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## *Physical and Inorganic Chemistry*

# Structural and Energetic Predictions for Simple Hydrocarbons from the NDDO and CNDO Semiempirical Molecular Orbital Methods[1]

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**Abstract:** The abilities of NDDO and CNDO molecular orbital calculations to predict equilibrium bond lengths, equilibrium bond angles, isomerization energies, rotational barriers, ionization potentials, dipole moments, and force constants are tested in a representative series of simple hydrocarbons.

Organic chemistry has derived great benefit from the recent renaissance of approximate molecular orbital theories.[2] There has, however, been insufficient critical evaluation of the ability of these theories to successfully predict those quantities of most interest to organic chemists: molecular geometry, relative energy, and physical properties. The present work attempts to assess some of the predictive abilities of two of these theories, CNDO/2[3] and NDDO,[2b,4] in applications to simple hydrocarbons. These two theories were chosen for study because they represent, respectively, a fairly simple and a fairly complex computational procedure, each arising by systematic approximation to the Hartree–Fock equations, each retaining the invariance to hybridization and change of coordinate system inherent to the exact theory.

It is worthwhile noting that the mnemonics CNDO and NDDO describe only which one-electron and two-electron integrals are to be omitted. There are many other approximations involved in these calculations, notably those used in the actual evaluation of the integrals that are to be retained. CNDO and NDDO thus denote whole families of methods, and the success of any particular scheme probably depends at least as much on, *e.g.*, the method of approximation of one-electron integrals as on the choice of integrals to be retained. The particular versions of CNDO and NDDO used in this study utilized those integral approximation prescriptions most commonly followed in previously published work using these methods. As few parameters as possible were varied, as indicated in the following section. The integrals retained in the two schemes were calculated similarly by both methods whenever possible.[5]

### Details of Approximation and Parametrization

The basic approximations involved in CNDO/2 calculations have been described by Pople and Segal.[3] The NDDO scheme used in this work has been described by Sustmann, *et al.*[4] For integrals retained in both methods, the two algorithms are identical with the following exception: CNDO/2 sets the resonance integral parameter $\beta_{HC}^0$ equal to the arithmetic mean of the corresponding parameters for carbon and hydrogen; NDDO calculations in this work used a value of $\beta_{HC}^0$ chosen to reproduce carbon–hydrogen bond lengths.

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1625.

[2] (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (b) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

[3] J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

[4] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).

[5] In the case of the CNDO resonance integrals, it was necessary to decide whether to use the same algorithm as the vast majority of previously published work, or a somewhat superior, though basically similar, evaluation scheme used in the NDDO programs. The former alternative was chosen.

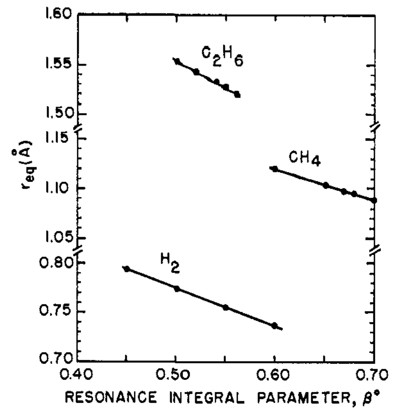

Figure 1. Effect of variation in parameters on equilibrium bond lengths.

Both methods employ a basis set of single exponent Slater orbitals.

