms that involve the lattice summation of the intermolecular density submatrices, ${}^{\mathrm{RS}}P$

$$W_{\mathrm{intermolecular}} = {}^1/_2\sum_{\mathrm{S}}^{\mathrm{Xstal}}\sum_{\mu}^{\mathrm{R}}\sum_{\nu}^{\mathrm{S}}[2({}^{\mathrm{RS}}P_{\mu\nu}{}^{(1)} + {}^{\mathrm{RS}}P_{\mu\nu}{}^{(2)}){}^{\mathrm{RS}}H_{\mu\nu}{}^{(1)} - {}^1/_2{}^{\mathrm{RS}}P_{\mu\nu}{}^{(1)} \times ({}^{\mathrm{RS}}P_{\mu\nu}{}^{(1)} + 2{}^{\mathrm{RS}}P_{\mu\nu}{}^{(2)})\gamma_{\alpha\beta}{}^{\mathrm{RS}}] \quad (16)$$

where ${}^{\mathrm{RS}}H^{(1)}$ is an intermolecular Hamiltonian submatrix.[13,14] A large fraction of the time required for the crystal calculation goes into the evaluation of this contribution, since each term requires separate SCF perturbation calculations. Fortunately, ${}^{\mathrm{RS}}P$ decreases very strongly as the separation between the molecules R and S increases, so relatively few terms need be included.

Finally, $W_{\mathrm{intramolecular}}$ includes all contributions to the crystal energy involving elements of the intramolecular submatrices, ${}^{\mathrm{RR}}P$, ${}^{\mathrm{RR}}H$, and ${}^{\mathrm{RR}}F$, for the reference molecule R.

$$W_{\mathrm{intramolecular}} = {}^1/_2\sum_{\alpha\beta}\sum(Q_\alpha{}^{(1)}Q_\beta{}^{(1)} + 2Q_\alpha{}^{(0)}Q_\beta{}^{(2)} + 2Q_\alpha{}^{(1)}Q_\beta{}^{(2)} + 2Q_\alpha{}^{(0)}Q_\beta{}^{(3)})\gamma_{\alpha\beta}{}^{\mathrm{RR}} + \sum_{\mu\nu}\sum[({}^{\mathrm{RR}}P_{\mu\nu}{}^{(2)} + {}^{\mathrm{RR}}P_{\mu\nu}{}^{(3)}){}^{\mathrm{RR}}H_{\mu\nu}{}^{(0)} - {}^1/_4({}^{\mathrm{RR}}P_{\mu\nu}{}^{(1)}{}^{\mathrm{RR}}P_{\mu\nu}{}^{(1)} + 2{}^{\mathrm{RR}}P_{\mu\nu}{}^{(2)}{}^{\mathrm{RR}}P_{\mu\nu}{}^{(0)} + 2{}^{\mathrm{RR}}P_{\mu\nu}{}^{(1)}{}^{\mathrm{RR}}P_{\mu\nu}{}^{(2)} + 2{}^{\mathrm{RR}}P_{\mu\nu}{}^{(0)}{}^{\mathrm{RR}}P_{\mu\nu}{}^{(3)})\gamma_{\alpha\beta}{}^{\mathrm{RR}}] \quad (17)$$

This term gives the intramolecular interaction for the polarized charge distributions of the lattice molecules. As might be expected from the variational theorem, the first-order charge in the intramolecular energy is zero, so all terms in eq 17 are of second or higher order.

Expressions 13–16 suggest that, at the present level of approximation, the crystal energy can be represented by a lattice sum of terms that involve no more than two molecules at a time, *i.e.*, sums of pair potentials. However, the crystal density submatrices included in these equations are obtained as the iterative solutions to the SCF crystal perturbation equations and are, therefore, complicated implicit functions of the Coulomb lattice sums as well as other interaction parameters. Thus, all of these crystal matrices are implicit functions of all of the interactions within the lattice, and the deceptively simple energy expressions that depend on them, in fact, include complicated multicenter interactions.

