# ALL VALENCE ELECTRONS LCAO–MO–SCF STUDIES OF HYDROGEN BONDING. CNDO/2 AND INDO CALCULATIONS OF THE INTRAMOLECULAR HYDROGEN BONDING IN 5-SUBSTITUTED FURFURYL ALCOHOLS

AHMED A.HASANEIN and Š.KOVÁČ

*Institute of Organic Chemistry,*
*Slovak Institute of Technology, 880 37 Bratislava 1*

Received November 5th, 1973

The properties of hydrogen bonding in furfuryl alcohol, 5-nitro- and 5-methylfurfuryl alcohols have been investigated using both the CNDO/2 and INDO methods. Both methods have predicted the same correlation of relative hydrogen bonding strengths in compounds studied.

Many theoretical approaches have been used to investigate the nature of hydrogen bonding[1,2]. Schuster[3,4] has successfully applied CNDO/2 and INDO MO methods to numerous structures with hydrogen bonding of different strengths. Abha and coworkers[5] reported that the CNDO/2 method proved to give more realistic proton potential function than the EHT method. Some intramolecularly hydrogen-bonded systems have been investigated using also CNDO/2[6–8], where a good agreement between calculated and experimental hydrogen bonding enthalpies have been found. Both INDO and the CNDO/2 methods have been used extensively for investigating intermolecular hydrogen bonding[9–11].

Gordon and Tallman have presented a method[12] for investigating the nature of inter- and intramolecular hydrogen bonding utilizing INDO localized MO's of the fully geometry-optimized molecules.

Here, the intramolecular hydrogen bonding in furfuryl alcohol and some of its derivatives have been studied by CNDO/2 and INDO methods.

## CALCULATIONS

The calculations have been carried out on the IBM 7040 computer using a Fortran IV program written for the CNDO/2, INDO and MINDO methods[13] in which the same mathematical formalism and parametrization scheme developed by Pople and coworkers[14–16] has been used. The geometry of the furane part in compounds studied is assumed to be the same as reported for furane[17] while the bond lengths and angles of the hydroxymethyl part are assumed to be as follows: C—C = 1·55 Å, C—O = 1·431 Å, O—H = 0·97 Å, C—H = 1·097 Å, ∢ CCH =

* Permanent address: Department of Chemistry, Faculty of Science, Alexandria University, Egypt.

= 109·7 Å and ∢ HCH = 109·7 Å (ref.[18]). As assumed before[8], the enthalpy of hydrogen bonding formation can be obtained by comparing the total energy of the system having two conformations *A* and *B* with the angle $\delta$ equal to 0° and 180°, respectively (Fig. 1).

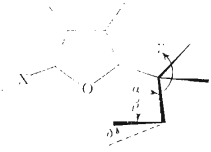

FIG. 1
Dreiding Molecular Model of Furfuryl Alcohol Derivatives

## RESULTS AND DISCUSSION

The total energy of furfuryl alcohol is calculated as a function of the angle $\alpha$, where the side chain is taken to be in the same plane as the furane ring and the angle $\beta$ is kept constant (106·3°). The energy of the system showed a minimum value at $\alpha$ = 111·5° with an O···O distance of 2·63 Å (Fig. 2). Keeping the $\alpha$ angle constant (111·5°) the total energy of furfuryl alcohol is then minimized as a function of the $\beta$ angle where the energy minimum is at $\beta$ = 106°. The effect of free rotation of the hydroxymethyl group around the bond joining it with the furane ring on the energy of the system is studied for small rotations. The results make it clear that the most stable conformation is when $\gamma$ = 0° (Fig. 2). Then the angles $\alpha$, $\beta$ and $\gamma$ being kept

