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A Model Study of the Interaction of a Hydrogen Bond with a π-Electron System

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A semi-empirical CNDO/2 calculation of the structure of the diimide-hydrogen fluoride hydrogen bonded complex is reported. The results are compared to calculations on a similar saturated system in an attempt to elucidate the effect of a neighboring π-system on a hydrogen bond, and to uncomplexed diimide to study the effect of the hydrogen bond on the π-system.

Introduction

The question of the interaction of π-electron systems with hydrogen bonds has long been of theoretical interest, as entities of this type are not uncommon. In the past few years, there has been a variety of semi-empirical calculations reported on systems of biological importance, such as the base pairs of DNA [1–6], which contain just such π-bond/hydrogen bond units. One problem encountered in such work is that the methods which have been used are of the Pariser-Parr-Pople or Hückel type, and have not taken the coupling of π and hydrogen bond electrons properly into account [5, 7].

With the recent availability of large, very fast computers, problems of this type, such as the DNA base pairs, can now be handled in an *ab initio* fashion [8]. The extreme expense of such calculations makes it desirable to take a middle course, however, and attempt to treat such problems with a semi-empirical, but all valence electron treatment. In this way, it is hoped that the important qualitative features of such valence electron interactions as the π-bond/hydrogen bond interaction can be profitably investigated.

To this end, a CNDO/2 calculation has been carried out on a very simple system containing both a π-bond and a hydrogen bond; namely the diimide-hydrogen fluoride complex. The results of this calculation are compared to calculations on the separated species and on similar non-π-bonded complexes, in order to draw conclusions concerning the effect of a π-bond on a neighboring hydrogen bond and vice versa.

Calculational Method

Recent studies [9] have shown that the all-valence-electron semi-empirical CNDO/2 method works quite well in a semiquantitative sense for describing the properties of hydrogen bonds among first row hydrides. As this method has the two qualities desired for this calculation, namely speed and consideration of all of the valence electrons, and has been shown to give reasonable results, it was used. As the method is well known [10], it will not be described here other than to say it is a semi-empirical, all-valence-electron, SCF-MO method. The program used is a modified version of Dobosh's CNDO/INDO program [11] and employs the CNDO/2 parametrization scheme [10].

Results and Discussion

One of the simplest molecules containing a π-bond which will participate in hydrogen bonding is diimide (HN=NH). Consequently, the diimide-hydrogen fluoride hydrogen bonded complex was chosen as a model system for this study.

Calculations were initially carried out on the HF and N_2H_2 fragments in order to determine their minimum energy geometries and properties. The results obtained for HF are presented in Table 1. It should be noted that the calculated results agree exactly with those previously published [9, 10] except for the stretching force constant, which is reported to be 19.2 mdyn/Å by Pople and Beveridge [10].

For diimide, the N—H and N—N distance, as well as the H—N—N angle (θ) and the internal rotation angle (φ) about the N—N bonds were varied. The minimum energy geometry was found to be the *cis* configuration ($\varphi = 0°$) with $R_{NH} = 1.07$ Å, $R_{NN} = 1.22$ Å, and $\theta = 115.5°$. The molecular parameters calculated at this geometry are given in Table 2.

Table 1. Calculated and experimental properties of HF

	Calculated	Experimental [10]
r_e	1.00 Å	0.917 Å
μ	1.861 D	1.819 D
B.E.	6.771 eV	6.11 eV
I.P.	21.14 eV	15.77 eV
k_{st}	18.92 mdyn/Å	9.6 mdyn/Å
$\left\lvert \frac{\partial\mu}{\partial r} \right\rvert_{av}$	0.0136	—
E_{tot}	−28.436693 a.u.	—

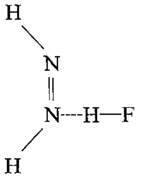
Table 2. Calculated and experimental molecular properties of diimide

	Calculated	Experimental
R_{NH}	1.07 Å	—
R_{NN}	1.22 Å	—
θ	115.5°	—
μ	3.066 D	—
I.P.	13.548 eV	9.85 eV[a]
E_{tot}	− 24.710500 a.u.	—

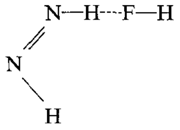
[a] See Ref. [12].

When the barrier to internal rotation was calculated, the *cis* configuration was found to be more stable than the *trans* configuration by 3.44 kcal/mole, with a maximum in the potential at $\varphi = 90°$ which was 67.62 kcal/mole above this *cis* configuration. This result is in agreement with previous semi-empirical calculations [13], but not with more recent *ab initio* results [14], which show the *trans* form to be the most stable. Although it would be nice to agree with more elaborate calculations, agreement is not necessary in this case, since changes in the properties of diimide when it undergoes hydrogen bonding are what are of interest here.

