

CNDO/2 Localized Molecular Orbital Studies on Disulfur Dinitride and Tetrasulfur Dinitride^{†‡}

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Abstract: The localized molecular orbital structures of disulfur dinitride and tetrasulfur dinitride have been investigated using energy localized CNDO/2 molecular orbitals. Disulfur dinitride was found to have six π electrons in three center bonds, four unshared electron pairs, and a σ bond structure. Tetrasulfur dinitride possesses a σ bond structure, limited π bonding over the NSN segment of the molecule, three divalent sulfur atoms having two lone electron pairs each, and an unshared electron pair on each nitrogen atom.

I. Introduction

The large number of binary sulfur–nitrogen molecules and ions offers a fruitful area for theoretical chemistry. For many species, e.g., S_4N_4 , S_4N_2 , S_2N_2 , and $S_5N_5^+$, a large number of classical valence structures¹ can be written and the “real” structure is difficult to select. Developments in molecular orbital theory concerned with localized molecular orbitals suggest that one might obtain some insight into the electronic structures of this class of molecules.

Tetrasulfur tetranitride, S_4N_4 , is well understood from both a bonding and structural point of view, owing to numerous theoretical² and experimental³ studies. The geometrical structure is from careful x-ray diffraction experiments,⁴ while the electronic structure has been inferred primarily from the localized molecular orbital studies of Gopinathan and Whitehead,⁵ and the ¹⁴N chemical shift studies of Mason.

Disulfur dinitride, S_2N_2 , and tetrasulfur dinitride, S_4N_2 , have had some attention given to their geometrical structures^{6–10} but little to their electronic structures.¹¹ CNDO/2 type molecular orbital calculations and energy localized molecular orbitals are presented below in an attempt to elucidate their electronic structures.

II. Calculations

CNDO/2 molecular orbital calculations gave canonical orbitals for the molecules.¹² Since our interest is in the density matrix and molecular orbitals, and not energies, the CNDO/2 parametrization is adequate. The disulfur dinitride (D_{2h}) calculations were for the molecule in YZ plane with the Z axis passing through the nitrogen atoms (Figure 1). The coordinate system for S_4N_2 placed the molecule in the YZ plane with the origin at the midpoint of a line through the two nitrogens atoms and the Z axis through sulfur atoms one and four (Figure 2).

The localized molecular orbitals have been calculated from the CNDO/2 canonical molecular orbitals using the energy localization method of Edmiston and Ruedenberg,¹³ as applied to CNDO wave functions by Trindle and Sinanoglu.¹⁴

A convergence criteria requiring two successive iterations to produce no more than a 10^{-5} change in the sum of the self-repulsion energies was used. For S_2N_2 a second-order curvature analysis^{15,16} was performed; all eigenvalues of the derivative matrix were negative, assuring that a true maximum had been obtained for the sum of the self-repulsion energies. Disulfur dinitride converged after six iterations and required about 3 h of computer time (Burroughs 5700). Tetrasulfur

dinitride converged in nine iterations and required about 40 h. Both calculations required considerably more computer time than localization on the basis of the Boys criteria.¹⁶

Results for Disulfur Dinitride, S_2N_2 . The structure of S_2N_2 was studied by infrared spectra by Warn and Chapman⁷ and later Bragin and Evans.⁸ Vibrational analysis led to the assignment of five frequencies (three IR and two Raman) and to a postulated cyclic, planar, rhombic structure of alternating sulfur and nitrogen atoms. Accurate bond angles and bond lengths could not be determined. Recently the crystal structure of S_2N_2 from x-ray diffraction¹⁰ led to a square planar structure with a single sulfur–nitrogen distance of 1.65 Å (Figure 1). Previous molecular orbital studies in this laboratory supported a structure having a single sulfur–nitrogen distance (1.71 Å), a SNS angle of 92°, and a NSN angle of 88°, respectively.¹¹ The experimental and theoretical studies agree within the limitations of the CNDO/2 approximation.¹⁷ The orbital charges and gross atomic charges are shown in Table I. A molecular orbital energy diagram is given in Figure 2. Table II lists the localized molecular orbitals for disulfur dinitride. Listed are the atomic orbital coefficients for the localized molecular orbitals, together with the percentage localization. The latter is determined by associating the localized orbital with a bond or atom in the molecule and truncating it so as to include only contributions from the atomic orbitals of the atom or atoms included in the pair or bond, respectively. The coefficients of this truncated localized molecular orbital, C_{TLMO}^i , when squared do not sum to unity. The percentage localization is defined as

$$\% \text{ localization} = \sum_i (C_{TLMO}^i)^2 \times 100$$

The 11 MOs are transformed into a set of four N–S σ bonding type orbitals, one lone electron pair orbital on each sulfur atom, one lone pair orbital on each nitrogen atom, two π -type orbitals which span three atomic centers, S–N–S, and a S–S non-bonding orbital. All orbitals calculated are highly localized with the three-center π -type bond orbital being the least localized, 97.88%. The d-type atomic orbitals for the sulfur atom were included in the calculation but are omitted from Table II because they enter the localized orbitals with very small coefficients.

