

they are used in close conjunction with *ab initio* results and experimental data, they frequently can be of considerable value.

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Hydrogen Bonded Dimers and Polymers Involving Hydrogen Fluoride, Water, and Ammonia^{1a}

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Abstract: A theoretical investigation employing semiempirical molecular orbital methods has been carried out on various dimers and polymers involving hydrogen fluoride, water, and ammonia. Different semiempirical MO techniques were compared with each other as well as with *ab initio* results. The CNDO/2 procedure was shown to be an appropriate tool for study of some aspects of hydrogen bonding. Hydrogen bond properties such as geometry, infrared intensity, and frequency shifts, as well as charge redistribution, were investigated. A number of mixed dimers, H₂O-HF, NH₃-HF, and NH₃-H₂O, not heretofore studied experimentally, were considered and found to possess unusually high heats of formation. Linear and cyclic HF polymers were studied. Rather surprisingly, the five-membered chain was found to have the largest energy per H bond among the linear species. For cyclic structures, the hexamer proved the most stable. A charge distribution investigation of the water pentamer provides a beginning toward a detailed electronic structure understanding of liquid water. In both water and H-F polymers, nonlinear energy increments were found.

The hydrogen bond has been of interest to chemists since Latimer and Rodebush² proposed it in 1920.³ This interest greatly increased in 1953 when Watson and Crick⁴ postulated that hydrogen bonding was a key feature of the structure of DNA. Since that time there have been numerous semiempirical studies by π electron methods on some biological systems involving hydrogen bonds.⁵ With the advent of extended Hückel theory, some hydrogen bonded systems were studied with this method.⁶ More recently, valence electron schemes which take electron repulsion into account have been proposed; of special interest have been the CNDO and NDDO methods proposed by Pople.⁷ The CNDO method has been applied to a number of hydrogen bonded systems.⁸

(1) (a) National Science Foundation Predoctoral Fellow, 1966-1970; (b) research supported in part by the Directorate of Chemical Sciences of the Air Force Office of Scientific Research, Contract No. AF 49(638)-1625.

(2) W. M. Latimer and W. H. Rodebush, *J. Amer. Chem. Soc.*, **42**, 1419 (1920).

(3) (a) For additional references, see P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969); (b) for the most recent theoretical review, see S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1966); the most recent spectroscopic review, A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 69 (1968).

(4) J. D. Watson and F. H. C. Crick, *Nature*, **171**, 737 (1953).

(5) For example, see B. Pullman and A. Pullman, *J. Mol. Biol.*, **22**, 373 (1966), and earlier articles; R. Rein and F. E. Harris, *J. Chem. Phys.*, **43**, 4415 (1965); P. O. Löwdin, *Advan. Quantum Chem.*, **2**, 213 (1965); S. Lunnell and G. Sperber, *ibid.*, **46**, 2119 (1967).

(6) See, for example, W. Adam, A. Grimson, R. Hoffman, and C. Ortiz, *J. Amer. Chem. Soc.*, **90**, 1509; (1968); A. S. N. Murthy and C. N. R. Rao, *Chem. Phys. Lett.*, **2**, 123 (1968); R. Rein, G. A. Clarke, and F. E. Harris, *J. Mol. Struct.*, **2**, 103 (1968).

(7) J. A. Pople, *J. Chem. Phys.*, **43**, S129, S135 (1965).

(8) A. S. N. Murthy and C. N. R. Rao, *Theor. Chim. Acta*, **13**, 81 (1968); *Chem. Phys. Lett.*, **2**, 123 (1968); T. Ocvirk, *Theor. Chim. Acta*,

This paper examines several of the semiempirical methods in light of recently carried out *ab initio* calculations on the hydrogen bond.^{3a} It is important to get agreement with experiment for the most favored geometry and heat of formation of the hydrogen bonded dimers and to see how well the semiempirical methods represent other properties of the hydrogen bond. In light of the above, this paper sets out to accomplish the following: (1) Compare the *ab initio* and semiempirical geometry and energy of formation predictions for various hydrogen bonded dimers. (2) Compare the spectroscopic properties predicted by *ab initio* and semiempirical methods choosing the linear water dimer and hydrogen fluoride dimer as test cases. (3) Compare the details of the CNDO and *ab initio* wave functions. (4) Consider the extension of the CNDO method to systems where an *ab initio* calculation would presently be impractical.

Description of Calculation

The *ab initio* calculations have been previously described.^{3a,9} The essential features of the CNDO/2 (CNDO = Complete Neglect of Differential Overlap)^{7,10} procedure are: (1) neglect of overlap between different AO's; (2) neglect of differential overlap in the calculation of energy integrals; (3) further approxima-

10, 187 (1968); A. Pullman and H. Berthod, *ibid.*, **10**, 461 (1968); P. Schuster and Th. Funck, *Chem. Phys. Lett.*, **2**, 587 (1968).

