Hydrogen Bonds Involving Sulfur.
I. The Hydrogen Sulfide Dimer

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Abstract: A theoretical investigation of S···H—S type hydrogen bonds in the hydrogen sulfide dimer is presented. Calculations utilizing both *ab initio* and CNDO techniques on a variety of possible dimer configurations are reported, and the results are compared. CNDO results are found to agree very poorly with *ab initio* predictions. The linear form of the dimer is found to be most stable in this system, and the properties of the hydrogen bond in this dimer configuration are discussed.

Until comparatively recently, weak hydrogen bonds involving sulfur as both donor and acceptor were unknown and thought not to exist.[1] The elucidation of the crystal structure of H_2S by Harada and Kitamura[2] in 1964 gave strong indications that such S···H—S hydrogen bonds do indeed exist, and since then a number of workers have measured properties of various species which associate *via* S···H—S intermolecular hydrogen bonds.[3–7] Most of the recent work, however, is concerned with ir spectroscopy and determination of association constants, and very little is known about the structure of such hydrogen-bonded species.

Consequently, the present work was undertaken in order to shed some light on the problem of the structure of the S···H—S hydrogen bond, and to look at some of the physical properties of a system containing such a bond.

As sulfur is already a reasonably large atom, it was necessary to choose a system with small substituents, so that the desired calculations could be carried out with reasonable expenditure of computer time. With this in mind, the hydrogen sulfide dimer was chosen as a model system, since it is both simple and chemically plausible.

In a recent paper, Kollman and Allen[8] show that the semiempirical CNDO/2 (CNDO = complete neglect of differential overlap) method gives quite reasonable results when applied to hydrogen-bonded dimers of first row hydrides. Thus it was felt that it would be useful to carry out CNDO as well as *ab initio* calculations on this system in order to see if the CNDO method could be extended to second-row hydrides, and to provide further needed calibration of the CNDO method for molecules containing second-row atoms.

Calculational Methods

The two methods employed in this work are both described elsewhere, and need be only briefly mentioned here.

The semiempirical CNDO scheme[9] considers explicitly only the valence electrons of the considered system and employs a number of approximations to simplify the matrix elements of the Roothaan equations. These approximations may be summarized in the following way.[9] (1) The overlap matrix for the system is considered to be the unit matrix, and overlap integrals are neglected for normalization of the molecular orbitals. (2) Differential overlap is neglected in all two-electron integrals. (3) Coulomb integrals not zero by assumption 2 are given a single value for each atom pair. (4) Monatomic differential overlap is neglected for interaction integrals involving cores of other atoms. (5) Off-diagonal core matrix elements are taken to be proportional to the appropriate overlap integrals. When these assumptions are made, the parameters to be used must then be chosen, and in this case the CNDO/2 parameters of Santry and Segal were used.[10]

For the *ab initio* calculations, a slightly modified version of program IBMOL, version 4,[11] was used. In this case, a minimal gaussian basis set of the type (12s, 9p) contracted to (3s, 2p) was used for each sulfur atom,[12] and a (3s) basis contracted to (1s) was used for each hydrogen atom[13]. These basis sets were used for all calculations, and gave energies of -0.496979 au for hydrogen and -396.97309 au for sulfur. (All results are reported in atomic units (1 au = 627.709 kcal/mol) unless otherwise indicated.) These results may be compared to a value of -0.499891 au for hydrogen, obtained with a (8s, 2p) contracted to (4s, 2p)[14] basis set, and to -396.62761 au for sulfur, obtained from an

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(1) R. Benesch, R. E. Benesch, P. D. Boyer, I. M. Klotz, W. R. Middlebrook, A. G. Szent-Gyorgyi, and D. R. Schwartz, Ed., "Sulfur in Proteins," Academic Press, New York, N. Y., 1959, p 440 ff.

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(4) D. H. McDaniel and W. G. Evans, *Inorg. Chem.*, **5**, 2180 (1966).

(5) S. H. Marcus and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3719 (1966).

(6) J. G. David and H. E. Hallan, *Spectrochim. Acta*, **21**, 841 (1965).

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

(9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. References to the original work describing the CNDO approximation may be found in this book.

(10) Program No. 141 from the Quantum Chemistry Program Exchange, Bloomington, Ind.