Parametrization was directed toward the accurate prediction of bond lengths in simple hydrocarbons. It was hoped that such parametrization might also provide good quantitative estimates of other geometric quantities. Fortunately, Wiberg[6] has already carried out such a parametrization of the CNDO/2 scheme,[3] and his optimized parameters were used in all the present CNDO calculations.[7] As the resonance integral proportionality constant, $\beta_{\mu\nu}$, is the most important determinant of predicted equilibrium bond lengths,[4,6] the following simple procedure was used in choosing parameters for the NDDO method. All parameters except the proportionality constants were taken from work of Sustmann, *et al.*,[4] and $\beta_{HH}{}^0$ was chosen to reproduce the equilibrium internuclear distance in the hydrogen molecule. Using the newly found value of $\beta_{HH}{}^0$, $\beta_{CH}{}^0$ was chosen to reproduce the equilibrium C-H bond length in methane (assuming $T_d$ symmetry). Finally, using these two parameters, $\beta_{CC}{}^0$ was determined so as to reproduce the C-C bond length in ethane.[8] The results of this parametrization process are summarized in Table I. As bond length predictions using these parameters are excellent (±0.015 Å), no further optimization was attempted. The experience of the authors in parameterizing the NDDO procedure paralleled the finding of Wiberg[6] that the predicted equilibrium bond lengths in the reference molecules are linear functions of the resonance integral parameters (with all other parameters held constant). These results are displayed in Figure 1.

**Table I.** Resonance Integral Parametrization

| Molecule | —Parameter— Bond | Value | —Bond length, A— NDDO | Exptl |
|---|---|---|---|---|
| Hydrogen | H-H | 0.55 | 0.755 | 0.741 |
| Methane | C-H | 0.67 | 1.098 | 1.106 |
| Ethane | C-C | 0.55 | 1.527 | 1.526 |

It is useful to compare the number of functional and parametric adjustments in the present work with similar numbers for other studies. As mentioned previously, our NDDO parameterization involved the modification of three resonance integral parameters; otherwise the original values of Sustmann, *et al.*,[4] were retained. The present CNDO calculations changed two resonance integral parameters and two ionization potentials within the original CNDO/2 formalism of Pople,[3] using the modified values of Wiberg.[6] Fischer and Kollmar[9] have changed the functional forms for resonance integrals and certain nuclear attraction integrals from those in CNDO/2 in an attempt to predict equilibrium geometries, heats of atomization, and force constants. In all they have adjusted a total of eight parameters, and the requirement of hybridization invariance was relaxed. Clark[10] sought to improve CNDO excitation energies and dipole moment predictions by changing two repulsion integral formulas, the resonance integral formula, the one-center core attraction integrals, and the method of selecting orbital exponents. He also abandoned hybridization invariance. Sichel and Whitehead[11] modified CNDO/2 by adjusting two resonance integral parameters and changing the nuclear repulsion energy expressions, the electron repulsion integral formulas, and the method of selection of one-center core attraction integrals in order to reproduce experimental binding energies, ionization potentials, dipole moments, and nuclear quadrupole coupling constants.

## Results

The results of bond length calculations are presented in Table II. Since the resonance integral parameters

**Table II.** Bond Lengths[a]

| Molecule | Bond | CNDO | NDDO | Exptl |
|---|---|---|---|---|
| Hydrogen | H—H | 0.735 | 0.755 | 0.741[b] |
| Methane | C—H | 1.128 | 1.098 | 1.106[c] |
| Acetylene | C—H | 1.101 | 1.057 | 1.059[d] |
|  | C≡C | 1.240 | 1.225 | 1.205 |
| Ethylene | C—H | 1.119 | 1.080 | 1.086[e] |
|  | C=C | 1.362 | 1.359 | 1.337 |
| Ethane | C—H | 1.126 | 1.094 | 1.093[f] |
|  | C—C | 1.516 | 1.527 | 1.526[g] |
| Propene | C=C | 1.365 | 1.361 | 1.336[h] |
|  | C—C | 1.501 | 1.493 | 1.501 |
| Cyclopropane | C—H | 1.122 | 1.084 | 1.089[i] |
|  | C—C | 1.520 | 1.517 | 1.510 |
| Propane | C—C | 1.518 | 1.521 | 1.526[j] |
| Benzene | C—H | 1.123 | 1.075 | 1.084[k] |
|  | C┄C | 1.424 | 1.410 | 1.397 |

