A Systematic Study of the Nine Hydrogen-Bonded Dimers Involving NH_3, OH_2, and HF

J. D. Dill,[1a] L. C. Allen,*[1a] W. C. Topp,[1b] and J. A. Pople[1c]

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540, Cold Spring Harbor Laboratory, Cold Spring Harbor, New York 11724, and the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received April 28, 1975*

Abstract: The nine H-bonded dimers of NH_3, OH_2, and HF have been calculated by ab initio molecular orbital theory at the 6-31G* level with geometry optimization. Calculated dimerization energies (kilocalories/mole) are: $H_3N\cdots HNH_2$, 2.9; $H_3N\cdots HOH$, 6.5; $H_3N\cdots HF$, 12.2; $H_2O\cdots HNH_2$, 2.8; $H_2O\cdots HOH$, 5.6; $H_2O\cdots HF$, 9.2; $HF\cdots HNH_2$, 2.6; $HF\cdots HOH$, 4.0; $HF\cdots HF$, 5.9. Energies and geometries are compared with available experimental and ab initio values from the literature. The 6-31G* results are found to be internally consistent and of reasonable accuracy. The paucity of experimental measurements on gas-phase dimers makes the present set of results of special significance for understanding the mechanism of hydrogen bonding, and for stimulating further experimental work.

Although hydrogen bonding has been actively studied for over 50 years,[2-4] very few attempts have been made to unify the vast body of collected data into a simple predictive theory. Such a theory should, by analogy with other "textbook" theories such as Pauling's's[5] electronegativity-bond strength or bond length-bond order relations, be capable of providing useful quantitative information given a small number of well-defined empirical quantities, and should provide a simple, general description of the characteristics of the hydrogen bond.

The reason for this lack is clear. In order to develop such a theory, it is necessary to assess the appropriate trends in series of hydrogen-bonded systems. Although experimental work has been carried out on a variety of systems, many difficulties prevent straightforward interpretation of results. For example, vibrational spectroscopy, one of the methods most sensitive to the presence of hydrogen bonding, is complicated by broad or overlapping bands, and high degrees of association in the liquid phase; calorimetric methods suffer from errors due to self-association of solvent and the accompanying temperature dependencies; gas-phase data are relatively sparse, difficult to obtain, and limited to those species having relatively strong hydrogen bonds. Limitations of the various methods have been described,[2,3] and it has been pointed out[6] that measurements made by different methods often lead to serious discrepancies in hydrogen-bond energies. Furthermore, those systems which are experimentally available are often sufficiently complex that measurements of hydrogen bonding information must be made indirectly, and complicating peripheral groups perturb hydrogen bonds to varying extents. Thus a series of internally consistent experimental values has not become available.

Theory therefore plays an important role in these studies. Molecular orbital techniques permit direct, uniform examination of hydrogen-bond energies and geometries. However, theoretical predictions of weak bonds require that small differences between large quantities be obtained, and this leads to varying results with different basis sets. Often the variations are unpredictable; they do not appear to diminish smoothly with increasing basis set size. This difficulty can be circumvented by considering a series of model systems at a single level of approximation, provided the level is sufficiently high to describe the entire series consistently. In this manner, trends can be assessed, based on which a simple theory might be developed. In this paper we present a complete series of calculations which appear to be more accurate and consistent than previous series. The species considered are the nine hydrogen-bonded dimers which can be formed from NH_3, OH_2, and HF, each as both proton donor and acceptor. On the basis of these and other[7] results, a simple theory of hydrogen bonding has been proposed in recent publications.[8]

Basis Set

Hartree-Fock calculations were performed at Carnegie-Mellon University, using the 6-31G* basis set developed by Hariharan and Pople.[9-11] The designation 6-31G* indicates a polarized, split-valence basis comprised of six Gaussians for inner shells, three plus one Gaussians for (split) valence shells and hydrogens, and six d-type Gaussians on heavy atoms. Standard exponents and molecular scaling factors were used, as described previously.[9] The 6-31G* basis has been demonstrated to reproduce hydrogenation energies[10] and geometries[11] of first-row species consistently. For a typical dimer calculation, integral + SCF time on a Univac 1108 was around 15 min.

Geometries

Dimer geometries were optimized at the 6-31G* level, apart from the following constraints: (A) all monomer units were held at experimental geometries, as specified in Table I; (B) hydrogen bonds were assumed to be linear, i.e., $A-H\cdots B$ angles were held at 180°; (C) for the three $H_3N\cdots H-A$ dimers, the symmetry axis of the NH_3 was assumed to lie along the N-A axis, i.e., θ was fixed at 0°; and (D) the lowest symmetry assumed for all nine dimers was C_s. Given these assumptions, at most three parameters remained variable: R, the A-B distance; θ, the angle between the A-B axis and the local symmetry axis of the proton acceptor; and φ, the dihedral angle about the A-B axis (for proton donors other than HF). For the latter, we have assumed the values obtained[12] at the STO-3G level: for $H_nB\cdots H-AH_m$ configurations the values are HN-N: = 180°, HN-OH = 180°, :O-N: = 180°, :O-OH = 0°, HF-N: = 0°, and HF-OH = 180°, where ":" represents the fourth tetrahedral direction at $-XH_2$. The remaining parameters R and, where appropriate, θ were optimized at the 6-31G* level, leading to the equilibrium values given in Table I. Also given in Table I are the total energies, dimerization (hydrogen-bond) energies, and dipole moments calculated at the 6-31G* level and at four other levels, described below. The definitions of R and θ are illustrated in Figure 1, where the above values of φ are represented pictorially.

