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Molecular Orbital Treatments of Hydrogen Bonded Systems. 2. Dimers of Water and HCN*

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Calculations were performed to investigate the reliabilities of the CNDO/2, PRDDO, and MNDO approximate molecular orbital methods. Systems selected for study included the linear, cyclic, and bifurcated dimers of water as well as the linear and cyclic dimers of HCN. The PRDDO method was found to provide the most consistently accurate reproduction of *ab initio* and experimental data. CNDO/2 performed fairly well in a number of cases but yielded extremely poor results for the cyclic dimers of both H_2O and HCN. Hydrogen bond strengths were consistently underestimated by MNDO which also furnished erroneously large intermolecular separations. In addition, MNDO calculations indicate the bifurcated water dimer to be most stable in contrast to other quantum mechanical and experimental information.

Key Words: PRDDO – CNDO/2 – MNDO.

1. Introduction

Hydrogen bonding plays an important role in a large number of chemical and biological problems, e.g. conformational analysis of proteins and nucleic acids, solvation phenomena, etc. It is therefore a prerequisite of any theoretical technique that is to be applied to related systems that it take accurate account of hydrogen bonding interactions. As there are currently available a wide array of quantum mechanical methods ranging from semiempirical to *ab initio*, it would be useful to have at hand a comparison of calculated results obtained by several of these procedures to serve as a basis on which a choice of technique may be made. A promising start in this direction has been made in a recent paper by Halgren et

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* See Ref. [1] for Paper 1 of this series.

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al. [2a] and a subsequent addendum by Dewar and Ford [2b]. These studies, however, did not include comparisons of hydrogen bonded systems and it is this topic on which we focus our attention here.

The water dimer has been studied perhaps more extensively than any other hydrogen bonded system. There exist experimental data [3–5] as well as results of sophisticated theoretical treatments [6–14] with which less rigorous calculations may be compared. Three types of water dimer which have received some attention are illustrated in Fig. 1. The linear dimer which contains a single O—H···O hydrogen bond has been most thoroughly investigated and has in fact been observed in a microwave experiment [5]. The bifurcated dimer contains a "double" hydrogen bond in which both protons are covalently bonded to the same oxygen. Two protons are also involved in hydrogen bonding in the cyclic dimer but in this structure one hydrogen is bonded to each oxygen atom.

Various quantum mechanical calculations have found all three dimer types to be stable minima in the potential surface [6–15]. In addition, Thiel recently reported [15] that the semiempirical CNDO/2 method [16] indicates the existence of two distinct cyclic dimers. One of these structures compares reasonably well with findings from more rigorous calculations while the second contains an extremely short R(00) distance of 1.49 Å. The latter geometry was described by Thiel as an "artifact" of the CNDO/2 method. The same procedure had been found earlier [17] to yield rather short intermolecular distances for all three dimer types. In addition, the popular MINDO/3 procedure has been shown [18] to fare quite poorly in treatments of hydrogen bonded systems including the water dimer.