(11) IBMOL was provided by Dr. Enrico Clementi of IBM Research Laboratories, San Jose, Calif. For a more complete description, see E. Clementi and D. R. Davis, *J. Comput. Phys.*, **1**, 223 (1966).

(12) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).

(13) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(14) A. Rauk, L. C. Allen, and E. Clementi, *ibid.*, **52**, 4133 (1970).

Table I. Calculated and Experimental Properties of H_2S

	Calcd geometry		Exptl geometry		
	Ab initio	CNDO	*Ab initio*	CNDO	Exptl
R_{HS}, Å	1.478	1.435			1.336[a]
HSH angle, deg	94.0	91.8			92.2[a]
E_{tot}, au	−398.07685	−12.35281	−398.05621	−12.33777	−400.81[a]
IP, eV	11.33	13.39	11.73	13.36	10.44[a]
$\|\mu\|$, D	1.523	0.111	1.558	0.043	1.02[b]
Net atomic charges					
S	−0.156332	+0.0058	−0.158419	−0.0047	
H	+0.078163	−0.0029	+0.079214	+0.0024	
S–H overlap population	0.325749		0.345452		
$k_\delta/l^2 \times 10^5$ dyn/cm	0.377	0.300			0.45[c]
$k_{str} \times 10^5$ dyn/cm	3.814	7.265			4.14

[a] As reported by P. Moccia, *J. Chem. Phys.*, **40**, 2186 (1964). [b] See C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955. [c] See G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945.

Table II. Comparison with Other Representative Calculations

	Rauk and Csizmadia[a]	Moccia[b]	Hake and Banyard[c]	Santry and Segal[d]
R_{HS}, Å		1.328	1.328	1.333
HSH angle, deg		89.4	89.4	93.3
E_{tot}, au	−381.03894	−397.58906	−396.3574	
IP, eV	3.25	9.540		
$\|\mu\|$, D	1.75	1.726		0.69
Net atomic charges				
S	−0.9110			
H	+0.4555			
$k_\delta/l^2 \times 10^5$ dyn/cm				0.41
$k_{str} \times 10^5$ dyn/cm				
S–H overlap population	0.4853			

[a] Gaussian basis (9s, 2p, 1d) on S, (1s) on H, experimental geometry: A. Rauk and I. G. Csizmadia, *Can. J. Chem.*, **46**, 1205 (1968). [b] One-center expansion SCF MO's; see ref *a*, Table I. [c] United atom, R_{HS} and ∠HSH preselected: R. B. Hake and K. E. Banyard, *J. Chem. Phys.*, **43**, 657 (1965). [d] CNDO, R_{HS} fixed: D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

Table III. Orbital Energies of Occupied Molecular Orbitals of H_2S in the Configuration $(a_1)^{10}(b_1)^4(b_2)^4$

	Calcd geometry		Exptl geometry[c]	
Orbital	*Ab initio*[a]	CNDO[b]	*Ab initio*	CNDO
a_1	−91.656140	Core	−91.680260	Core
	−8.7455478	Core	−8.7681930	Core
	−6.6033563	Core	−6.6266307	Core
	−0.9539634	−0.9751	−1.0042073	−0.9964
	−0.4926218	−0.5794	−0.5120799	−0.5882
b_1	−6.6012492	Core	−6.6237290	Core
	−0.4163761	−0.4921	−0.4309209	−0.4908
b_2	−6.6053259	Core	−6.6290477	Core
	−0.5673266	−0.6173	−0.6103974	−0.6367
Total energy	−398.07685	−12.35281	−398.05621	−12.33777

[a] R = 1.478 Å, HSH angle = 94.0°. [b] R = 1.435 Å, HSH angle = 91.8°. [c] R = 1.336 Å, HSH angle = 92.2°.

optimized single-ζ STO basis,[15] or −397.49776 using the (12s, 9p) basis set of this work, but uncontracted.[12]

Results

H_2S Monomer. The isolated H_2S molecule was the subject of initial calculations using both *ab initio* and CNDO methods, in order to compare the two methods against each other and against experimental and calculated results given in the literature. In each case, a thorough geometry search was carried out, varying both the HSH angle and the S–H bond distance. At the minimum-energy configurations, a Mulliken population analysis was carried out, and the dipole moment was calculated. Symmetric stretching and bending potential curves were developed, and the force constants were calculated. The results of these calculations, along with the experimental values, values calculated at the experimental geometry, and some representative other calculations from the literature are given in Tables I and II.

