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# Semiempirical Calculations of One-Bond Nitrogen-15–Hydrogen Coupling Constants and Inversion Barriers at Nitrogen[1]

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**Abstract:** The accuracy of several CNDO/2 methods is compared to INDO for the calculation of the Fermi-contact contribution to the one-bond $^{15}$N–H coupling constant and the inversion barrier at nitrogen for molecules containing first-row atoms. The CNDO/2 methods use (i) the inversion-optimized parameter set of Rauk, Andose, Frick, Tang, and Mislow; (ii) two other inversion-optimized parameter sets (sets A and B), which parameterize on ammonia, and (iii) the standard Pople–Segal parameters. Parameters are reported for first-row atoms boron through fluorine. Comparisons of calculated vs. experimental barriers and coupling constants for the various parameter sets are made employing nonparametric statistical methods. From a comparison of the calculated and experimental coupling constants, it is concluded that results obtained from the CNDO/2 inversion-optimized parameter sets of Rauk et al. and set B are as accurate as INDO, while those obtained from the Pople–Segal parameters are not. Inversion barriers and their trends calculated from these inversion-optimized CNDO/2 parameters are as accurate as those obtained from INDO; a conclusion which disagrees with the work of Stevenson and Burkey. Suggestions are made for further experimental and theoretical work.

There is at present theoretical and experimental interest in the one-bond $^{15}$N–H coupling constant, $^1J(^{15}\mathrm{N,H})$.[2] An objective of this paper is to compare the accuracy of semiempirical methods for the calculation of the Fermi-contact contribution to the coupling constant, which, in this case, is the principal contribution to the nuclear spin-spin interaction.[3]

Of the two commonly used semiempirical methods, CNDO/2[4,5] and INDO,[5,6] the former is apparently less effective because it ignores one-center exchange integrals, which are an important contribution to the coupling constant.[7] The suitability of the latter is at the cost of additional computer time.

Experimental evidence has indicated that the value of the one-bond $^{15}$N–H coupling constant is markedly affected by the hybridization of the nitrogen orbitals.[8] In addition, due to the inflexibility of the CNDO/2 or INDO basis set, this hybridization is also an important ingredient in the inversion barrier at nitrogen; the barrier being largely governed by the energy associated with the hybridization changes that occur in the highest occupied molecular orbitals during inversion.[9]

Rauk, Andose, Frick, Tang, and Mislow[9] (RAFTM) have developed a revised set of CNDO/2 parameters which are specific for pyramidal inversion, and, by using these parameters, they have obtained good agreement between calculated and experimental barriers for some hundred structures. It is reasonable to hypothesize that these same parameters will assist in the calculation of $^1J(^{15}\mathrm{N,H})$ from CNDO/2, whenever nitrogen is a center of pyramidal inversion. This supposition is tested by calculations which are reported in the results and discussion section.

In the RAFTM paper, 1-methylaziridine is chosen as the molecule which is representative of inversion at nitrogen. However, for our purposes, which is the calculation of $^1J(^{15}\mathrm{N,H})$, a molecule with a directly bonded nitrogen and hydrogen may be more suitable. Thus the approach of RAFTM is repeated with ammonia as the representative molecule. Ammonia is chosen because it has both a well-studied inversion barrier and $^{15}$N–H coupling constant, in addition to being economical to parameterize on.

In a recent paper Stevenson and Burkey[10] have studied inversion barriers at first-row elements using CNDO/2, INDO, and "CNDO-Mislow", the latter being the reparameterized CNDO/2 scheme of RAFTM. In a comparison of the three methods for inversion at nitrogen, they conclude that INDO is the most suitable method, closely followed by CNDO-Mislow. They infer this from calculations on six acyclic amines, where, for four of these, a tetrahedral ground state conformation is assumed. It is therefore important to determine if their conclusion is still valid for a wider variety of molecules, without assuming the value of the ground state out-of-plane angle.

In summary, the inversion barrier at nitrogen and the Fermi-contact contribution to the directly bonded $^{15}$N–H coupling constant, $^1J(^{15}\mathrm{N,H})$, are calculated. For a variety of molecules three methods are used and compared: "CNDO-Mislow", CNDO/2 which is reparameterized using $NH_3$ as the representative molecule, and INDO.