The d orbitals make their largest contribution to the π -type orbitals where the coefficient of the d_{xz} orbital is 0.1059. Among the σ type orbitals and the lone pair orbitals the maximum neglected coefficient is 0.06684. The small orbital charges for the d orbitals in Table I are a reflection of their contribution to the charge density. The d orbitals have a negligible role in the development of the form of the localized molecular orbitals.

The four nitrogen–sulfur σ bonding orbitals are from one

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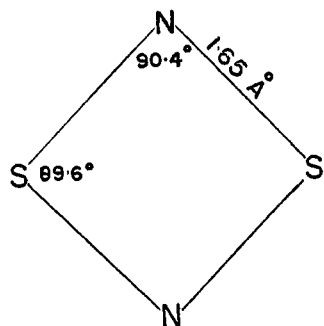


Figure 1. The structure of disulfur dinitride (ref 10).

Table I. CNDO Population Analysis for Disulfur Dinitride

Orbital Charges	
N	S
2s 1.6916	3s 1.7398
2p _x 1.4264	3p _x 1.5144
2p _y 0.9198	3p _y 1.3136
2p _z 1.1698	3p _z 1.1018
	3d _{z²} 0.0296
	3d _{xz} 0.0449
	3d _{yz} 0.0221
	3d _{x²-y²} 0.0119
	3d _{xy} 0.0144
Atomic Charges	
(S) = +0.2075	
(N) = -0.2075	

nitrogen atom and *one* of the sulfur atoms, and account for 99.17% of the localized molecular orbital. The four orbitals taken together imply the presence of four N-S single bonds. The population analysis indicated the following orbital charges; N-2s, 1.6916; N-2p_y, 0.9198; N-2p_z, 1.1698; S-3s, 1.7398; S-3p_y, 1.3136; S-3p_z, 1.1018.

Two types of lone pair orbitals were obtained, one for the nitrogen atoms and one for the sulfur atoms. These orbitals are highly localized—99.15 and 99.78%, respectively.

Three π -type localized molecular orbitals were obtained. Two of the LMOs contained large positive contributions from the out of plane p_x orbitals of nitrogen and the adjacent sulfur atoms and a small negative contribution from the p_x orbital of the remaining nitrogen atom. The largest contribution is from the p_x nitrogen orbital. The orbital is nodeless over three centers. These orbitals each are of the type $\pi|3$ as defined by England, Salmon, and Ruedenberg.¹⁸ The remaining out of plane type LMO is antibonding and involves primarily the out of plane p_x orbitals of the two sulfur atoms combined with opposite signs (a small contribution from the d_{xy} orbitals is also present). Together they may be interpreted as giving rise to a 6 π electron delocalized system. An analogy can be drawn with the cyclobutadienyl dinegative anion.¹⁹ A set of three localized orbitals can be generated from the π orbitals of C₄H₂²⁻ which are virtually identical with the localized orbitals calculated herein.²⁰ The π -type MOs coming from the CNDO/2 calculation are effectively those orbitals which would be obtained in a Hückel-type treatment.

Jolly¹ suggested that the disulfur dinitride molecule would possess 6 π type electrons, be planar, and satisfy the 4n + 2 Hückel rule.²¹ The LMO analysis is consistent with this model. Disulfur dinitride has been recently studied by the X α method²² and also by ab initio techniques.²³ The later studies show that the CNDO/2 tends to lower the energy of the π -type orbitals below several of the σ orbitals. The ab initio studies (double ζ basis set—full optimization) led to a square planar structure (d_{N-S} = 1.62 Å) which was in agreement with experiment. The d-type orbitals on sulfur were critical to the prediction of the correct geometry. The CNDO/2 method does not yield a

