Semiempirical Calculation of Barriers to Pyramidal Inversion for First- and Second-Row Elements[1]

Arvi Rauk,[2a] Joseph D. Andose,[2b] Willis G. Frick, Reginald Tang, and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received February 9, 1971*

Abstract: This paper describes an application of the Pople CNDO/2 semiempirical molecular orbital theory to the calculation of pyramidal inversion barriers in systems containing elements from both the first and the second row of the periodic table. It has been found that use of the standard Pople–Santry–Segal parameters consistently leads to calculated barriers which are appreciably higher than experimentally measured values and that, in certain cases involving second-row substituents adjacent to either first- or second-row inverting centers, anomalous potential curves for inversion are obtained. In an attempt to remedy these shortcomings, a revised set of parameters has been developed *specifically* for pyramidal inversion (Table I), empirically based to give agreement between reported and calculated barriers for one or two representative compounds for each inverting center. By use of these parameters, barriers to inversion have been calculated for some 100 structures (Table II). From a comparison of the calculated and reported values, it is concluded that the present method, while not infallible, is capable of yielding surprisingly accurate values for barriers to pyramidal inversion in a wide variety of systems, and thus can be used with considerable confidence to predict barriers for as yet unexamined or experimentally inaccessible structural types. In a number of cases, recent experimental studies have confirmed predictions made by using the present method.

The dependence of pyramidal inversion barriers on molecular structure has been the subject of intensive experimental and theoretical study.[3] It has been shown[4] that the nonempirical LCAO–MO–SCF method within the Hartree–Fock approximation can yield a quantitative estimate to the barrier height in the simplest of invertible systems, ammonia, and analysis of the results of such calculations[4–13] is expected to provide some understanding of the physical origin of the barrier to inversion. However, the necessity for the use of a relatively large and flexible basis set to ensure computational reliability precludes the application of this method, for practical reasons, to systems involving more than about three heavy atoms along with their complement of hydrogen atoms. Thus, while the nonempirical MO method has the potential for use in both the analysis of barrier origin *and* for the prediction of as yet unreported barriers, this last capability is, for technical reasons, severely restricted.

On the other hand, with some exceptions, semiempirical calculations of inversion barriers in complex systems, using parameters chosen for other molecular properties (*e.g.*, ground-state geometry, dipole moment, etc.), have heretofore proven generally unreliable.[14] In the case of the INDO[15a] and MINDO[15b] schemes, reasonable agreement with experiment has been obtained, but results have been reported only for systems involving first-row elements. Our current interest in the stereochemistry of second-row elements[16] led us to examine the utility of the CNDO/2 method,[17–19] as extended by Santry[18] to the second row, for the calculation of inversion barriers in systems containing first- *and* second-row elements.

Method

In the present study, barriers were obtained from potential curves for inversion (total energy *vs.* out-of-plane angle, θ). The calculated barrier is the difference in

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(19) The program CNINDO (P. A. Dobosh) received from the Quantum Chemistry Program Exchange (QCPE), Bloomington, Ind., was modified for use in the present study.

total energy of the pyramidal ground state at its calculated equilibrium angle, θ_{eq}, and the total energy of the transition state.[20]

In order to render this method convenient for complex as well as for simple systems, no geometry optimization was performed. Bond lengths and those bond angles not dependent on the out-of-plane angle were taken from the experimental ground-state geometry, where known, or were taken from standard tables.[21] Rings were taken to be planar and conformations about single bonds to be staggered. In most cases where choice of conformation about a single bond might be expected to influence the barrier to inversion, the dihedral angle about that bond as well as the out-of-plane angle of the inverting center were simultaneously varied. No allowance was made for bond length variation during the course of inversion.[4] Cartesian coordinates, required as input to the calculations, were obtained from the program COORD (M. J. S. Dewar and N. C. Baird), available from the QCPE.

Initial studies using the Pople–Santry–Segal parameters showed that the CNDO/2 method generally led to barriers to inversion approximately two or three times as large as expected. Furthermore, in several trial cases (for example, *N*-chloroaziridine, *N*-silylaziridine, and silyldimethylphosphine) in which a second-row substituent was attached to the inverting center, anomalous potential curves for inversion were obtained.[22] A new self-consistent set of parameters was therefore sought which would give satisfactory agreement between calculated and experimental values.

In choosing the new set of parameters, an attempt was made to do as little "curve fitting" as possible, in order that the predictive capability of the method could then be gauged against the many known barriers presently available. Hence, for each element to be parametrized, one or at most two compounds of known barrier height[23] were chosen in which the element in question was the inverting center,[24] and the empirical parameters for that element were adjusted to give a calculated barrier in agreement with the known value.

In the CNDO/2 method, there are several potentially adjustable parameters: orbital exponents, which are normally chosen by Slater's rules;[25] the electronegativities (χ_s, χ_p, χ_d) of the individual atomic orbitals, defined in the Mulliken sense;[26] the empirical bonding parameter, $\beta°_{AB}$, which largely determines the bond length between atoms A and B;[27] and the composition of the basis set, normally 2s and 2p for the first row and 3s, 3p, and 3d for second-row elements. Because of the relative inflexibility of this valence basis set, the origin of the inversion barrier is largely governed by the energy associated with the hybridization changes (approximately sp^3 → p) that occur in the highest occupied molecular orbital, *i.e.*, the lone-pair orbital, during inversion. These changes entail charge transfer from the s orbital on the inverting center to a p orbital, and a localization of the molecular orbital which is accompanied by charge transfer from the substituents to the inverting center. While detailed *ab initio* calculations indicate that the origin of the barrier to inversion is not localized on the inverting center in such a manner,[13] for our purpose it was convenient to adjust the calculated barrier by altering the s → p promotion energy, *i.e.*, by varying the s- and p-orbital electronegativities of the elements.