Computational Details

The oxygen atoms of ice-1h form a tetramolecular hexagonal sublattice of symmetry *P*6$_3$/*mmc*.[17] The four atoms in the unit cell occupy the special positions (4f)[17] with coordinates $\pm({}^1/_3, {}^2/_3, u; {}^2/_3, {}^1/_3, u + {}^1/_2)$, where u is the c coordinate of the first or reference oxygen atom, 1. This quantity is in principle completely arbitrary since no special value is required for the space-group symmetry *P*6$_3$/*mmc*. However, for a regular tetrahedral sublattice of oxygen atoms, certain restrictions must be placed on u and, in addition, on the unit cell dimensions a_0, b_0 $(=a_0)$, and c_0. The equality of all four nearest neighbor O–O distances requires

$$u = {}^1/_8 - (a_0/c_0)^2/6 \quad (18)$$

For all angles to be tetrahedral

$$u = {}^1/_{16} \quad (19)$$

Thus, for a tetrahedral lattice, both conditions must hold and, therefore

$$a_0 = \sqrt{0.375}c_0 \quad (20)$$

The observed ice-1h crystal structure data conform rather closely to these requirements, although there is a small, yet significant, deviation that appears to persist even at low temperatures.[8]

For the purpose of the present calculations, we smooth out the small observed asymmetries by setting $u = {}^1/_{16}$ and calculating a_0, and hence b_0, from c_0 using eq 20.

The position of the protons in the ice-1h lattice is not well established, but it is clear that the water molecules are intact and randomly oriented. Neutron diffraction[9] and broad line nmr[10] experiments suggest the HOH bond angle of a water molecule in ice-1h is increased, from the gas-phase value of 104°, to a value of about 109° so that each proton lies approximately on a nearest neighbor O···O direction. There is also evidence[10] for a slight increase in OH bond length for H_2O in ice-1h.

As the present theory specifically neglects thermal effects, it is necessary to carry through the calculations on some hypothetical ice-1h structure in which the protons are frozen to give an ordered arrangement. The proton assignment chosen for this purpose is shown in Figure 1. It can be seen from this figure that the inclusion of the protons in the frozen structure in this manner lowers the overall symmetry of the crystal, so that the four unit cell molecules are no longer crystallographically equivalent as required by the present version of the theory.[14] The application of the theory under these circumstances assumes a single average charge distribution for all four molecules in the unit cell. The difference in the charge densities of the two protons of molecule 1 (Table III) probably gives some measure of the error incurred.

The dimensions of the water molecules in the lattice were determined by calculating the crystal energy, W_{crystal}, as a function of θ and r_{OH} shown in Figure 2.

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[16] J. Larkindale and D. P. Santry, to be submitted for publication.

[17] R. W. G. Wykoff, "Crystal Structures," Vol. 1, Wiley, New York, N. Y., 1963.

Table I. List of Molecules and Contributions, $W_{AB}^{(2)}$ and $W_{AB}^{(3)}$, Explicitly Included in the Calculation of $W_{\text{intermolecular}}$

Molecule	Unit cell, in units of a_0, b_0, and c_0	Unit cell site[a]	Shortest intermolecular interatomic distance, Å	Second- and third-order contributions to $W_{\text{intermolecular}}$, kcal/mol $\lvert W_{AB}^{(2)}\rvert$	$\lvert W_{AB}^{(3)}\rvert$
1	000	I			
2	100	I	3.7	6.8×10^{-3}	8.8×10^{-5}
3	$\bar{1}00$	I	3.7	6.8×10^{-3}	8.8×10^{-5}
4	110	I	3.7	6.8×10^{-3}	8.8×10^{-5}
5	$\bar{1}10$	I	4.6	7.7×10^{-4}	6.3×10^{-6}
6	$1\bar{1}0$	I	4.6	7.7×10^{-4}	6.3×10^{-6}
7	$\overline{11}0$	I	3.7	6.8×10^{-3}	8.8×10^{-5}
8	000	II	3.7	6.8×10^{-3}	6.9×10^{-5}
9	010	II	3.7	6.8×10^{-3}	6.9×10^{-5}
10	$\bar{1}00$	II	3.7	1.1×10^{-1}	7.0×10^{-4}
11	$10\bar{1}$	II	7.3	$<10^{-6}$	$<10^{-6}$
12	$\bar{1}0\bar{1}$	II	3.7	1.1×10^{-1}	7.0×10^{-4}
13	$00\bar{1}$	II	3.7	6.8×10^{-3}	6.9×10^{-5}
14	000	III	1.7	1.6	2.6×10^{-1}
15	100	III	4.8	6.3×10^{-5}	$<10^{-6}$
16	$\bar{1}00$	III	4.8	8.9×10^{-4}	6.3×10^{-6}
17	110	III	4.8	6.3×10^{-5}	$<10^{-6}$
18	010	III	4.8	6.3×10^{-4}	$<10^{-6}$
19	010	III	4.8	6.3×10^{-4}	$<10^{-6}$
20	$\overline{11}0$	III	4.8	8.9×10^{-4}	6.3×10^{-6}
21	$00\bar{1}$	III	4.4	1.6×10^{-3}	1.8×10^{-5}
22	$10\bar{1}$	III	6.3	$<10^{-6}$	$<10^{-6}$
23	$\bar{1}0\bar{1}$	III	5.6	6.9×10^{-5}	$<10^{-6}$
24	$11\bar{1}$	III	6.3	$<10^{-6}$	$<10^{-6}$
25	$01\bar{1}$	III	5.6	$<10^{-6}$	$<10^{-6}$
26	$0\overline{11}$	III	5.6	6.3×10^{-6}	$<10^{-6}$
27	$\overline{111}$	III	5.6	6.9×10^{-5}	$<10^{-6}$
28	000	IV	1.7	1.6	2.6×10^{-1}
29	010	IV	1.7	1.6	3.4×10^{-1}
30	$\bar{1}00$	IV	1.7	1.6	3.4×10^{-1}

