NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2196—2197(1972)

CNDO/2 Calculations of Hydrogen Bonding; Phenol- and *p*-Nitrophenol-Ammonia Systems

Akio MATSUYAMA and Akira IMAMURA
Biophysics Division, National Cancer Center Research Institute, Tokyo 104

(Received July 24, 1971)

Detailed information on the double minimum potential curve for the proton of a hydrogen-bonded complex is especially useful for understanding the nature of hydrogen bonding and of great interest in connection with many biological problems. Baba, Matsuyama, and Kokubun showed[1] that in the *p*-nitrophenol–triethylamine system the second potential minimum which corresponds to an ion pair becomes stable upon excitation, while unstable in the ground state. On the other hand, recent development of the semi-empirical MO method which can treat all valence electrons has made it possible to calculate directly the potential energy curve of a rather complicated hydrogen-bonding system. Along this line, the CNDO/2 method[2,3] has been applied recently to some simple hydrogen-bonding systems[4] and guanine–cytosine base pair.[5] The main purpose of the present study was to see whether the CNDO/2 method can explain successfully the previous experimental results or not. Owing to the limited capacity of the computer used, ammonia was used as a proton acceptor instead of triethylamine throughout the calculations. However, this does not seem to have caused any essential effects.

Method of Calculation

The method of calculation was the same as described previously.[6] Molecular constants of phenolic compounds were taken from the results of X-ray diffraction analysis,[7] ammonia being assumed to be tetrahedral. Proton-donor and -acceptor molecules were arranged as shown in Fig. 1. In order to obtain the hydrogen-bonding energies and potential energy curves for the hydroxyl proton, the total energies of the hydrogen-bonded complexes were calculated at intervals of 0.1 or 0.2 Å of the O···N and O–H distances, respectively.

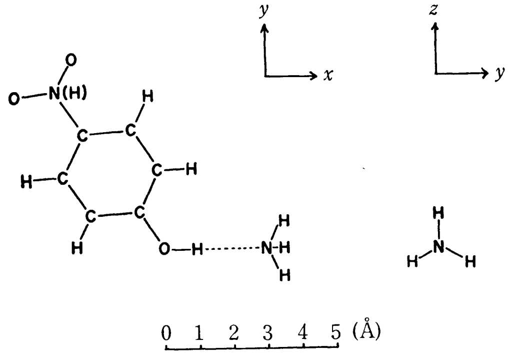

Fig. 1. Molecular arrangement of *p*-nitrophenol or phenol and ammonia.

Results and Discussion

First the total energies of the two hydrogen-bonded complexes, phenol–ammonia and *p*-nitrophenol–ammonia, were calculated as a function of the O···N distance. Distinct minima of the energies were obtained at 2.6 Å for both complexes. The hydrogen-bonding energies were found to be 10.2 and 11.1 kcal for phenol- and *p*-nitrophenol–ammonia complexes, respectively. These values seem to be slightly larger than those reported as the usual hydrogen-bonding energy.[8] However, the stronger proton-donating power of *p*-nitrophenol can be reasonably predicted by the present calculations.

Next, the potential energy curves for the hydroxyl proton in both the ground and excited states were calculated by varying the coordinate of the proton, keeping the O···N distance constant. The O···N distance of 3.0 Å was used instead of the calculated value (2.6 Å), since the latter seems to be short for the hydrogen-bonding distance related to a weak base such as ammonia.[8] The potential energy curves in the excited states were obtained using the ground state wave functions in the virtual orbital approximation. Although the CNDO/2 method is recognized as unreliable for the interpretation of electronic spectra, it should be noted that the energy concerned is not an absolute value but a relative one on varying the coordinate of the proton. Kroto and Santry[9] have shown that this virtual orbital approximation can predict successfully conformations of molecules in the excited state. These facts will permit us to adopt this procedure as a first approximation. The total energies in the ground and excited states are plotted against the coordinate of the proton in the phenol–ammonia system in Fig. 2. With regard to the excited states, only the lowest states of a (π,π^*) type are shown. In addition to potential minima at 1.0 Å, distinct shoulders

---

[1] H. Baba, A. Matsuyama, and H. Kokubun, *Sepctrochim. Acta*, **25A**, 1709 (1969).