(15) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

Table IV. Minimum-Energy Configuration, Total Energy, and Hydrogen Bond Energy for $(H_2S)_2$

	R, Å	α	β	γ	E_{tot}	ΔE, kcal/mol
		(a) Linear				
CNDO						
H_2S exptl geometry	3.00		0	0	−24.70990	21.6[a]
H_2S calcd geometry	3.10		0	0	−24.74012	21.6[a]
Ab initio						
H_2S calcd geometry	4.500	0	0	0	−796.15483	0.709
		(b) Bifurcated				
CNDO	2.30				−24.82923	78.4
Ab initio	4.425				−796.15477	0.672
		(c) Cyclic	θ			
CNDO	2.15		42.5		−24.94315	149.1
Ab initio	4.225		57		−796.15428	0.364

[a] For α = 0.

Table III gives the orbital energies for H_2S at the calculated equilibrium geometry and experimental geometry for both methods.

It should be noted that the CNDO calculation gives slightly better predictions of molecular geometry than does the *ab initio* calculation. All properties other than geometry, however, are in much better agreement with experiment when calculated by the *ab initio* method.

H_2S Dimers. Calculations were carried out for three general configurations of the H_2S dimer. The general form of these is shown in Figure 1. In all calculations, the configuration of the monomeric H_2S units was fixed at either the experimental or calculated geometry.

In the linear structure, one monomer was fixed at the origin, and the other monomer was moved with respect to it. Variations were carried out for the S–S distance, R; the yz plane bend, α; the xz plane bend, β; and the rotation, γ The minimum energy configuration for each method of calculation and the corresponding hydrogen bond energy, ΔE, are presented in Table IVa.

It is clear from Table IVa that the results of the CNDO calculation agree very poorly with those obtained from the *ab initio* calculation. In addition, it was found that increasing α led to rapidly decreasing energies for $\alpha < 20°$ using CNDO, while the same variation in α led to increased energies in the *ab initio* calculation.

The discrepancy in R and ΔE for the minimum-energy configuration determined by the two types of calculation is great, and it appears that CNDO underestimates R and greatly overestimates ΔE. If S···H—S type hydrogen bonds do exist, they would be expected to be quite weak, at least in the case of neutral species such as this. Such hydrogen bond energies have been estimated to be considerably less than the hydrogen bond energies of ~5 kcal/mol in water.[16] The CNDO predicted S–S internuclear distance is equally disappointing. The measured S–S distance in solid H_2S is 3.86 Å,[2] and generally one would expect the internuclear distance in the isolated dimer to be somewhat greater than this. One can also obtain an approximation to the S–S distance by plotting the van der Waals radius of a number of atoms X, forming hydrogen bonds of the type X···H—X, against an average observed X–X distance for that type of bond.

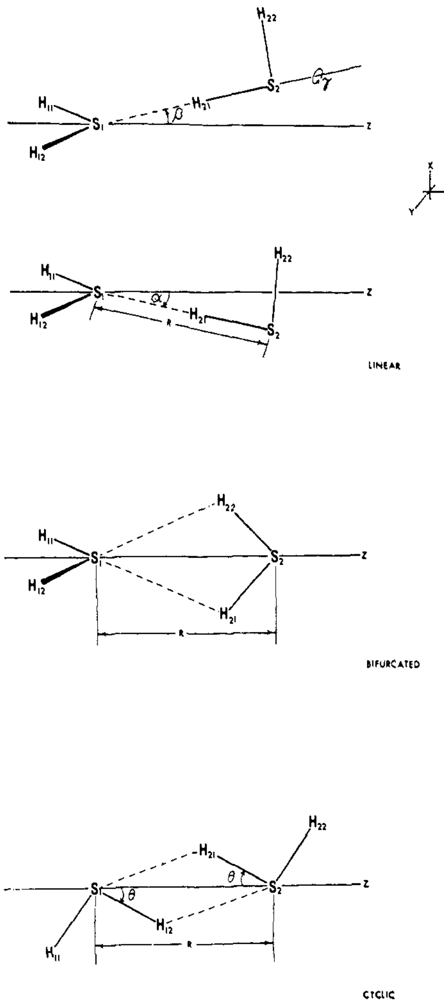

Figure 1. Configurations of the H_2S dimer.