Table I. Parameters for Pyramidal Inversion[a]

Atom	χ_s	χ_p	$\beta°$
B[b]	8.2	4.4	
C[c]	12.7	6.1	
N[d]	17.6	7.91	
O[e]	22.1	10.1	
F[b]	26.8	11.9	
Si	10.8[i]		−22.0[f]
P			−24.0[g]
S	18.5[h]	6.64[h]	−29.0[f]
Cl			−35.5[f]

[a] Unlisted parameters are unmodified from those given by Tables 3.2, 3.4, and 3.5 in Chapter 3 of ref 59b. [b] Obtained by a linear extrapolation from C, N, and O values. [c] Parametrized to reproduce the barrier of 5.2 kcal/mol calculated for methyl anion (ref 10). [d] Parametrized to reproduce the barrier of 19 kcal/mol found for 1-methylaziridine (ref 28) using modified parameters for carbon.[c] [e] Parametrized to reproduce the barrier of 10 kcal/mol found for 1-isopropyloxiranium ion (ref 29) using modified parameters for carbon.[c] [f] Calculated from the $\beta°$ value for phosphorus[g] by assuming the same proportional change reported for Santry $\beta°$ values (ref 18). [g] Obtained by simultaneously fitting barriers of 36 kcal/mol to trimethylphosphine, assumed to be typical of trialkylphosphines [R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970)] and 37.2 kcal/mol to phosphine (ref 6), and using modified parameters for carbon.[c] [h] Orbital electronegativities adjusted to give a barrier of 29 kcal/mol for trimethylsulfonium ion, taken to be typical of trialkylsulfonium ions, and using modified parameters for carbon.[c] [i] Orbital electronegativity adjusted to reproduce the calculated LCAO-MO-SCF (Hartree-Fock) barrier of 39.6 kcal/mol for silyl anion [A. Rauk, L. C. Allen, and K. Mislow, unpublished results].

In order to lower the generally high barriers calculated for systems containing first-row elements by use of the Pople–Segal parameters,[17] χ_p of the inverting atom was decreased and χ_s proportionately increased relative to the original parameters. This procedure has the advantage of leaving the overall electronegativities of the atoms substantially unaltered, while lowering the inversion barrier. A set of parameters for carbon was thus obtained which reproduces the best available LCAO–MO–SCF (Hartree–Fock) value for the inversion barrier of methyl anion (5.2 kcal/mol[10]). Using the optimized orbital electronegativities for carbon, the nitrogen and oxygen parameters were obtained in the same manner by matching, respectively, the barrier of 1-methylaziridine (19 kcal/mol[28]) and 1-methyloxiranium ion

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(20) In the absence of any intermediate in the interconversion of invertomers, the inverting center and its immediately bonded atoms *must* form a planar array at the transition state when the invertomers are related by a congruent transformation (isometry), *i.e.*, when the interconversion is either an automerization or an enantiomerization. However, when the invertomers are diastereomers, the probability is vanishingly small that the inverting center and its immediately bonded atoms form an *exactly* planar array. No such deviation from planarity was found in the present study, due to the rather coarse ($\Delta\theta = 8°$) increment in θ employed for the determination of the potential surface, and no attempt was made to search for a maximum in the neighborhood of $\theta = 0°$.

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(22) No minimum was obtained in the potential curve for inversion for reasonable values of the out-of-plane angle.

(23) In certain cases, *e.g.*, methyl and silyl anions, where experimentally determined barriers to inversion are not known, values calculated by the LCAO-MO-SCF method were employed.

(24) The calculated barrier to inversion is more sensitive to the choice of parameters for the inverting center than for that of the substituents.

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Table II. Barriers for Pyramidal Inversion

Entry no.^{ttt}	Compound	Barrier, kcal/mol^{a}		Ref
		Present work	Reported^{b,c}	
	(a) Inversion at Carbon			
1	Methyl anion	Parametrize	5.2^{b}	*k*
2	Cyclopropyl anion	14.2	20.8^{b}	*l*
3	Cyclopropenyl anion	39.3	52.3^{b}	*m*
	(b) Inversion at Nitrogen			
4	Ammonia	3.2	5.8^{c}	*n*
5	Methylamine	4.0	4.8^{c}	*o*
6	Dimethylamine	5.2	4.4^{c}	*p*
7	Trimethylamine	6.9	6.0^{c}	*q*
8	Aniline			
	In conjugation^{d}	0.7	1.6^{c}	*r*
	Out of conjugation^{e}	3.3		
9	Formamide			
	In conjugation^{d}	0.01	1.1^{c}	*s*
	Out of conjugation^{e}	2.1		
10	Nitramide			
	In conjugation^{d}	2.5	2.7^{c}	*t*
	Out of conjugation^{e}	5.8		
11	Cyanamide	0.2	2.0^{c}	*t*
12	Fluoroamine	12.2	20.3^{b}	*u*
13	Chloroamine	9.2	10.2^{c}	*v*
14	Silyldimethylamine	3.1	0.7^{b}	*w*
15	Methyldisilylamine	14.2	Planar^{c}	*x*
16	Trisilylamine	>50^{f}	Planar^{c}	*y*
17	Hydroxylamine	11.5^{g}		
18	Trimethylhydroxylamine	11.8^{g}	12.9^{c}	*z*
19	Hydrazine	7.4^{g}	7.5^{c}	*aa*
			6.8, 8.0^{c}	*bb*
20	Trimethylsulfenamide	5.9^{h}		
21	Dimethylaminodifluorophosphine	2.1^{h}		*cc*
22	Trisdimethylaminoborane	0.0	Planar^{c}	*dd*
23	Tetramethylaminoborane			
	In conjugation^{d}	0.0		
	Out of conjugation^{e}	11.5		
24	Aziridine	21.4	18.3^{b}	*ee*
			>11.6^{c}	*ff*
25	1-Methylaziridine	Parametrize	19^{c}	*gg*
26	1,2,2-Trimethylaziridine	18.0	17.9^{c}	*hh*
27	1-Methyl-2-methyleneaziridine	16.5	10.0^{c}	*ii*
28	1-Phenylaziridine			
	In conjugation^{d}	11.0	12.8^{c}	*jj*
	Out of conjugation^{e}	18.0		
29	1-(*p*-Nitrophenyl)-2,2-dimethylaziridine^{d}	7.1	8.2^{c}	*kk*
30	1-Phenyl-2,2-dimethylaziridine			
	In conjugation^{d}	10.8	11.2^{c}	*ll*
	Out of conjugation^{e}	15.1		
31	1-Acetylaziridine			
	In conjugation^{d}	3.6	<6^{c}	*jj*
	Out of conjugation^{e}	17.8		
32	1-Aminoaziridine	30.0^{g,i}	>22^{c}	*mm*
33	1-Ammonioaziridine	36.5		
34	1-Fluoroaziridine	49.4	>20.5^{c}	*nn*
35	1-Chloroaziridine	33.4	>21^{c}	*oo*
36	1-Benzenesulfenylaziridine	15.0^{h}	13.0^{c}	*pp*
37	1-Benzenesulfinylaziridine	14.4^{h}	13.5^{c}	*pp*
38	1-Benzenesulfonylaziridine	15.4^{h}	12.8^{c}	*pp*
39	1-Dimethylphosphinoxyaziridine	10.4^{h}	8.2^{c}	*pp*
40	1-Dimethylphosphinoaziridine	10.6^{h}	<6^{c}	*qq*
41	1-Silylaziridine	4.9	<5.5^{c}	*rr*
42	1-Trifluoromethyl-2,2-difluoroaziridine	15.4	11.1^{c}	*ss*
43	2-Azirene	34.0	35.1^{b}	*tt*
44	1,2-Dimethyl-2-azirene	29.1		
45	Oxaziridine	33.9	32.4^{b}	*ee*
			31–34^{c}	*uu*
46	1,2-Dimethyldiaziridine	27.2^{j}	27.3^{c}	*vv*
47	1-Methylazetidine	7.6	8.2^{c}	*ww*
48	Pyrrole	0.0	Planar^{c}	*xx*
	(c) Inversion at Oxygen			
49	Hydroxonium ion	0.0	Planar^{b}	*yy*
50	1-Methyloxiranium ion	Parametrize	10^{c}	*zz*
	(d) Inversion at Silicon			
51	Silyl anion	Parametrize	39.6^{b}	*aaa*
	(e) Inversion at Phosphorus			
52	Phosphine	Parametrize	37.2^{b}	*bbb*
53	Trimethylphosphine	Parametrize	35.6^{c}	*ccc*