[2] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, S136 (1965).

[3] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[4] A. S. N. Murthy, R. E. Davis, and C. N. R. Rao, *Theoret. Chim. Acta*, **13**, 81 (1969).

[5] A. C. Blizzard and D. P. Santry, *J. Theoret. Biol.*, **25**, 461 (1969).

[6] A. Imamura, H. Fujita, and C. Nagata, This Bulletin, **42**, 3118 (1969).

[7] P. Coppens and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 654 (1965).

[8] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San Francisco, Calif., (1960).

[9] H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 792 (1967).

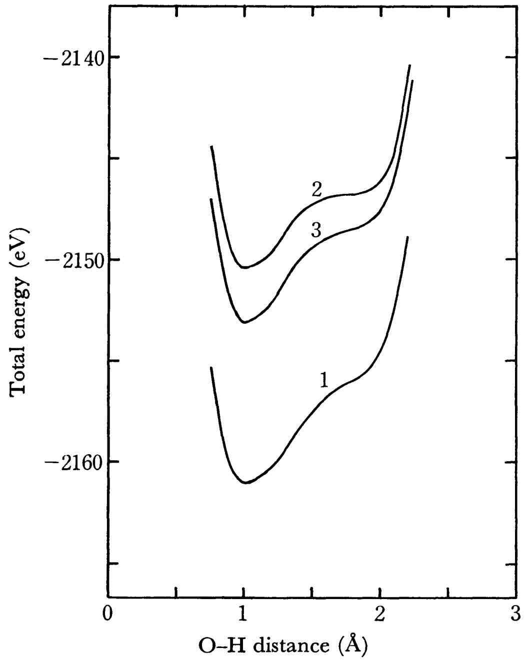

Fig. 2. Variations of the total energies in the ground and excited states of a phenol–ammonia complex as a function of the coordinate of the hydroxyl proton. 1; ground state, 2; the lowest singlet-excited state, 3; the lowest triplet-excited state.

or minima are found at 1.8 Å in all curves, which correspond to a proton-transferred species or an ion pair. The ion pair is unstable in both the ground and excited states, apparently due to the use of ammonia instead of more basic triethylamine as proton acceptor. It is evident, however, that the ion pair becomes less unstable upon excitation. Similar curves were obtained also for the *p*-nitrophenol–ammonia system. This finding is in qualitative agreement with the experimental evidence that the ion pair is more stable than the hydrogen-bonded complex in the singlet-excited state of *p*-nitrophenol–triethylamine system, but less stable in the ground state.[1]

Table 1. The energy differences between the hydrogen-bonded complex and ion pair

State	Energy difference (eV)	
	Phenol–Ammonia	*p*-Nitrophenol–Ammonia
Ground state	5.082	4.686
Singlet-excited state	3.574	3.697
Triplet-excited state	4.001	4.417

The energy differences between the hydrogen-bonded complex and ion pair in the ground and excited states are summarized in Table 1. The values indicate the differences between the total energies at the O–H distances of 1.8 and 1.0 Å. In the ground state, the energy differences are 5.082 and 4.686 eV for phenol and *p*-nitrophenol complexes, respectively. Greater lowering of the second potential minimum in the *p*-nitrophenol system can be reasonably interpreted in terms of the stronger acidity of the molecule. In both systems the energy differences in the singlet-excited state are smaller than those in the triplet-excited state, *viz.*, the ion pair is more stable in the singlet state than in the triplet state. This is consistent with the fact that the acidity of a phenolic compound is in general weaker in the triplet-excited state than in the singlet-excited state.[10]

In conclusion, it can be said that the present calculations could explain at least qualitatively the following experimental results: Existence of the second potential minimum, lowering of the minimum in the excited state, greater lowering in the singlet-excited state than in the triplet-excited state and a stronger proton-donating power of *p*-nitrophenol.

The authors wish to thank Dr. Chikayoshi Nagata of our Laboratory and Professor Hiroaki Baba of Hokkaido University for their helpful discussions and encouragement.

---

[10] G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961).