Charge Distributions

In Table II are given selected values from Mulliken population analyses of the 6-31G* wave functions. Several quantities are of interest for a hydrogen-bonded H_mA-$H \cdots BH_n$ dimer, as follows. For ease of interpretation, all values refer to charge changes upon dimerization rather than to absolute charges.

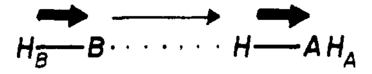
1. Loss of Charge from B Hydrogens ("B Ligands"), δ_{BL}. To the extent that charge is being transferred from H_nB to H-AH_m, the hydrogens on B become more positive upon dimerization. The quantity δ_{BL} gives the total number of electrons lost from the n hydrogens, relative to monomer values; accordingly, it varies almost linearly with n.

2. Change in Charge at B, δ_B. Atom B is donating charge to H-AH_m but receiving compensation from its own hydrogens. As δ_B values show, except for HF proton acceptors the net result is a slight buildup of charge at B compared to its monomer value.

3. Change in Charge at the Binding Hydrogen, δ_H. This H becomes more positive upon dimerization, especially with NH_3 proton acceptors.

4. Change in Charge at A, δ_A. The effect of dimerization is to increase electron density at A, as shown by δ_A values.

5. Total Charge Transfer, CT. CT represents the total number of electrons lost by H_nB, or, equivalently, gained by H-AH_m. These values (quantities 1-5) taken together lead to a picture of the overall redistribution of electrons upon dimerization as follows:



This indicates reduction of charge at H_B and the binding H, but buildup of charge at A and slightly at B. Although full discussions of dimer charge distributions have appeared elsewhere[4,8,13,15,21] and need not be repeated, we call attention to the rough correlation between trends in δ and CT values and the dimerization energies, E_D. In general, the stronger the hydrogen bond, the greater the extent to which monomer charge distributions are perturbed.

6. Ionization Potential, *I*. These values are the absolute values of the one-electron energies for the highest occupied molecular orbitals of the dimers, and may be compared with those of the monomers (11.42 eV for NH_3, 13.55 for H_2O, 17.10 for HF). In most cases, the HOMO of the dimer is localized on the lone pair of the proton donor.

Literature Results

Quantities available for comparison fall in two categories: those which have been calculated at a uniform level for the complete set of nine first-row dimers (Table I), and those, both calculated and experimental, which refer to smaller subsets (Tables III-V). We discuss these in turn, restricting our attention throughout this paper to ab initio methods of calculation. (A thorough INDO study has recently appeared;[32] earlier semiempirical work has been tabulated in ref 33.)

Five levels of approximation, including the present 6-31G*, have been applied to the entire series of dimers. Results of these studies are collected in Table I. The first involves the minimal STO-3G Gaussian basis developed by Pople and coworkers.[34] These calculations are taken from a comprehensive study of two-heavy-atom first-row systems;[12] they represent (within the constraint of C_s symmetry) complete geometry optimizations of all nine species, two[35] having been optimized also in alternate rotational conformations. Only the lower-energy rotamers are given here. Complete geometry searches have not been performed previously, so the STO-3G results are useful for assessing the validity of our geometry assumptions.

In the same compilation,[12] the split-valence 4-31G basis set[36] was used to calculate a single energy of each STO-3G-optimized structure. These values comprise the second set. They are claimed[12] to give unreliable E_D values due to the assumption of STO-3G geometries, but are useful for comparison with optimized 4-31G results.

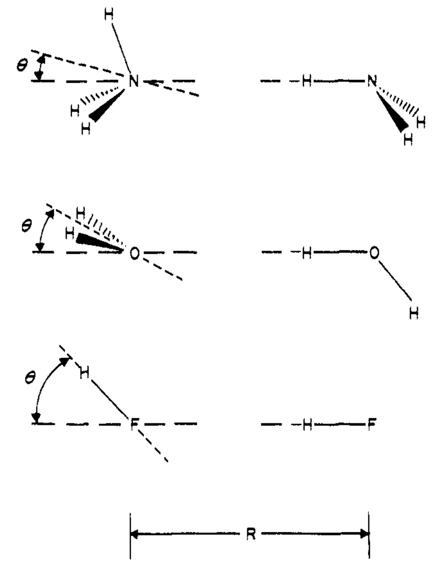


Figure 1. Definitions of R and θ. Dimers were calculated in conformations shown except $(NH_3)_2$ (Figure 2). Dotted line is center-of-gravity axis of acceptor.