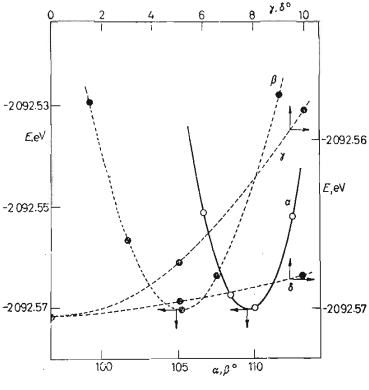


FIG. 2
Total Energy of Furfuryl Alcohol Calculated as a Function of $\alpha$, $\beta$, $\gamma$ and $\delta$ Angles

constant at their equilibrium values, the total energy is optimized as a function of the $\delta$ angle. An increase in angle leads to an increase in the total energy of the system and then to a decrease again until the value $\delta = 180°$. Since by calculation the two angles $\gamma$ and $\delta$ have equilibrium values equal to zero the proton of the hydroxyl group is directed toward the furane oxygen, we can deduce that the proton is equally interacting with the two lone pairs of electrons located on the oxygen atom of the furane ring. These obtained optimum values of $\alpha$, $\beta$, $\gamma$ and $\delta$ angles have been taken to be the same for the side chain in 5-nitro- and 5-methylfurfuryl alcohols. Conformation *B* was found to be more stable than *A* in all cases. This may indicate that the CNDO/2 method predicts that there is no hydrogen bonding interaction in either of the three compounds. On the other hand, the INDO method shows weak hydrogen bonding interactions indicated by the energy differences obtained: 0·32, 0·35 and 0·09 kcal/mol in furfuryl alcohol, 5-methyl- and 5-nitrofurfuryl alcohol derivatives, respectively (Table I). However, in all the compounds studied, the CNDO/2 method has given an equilibrium O—H bond length of 1·03 Å in both conformations *A* and *B* the latter being less stable than the former by 0·36, 0·38 and 0·30 kcal/mol for furfuryl alcohol, 5-methyl- and 5-nitrofurfuryl alcohol derivatives, respectively. This indicates that the method gives an energy difference between hydrogen bonded and nonbonded conformations, which is larger if calculated equilibrium O—H bond length 1·03 Å is used than when its approximate experimental bond length is taken 0·97 Å. This has been also found before[8]. It was thought that optimization of the $\alpha$ and $\beta$ angles in conformation *B* was necessary and might affect the CNDO/2

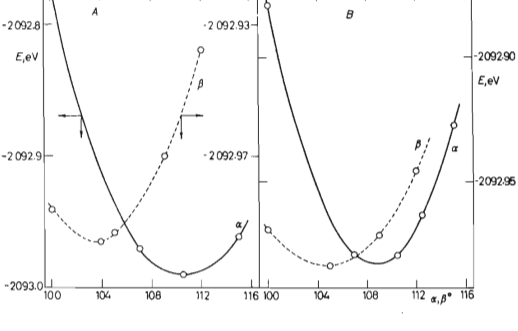


FIG. 3

Optimization of the $\alpha$ and $\beta$ Angles in Furfuryl Alcohol for Conformation *A*, Conformation *B*

prediction of hydrogen bonding energy when O—H is taken as 0·97 Å. A second optimization of the parameters $\alpha$, $\beta$ and also the O—H bond in both conformations *A* and *B* of furfuryl alcohol is then performed, starting with optimum values obtained before and keeping the angles $\gamma$ and $\delta$ at zero (Fig. 3 and 4). Different new equilibrium values of these parameters are obtained for each conformation but *A* is again less stable than *B* when O—H = 0·97 Å and more stable by 0·26, 0·24 and 0·08 kcal/mol, when O—H = 1·03 Å in case of furfuryl alcohol and 5-methyl- and 5-nitro-furfuryl alcohol derivatives, respectively. In comparison with the ex-

TABLE I

Energy and Dipole Moments of Conformations *A* and *B* of Furfuryl Alcohol (*I*), Its 5-Methyl (*II*) and 5-Nitro (*III*) Derivatives

| No | Method | *A* | | *B* | |
|---|---|---|---|---|---|
| | | *E*, eV | $\mu$, D | *E*, eV | $\mu$, D |
| *I* | CNDO/2 | −2 092·753 | 2·610 | −2 092·767 | 2·452 |
| | INDO[a] | −2 012·031 | 2·642 | −2 012·018 | 2·329 |
| *II* | CNDO/2 | −2 329·655 | 2·659 | −2 329·664 | 3·603 |
| | INDO[b] | −2 241·955 | 2·747 | −2 241·940 | 2·113 |
| *III* | CNDO/2 | −3 394·148 | 5·043 | −3 394·158 | 7·283 |
| | INDO[c] | −3 254·326 | 4·792 | −3 254·322 | 6·962 |

The enthalpy, $-\Delta H$, was found to be [a] 0·323 kcal/mol, [b] 0·335 kcal/mol, and [c] 0·085 kcal/mol.