There are two possible structures for the hydrogen-bonded N_2H_2–HF complex, $H_2N_2 \cdot HF$(I) and HNNH · FH(II).



(I)



(II)

A geometry search, holding the N_2H_2 and HF fragments at their previously determined geometries, showed both structures to be stable with respect to the separated fragments, but that structure I was much more stable than structure II. The minimum energy was obtained when the H–F bond bisected the N–N–H angle, and the N–F distance was 2.48 Å. In this configuration (see Fig. 1), the total energy of the complex was found to be −53.172282 a.u., corresponding to a hydrogen bond energy of 15.73 kcal/mole. Small variations of the placement of HF, such that the NHF line deviated from the Z-axis by 10–15°, led to energy changes of considerably less than 1 kcal/mole as long as the N–F distance was kept at 2.48 Å. It thus appears that the HF molecule is only weakly held in place in an angular sense, and considerable thermal wagging may be expected in the complex.

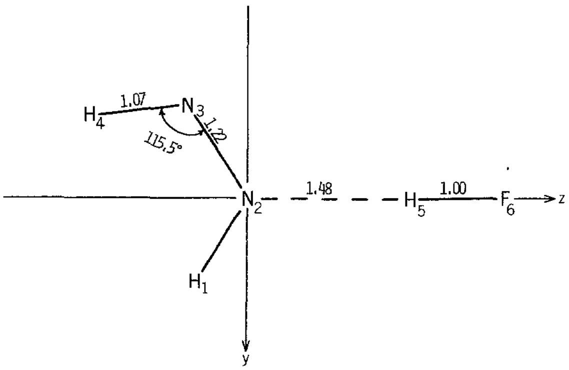


Fig. 1. The minimum energy geometry and coordinate system for N_2H_2–HF

Keeping all other atoms fixed, the hydrogen atom in the bond was moved along the N—F line of centers to obtain the protonic potential curve. This was found to be an asymmetric single well, with an energy minimum at $R_{NH} = 1.48$ Å, which corresponds to $R_{HF} = 1.00$ Å. From the curvature of the potential at the minimum, the quadratic force constant was found to be 17.39 mdyn/Å, and $\left|\frac{\partial\mu}{\partial r}\right|$ to be 2.998. Thus the H—F stretching force constant decreases on hydrogen bond formation, which is the expected result.

Table 3. Density matrix elements between orbitals involved in the N—N π-bond

	N_2H_2	HF	$H_2N_2 \cdot HF$
(N2X, N2X)	1.0000	—	1.0427
(N3X, N3X)	1.0000	—	0.9573
(N2X, N3X)	1.0000	—	0.9991
H_1	0.9615	—	0.9359
N_2	5.0385	—	5.0443
N_3	5.0385	—	5.0079
H_4	0.9615	—	0.9426
H_5	—	0.7737	0.7557
F_6	—	7.2263	7.3136

There are two questions which we now wish to consider. Namely, what is the influence of the hydrogen bond on the π-system of N_2H_2 and what is the influence of the π-system of N_2H_2 on the N—H—F hydrogen bond. Some light can be shed on the first question by consideration of the results presented above. A summary of the density matrix elements for the orbitals involved in the N—N π-bond are presented in Table 3, along with the atomic populations for the various atoms involved. Consideration of the Table shows that hydrogen bonding causes a buildup of charge in the $2p_x$ π-bonding AO of N_2 at the expense of the $2p_x$ orbital charge at N_3 and the bond population. This charge shift is also reflected in the decrease in gross atomic charge on N_3 and increase in net atomic charge on N_2 on hydrogen bond formation. The orbital energy of the N—N π-bonding orbital is -0.6604 a.u. in N_2H_2, but combines in a bonding and antibonding way with the $2p_x$ orbital on F_6 to give a pair of π-orbitals of energies -0.7119 and -0.7009 a.u. in the complex. Thus, the effect of the hydrogen bond on the π-system seems to be to polarize the orbital significantly, and to stabilize it via combination with the $2p_x$ orbital of fluorine. This is just what might be expected from intuitive reasoning.