All other values in the table were obtained by partial geometry optimization (R and θ only) exactly as described above. In the third series ("4-31G(0)"), the 4-31G basis was used for this purpose, both by Topp and Allen[7] and Kollman et al.,[13] in two identical studies. Some discrepancies occur between the two sets of published results, but they are sufficiently small to preclude mentioning. We list Topp's values, since total energies and dipole moments were not given by Kollman.

The HFAO basis of Kollman and Allen[15,21,37] was used for the fourth series. This basis gives lower total energies than 4-31G but is somewhat less flexible in valence regions. A strictly uniform basis was not applied to the HFAO series; five systems (see footnotes Table I) were studied with a very slightly improved HFAO basis which we estimate may give inconsistencies in E_D values of at most 0.5 kcal/mol.

Comparisons of the four complete series of results with 6-31G* are discussed below. Other theoretical studies dealing with fewer than nine dimers each have been reviewed in an excellent compilation by Schaad.[33] We supplement his discussion by mentioning a few ab initio studies which have appeared since. Lischka[38] examined the HF dimer with a Hartree–Fock quality basis set, and assessed the correlation energy by three separate methods (IEPA, CEPA, and PNO-CI). Curtiss and Pople[39,40] studied the water dimer[39] and the HF dimer[40] at several levels, with full or partial geometry optimization at each; these include 4-31G, 6-31G, 6-31G*, and 6-31G** (6-31G* plus p-type polarization functions on hydrogens). Schaefer, Bender, and coworkers have performed an extensive potential surface scan for the HF dimer.[41] Finally, Diercksen et al.[24] have recently calculated the correlation energy for the water dimer. Although Schaad has given a thorough discussion of the theoretical situation with regard to the water dimer, we feel that a complete tabulation of calculated ab initio results on all nine systems is useful for calibrating the present 6-31G* results and for directing future studies. Listing the calculated energies (not done by Schaad) allows us to assess trends which may occur with changing basis sets. Thus, we present

Table I. First-Row Monomers and Dimers, 6-31G* Energies, Geometries, and Dipole Moments[x]