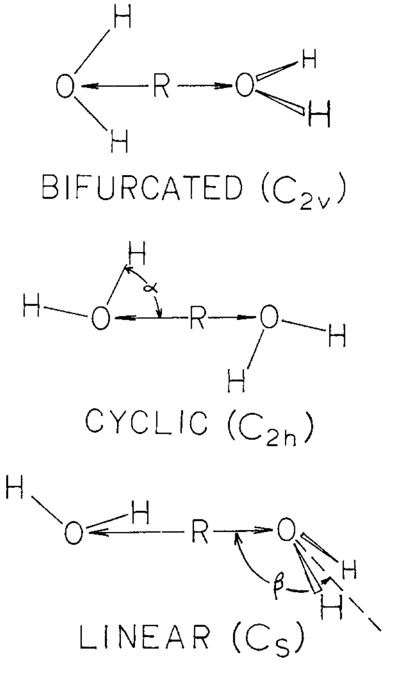

Fig. 1. Dimers of Water

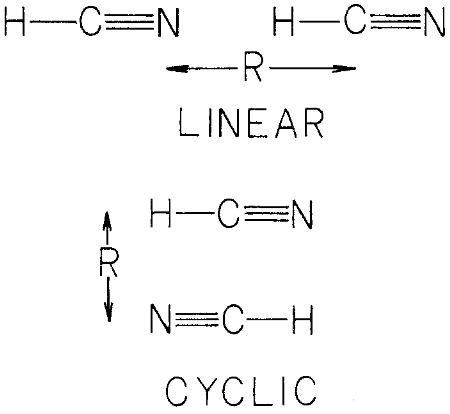

Fig. 2. Dimers of HCN

The dimer of HCN is another hydrogen bonded system for which more than one configuration may be envisioned. The linear arrangement in which a single N···H—C hydrogen bond is present has been observed by IR [19–21] and microwave [22] measurements in the gas phase and in an inert matrix. The crystalline form of HCN is composed of infinite linear chains with similar bonding [23]. A second mode of interaction shown in Fig. 2 is the antiparallel or cyclic dimer in which two hydrogen bonds may exist simultaneously. However, the spatial constraints of this system, which include hydrogen bond angles of 90°, would act to weaken the interaction considerably. It is therefore not surprising that the latter dimer type has not been observed experimentally. Although CNDO/2 calculations [24] indicated an extremely stable cyclic HCN dimer, a more recent *ab initio* study [25] found the linear dimer much more stable and attributed the previous CNDO/2 result to neglect of three and four center repulsions.

This paper reports calculations of the various dimer types of water and HCN using the recently developed approximate *ab initio* PRDDO [26] and semi-empirical MNDO [27] procedures. Because of the reported speed and accuracy of these two methods, they are both potentially useful for studies of large systems containing hydrogen bonds. It is therefore important to determine their reliabilities with smaller model systems and whether they, like CNDO/2, lead to any spurious results.

2. Water Dimers

Full geometry optimizations subject to the indicated symmetry constraints were carried out for each of the three dimers shown in Fig. 1 using the PRDDO and MNDO methods. All OH bond lengths were found to be equal to 1.00 Å by PRDDO and 0.94 Å by MNDO. The Θ(HOH) bond angles were all optimized to 107° by MNDO. PRDDO calculated these angles to be 100° for the cyclic and linear dimers as well as for the H_2O unit in the bifurcated dimer whose hydrogens are not involved in hydrogen bonding. Interactions with the oxygen lone pairs caused the HOH angle of the remaining H_2O unit to contract slightly to 98°. A true "linear" hydrogen bond was found by PRDDO and MNDO for the C_s dimer as the OOH angle was optimized to 0°.

Dimerization energies, E_d, are defined here as the difference in energy between the optimized dimers and the pair of infinitely separated monomers.

2.1. *Bifurcated*

The results obtained for the bifurcated dimer are summarized in Table 1 along with data from previous CNDO/2 and *ab initio* calculations. All *ab initio* estimates of the intermolecular separation R(OO) lie in the range between 3.0 and 3.1 Å. The dimerization energy is not as unambiguously evaluated but, with the exception of one minimal basis set calculation [6], varies between 3.3 and 5.5 kcal/mol. Both the PRDDO and CNDO/2 estimates of the latter quantity lie within this range although the calculated intermolecular distances are too small. It may be noted that the PRDDO separation is considerably closer to the *ab initio* value than is the CNDO/2 distance. The MNDO procedure, on the other hand, leads to a large overestimation of R as well as a calculated dimerization energy much smaller than *ab initio* values.

Rotations of one water molecule relative to the other about the O—O internuclear axis, thereby destroying the C_{2v} symmetry of the system, were found by CNDO/2, PRDDO, and MNDO to result in an increase in energy, in agreement with *ab initio* data [8, 9].

Table 1. Bifurcated Dimers of Water

Method	R, Å	E_d, kcal/mol	Reference
CNDO/2	2.36	3.8	15
PRDDO	2.71	3.7	This work
MNDO	3.88	1.0	This work
MBS[a]	3.00	9.2	6
[31/1][b]	3.0	4.5	7
DZ[a]	3.0[c]	5.5	7
DZ+P[a]	3.12	3.4	8
DZ+P	3.09	3.3	9
DZ+P+CI[a]	3.01	4.2	9

[a] Abbreviations used: MBS, minimal basis set; DZ, double zeta; P, polarization functions; CI, configuration interaction; HF, Hartree–Fock limit including f functions on O and d functions on H.