Table II (*Continued*)

Entry no.[ttt]	Compound	Barrier, kcal/mol[a]		Ref
		Present work	Reported[b,c]	
54	Dimethylphenylphosphine			
	In conjugation[d]	28.2	32.1[c]	*eee*
	Out of conjugation[e]	36.0		
55	Acetyldimethylphosphine			
	In conjugation[d]	22.6		
	Out of conjugation[e]	35.6		
56	Dimethylphosphonitrile	31.9		
57	Tetramethylphosphinoborane			
	In conjugation[d]	5.3		
	Out of conjugation[e]	35.0		
58	Aminodimethylphosphine	40.0[h]		
59	Methoxydimethylphosphine	54.8[h]		
60	Fluorodimethylphosphine	54.1		
61	Chlorodimethylphosphine	40.4		
62	Silyldimethylphosphine	18.7	18.9[c]	*fff*
63	Methyldisilylphosphine	13.2		
64	Trisilylphosphine	>50[f]		
65	Trimethoxysilyldimethylphosphine	16.0		
66	Methyl dimethylthiophosphinite	32.6[g]	<33[c]	*ggg*
67	Dimethyl methyldithiophosphonite	32.1[h]	24.5[c]	*hhh*
68	Dimethylphosphinite	51.3		
69	Dimethylphosphinite anion	31.3		
70	Diphosphine	27.9[g]		
71	Tetramethyldiphosphine	24.1[g]	24[c]	*iii*
72	Phosphirane	80.4		
73	1-Methylphosphetane	44.3	40[c]	*jjj*
74	1-Methylphospholane	41.4	39[c]	*kkk*
75	1-Methyl-2-phospholene	33.9		
76	1-Methyl-3-phospholene	39.3		
77	1-Methyl-2,5-dimethylenephospholane	31.7		
78	1-Methylphosphole	16.7		
79	1,2,5-Trimethylphosphole	18.4	16[c]	*lll*
80	1,2-Dimethylphosphindole	23.2	23.3[c]	*mmm*
81	1-Methylisophosphindole	6.9		
82	1-Methylphosphindoline	36.4	35[c]	*nnn*
83	1-Methyl-2-methylenephosphindoline	31.2		
84	1-Silylphosphole	6.0		
85	1-Silylphosphindole	9.3		
86	1-Methyl-2,5-diketophospholane	18.0		
87	1-Methylphosphorinium ion	0.0		
88	1-Methyl-2,5-dibora-3-phospholene	0.0		
89	1-Methyl-2,5-diboraphospholane	0.0		
	(f) Inversion at Sulfur			
90	Hydrosulfonium ion	29.3	30.0[b]	*aaa*
91	Trimethylsulfonium ion	Parametrize	26–29[c]	*ooo*
92	1,2-Dimethylbenzothiophenium ion	22.5	>15.9[c]	*ppp*
93	Dimethyl sulfoxide	37.5	39.7[c]	*qqq*
94	Methyl methanesulfinate	53.3		
95	Methyl methanethiolsulfinate	36.4	23[c]	*rrr*
96	Methanesulfinyl fluoride	57.0		
97	Methanesulfinyl chloride	42.5		
98	Methyl silyl sulfoxide	18.8		
99	Acetyl methyl sulfoxide[d]	28.6		
100	2,5-Dimethylthiophene *S*-oxide	13.3	14.8[c]	*sss*
101	1-Methylthiabenzene	42.5		

[a] No distinction was made in barrier values, which have been variously reported as $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, E_a, or V_i. [b] Value obtained by LCAO-MO-SCF calculation. [c] Experimentally measured value. [d] The conformation permitting maximum overlap of the lone electron pair with an adjacent pπ orbital. [e] The conformation imposing minimum overlap of the lone electron pair with an adjacent pπ orbital. [f] An anomalous potential curve for inversion was obtained (ref 22). [g] The value calculated is the result of an examination of the full inversion–rotation surface. [h] The calculated value refers to a conformation chosen to minimize lone pair–lone pair interactions. [i] Inversion of ring nitrogen. [j] The barrier calculated is obtained from the full potential surface for inversion at both centers. [k] See ref 10. [l] See ref 12. [m] See ref 11. [n] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962). [o] M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967). [p] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). [q] Value reported for dibenzylmethylamine (C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970)). See, however, C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *ibid.*, **92**, 6349 (1970), and S. Brownstein, E. C. Horswill, and K. U. Ingold, *ibid.*, **92**, 7217 (1970). J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectrosc.*, **20**, 359 (1966). See also footnote *t*. [s] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960). [t] D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966). [u] See ref 7. [v] Value reported for chlorodiethylamine (see W. B. Jennings and R. Spratt, *Chem. Commun.*, 54 (1971)). [w] Value calculated for silylamine (see ref 8). [x] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*. **4**, 215 (1969). [y] K. Hedberg, *J. Amer. Chem. Soc.*, **77**, 6491 (1955). [z] Value reported for *N*-benzyl-*O*,*N*-dimethylhydroxylamine (see D. L. Griffith and J. D. Roberts, *ibid.*, **87**, 4089 (1965)). [aa] Y. Hamada, A. Y. Hirakawa, K. Tamagake, and M. Tsuboi, *J. Mol. Spectrosc.*, **35**, 420 (1970). [bb] Value reported for benzyltrimethylhydrazine (6.8 kcal/mol, see J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6371 (1969)) and 1,1-dibenzylhydrazine (8.0 kcal/mol, see M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970); *J. Amer. Chem. Soc.*, **91**, 3655 (1969)). [cc] Nitrogen in dimethylaminodifluorophosphine is reported to be planar in the crystalline state [E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969)] but pyramidal in the gas phase

