## Inversion Barriers by the MINDO Method[1]

*Sir:*

Recent work in these laboratories has led to the development of a semiempirical SCF MO treatment (MINDO approximation[2]) of molecular ground states, including all the valence electrons, which seems to give very good estimates of the heats of formation of organic molecules composed of carbon, hydrogen, nitrogen, and oxygen. Here we report some preliminary applications of the method to a problem of current interest, namely the barriers to inversion in compounds of trivalent nitrogen and the geometry and barriers to inversion in compounds of trivalent carbon (*i.e.*, radicals and carbanions).

In its present form the MINDO method does not give good estimates of bond lengths; it is therefore necessary to use assumed geometries in which the bond lengths are assigned standard values. The calculations reported here were carried out using the standard bond lengths of ref 2 for geometries in which the tricovalent atom is either planar or pyramidal with tetrahedral bond angles. In cases where the pyramidal structure has the lowest energy, the difference in energy ($\Delta E$) between the pyramidal and planar structures is taken as a measure of the barrier to inversion. In this preliminary study, we did not try to calculate the whole potential surface; in the case of ammonia, the minimum energy corresponded quite closely to tetrahedral geometry, in agreement with experiment.

Table I compares values calculated in this way for a number of amines and hydrazines with those estimated by nmr or microwave spectroscopy. In hydrazine $R_2NNR'_2$ it was assumed that the lines RR and R'R' are mutually perpendicular; this is equivalent to assuming a minimum interaction between the nitrogen lone pairs in a simple valence picture.

**Table I.** Calculated and Observed Barriers to Inversion of Trivalent Nitrogen

| Compd | Barrier height (kcal/mole) Calcd | Obsd |
|---|---|---|
| Ammonia | 3.7 | 5.9[a] |
| Methylamine | 5.8 | 6.0[b] |
| Ethylamine | 5.7 | |
| Dimethylamine | 6.7 | |
| Trimethylamine | 6.5 | 8.5[a] |
| Aziridine | 13.8 | 12.0[c] |
| N-Aminoaziridine; ring N | 22.3 | >22[d] |
| NH$_2$ | 9.7 | |
| N-Methylmethyleneaziridine | 10.5 | 6.4[e] |
| Formamide | 1.5 | 1.0[f] |
| Hydrazine | 10.3 | 2.8[g] |

[a] R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954). [b] M. Tsuboi, A. Y. Hirakawa, T. Ino, T. Sasaki, and K. Tamagak, *J. Chem. Phys.*, **41**, 2721 (1964). [c] W. M. Tolles and W. D. Gwinn, *ibid.*, **42**, 2253 (1965); value given as a "lower barrier limit." [d] S. J. Brois, *Tetrahedron Letters*, 5997 (1968). [e] A. Loewenstein, J. F. Neumer, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3599 (1960). [f] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960). [g] T. Kosuya and T. Kojuna, Proceedings of the International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, p C204; *Chem. Abstr.*, **61**, 2616*d* (1964).

The agreement between the calculated and observed barriers is clearly very good. The calculated values not only follow all the observed trends but even give good numerical estimates of the barrier heights.[3] Thus our calculations reproduce closely the great increase in barrier height in passing from open-chain amines to aziridine, the significant decrease on passing from aziridine to its methylene derivative, and the large increase in passing from aziridine to the corresponding hydrazine. This last difference is clearly due to an increase in the nitrogen lone-pair–lone-pair repulsion when one of the nitrogen atoms in hydrazine assumes a planar form; a similar effect no doubt accounts for the analogously high inversion barriers observed in N-chloroaziridines.[5] The calculations also reproduce correctly the increase in the inversion barrier with alkyl substitution and the decrease in passing from ammonia to an amide; both these effects would of course also be expected in terms of simple valence theory.