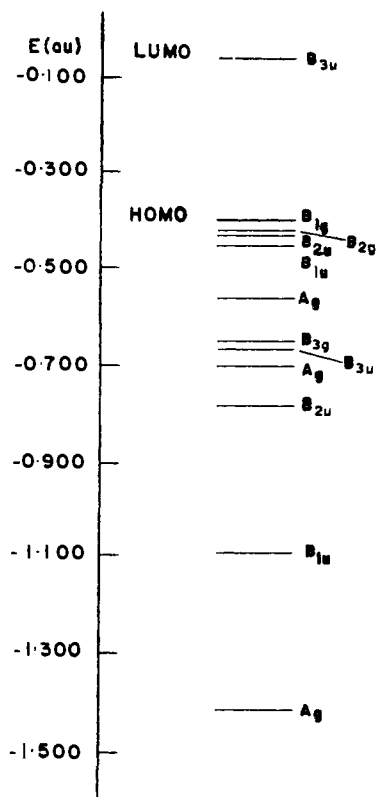


Figure 2. Orbital energy diagrams for N₂S₂.

Table II. Localized Orbitals for S₂N₂

LMO type	Atomic orbital coefficients	% localization ^a
4 N-S σ bonds	N _{2s} -0.2426	99.17
	N _{2p_y} -0.4792	
	N _{2p_z} 0.3980	
	S _{3s} -0.2702	
	S _{3p_y} 0.4369	
	S _{3p_z} -0.5248	
	and the same for N and S orbitals	
2-Sulfur lone pair	S _{3s} 0.8504	99.78
	S _{3p_y} \pm 0.5238	
2-Nitrogen lone pair	N _{2s} -0.8532	99.55
	N _{2p_z} \pm 0.5173	
2-Three center π	S _{3p_x} 0.3595	97.88
	S _{3p_x} 0.3595	
	N _{2p_x} 0.8319	
	N _{2p_x} -0.1454	
Sulfur-sulfur nonbonding	S _{3p_x} 0.7061	100.00
	d _{xy} 0.0369	
	S _{3p_x} -0.7061	
	d _{xy} 0.0369	

^a Defined in text.

structure which is perfectly in agreement with experiment but rather one in which the N-S bond length is elongated and the bonds angles are slightly distorted from 90°. The d-type orbitals seem to play a major role in structure determination in ab initio calculations but not show major effects in the localized molecular orbitals. This may reflect truncating the basis set, the higher angular momentum orbitals being necessary to obtain an accurate energy. The X α calculations led to a rhomboid structure and d-type partial waves were of minor importance. The calculations show an even distribution of bonding around the ring. The two highest occupied MOs (B_{2g}, B_{3g}) are antibonding combinations of sulfur or nitrogen 2p

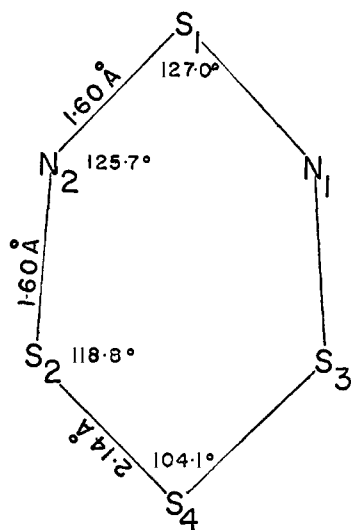


Figure 3. The calculated structure of tetrasulfur dinitride. Bond distance are assumed, bond angles have been calculated.

Table III. CNDO/2 Results for S_4N_2

		$d_{N-S} = 1.60 \text{ \AA}$	
		$d_{S-S} = 2.14 \text{ \AA}$	assumed
Bond angles	NSN	127	
	SNS	126	$E_T = -64.7308$ hartrees
	NSS	119	$BE = 0.4862$ (305 kcal/mol)
	SSS	104	
Wiberg bond orders ^a		Atomic charges	
	S_1-N_1	1.558	$N = -0.224$
	N_1-S_3	1.164	$S_1 = +0.376$
	S_3-S_4	1.040	$S_2 = +0.066$
	N_1-N_2	0.192	$S_4 = -0.060$
	S_1-S_3	0.154	
	S_2-N_1	0.052	
	S_2-S_3	0.044	

^a See text for definition (ref.26).

orbitals. The localized molecular orbital analysis indicated that this is antibonding. We obtained no antibonding orbitals composed of only nitrogen-nitrogen AOs.