## Computational Methods

**Optimization Method.** The method of obtaining pyramidal inversion optimized CNDO/2 parameters follows the spirit of the work of RAFTM: the standard (Pople–Segal) CNDO/2 parameters[4] are adjusted until agreement is found between the calculated and reported barriers in a "representative" molecule for each inverting center. The "representative" molecules chosen are $NH_3$ and $CH_3^-$, which provide the nitrogen and carbon parameters, respectively. The hydrogen parameters are unchanged from their Pople–Segal values.

Both equilibrium and variable bond distances, as a function of out-of-plane angle, have been reported for the representative molecules, so it is possible to obtain *two* sets of inversion optimized CNDO/2 parameters: optimization with a fixed (equilibrium) XH distance (set A), optimization with a variable XH distance (set B).

For oxygen, the appropriate "representative" molecule of the form $XH_3$ is, of course, hydroxonium ion. Unfortunately, the ion is probably planar,[11] and a wide variety of CNDO/2 parameters will yield a zero calculated barrier. Thus, the oxygen parameters have to be calculated by linear extrapolation of the carbon and nitrogen values.

The adjustable parameters for first-row elements are the 2s and 2p electronegativities, $\chi_s$ and $\chi_p$, respectively. For methyl anion, both parameter sets reproduce the ab initio inversion barrier reported in ref 12. Set A uses a fixed CH bond distance (1.079 Å), which contrasts with the longer, methane value (1.095 Å) used by RAFTM. Set B uses a variable CH distance.[13]

For inversion at nitrogen, two parameter sets are found which reproduce the experimental ammonia inversion barrier[14] from reported fixed equilibrium[15] (set A) and variable[13] (set B) NH bond distances.

The above optimization scheme yields the inversion-optimized CNDO/2 parameters listed in Table I.[16]

**Finite Perturbation Theory.** In the finite perturbation formalism, using the method of finite differences,[7a] the coupling constant between two nuclei, A and B, is given by eq 1.

$$J_{AB} = (\hbar/2\pi)(8\pi\beta/3)^2\gamma_A\gamma_B S_A^2(0)S_B^2(0)\rho_{S_AS_A}{}^{spin}(h_B)/h_B \tag{1}$$

In the above equation, $\beta$ is the Bohr magneton, $\gamma_A$ and $\gamma_B$ are the magnetogyric ratios of nuclei A and B, $S_A^2(0)$ and $S_B^2(0)$ are the valence s-orbital electron densities at nuclei A and B,[17] respectively, and $\rho_{S_AS_A}{}^{spin}(h_B)$ is the diagonal element of the spin matrix, in the presence of the contact perturbation $h_B$.

As suggested by Pople et al.[7a] and Wasylishen and Shaffer,[18] $h_B$ is taken as approximately $10^{-3}$ au. In order to obtain reasonably accurate coupling constants in a small number of SCF iterations, the convergence criterion is

$$10^{-3} \geq |(\rho_{ii}{}^{old} - \rho_{ii}{}^{new})/\rho_{ii}{}^{old}| \tag{2}$$

for all $i$.[16] Should a calculation not satisfy this criterion after 40 SCF cycles, it is assumed that it has converged sufficiently well if eq 2 is obeyed for $i = S_A$. Note that a change of $10^{-3}$ au in $\rho_{S_AS_A}{}^{spin}$ in one SCF cycle will affect a calculated coupling constant of 10 Hz by about 0.01 Hz.[18]

## Results and Discussion

The pyramidal inversion barrier is the energy difference between the pyramidal ground state and the (assumed planar) transition state. Total energy curves are obtained using a 5° out-of-plane interval for all structures except the parameterized molecules, where a 2° interval is used. Except for the bond distances in the parameterized molecules, the molecular geometry during inversion follows the convention outlined in RAFTM.[19]