[a] Bond lengths, A. [b] B. P. Stoicheff, *Can. J. Phys.*, **35**, 730 (1957). [c] L. S. Bartell, K Kuchitsu, and R. J. de Neui, *J. Chem. Phys.*, **35**, 1211 (1961). [d] J. H. Callomon and B P. Stoicheff, *Can J. Phys.*, **35**, 373 (1957). [e] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [f] H. C. Allen and E. K. Plyler, *J. Chem. Phys.*, **31**, 1062 (1959). [g] D. R. Lide, Jr., *ibid.*, **33**, 1519 (1960). [h] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35**, 1374 (1961). [i] O Bastiansen, F. N. Fritsch, and K. Hedberd, *Acta Cryst.*, **17**, 538 (1964). [j] D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960). [k] A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

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(6) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).

(7) A number of the CNDO calculations done in this laboratory repeat those of Wiberg. They were included in this study to ensure uniformity in the method of geometry calculation and in the choice of experimental reference values for the geometric parameters. However, Wiberg's linear adjustment of energy values was not used, but rather the calculated energies as they came from the usual CNDO procedure.

(8) Whenever possible, spectroscopic substitution values (or the equivalent) were chosen for the geometric quantities. Thus, the probable substitution value of the C-C bond length in ethane, 1.526 Å, was used as the target value in the parametrization (see ref *g*, Table II).

(9) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

(10) D. T. Clark, *ibid.*, 10, 111 (1968).

(11) J. M. Sichel and M. A. Whitehead, *ibid.*, **11**, 220 (1968).

were chosen to reproduce specific single bond lengths, it is not suprising that agreement between most experimental and calculated single bond lengths is very good. The NDDO calculations predict carbon–hydrogen bond lengths and carbon–carbon single bond lengths particularly well (within 0.01 Å of the experimental value in every case). CNDO estimates carbon–carbon single bond lengths approximately as well as NDDO; carbon–hydrogen bonds, however, are consistently computed to be 0.03–0.04 Å too long.

Both semiempirical techniques fail to predict carbon–carbon multiple bond lengths as accurately as single bond lengths. The NDDO method calculates multiple bonds in acetylene, ethylene, propene, and benzene which are 0.015–0.025 Å too long, while CNDO predicts them to be 0.025–0.035 Å too long. Overall, the NDDO method gives quantitatively better bond length estimates than the CNDO scheme; however, had the CNDO method used the same resonance integral parametrization as the NDDO calculations, the difference between the two set of results would probably have been very small.

The results of bond angle calculations using NDDO and CNDO are displayed in Table III. Both methods provide equally good quantitative predictions of bond angles in hydrocarbons. The bond angles agree with the experimental ones to within approximately 2°. Closer examination shows that the CNDO scheme produces bond angles greater than the observed values, whereas the NDDO method calculates them to be smaller (except for the H–C–H angle in propane). The CNDO predictions are consistent with the tendency of *ab initio* LCAO–SCF calculations which exclude d orbitals to overestimate bond angles.

**Table III.** Bond Angles[a]

| Molecule | Angle | CNDO | NDDO | Exptl |
|---|---|---|---|---|
| Ethylene | C–C–H | 123.4 | 120.2 | 121.3[e] |
| Ethane | C–C–H | 111.0 | 107.3 | 109.2[f] |
| Propane | C–C–C | 112.9 | 111.8 | 112.4[j] |
| | H–C–H[b] | 106.1 | 108.1 | 106.1[j] |

[a] Bond angles in degrees. Footnotes *e*, *f*, and *j* are to references in Table II. [b] Methylene H–C–H angle.