The electron-rich centers of the S_2N_2 molecule are on the nitrogen atoms. One would predict the addition of Lewis acids to occur at these points. Similarly, Lewis base additions should occur at the sulfur centers. The compound $S_2N_2(SbCl_5)_2$ is known to have the $SbCl_5$ groups bonded to the nitrogen atoms.²⁴ The compounds $S_2N_2(BCl_3)$ and $S_2N_2(BCl_3)_2$ have been identified,²⁵ and may represent Lewis acid addition compounds with bonding through the nitrogen atoms.

Results for Tetrasulfur Dinitride, S_4N_2 . The structure of tetrasulfur dinitride has been investigated twice, once by Nelson and Heal⁶ and in our laboratory.⁹ A combination of mass spectra, infrared analysis, dipole moment studies, and ^{14}N NMR measurements point to a cyclic structure where the nitrogen atoms are in the 1,3 positions. Normal coordinate analysis indicates the molecule to be near planar, but does not enable assignment of bond distances and angles.⁹ A rather lengthy series of CNDO/2 molecular orbital studies was performed in order to obtain the structure of minimum energy. The calculations were carried out assuming a S-N distance of 1.60 Å and a S-S distance of 2.14 Å. These distances were selected on the basis of the known distance in S_4N_4 (1.62 Å) and previous results obtained for S_2N_2 as well as the known S-S single bond distance (2.136 Å) in the $S_3N_2Cl^+$ molecule.²⁶

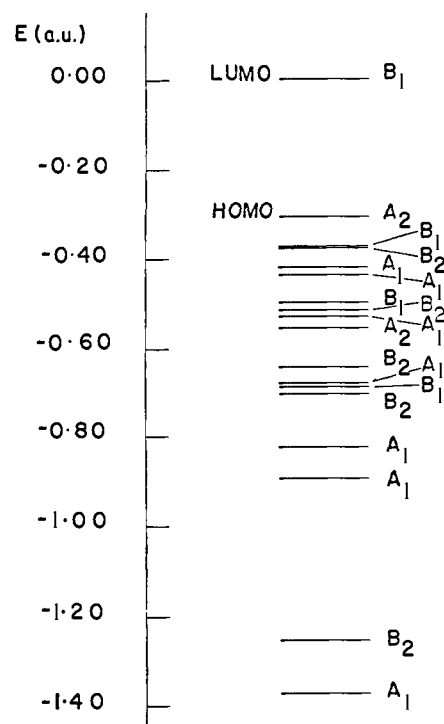


Figure 4. Orbital energy diagram for tetrasulfur dinitride.

Table IV. Results of Nonplanar S_4N_2 Calculations

ϕ^a	E_T , hartrees	ϕ^a	E_T , hartrees
0	-64.7308	30	-64.7153
15	-64.7264	45	-64.7050

^a ϕ represents the angle defined by the molecular plane and the plane of the three sulfur atoms ($S_2S_4S_3$).

The NSN, SNS, NSS, and SSS angles were varied in order to minimize the total electronic energy. The results are given in Table III. The population analysis of these calculations was utilized as a guide in the selection of force constants for the normal coordinate analysis. The details of this study will be published later.²⁷ The population analysis for S_4N_2 is given in Table III.

The Wiberg bond orders are defined as²⁸

$$BO_{R-S}(\text{Wiberg}) = \sum_{\alpha \text{ on R}} \sum_{\beta \text{ on S}} p_{\alpha,\beta}^2$$

The bond orders indicate that the S_1-N_1 and S_1-N_2 bonds have a higher multiplicity than other bonds around the ring.

It has been suggested previously that the S_4N_2 molecule might be nonplanar with sulfur atom 4 lying above the plane of the other five atoms.¹ A series of CNDO/2 calculations was carried out to test this hypothesis, by allowing sulfur atom 4 to be positioned such that the $S_2S_4S_3$ plane makes an angle ϕ with the molecular plane (Table IV). The planar structure was always favored over any nonplanar geometry. An orbital energy diagram for the planar structure is given in Figure 4.

The CNDO/2 orbitals for the structure of the minimum energy were transformed to energy localized molecular orbitals (Table V). The numbering of the atoms refers to Figure 2. In the absence of a curvature analysis we cannot be certain that a true maximum was obtained for the sum of self-repulsion energies. Under the given definition of localization all localized orbitals are greater than 94% localized.