Structure	Basis	Energy, au	R, Å[a]	θ, deg[a]	μ, D	E_D, kcal/mol[b]
NH_3	STO-3G[c]	−55.45542	1.033	104.2	1.66	
	4-31G[d]	−56.09829	1.033	104.2	2.28	
	4-31G(0)[e]	−56.10269	1.0136[f]	107.05[f]	2.28	
	HFAO[g]	−56.14176	1.0116[h]	106.7[h]	2.31	
	6-31G*[i]	−56.18404	1.0136	107.05	1.93	
	Exptl		1.012[h]	106.7[h]	1.47[j]	
OH_2	STO-3G	−74.96590	0.990	100.0	1.78	
	4-31G	−75.90324	0.990	100.0	2.61	
	4-31G(0)	−75.90740	0.957[k]	104.52[k]	2.61	
	HFAO	−75.97638	0.957	105	2.48	
	6-31G*	−76.01054	0.957	104.52	2.22	
	Exptl		0.957[k]	104.5[k]	1.85[j]	
FH	STO-3G	−98.57285	0.956		1.41	
	4-31G	−99.88613	0.956		2.28	
	4-31G(0)	−99.88726	0.917[l]		2.28	
	HFAO	−99.99767	0.915		2.12	
	6-31G*	−100.00286	0.917		1.98	
	Exptl		0.917[l]		1.82[j]	
$H_3N\cdots H{-}NH_2$	STO-3G	−110.91690	3.08	5.9[m]	3.6	3.8
	4-31G	−112.20381	3.08	5.9[m]	4.6	4.5
	4-31G(0)	−112.21198	3.31	0.0	4.2	4.1
	HFAO	−112.28767	3.49	0.0		2.7
	6-31G*	−112.37277	3.44	0.0	3.6	2.9
	Exptl					4.5[n]
$H_3N\cdots H{-}OH$	STO-3G	−130.43071	2.91	4.0[m]	3.9	5.9
	4-31G	−132.01805	2.91	4.0[m]	5.4	10.4
	4-31G(0)	−132.02437	2.95	0.0	5.0	9.0
	HFAO	−132.12801	3.12	0.0		5.8
	6-31G*	−132.20491	3.05	0.0	4.3	6.5
$H_3N\cdots H{-}F$	STO-3G	−154.04144	2.77	0.0[m]	4.0	8.3
	4-31G	−156.01309	2.77	0.0[m]	5.7	18.0
	4-31G(0)	−156.01595	2.69	0.0	5.4	16.3
	HFAO	−156.15870	2.75	0.0		11.7
	6-31G*	−156.20634	2.77	0.0	4.7	12.2
$H_2O\cdots H{-}NH_2$	STO-3G	−130.42787	2.89	60.9	2.2	4.1
	4-31G	−132.00687	2.89	60.9	3.0	3.3
	4-31G(0)	−132.01662	3.21	55.0	2.8	4.1
	HFAO	−132.12237	3.41	0.0		2.3
	6-31G*	−132.19912	3.40	68.7	2.0	2.8
$H_2O\cdots H{-}OH$	STO-3G	−149.94139	2.73	58.7	2.8	6.0
	4-31G	−151.82176	2.73	58.7	3.9	9.6
	4-31G(0)	−151.82767	2.87	36.0	4.4	8.1
	HFAO[o]	−151.95768	3.00	25.0		5.3
	6-31G*	−152.03007	2.99	55.0	3.2	5.6
	Exptl		2.98[p]	60[p]	2.6[p]	5.1[q]
$H_2O\cdots H{-}F$	STO-3G	−173.55071	2.63	51.8	3.4	7.5
	4-31G	−175.81126	2.63	51.8	5.3	13.7
	4-31G(0)	−175.81600	2.63	0.0	5.6	13.4
	HFAO[o]	−175.98396	2.72	0.0	5.1[r]	9.4
	6-31G*	−176.02807	2.74	40.4	4.6	9.2
	Exptl		2.68[v]	(0.0)[v,w]	(3.7)[v,w]	
$HF\cdots H{-}NH_2$	STO-3G	−154.03358	2.81	75.1	1.5	3.3
	4-31G	−155.98756	2.81	75.1	2.1	2.0
	4-31G(0)	−155.99557	3.26	80.0	4.9	3.5
	HFAO	−156.14215	3.45	0.0		1.3
	6-31G*	−156.19110	3.38	82.8	1.1	2.6
$HF\cdots H{-}OH$	STO-3G	−173.54583	2.68	72.0	2.0	4.4
	4-31G	−175.79668	2.68	72.0	3.0	4.6
	4-31G(0)	−175.80326	2.97	60.0	3.1	5.4
	HFAO[o]	−175.97396	3.08	52.0	4.3[s]	3.0
	6-31G*	−176.01976	3.11	69.8	2.4	4.0
$HF\cdots H{-}F$	STO-3G	−197.15447	2.57	70.9	2.6	5.5
	4-31G	−199.78434	2.57	70.9	4.3	7.6
	4-31G(0)	−199.78682	2.72	30.0	4.8	7.7
	HFAO[o]	−199.99647	2.88	20.0	4.5[s]	4.6
	6-31G*	−200.01506	2.78	63.0	3.8	5.9
	Exptl		2.79[t]	72[t]	3.0[t]	5–7[u]

Footnotes to Table I

[a] For monomers, R is the X–H distance, θ is the H–X–H angle. For dimers, R is the heavy-atom separation, θ is defined in the text and Figures 1 and 2. [b] E_D = dimerization energy = total energy of dimer minus sum of monomer total energies. In this and subsequent tables, slight discrepancies may occur between E_D values given here and in the original literature, due to recalculation from published total energies using 1 hartree = 627.50916 kcal/mol.[70] Published total energies correspond in some cases to geometries near but not at predicted minima. [c] STO-3G fully optimized, ref 12. [d] 4-31G at STO-3G equilibrium geometries, ref 12. [e] 4-31G optimized, ref 7. Cross checking with P. Kollman and the original computer output led to some slight deviations between these (recommended) values and those of ref 7 and 13. [f] Experimental structure, ref 14 (1969). [g] Hartree–Fock AO Gaussian (minimal) basis, ref 15, unless noted otherwise. Values reported here refer to "unsplit" basis on F, "GLF" basis on NH_3. Dimer dipole moments not available in ref 15 or at Princeton. [h] Experimental structure, ref 16 (1968). [i] 6-31G* optimized, this work. [j] Reference 17. [k] Reference 18. [l] Reference 19. [m] Calculated angle between N–A axis and "center of gravity" axis of NH_3 (see Figures 1 and 2). Assumed to be 0.0° at 4-31G(0), HFAO, and 6-31G* levels. [n] Reference 20. [o] These values were obtained with a slightly inferior HFAO basis, ref 21. Corresponding monomer energies are HF = −99.99457, H_2O = −75.97468. [p] Reference 22. [q] Reference 23. [r] μ calculated at R = 2.65 Å. [s] μ calculated at θ = 0°. [t] Reference 29. [u] References 30 and 31. [v] Reference 69. [w] θ = 0° assumed (see text); μ = 3.7 found assuming planar (θ = 0°) structure. [x] Comparisons with experimental results and previous complete ab initio studies.