Footnotes to Table II (*Continued*)

[G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A.*, 785 (1971)]. [dd] A. H. Clark and G. A. Anderson, *Chem. Commun.*, 1082 (1969). [ee] See ref 9. [ff] M. K. Kemp and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 6267 (1968). [gg] See ref 28. [hh] M. Jautelat and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 642 (1969). [ii] The value quoted refers to $\Delta G^{\ddagger}$ at $-60°$ and was calculated from the reported values $E_a = 6.4$ kcal/mol and log $A = 9$ (A. Loewenstein, J. F. Neumer, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 3599 (1960)). [jj] F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967). [kk] J. D. Andose, J. M. Lehn, K. Mislow, and J. Wagner, *ibid.*, **92**, 4050 (1970). [ll] See Andose, *et al.*, footnote *kk*. [mm] S. J. Brois, *Tetrahedron Lett.*, 5997 (1968). [nn] Value calculated from data reported for 1-fluoro-2,2-bis(trifluoromethyl)aziridine (R. G. Kostyanovsky, I. I. Tchervin, A. A. Fomichov, Z. E. Samojlova, C. N. Makarov, Yu. V. Zeifman, and B. L. Dyatkin, *ibid.*, 4021 (1969)). [oo] Value reported for 1-chloro-2,2-dimethylaziridine [S. J. Brois, *J. Amer. Chem. Soc.*, **90**, 506 (1968)]. [pp] Value calculated from data reported in F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967). [qq] Value reported for 1-(diphenylphosphino)-2,2-dimethylaziridine [A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *ibid.*, **92**, 5206 (1970)]. [rr] See ref 3b. [ss] The value quoted refers to $\Delta G^{\ddagger}$ at 25° and was calculated from the reported values $E_a = 5.5$ kcal/mol and $A = 5 \times 10^8$ sec^{-1} [A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964)]. [tt] See ref 11. [uu] A. Mannschreck, J. Linss, and W. Seitz, *Justus Liebigs Ann. Chem.*, **727**, 224 (1969); F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 1086 (1969). [vv] Value reported for 1,3-dimethyl-2,3-dibenzyldiaziridine [A. Mannschreck and W. Seitz, *Angew. Chem., Int. Ed. Engl.*, **8**, 212 (1969)]. Examination of the energy surface for inversion at both nitrogen centers indicates that the preferred process corresponds to consecutive, rather than simultaneous, inversion, in agreement with the suggestion of Mannschreck and Seitz. [ww] Value reported for 1,3,3-trimethylazetidine (J. M. Lehn and J. Wagner, *Chem. Commun.*, 148 (1968)). [xx] L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sørensen, *J. Mol. Struct.*, **3**, 491 (1969). [yy] J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **43**, 3550 (1965). [zz] Value reported for 1-isopropyloxiranium ion (see ref 29). [aaa] A. Rauk, L. C. Allen, and K. Mislow, unpublished results. [bbb] See ref 6. [ccc] Value reported for cyclohexylmethyl-*n*-propylphosphine (see footnote *ddd*). [ddd] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970). [eee] Value reported for methylphenyl-*n*-propylphosphine (see footnote *ddd*). [fff] Value reported for isopropylphenyltrimethylsilylphosphine (R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 4758 (1970)). [ggg] Value reported for allyl methylphenylthiophosphinite (W. B. Farnham, A. W. Herriott, and K. Mislow, *ibid.*, **91**, 6878 (1969)). [hhh] Value found for diisopropyl phenyldithiophosphonite (J. P. Casey and K. Mislow, unpublished results). [iii] Value reported for 1,2-dibenzyl-1,2-dimethyldiphosphine (J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, **92**, 3093 (1970); J. B. Lambert and D. C. Mueller, *ibid.*, **88**, 3669 (1966)). [jjj] Value quoted for 1,2,2,3,4,4-hexamethylphosphetane [S. E. Cremer, private communication]. [kkk] Value estimated for 1-cyclohexyl-3-methylphospholane (W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970)). [lll] Value reported for 1-isopropyl-2-methyl-5-(2-phenylethyl)phosphole (W. Egan, R. Tang, G. Zon, and K. Mislow, *ibid.*, **93**, 6205 (1971)). [mmm] Value found for 1-(1,1-dideuterio-2-phenylethyl)-2-phenyl-3-*n*-butylphosphindole (see Egan, *et al.*, footnote *lll*). [nnn] Value reported for 3-methyl-1-phenylphosphindoline (see Egan, *et al.*, footnote *lll*). [ooo] Taken to be typical of trialkylsulfonium ions (R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967)). [ppp] A lower limit calculated from the nmr chemical-shift nonequivalence of the methylene protons reported for 1-ethyl-3-bromobenzothiophenium ion (R. M. Acheson and D. R. Harrison, *Chem. Commun.*, 724 (1969)). [qqq] Value obtained for adamantyl methyl sulfoxide (D. R. Rayner, A. J. Gordon and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4854 (1968)). [rrr] Value reported for *p*-tolyl *p*-toluenethiolsulfinate (P. Koch and A. Fava, *ibid.*, **90**, 3867 (1968): see, however, F. Wudl, R. Gruber, and A. Padwa, *Tetrahedron Lett.*, 2133 (1969)). [sss] Value reported for a 2,5-dialkylthiophene 1-oxide (W. L. Mock, *J. Amer. Chem. Soc.*, **92**, 7610 (1970)). [ttt] Structures for many of the compounds are given on p 6513.

(10 kcal/mol, taken to be the same as that of 1-isopropyloxiranium ion[29]). Parameters for boron and for fluorine were determined by a linear extrapolation of the carbon, nitrogen, and oxygen values. The parameters thus obtained for the first-row elements together with the structures used in their parametrization are given in Table I.

For the second row, modification of χ_s and χ_p as above led to satisfactory results for systems involving inversion at second-row centers bearing substituents from the first row. However, with second-row atoms adjacent to both first- and second-row inverting centers, anomalous potential curves for inversion[22] were still obtained. Since recent *ab initio* studies of phosphine[5,6] and silylamine[8] have indicated that d-type functions contribute to the wave function as polarization functions only, rather than as d orbitals in the usual sense, it is possible that inclusion of such functions for the second row, and not for the first row, serves only to unbalance the basis set. Indeed, it was found that the above-mentioned difficulties with second-row substituents were largely overcome by deletion of d orbitals from the basis set, major modification of the bonding parameters,[30] and minor adjustment to the orbital electronegativities. Values thus obtained for second-row elements together with details of the parametrization are given in Table I.