TABLE II

Charges on Interacting Atoms >O...H—O—R (Multiplied by $10^5$) in Conformations *A* and *B* (in Parentheses) of Furfuryl Alcohols *I*—*III*

$r_{OH}$ for CNDO/2 and INDO calculations taken as 1·03 Å and 0·97 Å, respectively.

| No | Method | >O | H | —O— |
|---|---|---|---|---|
| *I* | CNDO/2 | −16 274 (−14 999) | 14 772 (12 558) | −24 964 (−23 000) |
| | INDO | −19 178 (−17 900) | 17 475 (16 039) | −30 922 (−29 421) |
| *II* | CNDO/2 | −17 523 (−16 257) | 14 695 (12 430) | −25 084 (−23 063) |
| | INDO | −20 355 (−19 083) | 17 348 (15 862) | −30 950 (−29 395) |
| *III* | CNDO/2 | −14 767 (−13 407) | 15 458 (13 478) | −24 225 (−22 465) |
| | INDO | −17 303 (−15 959) | 17 914 (16 671) | −28 794 (−30 116) |

perimental value of the enthalpy of intramolecular hydrogen bonding formation in furfuryl alcohol, 0·46 kcal/mol, obtained from IR spectral data[19], it can be concluded that the INDO method is predicting better results than CNDO/2 in the systems investigated. The strongest hydrogen bonding calculated for 5-methyl derivative is in accordance with the electronic effects of the substituents attached to the furane ring. Changes in the charges on hydrogen and the two oxygen atoms forming the hydrogen bonding in going from conformation *B* to conformation *A* are shown in Table II. Not only is the O—H···O part the molecule affected but changes on all the atoms are also observed. Both the CNDO/2 and INDO methods are giving nearly the same results. It seems as if the O—C—C—O part of the molecule has gained a negative charge from the rest of the molecule including the proton situated between the two oxygen atoms. This is not consistent with the expected changes on hydrogen bonding formation. Similar changes have also been found by CNDO/2 study of some intermolecularly hydrogen bonded systems[20–22] where an increase of the positive charge on hydrogen and negative charges and X and Y atoms have been observed. This may indicate that the CNDO/2 and INDO methods are not well predicting changes of atomic charges on hydrogen bonding formation in such systems.

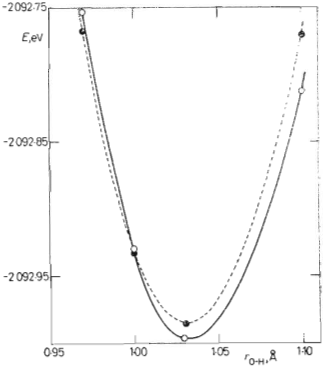


FIG. 4

Total Energy Furfuryl Alcohol Calculated as a Function of O—H Bond Length in Both Conformations *A* (———) and *B* (- - - - -)

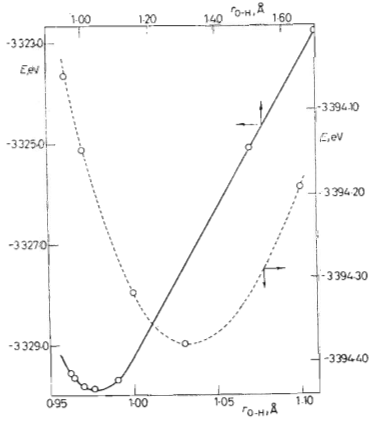


FIG. 5

Proton Potential Function for 5-Nitro- (- - - -) and 5-Methylfurfuryl Alcohol (———)

*The proton potential function.* The total energy of the systems studied has been calculated by the CNDO/2 method as a function of the O—H bond length, keeping the O···O distance constant at its equilibrium value of 2·63 Å. In all cases a single minimum proton potential function is obtained having a minimum energy value at O—H = 1·03 Å and O···H— distance of 1·90 Å (Fig. 4 and 5). A structure, in which the proton is located at nearly equal distance from the two oxygen atoms, was found not to exist since only one minimum in the potential energy curve is observed.