Table I. Inversion-Optimized CNDO/2 Parameters

| | Set A[a] | | Set B[a] | | RAFTM[b] | |
|---|---|---|---|---|---|---|
| Atom | $\chi_s$ | $\chi_p$ | $\chi_s$ | $\chi_p$ | $\chi_s$ | $\chi_p$ |
| B | 6.6 | 4.8 | 8.3 | 6.0 | 8.2 | 4.0[c] |
| C | 12.4[d] | 6.2[d] | 12.5[e] | 6.8[e] | 12.7[f] | 6.1[f] |
| N | 18.1[g] | 7.61[g] | 16.6[h] | 7.61[h] | 17.6[i] | 7.91[i] |
| O | 23.9 | 9.05 | 20.8 | 8.4 | 22.1[j] | 10.1[j] |
| F | 29.5 | 10.5 | 24.9 | 9.2 | 26.8 | 11.9 |

[a] The boron, oxygen, and fluorine parameters are obtained by a linear extrapolation of the carbon and nitrogen values. [b] The boron and fluorine parameters are obtained by a linear extrapolation of the carbon, nitrogen, and oxygen values. [c] Linear extrapolation gives 4.0, not 4.4 as reported in ref 9. [d] Parameterized to reproduce the ab initio barrier of 2.8 kcal/mol calculated for methyl anion (ref 12) with fixed CH bond distance of 1.079 Å. [e] Parameterized to reproduce the ab initio barrier of 2.8 kcal/mol calculated for methyl anion (ref 12) with variable CH bond distance (ref 13). [f] Parameters reproduce the ab initio barrier of 5.2 kcal/mol calculated for methyl anion (Ph. Millié and G. Berthier, *Int. J. Quantum Chem., Symp.*, **2**, 67 (1968)) with a fixed CH bond distance of 1.095 Å (methane distance). [g] Parameterized to reproduce the experimental barrier of 5.8 kcal/mol (ref 14) for ammonia with fixed NH bond distance (ref 15). [h] Parameterized to reproduce the experimental barrier of 5.8 kcal/mol (ref 14) for ammonia with variable NH bond distance (ref 13). [i] Parameterized in ref 9 to reproduce the experimental barrier of 19.0 kcal/mol (see ref 9, footnote 28) in 1-methylaziridine, calculated from a potential curve at 8° intervals in the out-of-plane angle, and using modified parameters for carbon. Using the geometry of footnote *k* (Table I) and the modified parameters for carbon, we calculate a barrier of 19.3 kcal/mol from a potential curve at 5° intervals in the out-of-plane angle. [j] Parameterized in ref 9 to reproduce the experimental barrier of 10 kcal/mol (footnote *m*, Table I) in 1-methyloxiranium ion, calculated from a potential curve at 8° intervals in the out-of-plane angle, and using modified parameters for carbon. Using the geometry of footnote *n* (Table I) and the modified parameters for carbon we calculate a barrier of 11.2 kcal/mol from a potential curve at 5° intervals in the out-of-plane angle. [k] The aziridine ring framework of J. M. Lehn, B. Munsch, Ph. Millié, and A. Veillard, *Theor. Chim. Acta*, 13, 313 (1969) is used. The remaining molecular fragments are obtained from tables (footnote *l*, Table I). [l] (a) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Burlington House, London, 1971; (b) ref 5, Tables 4.16 and 4.17. [m] Value reported for 1-isopropyloxiranium ion reported by J. B. Lambert and D. H. Johnson, *J. Amer. Chem. Soc.*, 90, 1349 (1968). [n] The oxirane ring framework of G. L. Cunningham, A. W. Boyd, R. J. Meyers, W. D. Gwinn, and W. I. Le Van, *J. Chem. Phys.*, 19, 676 (1951) is used. The remaining molecular fragments are obtained from tables (footnote *l*, Table I).

Table II contains the results obtained where the inversion-optimized CNDO/2 parameters in Table I and INDO are employed.

Coupling constants are calculated using eq 1, and they are computed for various parameterizations using the experimental geometry for 11 molecules. The parameterizations are (i) CNDO/2 (the inversion-optimized parameters and the Pople–Segal parameterization)[4] and (ii) INDO. The results are in Table III.