Table II. 6-31G* Charge Distributions and Ionization Potentials for First-Row Hydrogen-Bonded Dimers [a]

$H_nB\cdots H{-}AH_m$	δ_{BL}	δ_B	δ_H	δ_A	CT[b]	I[c]	E_D[d]
$H_3N\cdots H{-}NH_2$	0.026	−0.010	0.054	−0.041	0.016	10.66	2.94
$H_2O\cdots H{-}NH_2$	0.016	−0.002	0.033	−0.036	0.018	10.96	2.85
$HF\cdots H{-}NH_2$	0.008	+0.010	0.010	−0.025	0.018	11.21	2.64
$H_3N\cdots H{-}OH$	0.054	−0.032	0.063	−0.064	0.022	12.19	6.48
$H_2O\cdots H{-}OH$	0.032	−0.007	0.042	−0.056	0.025	12.72	5.64
$HF\cdots H{-}OH$	0.013	+0.011	0.012	−0.032	0.024	13.10	3.99
$H_3N\cdots H{-}F$	0.087	−0.054	0.044	−0.078	0.033	12.81	12.20
$H_2O\cdots H{-}F$	0.048	−0.018	0.032	−0.062	0.030	14.78	9.20
$HF\cdots H{-}F$	0.020	+0.012	0.009	−0.041	0.032	16.38	5.86

[a] See text for definitions. All values in electrons unless noted otherwise. Negative δ value indicates excess of electron density compared to monomer value. [b] Charge transfer in the direction $H_nB \rightarrow HAH_m$. [c] In eV. [d] Dimerization energies (kcal/mol) included for comparison.

Table III. Ab Initio Studies of the Water Dimer

Basis	Energy, au	E_D, kcal/mol	Ref[a]
STO-3G counterpoise	−149.93396	4.9	42
STO-3G optimized	−149.94139	6.0	12*
STO-4G	−151.00998	6.1	43
Minimal Gaussian	−151.11887	12.6	44
Bond orbital approximation	−151.30781	8.1	45
Minimal Slater	−151.41730	6.6	46
Minimal Slater	−151.42014	6.1	45
Minimal Slater	−151.42051	6.6	47
4-31G (at STO-3G geometry)	−151.82176	9.6	12*
4-31G (partially optimized)	−151.82767	8.1	7*
4-31G (fully optimized)	−151.83038	8.2	39, 48
HFAO Gaussian	−151.95775	5.3	21, 37*
6-31G	−151.98315	7.8	39
Double ζ "split-out"	−152.01507	7.9	21, 37
6-31G*	−152.03007	5.6	This work*
6-31G*	−152.03043	5.6	39
6-31G**	−152.05598	5.5	39
Extended Gaussian + polarization	−152.09069	4.7	49
Extended Gaussian + polarization	−152.09110	5.0	50
Extended Gaussian + polarization	−152.11167	4.8	51
Extended Gaussian + polarization	−152.11215	5.1	24
Hartree–Fock limit	−152.13781	3.7	52
SCF + CI	−152.52168	6.0	24
Experiment		5.1	23

[a] Entries marked with an asterisk are also given in Table I.

a complete list of literature values (total energies and E_D values) in Tables III (H_2O dimer) and IV (HF dimer), to be discussed below.

Studies on systems other than $(H_2O)_2$ and $(HF)_2$ are relatively few, but are noteworthy. Diercksen[61] has employed a large Gaussian basis, including d functions on heavy atoms and p functions on hydrogen, in studies of H_3NHOH and H_2OHNH_2. Kollman and Allen supplement their HFAO studies[15] on dimers of NH_3 and HF by employing a "split p" basis on fluorine. These and other results are given in Table V.

Comparisons

A. Dipole Moments. The ability of a given level of theory to predict hydrogen-bonding energies is reflected to a considerable degree in its ability to reproduce monomer dipole moments.[7,13] In this regard the 6-31G* basis set is superior to the other basis sets in Table I. For H_2O, for example, the quality of calculated μ values changes from STO-3G (1.78 D) to 4-31G (2.61) to HFAO (2.48) to 6-31G* (2.22) to the Hartree–Fock limit (1.99)[62] to experiment (1.85);[17] for HF, the progression is 1.41 (STO-3G), 2.28 (4-31G), 2.12 (HFAO), 1.98 (6-31G*), 1.94 (HF limit[63]), 1.84 (PNO-CI[38]), 1.82 (exptl[17]). STO-3G μ values are perhaps fortuitously good, and often STO-3G calculations lead to better hydrogen-bond energies than 4-31G; however, deviations between STO-3G and experimental results are not as systematic as those involving 6-31G*, so trends are more reliably given at the higher level.[64]

For dimers, three experimental dipole moments are available: $(H_2O)_2$ = 2.60 D,[22] $(HF)_2$ = 2.99 D,[29] $H_2O\cdots HF$ = 3.68 D[69] (see below). For the first two, agreement with 6-31G* values (3.2, 3.8) is better than with 4-31G (4.4, 4.8), but STO-3G values (2.8, 2.6) are superior to both. For $H_2O\cdots HF$, θ is not well established; assuming θ = 0° leads to μ = 3.68 D, but it is likely that θ is larger (6-31G* gives 40.4°) which would lead to a smaller value of μ.