Results

Using the parameters given in Table I, barriers for pyramidal inversion were calculated for a wide variety of systems involving first- and second-row elements. Results of these calculations are collected in Table II. As shown by comparison with known values from other sources (Table II), agreement between calculated and reported barrier heights is generally quite good. Before a discussion of these results is undertaken, however, it is appropriate to examine the sensitivity of the computed barriers to the choice of geometry used in the calculations.[31]

It was found that the major geometric factors affecting the barrier height are those pertaining to the inverting center itself. Generally, variations in bond lengths and bond angles distant from the inverting center did not crucially affect the barrier height. Care was taken to choose conformations in which steric crowding is minimized during the course of inversion. At the inverting center, model studies on MH_3 (M = N or P) indicated a moderate sensitivity of the computed barrier to input bond length. Thus a decrease of all three M–H bonds by 0.01 Å from some initial value causes a decrease in barrier of about 0.5 kcal/mol. However, in cases where the structure is accurately known, or in cases where bond lengths can be reasonably assumed to approximate those found in similar compounds of known structure, the choice of bond length is expected to present no major problem.

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(29) J. B. Lambert and D. H. Johnson, *J. Amer. Chem. Soc.*, 90, 1349 (1968).

(30) Modification of the bonding parameters was necessitated by the change in basis set.

(31) For the most part, where structural data are available, fair agreement (θ within ±10°) was found between the calculated equilibrium value of θ and the experimentally determined value. However, the present parameters do not satisfactorily reproduce experimental bond lengths. While most calculated bond lengths were found to be within 0.1 Å of the experimental value, significant deviations (*e.g.*, 0.18 Å for N–N in hydrazine, up to 0.56 Å for molecular fluorine) were encountered when both atoms of the bond pair possess nonbonded electron pairs. The calculated bond length in these cases is always shorter than the experimentally found value.

Bond angles about the inverting center were handled differently for acyclic and for cyclic compounds. All acyclic compounds MR′R′′R′′′ were treated as threefold rotors. Thus, the three bond angles about M in the planar species were all taken to be equal ($2\pi/3$ radian), and all three ligands symmetrically deformed out of the plane as the molecule became pyramidal. The bond angles in the ground state were determined from the equilibrium out-of-plane angle, which in turn was determined from the potential curve for inversion. While such a treatment is only valid when $R' = R'' = R'''$, the errors introduced are assumed to be small. For cyclic compounds, the endocyclic angle at the inverting center was held fixed during the inversion processes. Model studies on the structure MH_3 (M = N or P), in which one HMH angle is held fixed during inversion, showed that phosphorus is about twice as sensitive to a given degree of angular constraint as nitrogen (P, 0.70 kcal mol^{-1} deg^{-1}; N, 0.35 kcal mol^{-1} deg^{-1}). These latter figures may be taken as approximate indicators of the sensitivity of the calculated barrier to the assumed geometry in cases where structural data for the cyclic compound are lacking.

Discussion

Nonempirical LCAO–MO–SCF calculations can yield insight into the physical origin of barriers to inversion,[32] provided that use is made of a sufficiently large and flexible basis set. However, in semiempirical treatments such as the present, only valence electrons are explicitly treated, and since analysis of all-electron nonempirical calculations shows that the variation in energy of the "inner shell" electrons during inversion can be as large as the barrier itself,[13] only the most limited significance may be attached to a physical interpretation of the computed results here reported.[33] For this reason, the following discussion will be restricted to an assessment of the ability of the present treatment to reflect those factors, *e.g.*, angular constraint, steric size, conjugation, and heteroatomic substitution, which have been adduced in an *ad hoc* manner to rationalize structural effects on barriers to pyramidal inversion.[3]

Angular Constraint and Steric Size. The anticipated increase in barrier height when the inverting center is incorporated into a small ring is realized for all systems studied. Furthermore, the expected ordering of barriers along the series three-membered ring > four-membered ring > five-membered ring > acyclic is obtained, as for example in 1-methylaziridine (**25**) > 1-methylazetidine (**47**) > trimethylamine (**7**), and in phosphirane (**72**) > 1-methylphosphetane (**73**) > 1-methylphospholane (**74**) > trimethylphosphine (**53**).

Since accurate structural data are lacking for most five-membered ring compounds containing tricoordinate phosphorus, the internal CPC angle was arbitrarily taken as 95° for systems (*i.e.*, **74–77**, **82**, **83**, **86**, **88**, and **89**) other than phospholes or phosphindoles.[35] For these latter compounds (*i.e.*, **78–81**, **84**, and **85**) an internal CPC angle of 90.7° was employed.[36] From the agreement obtained between reported and calculated values in the cyclic systems studied, we conclude that the present method is capable of satisfactorily reflecting effects attributed to angular constraint.

Trends in inversion barrier magnitude due to small differences in steric size appear to be less satisfactorily reproduced by the present treatment. Thus, while the decrease in barrier height for 1,2,2-trimethylaziridine (**26**),[37] relative to 1-methylaziridine (**25**),[28] properly reflects the effect of B strain, the similar decrease expected for 1-phenyl-2,2-dimethylaziridine (**30**),[38] relative to 1-phenylaziridine (**28**),[39] is poorly reproduced in the calculation. However, it must be recalled that a molecule is represented in these calculations as a rigid framework from which a total energy is computed. Successive calculations for different values of the out-of-plane angle serve to define the potential curve for inversion. Thus, subtle adjustments of bond length and especially bond angle to relieve steric crowding, which are automatic for a real molecule, can be computationally handled only by a geometry search, with a resulting increase in time and expense. Such a procedure was not followed in the present work although care was taken that for the conformations chosen, no unintentional buttressing of groups occurs during the course of inversion.

(p–p)π Conjugation. Interaction of the lone-pair orbital on an inverting center with an adjacent pπ orbital (or orbitals) can lead to an increase or to a decrease in barrier height, relative to a suitable model in which such interactions are absent. Both features are successfully reflected by the present method. Thus, substitution of a phenyl (**8**, **28**, **29**, **30**, and **54**), olefinic (**27**, **75**, **77**, and **83**), nitro (**10**), cyano (**11** and **56**), or acyl (**9**, **31**, **55**, **86**, and **99**) substituent adjacent to the inverting center leads to the anticipated barrier lowering (Table II). That the factor actually responsible for the decrease in calculated barrier height is indeed due to (p–p)π delocalization is seen from examination of the conformational dependence of these barriers. In all appropriate cases studied, the calculated barrier to inversion is lowest in that conformation which permits maximum overlap between the lone-pair orbital and the adjacent p orbital of the substituent, *i.e.*, when the orbital axes are parallel. Furthermore, a measure of the magnitude of the delocalization effect for each compound may be obtained by a comparison of the barrier for the conformation in which such overlap is maximal with the value when such overlap is minimal, *i.e.*, when the orbital axes are orthogonal.