[b] Basis sets denoted by the standard notation [IJK/LM] refer to a contracted set of Gaussian-type functions including I s-orbitals, J sets of 3 p-orbitals, K sets of 6 d-orbitals on oxygen and L s-orbitals, M sets of 3 p-orbitals on hydrogen.

[c] Not optimized.

Table 2. Cyclic Dimers of Water

Method	R, Å	α, deg	E_d, kcal/mol	Reference
CNDO/2(IV)[a]	1.49	103	14.3	15
CNDO/2 (II)[a]	2.24	51	4.3	15
PRDDO	2.53	98	4.4	This work
MNDO	4.26	51	0.5	This work
MBS[b]	2.75	42	7.8	6
[31/1][b]	2.9	50	4.0	7
DZ[b]	2.9[c]	50[c]	6.0	7
DZ+P[b]	2.95	62	3.7	9
DZ+P+CI[b]	2.87	62	4.9	9

[a] Notation II and IV used in Ref. [15].
[b] See footnotes of Table 1.
[c] Not optimized.

2.2. *Cyclic*

Results for the cyclic dimer are reported in Table 2. As in the previous case, *ab initio* data provide a consistent intermolecular separation ($R = 2.9$ Å) but the dimerization energy is rather uncertain, with a range of 3.7–6 being observed. (The results of reference 6 are again in disagreement with other calculations.) Once again, PRDDO and CNDO/2 (dimer "II") furnish an acceptable estimate of the dimerization energy but underestimate R with PRDDO providing a closer approximation to the *ab initio* value than does CNDO/2.

Thiel [15] has located a second (and unrealistically deep) minimum in the CNDO/2 potential energy surface which, as may be seen in Table 2, contains the extremely short interoxygen distance of 1.49 Å. As indicated by Thiel, this C_{2h} dimer (designated IV in Ref. 15) is apparently an artifact of the CNDO/2 procedure and illustrates an important failure of the method.

As with the bifurcated dimer, MNDO greatly overestimates R (by 50%) and yields a very low dimerization energy.

An interesting point concerns the optimized values of the OOH angle α (see Fig. 1). For a cyclic hydrogen bonded system, it would be reasonable to expect α to be somewhat less than 90°. Indeed, a value of 51° is obtained by CNDO/2 (for dimer II) and by MNDO, in good agreement with *ab initio* values ranging from 42° to 62°. However, the other CNDO/2 dimer (IV) includes a value of $\alpha = 103°$ and the PRDDO structure contains an angle of 98°. Such configurations with large values of α might more appropriately be described as containing an $O \cdots O$ bond rather than a hydrogen bond. A further and not inconsistent finding is that if α is held fixed at the CNDO/2 value of 103°, only PRDDO and CNDO/2 predict the dimer to be stable with respect to dissociation to monomers. MNDO as well as the *ab initio* STO-3G [28] and 4-31G [29] methods yield purely repulsive potentials between the two molecules in this orientation.

Table 3. Linear Dimers of Water

Method	R, Å	β[a], deg	E_d, kcal/mol	Reference
CNDO/2	2.54	173	8.6	14
PRDDO	2.65	135	9.2	This work
MNDO	4.30	126	0.6	This work
MBS	2.68	180	12.6	6
STO-3G	2.73	121	6.0	14
4-31G	2.83	149	8.2	13
[531/21]	3.00	140	4.7	10
[541/31]	3.00	140	4.8	8
HF[b]	3.00	180[c]	3.7	11
[431/21]+CI	2.98	155	5.6	9
[541/31]+CI	2.92	138	6.1	12
Experiment	2.98 ± 0.04^5	120 ± 10^5	5.1 ± 0.3^{12} 6.2 ± 1.5^4	4, 5, 12

[a] β is defined as the angle between the HOH bisector and the O—O internuclear axis (see Fig. 1).

[b] See footnote a of Table 1.

[c] Not optimized.