Summarizing, it can be stated that *a*) in furfuryl alcohol and its derivatives the planar conformation, in which the hydroxy methyl group is included in the same plane of the furane ring, is the most stable one. *b*) Either the CNDO/2 or the INDO method is proved to be an appropriate tool in studying the properties of intramolecular hydrogen bonding in compounds investigated. *c*) The enthalpies of hydrogen bonding formation are predicted somewhat better by the INDO method than by CNDO/2 one as compared with experimental results as far as they are available. *d*) A fairly good agreement between calculated and experimental dipole moments is found but the changes of atomic charges on hydrogen bonding formation are not well predicted by the two methods.

*The authors are grateful to Dr R. Zahradnik and Dr P. Čársky, both of the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, for providing the program used in these calculations and appreciate helpful discussions with them. The authors are also greatly indebted to Dr I. Hubač of this Institute for valuable discussions. One of us (A. A. H.) thanks the University of 17th November for fellowship support.*

REFERENCES

1. Bartoš S.: Advan. Quantum Chem. *3*, 209 (1966).
2. Murthy A. S. N., Rao C. N. R.: J. Mol. Struct. *6*, 253 (1970).
3. Schuster P.: Theor. Chim. Acta *19*, 212 (1970).
4. Schuster P., Funck Th.: Chem. Phys. Lett. *2*, 587 (1968).
5. Goel Abha, Murthy A. S. N., Rao C. N. R.: Ind. Chem. Soc. *9*, 56 (1971).
6. Murthy A. S. N., Rao C. N. R.: Theor. Chim. Acta *13*, 81 (1968).
7. Murthy A. S. N., Bhat S. N., Rao C. N. R.: J. Chem. Soc. *A 1970* 1251.
8. Hasanein A. A., Kováč Š.: J. Mol. Struct. *52*, 457 (1974).
9. Schneider M., Ciguére P. A.: Can. J. Chem. *47*, 4685 (1969).
10. Kollman P. A., Allen L. C.: J. Am. Chem. Soc. *93*, 499 (1971),
11. Kollman P. A., Allen L. C.: Chem. Rev. *72*, 283 (1972).
12. Gordon S., Tallonan D. E.: Chem. Phys. Lett. *17*, 385 (1972).
13. Čársky P.: Private communication.
14. Pople T. A., Santry D. P., Segal G. A.: J. Chem. Phys. *43*, S 129 (1965).
15. Pople J. A., Segal G. A.: J. Chem. Phys. *S 136* (1965).
16. Pople J. A., Segal G. A.: J. Chem. Phys. *1966*, 3282.
17. Ejdus J. A., Ekmane A. J., Venter K. K., Giller S. A.: *Atlas* of *Electronic Spectra of 5-Nitrofurane Compounds*, p. 9. Zinatne, Riga 1968.

18. Sutton L. E. in the book: *Tables of Interatomic Distances and Configurations in Molecules and Ions* (A. D. Mitchell, Ed.). Chemical Society (London), Special Publ. No. 11 1958; Suppl. 1956—1959, Special Publ. No. 18, 1965.
19. Nazarova Z. N., Novikov V. N.: Ž. Obšč. Chim. *34*, 767 (1964).
20. Pullman A., Berthod H.: Theor. Chim. Acta *10*, 461 (1968).
21. Ocvirik A., Ažman A., Hadži D.: Theor. Chim. Acta *10*, 187 (1968).
22. Schuster P.: Internat. J. Quantum Chem. *3*, 851 (1969).
23. McClellan A. L.: *Tables of Experimental Dipole Moments*. Freeman, San Francisco 1963.

Translated by A. A. Hasanein.