Ethylenimines and Phosphiranes. An Iterated Extended Hückel Theory View

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Abstract: Iterated extended Hückel theory calculations on ethylenimines and phosphiranes have led to a rationalization of rotation and inversion barrier magnitudes in terms of electronic effects. It has been found that the extent of electron density shifts within basis set orbitals at the ring heteroatom and/or the substituent atom or group bonded to it correlates well with the known or estimated barrier magnitudes in these molecular systems. In addition, an empirical method has been developed which allows a more accurate estimate of ground-state geometry than does the traditional molecular orbital energy summation technique.

The wealth of information on ethylenimine[2a] and the preparation[2b] and structural analysis of phosphirane[3] have afforded a convenient opportunity to compare the characteristics of nitrogen and phosphorus chemistry in small-ring compounds as described by iterated extended Hückel theory (IEHT). Descriptions of this theory have been reported,[4] and the options utilized, including the use of phosphorus 3d orbitals, are described in the text. In this report, the discussion will center on point-charge dipole moments, evaluation and rationalization of rotation and inversion barriers, and a new method of molecular geometry evaluation in the systems ethylenimine (**1**), 1-methylethylenimine (**2**), 1-chloroethylenimine (**3**), phosphirane (**4**), and 1-methylphosphirane (**5**).

Description of the Method

The choice of one set of parameters in IEHT is often facilitated by imposing the criteria of "parameter transferability." In this technique, the set of parameters chosen for use must be that set which produces the best average set of predictions over the range of molecular systems studied. Evaluation of resonance integral formulations and valence-state ionization potential (VSIP) parameters has been carried out here. The VSIP's which produced the most uniform set of predictions were those reported by Basch, *et al.*,[5] for 2s and 2p orbitals, by Carroll, *et al.*,[6] for the hydrogen 1s orbital, and by Cusachs[7] for 3d orbitals. The resonance integral formulation found to be most satisfactory in conjunction with these VSIP's was that given by Cusachs.[8] This formulation has been programmed in a coordinate-invariant fashion in these calculations. Slater-type orbital (STO) exponents were calculated according to Slater's rules[9] for s and p orbitals, with the exception that a value of 1.2 was used for the hydrogen 1s orbital. The phosphorus 3d orbital exponent was taken as 1.4[10].

All calculations are carried out with iteration to charge consistency. In this procedure, orbital energies are adjusted for atomic charge after each iteration, and the calculation is repeated until input and output charges match within a preset limit. In this study, the limit was 0.001 or 0.003 unit of charge, as described below.

Cartesian coordinates have been evaluated from published molecular geometries for **1**,[11] **2**,[12] and **4**.[3] The N–Cl distance in **3** has been estimated as 1.75 Å,[13] while the coordinates of the remainder of the molecule have been assumed to be the same as those of the parent molecule. The coordinates of **5** were calculated using a P–C_{methyl} distance of 1.88 Å,[13] normal tetrahedral methyl group angles, 1.091-Å C_{methyl}–H bond distances, and ring coordinates from **4**. The major ring axis is defined as the *x* axis, the out-of-plane direction as the *z* axis, and the *y* axis as parallel to the ring C–C bond axis. Thus the bond from nitrogen to the substituents lies in the *x–z* plane. The origin of the coordinate system is taken as the ring heteroatom.

The molecular properties which were evaluated include point-charge dipole moments, inversion barrier and rotation barrier magnitudes, and equilibrium bond angles between an extension of the ring plane and the ring heteroatom–Y bond, where Y is H, CH_3, or Cl. This angle is hereafter referred to as θ, and was varied in increments of 10° or less.

Inversion barriers are calculated from motion of the atom or group attached to the ring heteroatom in the vertical plane of symmetry of the ring atoms. At $\theta = 0°$, the inverting atom or carbon atom of the inverting methyl group lies in an extension of the plane of the ring.

Rotation barriers are evaluated from a rotation of the methyl group about the C(methyl)–X bond axis, where

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[1] Abstracted in part from M.S. thesis of Robert L. Brisotti, Jr.

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Table I. Charge Distributions in PE Predicted or Observed Ground-State Geometries

Molecular system	θ, deg[b]	Gross atomic charges[a]				
		C_{ring}	H_{cis}[c]	H_{trans}	X[d]	Y[d]
Ethylenimine (**1**)	70	+0.040	+0.013	+0.014	−0.166	+0.033
1-Methylethylenimine (**2**)	63.15	+0.033	+0.010	+0.010	−0.173	+0.037
1-Chloroethylenimine (**3**)	50	+0.058	+0.021	+0.021	−0.120	−0.081
Phosphirane (**4**)	82.3					
	(No 3d)	−0.008	−0.005	−0.004	+0.061	−0.028
	(3d incl)	−0.015	−0.011	−0.010	+0.089	−0.018
1-Methylphosphirane (**5**)	72	−0.014	−0.009	−0.011	+0.122	−0.024

[a] In units of electrons. [b] Observed ground-state angle or calculated angle closest to PE predicted geometry. [c] Hydrogen on the same side of the ring as Y. [d] X = N or P and Y = H, Cl, or C(methyl), as indicated by the molecular system. For **2**, methyl hydrogen charges are +0.010 electron each, and for **5**, the methyl hydrogen charges are −0.010 electron each.