It was decided to limit studies of heats of reaction to conformational changes and isomerizations. This is because we have taken the approach that these semiempirical schemes are to be regarded as approximations to Hartree–Fock theory, and it seemed appropriate to concentrate on properties which are calculable within the framework of that theory.[12]

The results of isomerization energy calculations are shown in Table IV. Both methods correctly predict that the chair form of cyclohexane is more stable than the boat. NDDO erroneously finds transoid 1,3-butadiene to be less stable than the cisoid form; CNDO makes the correct prediction. In the butene series, NDDO correctly shows *trans*-2-butene to be less stable than isobutylene; all other predictions by both methods are wrong. For the butanes, CNDO finds isobutane to be the most stable isomer. NDDO predicts the *anti* conformer of *n*-butane to be less stable than isobutane. Other predictions in this series are incorrect.

**Table IV.** Isomerization Energies

| Molecule | Relative energies, kcal/mol<br>CNDO | <br>NDDO | <br>Exptl |
|---|---|---|---|
| Transoid 1,3-butadiene | 0.00 | 0.00 | 0.00 |
| Cisoid 1,3-butadiene | 0.63 | −1.42 | 2.30[a] |
| Isobutylene | 0.00 | 0.00 | 0.00 |
| *trans*-2-Butene | −3.08 | 0.87 | 1.37[b] |
| *cis*-2-Butene | −3.33 | −3.14 | 2.37[b] |
| Isobutane | 0.00 | 0.00 | 0.00 |
| *n*-Butane (*anti*) | 0.19 | 0.11 | 2.00[b] |
| *n*-Butane (*gauche*) | 0.12 | −1.39 | 2.80[c] |
| Cyclohexane (chair) | 0.00 | 0.00 | 0.00 |
| Cyclohexane (boat) | 5.02 | 4.83 | 6.59[d] |

[a] J. G. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946). [b] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project No. 44, Carnegie Press, Pittsburgh, Pa., 1953. [c] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, pp 8–9. [d] Computed by molecular mechanics: N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminsky, and F. A. Van Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

In finding the *cis* hydrocarbon isomers more stable than the *trans*, it appeared that the NDDO method was underestimating nonbonded carbon–carbon interactions. Although the interaction between the methyl carbons in *cis*-2-butene was found to be antibonding, it was not antibonding enough to make it less stable than the *trans* isomer. An attempt to correct this situation was made by increasing the carbon–carbon resonance integral parameter from 0.55 to 0.60. The effect of this change on the isobutylene, *cis*-2-butene, and *trans*-2-butene calculations was that the *cis* isomer was then 3.37 and the *trans* isomer 0.17 kcal/mol more stable than isobutylene. Even though the *cis* form was still lower in energy than the *trans*, their relative energies were brought almost 1 kcal/mol closer together. Unfortunately, isobutylene was found to be less stable than *trans*-2-butene. This was expected, however, because the interaction between the methyl groups in isobutylene is also antibonding. The carbon–carbon resonance integral parameter was not further increased, as this would result in absurd geometry predictions. Nevertheless, this test indicated that it might be possible to parametrize the NDDO method expressly for the prediction of relative stabilities of *cis* and *trans* isomers at the sacrifice of predictions of other geometric properties.

Results of calculations of barriers to internal rotation are presented in Table V. The CNDO values are consistently lower than experiment, while the NDDO results display no simple pattern. CNDO orders the barrier magnitudes better than NDDO, but neither method yields results which are systematic enough to be quantitatively useful. The torsional potential surfaces predicted by the two methods for *n*-butane are compared with experiment in Figure 2.

Koopman's theorem first ionization potentials for the molecules studied are given in Table VI. Both CNDO and NDDO give results which are too high by 35–50%. CNDO orders the values more consistently than NDDO, but still reverses some.

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(12) R. M. Pitzer and W. N. Libscomb, *J. Chem. Phys.*, **39**, 1995 (1963); W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261, 2276 (1967); L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967); J. R. Hoyland, *ibid.*, **49**, 2563 (1968), **50**, 2775 (1969); R. J. Buenker and J. L. Whitten, *ibid.*, **49**, 5381 (1968).