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(16) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

Table V. Mulliken Population Analysis and Dipole Moment for H_2S Dimers

	Ab initio			CNDO		
Atom	Linear $R = 4.500$	Bifurcated $R = 4.425$	Cyclic $R = 4.225$	Linear $R = 3.10$	Bifurcated $R = 2.30$	Cyclic $R = 2.15$
H_{11}	0.915	0.916	0.920	1.026	1.051	1.070
H_{12}	0.915	0.916	0.915	1.026	1.051	0.873
S_1	16.167	16.167	16.164	6.039	6.121	6.057
S_2	16.168	16.168	16.164	5.971	6.034	6.057
H_{21}	0.908	0.916	0.915	0.949	0.871	0.873
H_{22}	0.926	0.916	0.920	0.990	0.871	1.070
$\lvert\mu\rvert$, D	3.00	0.547	0.008	1.748	3.241	0.000

If this is done, an S–S distance of 4.7–4.9 Å is obtained.[17]

In both types of calculation, movement of H_{21} off the S–S line of centers leads to an increase in energy. When H_{21} was moved along the S–S line of centers to develop the potential, a single well with a shoulder was observed. The quadratic force constant from the *ab initio* calculation for the H–S stretch in the hydrogen bond was found to be 3.701×10^5 dyn/cm.

In the case of the bifurcated dimer, the S–S line of centers bifurcates the HSH angle in both monomers, which were kept in orthogonal planes. Only the S–S distance was varied in this case, and the H_2S monomers were kept at their calculated geometries. The results of this calculation are presented in Table IVb.

For the cyclic dimer, the monomers were kept coplanar. The S–S distance and angle, θ, between the S–H bond and S–S line of centers, were varied. θ was restricted to be the same for both monomers, and calculated monomer geometries were used. The results for these calculations are presented in Table IVc.

The Mulliken population analysis and dipole moment for the three minimum energy dimer structures are presented in Table V.

From Tables IV and V it is apparent that the CNDO calculation gives very poor results. The equilibrium S–S bond distances are much too small to be realistic, while the hydrogen bond energies are much too large. The *ab initio* calculation, on the other hand, gives both S–S distances and bond energies which seem quite reasonable. The CNDO population analysis is also in poor agreement with the *ab initio* result, generally giving the monovalent hydrogen atoms a net negative charge at the expense of the divalent hydrogens. Although it is not easy to show that this is not the case, it is an unexpected result and does not agree with *ab initio* result which gives all hydrogen atoms a net positive charge.

Discussion

Since the idea that 3d orbitals might be important in the bonding of molecules involving second-row atoms was first put forward by Pauling,[18] there has been a variety of calculations which have attempted to assess the importance d orbitals in chemical bonding. As hydrogen sulfide is a chemically well-characterized species and is small enough to be treated by rigorous theoretical techniques, it has been the subject of many of these investigations.[19–23] In these studies, it has been found that certain properties, such as dipole moment, are very much improved[23b,f] when 3d orbitals are added to the basis set, while other properties, such as molecular geometry, are quite insensitive to it.[20,23b]

Before proceeding to the question of the importance of d orbitals in H_2S calculations, it should be pointed out that one must be wary of making general assertions concerning d-orbital importance in calculations involving second-row atoms. In the case of restricted Hartree–Fock calculations on molecular ground states, what one is attempting to do by adding 3d orbitals to the basis set is to improve the LCAO–MO representation of an occupied MO of the molecule. That is, one is attempting to improve the approximation to a complete basis by addition of 3d orbitals. The MO's in question will belong to one of the irreducible representations of the point group of the molecule. The addition of any set of functions such that the functions themselves or linear combinations of them transform according to the irreducible representation of the MO in question would be expected to contribute to the MO and improve the calculation. In this sense, d functions are in no way unique.

One would expect, then, that inclusion of d orbitals would be particularly important when there are occupied MO's of the system belonging to irreducible representations not spanned by s- and p-type functions. It should be noted that calculations of properties involving excited states will need d functions, as there will be unoccupied MO's with d-function symmetry which should be included in the calculation.

Rauk and Csizmadia[20] have carried out a detailed analysis of the problem of d-orbital participation in H_2S, based on a gaussian orbital calculation. Using

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[17] (a) van der Waals radii from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260; (b) X—X distances in X···H—X from G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, pp 282, 289, and 292.