X is N or P, at an inversion angle θ corresponding to the calculated equilibrium geometry. A 0° rotation is defined as that geometry in which two C–H(methyl) bonds straddle the lone pair of N or P.

A molecular energy is taken as[4] the sum of filled-orbital energies, referred to below as an MO energy. A barrier magnitude is taken as the difference between mimimum and maximum in a plot of MO energy *vs.* θ. An equilibrium geometry is taken as the angle corresponding to the minimum in an MO plot or from a plot of point charge potential energy (PE) *vs.* θ. The latter of these two plots is constructed from the summation described in eq 1, where q_i is the gross atomic

$$\mathrm{PE} = \sum_{i<j} \frac{q_i q_j}{r_{ij}} \qquad (1)$$

charge on atom *i*, and r_{ij} is the distance between atoms *i* and *j*. This summation is carried out over all atoms of the molecule at each value of θ, and is plotted *vs.* θ. The turning point of such a plot is taken as the equilibrium geometry.

Discussion of the phenomenological aspects of inversion or rotation is divided into two general areas. The first of these is termed the orbital level, and discussion in this area is centered on changes that occur in the eigenvector or charge matrices. The second area is centered on observations of the molecule as a whole, such as basis-set orbital populations, net atomic charges, equilibrium geometry, and barrier heights.

Results and Discussion

General. The molecular systems chosen for this study provide a convenient context for comparison of size, electronegativity, and electronic effects of N and P. The systems are large enough so that trends in orbital populations, charge distributions, and bonding characteristics can be seen over several atoms, but not so large that a considerable amount of calculation time is needlessly spent on molecular fragments whose characteristics do not change as geometry and/or atomic variations are made.

A utilitarian, if not theoretical justification for the iterative procedure described above stems from the fact that, in this study, molecular geometries predicted from noniterated results are far less accurate than iterated values. Noniterated calculations of geometries are as much as 10° poorer, barriers are as much as eight times lower, and dipole moments are as much as four times larger than values obtained from iterated calculations. This effect is most pronounced in the barrier and angle calculations when there is a relatively large calculated separation of charge in a molecular system. Thus, the effect is larger in **1** and its derivatives than in the phosphorus analogs, as implied by the larger separation of charge in the N series shown in Table I. In conjunction with this iterative procedure, smooth plots of PE *vs.* inversion or rotation angle in small-barrier cases could only be obtained if very restrictive test limits were used. Hence, a test limit of 0.001 unit of charge was used in **2** (rotation and inversion), **5** (rotation), and **3**. A somewhat relaxed test limit of 0.003 unit of charge was used in **1**, **4**, and **5** (inversion).

It is recognized that barrier magnitudes and molecular geometry are affected by several factors in addition to potential energy;[14] however, the observation of changes in atomic charge distributions with geometry variation has prompted us to apply a simple point-charge potential energy function (eq 1) to the charge distributions at each calculated molecular geometry. Variation in this sum with geometry should not be interpreted as variation in the true potential energy of the system, as no explicit potential energy terms are utilized in the semiempirical molecular orbital theory itself. Rather, the variation in overlap integral magnitudes which accompany any molecular geometry change naturally lead to changes in resonance integrals through use of the resonance integral formulation and ultimately to changes in the basis-set orbital coefficients. The Mulliken gross atomic charge for an atom,[15] which is evaluated from these coefficients and overlap integral magnitudes, reflects this change.

Looking at this from the orbital level, a parallel can be found between the trends in degree of antibonding or bonding character between atoms and the change in molecular geometry. This results from the changes in basis-set atomic orbital coefficients of the eigenvectors produced by inversion or rotation of an atom or group. It is therefore anticipated that the summation in eq 1, which also depends on these coefficients, might also follow a trend and thereby yield an alternate mechanism for the prediction of molecular geometry.

The degree of correlation between the relative magnitudes of atom–atom interactions as predicted from this

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equation with conclusions drawn from other evidence is examined below.

Dipole Moments. Point-charge dipole moments, neglecting lone-pair contributions, were calculated for those systems for which experimental evidence has been reported. These results are shown in Table II.

Table II. Point-Charge Dipole Moments

Molecular system		μ_{calcd}, D	μ_{obsd}, D
1		0.83[a]	1.89[b]
		(3.98)	1.73[c]
2		0.64[d]	1.236[e]
4	(No 3d)	0.33[f]	1.121[g]
	(3d incl)	0.64[f]	

[a] $\theta = 70°$. [b] R. D. Johnson, A. J. Myers, and W. D. Gwinn, *J. Chem. Phys.*, **21**, 1425 (1953). [c] R. W. Kiser and T. W. Lapp, *Inorg. Chem.*, **1**, 401 (1962). [d] $\theta = 63.15°$. [e] Reference 12. [f] $\theta = 82.3°$. [g] Reference 3.

It can be seen that the trends in experimental values are paralleled by these calculations, which we have taken as support at least for the trends in charge distributions reported here.