2.3. Linear

The linear dimer has been studied extensively at various levels of *ab initio* theory ranging from minimal basis set to the Hartree–Fock limit including configuration interaction. Much of this data has been recently compiled by Dill et al. [13] and is summarized in Table 3 along with CNDO/2, PRDDO, and MNDO results. Increasing the basis set size and inclusion of correlation energy leads to convergence in the calculated intermolecular separation and the resulting value of R agrees well with experimental data. The dimerization energy does not appear to have achieved convergence but *ab initio* values of this quantity are nevertheless in reasonable agreement with estimates derived from experimental information [4, 12].

PRDDO and CNDO/2 optimizations provide underestimates of the intermolecular separation, with PRDDO yielding a value of R closer to experiment. In fact, the PRDDO separation is nearly identical to an *ab initio* value calculated with a minimal basis set [6]. Both PRDDO and CNDO/2 overestimate the dimerization energy but, as may be noted in Table 3, *ab initio* minimal basis set [6] and split-valence shell [13] calculations produce similarly high values of E_d. As in the two previous dimer types, the MNDO procedure overestimates the intermolecular distance and underestimates the dimerization energy.

Some consistency may be observed in the data reported above. The CNDO/2 and PRDDO methods yields excellent estimates of dimerization energies although some overestimation is noted in the linear dimer. The intermolecular distances are slightly underestimated with PRDDO producing significantly better results than CNDO/2. In addition, PRDDO does not yield a spurious minimum with an anomalously short separation for the cyclic dimer as does CNDO/2. The high value of α observed for the cyclic dimer in the PRDDO approximation does indicate, however, that some care may be required in interpreting results for certain hydrogen bonded systems.

MNDO, on the other hand, does not appear to deal adequately with the water dimers. Dimerization energies are consistently underestimated by a great deal and intermolecular separations are too large by 30–50%. It may be noted that the interoxygen distance calculated by MNDO for the bifurcated dimer is 0.4 Å less than those predicted by this method for the linear and cyclic dimers.

One may also be concerned with the relative order of stability of the three types of dimers. *Ab initio* calculations as well as experiment [5] indicate that the linear dimer is most stable, followed by the cyclic and bifurcated structures. Both PRDDO and CNDO/2 predict the same order of stability (if the spurious CNDO/2 dimer (IV) is not considered) whereas MNDO finds the *bifurcated* dimer most stable with the linear and cyclic structures approximately equally stable.

Very recent CNDO/2 calculations [30] indicate that when symmetry restraints are relaxed, the bifurcated and cyclic (II) dimers may spontaneously rearrange to the linear C_s structure. Similar results were obtained here with PRDDO except that a barrier on the order of 1 kcal/mol was found for rearrangement of the cyclic dimer. In addition the conversion of the bifurcated to linear dimer with no energy barrier has been noted previously via *ab initio* calculations using an extended basis set including polarization functions [8]. MNDO, on the other hand, does not predict the facile rearrangement of either the bifurcated or cyclic dimers. This result is not unexpected as the bifurcated dimer is found more stable than the linear type by MNDO.

3. HCN Dimer

Following Johannson, et al. [25] the HCN units of the dimer were held fixed in their experimental linear geometries ($r(\mathrm{CH}) = 1.07$ Å, $r(\mathrm{CN}) = 1.15$ Å). The intermolecular separations of the cyclic and linear dimers (see Fig. 2) were then optimized by the CNDO/2, MNDO, and PRDDO methods. The results obtained are shown in Table 4 along with *ab initio* STO-3G [28] data and ranges of values obtained from experimental information for the linear dimer. The equilibrium separation for this dimer, determined by infrared [19] and microwave [22] measurements of the gas phase and X-ray diffraction of the crystal [23], is quite well characterized as having a value of 3.2–3.3 Å. The dimerization energy is not as well determined but appears to lie in the range of 3.3 to 5.7 kcal/mol. The *ab initio* STO-3G method predicts values for the separation and dimerization energy in excellent agreement with experiment. The PRDDO value of R is too low by about 0.1 Å and the predicted dimerization energy, while higher than that calculated by STO-3G, is within the experimental range. CNDO/2 once again yields a still lower estimate of the intermolecular separation and the dimerization