It is known that calculated coupling constants are often very sensitive to molecular geometry. For example, in the calculations of Wasylishen and Schaffer,[18] using the INDO level of approximation, the $^{15}N$-H coupling constant in ammonia changes from −36 to −43 Hz upon a change from the experimental to the cruder molecular geometry obtained from standard tables.[5] In order to study this effect,

**Table II.** Barriers for Pyramidal Inversion for Various Parameter Sets[a]

| Compound | Set A[b] | Set B[b] | RAFTM[b] | INDO[c] | Reported[d] | Geometry |
|---|---|---|---|---|---|---|
| (i) Inversion at Carbon | | | | | | |
| Methyl anion | | | 5.1[e] | | (5.2)[f] | *g* |
| | 2.8[e] | | | 10.4 | (2.8)[h] | *f* |
| | | 2.8[e] | | | (2.8)[h] | *i* |
| Cyclopropyl anion | 12.2 | 9.2 | 15.0 | 20.7 | (20.8)[j] | *j* |
| Cyclopropenyl anion | 34.8 | 29.3 | 38.9 | 55.4 | (52.3)[k] | *k* |
| (ii) Inversion at Nitrogen | | | | | | |
| Ammonia | 5.8[e] (4) | | 3.3 (23) | 5.0 (11) | 5.8[l] | *m* |
| | | 5.8[e] (4) | | | 5.8[l] | *i* |
| Methylamine | 7.1 (21.5) | 3.0 (20) | 4.4 (8) | 4.8 (4) | 4.8[n] | *n* |
| Dimethylamine | 8.5 (29) | 3.3 (14.5) | 5.7 (16) | 5.1 (9) | 4.4[o] | *o* |
| Fluoroamine | 15.8 (30) | 8.9 (36) | 12.1 (33) | 17.6 (24) | (20.3)[p] | *q* |
| Difluoroamine | 54.9 | 45.6 | 51.6 | 60.4 | | *r* |
| Cyanamide | 3.0 (13) | 0.4 (19) | 1.2 (11) | 0.9 (14.5) | 2.0[s] | *t* |
| Aziridine | 27.3 (34) | 19.1 (11) | 21.8 (27) | 24.7 (31) | (18.3)[u] | *u* |
| Oxaziridine | 39.8 (32) | 29.6 (25.5) | 33.8 (17) | 42.4 (35) | (32.4)[u] | *u* |
| Pyrrole | 0 (4) | 0. (4) | 0 (4) | 0 (4) | Planar[v] | *v* |
| Formamide | 5.1 (28) | 2.6 (18) | 3.4 (21.5) | 3.9 (25.5) | 1.1[w] | *x* |
| Acetamide | 3.2 | 1.2 | 1.7 | 1.5 | | *q* |
| $\bar{\delta}$[y] | 4 | 3 | 2 | 3 | | |
| $\bar{R}$[z] | 21.7 | 16.9 | 17.8 | 17.6 | | |

[a] Barriers are in kcal/mol. Where relevant, the rank of $|\Delta E_i^{\text{calcd}} - \Delta E_i^{\text{reported}}|$ is in parentheses, where average ranks are used for ties. [b] Parameters listed in Table I. [c] See ref 5 and 6. [d] Values obtained by LCAO–MO–SCF calculations are in parentheses. [e] Parameterize. [f] Ph. Millié and G. Berthier, *Int. J. Quantum Chem., Symp.*, **2**, 67 (1968). [g] Fixed CH bond distance of 1.095 Å. [h] See ref 12. [i] See ref 13. [j] D. T. Clark and D. R. Armstrong, *Chem. Commun.*, 850 (1969). [k] D. T. Clark, *Chem. Commun.*, 637 (1969). [l] See ref 14. [m] See ref 15. [n] M. Tsuboi, A. Y. Kirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967). [o] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). [p] J. M. Lehn and B. Munsch, *Chem. Commun.*, 1062 (1970). [q] See Table I, ref *l*(a). [r] D. Lide, *J. Chem. Phys.*, **38**, 456 (1963). [s] W. H. Fletcher, *ibid.*, **39**, 2478 (1963). [t] D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966). [u] J. M. Lehn, B. Munsch, Ph. Millié, and A. Veillard, *Theor. Chim. Acta*, **13**, 313 (1969). [v] L. Nyaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sørensen, *J. Mol. Struct.*, **3**, 491 (1969). [w] See ref 9, Table II, entry number 9. [x] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960). [y] Mean deviation: $\bar{\delta}_j = \Sigma\delta_{ij}/n_j$, where $\delta_{ij} = |\Delta E_{ij}^{\text{calcd}} - \Delta E_i^{\text{reported}}|$, for inversion at nitrogen, for the *j*th treatment. [z] Average rank per treatment: $\bar{R}_j = \Sigma r_{ij}/n_j$, where $r_{ij}$ is the rank of the *i*th sample ($\delta_{ij}$) for the *j*th treatment.