An interesting observation was made by Veillard, *et al.*,[16] in an *ab initio* SCF calculation on **1**. The calculated dipole moments at the experimental geometry and in the transition state were 2.31 and 0.22 D, respectively, indicating the expected rather large contribution from the lone-pair moment.

We have carried out calculations on **4** with and without 3d orbital inclusion. The inclusion of these orbitals leads to a migration of charge toward the CH_2 groups of the molecule (see Table I), an improved dipole moment, and a better ground-state geometry prediction when compared to results obtained by using only P 3s and P 3p orbitals.

Ethylenimine. The search for a nitrogen system which inverts slowly on the nmr time scale has led several workers to examine the ethylenimine system or its derivatives.[17-22] It has long been proposed that constrictions inherent in a three-membered ring system would slow the inversion process at nitrogen, although slowly inverting five- and seven-membered heterocyclic nitrogen systems have also recently been observed.[23]

Lower limits to the inversion barrier at nitrogen shown in Table III have been determined to be 12.0[24] and 11.6 kcal/mol.[25] No experimentally determined upper limit has yet been reported. The barrier of the tetramethyl carbon-substituted derivative has been determined by nmr analysis to be 11.0 or 11.9 kcal/mol (two different methods of analysis).[26]

The inversion barrier of **1** has also been evaluated from theoretical studies. Koeppl, *et al.*,[27] have used a method based on a valence force field to calculate a barrier of 34 kcal/mol. Using the MINDO method, Dewar and Shanshal[28] have obtained a value of 13.8 kcal/mol. Veillard, *et al.*,[16] in an *ab initio* SCF study, report a value of 18 kcal/mol.

In this study, we have examined the predicted ground-state geometry and the inversion barrier at nitrogen. Results are listed in Table III. In accordance with the PE model, the 68° turning point is taken to represent the ground-state geometry of the system. In the nitrogen series, these plots exhibit maxima. In this case, the PE value is found to be coincident with the experimentally determined value[11] while the MO value is some 8° lower. The MO barrier magnitude of 20.9 kcal/mol is somewhat higher than the values found by Bardos, *et al.*,[26] for the tetramethyl derivative, and is in very good agreement with Veillard's SCF value.[16]

Table III. Rotation and Inversion Barriers and Angles

	Predicted			Observed	
Molecular system	Angle, deg MO	Angle, deg PE	Barrier, kcal/mol	Angle, deg	Barrier, kcal/mol
1	60	68	20.9	68[a]	11.6[b] > 12.0[c] 11.0 or 11.9[d] 13.8[e] 18[f] 34[g]
2 (Inv)	45	63	9.8	63.15[h]	19[i]
(Rot)	0	0	3.9 (45°) 8.5 (63°)		3.462[h]
3	0	53	0.0	>0[j]	≥25[j]
4	74	81	39.9	82.3[k]	
5 (Inv)	72	73	37.3		
(Rot)	0	0	0.75		

[a] See ref 11. [b] See ref 25. [c] See ref 24. [d] See ref 26. [e] See ref 28. [f] See ref 16. [g] See ref 27. [h] See ref 12. [i] See ref 33. [j] See the text for an explanation of this number. [k] See ref 3.

At the orbital level, examination of the charge matrices determined at $\theta = 70°$ (the calculated value closest to the turning point of the PE curve) and at 0° (the planar transition state) reveals that the major shifts in electron density between atoms during the inversion process involve the two carbons and the nitrogen of the ring, and the N–H hydrogen. The methylene hydrogens are less significantly involved in the inversion process. This observation is reflected in the fact that substitution of methyl groups for each of the four methylene hydrogens does not have a large effect on the inversion barrier magnitude.[26] The relative ratio of atom–atom interaction magnitudes shown in Table IV indicates that the shape of the PE barrier is dominated by N–H and N–C_2 interactions, in consonance with the above observation.

The highest filled molecular orbital in the ground-state geometry corresponds to the "lone-pair" orbital on nitrogen. The orbital is considerably delocalized, with only 76.3% of the two electrons in this orbital localized on nitrogen. Although there are changes in several other basis-set orbital coefficients in this and

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Table IV. PE Atom–Atom Interaction Magnitudes. Ethylenimine

Atom–atom interaction	Interaction magnitude (×10^2) 0° [b]	70° [b]	Δ (×10^4)[a]	Ratio
N-H	−0.760	−0.541	+18.3	10.0
N-C_2	−1.004	−0.881	+10.3	5.6
N-H_4	−0.423	−0.409	+1.2	0.7
H-C_2	+0.148	+0.128	−1.7	0.9
H-H_4	+0.074	+0.069	−0.5	0.3
Σ(CH_2-CH_2)	+0.455	+0.440	−1.3	0.7
			+26.3	

[a] The Δ in this expression is the difference in interaction magnitudes for the two configurations listed divided by the sum of the PE atom–atom interaction magnitudes for the more stable geometry listed. The total difference in the PE summation for the two configurations relative to the more stable geometry is the sum of these terms and is indicated at the bottom of the column. The plus or minus sign in this column indicates the relative direction of the shift in each interaction. [b] See the text for a definition of this inversion angle.

other MO's as θ is reduced to 0°, it is found that a dominant change occurs in this MO at nitrogen. As θ approaches 0°, the lone pair becomes essentially a p_z orbital on nitrogen (92.4% of the two electrons in this orbital reside on nitrogen in the transition state). Use of the orbital coefficients on nitrogen for the lone pair at θ = 70° indicates that the lone pair is directed below the ring plane at an angle of 54°. Thus, a principal phenomenological change that occurs as inversion takes place is the change in orbital character of the lone pair on nitrogen. The fact that several other variations also occur as inversion proceeds, however, indicates that the change in lone-pair character cannot be cited as the *only* change coincident with inversion.