[18] L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931).

[19] R. Moccia, *J. Chem. Phys.*, **40**, 2186 (1964).

[20] A. Rauk and I. G. Csizmadia, *Can. J. Chem.*, **46**, 1205 (1968).

[21] R. B. Hake and K. E. Banyard, *J. Chem. Phys.*, **43**, 657 (1965).

[22] D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

[23] Some representative calculations on H_2S: (a) I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **5**, 384 (1970); (b) I. H. Hillier and V. R. Saunders, *ibid.*, **4**, 163 (1969); (c) K. E. Banyard and R. B. Hake, *J. Chem. Phys.*, **41**, 3221 (1964); (d) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966); (e) F. P. Boer and W. N. Lipscomb, *ibid.*, **50**, 989 (1969); (f) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199 (1970).

the Boys[24] definition of nonnormalized gaussian functions

$$\eta = X^{a_1} Y^{a_2} Z^{a_3} e^{-\alpha r^2} \tag{1}$$

one obtains ten functions of s, p, and d type

$$\begin{aligned} &\text{one s function:} \quad a_1 + a_2 + a_3 = 0 \\ &\text{three p functions:} \quad a_1 + a_2 + a_3 = 1 \\ &\text{six d functions:} \quad a_1 + a_2 + a_3 = 2 \end{aligned} \tag{2}$$

Linear combinations of the X^2, Y^2, and Z^2 functions give rise to a spherically symmetric, s-type function

$$\begin{aligned} \eta_s &= (X^2 + Y^2 + Z^2)e^{-\alpha r^2} \\ &= r^2 e^{-\alpha r^2} \end{aligned} \tag{3}$$

plus two others which are the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ AO's.

Using the above Boys-type gaussian functions (1), Rauk and Csizmadia carried out an SCF-LCAO-MO calculation on H_2S. Since the H_2S molecule is not spherically symmetric, the coefficients of X^2, Y^2, and Z^2 in the a_1 MO's (the only ones where they contribute) are not identical, but are close enough to each other so that they may be regarded as forming a distorted s-type function of the type η_s. In the high exponent case ($\alpha = 5.42$) the X^2, Y^2, and Z^2 d functions mixed primarily with the low-lying $1a_1$ and $2a_1$ inner-shell orbitals of sulfur.

The XZ and YZ orbitals, which contribute to MO's of b_1 and b_2 symmetry, respectively, have negligible coefficients. The XY orbital has a_2 symmetry, and does not contribute to an occupied MO.

Thus, from the results of this analysis, Rauk and Csizmadia conclude that the effect of including d-type functions in an H_2S calculation of this sort is to stabilize the system by interaction with low-lying a_1 MO's, and that there is no appreciable participation of d orbitals in the bonding of the system. This leads to the conclusion that in H_2S the bonding may be described by s and p functions only.

Such a conclusion is supported by comparison of various calculations of molecular properties using sp and spd basis sets.

Boer and Lipscomb[23e] have compared calculations using an STO basis with and without d orbitals. Their results show a lowering of 0.0534 au in the total energy when d orbitals are included. The total occupation of d orbitals is 0.147 electron, and the dipole moment improves. This seems to arise from a small charge redistribution, with the hydrogens becoming more positive.

The question of d-orbital participation in bonding in H_2S considered for gaussian basis sets by Roos and Siegbahn,[23f] who obtained results very similar to those of Boer and Lipscomb. Using a (9s, 5p) basis with and without additional d orbitals, they found an energy improvement of 0.022 au on addition of a single d-set to their sp basis. The charge on the hydrogens went from +0.067 to +0.121 and from −0.133 to −0.242 on sulfur when d orbitals were included. The dipole moment improved from 1.477 to 0.881D.

Rauk and Csizmadia[20] studied H_2S geometry with sp and spd basis sets. Keeping the S–H distance fixed at 1.335 Å, they found the minimum energy angle to be 99.9° without d functions and 98.8° with d functions. The barrier to inversion through 180° was 76 kcal/mol and 92.3 kcal/mol when calculated with the sp and spd basis, respectively.

Santry and Segal,[22] using the CNDO formalism, find that the geometry of H_2S can be well predicted without using d orbitals.