(9) (a) P. A. Kollman, J. F. Liebman, and L. C. Allen, "The Lithium Bond," *J. Amer. Chem. Soc.*, in press; (b) P. A. Kollman and L. C. Allen, "HF Dimers and Mixed Water-HF Dimers," and "Mixed Dimers Involving Ammonia," submitted for publication.

(10) The CNDO/2 calculations were carried out with the Pople and Segal parameters (program QCPE 91).

Table I. Monomer Geometries

Molecule	R, Å	CNDO Results		
		θ , deg	E, au	μ , D
HF	1.00		-28.4366	1.86
H ₂ O	1.03	105	-19.8910	2.11
NH ₃	1.06	106.7 (assumed)	-13.8890	2.10

Molecule	R, Å (fit)	NDDO Results	
		θ , deg	E, au
HF	0.91		-29.3589
H ₂ O	0.96	105 (assumed)	-19.8134

β Parameters Found in the NDDO Calculations	
Atom pair	β
H-F	0.8
F-F	0.15
O-O	0.20
H-H	0.32
O-H	0.75

Table II. Dimerization Energies and Geometries Using Experimental Monomer Geometries

System	CNDO			NDDO			Ab initio ^a		
	R, Å	θ , deg	ΔE , kcal	R, Å	θ , deg	ΔE , kcal	R, Å	θ , deg	ΔE , kcal
(H ₂ O) ₂ linear	2.53	0	5.94	2.2	0	76	3.01	25	5.3
(H ₂ O) ₂ cyclic	2.25	60	2.31	1.6	60	76	2.90	50	4.0
(H ₂ O) ₂ bifurcated	2.44		2.50	2.0		60	3.00		4.45
H ₂ OHF linear	2.41	0	10.70				2.71	0	9.29
HFHOH linear	2.55	0	3.38				3.15	60	2.66
HFH ₂ O cyclic	2.30	60	2.82				3.00	45	3.03
HFH ₂ O bifurcated	2.48		1.69				3.02	0	2.75
(HF) ₂ linear	2.42	20	6.58	2.0		124	2.88	20	4.58
(HF) ₂ cyclic	2.3	60	2.50	2.0	45	64	2.88	60	2.75
(NH) ₂ linear	2.82		3.69						
(NH ₃) ₂ cyclic	2.80	60	0.5						
((NH ₃) ₂ bifurcated	3.0		0.1						
NH ₃ HF linear	2.47	0	13.08						
H ₂ NHFH linear	2.75		1.50						
NH ₃ HF cyclic	2.8	45	2.10						
NH ₃ HF bifurcated	2.81		0.2						
NH ₃ HOH linear	2.64		10.51						
H ₂ NHOH ₂ linear	2.83		1.26						
NH ₃ H ₂ O cyclic	2.4	60	1.50						
NH ₃ H ₂ O bifurcated	2.60		5.32						
H ₂ ONH ₃ bifurcated	2.80		1.30						

^a Ab initio calculations on the ammonia systems are now being carried out.

tion of some particular types of electron repulsion integrals, to ensure invariance with respect to different coordinate systems; (4) use of atomic spectral data for some of the one-electron matrix elements; and (5) employment of energy matrix elements in an LCAO-MO-SCF procedure analogous to that used in the *ab initio* method. The NDDO (NDDO = No Diatomic Differential Overlap)¹¹ method differs from the CNDO in the retention of more of the two-center repulsion and attraction integrals, neglecting only diatomic differential overlap. The two methods also differ in the selection of the two-center attraction parameter β_{XY} . In the CNDO, β_{XY} is proportional to the arithmetic mean of β_X^0 and β_Y^0 and the overlap between the valence orbitals considered; in the NDDO, this parameter is adjusted to fit the X-Y distance in simple monomers. β_{HF} and β_{OH} were found by fitting the hydrogen fluoride

(11) The authors gratefully thank R. Sustmann for the use of his NDDO program.

and water bond distances (see Table I); β_{HH} , β_{OO} , and β_{FF} were computed by fitting the experimental bond lengths in the homonuclear diatomics. The energies of dimerization were not particularly sensitive to small parameter change.

Geometry Searches with CNDO and NDDO

First, CNDO calculations on hydrogen fluoride, water, and ammonia monomers were carried out. In the case of hydrogen fluoride, the bond length was varied; for water, both the angle and bond length were varied; for ammonia, the bond angle was kept at the experimental value and the bond length varied (Table I).

Secondly, dimer calculations on the water dimer, the hydrogen fluoride dimer, the ammonia dimer, and various mixed dimers were performed with the CNDO program. In each calculation the monomers were kept at the experimental geometries (see Figure 1 for geometries considered and Table II for results). For each dimer, the energy of dimerization, the equilibrium

X-Y distance, and the optimum angle θ (where appropriate) were found.