[a] Coordinates, in units of a_0, b_0, and c_0, for sites I, II, III, and IV are $(^1/_3, {}^2/_3, u)$, $(^2/_3, {}^1/_3, u + {}^1/_2)$, $(^1/_3, {}^2/_3, {}^1/_2 - u)$, and $(^2/_3, {}^1/_3, \bar{u})$, respectively.

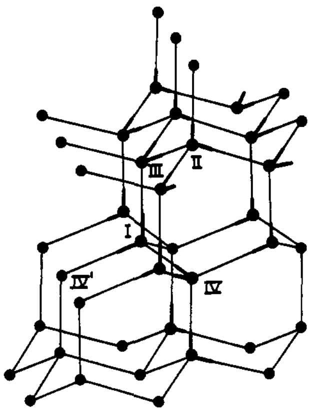

Figure 1. Assumed structure for the ice-1h crystal. The short heavy lines represent the OH bonds of the lattice water molecules, and the Roman numerals refer to the unit cell sites of Table I. Site IV′ corresponds to the oxygen atom so numbered in Figure 2.

Note that throughout these calculations the water molecules were maintained in symmetrical positions relative to the oxygen atoms to which they are hydrogen bonded. This is an unwarranted, but hopefully not serious, assumption since such an arrangement is not required by the local crystal symmetry. Interestingly, the crystal symmetry does not require the two OH bonds to be equal either. However, investigation of these interesting possibilities, along with deviations of u from $^1/_{16}$, must await more detailed calculations based on the more general version of the theory.

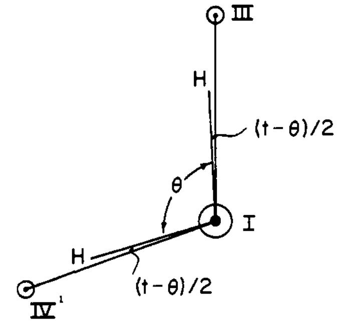

Figure 2. Assumed orientation for the water molecules of the ice-1h lattice. t is the tetrahedral angle.

Lattice Sums

The intramolecular Fock matrices, the electrostatic energy, and the polarization energy all require the calculation of lattice sums of Coulomb integrals, $\Gamma_{\alpha\beta}$. The electrostatic energy requires, in addition, the summation of the nuclear repulsion energy for the lattice. Although these lattice sums are divergent, the elements of the Fock matrices and the electrostatic and polarization are slowly convergent. One reason for this slow convergence is that as the summation is extended into the lattice, away from the reference molecule, the number of molecules at a given distance R increases roughly as R^2. The Coulomb and nuclear repulsion lattice sums used in the present study include all the molecules, save the original molecule, in a block of 7 × 7 × 7 unit cells, or rather more than 1300 mole-

Table II. Perturbation Density Matrix for the Reference Molecule 1 of Figure 1[a]

	1s	1s	2s	$2p_a$	$2p_{b'}$	$2p_c$
1s	−0.03703	0.00166	−0.00064	0.00929	0.00533	−0.02899
1s	0.00166	−0.04410	−0.00284	0.02305	0.01332	−0.00180
2s	−0.00064	−0.00284	−0.00509	−0.02968	−0.01848	0.02169
$2p_a$	0.00929	0.02305	−0.02969	0.03649	0.03605	0.00612
$2p_{b'}$	0.00533	0.01332	−0.01848	0.03605	−0.00525	0.00370
$2p_c$	−0.02899	−0.00180	0.02169	0.00612	0.00370	0.05498

[a] The first proton lies on the *c* axis of the crystal.

