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A MINDO/2′-MO Study of the Inversion Barriers of Some Molecules Involving First-Row Atoms

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Synopsis. The inversion barriers of CH_3^-, NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, NH_2OH, NH_2CHO, and OH_3^+ were investigated by means of the MINDO/2′ method. Although the calculated bond lengths are in satisfactory agreement with the experimental values, the calculated bond angles are too large and resulted in relatively low inversion barriers in comparison with the observed values.

In general, pyramid-like molecules involving an unshared pair on its central atom instead of a fourth substituent indicate the intramolecular motions which lead to inversion.

Inversion barriers are intimately related to the configurations (especially, bond angles) of molecules,[1)] for instance, the smaller angles of phosphine, arsine, *etc.*, as compared with those of ammonia, make inversion more difficult.[2)]

Recently, Allen and Arents[3)] have argued that carefully parametrized semiempirical adaptations of the SCF-MO method can be useful for investigating inversion barriers. Stevenson and Burkey[4)] have compared the effectiveness of several different versions of the CNDO and INDO methods in predicting the inversion barriers of AR(R′) (R″), where A=C, N, O, Si, P, and S, and they demonstrated a predominant utility of the INDO method. However, all previous semiempirical calculations of the inversion barriers[5)] were performed without optimization of the molecular geometries for the compounds investigated.[6)]

On the other hand, a few *ab initio* calculations have also been performed on the inversion barriers of small molecules such as NH_3; Rauk *et al.*[7)] have obtained an inversion barrier of 5.08 kcal/mol (exptl.=5.8 kcal/mol[8)]) for NH_3 using an *ab initio* method with a large gaussian basis set, while Sambe and Felton[9)] have reported a negative barrier of −62.77 kcal/mol for the same molecule using an LCAO-X$_\alpha$ method without the nitrogen d-orbitals.

The present authors report, here, on an extensive study of the inversion barriers of CH_3^-, NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, NH_2OH, NH_2CHO, and OH_3^+, which were investigated by means of the MINDO/2′ method.[10)]

Method of Calculation

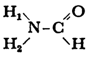
The MINDO/2′ method used for the present study is a modified version of MINDO/2[11)] which has already been found to suffer from serious defects, including: (a) an overestimation of the dipole moments, (b) an underestimation of the strain energies of small rings, and (c) an incomplete treatment of heteroatoms.[12)] The integrations and parametrizations involved in the present method will not be repeated here, because they have been described in detail in Ref 10.

The optimizations were performed on the geometrical parameters for the ground-state and transition-state molecules in which the geometries of the substituents (R, R′, and R″) were fixed by the use of the standard bond lengths and angles[13)] in order to simplify the computation.

Results and Discussion

Let us first examine the optimized geometries of the compounds investigated in their ground and transition states. As can be seen from Table 1, the calculated bond lengths except that of the N–O bond in NH_2OH are in satisfactory agreement with the observed values and the differences between the ground-state and transition-state configurations are not too great. The bond length for the N–O bond in NH_2OH, which is too short, is mainly attributable to an underestimation (caused by the neglect of two-center integrals involving one-center overlap) of the lone pair-lone pair interactions in the present method.[14)] This trend was also found for the bond lengths of O–O (in H_2O_2) and N–N (in N_2H_4) calculated by the MINDO/2′ method,[14)] which were also too short. The calculated bond angles are too large in comparison to the observed values except for

Table 1. Estimated molecular geometries, ionization potentials, and dipole moments obtained using the MINDO/2′ method

Compound	Molecular geometry		I_p/eV Calcd (Obsd)	μ/Debye Calcd (Obsd)
	Ground-state	Transition-state		
CH_3^-	CH, 1.12;	CH, 1.05;	1.30	6.05
	CHC, 95.05	CHC, 120.0		
NH_3	NH, 0.979 (1.012$^{a)}$);	NH, 0.956;	10.483	2.117
	HNH, 104.62 (106.7$^{a)}$)	HNH, 120.0	(10.154$^{f)}$)	(1.468$^{i)}$)
CH_3NH_2	NH, 0.975 (1.014$^{b)}$);	NH, 0.963;	9.336	0.595
	NC, 1.43 (1.47$^{b)}$);	NC, 1.43;	(9.56$^{g)}$)	(1.29$^{i)}$)
	HNH, 109.02 (105.8$^{b)}$);	HNH, 115.5;		
	HNC, 123.49 (112.2$^{b)}$)	HNC, 123.23		
$(CH_3)_2NH$	NH, 0.989;	NH, 0.986;	8.975	0.263
	NC, 1.44 (1.46$^{c)}$);	NC, 1.44;	(9.01$^{g)}$)	(1.03$^{i)}$)
	HNC, 116.93;	HNC, 117.69;		
	CNC, 126.22 (108.11$^{c)}$)	CNC, 123.86		
$(CH_3)_3N$	NC, 1.45 (1.47$^{d)}$);	NC, 1.45;	8.748	0.182
	CNC, 119.99 (108.7$^{d)}$)	CNC, 120.0	(8.66$^{g)}$)	(0.612$^{d)}$)
NH_2OH	NH, 1.02 (1.01$^{b)}$);	NH, 0.978;	9.602	2.665
	NO, 1.27 (1.46$^{b)}$);	NO, 1.26;		(2.45$^{j)}$)
	HNH, 94.15 (107$^{b)}$);	HNH, 121.04;		
	HNO, 112.05 (105$^{b)}$)	HNO, 118.57		
	NH, 0.981 (1.002$^{e)}$);	NH, 0.980;	10.001	4.880
	NC, 1.36 (1.38$^{e)}$);	NC, 1.36;	(10.83$^{h)}$)	(3.79$^{i)}$)
	H_1NH_2, 106.04 (118.98$^{e)}$);	H_1NH_2, 106.60;		
	H_1NC, 127.9 (117.2$^{e)}$);	H_1NC, 128.11;		
	H_2NC, 126.1 (120.5$^{e)}$)	H_2NC, 125.89		
OH_3^+	OH, 0.965 (0.96$^{b)}$);	OH, 0.964;	22.778	4.810
	HOH, 119.99 (117$^{b)}$)	HOH, 120.0		