The question of the effect of the π-system on the hydrogen bond is a much more difficult one to treat. In order to prepare a non-π-bonded system with which the results on $H_2N_2 \cdot HF$ could be compared, a hydrazine-type molecule was considered. Here, hydrogen atoms were added 1.07 Å above and below N_2 and N_3 respectively (see Fig. 1), but all other distances and angles were maintained as in $H_2N_2 \cdot HF$. Thus a complex, $H_4N_2 \cdot HF$ was considered which is as like $H_2N_2 \cdot HF$ as possible, but without the double bond. Because of the desire to maintain similarity with $H_2N_2 \cdot HF$, the N_2H_4 fragment in this complex does not have the hydrazine minimum energy geometry [15].

The energy of the N_2H_4 fragment in the configuration described above was found to be −26.301064 a.u., while that of the $H_4N_2 \cdot HF$ complex was −54.760843 a.u., giving the complex an hydrogen bond energy of 14.49 kcal/mole. Table 4 presents some of the density matrix elements and gross atomic populations of interest.

Table 4. Density matrix elements and atomic populations involved in the N---H—F bond

	$H_4N_2 \cdot HF$	$H_2N_2 \cdot HF$
(H5S, F6X)	0.3660	0.3661
(H5S, F6Z)	−0.8448	−0.8447
(H5S, N2S)	0.1691	0.1781
(H5S, N2Z)	0.2447	0.2448
(N2X, N2X)	1.1670	1.0427
(N3X, N3X)	1.1579	0.9573
(N2X, N3X)	0.2051	0.9991
(F6S, N2S)	−0.0615	−0.0642
(F6Z, N2Z)	0.1126	0.1148
(N2S, N2S)	1.4569	1.5447
(N2Z, N2Z)	1.3801	1.3949
N2	5.0681	5.0443
H5	0.7544	0.7557
F6	7.3140	7.3136
ΔE (kcal/mole)	−14.49	−15.73

The most striking feature of Table 4 seems to be the excellent agreement between the two cases. That is, it seems that the breaking of the π-bond between N_2 and N_3 has remarkably little effect on the hydrogen bond, except for the 2*s* orbital population on N_2 which decreases by ~0.1 electron. Thus the 1sH-2sN interaction becomes less bonding, as reflected in the lower (H5S, N2S) density matrix element. This destabilization is slight, however, and the hydrogen bond energy is decreased by only 1.24 kcal/mole. The remarkable lack of influence of the π-bond on the hydrogen bond is most probably due to the nearly constant gross charge distribution in the two cases, and consequent nearly equivalent electrostatic contribution to the hydrogen bond. For example, the HF fragment has a gross population of 8.0685 in $H_4N_2 \cdot HF$, and of 8.0693 in $H_2N_2 \cdot HF$.

It appears then that the effect of a π-bond on an adjacent hydrogen bond is small, and consists primarily of a destabilization with respect to an equivalent non-π-bonded case. The opposite effect, that of the hydrogen bond on the π-system, seems to be much more pronounced, and consists primarily of polarization and stabilization of the delocalized bond.

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References

1. Pullman, A., Pullman, B.: Biochim. biophysica Acta **36**, 343 (1959).
2. Hoffman, T. A., Ladik, J.: Advances chem. Physics **7**, 84 (1964).
3. Ladik, J., Appel, K.: Theoret. chim. Acta (Berl.) **4**, 132 (1966).
4. Rein, R., Ladik, J.: J. chem. Physics **40**, 2466 (1964).
5. — Harris, F. E.: J. chem. Physics **42**, 2144 (1965).
6. Lunnell, S., Sperber, G.: J. chem. Physics **46**, 2119 (1967).
7. Sabin, J. R.: Int. J. quant. Chemistry **2**, 23 (1968).
8. Clementi, E., Mehl, J., Niessen, W. von: J. chem. Physics **54**, 508 (1971).
9. Kollman, P. A., Allen, L. C.: J. Amer. chem. Soc. **92**, 753 (1970).
10. For a full description of the method and reference to the original literature, see Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970.
11. Dobosh, P. A.: Program CNINDO, No. 141 from the Quantum Chemistry Program Exchange, Bloomington, Indiana.
12. Foner, S. N., Hudson, R. L.: Advan. chem. Ser. **36**, 34 (1962).
13. Gordon, M. S., Fischer, H.: J. Amer. chem. Soc. **90**, 2471 (1968).
14. Wong, D. P., Fink, W. H., Allen, L. C.: J. chem. Physics **52**, 6291 (1970). See this paper for a bibliography of recent calculations on N_2H_2.
15. For an *ab initio* determination of the structure of hydrazine see: Fink, W. H., Pan, D. C., Allen, L. C.: J. chem. Physics **47**, 895 (1967), and references contained therein.

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