Cyclic conjugation effects which involve either aromatic or antiaromatic systems are also successfully reflected by the present method. Thus, not only do the calculations reproduce the low barrier to inversion observed for phospholes (**78**, **79**), but the increase in barrier height upon fusion of a benzene ring to the 2,3 positions of the phosphole ring (1,2-dimethylphosphindole (**80**)) is also reproduced.[40] By contrast, fusion of a benzene

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(32) See, for example, ref 4 and 13.

(33) This statement may be illustrated by a comparison of the present results for ammonia with those obtained by the *ab initio* technique.[4] Mulliken population analysis[34] indicates that, according to both methods, the overlap population of the N–H bond increases as the molecule becomes planar. However, whereas according to the *ab initio* calculation nitrogen *loses* negative charge, the present semiempirical calculations show nitrogen to *gain* negative charge.

(34) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(35) A value of 94.8° has been reported for the internal CPC angle of phospholanic acid [E. Alver and H. M. Kjøge, *Acta Chem. Scand.*, **23**, 1101 (1969)].

(36) This is the internal CPC angle reported for 1-benzylphosphole by P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970).

(37) See Table II, footnote *hh*.

(38) See Andose, *et al.*, Table II, footnote *kk*.

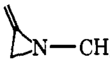
(39) See Table II, footnote *jj*.

$(CH_3)_2NMCH_3$
18, M = O
20, M = S

$(CH_3)_2NPF_2$
21

$B(N(CH_3)_2)_3$
22

$(CH_3)_2BN(CH_3)_2$
23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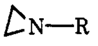
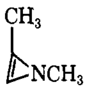

33, R = NH_3^+
36, R = SC_6H_5
37, R = $S(O)C_6H_5$
38, R = $SO_2C_6H_5$
39, R = $P(O)(CH_3)_2$
40, R = $P(CH_3)_2$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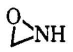
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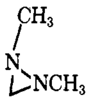
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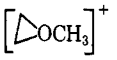
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$(CH_3)_2BP(CH_3)_2$
57

$(CH_3)_2PSi(OCH_3)_3$
65

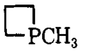
$(CH_3)_2PSCH_3$
66

$CH_3P(SCH_3)_2$
67

$(CH_3)_2POH$
68

$((CH_3)_2PO)^-$
69


72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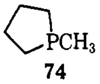
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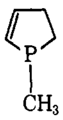
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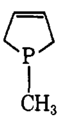
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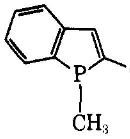
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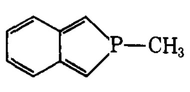
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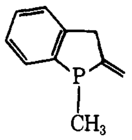
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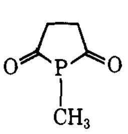
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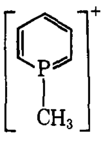
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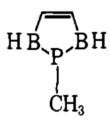
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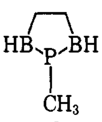
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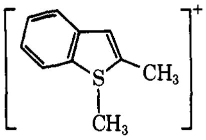
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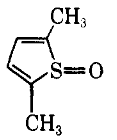
$CH_3S(O)MCH_3$
94, M = O
95, M = S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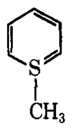
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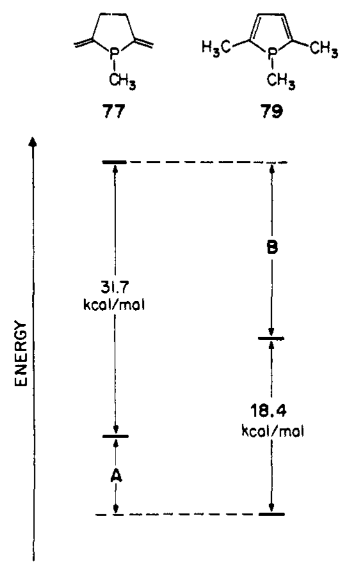

Figure 1. Comparison of calculated ground- and transition-state energies of **77** and **99**.

ring to the 3,4 positions of the phosphole ring is predicted to effect a substantial decrease in barrier height (1-methylisophosphindole (**81**), 6.9 kcal/mol), a result which is yet to be experimentally verified. Both phenomena may be explained by a consideration of the delocalization of the lone pair on phosphorus in the phosphole moiety and the manner in which such delocalization is affected by annulation. For the 3,4-annulated systems, such delocalization will be particularly favorable in the transition state to inversion, the result of increased benzenoid character for the carbocyclic portion of the bicyclic structure. The opposite is true for the 2,3-annulated systems.

Calculations have been performed for model systems in order to gauge the magnitude of the barrier lowering phenoma specifically due to cyclic conjugation. Comparison of the barrier calculated for 1,2,5-trimethylphosphole (**79**) with that calculated for its tautomer 1-methyl-2,5-dimethylenephospholane (**77**), in which cyclic π conjugation is precluded, gives a value of 13.3 kcal/mol as the barrier decrease which results from incorporation of phosphorus into a phosphole ring. A similar comparison for 1,2-dimethylphosphindole (**80**) and its tautomer 1-methyl-2-methylenephosphindoline (**83**) gives 8.0 kcal/mol as the additional barrier lowering due to the phosphindole ring structure. Although these values (13.3 and 8.0 kcal/mol) are significantly lower than the values independently obtained from other types of estimates[40b] (18 and 11 kcal/mol, respectively), both methods indicate a barrier lowering for the phosphole greater than that of the phosphindole. That the calculated barrier lowerings are less than the estimated[40b] values results principally from the difference in barrier heights obtained for the model compounds by the two methods. Barriers of about 35 kcal/mol might be expected[40b] for these compounds (**77** and **83**) whereas barriers of 31.7 and 31.2 kcal/mol, respectively, are calculated.