**Table III.** Comparison of Calculated Coupling Constants $^1J(^{15}N,H)$ for Various Parameter Sets Using Experimental Geometry[a]

| Compound | Set A[b] | Set B[b] | RAFTM[b] | CNDO/2[c] | INDO[d] | Reported | Ref[e] |
|---|---|---|---|---|---|---|---|
| Ammonia | −32.6 (34) | −41.0 (20) | −37.7 (24) | −23.1 (42) | −32.8 (33) | −61.2 | *f, g* |
| Methylamine | −36.3 (32) | −44.8 (18) | −41.5 (23) | −26.0 (43) | −39.8 (27) | −64.5 | *h, g* |
| Dimethylamine | −27.6 (44) | −36.6 (36) | −33.2 (38) | −16.6 (95) | −32.1 (39.5) | −67.0 | *i, g* |
| Fluoroamine | −28.0 | −37.2 | −35.0 | −17.2 | −18.9 | | *j* |
| Difluoroamine | −13.8 | −21.6 | −21.7 | −4.6 | +1.4 | | *k* |
| Cyanamide | −61.8 (30) | −68.0 (21) | −65.4 (25.5) | −53.9 (41) | −72.7 (15) | (−)89.4 | *l, m* |
| Aziridine | −19.9 | −31.3 | −27.0 | −7.4 | −7.6 | | *n* |
| Oxaziridine | −17.3 | −29.7 | −25.8 | −3.1 | +8.8 | | *n* |
| Pyrrole | −65.8 (37) | −69.5 (29) | −67.5 (35) | −61.6 (39.5) | −79.1 (16) | −96.5 | *o, p* |
| Formamide | −76.3 (13) | −79.8 (7) | −77.8 (9) | −72.0 (17) | −87.5 (3) | −91.3[q] | *r, s* |
| | −71.4 (14) | −74.8 (8) | −73.0 (10.5) | −67.0 (19) | −84.2 (2) | −86.9[t] | |
| Acetamide | −78.4 (6) | −80.7 (4) | −79.0 (5) | −75.3 (10.5) | −88.8 (1) | (−)89.2[q] | *u, v* |
| | −61.5 (28) | −63.9 (22) | −62.4 (25.5) | −58.7 (31) | −71.8 (12) | (−)86.4[t] | |
| $\bar{\delta}$[w] | 25 | 19 | 22 | 31 | 16 | | |
| $\bar{R}$[x] | 26.4 | 18.3 | 21.7 | 32.0 | 16.5 | | |

[a] Coupling constants are in Hz. Where relevant the rank of the difference $|^1J^{\text{calcd}} - {}^1J^{\text{exptl}}|$ is in parentheses, where average ranks are used for ties. [b] Parameters listed in Table I. [c] See ref 4 and 5. [d] See ref 5 and 6. [e] Geometry reference then coupling constant reference, separated by comma. [f] See ref 15. [g] M. Alei, Jr., A. E. Florin, W. M. Litchman, and J. F. O'Brien, *J. Phys. Chem.*, **75**, 932 (1971). [h] See Table II, footnote *n*. [i] See Table II, footnote *o*. [j] See Table I, ref *l*(a). [k] See Table II, footnote *r*. [l] See Table II, footnote *t*. [m] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964). [n] See Table II, footnote *u*. [o] See Table II, footnote *v*. [p] E. Rahkamaa, *Mol. Phys.*, **19**, 727 (1970). [q] Trans proton with respect to the carbonyl oxygen. [r] See Table II, footnote *x*. [s] R. J. Chuck, D. G. Gillies, and E. W. Randall, *Mol. Phys.*, **16**, 121 (1969). [t] Cis proton with respect to the carbonyl oxygen. [u] W. A. Denne and R. W. H. Small, *Acta Crystallogr., Sect. B*, **27**, 1094 (1971). [v] M. Liler, *J. Magn. Reson.*, **5**, 333 (1971). [w] Mean deviation: $\delta_j = \Sigma\delta_{ij}/n_j$, where $\delta_{ij} = |^1J_{ij}^{\text{calcd}} - {}^1J_i^{\text{exptl}}|$ for the *j*th treatment. [x] Average rank per treatment: $\bar{R}_j = \Sigma r_{ij}/n_j$, where $r_{ij}$ is the rank of the *i*th sample ($\delta_{ij}$) for the *j*th treatment.

coupling constant calculations are repeated using the theoretical equilibrium N–H out-of-plane angle obtained in the inversion barrier calculations. Here the Pople–Segal parameters are not used, since they give a poor out-of-plane angle. The results are in Table IV.