Next, NDDO calculations were carried out for the hydrogen fluoride and water monomers and dimers. The β parameters were varied to fit experimental monomer geometries,¹² and using these parameters, various dimer geometries were studied.

Finally, force constants and infrared intensity increases for the X-H stretch were computed for the hydrogen fluoride and water dimers.

CNDO Dimer Results

(H₂O)₂. In the water dimer the linear structure is the most stable, with an energy of dimerization of 5.94 kcal/mol. This structure is predicted to be considerably more stable than the cyclic and bifurcated structures. Experimental infrared data on dimers trapped

(12) See W. H. Fink and L. C. Allen, "Ten Electron Polyhydrides," for experimental monomer distances, to be submitted for publication.

in a matrix were interpreted to favor a cyclic structure for the water dimer.¹³

(H₂O-HF). Of the four structures considered for the mixed water-hydrogen fluoride dimer, the linear H₂O-HF is by far the most stable. This system has not been experimentally studied and would be interesting to investigate by microwave spectroscopy, to obtain structural information. It is the feeling of the authors that the energy of dimerization is high enough that a reasonable percentage of dimers would exist even at relatively low pressures. Of the three weaker HF-H₂O dimers, the relative stabilities predicted by CNDO disagree with *ab initio* results, but this is not so surprising for cases where the relative energies of dimerization are not very different.

(HF)₂. The linear HF dimer is predicted to be twice as stable as the cyclic structure, in reasonable agreement with *ab initio* findings.

(NH₃)₂. The linear dimer is predicted to be far more stable than the other two structures.¹⁴

(NH₃-HF). The linear NH₃-HF is the strongest dimer studied, with an energy of dimerization of 13.08 kcal/mol. This is also of interest for gas phase structure studies, since at low concentrations in the gas phase, one would expect the dimer to be nonionic (proton transfer is not predicted in this calculation) and stable with respect to separated ions. The other mixed ammonia-hydrogen fluoride dimers are too weak to be observed.

(NH₃HOH). The linear NH₃HOH system is comparable in energy of dimerization to the mixed H₂O-HF dimer; this makes this system also of experimental interest. The bifurcated NH₃H₂O is also quite strongly bound with respect to isolated monomers, but the other geometries considered are much less stable than the linear or bifurcated.

Critical Evaluation of Dimerization Results

It is clear from the geometry searches that the CNDO method appears very promising. In each dimer system considered, the CNDO and *ab initio* methods predict the same type of structure to be the most stable, and the energy of dimerization is quite comparable in both. There are some discrepancies in the weaker bonded structure between the orders predicted by the *ab initio* and CNDO, but the energy differences between the various geometries are quite small in these cases. However, the equilibrium separation of the dimers is invariably too small by CNDO. For example, the equilibrium separation of the linear water dimer in the CNDO calculation is found to be 2.53 Å. The crystal distance in hexagonal ice is known to be 2.75 Å,¹⁵ and it is certain that the separation in a gas phase dimer is larger than the crystal value.¹⁶ Also, many of the angular effects ($\theta \neq 0^\circ$ in the linear water dimer) found in the *ab initio* results are not reproduced. This is not surprising because not only are these surfaces quite

(13) M. van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 486 (1957).

(14) A linear structure for the ammonia dimers is found in rare gas matrix work: G. C. Pimentel, M. O. Bulanin, and M. van Thiel, *ibid.*, **36**, 500 (1962).

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

(16) The formation of one hydrogen bond increases the energy of formation of a second to the same center: L. J. Bellamy and R. Pace, *Spectrochim. Acta*, **22**, 525 (1966); therefore, one would expect a stronger bond in ice than in water and thus a shorter O-O distance.