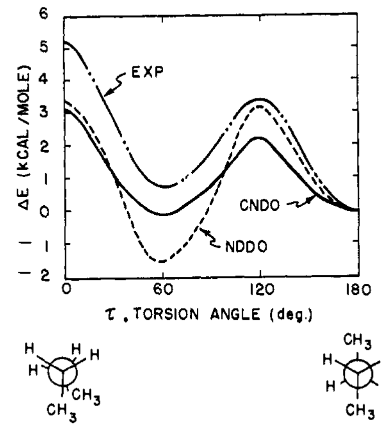

Figure 2. Torsional potential surfaces for *n*-butane. The experimental value of $\Delta E$ for the *cis* isomer ($\tau = 0°$) is shown as the arithmetic mean of the range given in Table V.

Calculated dipole moments are compared with experiment in Table VII. The general trends of the values for both schemes are not unreasonable, especially in view of the rather erratic results generated by *ab initio* calculations using the same single exponential orbitals employed by the semiempirical methods.

Table V. Rotational Barriers[a]

| Molecule | CNDO | NDDO | Exptl |
|---|---|---|---|
| Ethane | 2.32 | 2.39 | 2.928[b] |
| Propene | 1.00 | 1.68 | 1.98[c] |
| Propane | 2.20 | 2.61 | 3.4[d] |
| Isobutylene | 0.94 | 1.69 | 2.21[e] |
| *cis*-2-Butene | 0.44 | 2.54 | 0.73[f] |
| *n*-Butane (180° → 120° [i]) | 2.26 | 3.17 | 3.40[g] |
| *n*-Butane (120° → 60°) | −2.33 | −4.67 | −2.60 |
| *n*-Butane (60° → 0°) | 3.27 | 4.92 | 3.60–5.30 |
| Isobutane | 2.64 | 2.01 | 3.9[h] |

[a] Barrier heights in kcal/mol. [b] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968). [c] D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957). [d] See Table II, ref *j*. [e] V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961). [f] T. N. Sarachman, *ibid.*, **49**, 3146 (1968). [g] See Table IV, ref *c*. [h] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958). [i] Dihedral angle between C–C bonds.

Table VI. Ionization Potentials[a]

| Molecule | MO | CNDO | NDDO | Exptl[b] |
|---|---|---|---|---|
| Hydrogen | $\sigma_g^+$ | 21.4 | 23.1 | 15.4 |
| Methane | $t_2$ | 19.4 | 19.2 | 13.6 |
| Acetylene | $\pi_u$ | 17.4 | 15.4 | 11.4 |
| Ethylene | $b_{3u}$ | 16.0 | 13.3 | 10.6 |
| Ethane | $e_g$ | 16.2 | 15.0 | 11.2 |
| Propene | $a''$ | 14.5 | 11.8 | 9.8 |
| Cyclopropane | $e'$ | 15.6 | 13.9 | 10.2 |
| Propane | $b_2$ | 15.3 | 13.7 | 11.2 |
| 1,3-Butadiene | $b_g$ | 13.5 | 11.0 | 9.2 |
| Isobutylene | $b_1$ | 13.8 | 11.1 | 9.4 |
| *cis*-2-Butene | $b_1$ | 13.4 | 10.6 | 9.3 |
| *trans*-2-Butene | $a_u$ | 13.3 | 10.6 | 9.3 |
| Isobutane | $a_1$ | 14.7 | 12.9 | 10.4 |
| *n*-Butane | $b_g$ | 15.0 | 13.2 | 10.8 |
| Benzene | $e_{1u}$ | 14.0 | 11.3 | 9.2 |
| Cyclohexane | $e_g$ | 13.8 | 11.8 | 10.4 |

[a] Ionization potentials in eV. [b] F. H. Field and J. L. Franklin, "Electron Impact Phenomenon," Academic Press New York, N. Y., 1957, Table 10a.