Table V. Atomic Orbital Population Shifts[a]

Molecular system		X[b] s[c]	X[b] p_x	X[b] p_y	X[b] p_z	Y[b] p_x	Y[b] p_y	Y[b] p_z	Barrier, kcal/mol
1		−0.11	−0.47		+0.62				∼16[d]
2	(Inv)	−0.08	−0.34		+0.45	−0.10		+0.10	19[e]
	(Rot)			+0.008		−0.008	+0.013		3.462[f]
3		−0.08	−0.36		+0.49	−0.47		+0.45	≥25[g]
4		−0.19	−0.47		+0.73				
5	(Inv)	−0.16	−0.39		+0.66				
	(Rot)					−0.006	+0.007		

[a] All other shifts are small in comparison with those shown. [b] X = N or P, and Y = H, Cl, or C(methyl), as indicated by the molecular system. [c] A minus sign indicates a shift from the orbital as θ approaches 0°. [d] An approximate value based on reported data (see Table III). [e] See ref 33. [f] See ref 12. [g] See the text for an explanation of this number.

There is also an effect which characterizes the molecule as a whole, *i.e.*, reflecting net trends of all variations occurring in all the molecular orbitals. As such it is termed a molecular level effect, as opposed to an orbital level effect, and is more representative of the net electronic consequences of inversion than are the molecular orbital character changes cited above. This effect is given in Table V, which shows the major shifts which occur in basis-set orbital populations as each of the systems studied reaches the transition state. In this case, there is a shift of 0.11 electron out of the N 2s, a shift of 0.47 electron out of the N $2p_x$, and a shift of 0.62 electron into the N $2p_z$ orbital as θ is lowered from 70 to 0°. Shifts in other orbital populations are small in comparison with these. A similar effect was observed for this system by Viellard[16] in which *ca.* 0.3 electron shifted from the N 2s to the N $2p_z$ orbital. It is encouraging to find this similarity between *ab initio* SCF results and those of this semiempirical calculation. The relationship of these shift magnitude trends with the barrier magnitude trends is noted in each of the remaining systems.

1-Chloroethylenimine. The initial nmr spectrum of this system, obtained on a 20-MHz instrument, was reported[29] as a single line, implying that the four methylene hydrogens were equivalent on the nmr time scale. Later investigations of carbon-substituted derivatives[21] of this compound revealed that these systems represent stable nitrogen pyramids. Subsequently,[20] the spectrum of **3** was reinvestigated at 60 and 100 MHz and found to be an AA′BB′ system. The apparent singlet at 20 MHz is therefore assumed to be a closely spaced unresolved multiplet. Indeed, the 1-bromoethylenimine spectrum also appears to be a singlet even at 60 MHz and is assumed[20] to also correspond to a closely spaced unresolved multiplet, based on the resolved spectra of its carbon-substituted derivatives.

We have taken this evidence to support a high-barrier, bent-ground-state configuration for **3**. Bottini and Roberts[22] have estimated that a barrier of at least 25 kcal/mol is required for a stable pyramid to exist. As indicated in Table III, the MO predicted geometry is θ = 0°, in opposition to the observed nmr results. The PE predicted ground state, on the other hand, is a bent configuration with θ = 53°, an angle somewhat lower than in the case of **1**. This represents one of two instances in this study where the geometry predicted on the basis of the PE plot is in much closer agreement with experimental observations than is the geometry predicted from the MO energy plot. The other case, that of **2**, is discussed below.

As in the case of **1**, it is possible to restrict inversion barrier arguments at the orbital level to changes that occur in one specific MO only if all other orbital descriptions remain essentially constant as the process occurs. To the extent that the use of trends in orbital characteristics is allowed, a comparison of shifts in electron density exhibited in the charge matrices of **1** *vs.* **3** indicates that the large barrier in the latter case is accompanied by electron density shifts involving more atoms and to a larger extent than in **1**.

Examination of the relative magnitudes of PE interactions in these two systems as shown in Tables IV and

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Table VI. PE Atom–Atom Interaction Magnitudes. 1-Chloroethylenimine

Atom–atom Interaction	Interaction magnitude ($\times 10^2$) 0° [b]	50° [b]	Δ ($\times 10^4$)[a]	Ratio
N–Cl	+0.444	+0.558	+29.9	10.0
N–C_2	−1.070	−0.945	+33.0	11.0
N–H_4	−0.478	−0.465	+3.3	1.1
Cl–C_2	−0.212	−0.331	−31.2	10.4
Cl–H_4	−0.120	−0.207	−23.0	7.7
$\Sigma(CH_2–CH_2)$	+0.927	+1.010	+21.9	7.3
			+33.9	

[a] See footnote *a* of Table IV. [b] See the text for a definition of this inversion angle.