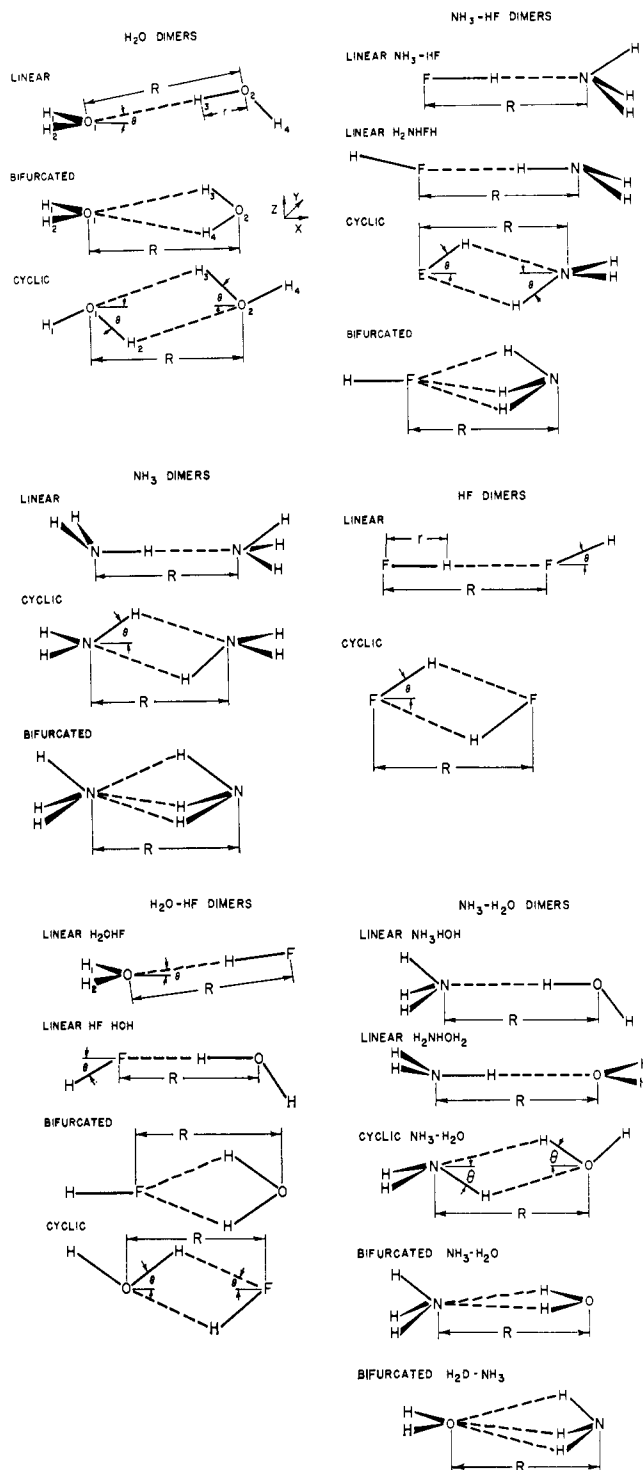


Figure 1. Geometries studied.

shallow, but a smaller basis set *ab initio* calculation by Pederson and Morokuma¹⁷ also predicts $\theta = 0^\circ$ for the linear water dimer.

The NDDO method greatly overestimates the attraction between the molecules considered, and in one case (cyclic *vs.* linear water) predicts the wrong order for stability. Thus it appears that the CNDO/2 method is the most appropriate for study of hydrogen bonded systems. With this in mind, a more careful analysis of the CNDO method was made. One would like to have some estimate of the confidence one could have in the

(17) K. Morokuma and L. Pederson, *J. Chem. Phys.*, **48**, 3275 (1968).

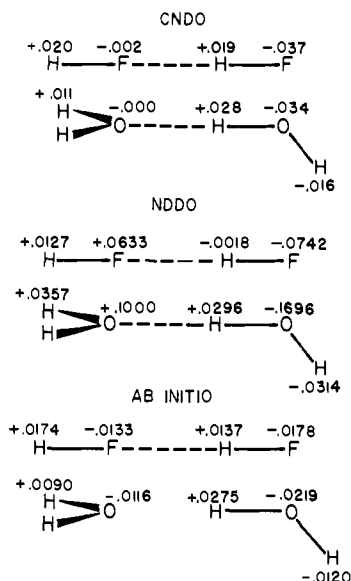


Figure 2. Comparison of population analysis of CNDO, NDDO, and *ab initio*.

energy of formation found by the CNDO procedure. All of the hydrogen bonded studies carried out thus far by CNDO⁸ have used experimental monomer geometries; however, when one investigates the effect of changes in monomer geometry on dimerization energies, as has been done in this study, considerable sensitivity is found. That is, the dimer energy of formation for HF using experimental monomer geometries is 6.58 kcal; when CNDO-determined theoretical geometries are used, a dimerization energy of 8.95 kcal is found. Similar results are found for other dimers. In contrast to this, *ab initio* dimer results are not strongly dependent on monomer geometries (4.58 kcal dimerization energy predicted using experimental monomer geometries in HF; 4.98 kcal predicted using *ab initio* calculated monomer geometries). This is primarily a reflection of the relatively poor monomer geometry prediction achieved by CNDO and suggests that reparameterization of the CNDO might improve the situation.

The degree of confidence one has for intersystem comparisons is also an important question. For example, CNDO predicts the hydrogen fluoride dimer to be more stable than the water dimer. *Ab initio* results predict that the opposite is the case.¹⁸ Therefore, one should be cautious in intersystem comparisons of energies of dimerization.

Finally, it is appropriate to cite the extended Hückel results of Murthy, *et al.*⁶ Their calculations show that not only is the monomer O-H distance very poorly represented in the water dimer, but that $\text{H}_3\text{O}^+\text{OH}^-$ is more stable than a neutral water dimer—a situation which is physically unreasonable. Therefore, it is concluded here that further consideration of the extended Hückel method to attack this problem would be unfruitful.

