

# INDO and MINDO/2 study of hydrogen-bonded systems

\*A. A. HASANEIN and <sup>b</sup>I. HUBAČ

<sup>a</sup>Department of Chemistry, Faculty of Science,  
Alexandria University, Alexandria, Egypt

<sup>b</sup>Department of Biophysics, Faculty of Natural Sciences,  
Komenský University, 816 31 Bratislava

Received 4 June 1979

Accepted for publication 1 September 1980

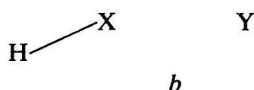
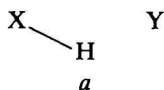
The INDO and MINDO/2 methods are used to calculate the energies of intra- and intermolecular H bonds in 1,2-, 1,3-, 1,4-butanediols and the MeOH...OEt<sub>2</sub>, MeOH...NMe<sub>3</sub> H-bonded systems. The results are discussed in relation to experimentally obtained values.

Методы INDO и MINDO/2 использованы для вычислений энергий внутри- и межмолекулярных водородных связей в 1,2-, 1,3-, 1,4-бутандиолах и в системах MeOH...OEt<sub>2</sub>, MeOH...NMe<sub>3</sub>. Результаты обсуждаются относительно экспериментальным данным.

During the last 15 years the hydrogen bond (H bond) has been a subject of intensive quantitative quantum chemical research. The properties and wide variety of H-bonded systems have been calculated by various quantum chemical methods. For detail information in this respect we refer the reader to the paper by *Schuster* [1]. Of the semiempirical MO methods the CNDO/2 method is the most extensively applied to the study of H bond [1]. In this paper we report on the INDO and MINDO/2 calculation of intramolecular H bonds in 1,2-, 1,3-, and 1,4-butanediols and intermolecular H bonds in the MeOH...OEt<sub>2</sub> and MeOH...NMe<sub>3</sub> systems.

## Method of calculation

The calculations were carried out using CNDO/2, INDO, and MINDO/2 programs [2] with standard parametrization [3—7]



The experimental molecular geometries and structural parameters [8] are used. The intermolecular H-bond energy is taken to be the calculated interaction energy at the equilibrium intermolecular distance while the intramolecular H-bond energy is taken to be the difference in energy of system when the H bond does exist and the energetically most closest system when H bond does not exist (see structures *a* and *b* shown above).

## Results and discussion

The H-bond interactions in 1,2-, 1,3-, 1,4-butanediols and in the MeOH...OEt<sub>2</sub> and MeOH...NMe<sub>3</sub> systems were studied in detail earlier [9–11] using the CNDO/2 method. The intermolecular H bonds are assumed to form a linear X—H...Y conformation. Complete potential energy curves for the approach of proton donor molecule toward the proton acceptor molecule are calculated [9–11]. For butanediols a detailed analysis of conformation has been discussed [10, 11] and potential energy curves showing the most preferable conformations for the intramolecular H bonds are also calculated together with the proton potential functions within the O—H...O part of the molecules.

In the calculations presented here, potential energy curves are not reproduced again, but we rather make use of the equilibrium distance obtained before [9–11]. This may indicate that we assume the equilibrium distances to be the same in the three approximations (CNDO/2, INDO, and MINDO/2) which probably is not true due to the difference in the intimate structure of the three approximations. As has been shown [12], the CNDO/2 method satisfactorily reproduces bond angles, bond lengths, and bending but not stretching force constants for a large number of molecules. The same agreement with experiment has been obtained at the INDO level and equally good values for bond distances and force constants are provided by the MINDO/2 method [12].

### INDO calculations

The total energy of 1,2-butanediol having a conformation with H bond and with O...O and H...O distances of  $2.46 \times 10^{-10}$  and  $1.75 \times 10^{-10}$  m, respectively is calculated to be  $-185421.76 \text{ kJ mol}^{-1}$ , with a dipole moment of  $13.10 \times 10^{-30}$  Cm. When the molecule is present in the conformation without H bond, the total energy is calculated to be  $-18541.80 \text{ kJ mol}^{-1}$  with a dipole moment of  $10.40 \times 10^{-30}$  Cm. This indicates that the dipole moment decreases on H-bond formation and the calculated stabilization energy due to the H bond is  $10.95 \text{ kJ mol}^{-1}$ .