A comparison of the importance of d-orbital participation in calculations on H_2S and H_2O was made by Roos and Siegbahn.[23f] In each case they reported results using sp and spd basis sets on the heavy atom. The improvement in total energy was found to be comparable in both cases, but charge redistribution was found to be considerably greater in H_2O than in H_2S. That is, H_2O was found to be much more sensitive to the inclusion of polarization functions in the basis than was H_2S. It is well known, however, that chemically useful calculations on hydrogen-bonded water dimers can be carried out without the use of polarization functions. Kollman and Allen[26] have commented on this point in the case of water dimers. Since the symmetry of H_2O dimers is lower than in the monomers, and since the two molecules are relatively distant from one another compared to intramolecular distances, Kollman and Allen expect that inclusion of d orbitals will not be likely to produce significant changes in the potential surface. Inclusion of d orbitals would be expected to lower monomer energies more than dimer energies, and thus dimerization energies are expected to decrease uniformly. Exactly the same comments would be expected to apply to H_2S and its dimer.

From the foregoing discussion and examples, it appears that addition of d orbitals to the basis set for H_2S will surely improve the quality of the calculation, but will not introduce anything qualitatively new into the description of the bonding of the system. Thus we are justified in considering H_2S and $(H_2S)_2$ from the standpoint of an sp basis.

Comment may be in order concerning the comparison of CNDO and minimal-basis *ab initio* calculations, as they are very different approaches to the problem using very different basis sets. Both of these methods are frequently used in chemically interesting problems, and both have given reasonable results in studies of this kind.[8] As there is still some problem with CNDO parameters for second-row atoms,[25] it is hoped to provide a further *ab initio* calculation against which to compare CNDO results.

The basis sets in these two calculations are quite different, CNDO using 3d orbitals and no inner shell 1s, 2s, or 2p orbitals on sulfur, *ab initio* using an AO basis comprised of all occupied AO's of sulfur, but no 3d functions. The inclusion of the 3d functions is discussed above, where it was concluded that they add no

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(24) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).

(25) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).

Table VI. Differences between Monomer and Dimer Atomic Charges of Water for Various Calculations[a]

	Method	H_{11}	H_{12}	O_1/S_1	H_{21}	O_2/S_2	H_{22}
Morokuma and Pedersen[b]	LCAO–MO–SCF, gaussian basis	+0.0415	+0.0415	−0.019	+0.007	−0.060	−0.011
Kollman and Allen[c]	CNDO	+0.011	+0.011	−0.000	+0.028	−0.034	−0.016
Del Bene and Pople[d]	Gaussian fits to STO's	+0.023	+0.023	−0.002	+0.035	−0.053	−0.026
Kollman and Allen[e]	Contracted gaussian basis	+0.009	+0.009	−0.0116	+0.0275	−0.0219	−0.0120
H_2S, this work	Contracted gaussian basis	+0.006	+0.006	−0.011	+0.013	−0.012	−0.005

[a] Numbering system as shown in Figure 1. [b] K. Morokuma and L. Pedersen, *J. Chem. Phys.*, **48**, 3275 (1968). [c] Reference 8. [d] J. De Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970). [e] Reference 24.

new qualitative features to the calculations. This is supported by Santry's[25] test calculations on molecules involving second-row atoms where he concludes that in the CNDO formalism the addition of 3d orbitals helps to stabilize the molecule rather than help to determine molecular geometry. The same conclusion was reached by Manne[26] who found he could predict the geometry of ClF_3 using only s and p orbitals in an approximate MO scheme.

Thus, the inclusion of d orbitals in the CNDO scheme should not invalidate comparison with *ab initio* minimal-basis calculations.

The CNDO/2 second-row parameters used in this work were those of Santry and Segal[22] rather than the more recent parameters of Santry.[25] These parameters were used since one purpose of this work was to point out that caution was needed when applying CNDO to hydrogen-bonded molecules involving second-row atoms, and many of the CNDO programs currently in use[10] still retain the original[22] parameters. In test calculations using the new parameters, Santry[25] reports better dipoles and charge distributions in H_2S, but slightly poorer bond angles. Thus the new parameterization would not be expected to give significantly better geometries in the case of $(H_2S)_2$. Test calculations on $(H_2S)_2$ have been made to verify this, and although the results were better, the R_{SS} distance was still too small, leading to hydrogen bond energies that were too high by nearly an order of magnitude.