Properties

It is of interest to compare the dipole moment, force constant, and population analysis results of CNDO, NDDO, and *ab initio* calculations (Figure 2 and Table III). Since one of the most dramatic evidences for hy-

(18) Both minimal basis double ζ calculations and a less contracted basis set show $(\text{HF})_2$ to be 1–2 kcal less stable than the water dimer.

drogen bond formation is the increase of intensity of the X-H stretch in the infrared, we computed $|\partial u/\partial r|^2$ for the *ab initio* and CNDO calculations on the water dimer and the hydrogen fluoride dimer. The *ab initio* wave function for the water dimer gives an intensity increase of eight, in good agreement with experiment;¹³ the CNDO value is reasonably close to this (16). On the other hand, there is a large disagreement between the intensity increases predicted for hydrogen fluoride. The CNDO value is far too high and the *ab initio* surprisingly low (CNDO intensity prediction = 180; *ab initio* = 2).¹⁹ It was thought that the excessive predicted intensity for the hydrogen fluoride dimer in the CNDO approximation might be due to the fact that the equilibrium distance is too short, thus exaggerating the charge shifts. Therefore, the intensity increases predicted by CNDO near the *ab initio* equilibrium X-Y separation were studied ($R(\text{F-F})$, 2.78; $R(\text{O-O})$, 2.9 Å), and the values are given in Table III. In this case the intensity increase predicted for the hydrogen fluoride dimer is reasonable, but no intensity increase at all is predicted for the water dimer.

Table III

$(\text{HF})_2(\text{CNDO})_s$ $R(\text{F-F}) = 2.45 \text{ \AA}$			$(\text{HF})_2(\text{CNDO})_s$ $R(\text{F-F}) = 2.78 \text{ \AA}$		
$r(\text{F-H})$, Å	E , au	u, D	$r(\text{F-H})$, Å	E , au	u, D
0.9	-56.8569	4.05	0.91	-56.8580	3.88
0.93	-56.8724	4.11	0.94	-56.8710	3.90
0.96	-56.8821	4.17	0.97	-56.8786	3.93
0.99	-56.8870	4.24	1.00	-56.8815	3.96
1.02	-56.8887	4.32	1.03	-56.8806	4.00
1.05	-56.8850	4.40	1.06	-56.8764	4.04
$(\text{H}_2\text{O})_2(\text{CNDO})_s$ $R(\text{O-O}) = 2.55 \text{ \AA}$			$(\text{H}_2\text{O})_2(\text{CNDO})_s$ $R(\text{O-O}) = 2.90 \text{ \AA}$		
$r(\text{O-H})$, Å	E , au	u, D	$r(\text{O-H})$, Å	E , au	u, D
0.95	-39.7777	4.138	0.96	-39.7771	3.952
0.98	-39.7878	4.180	0.99	-39.7851	3.961
1.01	-39.7934	4.232	1.02	-39.7888	3.779
1.04	-39.7953	4.284	1.05	-39.7890	3.984
1.07	-39.7941	4.355	1.08	-39.7863	4.012

System	$ \partial u/\partial r ^2_d/ \partial u/\partial r ^2_m^a$	K_d/K_m^a	$\Delta r_d/(H-X)^a$, Å
$(\text{HF})_2$ CNDO, $R = 2.45$	180	1.08	0.011
$(\text{HF})_2$ CNDO, $R = 2.78$	20		
$(\text{HF})_2$ <i>ab initio</i> , $R = 2.88$	2	1.00	0.004
$(\text{H}_2\text{O})_2$ CNDO, $R = 2.55$	16	0.51	0.0135
H_2O_2 CNDO, $R = 2.90$	1		
H_2O_2 <i>ab initio</i> , $R = 3.00$	8	0.97	0.010

^a d = dimer, m = monomer.

Experimentally, the X-H stretching frequency is usually found to decrease by 10% upon H-bond formation. The CNDO computed water dimer and HF dimer stretching force constants are compared with the *ab initio* results in Table III. For this property both theoretical methods show a clear decrease in stretching force constant in the water dimer, but for HF dimer,

(19) D. F. Smith, *J. Mol. Spectrosc.*, **3**, 473 (1959), has viewed the HF spectra by ir. Because of the overlapping nature of the spectra, he makes no estimate of the intensity enhancement due to dimer formation. He estimates the heat of formation to be between 5 and 7 kcal.

CNDO actually predicts an increase in the HF force constant.

Because the equilibrium separations of the two monomers in the CNDO and NDDO calculations are so much smaller than the *ab initio*, one would expect the electron redistribution to be much more drastic in the semiempirical than in the *ab initio* wave function. This is true for the NDDO calculation, but the CNDO and *ab initio* are quite comparable (Figure 2). The CNDO fails to show the increased charge on the electron pair donor heavy atom, but otherwise reproduces the *ab initio* populations quite well. Note that all the water wave functions display an increased electron density on one of the hydrogens. It is worthwhile reiterating the previous point that one has little hope of representing the properties of liquid water with a dimer wave function, since in the liquid all the hydrogens are expected to have equal electron populations.