**Table II.** Calculated Barriers to Inversion in Radicals and Carbanions

| Radical or ion | Calculated barrier height (kcal/mole) Radical | Anion |
|---|---|---|
| Methyl | −4.9 | 20.2 |
| Isopropyl | −3.3 | 23.2 |
| Vinyl | 4.3 | 31.1 |
| Cyclopropyl | 4.8 | 36.6 |

The only discrepancy occurs in the case of hydrazine itself where the MINDO method predicts the barrier to be much larger than in ammonia, whereas microwave studies have led to a much lower value. However the "experimental" value was based on an assumed form of the potential function which may well not be correct; certainly it is very difficult to believe that the barrier in hydrazine can in fact be lower than in ammonia in view of the evidence in the case of N-aminoaziridine and the calculations reported here.

Since the MINDO method seemed so successful in this connection, we also carried out calculations for some carbon radicals and carbanions (Table II). Here no quantitative data are available for comparison, but the available evidence is certainly well interpreted by our calculations. Thus simple radicals (*e.g.*, methyl) are known to be coplanar,[6] whereas the cyclopropyl radical is probably pyramidal with a significant barrier to inversion;[7] the calculations also correctly predict the vinyl radical to be nonlinear, the calculated barrier being for inversion through a linear intermediate.[8]

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(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustman, *ibid.*, **50**, 1275 (1969); M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

(3) Previous calculations have been unsatisfactory in this respect; thus the barrier calculated[4] by a very elaborate *ab initio* method for NH$_3$ was more than double that observed.

(4) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **45**, 888 (1966).

(5) (a) S. J. Boris, *J. Am. Chem. Soc.*, **90**, 506 (1968); S. J. Brois, *ibid.*, **90**, 508 (1968); J. M. Lehn and J. Wagner, *Chem. Commum.*, 148 (1968). (b) Our calculations indicate that the increase in barrier height cannot be due to an inductive effect of the group attached to nitrogen. The barriers calculated for amines are less than those for the isoconjugate carbanions (Table II), implying that an increase in electronegativity of the trivalent atom leads to a *decrease* in barrier height.

(6) See B. Mile, *Angew. Chem.*, **80**, 519 (1968).

(7) M. J. S. Dewar and J. M. Harris, *J. Am. Chem. Soc.*, **91**, 3652 (1969), and papers cited therein.

(8) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

In the case of carbanions, it is known that the cyclopropyl carbanion has a much higher barrier to inversion that its open-chain analogs[9] and that the vinyl anion also retains its geometry tenaciously (estimated barrier to inversion >25–35 kcal/mole[10]). This evidence refers, however, not to the free anions but to their lithium derivatives; one cannot therefore be sure that we are right in predicting that the barriers in carbanions are much higher than in their corresponding amines, although this certainly does seem to be the case.

[9] See H. M. Walborsky, *Record Chem. Prog.*, 23, 75 (1965).

[10] S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, 81, 6313 (1959).

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*Received February 1, 1969*

## Rotation–Inversion Barriers in Hydrazines[1]

*Sir:*

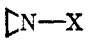
We wish to report the discovery of considerable barriers to rotation and/or inversion in some simple hydrazines. Previous work has shown the existence of surprisingly large barriers to rotation about P–N bonds in aminophosphines[2] and N–As bonds in aminoarsines,[2a] and similar rotational barriers have been observed about N–S[3] and N–O[4] bonds. These barriers are much too large to be due to conformational effects of the kind that operate in ethane; they must be attributed to lone-pair interactions. On this basis one might expect to find comparable barriers to rotation about the N–N bond in hydrazines. Barriers to rotation have indeed been reported for di- and tetraacylhydrazines, where both nitrogen atoms are of amide type,[5] and in hydrazones,[6] triazines,[7] and tetrazines.[8] Here, however, one might expect $\pi$ bonding or steric effects to lead to enhanced barriers to rotation; no measurements have as yet been reported for hydrazines of simpler types.

Table I. Spectral Data and Free Energy of Activation ($\Delta G^{\ddagger}_c$) Estimated at the Coalescence Temperature ($T_c$)

| Compd | Solvent | $\Delta\nu_{AB}{}^a$ (at $T$), Hz | $J_{AB}$, Hz | $T_c$, °C | $\Delta G^{\ddagger}_c$, kcal/mole |
|---|---|---|---|---|---|
| II | $CCl_3F\text{-}CH_2Cl_2{}^b$ | ~50 | | −95 | ~8.5 |
| III | $CDCl_3$ | 27.0 (0°) | 12.8 | 59 | 16.6 |
| IV | $CDCl_3$ | 12.3 (0°) | 12.8 | 50 | 16.2 |
| V | $CDCl_3$ | 29.7 (−60°) | 13.3 | −38 | 11.5 |

[a] At 100 MHz. [b] ~3:1.