There are a number of calculations presently available in the literature on the water dimer. As this system is analogous the hydrogen sulfide dimer presented here, it is instructive to compare our results to some representative $(H_2O)_2$ calculations. As these methods all use different basis sets and methods, it is difficult to compare absolute values of many of the interesting properties. Consequently, differences between monomer and dimer properties are reported.

All the calculations on the water dimer predict a system with a single hydrogen bond with a linear O–H–O fragment. Variations in the dihedral angle between planes of the two H_2O fragments at the minimum-energy geometry exist, but they are reasonably small. This is the same result that we get for $(H_2S)_2$.

The differences in atomic charges between the monomer and dimer are presented in Table VI for various calculations.

From Table VI it can be seen that the charge shifts on dimer formation are very similar in all the water dime calculations. In H_2S, the shifts are qualitatively the same as those calculated for water, but are slightly smaller in magnitude. All the calculations show an increased population on H_{22}, the hydrogen atom on the proton donor molecule which is not involved in the hydrogen bond, which emphasizes the difference in environment between H_{21} and H_{22}. As Kollman and Allen[24] have pointed out, this precludes the use o dimer wave functions in attempting to draw conclusion about liquid H_2O or H_2S, where one would expect al hydrogen atoms to be hydrogen bonded to neighboring molecules.

A straightforward comparison between $(H_2O)_2$ and $(H_2S)_2$ may be made on the basis of dimerization energies. Table VII presents the dimerization energie for a variety of different calculations.

Table VII. Dimerization Energies for Various H_2O Dimer Calculations

Ref	$-\Delta E$, kcal/mol
Morokuma and Winick[a]	6.55
Del Bene and Pople[b]	6.09
Kollman and Allen[c]	5.94
	5.27
Morokuma and Pedersen[d]	12.6
Rein, Clarke and Harris[e]	<0
$(H_2S)_2$, this work	0.71

[a] K. Morokuma and J. Winick, *J. Chem. Phys.*, **52**, 1301 (1970) [b] Reference *d* of Table VI. [c] References 8 and 24. [d] Reference *b* o Table VI. [e] R. Rein, G. A. Clarke, and F. E. Harris, *J. Mol Struct.*, **2**, 103 (1968).

From Table VII, it can be seen that aside from the early paper of Morokuma and Pedersen, who find too large a dimerization energy, and the iterative extended Hückel calculation of Rein, Clarke, and Harris, who found no binding, the reported calculations all give reasonable agreement with each other and are in quite good agreement with experimentally determined value of 5 kcal/mol[27] for the water dimerization energy. The

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(26) R. Manne, *Theor. Chim. Acta*, **6**, 312 (1966).

(27) J. S. Rowlinson, *Trans. Faraday Soc.*, **47**, 120 (1951); J. D Lambert, *Discuss. Faraday Soc.*, **15**, 226 (1953).

value obtained in this work is nearly an order of magnitude less than this, indicating a much weaker bond in $(H_2S)_2$ than in $(H_2O)_2$.

The force constant for the hydrogen stretching mode in the hydrogen bond is reported by Kollman and Allen[24] to be 6.23×10^5 dyn/cm compared to our value of 3.7×10^5 dyn/cm for $(H_2S)_2$. This is again an indication that the bond is considerably looser in $(H_2S)_2$ than in $(H_2O)_2$. The ratio of $k_{\text{dimer}}/k_{\text{monomer}}$ is 0.97 in each case, indicating the normal shift to lower frequency on hydrogen bond formation.

Thus it appears that there are similarities in terms of charge distribution changes in going from monomers to dimers for H_2O and H_2S. The bond strengths in the two species differ by nearly a factor of 10, however, and this would be expected to lead to differences in chemical behavior.

Conclusions

From the results presented above, it is apparent that the CNDO formalism in its present form is not adequate to describe the properties of weak hydrogen bonds of the type S···H—S. The CNDO predictions of S–S bond length are too small by a factor of 2, more than the usual CNDO underestimate of bond lengths,[8] while bond energies are predicted to be one to two orders of magnitude too high. The CNDO predictions not only disagree with the *ab initio* results, but are in conflict with what little is known experimentally about S···H—S type systems. The choice of experimental or calculated monomer geometries for dimer calculations has a small but not significant effect on the result.