B. Geometries. There are several factors to consider in comparing dimer geometries predicted at different levels of calculation. First, it is important to examine agreement between calculated and experimental geometries of the monomers in order to assess the overall quality of geometry predictions. Second, the validity of the three assumptions, H bond linearity, fixed monomer geometries, and θ = 0° for NH_3 proton acceptors, should be discussed. Finally, predicted dimer geometries should be compared with experimental and Hartree–Fock values where possible.

Monomer geometries are predicted satisfactorily at all levels, but it is well known[11] that accuracy increases with basis set size. For our purposes, it is most instructive to consider not only differences in geometries, but also *energy* differences between experimental and theoretical equilibrium

Table IV. Ab Initio Studies of the HF Dimer

Basis	Energy, au	E_D, kcal/mol	Ref[a]
STO-3G counterpoise	−197.14968	4.4	42
STO-3G	−197.15016	5.6	53
STO-3G (optimized)	−197.15447	5.5	12*
STO-4G	−198.54876	5.2	54
4-31G (STO-3G geometry)	−199.78434	7.6	12*
4-31G (partially optimized)	−199.78682	7.7	7*
4-31G (fully optimized)	−199.78733	8.0	40
6-31G	−199.97877	7.5	40
HFAO Gaussian	−199.99647	4.6	21*
6-31G*	−200.01506	5.9	This work*
6-31G*	−200.01543	6.0	40
HFAO + CI	−200.01845	5.3	55
6-31G**	−200.03289	6.0	40
Double δ "split p"	−200.03726	6.5	21
Extended Gaussian	−200.04926	6.4	56
Extended Gaussian + polarization	−200.0953	4.6	41
Extended Gaussian + polarization	−200.11989	4.5	57
Extended Gaussian + polarization	−200.13074	3.5	38
PNO-CI (correlation)	−200.54462	3.5	38
CEPA (correlation)	−200.57761	3.4	38
IEPA (correlation)	−200.67541	3.3	38
Experiment		5−7	30, 31

[a] Entries marked with an asterisk are also given in Table I.

Table V. Other ab Initio First-Row Dimer Studies Compared with 6-31G* Results

Dimer	Basis	Energy, au	E_D, kcal/mol	Ref
$H_3N\cdots HOH$	Minimal Slater	−131.564	7.2	58
	Minimal Slater	−131.721	7.7	59
	Extended Slater	−132.079	6.4	58
	Extended Gaussian	−132.17986	7.9	60
	6-31G*	−132.20491	6.5	This work
	Extended Gaussian + polarization	−132.27418	6.3	61
$H_3N\cdots HF$	STO-3G	−154.03816	8.5	53
	Double ζ "split p"	−156.17816	15.9	15
	6-31G*	−156.20634	12.2	This work
$H_2O\cdots HNH_2$	6-31G*	−132.19912	2.8	This work
	Extended Gaussian + polarization	−132.26788	2.3	61
$H_2O\cdots HF$	STO-3G	−173.54581	7.7	53
	6-31G*	−176.02807	9.2	This work
$HF\cdots NHN_2$	Double ζ "split p"	−156.15577	1.4	15
	6-31G*	−156.19110	2.6	This work

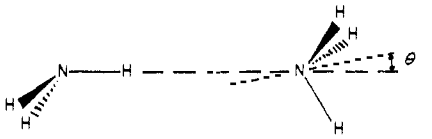


Figure 2. Conformation of NH_3 dimer.

geometries. At STO-3G, the total energy of H_2O at the optimized geometry[12] (r = 0.990, HOH = 100.0) is −74.96590; at the experimental geometry (r = 0.957, HOH = 104.5) the STO-3G energy[65] is −74.96293. The difference is 1.86 kcal/mol. At 4-31G the predicted geometry[66] (r = 0.951, θ = 111.2) is poorer but the energy difference is reduced to 0.78 kcal/mol. At the 6-31G* level,[67] both the predicted geometry (r = 0.948, θ = 105.5) and the energy difference (0.13 kcal/mol) are better still. Similarly, for NH_3 the theoretical vs. experimental geometry energy differences are 0.89 kcal/mol (STO-3G), 2.65 (4-31G), and 0.19 (6-31G*); for HF they are 1.30 (STO-3G), 0.02 (4-31G), and 0.03 (6-31G*). Clearly, the 6-31G* geometries are the most consistently accurate, according to this analysis, assuming experimental geometries for monomers at the 4-31G level may lead to small nonsystematic errors, as has been pointed out by Del Bene.[68]

We do not present the fully optimized STO-3G geometries for the dimers, which are available elsewhere.[12] Instead, we comment on the following features. In the 11 dimers studied (two[35] were considered in more than one rotational conformation), we may consider the deviations between dimer-optimized geometrical parameters and the corresponding monomer-optimized values, in order to assess the distortions undergone upon dimerization. For example, the complete series involves a total of 18 independently varied N–H bonds. STO-3G optimized N–H bond lengths range from 1.031 to 1.035 Å, the average and its standard deviation being 1.032 ± 0.001 Å. This agrees closely with the value of 1.033 obtained by optimizing NH_3 alone, and indicates that, to a first approximation, N–H bond lengths do not change upon dimerization. Bond angles behave similarly: the 18 independent H–N–H angles have values ranging from 103.5 to 105.0°, averaging 104.5 ± 0.5; for the NH_3 monomer, the optimized value is 104.2°. Similar observations apply to H_2O and HF. Thus the assumption of fixed monomer geometries appears to be justified.