For the *i*th treatment (set A, set B, etc.), the mean deviation ($\bar{\delta}_i$) is a reliable measure of the calculated vs. experimental values. These values are accordingly cited in the tables.

To establish the confidence level for apparent differences in the $\bar{\delta}$ values, it is necessary to use nonparametric statistical methods, for the deviation of the calculated vs. reported value for each molecule need not be normally distributed about the mean $\bar{\delta}_i$, due to systematic errors in the theory.

The statistical treatments used here are the Kruskal–Wallis analysis of variance rank sum test and the Dunn multiple comparison test.[20]

The rank of the *j*th deviation for the *i*th treatment ($r_{ij}$) is computed, where average ranks are used for ties, and these plus the average rank ($\bar{R}_i$) for the treatment are re-

Table IV. Comparison of Calculated Coupling Constants $^1J(^{15}N,H)$ for Various Parameter Sets Using Equilibrium Geometry from Inversion Barrier Calculations[a,b]

| Compound | Set A[c] | Set B[c] | RAFTM[c] | INDO[d] | Reported[e] |
|---|---|---|---|---|---|
| Ammonia | −43.1 (6) | −49.1 (3) | −52.7 (1) | −42.3 (7) | −61.2 |
| Methylamine | −34.7 (18) | −53.9 (2) | −45.2 (8) | −37.0 (15) | −64.5 |
| Dimethylamine | −28.3 (24) | −49.1 (5) | −39.8 (14) | −38.8 (16) | −67.0 |
| Fluoroamine | −32.5 | −47.3 | −39.7 | −18.8 | |
| Difluoroamine | −24.0 | −34.6 | −33.9 | +0.5 | |
| Cyanamide | −44.0 (28) | −69.9 (9) | −58.4 (20) | −65.3 (11) | (−)89.4 |
| Aziridine | −22.4 | −39.8 | −35.2 | −9.3 | |
| Oxaziridine | −16.6 | −33.5 | −25.1 | +8.3 | |
| Pyrrole | −65.8 (19) | −69.5 (13) | −67.5 (17) | −79.1 (4) | −96.5 |
| Formamide | −44.7 (27) | −51.7 (23) | −49.0 (26) | −49.6 (25) | −89.1[f] |
| Acetamide | −51.6 (22) | −67.5 (10) | −55.3 (21) | −61.0 (12) | (−)87.8[f] |
| $\bar{\delta}$[g] | 35 | 21 | 27 | 26 | |
| $\bar{R}$[h] | 20.6 | 9.3 | 15.3 | 12.9 | |

[a] Coupling constants are in Hz. Where relevant the rank of the difference $|^1J^{\text{calcd}} - {}^1J^{\text{exptl}}|$ is in parentheses, where average ranks are used for ties. [b] The N–H out-of-plane angle is the same as the corresponding angle which gives the minimum energy in the inversion barrier calculations for the given parameter set. Bond angles not dependent on the out-of-plane angle and all bond lengths are taken from the experimental references in Table III. Conformations about single bonds are assumed staggered. [c] Parameters listed in Table I. [d] See ref 5 and 6. [e] References for the experimental values are in Table III. [f] In view of footnote *b*, the cis proton with respect to the carbonyl oxygen is identical with the trans proton. Hence the reported coupling constant is taken as the average of the experimental value for the cis and trans protons. [g] Mean deviation: $\delta_j = \Sigma\delta_{ij}/n_j$, where $\delta_{ij} = |^1J_{ij}^{\text{calcd}} - {}^1J_i^{\text{exptl}}|$ for the *j*th treatment. [h] Average rank per treatment: $\bar{R}_j = \Sigma r_{ij}/n_j$, where $r_{ij}$ is the rank of the *i*th sample ($\delta_{ij}$) for the *j*th treatment.