VI shows that the shape of the PE model barrier is dictated by the sum of several interactions in the case of **3**, but is mainly determined by the N–H and N–C_2 interactions in the case of **1**. Hence the same qualitative conclusion can be drawn from the PE model as from the shifts in electron density exhibited in the charge matrices; namely, a more delocalized effect accompanies the barrier in **3**.

There is another dominant feature of the inversion process at the orbital level. At $\theta = 50°$, the highest filled MO (no. 9) is of lone-pair symmetry; however, only 65.9% of the electron density in this MO is localized at nitrogen. At this ground-state geometry, MO no. 11 is primarily a nonbonding orbital on Cl (containing 72.7% of the electron density in this MO). As θ is reduced to 0°, these two MO's become even more localized. Molecular orbital no. 9 becomes 80.4% localized on nitrogen, and MO no. 11 becomes 86.9% localized on chlorine, both as p_z orbitals. Additional shifts, some fairly large, indicating the delocalized nature of this barrier process as opposed to **1**, occur in other more delocalized MO's, but MO's 9 and 11 are initially localized on N and Cl at $\theta = 50°$, and become even more localized on these two atoms as θ approaches 0°. The increased localization of electron density on nitrogen as the transition state is reached is a phenomenon common to all the ethylenimine derivatives studied here, and in this case is accompanied by an additional localization on Cl. Since this is a more dominant effect in the MO trends, and can therefore be taken as qualitatively representing a phenomenon characteristic of this molecule as a whole, it can be used to correlate with valence-bond arguments of increased electron–electron repulsions in the transition state.

At the molecular level, shown in Table V, variations in basis-set orbital populations with θ are concentrated on nitrogen and chlorine. As in the case of **1**, nitrogen undergoes two shifts, an s–p shift and a p–p shift, as the transition state is reached. In addition, there is also a significant shift on chlorine. The nitrogen shifts are all slightly smaller than the corresponding shifts in the parent compound, yet the inversion barrier is larger. Resolution of this apparent contradiction is found in the p–p shift on chlorine. If the orbital population shift magnitudes can always be associated with barrier height, *vida infra*, then these two sets of shifts must complement each other and lead to the larger barrier. As the orbital character trends cited above also indicate chlorine participation in the barrier, these two features complement each other.

Phosphirane. The preparation of **4** by Wagner, *et al.*,[2] has afforded an opportunity to compare the properties of this system with the analogous properties of **1**. The initial report of the proton nmr spectrum[2] of this system indicates that inversion at phosphorus is slow on the nmr time scale. Subsequent preparation of various derivatives[30] confirms this observation. The structure of this system determined by Bowers, *et al.*,[3] supports a bent ground state with $\theta = 82.3°$.

We have examined the ground-state geometry, inversion barrier, and electronic structure of this system for comparison with **1**. The MO predicted ground state shows $\theta = 74°$, while the PE predicted ground state is 81° (Table III), again virtually coincident with the observed angle. In this case, as in **5** below, a minimum rather than a maximum is observed in the PE plot.

Examination of charge matrices evaluated at $\theta = 80°$ (the calculated value closest to the predicted geometry of 81°) and at 0° reveals that all atoms of the ring, including the methylene hydrogens as well as the P–H hydrogen, are involved in the inversion process. This is in contrast to the results on **1** in which the ring hydrogens were involved to a lesser extent. Two observations are consonant with this trend. First, Bowers, *et al.*,[3] reported that the methylene hydrogens are not symmetrically disposed above and below the ring plane. Rather, the H_{cis}–P and H_{trans}–P distances are 2.562 and 2.527 Å, respectively, and the two trans hydrogens are closer together than the two cis hydrogens. This can be interpreted as a result of P–H hydrogen–H_{cis} interactions in this system, indicating that the methylene hydrogens may very well play a part in the inversion process. Second, examination of the PE atom–atom interactions indicated in Table VII also indicates that interactions between the methylene hydrogens and other atoms are larger in this case than in the case of **1**. As a result, the shape of the PE curve is more the sum of several interactions here, as opposed to domination by the N–H and N–C_2 interactions in the case of **1**.

Table VII. PE Atom–Atom Interactions. Phosphirane

Atom–atom interaction	Interaction magnitude ($\times 10^2$) 0° [b]	80° [b]	Δ ($\times 10^4$)[a]	Ratio
P–H	+0.034	−0.115	−64.9	10.0
P–C_2	−0.062	−0.141	−34.4	5.3
P–H_4	−0.100	−0.149	−21.1	3.3
H–C_2	−0.005	+0.021	+11.6	1.8
H–H_4	−0.010	+0.026	+15.6	2.4
$\Sigma(CH_2–CH_2)$	+0.102	+0.129	+11.5	1.8
			−81.7	

[a] See footnote *a* of Table IV. [b] See the text for a definition of this inversion angle.