The molecular orbital energies obtained by CNDO follow the same trend as that found in the *ab initio* calculations done in this laboratory. The orbitals on the electron pair donor decrease in energy and those on the electron pair acceptor increase.²⁰ This characterizing feature has been found in a wide variety of donor acceptor interactions involving closed shell systems,^{9a} and it is the fundamental distinguishing factor between normal covalent bond formation (where all the MO's are usually raised in energy) and intermolecular bond formation between closed shell species.

Extension to Larger Systems: HF Polymers and the Water Pentamer

A main purpose of this paper is to assess the validity of the CNDO/2 procedure as a tool for studying larger H-bonded systems where a complete *ab initio* potential surface would be impractical. Here, the concentration is on polymers of hydrogen fluoride and on water surrounded by a tetrahedral environment of water molecules.

HF Polymers. Hydrogen fluoride has been found to be a gas phase hexamer by electron diffraction, with F-F distances of 2.53 Å and F-F-F angles of 104°. Linear dimer, trimer, tetramer, pentamer, hexamer, heptamer, and octamers of hydrogen fluoride have been studied and compared with equilateral and equiangular 4, 5, 6, and 8-gons, and with cyclohexane-like boat and chair and cyclooctane-like structures. In each case, the F-F distance was kept at 2.45 Å, the theoretically found equilibrium distance for the dimer, and the H-F distance was kept at the CNDO theoretically calculated minimum of 1.00 Å. In the cyclohexane and cyclooctane structures, all F-F-F angles were kept tetrahedral.

Three important features emerge. First, in the linear configurations, the average energy gained per H bond goes through a maximum at the pentamer (Table IV).

(20) A. Pullman (*J. Chim. Phys.*, 61, 226 (1964)) has carried out π electron Hückel calculations on a variety of biologically interesting nucleotides. In some of her calculations she increased the value of the Coulomb parameter, α , for the proton acceptor and simultaneously decreased α for the proton donor. For the π electrons this produces a raising and lowering of the molecular orbital energies, which parallels our findings.

(21) J. Janzen and L. S. Bartell, *J. Chem. Phys.*, 50, 3611 (1969). They note, however, that "the pucker may simply be a consequence of thermal binding of the extremely flexible ring." They also find that a substantial number of ring protons migrate to positions halfway between the fluorines.

ACCEPTOR MODEL OF HF POLYMER

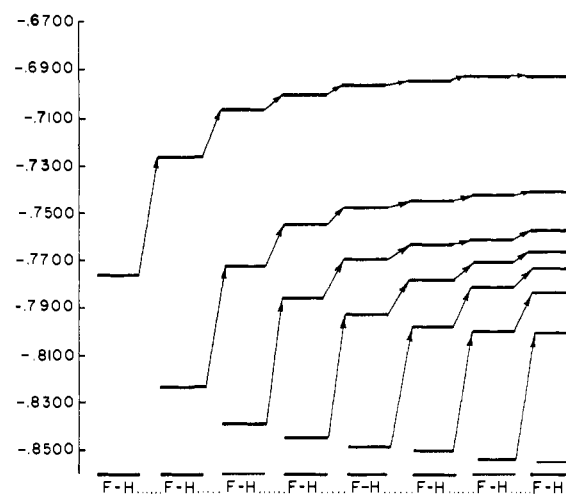


Figure 3. Acceptor model of HF polymer (all MO's are raised).

This result is somewhat surprising; one might expect the average H-bond energy to increase monotonically to a limiting value as the chain length becomes infinite. It is quite evident, however, that the average H-bond

Table IV. HF Polymers

Linear system	E , au	ΔE gained/HF fragment, kcal	ΔE gained/H bond, kcal
(HF) ₂	-56.8876	4.505	9.01
(HF) ₃	-85.3425	6.819	10.22
(HF) ₄	-113.7983	8.117	10.82
(HF) ₅	-142.2545	8.946	11.18
(HF) ₆ ^a	-170.7011	8.498	10.20
(HF) ₇	-199.1519	8.553	9.98
(HF) ₈	-227.6022	8.555	9.77

Cyclic system	E , au	ΔE /HF fragment, kcal	ΔE /bond, kcal
(HF) ₄ square	-113.8132	10.45	10.45
(HF) ₅ regular pentagon	-142.2685	10.70	10.70
(HF) ₆ regular hexagon	-170.7243	10.92	10.92
(HF) ₆ cyclohexane boat	-170.7133	9.73	9.73
(HF) ₆ cyclohexane chair	-170.7119	9.62	9.62
(HF) ₈ regular octagon	-227.6271	10.50	10.50
(HF) ₈ cyclooctane-like	-227.6168	9.70	9.70

^a A zig-zag hexamer with F-F-F = 160° (in view of the fact that the equilibrium geometry in the H-F dimer has $\theta = 20^\circ$) is less stable than the linear structure.