The total energy of 1,3-butanediol having a conformation [10] with O...O distance of  $2.51 \times 10^{-10}$  m is calculated to be  $-185425.80 \text{ kJ mol}^{-1}$  when it is

H-bonded with H...O distance of  $1.65 \times 10^{-10}$  m and a dipole moment of  $13.10 \times 10^{-30}$  Cm. If the H bond does not exist the calculated total energy and dipole moment are found to be  $-185411.35$  kJ mol $^{-1}$  and  $7.80 \times 10^{-30}$  Cm, respectively. This amounts to a decrease in dipole moment on H-bond formation and a stabilization energy of  $14.45$  kJ mol $^{-1}$ .

In the case of 1,4-butanediol in conformation [10] with the O...O distance of  $2.51 \times 10^{-10}$  m, the total energy is calculated to be  $-185460.49$  kJ mol $^{-1}$  when it is H-bonded with the H...O distance of  $1.53 \times 10^{-10}$  m. For the non-H-bonded case the total energy is calculated to be  $-185428.53$  kJ mol $^{-1}$ . This amounts to the H-bond stabilization energy of  $31.96$  kJ mol $^{-1}$ . The dipole moment decreases from  $13.94 \times 10^{-30}$  to  $3.33 \times 10^{-30}$  Cm on H-bond formation.

For the MeOH...OEt $_2$  system with the O...O distance of  $2.59 \times 10^{-10}$  m and the H...O distance of  $1.63 \times 10^{-10}$  m and with a linear O—H...O H bond, the total energy is calculated to be  $-211468.86$  kJ mol $^{-1}$  with a dipole moment of  $12.20 \times 10^{-30}$  Cm. If this value is compared with the calculated values for the individual molecules given in Table 1, the value of  $46.28$  kJ mol $^{-1}$  for the calculated H-bond stabilization energy is obtained.

Table 1

INDO and MINDO/2 results

System	INDO		MINDO/2		
	<i>E</i> kJ mol $^{-1}$	$\mu$ 10 $^{-30}$ Cm	<i>E</i> kJ mol $^{-1}$	$\Delta H$ kJ mol $^{-1}$	$\mu$ 10 $^{-30}$ Cm
MeOH	- 72340.80	6.33	- 48723.78	- 27.85	8.37
Et $_2$ O	- 139081.78	5.37	- 95204.89	- 13.27	7.27
Me $_3$ N	- 101953.23	4.90	- 70719.98	+ 322.22	6.70
MeOH...OEt $_2$	- 211468.86	12.20	- 143753.73	+ 58.17	16.40
MeOH...NMe $_3$	- 174345.48	12.50	- 119354.08	+ 384.09	15.34

Similarly, with a linear O—H...N H bond where the O...N and H...N distances are  $2.59 \times 10^{-10}$  and  $1.63 \times 10^{-10}$  m, respectively, the total energy of the MeOH...NMe $_3$  system calculated is  $-174345.48$  kJ mol $^{-1}$  with a dipole moment of  $12.50 \times 10^{-30}$  Cm. Comparing with the total energies of the individual molecules given in Table 1, the calculated H-bond stabilization energy is found to be  $51.45$  kJ mol $^{-1}$ .

The INDO calculated H-bond energies together with the experimental values for butanediols [13] and the MeOH...OEt $_2$  [14] and MeOH...NMe $_3$  [15] systems are given in Table 2. The results show that the INDO method is successful in predicting

Table 2

INDO calculated H-bond energies and experimental values for butanediols and the MeOH...OEt<sub>2</sub> and MeOH...NMe<sub>3</sub> systems

System	H bond (kJ mol <sup>-1</sup> )	
	INDO	Exp
1,2-Butanediol	10.96	3.19 ± 1.68 <sup>a</sup>
1,3-Butanediol	14.45	5.67 ± 0.42 <sup>a</sup>
1,4-Butanediol	31.96	12.60 ± 0.84 <sup>a</sup>
MeOH...OEt <sub>2</sub>	46.28	19.74 ± 0.42 <sup>b</sup>
MeOH...NMe <sub>3</sub>	51.45	31.50 ± 2.10 <sup>c</sup>

a) Ref. [13]; b) Ref. [14]; c) Ref. [15].

the relative H-bond strength in the systems studied. Irrespective of the overestimation in the INDO calculated H-bond energies, it is also clear that the agreement with experimental H-bond enthalpies is reasonable. However, the calculated H-bond energy is particularly sensitive to molecular conformations adopted by the molecules and the molecular geometries dealt with and the accuracy of the experimentally obtained values of the H-bond energy has to be taken into consideration.