Table V. Deviations in Barrier Trends for Acyclic Amines from Data of Table II[a]

| Sequence | Set A | Set B | RAFTM | INDO |
|---|---|---|---|---|
| $NH_3$ to $NH_2CH_3$ | 2.3 (11) | 1.8 (7) | 2.1 (9.5) | 0.8 (4) |
| $NH_2CH_3$ to $NH(CH_3)_2$ | 1.8 (7) | 0.7 (2.5) | 1.7 (5) | 0.7 (2.5) |
| $NH(CH_3)_2$ to $NH_2CN$ | 3.1 (14) | 0.5 (1) | 2.1 (9.5) | 1.8 (7) |
| $NH_2CN$ to $NH_2CHO$ | 3.0 (12) | 3.1 (14) | 3.1 (14) | 3.9 (16) |
| $\bar{\delta}$ | 2.6 | 1.5 | 2.2 | 1.8 |
| $\bar{R}$ | 11.0 | 6.1 | 9.5 | 7.4 |

[a] Deviations in kcal/mol. The rank of each deviation is in parentheses, where average ranks are used for ties.

ported in the tables. Small values for $\bar{\delta}$ and $\bar{R}$ indicate an accurate treatment.

In the inversion barrier calculations, Table II, the apparent differences in $\bar{\delta}$, for the inversion-optimized CNDO/2 parameters and INDO, are not significant to a 90% level of confidence.

Table V reports the deviations in the calculated barrier trends vs. the experimental barriers for the sequence $NH_3$ to $NH_2CH_3$ to $NH(CH_3)_2$ to $NH_2CN$ to $NH_2CHO$. The apparent differences in $\bar{\delta}$, for the inversion-optimized CNDO/2 parameters and INDO, are not significant to a 90% level of confidence.

In the calculation of coupling constants using experimental molecular geometries, Table III, the mean deviation of CNDO/2 (Pople–Segal parameterization) is inferior to that of INDO, to a 90% level of confidence. Upon redoing the statistics for the combined population Set B-RAFTM vs. CNDO/2 and INDO, the mean deviation of CNDO/2 is inferior to each of the others to at least a 90% confidence level.

In Table IV, where the coupling constants are calculated using the theoretical equilibrium N–H out-of-plane angle obtained in the inversion barrier calculations, the mean deviation of set A is inferior to that of set B, to a 90% level of confidence. Upon redoing the statistics for the combined populations set B-RAFTM vs. INDO, the mean deviation of these CNDO sets does not differ significantly from the INDO result.

In view of these results, set A has no apparent computational advantage over set B or RAFTM.

The apparent deterioration in the $\bar{\delta}$ values of Table IV with respect to the corresponding entries in Table III is significant for INDO (90% confidence level).

For Tables III–V all the apparent differences in $\bar{\delta}$ not already stated are deemed to be statistically insignificant.

These results lead to the following conclusions concerning semiempirically calculated inversion barriers at nitrogen and directly bonded $^{15}N$–H coupling constants.

For molecules containing first-row atoms, inversion barriers and trends calculated from inversion-optimized CNDO/2 parameters are as accurate as those calculated in the INDO level of approximation, while it is already known that those calculated from CNDO (Pople–Segal parameterization) are not.[21] This conclusion differs from that of Stevenson and Burkey,[10] whose calculations often assume tetrahedral ground state geometries.

Coupling constants calculated from the inversion-optimized CNDO/2 parameter set of RAFTM and set B are as accurate as those calculated from INDO, while those calculated from CNDO/2 (Pople–Segal parameterization) are not.

Three recommendations for further work arise from those calculations. First, INDO and the inversion-optimized CNDO/2 parameter sets predict very different coupling constants for molecules which apparently have not been studied. Thus experimental work on these systems is important. Second, in view of the different carbon parameters for set B and RAFTM, the calculation of $^1J(^{13}C,^{15}N)$ should provide a useful framework in which to compare these methods. Third, the overall accuracy of our INDO coupling constants is apparently more sensitive to assumed molecular geometry than the inversion-optimized CNDO/2 methods of RAFTM and set B. It is important to determine by further study if this is true in general.