Orbital population shifts shown in Table V indicate a larger barrier in **4** than in **1**, assuming shift magnitudes are proportional to barrier height. The MO predicted inversion barrier is 39.9 kcal/mol, in agreement with this implication. This is also in consonance with the generally high barriers observed in acyclic phosphorus compounds[31] and the expected increase in these barriers

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(30) S. Chan, H. Goldwhite, H. Keyzer, D. G. Rowsell, and R. Tang, *Tetrahedron*, **25**, 1097 (1969).

(31) M. J. Gallagher and J. D. Jenkins, *Top. Stereochem.*, **3**, 11 (1968).

in small ring cyclic compounds.[32] As in **1**, ring heteroatom population shifts are the only significant intraatom shifts in the molecule as the transition state is approached.

Accompanying the inversion process are changes in the basis-set orbital coefficients in MO's. Within the limits imposed by the theory itself, as described above, the highest filled molecular orbital is again that orbital which can be termed the lone-pair orbital. In the bent configuration, this orbital is similar in basis-set orbital coefficient magnitudes to that of **1**. Using the magnitudes of p_x and p_z coefficients on phosphorus, the lone pair is directed at an angle 45° below the plane of the ring (P–H bond 81° above the ring). This yields essentially the same angle between the lone-pair orbital and the P–H bond (126°) as found between the lone-pair orbital and the N–H bond in **1** (124°). The net difference in this respect between the two systems lies in the ring–lone pair angle of 135° in **4** as opposed to 126° in **1**. This also means that the P–H bond makes an angle of 99° with the ring in **4** as opposed to the 110° angle between the N–H bond axis and the ring in **1**. Such effects undoubtedly arise from features in addition to the lone-pair orbital; however, ring–lone pair repulsion *vs.* ring-bonded pair repulsion arguments favor the larger ring–lone pair angle in **4**, as observed. The main difference in the character of the lone-pair orbital in these two systems is the extent of its delocalization. Only 62.3% of the electron density in this orbital is localized on phosphorus, as opposed to 76.3% on nitrogen in **1**. Delocalization extends primarily to the ring carbon atoms in **4**, with only small differences in the extension to the methylene hydrogens in the two systems. In the transition state, there is a shift of electron density from other atoms in the molecule to phosphorus, such that 88.5% of the electron density then resides in the p_z orbital of phosphorus. There are also other significant shifts of electron density in other MO's as inversion occurs, however, so it cannot be said that the dominant shift in the lone-pair molecular orbital is or is not the only factor contributing to the inversion barrier magnitude, but the orbital population shifts of Table V do support this notion.

There appears to be very little participation of P 3d orbitals in any of the filled molecular orbitals of the eigenvector or charge matrices. Their presence is evident, however, in the empty orbitals. The effect of their inclusion is most evident at the molecular level in the gross atomic charge distributions, and has been referred to above in the section on dipole moments. This is an interesting case where examination of the filled orbitals of the eigenvector matrix leads one to the initial conclusion that the 3d orbitals of phosphorus do not affect the nature of bonding in the molecule; however, their effect is seen upon closer examination of the entire eigenvector matrix and again when molecular properties such as dipole moment and charge distributions are examined both before and after their inclusion.

1-Methylethylenimine. There have been many investigations of ethylenimines substituted at nitrogen with several reports of nmr analyses indicating slow inversion at nitrogen.[1,17–22] The geometry of 1-methylethylenimine, the system studied here, has been determined by Harmony and Sancho,[12] who report an angle of 63.15° between an extended ring plane and the N–C$_{\text{methyl}}$ bond axis. The rotation barrier about this axis is also reported by these authors[12] to be 3.462 kcal/mol. An inversion barrier of 19 ± 3 kcal/mol at nitrogen has been determined by Heeschen and Gutowsky.[33] Evidence that the magnitude of this barrier is only moderately increased by substitution in the ring has been obtained by Jautelat and Roberts,[22] who report a barrier of approximately 24 kcal/mol (solvent dependent) for 1,2,2-trimethylethylenimine. A value of 16 kcal/mol has been calculated for an N-substituted ethylenimine by Koeppel, *et al.*;[27] however, the authors list this value as uncertain.

We have examined both the inversion barrier at nitrogen and the rotation barrier about the N–C$_{\text{methyl}}$ bond in this system. Results are given in Table III. A plot of MO energy *vs.* inversion angle was carried out with the methyl group in the 0° rotation position, as described above, and shows a minimum at 45°. At the predicted ground-state geometry, the 0° rotation is most stable (see below), and in the transition state, only a 1-kcal/mol change in MO energy is observed with methyl group rotation. Hence, the minimum in this plot is not sensitive to methyl group rotation. The PE plot shows a maximum at 63°, which, using this model, is taken as the ground-state geometry. This angle is virtually coincident with the observed angle. The inversion barrier magnitude evaluated from the MO plot (45° minimum) is 9.8 kcal/mol, considerably lower than the observed value of 19 ± 3 kcal/mol.[33] The rotation barrier calculated at this 45° methyl group elevation is 3.90 kcal/mol, however, in excellent agreement with the observed value. In the light of this discussion, however, this agreement should be viewed only as fortuitous in nature. Evaluation of this barrier at the 63° PE predicted geometry (again using the MO energies) yields a value of 8.5 kcal/mol. Thus the MO-predicted low inversion barrier angle and magnitude is associated with a good rotation barrier calculation, and the PE-predicted accurate inversion barrier angle is associated with a high MO rotation barrier prediction. In both instances, the 0° rotamer is predicted to be most stable, and the 60° rotamer least stable, implying that the barrier origin lies in an interaction between the lone pair on nitrogen and the methyl group.