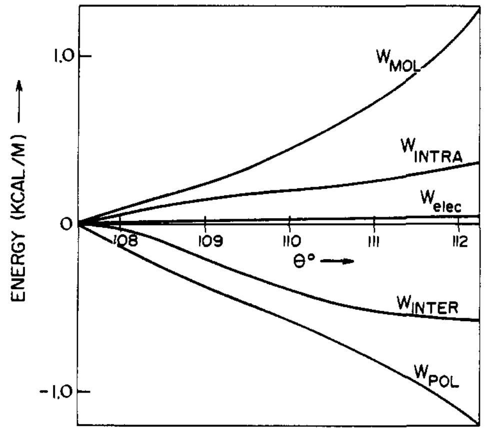

Figure 3. Contributions to the binding energy of the ice-1h crystal as functions of the bond angle of the lattice water molecules. The curves pass through a common value at 107° since all contributions are plotted relative to their values at this angle.

cules. The calculation of these sums was expedited by approximating $\gamma_{\alpha\beta}$ to $1/R_{\alpha\beta}$ when $R_{\alpha\beta}$ was greater than 10 Å. While this number of molecules may be excessive, it was found that limiting the sums to the molecules listed in Table I led to serious error.

The calculation of the intermolecular energy, eq 16, also involves a lattice summation. As each term in this series involves a fairly complicated calculation, it is fortunate that the series is very strongly convergent. That this is so may be judged from the data given in Table I for the first 30 molecules in the ice-1h lattice. It can be seen from these results that the intermolecular interaction is negligible beyond the next nearest neighbors. (The nearest neighbors are molecules 14, 28, 29, and 30; the important next nearest neighbors are molecules 10 and 12 of Table I.)

Molecular Geometry of Water in the Ice-1h Lattice

The calculations reported in this section are based on unit cell dimensions of 4.491752 and 7.335 Å, for a_0 ($=b_0$) and c_0, respectively. The c_0 value corresponds to the experimentally[17] observed value for ice-1h at −130°, and the a_0 value to that required, in conjunction with $u = {}^1/_{16}$, to give a tetrahedral sublattice of oxygen atoms.

The bond length, 1.038 Å, calculated for the water molecules of ice-1h is about 0.01 Å longer than that, 1.03 Å, calculated for an isolated molecule. A term-by-term examination of the crystal energy as a function of r_{OH} showed the most significant changes to be in W_{molecule} and $W_{\text{intermolecular}}$. The changes in these two quantities are opposed and balance out to give a small increase in bond length. Examination of Table I shows that $W_{\text{intermolecular}}$ is largely determined by nearest neighbor interactions, so that the bond length increase may be considered as a nearest neighbor effect. This is confirmed by the calculations of Kollman and Allen[18] which revealed a comparable bond length increase for the water dimer.

The calculated bond angle, 110.5°, for the lattice water molecules, on the other hand, shows a significant increase over the free molecule theoretical value of 104.7°. The reason for this increase may be partially understood from Figure 3, which shows the various terms of eq 10 as functions of θ. This figure shows the intermolecular energy to be minimized, as expected, near the tetrahedral angle, which corresponds to all of the OH bonds pointing directly at their nearest oxygen atom. However, it can also be seen that any decrease in this contribution, resulting from an increase in θ, is more than offset by corresponding increases in $W_{\text{molecular}}$ and $W_{\text{intermolecular}}$. In other words, the direct hydrogen-bonding interaction is not sufficiently strong to distort the water molecule. The dominant force tending to increase the bond angle originates from the polarization energy, which is relatively sensitive to this change in molecular geometry. It is interesting to note that, according to CNDO/2 theory, the hydrogen bonds in ice-1h are slightly bent.

The change in the intramolecular density (sub-) matrix for molecule 1, as represented by the sum for first, second, and third order contributions, is given in Table II. The diagonal elements of this matrix show a transfer of electron density from the hydrogen 1s and oxygen 2s orbitals into the oxygen 2p orbitals.

Calculation of the Unit Cell Dimensions

For the purpose of the calculations reported in this section, the molecular parameters r_{OH} and θ were maintained at their previously calculated values of 1.038 Å and 110.5°, respectively. The *c* unit cell dimension was varied, and a_0 recomputed each time to maintain a perfect tetrahedral lattice. This procedure yielded values of 7.04 and 4.31 Å for c_0 and a_0, respectively. These lengths were largely determined by a balance between the electrostatic and intermolecular energies.

Lattice Binding Energy

The calculated binding energy, −4.9 kcal/molecule, for the ice-1h lattice is rather less than half of the observed value of between −11 and −13 kcal/molecule.[19]

This is not surprising since the two approximations, of a single average charge density for all four unit cell

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(18) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 753 (1970).