Again we elect to neglect the contribution of the d orbitals to the localized molecular orbitals. The magnitude of the

Table V. Localized orbitals for tetrasulfur dinitride, S₄N₂

LMO type ^a	Atomic orbital coefficient		% localization	
S(1) lone pair	3s	0.7458	99.10	
	3p _z	0.6577		
S(1)-N(1) σ bond	S _{3s}	0.3587	N _{2s} 0.2906	97.93
	S _{3p_y}	-0.4923	N _{2p_y} 0.5755	
	S _{3p_z}	-0.3993	N _{2p_z} 0.1659	
S(1)-N(1) π bond	S _{3p_x}	0.5120	96.20	
	N _{3p_x}	0.8116		
N(1)-S(3) σ bond	S _{3s}	0.2841	N _{2s} 0.3320	98.06
	S _{3p_y}	-0.2226	N _{3p_y} -0.0308	
	S _{3p_z}	0.5811	N _{3p_z} -0.6302	
Nitrogen lone pair	N _{2s}	0.7692	95.58	
	N _{2p_y}	0.4777		
	N _{2p_z}	0.3687		
S(2) lone pair type 1	S _{3s}	0.8585	98.90	
	S _{3p_y}	-0.4380		
	S _{3p_z}	-0.2437		
S(2) lone pair type 2	S _{3p_x}	0.9710	94.32	
S(2)-S(4) σ bond	S _{3s}	0.2247	S _{3s} 0.2130	98.83
	S _{3p_y}	-0.5863	S _{3p_y} 0.4895	
	S _{3p_z}	-0.2849	S _{3p_z} 0.4618	
S(4) lone pair type 1	S _{3p_x}	-0.9894	97.89	
S(4) lone pair type 2	S _{3s}	-0.9075	99.30	
	S _{3p_y}	0.0000		
	S _{3p_z}	+0.4114		

^a The numbering system used for the atoms refers to Figure 2.

largest neglected coefficient is 0.0742. The role of the d orbitals in S₄N₂ appears to be similar to their role in disulfur dinitride. They make no important contribution to the localized molecular orbitals. The absence of an ab initio calculation for S₄N₂ makes it impossible to comment upon their role in development of the geometrical structure.

The localized molecular orbitals reflect a σ-π separation in the molecule. Both σ- and π-type localized orbitals were found for the bonds between S₁ and its two neighboring nitrogen atoms. σ bonding type orbitals were also found for N₁-S₃, S₃-S₄, S₄-S₂, and S₂-N₂. No π-type orbitals were found for these regions. The σ orbitals were about 98% localized, while the π-type orbitals were less localized (96%). One of the π-type orbitals is made up primarily of the p_x orbitals of S₁ and N₂ (coefficients 0.512 and 0.116, respectively) but also contains a small contribution from d_{xz} orbital of sulfur 2 (coefficient 0.1250). Similarly, the other π-type orbital is made from out of plane orbitals of S₁ and N₁ with a small contribution from the d_{xz} orbital of S₃. Interestingly the out of plane orbitals of S₄ contribute virtually nothing to these π orbitals. The two orbitals together give rise to a π-electron distribution through the system N₂-S₁-N₁.

The presence of small contributions from S₂ and S₃ implies a slight π delocalization extending over these atoms as well. The point group, however, does not contain a symmetry operation which interchanges S₁ with either S₂ or S₃ and thus full delocalization over the S₃-N₂-S₁-N₁-S₂ system is not possible. The Wiberg bond orders reflect this. The S(3)-N(1) bond order reflects the extent to which the adjacent π bond is delocalized over this center. The Wiberg order for the S(1)-N(1) multiple bond is 1.56.

Jolly predicted such a delocalization.¹ This study implies a lesser degree of π bonding for S₃-N₂ and S₂-N₁ than that which occurs for N₂-S₁ and S₁-N₁.

The LMOs and the Wiberg bond indexes both indicate that there is no appreciable bonding between sulfur atoms across the ring or between the two nitrogen atoms.

The localized orbitals attribute single lone electron pairs to S₁, N₁, and N₂. Sulfur atoms 2, 3, and 4 each have two lone pair localized orbitals. The electronic structure predicted from the LMO analysis is consistent with the known chemistry for

tetrasulfur dinitride. For example, an adduct is formed when S₄N₂ reacts with BF₃, S₄N₂(BF₃)₂.²⁹ This is explicable if it is assumed that the addition occurs to the nitrogen atoms. The lone pair orbitals for the nitrogen atoms represent the more electronegative centers of the molecule. The atomic charges are negative for these centers (see Table III).