At the STO-3G level, most dimers were found[12] to involve slightly nonlinear hydrogen bonds. The deviations from linearity varied from 0.0° ($H_3N\cdots HF$) to 4.3° ($H_3N\cdots HNH_2$), averaging 2.2°. No regular pattern of deviations is seen, but clearly the magnitudes are sufficiently small to be considered negligible.

Finally, the assumption of $\theta = 0°$ for NH_3 proton acceptors may be assessed by examination of Table I. We define the θ value for such dimers as the angle between the N–A axis and the vector obtained by summing the three (nonequivalent) N–H vectors, as shown in Figures 1 and 2. The latter vector corresponds to the NH_3 center-of-gravity axis. If the NH_3 monomer has a local C_3 axis, the two axes coincide, as is the case for $H_3N\cdots HF$. This is not true for $H_3N\cdots HNH_2$ and $H_3N\cdots HOH$, for which the STO-3G values of θ thus defined are 5.9 and 4.0°, respectively. Again, these are sufficiently small deviations to be reasonably approximated as zero.

We mention briefly the studies of Curtiss and Pople[39,40] in which the geometries of $(HF)_2$[40] and $(H_2O)_2$[39] were fully optimized at the 4-31G level. Deviations from monomer geometries were again found to be small. For H_2O, the bond length is calculated to be 0.951 Å, the bond angle 111.2°; in the fully optimized dimer, O–H bond lengths are 0.950, 0.951, and 0.958, and angles are 111.3 and 112.0. For $(HF)_2$, 4-31G values of r_{HF} are 0.927 and 0.925 Å, compared to 0.922 for HF itself. Also, deviations from linearity were found to increase with larger basis sets. For $(HF)_2$, optimized values of the deviation angle were 4.0° (STO-3G), 8.1° (4-31G), 8.2° (6-31G), 15.5° (6-31G*), and 15.3° (6-31G**); for $(H_2O)_2$, corresponding values were 0.4° (STO-3G), 0.0° (4-31G), 0.0° (6-31G), 4.5° (6-31G*), and 3.0° (6-31G**). Polarization functions thus tend to favor nonlinear dimers.

Experimental structures for $(HF)_2$,[29] $(H_2O)_2$,[22,25,26] and $H_2O\cdots HF$[69] (Table I) agree well with the 6-31G* structures. STO-3G structures give surprisingly good values of θ, but predict short internuclear separations, whereas 4-31G values are the opposite, giving acceptable distances but considerably underestimating angles.[68] It has been pointed out,[26] however, that the energy surface is extremely flat with respect to variations of θ, and binding energies are not too sensitive to geometry in this respect. In a recent microwave study of $H_2O\cdots HF$,[69] the observed data suggest either that $\theta = 0°$ or that there is a low barrier to inversion. This is in agreement with the optimized 4-31G result, which gives $\theta = 0°$, but differs from 6-31G*, which predicts $\theta = 40.4°$. However, a single 6-31G* calculation at $\theta = 0°$ implies an inversion barrier of 0.23 kcal/mol, sufficiently low to remain consistent with both 4-31G and experimental results.

C. Dimerization Energies. It is not appropriate to repeat recent discussions[24-28,33] concerning experimental uncertainties, zero-point vibration corrections, and other considerations dealing with experimental dimerization energies. Diercksen et al.[23,24] conclude that a reasonable estimate of E_D for the water dimer is 5.1 ± 0.3 kcal, in excellent agreement with our 6-31G* value (5.6). Less well established experimental estimates of E_D for the HF dimer[30,31] range from 5 to 7 kcal, compared with the 6-31G* value of 5.9. The NH_3 dimer value (4.5)[20] is somewhat higher than the 6-31G* (2.9), but this experimental result is also subject to question.

For internal comparisons, we may examine the values in Tables III to V. Without d functions, the E_D values increase from 5.6 (6-31G*) to 7.8 (H_2O dimer, 6-31G) and 6.0 to 7.5 (HF dimer, 6-31G* → 6-31G). Thus although a more accurate description of nuclear regions improves dimerization energies in going from 4-31G to 6-31G, the flexibility of valence regions must also be improved by adding polarization functions for accurate results. The further addition of polarization functions on hydrogen (6-31G** basis) leads to little change in E_D values.