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(2) See, for example, the review article by T. Axenrod in "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons", T. Axenrod and G. A. Webb, Ed., Wiley, New York, N.Y., 1974, p 81.

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# The Electronic Structure of Pyrazine. A Valence Bond Model for Lone Pair Interactions

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**Abstract:** A valence bond (VB) model is developed to describe the interaction of the lone pair excitations in pyrazine. Extensive ab initio minimal basis set (MBS) configuration interaction (CI) calculations show that the description of the n cations and $n\pi^*$ states of pyrazine afforded by the VB model is more accurate than that afforded by the molecular orbital (MO) model proffered by Hoffmann. The VB picture of the n cations and $n\pi^*$ states involves the interaction (resonance) of two *equivalent, localized* excitations. The resultant splitting is large (1 to 2 eV) because of a slight delocalization of the n orbitals induced by the Pauli principle. (The n orbitals remain 90% localized on the nitrogens.) The splitting of the $n\pi^*$ states is comparable to that of the n cations because the $\pi^*$ orbital is delocalized, even though the excitation process is localized on one nitrogen. The MBS CI calculations indicate that the lowest ionization potential of pyrazine corresponds to the ${}^2A_g(n)$ state. Calculations on the lowest Rydberg states indicate that they involve excitations out of an n orbital rather than a $\pi$ orbital, in opposition to earlier spectroscopic assignments. Finally, the calculations show that the forbidden $1\,{}^1B_{2g}(n\pi^*)$ state is 1 eV higher than the allowed $1\,{}^1B_{3u}(n\pi^*)$ state, so that the perturbations observed in the absorption spectrum must be ascribed to another source.

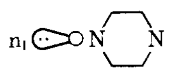
## I. Introduction

The nature of the excited states of pyrazine has generated great interest among spectroscopists and theoreticians for many years.[2] In addition to the $\pi \rightarrow \pi^*$ transitions, analogous to those of benzene, one expects new $n \rightarrow \pi^*$ transitions involving the nonbonding (or lone pair) orbitals on the nitrogen. Since there are two nitrogens in pyrazine, the question arises as to how the states involving excitations from the two different nitrogens interact with one another. With the advent of photoelectron spectroscopy,[3] the question has been extended to the interaction of the two possible n cations.

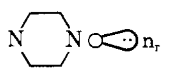
Two models for the interaction of the lone pairs have been previously developed, namely, the exciton model of El-Sayed and Robinson[4] and the molecular orbital (MO) model of Hoffmann.[5] The MO model has had good success in elucidating the photoelectron spectra (vide infra). In this paper we present an alternative model based on valence bond (VB) ideas. Ab initio minimal basis set (MBS) calculations have been carried out to test the usefulness of the VB model. In these calculations, emphasis has been placed on describing the $n\pi^*$ excited states and the n cations.

## II. Qualitative VB Model

**(A) n Cations.** To begin with, the VB view of the lone pairs in the ground state of pyrazine is represented by **1a** and **1b**.[6]

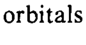


**1a**



**1b**

The nonbonding orbitals are represented by

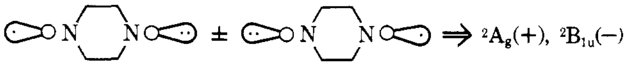


and the electrons by dots. In the VB model the lone pairs ($n_l$ and $n_r$) are localized and equivalent, so that the ground state wave function is

$$\Psi = \mathcal{A}(\Phi_{\mathrm{core}} n_l^2 n_r^2 \alpha\beta \ldots \alpha\beta)$$

where $\Phi_{\mathrm{core}}$ represents the remaining electrons.

Now consider ionization of one of the lone pair electrons. One can remove the electron from either the left or right lone pair. These equivalent ion states are combined (resonance) to form two n cation states, ${}^2A_g$ and ${}^2B_{1u}$



**2**

The wave functions in this approximation are[7]

$$\Psi({}^2A_g) = (\Psi_L + \Psi_R)/\sqrt{2(1 + S)} \quad (1)$$

$$\Psi({}^2B_{1u}) = (\Psi_L - \Psi_R)/\sqrt{2(1 - S)} \quad (2)$$