Table 4. HCN Dimers

Method	R, Å	E_d, kcal/mole
Linear		
CNDO/2	2.88	2.9
PRDDO	3.08	4.7
MNDO	4.29	1.1
STO-3G[a]	3.2	3.7
Experiment[b]	3.2–3.3	3.3–5.7
Cyclic		
CNDO/2	1.75	41.3
PRDDO	∞	0
MNDO	4.27	0.6
STO-3G	3.51	1.0

[a] From Ref. [25].
[b] From Refs. [19], [20], [22], [23], [31].

energy appears to be a bit too low as well. The latter result is in contrast to the calculated data for the linear water dimer where CNDO/2 *over*estimated the dimerization energy. As with the various water dimers, MNDO yields very weak intermolecular attractive forces, with R being overestimated here by 1 Å and an extremely low dimerization energy being predicted.

Although the cyclic dimer has not been observed experimentally, CNDO/2 predicts this structure to be extremely stable ($E_d = 41$ kcal/mol) with an equilibrium distance between the two monomers of less than 1.8 Å. This situation is reminiscent of the C_{2h} cyclic dimer (IV) of water reported by Thiel and represents a second major failure of the CNDO/2 procedure. The *ab initio* STO-3G method, on the other hand, predicts only a very slightly stable cyclic dimer (1.0 kcal/mol) with a much more reasonable intermolecular separation of 3.5 Å. In addition it was found here by STO-3G calculatons that the cyclic dimer may "open up" to form the more stable linear dimer with an energy barrier for this rearrangement of less than 0.1 kcal/mol. *Ab initio* calculations therefore indicate that observation of a cyclic HCN dimer in the gas phase is extremely unlikely. PRDDO is in agreement with the latter prediction as no evidence is found of a stable cyclic dimer. The PRDDO potential for this C_{2h} intermolecular orientation is purely repulsive. MNDO, like STO-3G, predicts a slightly stable cyclic structure but the MNDO intermolecular separation is larger by 0.8 Å than that found by *ab initio* calculations. It may also be noted that the MNDO cyclic and linear dimers have very similar values of both R and E_d. The opening of the cyclic to the slightly more stable linear dimer was found by MNDO to occur with no energy barrier. Thus, all molecular orbital procedures, with the exception of CNDO/2, predict the linear dimer of HCN to be the only dimer present in the gas phase.

4. Conclusions

Ab initio molecular orbital calculations appear to be quite capable of providing adequate descriptions of the hydrogen bonded dimers studied here. Calculated equilibrium geometries and dimerization energies are in excellent agreement with available experimental data. Of the approximate methods examined in this paper, PRDDO provides the most consistently accurate reproduction of *ab initio* results. Dimerization energies calculated by PRDDO all fall within the ranges obtained by various *ab initio* approaches. The most stable dimers of both water and HCN are correctly predicted to be the linear structures. PRDDO intermolecular distances appear to be consistently underestimated by approximately 10%.

For certain dimers, CNDO/2 provides results similar to PRDDO (but with considerably smaller values of R). However, the CNDO/2 procedure fails completely for the cyclic dimers of both water and HCN where the intermolecular separations are grossly underestimated. The latter shortcoming results in the failure of CNDO/2 to predict the most stable type of dimer for either system.

The MNDO procedure is quite unsuccessful in its treatment of the water and HCN dimers. The upper limit of MNDO dimerization energies for these systems is 1.1 kcal/mol. Equilibrium separations are all greatly overestimated, the smallest being 3.9 Å. In addition, the most stable dimer of water is erroneously predicted by MNDO to be the bifurcated structure. Thus MNDO, like its predecessor MINDO/3, would appear to be a poor choice for use with hydrogen bonded systems.

Although, of the semiempirical methods studied here, PRDDO appears to furnish the most reliable results, some caution needs to be excercised in its use. As noted here, hydrogen bond lengths are predicted to be up to 0.3 Å too short. The large value of α calculated for the cyclic water dimer may also indicate that PRDDO geometries for larger systems require critical evaluation.