(19) D. Eisenberg and W. Kauzman, "The Structure and Properties of Water," Oxford University Press, London, 1969.

Table III. Comparison of Theoretical Data for Lattice and Gas-Phase Water Molecules

	θ	r_{OH}	$Q_H{}^b$	$Q_0{}^a$	$a_0{}^c$	$c_0{}^c$	Stabilization energy,[d] kcal/mol
Crystal	110.5	1.038	0.8279, 0.8208	6.3513	4.32	7.06	−4.5
Isolated	104.7[a]	1.029[a]	0.8584, 0.8584	6.2832			

[a] CNDO/2 theoretical values. [b] Calculated assuming $c_0 = 7.335$, $a_0 = 4.491752$ Å. [c] Experimental values[8] at −186°: $a_0 = 4.4968$, $c_0 = 7.3198$ Å. [d] Experimental value[18] = −11 kcal/mol.

molecules and the symmetrical centering of the molecules in the lattice, both serve to increase the (negative) binding energy.

Summary and Conclusions

In the foregoing sections, we have reported molecular orbital calculation, based on the CNDO/2 method, for the ice-1h crystal. The more interesting results from these calculations are collected in Table III. The agreement between theory and experiment is encouraging and suggests that the CNDO/2 method will prove useful for the theoretical study of hydrogen-bonded systems.

The present calculation also provides some interesting insight into the nature of the hydrogen-bonded interaction within large molecular aggregates. According to the present calculations, the change in the HOH bond angle of water that accompanies crystallization is not due to a nearest neighbor effect as generally supposed, but rather is the result of long-range interaction between the polarized charge densities of the lattice molecules.

The Reactions of Sulfur Atoms. XIV. *Ab Initio* Molecular Orbital Calculations on the Ethylene Episulfide Molecule and the S + C_2H_4 Reaction Path

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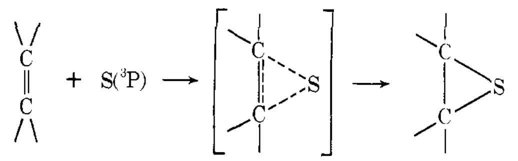
Abstract: A nonempirical SCF molecular orbital study has been made on thiirane and the thiirane-forming addition of sulfur atoms to ethylene. All the lower lying triplet and singlet excited states of thiirane have a ring distorted equilibrium conformation in which the terminal methylene plane is orthogonal to the CCS plane and the considerable energy barrier with respect to rotation of the terminal methylene is responsible for the maintenance of the stereochemical information content of the addition reaction. Since all the vertical excited states lie at higher energies than the sum of the enthalpy change and activation energy of the reaction, a ring distorted triplet state activated complex is implicated which, in the C_2H_4 + $S(^3P)$ system, correlates with the third vertical triplet state of thiirane. The reaction product, the lowest nonvertical $^3\Sigma(12\sigma \rightarrow 13\sigma^*)$ excited state of thiirane, arises *via* the sequence: $C_2H_4(^1A_1) + S(^3P) \rightarrow C_2H_4S[^3B_2(4\pi \rightarrow 14\sigma^*)] \rightarrow C_2H_4S[^3A_2(4\pi \rightarrow 13\sigma^*)] \rightarrow C_2H_4S[^3\Sigma(12\sigma \rightarrow 13\sigma^*)]$. The ultimate fate of the triplet C_2H_4S is collision-induced intersystem crossing to the ground state. The C_2H_4 + $S(^1D_2)$ system correlates with the electronic ground state of thiirane; therefore the addition is a simple concerted process.

The experimental observation that the addition of ground triplet state sulfur atoms to olefins follows a unique stereospecific path[2] may be rationalized by assuming that the product thiirane is formed essentially in its final nuclear configuration *via* a symmetric transition state.[3]



To conserve spin and orbital symmetry the thiirane should be in one of its low lying triplet states. According to Hoffmann and coworkers' extended Hückel MO calculation,[3] this triplet (n,σ^*) thiirane retains CC bonding but is unstable with respect to CS ring opening. The ring-opened intermediate has a computed CCS bond angle of 110° and the plane of the terminal meth-

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[1] (a) Department of Chemistry, University of Alberta; (b) Department of Chemistry, University of Toronto.

[2] H. E. Gunning and O. P. Strausz, in *Advan. Photochem.*, 4, 143 (1966); E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7164 (1968).

[3] (a) E. Leppin and K. Gollnick, *Tetrahedron Lett.*, 3819 (1969); (b) R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, **19**, 113 (1970).