Table VII. Dipole Moments[a]

| Molecule | CNDO | NDDO | Exptl |
|---|---|---|---|
| Propene | 0.525 | 0.629 | 0.364[c] |
| Propane | 0.020 | 0.084 | 0.083[d] |
| Isobutylene | 0.910 | 0.971 | 0.503[e] |
| *cis*-2-Butene | 0.200 | 0.231 | 0.257[f] |
| Isobutane | 0.010 | 0.213 | 0.132[h] |

[a] Dipole moments in debyes. Footnotes *c*, *d*, *e*, *f*, and *h* are to references in Table V.

The results of force constant calculations are presented in Table VIII(A). Values computed by both methods are too large by factors of 2–3. Though this is a large and somewhat variable error, it is qualitatively similar to that produced by *ab initio* Hartree–Fock calculations. Table VIII(B) indicates the ranges of force constants predicted for each type of bond. It is encouraging that these ranges are essentially in correct order and nonoverlapping.

Table VIII

(A) Force Constants[a]

| Molecule | Bond | CNDO | NDDO | Exptl |
|---|---|---|---|---|
| Hydrogen | H—H | 10.4 | 11.8 | 5.7[b] |
| Methane | C—H | 11.2 | 15.4 | 5.4[b] |
| Acetylene | C—H | 14.6 | 16.1 | 6.2[b] |
|  | C≡C | 35.2 | 36.8 | 17.2[b] |
| Ethylene | C—H | 13.5 | 15.2 | 6.1[b] |
|  | C=C | 23.6 | 25.4 | 10.9[b] |
| Ethane | C—H | 13.4 | 15.2 | 5.4[b] |
|  | C—C | 12.6 | 13.2 | 4.6[b] |
| Propene | C=C | 25.6 | 24.8 | 9.6[c,e] |
|  | C—C | 15.5 | 14.8 | 4.5[c,e] |
| Cyclopropane | C—H | 13.4 | 15.0 | 5.3[f] |
|  | C—C | 13.7 | 14.5 | 4.0[f] |
| Propane | C—C | 13.9 | 15.2 | 4.5[c,e] |
| Benzene | C—H | 13.4 | 14.8 | 5.1[b,e] |
|  | C⋯C | 21.3 | 22.6 | 7.6[d,e] |

(B) Force Constant Ranges[g]

| Method | C—C | C—H | C⋯C | C=C | C≡C |
|---|---|---|---|---|---|
| CNDO | 12.6 → 15.5 | 11.2 → 14.6 | 21.3 | 23.6 → 25.6 | 35.2 |
| NDDO | 13.2 → 15.2 | 14.8 → 16.1 | 22.6 | 24.8 → 25.4 | 36.8 |
| Exptl | 4.0 → 4.6 | 5.1 → 6.2 | 7.6 | 9.6 → 10.9 | 17.2 |

[a] Force constants in mdyn/A. [b] T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth and Co., London, 1958. [c] From group frequencies: G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945. [d] J. W. Linnett, *Quart. Rev.* (London), **1**, 73 (1947). [e] Not corrected for anharmonicity. [f] J. L. Duncan and G. R. Burns, *J. Mol. Spectrosc.*, **30**, 253 (1969). [g] All data are from part A.

## Conclusion

The success of NDDO in predicting bond lengths and its failure in the calculation of other properties confirm recent experience indicating that successful quantitative predictions by semiempirical molecular orbital theories which include electron repulsion usually depend upon specialization to a small group of closely related properties. The fact that CNDO, in general, more closely parallels experimental trends than NDDO indicates that the additional integrals included in the latter scheme are unnecessary for most purposes. Confident quantitative predictions do not yet seem to be within the province of either NDDO or CNDO. However, if they are used in close conjunction with *ab initio* results and experimental data, they frequently can be of considerable value.