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References

1. Scheiner, S., Kern, C. W.: J. Am. Chem. Soc. **101**, 4081 (1979)
2. (a) Halgren, T. A., Kleier, D. A., Hall, J. H., Brown, L. D., Lipscomb, W. N.: J. Am. Chem. Soc., **100**, 6595 (1978) (b) Dewar, M. J. S., Ford, G. P.: J. Am. Chem. Soc. **101**, 5558 (1979)
3. (a) Van Thiel, M., Becker, E. D., Pimentel, G. C.: J. Chem. Phys. **27**, 486 (1957) (b) Tursi, A. J., Nixon, E. R.: J. Chem. Phys. **52**, 1521 (1970) (c) Magnusson, L. B.: J. Phys. Chem. **74**, 4221 (1970)
4. Joesten, M. D., Schaad, L. J.: "Hydrogen bonding". New York: Dekker 1974
5. Dyke, T. R., Muenter, J. S.: J. Chem. Phys. **60**, 2929 (1974)
6. Morokuma, K., Pederson, L.: J. Chem. Phys. **48**, 3275 (1968)
7. Kollman, P. A., Allen, L. C.: J. Chem. Phys. **51**, 3286 (1969)
8. Diercksen, G. H. F.: Chem. Phys. Letters **4**, 373 (1970); Theor. Chim. Acta (Berl.) **21**, 335 (1971)

9. Matsuoka, O., Clementi, E., Yoshimine, M.: J. Chem. Phys. **64**, 1351 (1976)
10. Hankins, D., Moskowitz, J. W., Stillinger, F. H.: J. Chem. Phys **53**, 4544 (1970)
11. Popkie, H., Kistenmacher, H., Clementi, E.: J. Chem. Phys **59**, 1325 (1973)
12. Diercksen, G. H. F., Kraemer, W. P., Roos, B. O.: Theor. Chim. Acta (Berl.) **36**, 249 (1975)
13. Dill, J. D., Allen, L. C., Topp, W. C., Pople, J. A.: J. Am. Chem. Soc. **97**, 7220 (1975)
14. Curtiss, L. A., Pople, J. A.: J. Mol. Spect **55**, 1 (1975)
15. Thiel, W.: Theor. Chim. Acta (Berl.) **48**, 357 (1978)
16. Pople, J. A., Beveridge, D. L.: "Approximate molecular orbital theory". New York: McGraw-Hill 1970
17. Kollman, P. A., Allen, L. C.: J. Am. Chem. Soc. **92**, 753 (1970)
18. (a) Zielinski, T. J., Breen, D. C., Rein, R.: J. Am. Chem. Soc. **100**, 6266 (1978) (b) Klopman, G., Andreozzi, P., Hopfinger, A. J., Kikuchi, O., Dewar, M. J. S.: J. Am. Chem. Soc. **100**, 6267 (1978)
19. Jones, W. J., Seel, R. M., Sheppard, N.: Spectrochim. Acta **25A**, 385 (1969)
20. Mettee, H. D.: J. Phys. Chem. **77**, 1762 (1973)
21. King, C. M., Nixon, E. R.: J. Chem. Phys. **48**, 1685 (1968)
22. Legon, A. C., Millen, D. J., Mjöberg, P. J.: Chem Phys. Letters **47**, 589 (1977)
23. Dulmage, W. J., Lipscomb, W. N.: Acta Cryst. **4**, 330 (1951)
24. Hoyland, J. R.; Kier, L. B., Theor. Chim. Acta. **15**, 1 (1969).
25. Johannson, A., Kollman, P., Rothenberg, S.: Theor Chim. Acta (Berl.) **26**, 97 (1972)
26. Halgren, T. A., Lipscomb, W. N.: J. Chem Phys. **58**, 1569 (1973)
27. Thiel, W.: MNDO, Program No. 353, Quantum chemistry program exchange. Bloomington, Ind.: Indiana University; Dewar, M. J. S., Thiel, W.: J. Am. Chem. Soc. **99**, 4899 (1977)
28. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
29. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971)
30. Zhixing, C.: Theor. Chim. Acta (Berl.) **54**, 169 (1980)
31. Giauque, W. F., Ruehrwein, R. A.: J. Am. Chem. Soc. **61**, 2626 (1939)

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