In light of the excellent agreement with experiment and *ab initio* results obtained by Kollman and Allen on similar first-row systems,[8] better results might have been expected from the CNDO calculation. The problem probably lies with the 3d orbital parameterization, as there is a lack of rigorous SCF–LCAO calculations on molecules containing second-row atoms from which to obtain the CNDO parameters. In particular it has been pointed out[22] that the present parameterization leads to 3d Coulomb integrals which are too small, and leads to 3d–s overlap which is too large at large distances.[22] This in turn would be expected to give rise to bond distances which are too short, and thus hydrogen bond energies which are too high.

It seems, then, that one must be most careful about applying CNDO to hydrogen-bonded systems involving S···H—S hydrogen bonds, and probably to all systems with hydrogen bonds involving second-row atoms.

The properties of S···H—S type hydrogen bonds as predicted by the *ab initio* calculation seem quite reasonable and compare quite favorably with the scant available experimental information. All three dimeric structures are stable with respect to two isolated monomers, and all have stabilization energies of somewhat less than 1 kcal/mol. The linear structure is predicted to be most stable. From infrared measurements on associated thiols, Bulanin *et al.*,[3] concluded that, in the cases studied, a linear dimer fit their data better than a cyclic dimer. This agrees with the present result.

It is difficult to evaluate the reliability of the hydrogen bond energy for the linear dimer, as it is well known that Hartree–Fock methods can give poor values of bond energies. As these systems are all closed shell, one might expect that to a zero-order approximation the correlation energy might be conserved on hydrogen bond formation, and consequently some confidence might be placed in the result.

It should also be noted that the argument presented above to the effect that d-orbital contributions to the dimer energies will be small is qualitative, not quantitative. As the differences in hydrogen bond energy of the various dimer configurations are so small, there is thus no guarantee that addition of d orbitals to the basis set would preserve the energy ordering of the configurations.

There are no direct bond energy measurements with which to compare our result of $\Delta E = 0.7$ kcal/mol for the bond energy in the linear dimer. An indirect comparison may be made, however, if one considers work by Spurr and Byers[28] and by Marcus and Miller[5] on solutions of thiols in CCl_4. Both of these pairs of workers measured equilibrium constants for the reaction

$$2\text{RSH} \rightleftarrows (\text{RSH})_2 \qquad (4)$$

where R was a number of simple hydrocarbon groups. Most of the simple compounds gave $K \approx 0.01$–0.02 for temperatures near 25°. Taking $K = 0.015$ at 25° as a typical case, one may calculate the free energy of formation *via* $\Delta G° = -RT \ln K$. It is necessary to approximate the standard entropy of formation in order to calculate enthalpies for dimer formation. This may be done by taking a representative value of -12 eu from the known standard entropy of formation of the analogous alcohols.[29] This leads to an enthalpy of formation of -1.089 kcal/mol. Using $\Delta E° \approx \Delta H°$ since $P\Delta V \approx 0$, one finds an energy of formation of about -1.1 kcal/mol. As one would expect bond energies in thiol dimers to be not very different than those in $(H_2S)_2$, and considering the approximations made to obtain the value, this is quite good agreement and is consistent with predictions that if S···H—S does exist, it will have a small bond energy.[16]

As small variations of the angles α, β, and γ (see Figure 1) near the minimum give quite flat potential functions, it appears that the hydrogen bond in the H_2S linear dimer is quite loose as well as weak.

From the force constant calculation for the symmetric stretch, $k_{\text{monomer}}/k_{\text{dimer}}$ is found to be 1.031. This indicates that the S–H stretching frequency should decrease on hydrogen bond formation. Such a decrease is generally considered to be indicative of hydrogen bond formation[29] and is indeed observed in experimental work on thiols[3,5] and organic complexes such as tetramethylammonium hydrosulfide–H_2S.[4]

It thus appears that CNDO methods are inadequate to describe the weak S···H—S hydrogen bond formed in the linear H_2S dimer, but that a minimal-basis-set *ab initio* calculation will give a quite reasonable description of the bond. Further work is presently underway in an attempt to further characterize hydrogen bonds involving sulfur both of the S···H-S type and mixed dimers of H_2S with first- and second-row hydrides.

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(28) R. A. Spurr and H. F. Byers, *J. Phys. Chem.*, **72**, 425 (1968).
(29) Reference 17b, Appendix B.

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