### MINDO/2 calculations

The MINDO/2 calculated heats of formation and total energies for butanediols with the same geometrical and conformational conditions as used in the INDO calculations are given in Table 3. It is expected that the H-bonded conformations will be more stable than the non-H-bonded ones, when comparing either the calculated total energies or heats of formation. As seen from our results the

Table 3

MINDO/2 calculated heats of formation and the total energies for butanediols

System	Conformation without H bond			Conformation with H bond		
	<i>E</i> kJ mol <sup>-1</sup>	$\Delta H$ kJ mol <sup>-1</sup>	$\mu$ 10 <sup>-30</sup> Cm	<i>E</i> kJ mol <sup>-1</sup>	$\Delta H$ kJ mol <sup>-1</sup>	$\mu$ 10 <sup>-30</sup> Cm
1,2-Butanediol	-125332.91	-14.95	13.40	-125291.54	+22.22	17.64
1,3-Butanediol	-125335.47	-17.51	8.87	-125254.71	+63.25	16.74
1,4-Butanediol	-125311.62	+6.34	3.70	-125239.80	+78.12	17.94

reversed result is obtained for the MeOH...OEt<sub>2</sub> and MeOH...NMe<sub>3</sub> H-bonded systems shown in Table 1.

As it is known the MINDO/2 method was parametrized to give the heats of formation. Dewar *et al.* [4—7] have calculated the heats of formation of a large number of hydrocarbons with a good accuracy. Most of these calculations required the use of an artificially lowered nuclear-nuclear repulsion term. Such an approximation usually results also in unrealistically low values for the bond distances and one has to choose between the method that gives good heats of formation and poor bond distances and *vice versa* [12]. This problem may be related to the fact that the changes in correlation energy were neglected. This together with the fact that we are using experimentally obtained bond distances and angles may be responsible for the poor prediction of heats of formation of the H-bonded systems.

*Acknowledgements.* The facilities made available at the ICL 1905 computer centre, Cairo University and the PDP 11 computer centre, Alexandria University supported financially by the Faculty of Science, Alexandria University are very much appreciated.

## References

- Schuster, P., in *The Hydrogen Bond*. (Schuster, P., Zundel, G., and Sandorfy, C., Editors.) North Holland, Amsterdam, 1976.
- Čársky, P., private communication.
- Pople, J. A., Santry, D. P., and Segal, G. A., *J. Chem. Phys.* 43, S 136 (1965).
- Dewar, M. J. S. and Haselback, E., *J. Amer. Chem. Soc.* 92, 590 (1970).
- Bodor, N., Dewar, M. J. S., Harget, A., and Haselback, E., *J. Amer. Chem. Soc.* 92, 3854 (1970).
- Dewar, M. J. S. and Klopman, G., *J. Amer. Chem. Soc.* 89, 3089 (1967).
- Baird, N. C. and Dewar, M. J. S., *J. Chem. Phys.* 50, 1262 (1969).
- Tables of Interatomic Distances and Configurations of Molecules and Ions*. The Chemical Society, London, 1965.
- Hasanein, A. A., Kováč, Š., and Hubač, I., *J. Mol. Struct.* 22, 308 (1974).
- Hasanein, A. A. and Kováč, Š., *J. Mol. Struct.* 22, 457 (1974).
- Hasanein, A. A., *Ph.D. Thesis*. Slovak Technical University, Bratislava, 1974.
- Klopman, G. and O'Leary, B., *Fortschr. Chem. Forsch.* 15, 445 (1970).
- Fishman, E. and Chen, T., *Spectrochim. Acta, Part A*, 25, 1231 (1969).
- Iskeep, R. G., Dickson, F. E., and Kelliher, J. M., *J. Mol. Spectrosc.* 4, 477 (1960).
- Field, M., Swiniarski, M. F., and Holmes, R. R., *Inorg. Chem.* 9, 839 (1970).

Translated by I. Hubač