energy will stay higher than that for the dimer. This is additional support for the generality of Bellamy and Pace's experimental discovery that the presence of a hydrogen bond at a nucleophilic center increases the strength of another H bond to that site. This increase is what one would expect from purely electrostatic arguments.¹⁶

Secondly, all the planar cyclic structures are more stable than the linear structures, but the most stable energy per HF fragment is found for the cyclic hexamer. Both the boat and chair cyclohexane-like structures are less stable than the planar cyclic hexamer, and the cyclooctane structure is less stable than the planar cyclic octamer. Experimentally, HF exists in the gas phase mainly

Table V. MO Energies (for π Orbital) (au)

HF	(HF) ₂	(HF) ₃	(HF) ₄	(HF) ₅	(HF) ₆	(HF) ₇	(HF) ₈
-0.7766	-0.7249	-0.7073	-0.7000	-0.6962	-0.6954	-0.6935	-0.6933
	-0.8228	-0.7715	-0.7545	-0.7474	-0.7450	-0.7424	-0.7418
		-0.8377	-0.7863	-0.7694	-0.7633	-0.7593	-0.7580
			-0.8444	-0.7929	-0.7768	-0.7694	-0.7665
				-0.8479	-0.7968	-0.7798	-0.7735
					-0.8500	-0.7986	-0.7824
						-0.8514	-0.8003
							-0.8525
"Primary acceptor" changes, au		"Secondary acceptor" changes, au			"Tertiary acceptor" changes, au		
	+0.0517		+0.0176		+0.0073		
	+0.0513		+0.0170		+0.0071		
	+0.0514		+0.0169		+0.0061		
	+0.0515		+0.0161		+0.0074		
	+0.0511		+0.0170		+0.0063		
	+0.0514		+0.0162				
	+0.0511						
"Primary donor" change, au		"Secondary donor" change, au			"Tertiary donor" change, au		
	-0.0462		-0.0149		-0.0067		
	-0.0466		-0.0148		-0.0066		
	-0.0472		-0.0149		-0.0074		
	-0.0474		-0.0159		-0.0061		
	-0.0478		-0.0143		-0.0067		
	-0.0470		-0.0156				
	-0.0483						

as a cyclic hexamer²¹ with F-F distances of 2.45 Å and F-F-F angles of 104°. It is intriguing that the quantum mechanical internal energy calculations of this laboratory correctly predict a six-membered ring to be the most stable structure of gas phase hydrogen fluoride.

HF···HF··· donates the electrons from the approaching fluorine to the previously formed polymer, and each MO on the polymer is raised in energy. This trend continues on the addition of more HF fragments; gradually, the MO's contributed by the HF on the far end

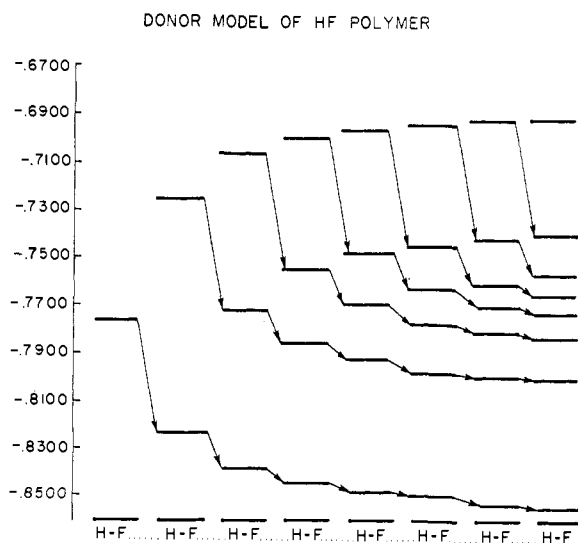


Figure 4. Donor model of HF polymer (all MO's are lowered).

Finally it is of interest to look at the MO energies of the various linear polymers of hydrogen fluoride, where a band-like structure emerges. Considering first the π MO's (since these are the easiest to assign to individual hydrogen fluoride monomer fragments²²), one can consider the addition of each HF fragment from either a donor or an acceptor point of view. The approach of an HF toward an already formed polymer HF →

(22) After the SCF procedure has been carried out, these MO's still look very much like AO's from different fluorines.

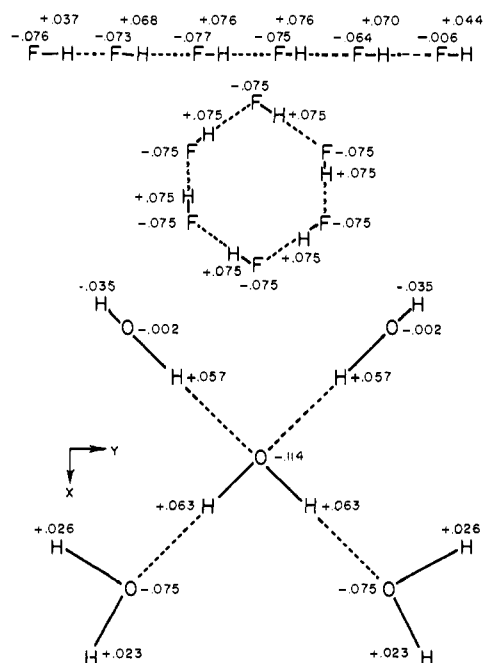


Figure 5. Population analysis of linear HF polymer, cyclic HF polymer, and pentameric water (tetrahedral, but projected onto a plane).