As the PE plots have led to better predictions of molecular geometry in this study, the following discussion is based on results calculated at $\theta = 63°$ rather than $\theta = 45°$ for the ground state of the system. There is again a rough correlation between the magnitudes of atom–atom interactions of the point charge PE model as shown in Table VIII and the extent of electron density shifts at the orbital level in the molecular orbitals of the charge matrix. The most noticeable difference between inversion in this system and that in the parent molecule **1** is the lack of N–C$_2$ interactions in the ring in this system. Electron density shifts in the charge matrix still show significant ring carbon involvement, however.

Other effects which accompany inversion in this system parallel those of **1**. At the orbital level, the lone-pair molecular orbital is 77.7% localized on nitrogen

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[32] S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968).

[33] (a) J. P. Heeschen, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1959; (b) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958).

Table VIII. PE Atom–Atom Interactions. 1-Methylethylenimine (Inversion)

Atom-atom interaction	Interaction magnitude (×10²) 0°[b]	63°[b]	Δ(×10⁴)[a]	Ratio
N-CH$_3$	−0.905	−0.686	+19.8	10.0
N-C$_2$	−0.776	−0.757	+1.8	0.9
N-H$_4$	−0.264	−0.315	−4.5	2.3
ΣCH$_3$	+0.200	+0.120	−7.2	3.6
Σ(CH$_2$-CH$_2$)	+0.221	+0.272	+4.6	2.3
CH$_3$-(CH$_2$)$_2$	+0.253	+0.254	+0.1	0.1
			+14.6	

[a] See footnote *a* of Table IV. [b] See the text for a definition of this inversion angle.

in the ground state, and increases to 87.1% as the transition state is reached. In the ground state of 63°, it is directed below the ring at an angle of 55.5°, much the same as in the parent system. On the molecular level, the basis-set orbital population shifts indicated in Table V accompany the reduction in θ from 63° to 0°. Again, using shift magnitudes as an inference of barrier height, the shifts observed on C_{methyl} and N lead to the prediction of a lower barrier height than in **3** as observed, and approximately the same as in **1** (a study of the quantitative use of these shift magnitudes is in progress).

Rotation of the methyl group about the N–C_{methyl} bond produces only very small shifts in the charge matrices and in the PE atom–atom interactions shown in Table IX. Note that on a ratio scale the effect is significantly delocalized, but that the actual magnitude of each interaction is small when compared to interactions in the other barriers studied. On a molecular level, there are also only small shifts in net orbital populations, as shown in Table V. The dominant shifts of *ca.* 0.01 electron occur in the p_x and p_y orbitals of the methyl group carbon and in the p_y orbital of nitrogen. Other shifts are *ca.* 0.004 electron, and in general far less than this value. Thus, using orbital population shifts as an indication of the electronic consequences of the barrier, this barrier originates in the shifts in nitrogen and the C_{methyl} carbon cited above induced by rotation of the methyl group hydrogens. Notably, there is only an insignificant 0.001-electron shift in each of the methyl hydrogen s orbital populations as rotation proceeds.

Table IX. PE Atom–Atom Interactions. 1-Methylethylenimine (Rotation)

Atom-atom interaction	Interaction magnitude (×10²) 60°[b]	0°[b]	Δ(×10⁴)[a]	Ratio
N-CH$_3$	−0.709	−0.686	+2.1	10.0
N-C$_2$	−0.783	−0.757	+2.3	11.3
N-H$_4$	−0.324	−0.315	+0.8	3.9
ΣCH$_3$	+0.126	+0.120	−0.5	2.6
Σ(CH$_2$-CH$_2$)	+0.280	+0.272	−0.7	3.5
CH$_3$-(CH$_2$)$_2$	+0.265	+0.254	+1.0	4.8
			+3.0	

[a] See footnote *a* of Table IV. [b] See the text for a definition of this rotation angle.

An interesting test of the correlation of electron density shift magnitude with barrier magnitude in this system can be made by comparing the shifts induced by methyl group rotation at θ = 45° (the MO predicted geometry) and at θ = 63° (the PE predicted geometry). At θ = 45°, MO predicted barrier height is 3.9 kcal/mol, and all but 1 of the 23 electron population shifts are less, many approximately half the magnitude, than the shifts observed at θ = 63°, where the MO calculated barrier is 8.5 kcal/mol. The one orbital population, p_z on the methyl group carbon, which does not follow this trend shows a slight increase in shift magnitude as θ is increased. This correlation, coupled with those of **1** *vs.* **3** and **1** *vs.* **4**, points to a meaningful parallel between barrier height and intraatom electron density shifts.