It is instructive to compare the ground- and transition-state energies for the tautomeric structures **77** and **79** (Figure 1). Granted the crudeness of such a comparison, the essential feature, *i.e.*, increased stabilization of the phosphole transition state over the ground state (B > A), is reasonable for a Hückel aromatic $(4n + 2)\pi$ system. It should be noted that for the antiaromatic system 1,2-dimethyl-2-azirene (**44**) and its tautomer 1-methyl-2-methyleneaziridine (**27**), a similar comparison shows that the increased barrier for the azirene is due to the greater destabilization of the transition state, relative to the ground state, in accord with what would be expected for an antiaromatic $(4n)\pi$ system.[11]

(p–d)π Conjugation. The question of (p–d)π conjugation as it affects barrier heights to pyramidal inversion is a topic of current interest.[8,41] This mechanism has been invoked to explain the planarity, or near planarity, of nitrogen in silylamines[42] and aminophos-

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[40] (a) See Egan, *et al.*, Table II, footnote *kkk*; (b) see Egan, *et al.*, Table II, footnote *lll*.

[41] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 773 (1971).

[42] (a) C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, 6, 231 (1970); (b) see Table II, footnote *x*; (c) see Table II, footnote *y*.

phines,[43] the low barriers reported for various sulfur and phosphorus substituted aziridines,[44] and the relatively low barriers in diphosphines,[45,46] diarsines,[46,47] and a thiolsulfinate.[48] It is therefore of interest to examine the ability of the present treatment, in which d orbitals are not included, to reproduce barriers in systems for which d-orbital participation has been invoked.

The compounds in question are represented by entries **14–16**, **21**, **36–40**, **71**, and **95**. Assuming that the assignment of the experimentally observed rate process to pyramidal inversion is correct,[49] comparison of the calculated values with reported barriers for the above compounds indicates that agreement is, for the most part, surprisingly good. Only in the case of the multisilyl-substituted amines (**15** and **16**) and of the thiolsulfinate (**95**) is agreement poor.[50]

Tempting as it is to regard this agreement as evidence that $(p-d)\pi$ conjugation effects are unimportant in influencing barrier heights, one must admit to the possibility that comparable results might have been obtained using some other suitable parametrization of an spd basis set. Thus, the present results cannot be taken as evidence relevant to the question of d-orbital participation in the inversion process.[3] Nevertheless, recent experimental[41] and theoretical[8] studies indicate that ligand electronegativity, rather than $(p-d)\pi$ conjugation, may be the dominant factor in determining inversion barriers for many of these compounds.

Heteroatomic Substitution. The presence of a heteroatom (*i.e.*, an atom other than carbon or hydrogen) adjacent to an inverting center can lead to either an increase or decrease in barrier, depending on the nature of the particular substituent. The attributes of heteroatoms invoked to explain this behavior have been previously enumerated.[3a] Thus, it is experimentally found that a nitrogen, oxygen, fluorine, or chlorine atom adjacent to an inverting center results in an elevated barrier, whereas an adjacent boron, silicon, phosphorus, or sulfur atom results in a barrier lowering, all relative to the corresponding methyl- or hydrogen-substituted analog.

While there is a general lack of quantitative experimental data on the barrier-elevating ability of adjacent nitrogen, oxygen, fluorine, or chlorine, the accuracy with which the present method duplicates barriers for cases where such values are known (*e.g.*, acyclic chloroamines,[51] oxaziridines,[52] diaziridines,[53] and acyclic hydrazines;[54] entries **13**, **45**, **46**, and **19**, respectively) generates confidence in the reliability of these calculations.

The capability of the present method to deal with neighboring silicon, phosphorus, and sulfur was discussed above. Boron as a substituent is expected to lower the barrier to inversion both for inductive (Pauling electronegativity[55] = 2.0) and for conjugative ($(p-p)\pi$) reasons. Indeed, nitrogen is reported,[56] and calculated to be planar in trisdimethylaminoborane (**22**). While no similar experimental data are available for boron adjacent to phosphorus, the present calculations predict quite a large effect; it is found that a single boron substituent lowers the barrier to phosphorus inversion to only about 5 kcal/mol (tetramethylphosphinoborane (**57**)). In an attempt to assess the relative importance of the inductive and the conjugative contributions to the barrier-lowering capability of boron, calculations were performed on tetramethylamino- and tetramethylphosphinoborane (**23** and **57**) in which the vacant p orbital on boron was held orthogonal to the lone pair on the inverting center and where $(p-p)\pi$ conjugation is thus eliminated. It was found (Table II) that while the inductive effect appears to be negligible in the phosphorus compound (35 kcal/mol for the out-of-conjugation conformation of **57**, as compared to 36.3 kcal/mol calculated for trimethylphosphine, **53**), the inductive effect in the amino compound appears to operate in the wrong direction (11.5 kcal/mol for the out-of-conjugation conformation of **23**, as compared to 6.9 kcal/mol for trimethylamine, **7**) and most probably represents a breakdown in the calculations similar to that observed for di- and trisilylamine and trisilylphosphine.[50]

Applications

An intriguing application of the present method concerns the determination of barriers to pyramidal inversion in systems where there exists an ambiguity in the assignment of the barrier to either inversion or rotation.[3a] Although CNDO (and INDO) appear to be poorly suited to the calculation of rotational barriers around heteroatom–heteroatom bonds[57] (since interactions due to directed lone pairs of electrons are not included[59]), a reliable calculated value for the inversion barrier, to be compared with the observed barrier for the compound in question, might hopefully lead to the proper assignment. For example, recent nmr evidence

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(43) (a) See Table II, footnote *cc*; (b) J. E. Smith, R. Steen, and K. Cohn, *J. Amer. Chem. Soc.*, **92**, 6359 (1970), and references therein.

(44) (a) See Anet, *et al.*, Table II, footnote *pp*; (b) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).

(45) See Lambert, *et al.*, Table II, footnote *iii*.

(46) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, 90, 6401 (1968).

(47) J. B. Lambert and G. F. Jackson, III, *ibid.*, **90**, 1350 (1968).

(48) See Koch and Fava, and Wudl, *et al.*, Table II, footnote *rrr*.

(49) For many of these compounds (36–40 and 71), the possibility of a rate-limiting torsional process has not been rigorously excluded by experiment.

(50) The failure of the present method in cases of multisilyl substitution appears general, invariably leading to inversion barriers that are larger than expected. Thus, in accord with experimental[42a] and theoretical[8] findings, we find nitrogen to be pyramidal with a low barrier to inversion in the case of silyldimethylamine (14).[50a] However, in the case of a di- and trisilylamine (15 and 16), both reported to be planar,[42b,c] we calculate barriers of 14.2 and >50 kcal/mol, respectively. Furthermore, while the calculated barriers for a mono- and a disilylphosphine (62 and 63) appear reasonable, an anomalous potential curve for inversion[22] is obtained for trisilylphosphine (64).