The bond lengths are in Å and the bond angles are in degrees.
a) W. S. Bennett and E. K. Plyler, *Can. J. Phys.*, **35**, 1235 (1957). b) Ref. 13. c) Ref. 17. d) Ref. 18. e) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960). f) W. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957). g) A. Stereitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960). h) Monograph Ser. Res. Instit. Appl. Elect. Hokkaido Univ., No. 4 (1954—7). i) A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif. (1963). j) S. Tsunekawa, *J. Phys. Soc.*, **33**, 167 (1972).

Table 2. Inversion barriers for some molecules involving first-row central atoms

Compound	CNDO/2[a]	INDO[b]	MINDO/2′	Obsd
CH_3^-	16.2	11.7	17.58	(5.2[c])
NH_3	11.8	4.9	3.14	5.9[d]
CH_3NH_2	12.9	4.7	1.38	4.8[e]
$(CH_3)_2NH$	13.6	4.4	0.12	4.4[f]
$(CH_3)_3N$	15.0	5.1	0.00	8.2[d]
NH_2OH			9.04	(13.3[g]) (12.9[h])
NH_2CHO			0.092	1.0[i]
OH_3^+	1.3	0.0	0.0	1.71[j]

Values are in kcal/mol.

a) From Ref. 4, the ground-state configurations were assumed to be tetrahedral except CH_3^- (optimized angle=107°), NH_3 (optimized angle=107°), and OH_3^+ (optimized angle=115°). b) From Ref. 4, the ground-state configurations were assumed to be tetrahedral except CH_3^- (optimized angle=106°), NH_3 (optimized angle=110°), and OH_3^+ (optimized angle=120°). c) *ab initio* result. P. Millie and G. Berthier, *Int. J. Quantum Chem., Symp.*, **2**, 67 (1968). d) R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954). e) M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967). f) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). g) MINDO/1 result. M. J. S. Dewar and M. Shanshal, *J. Chem. Soc., A*, **1971**, 25. h) Value for $C_6H_5CH_2N(OCH_3)_2$: D. J. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965). i) J. Issoire and C. V. Long, *Bull. Soc. Chim. Fr.*, **1964**, 2004. j) G. W. Koeppl, D. S. Safatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*. **89**, 3396 (1967).

those of NH_3. This may be a result of the fact that the MINDO/2′ method, as well as the original version called MINDO/2, is still unsatisfactory for the parametrization (α and B) of heteroatoms, such as nitrogen, and overestimates nonbonded hydrogen-hydrogen repulsions in such molecules as $(CH_3)_2NH$ and $(CH_3)_3N$.[15]

It should be stressed here that the present MINDO/2′ calculations for the compounds (with fixed geometries of the substituents) listed in Table 1 result in almost the same bond lengths and angles as the calculations with no geometrical assumptions (with all bond lengths and angles variable), for example, an MINDO/2′ calculation of $(CH_3)_3N$ with no geometrical assumptions gave N–C=1.44 Å, C–H=1.082 Å, ∠CNC=119.99°, and ∠NCH=114.91°. Therefore, there are no serious defects in the geometrical assumptions for the substituents (R, R′, and R″) in terms of the calculated bond lengths and angles.

In connection with the unsatisfactory results for the optimization of the bond angles, dipole moments (μ) are calculated incorrectly with marked deviations from the experimentally determined values, although the calculated ionization potentials (I_P)[19] are in good overall agreement with the observations (see Table 1).

Now, we turn our attention to the inversion barriers of the compounds investigated. In Table 2, the calculated inversion barriers were listed together with those evaluated by the CNDO/2 or INDO method. As Table 2 indicates, the CNDO/2 method results in remarkably high inversion barriers in comparison with the INDO or MINDO/2′ method, probably because it not only excludes the one-center atomic exchange integrals but suffers markedly from the parametrization.[20] With regard to the results of the present MINDO/2′ calculations, the inversion barriers were predicted to be relatively low in comparison with the experimental values. This is due to inadequate optimization (*viz.*, overestimation) of the bond angles for the ground-state configuration of the molecule.

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