1-Methylphosphirane. Initial attempts at the preparation of this system were reported by Wagner, *et al.*,[2] and later substantiated by Chan, *et al.*[30] The proton nmr spectrum of this system[30] is of the AA′BB′X type, implying, as expected, that the rate of inversion at phosphorus is slow on the nmr time scale. No barrier height or geometry elucidation studies have yet been reported; however, the nmr evidence indicates that the molecule is bent, and it is anticipated that methyl substitution for the P–H hydrogen in **4** should have only a small perturbing influence on molecular geometry, similar to that observed in **1** *vs.* **2**.

As in the case of **2**, we have studied both the methyl group rotation barrier and the inversion barrier at the ring heteroatom. The results are indicated in Table III. The inversion geometry was evaluated with the methyl group in the 0° rotation position. Both models predict a similar inversion angle in this instance. The rotation barrier was evaluated at a methyl group elevation of 72°, and again the 0° rotation configuration is predicted to be most stable by both models. From the MO plots, an inversion barrier of 37.3 kcal/mol and a rotation barrier of 0.75 kcal/mol were evaluated.

Atom–atom interactions shown in Tables X and XI for inversion and rotation, respectively, and the shifts in the charge matrices parallel those of **2**, except that in this case, a slightly more delocalized effect is predicted for both barriers. The lone-pair molecular orbital is again delocalized in the equilibrium position, with only 57.1% of the electron density in this orbital localized on P. At θ = 0°, it is 79.9% localized on P. This is the most delocalized lone-pair orbital in the series of compounds studied here. If base strength

Table X. PE Atom–Atom Interactions. 1-Methylphosphirane (Inversion)

Atom-atom interaction	Interaction magnitude (×10²) 0°[b]	72°[b]	Δ(×10⁴)[a]	Ratio
P-CH$_3$	−0.026	−0.309	−75.2	10.0
P-C$_2$	−0.120	−0.189	−18.4	2.5
P-H$_4$	−0.171	−0.191	−5.2	0.7
ΣCH$_3$	+0.001	+0.086	+22.8	3.0
Σ(CH$_2$-CH$_2$)	+0.148	+0.117	−8.2	1.1
CH$_3$-(CH$_2$)$_2$	+0.013	+0.110	+25.8	3.4
			−58.4	

[a] See footnote *a* of Table IV [b] See the text for a definition of this inversion angle.

Table XI. PE Atom–Atom Interactions. 1-Methylphosphirane (Rotation)

Atom–atom interaction	Interaction magnitude ($\times 10^2$)			
	60°[b]	0°[b]	Δ ($\times 10^4$)[a]	Ratio
P–CH_3	-0.321	-0.309	$+3.2$	10.0
P–C_2	-0.178	-0.189	-3.0	9.4
P–H_4	-0.184	-0.191	-1.8	5.6
ΣCH_3	$+0.093$	$+0.086$	-2.0	6.3
$\Sigma(CH_2–CH_2)$	$+0.108$	$+0.117$	$+2.6$	8.1
$CH_3–(CH_2)_2$	$+0.109$	$+0.110$	$+0.3$	0.9
			-0.7	

[a] See footnote *a* in Table IV. [b] See the text for a definition of this inversion angle.

can be correlated with electron density localization on the donor atom, then this system should be the poorest base of the series. The lone-pair orbital shape is similar to that in other members of the series, and is directed at an angle of 51.6° below the ring plane. This is a slightly larger angle than found in **4**, and is expected in the light of a lower θ value in the equilibrium geometry. A similar trend is found in **1** *vs.* **2**.

At the molecular level, as shown in Table V, inversion is accompanied by significant orbital population shifts on phosphorus. No significant C_{methyl} shifts are noted in this instance. Rotation, on the other hand, occurs with significant shifts on the C_{methyl} carbon, and not on the ring heteroatom as in **2**. As these rotation-induced shifts are of themselves small in magnitude (similar to rotation in **2**), the relative ratio of the listed shift magnitudes to those of other orbitals is notably smaller than in cases of inversion. The reduced magnitude of rotation-induced shifts in **5** as compared with **2** parallels the calculated reduction in MO predicted barrier magnitudes. The reduction in ring heteroatom orbital shifts in going from **1** to **2** is paralleled in the comparison of **4** and **5**, with the notable exception that no significant shift is found for the C_{methyl} carbon in **5**. Since inversion barrier magnitudes are only moderately affected by methyl substitution for hydrogen at the heteroatom position, as inferred from the MO plots of **4** and **5**, and a comparison of the estimated inversion barrier in **1** and the observed barrier in **2**, it is premature to make a more quantitative evaluation of the magnitude of these shift differences until more precise experimental evidence has been obtained.

Conclusion

Barrier magnitudes correlate well with net orbital population shifts. It has not been demonstrated that other electronic effects do not also occur as geometry variation takes place, but only that this is not manifested in orbital population shifts. Indeed, the empirical relationships developed from eq 1 may correlate with atom participation during such changes. At present, it has been found that such atom–atom interaction magnitudes do qualitatively reflect the extent of atom involvement in electron density shifts in molecular orbitals.

Traditional geometry and barrier height prediction techniques have been found to be of somewhat limited utility in these systems, with more accurate geometries predicted from a fitting of net atomic charge variations to a point-charge potential energy equation.

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