(50a) NOTE ADDED IN PROOF. A recent note by Szeimies indicates that the barrier in silylamine can be accounted for by a CNDO/2 calculation employing an sp basis set [G. Szeimies, *Tetrahedron Lett.*, 5073 (1970)].

(51) See Jennings and Spratt, Table II, footnote *v*.

(52) See Table II, footnote *uu*.

(53) See Mannschreck and Seitz, Table II, footnote *vv*.

(54) (a) See Table II, footnote *aa;* (b) see Dewar and Jennings, Table II, footnote *bb;* (c) see J. E. Anderson, *et al.*, Table II, footnote *bb*.

(55) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca. N. Y., 1960, Chapter 3.

(56) See Table II, footnote *dd*.

(57) In particular, the present method grossly fails to account for torsional barriers; in none of the cases examined was a barrier in excess of 3 kcal/mol obtained. Thus, using the geometries adopted by Allen and coworkers[58] for hydrazine and hydroxylamine, the difference in energy between the highest and lowest energy conformation was calculated to be only 1.9 and 1.8 kcal/mol, respectively, in contrast to the *ab initio* values of 11.9 and 12.0 kcal/mol.[58]

(58) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967), and references therein.

(59) (a) J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970); (b) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

has been interpreted as indicating that rotation is a slower process than inversion for simple acyclic hydrazines,[54b] and that the barrier to nitrogen inversion is 6.8–8.0 kcal/mol in these compounds.[54] This result is in excellent agreement with the present calculations (7.4 kcal/mol, **19**). For acyclic hydroxylamines, however, the interpretation of small steric effects within a related series of compounds has resulted in conflicting claims as to which is the rate-limiting process (inversion or rotation) in the isomerization.[60] The calculated barrier for nitrogen inversion in trimethylhydroxylamine (**18**, 11.8 kcal/mol) is near the observed barriers[60] of 12.3–12.9 kcal/mol, but *ab initio* calculations indicate a rotational barrier of similar magnitude (12.0 kcal/mol[58]). Perhaps only a single "coupled" barrier separates isomers,[61] and further attempts to assign the barrier to either rotation or to inversion may be bootless.

The success with which the present method duplicates known barriers to pyramidal inversion for a variety of chemical structures permits its application to the prediction of as yet unreported barriers (Table II) with a considerable degree of confidence. One such application, the prediction of barriers to pyramidal inversion in various thiophene *S*-oxides and S-alkylated thiophenium ions, has been recently reported.[62] Additionally, barriers to pyramidal inversion are predicted for an acylphosphine (**55**, 22.3 kcal/mol), for an acyl sulfoxide (**99**, 28.6 kcal/mol), and for silyl-substituted phosphorus and sulfur compounds (trimethoxysilyldimethylphosphine, **65**, 16.0 kcal/mol; methyldisilylphosphine, **63**, 13.2 kcal/mol; 1-silylphosphole, **84**, 6.0 kcal/mol; 1-silylphosphindole, **85**, 9.3 kcal/mol; methyl silyl sulfoxide, **98**, 18.8 kcal/mol). Finally, phosphorus is anticipated to be planar in phosphorinium ion (**87**), in 1-methyl-2,5-diboraphosphol-3-ene (**88**), and in 1-methyl-2,5-diboraphospholane (**89**). Other compounds listed in Table II with no accompanying reported barriers represent further predictions by this treatment.

Several of our predictions have since been confirmed by experiment. Thus, studies in these laboratories have yielded barriers for an acylphosphine (19.4 kcal/mol),[63] a trimethoxysilylphosphine (17.1 kcal/mol),[64] a disilylphosphine (12.2 kcal/mol),[65] and a phosphonitrile (>26 kcal/mol),[66] all in reasonable agreement with calculated values for **55**, **65**, **63**, and **56**, respectively.

In conclusion, the present method offers a relatively simple and reliable means for obtaining quantitative estimates to barriers of pyramidal inversion in systems comprised of first- and second-row elements, and hopefully will serve both to stimulate and to direct new research efforts in this field.

(60) (a) See Griffith and Roberts, Table II, footnote *z*; (b) M. Raban and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 1295 (1969); (c) J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 687 (1970).

(61) See section 3.2.4 in ref 3a.

(62) J. D. Andose, A. Rauk, R. Tang, and K. Mislow, *Int. J. Sulfur Chem. A*, **1**, 66 (1971).

(63) Value reported for acetylisopropylphenylphosphine: W. Egan and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 1805 (1971).

(64) Value found for isopropylphenyl(trimethoxysilyl)phosphine; R. D. Baechler and K. Mislow, unpublished results.

(65) Value found for bis(dimethylphenylsilyl)phenylphosphine; G. H. Senkler, Jr., and K. Mislow, unpublished results.

(66) A lower limit to the inversion barrier for isopropylphenylcyanophosphine; W. Egan and K. Mislow, unpublished results.

Hindered Rotation in Some Organometallic Carbamates, Thiocarbamates, and Dithiocarbamates

Claude H. Yoder,* Akira Komoriya, John E. Kochanowski, and Fred H. Suydam

Contribution from the Department of Chemistry,
Franklin and Marshall College, Lancaster, Pennsylvania 17064.

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Abstract: Hindered rotation in systems of the type $R'YC({=}X)NR_2$, where X,Y = O,O; O,S; S,O; S,S; R = CH_3, C_2H_5; R′ = CH_3, $Si(CH_3)_3$, $Sn(CH_3)_3$, has been investigated by variable temperature nmr spectroscopy. Rotational parameters were calculated by the total line shape and intensity ratio methods. Effects of substituent groups X, Y, and R′ on the free energy of activation are discussed in terms of their effect on the relative importance of the contributing resonance structures.

Although the synthetic aspects of the insertion of unsaturated species into the organometallic–nitrogen bond have been widely explored,[1] the structural details of the products have received little attention. Most of the insertion adducts contain the grouping $C({=}X)NR_2$ and might therefore be expected to exhibit hindered rotation about the C–N bond.

In order to explore hindered rotation in these systems we have prepared a number of trimethylsilyl carbamates and thiocarbamates of the type $R'YC({=}X)NR_2$ where X,Y = O,S; R = CH_3, C_2H_5; R′ = $(CH_3)_3Si$, and have measured their nmr spectra at various temperatures. The temperature dependence of the shape of the *N*-alkyl resonances can be used to determine the rotational energy and free energy of activation by what are now standard methods.[2,3]

The primary objectives of the study were: (a) to investigate the existence of hindered rotation about

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(1) M. F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5**, 225 (1965).

(2) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

(3) W. E. Stewart and T. H. Siddall, *Chem. Rev.*, 70, 517 (1970).

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