Hydrolysis studies of S₄N₂ indicate that the compound gives rise to sulfur atoms in three different valence states.^{1,29} The predicted electronic structure has sulfur atoms in three different electronic environments. S(2) and S(3) are equivalent and at the same time distinctly different from S(1) and S(4). The bond angle calculated for the sulfur atoms are 127° for S(1), 119° for S(2), and 104° for S(4).

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Molecular Orbital Theory of the Hydrogen Bond. 18. Methyl Substituent Effects on Amide Hydrogen Bonding

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Abstract: Ab initio SCF calculations have been performed to investigate the effect of methyl substitution on amide hydrogen bonding. Equilibrium structures and stabilization energies of amide-water dimers which contain methylformamide, acetamide, and methylacetamide have been determined, and compared with the structures and stabilization energies of corresponding formamide-water dimers. When the amide molecule is the proton donor, or when it is the proton acceptor and hydrogen bond formation occurs on that side of the carbonyl group "trans" to nitrogen, the presence of a methyl group has little effect on the equilibrium structure. However, when the amide is the proton acceptor molecule and hydrogen bonding occurs "cis" to nitrogen, a methyl group bonded to the nitrogen "s-cis" to CO prevents cyclization. Methyl substitution decreases the stabilities of dimers with the amide molecules as proton donors, and increases to a lesser extent the stabilities of dimers with amides as proton acceptors. Hydrogen bond formation at the carbonyl oxygen "trans" to nitrogen is more favorable than "cis" hydrogen bond formation except when the "cis" structure is cyclic. Methyl substitution has little effect on the stabilities of 2:1 water-amide trimers relative to the corresponding dimers, and on the nonadditivity of hydrogen bond energies in open trimers. Greater nonadditivities of hydrogen bond energies are found in trimers in which the amide molecule is either a proton donor or a proton acceptor, and which therefore contain uninterrupted N-H...O-H...O or O-H...O-H...O chains of hydrogen bonds.

Introduction

Hydrogen bonding involving the amide group is an important factor in determining the structures of proteins and polypeptides. In view of the important role which proteins and polypeptides play in biochemistry, it is not surprising that a number of theoretical studies of hydrogen bonding have focused on the amide group. The first such investigations using ab initio SCF techniques were reported by Dreyfus, Maigret, and Pullman,¹ and by Dreyfus and Pullman,² who examined hydrogen bonding in formamide dimers. Hydrogen bonding in formamide-water systems has been studied by Johansson and Kollman,³ by Johansson, Kollman, Rothenberg, and McKelvey,⁴ by Ottersen,⁵ and by Ottersen and Jensen.⁶ Earlier papers in this present series reported the results of studies of formamide as a proton donor and a proton acceptor molecule in dimers and trimers containing formamide and water.^{7,8} A very detailed study of the solvation of formamide by water molecules has been published by Alagona, Pullman, Scrocco, and Tomasi.⁹ This work was followed by a note on the solvation of methylacetamide.¹⁰

While formamide, the simplest amide, may serve as a model for studies of hydrogen bonding in proteins and polypeptides, alkyl-substituted formamides are more representative of these hydrogen bonded systems. How suitable a model formamide is, and the effect of methyl substitution on amide hydrogen bonding, are points addressed in this paper. To this end, a systematic investigation has been undertaken of the structures and hydrogen bond energies of 1:1 and 2:1 water-amide

complexes containing the methyl-substituted formamide molecules methylformamide, acetamide, and methylacetamide as proton donor and as proton acceptor molecules. It is the purpose of this paper to report the results of this investigation.

Method of Calculation

Basis Set. Wave functions for the closed-shell ground states of the monomers and hydrogen bonded complexes have been expressed as single Slater determinants consisting of doubly occupied molecular orbitals. These orbitals have been obtained variationally through the Roothaan SCF procedure as linear combinations of atomic basis functions.¹¹ The atomic basis set used for the molecular orbital expansions is the minimal STO-3G basis set with standard scale factors.¹²

Geometry Optimization of Monomers. It has been noted previously that spurious dimer stabilization may occur when nonoptimized geometries are used for the monomers which form hydrogen-bonded complexes.^{8,13} Since this may be a serious error when substituent effects in dimers with similar stabilization energies are being compared, the first step in this study was to optimize the structures of methylformamide, acetamide, and methylacetamide. For these molecules, intramolecular coordinates were optimized cyclicly and independently to ± 0.01 Å in bond distances and $\pm 1^\circ$ in bond angles, subject to C_s symmetry and the constraints noted in Table I. Parabolic interpolation was then used to estimate bond distances to 0.001 Å and bond angles to 0.1°, yielding the struc-