(furthest from the site of addition) converge (Figure 3) to a limiting energy. It is also interesting that the fragment on the end facing the approaching HF has its π MO raised in energy about 0.0513 au; the fragment next to the end has its π MO raised by about 0.0168 au;

and the fragment third from the end has its π MO raised about 0.0068 au (see Table V). One can also view the buildup of the polymer as $\text{FH} \rightarrow \text{FH} \cdots \text{FH} \cdots$; in this type of approach (hydrogen first), all the MO's on the previously formed polymer decrease and eventually converge (Figure 4). In this case the "primary donor" decrease is about 0.0472, the "secondary donor" decrease 0.0151, and the "tertiary donor" 0.0067 au. For both of these viewpoints, the σ MO's display the same general trends.

Water Pentamer. A single calculation was carried out on water in a tetrahedral water environment. Figure 5 shows the population changes. The stabilization energy for the pentamer is 8.3 kcal/H bond, very slightly less than that found in the dimer using CNDO determined monomer geometries. A more complete geometry search is now underway, in which we hope to map out the potential which a water molecule feels in hexagonal ice and liquid water. The many comparisons of CNDO with *ab initio* and experimental data given in the first section of this paper show quite conclusively that the *forte* of the CNDO is in distinguishing most stable geometries within a single system, so we may expect our multi-molecule water results to be physically meaningful.

In conclusion we emphasize that the CNDO/2 is the best of the three semiempirical schemes (CNDO, NDDO, and extended Hückel) for studying hydrogen bond interactions. One has most confidence in the

CNDO for studying different possible geometries involving the same molecules. However, one must be cautious in making intersystem comparisons or in attaching too much significance to the quantitative energy of dimerization found. The failure of the NDDO method to give physically meaningful results is somewhat disturbing and shows the not uncommon phenomenon that an increase in sophistication of the method (CNDO \rightarrow NDDO) causes worse agreement with reality.

The studies of the HF polymer indicate some interesting features: (1) the band-like MO-energy trend, (2) the nonlinear energy increments (the energy gain in trimerization is more than that of dimerization), and (3) the prediction that the cyclic hexamer is the most stable HF polymer.

A beginning was made on the structure of liquid water and hexagonal ice through a calculation on $(\text{H}_2\text{O})_5$.

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Combined Substituent and Angular Effects upon Vicinal Hydrogen-Fluorine Coupling Constants¹

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Abstract: The nmr spectra from a series of fluoro-substituted bicyclo compounds reveal that vicinal H-F coupling constants are extremely sensitive to substituent electronegativity with ${}^3J_{\text{HF}}$ *trans* exhibiting a 40-fold change. The magnitude of the substituent effect varies with dihedral angle (ϕ) and is largest for $\phi = 0$ and 180° . Limited data indicate that ${}^3J_{\text{HF}}$ may be estimated from Karplus-type expressions of the form $A \cos^2 \phi$, $0^\circ \leq \phi \leq 90^\circ$; $B \cos^2 \phi$, $90^\circ \leq \phi \leq 180^\circ$ where A and B are inversely proportional to the sum of the substituent electronegativities. Substituent effects on vicinal H-H coupling constants are also compared.

Recent empirical evidence confirms that the guidelines outlined in the Karplus equation²⁻⁴ for estimating vicinal H-H coupling constants apply equally well for vicinal H-F coupling constants.⁵⁻⁸

Parameters affecting 3J are (1) dihedral angle, (2) bond length, (3) bond angle, and (4) electronegativity of neighboring groups. Recently Williamson, *et al.*, elucidated the angular dependence of ${}^3J_{\text{HF}}$ in a series of rigid molecules having groups of similar electronegativity.^{6,9} Their data demonstrated that a 12° increase in the C-C-H and C-C-F bond angles at a constant dihedral angle ($\phi = 0^\circ$) causes ${}^3J_{\text{HF}}$ to vary from 30.8 to 0.9 Hz. Furthermore at a constant bond angle θ , ${}^3J_{\text{HF}}$ is related to the dihedral angle ϕ by the following expression.

$${}^3J_{\text{HF}} = \begin{matrix} 31 \cos^2 \phi & 0^\circ \leq \phi \leq 90^\circ \\ 44 \cos^2 \alpha & 90^\circ \leq \phi \leq 180^\circ \end{matrix} \quad (1)$$

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