**Acknowledgments.** The authors are grateful to Dr. Reiner Sustmann for the computer programs used for NDDO calculations in this work and for many helpful conversations. We also wish to thank the Quantum Chemistry Program Exchange for providing CNDO programs upon which the ones used here at Princeton are based. The assistance rendered by the Princeton University Computing Center, supported in part by National Science Foundation Grants GJ-34 and GU-3157, was appreciated. One of us (R. B. D.) is grateful to the Monsanto Company for fellowship support.

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# Hydrogen Bonded Dimers and Polymers Involving Hydrogen Fluoride, Water, and Ammonia[1a]

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*Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. Received July 8, 1969*

**Abstract:** A theoretical investigation employing semiempirical molecular orbital methods has been carried out on various dimers and polymers involving hydrogen fluoride, water, and ammonia. Different semiempirical MO techniques were compared with each other as well as with *ab initio* results. The CNDO/2 procedure was shown to be an appropriate tool for study of some aspects of hydrogen bonding. Hydrogen bond properties such as geometry, infrared intensity, and frequency shifts, as well as charge redistribution, were investigated. A number of mixed dimers, $H_2O$–HF, $NH_3$–HF, and $NH_3$–$H_2O$, not heretofore studied experimentally, were considered and found to possess unusually high heats of formation. Linear and cyclic HF polymers were studied. Rather surprisingly, the five-membered chain was found to have the largest energy per H bond among the linear species. For cyclic structures, the hexamer proved the most stable. A charge distribution investigation of the water pentamer provides a beginning toward a detailed electronic structure understanding of liquid water. In both water and H–F polymers, nonlinear energy increments were found.

The hydrogen bond has been of interest to chemists since Latimer and Rodebush[2] proposed it in 1920.[3] This interest greatly increased in 1953 when Watson and Crick[4] postulated that hydrogen bonding was a key feature of the structure of DNA. Since that time there have been numerous semiempirical studies by $\pi$ electron methods on some biological systems involving hydrogen bonds.[5] With the advent of extended Hückel theory, some hydrogen bonded systems were studied with this method.[6] More recently, valence electron schemes which take electron repulsion into account have been proposed; of special interest have been the CNDO and NDDO methods proposed by Pople.[7] The CNDO method has been applied to a number of hydrogen bonded systems.[8]

This paper examines several of the semiempirical methods in light of recently carried out *ab initio* calculations on the hydrogen bond.[3a] It is important to get agreement with experiment for the most favored geometry and heat of formation of the hydrogen bonded dimers and to see how well the semiempirical methods represent other properties of the hydrogen bond. In light of the above, this paper sets out to accomplish the following: (1) Compare the *ab initio* and semiempirical geometry and energy of formation predictions for various hydrogen bonded dimers. (2) Compare the spectroscopic properties predicted by *ab initio* and semiempirical methods choosing the linear water dimer and hydrogen fluoride dimer as test cases. (3) Compare the details of the CNDO and *ab initio* wave functions. (4) Consider the extension of the CNDO method to systems where an *ab initio* calculation would presently be impractical.

## Description of Calculation

The *ab initio* calculations have been previously described.[3a,9] The essential features of the CNDO/2 (CNDO = Complete Neglect of Differential Overlap)[7,10] procedure are: (1) neglect of overlap between different AO's; (2) neglect of differential overlap in the calculation of energy integrals; (3) further approxima-

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(1) (a) National Science Foundation Predoctoral Fellow, 1966–1970; (b) research supported in part by the Directorate of Chemical Sciences of the Air Force Office of Scientific Research, Contract No. AF 49(638)-1625.

(2) W. M. Latimer and W. H. Rodebush, *J. Amer. Chem. Soc.*, **42**, 1419 (1920).

(3) (a) For additional references, see P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969); (b) for the most recent theoretical review, see S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1966); the most recent spectroscopic review, A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Rev.*, **2**, 69 (1968).

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