A further complicating factor is the possibility of an enhanced barrier to inversion of nitrogen in compounds where nitrogen is attached to another atom carrying unshared electrons. Thus the barriers to inversion in aziridine derivatives I, where X is $NH_2$ or chlorine, are very much greater than in aziridine itself,[9] and indeed Roberts, *et al.*,[4b] attributed the barriers in simple hydroxylamines to inversion rather than rotation. It is true that the barrier to inversion in hydrazine has been reported[10] to be much lower than that for ammonia; this, however, is at variance with the evidence from N-aminoaziridine[9] and also with SCF MO calculations which predict a barrier height in hydrazine of ~10 kcal/mole.[11]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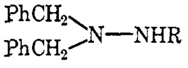
$\mathrm{(PhCH_2)_2N{-}NHR}$

II, R = H
III, R = 2, 4-dinitrophenyl
IV, R = picryl
V, R = 2-pyrimidyl

We have now examined the nmr spectra[12] of 1,1-dibenzylhydrazine (II), and of its 2,4-dinitrophenyl (III), picryl (IV), and 2-pyrimidyl (V) derivatives. All of the spectra showed a dependence on temperature that indicated significant barriers to inversion and/or rotation.

In the case of II, the benzyl protons must be equivalent unless the adjacent nitrogen atom is pyramidal and inverts slowly, effectively forming an asymmetric center. At room temperature the corresponding nmr signal was a sharp singlet, but below −80° in dichloromethane–fluorotrichloromethane the line broadened rapidly and at −104° had separated in two broad peaks. Although the limiting low-temperature spectrum was not attained, a reasonable estimate of the free energy of activation at the coalescence temperature (−95°) could be made (Table I). The barrier is in good agreement with that calculated theoretically; it seems clear that the value (3.5 kcal/mole) reported[10] for hydrazine itself must be incorrect.

In the case of the substituted dibenzylhydrazines III–V, the signal for the benzylic protons at low tem-

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[2] (a) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Am. Chem. Soc.*, 90, 4185 (1968); (b) M. P. Simonnin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. France*, 3544 (1967); (c) D. Imbery and H. Friebolin, *Z. Naturforsch.*, 23b, 759 (1968).

[3] H. J. Jacobsen and A. Senning, *Chem. Commun.*, 617 (1967); M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *Tetrahedron Letters*, 5055 (1968); J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).

[4] (a) B. J. Price and I. O. Sutherland, *ibid.*, 1070 (1967); (b) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 4089 (1965).

[5] B. H. Korsch and N. V. Riggs, *Tetrahedron Letters*, 5897 (1966); G. J. Bishop, B. J. Price, and I. O. Sutherland, *Chem. Commun.*, 672 (1967); A. Foucand and R. Roudant, *Compt. Rend., Ser. C*, 266, 726 (1968).

[6] A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 863 (1967).

[7] N. P. Marullo, C. B. Mayfield, and E. M. Wagener, *J. Am. Chem. Soc.*, 90, 510 (1968).

[8] W. M. Tolles, D. W. Moore, and W. E. Thun, *ibid.*, 88, 3476 (1966).

[9] S. J. Brois, *Tetrahedron Letters*, 5997 (1968); *J. Am. Chem. Soc.*, 90, 506, 508 (1968).

[10] T. Kasuya and T. Kojima, Proceedings of the International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, p C204; *Chem. Abstr.*, 61, 2616*d* (1964).

[11] M. J. S. Dewar and M. Shanshal, *J. Am. Chem. Soc.*, 91, 3654 (1969).

[12] The spectra were measured by Mr. E. J. Burshnick on a Varian HA-100 spectrometer using TMS as internal lock, with 5–10% (w/v) solutions.