For the water dimer, correlation and zero-point vibration energies appear to cancel. The near Hartree–Fock dimerization energy found by Diercksen et al.[24] is 5.14 kcal, which is increased to 6.05 by correlation corrections. This value is then decreased to 5.1 by zero-point vibration corrections. For the HF dimer, correlation is less important. Lischka[38] finds a Hartree–Fock dimerization energy of 3.46 kcal, which is raised (in the PNO-CI approximation) to 3.50 by correlation energy differences. Correcting this for zero-point vibration gives 2.90 kcal, which seems to be quite low. This may be due to the assumption of a linear $C_{\infty v}$ geometry for the dimer. The optimized near Hartree–Fock values of 4.47[57] or 6.02[40] kcal appear more reasonable.

Tables III–V illustrate the variation in total energy and E_D values with improvements in basis set. It is clear that dimerization energies do not improve monotonically with decreasing total energy. For $(H_2O)_2$, for example (Table III), many of the minimal-basis E_D values are close to experimental, while split-valence results overestimate E_D by up to 80%. Agreement becomes consistently good at 6-31G* and higher levels. The same is true for $(HF)_2$. In both cases, 6-31G* results are not significantly improved by calculation nearer or beyond the Hartree–Fock limit. For this reason the 6-31G* level appears to be the lowest level capable of consistently[64] providing experimental-quality results, and at the same time it is the highest level yet applied to the complete series of dimers.

Summary

The calculations presented here appear to be internally consistent and of sufficient accuracy to allow deductions of hydrogen-bond energy trends. The 6-31G* basis reproduces dipole moments, geometries, and dimerization energies more satisfactorily than other basis sets which have been applied to the full series of first-row dimers, since polarization functions on heavy atoms appear to be important in such studies. Furthermore, results obtained near but above the Hartree–Fock limit parallel those known experimentally, so that one can realistically draw quantitative as well as qualitative conclusions from these calculated values. Such conclusions will appear in a forthcoming publication.

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Effects of Formal Charge on the Heterogeneous Electron Transfer Rate at a Mercury–Dimethylformamide Interface for a Series of Organic Salts

Tadaaki Kakutani, C. Kenneth White, and Reuben D. Rieke*[1]

Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.

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Abstract: The heterogeneous electron transfer rate at a mercury–dimethylformamide interface was determined by ac polarography for a series of organic salts with a variety of formal charges. Several orders of magnitude difference in electron transfer rates were noted on going from +2 ions to −1 ions with the negatively charged ions having the higher electron transfer rate. These results were interpreted within the Marcus theory as arising primarily from solvation effects.

Since Hoijtink's original report, several papers have appeared regarding the heterogeneous electrochemical electron transfer rates to a wide variety of organic and organometallic compounds in aprotic media.[2-18] In the majority of cases, the results can be explained in terms of Marcus's theories for heterogeneous electron transfer.[19,20] In some cases, comparison with homogeneous electron transfer rates has also been made.[11,22] In the reduction of a series of nitrobenzene derivatives, a remarkably successful correlation has been obtained between kinetic parameters and predictions of the Marcus theory.[19] The results were interpretable in terms of the activation free energy for the heterogeneous electron transfer process coming mainly from reorganization of solvent molecules around the reacting species. Similar tendency has also been shown in the electrochemical kinetics of some quinone derivatives[7] and porphyrin derivatives.[12] Slow electron transfer rates due to major geometrical changes of the molecule being reduced have been observed for cyclooctatetraene,[3,8] phenyl-substituted cyclooctatetraenes,[41,42] stilbene derivatives,[5] and azocines.[9]

The majority of previous data has been limited to the one-electron reduction of neutral molecules (e.g., from neutral compound to anion radical) and anion radicals (e.g., from anion radical to dianion), and only a few papers have been published involving kinetic data for the systems containing a positively charged molecule as a reductant or an oxidant.[13,15,21]

We have applied the ac polarographic method to determine the kinetic parameters for one-electron reduction of some 1,4-diphosphoniacyclohexa-2,5-diene salts, nitrophenyltriphenylphosphonium salts, nitrophenyltrimethylammonium salts, and potassium *p*-nitrophenylacetate at a dropping mercury electrode in *N,N*′-dimethylformamide (DMF). We were particularly interested in determining the effect of formal charge on the electron transfer rate. The recent report that some of the diphosphoniacyclohex-2,5-diene salts show antileukemia activity made the elucidation of their redox properties much more urgent.[43]

Recent electrochemical and ESR studies[23-27] have revealed that in aprotic media the first reduction of the above-mentioned salts can occur in a one-electron step (e.g., from dication to cation radical or from monocation to radical product) and that the reduction product, cation radical, or radical is highly stable in the solvent. Thus the kinetic data on the first reduction of these compounds were obtained by the ac polarographic method. The results are presented here.

Experimental Section

Chemicals. All 1,4-diphosphoniacyclohexa-2,5-diene salts were