Linear Free Energy Correlations of Barriers to Pyramidal Inversion[1]

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Abstract: Linear relationships are found to correlate the pyramidal inversion barriers of identically substituted amines, phosphines, arsines, carbanions, oxonium ions, silyl anions, sulfonium ions, and sulfoxides. The slopes of the correlation lines are a convenient measure of the relative sensitivities of inversion centers to structural modification. The potential existence of reversal points in these linear free-energy correlations implies that for systems R^1R^2MX, the effect (barrier elevating or barrier depressing) of a given structural modification ($X \rightarrow Y$) may be dependent upon the remaining invariant ligands (R^1 and R^2). A relationship between planar and pyramidal stability is suggested: the ordering of substituents according to their effectiveness in decreasing pyramidal stability may be used to predict the effectiveness of these selfsame substituents toward increasing planar stability.

In previous studies it was shown that free-energy relationships of the standard Hammett type are applicable to a restricted class of pyramidal species—aryl-substituted sulfoxides,[2] phosphines,[3] and amines.[4] Subsequent investigations have revealed a marked parallelism in the effect of structure on the inversion barriers at nitrogen, phosphorus, and arsenic.[5] In this paper we describe our finding that these observations may be expressed in a quantitative fashion, for systems embracing a wide variety of structural types, through the use of linear free-energy correlations.

Inversion Centers of Group Va Elements

Figure 1 represents a correlation between barriers to pyramidal inversion at arsenic and phosphorus in which the only difference between the compared structures is the identity of the inversion center.[6] This plot represents a correlation between the inversion barriers of corresponding members of two *reaction series*, a term by which we describe a set of compounds possessing the same inversion center and differing solely in the nature of the ligands to that center.[7]

The correlation represented by the present treatment (illustrated by the plot in Figure 1) is far broader in scope than the earlier, standard Hammett correlations,[3,4] in which the structural variation within a given reaction series was severely restricted.[8]

The linear correlation between barriers to inversion at phosphorus and arsenic may be extended to nitrogen. However, the lack of experimental data for identically substituted pairs of compounds has dictated the use of values calculated by a semiempirical method. For this purpose, we have utilized the previously reported,[9] specially parametrized CNDO/2 scheme which has proven useful in the calculation of inversion barriers in systems comprised of elements from the first and second rows of the periodic table. Figure 2 represents a correlation of nitrogen and phosphorus inversion barriers obtained in this manner.[10] Since previous experience[9] has demonstrated acceptable agreement between experimental and calculated inversion barriers for amines and phosphines incorporating a variety of structural features, we believe that the correlation line in Figure 2 is not significantly different from that which would have been obtained through use of experimental data.

Inspection of Figures 1 and 2 reveals that barriers of first-, second-, and third-row inversion centers respond in a similar fashion to a given structural change. Despite the considerable variety of substituents examined, the points defining each correlation roughly fall on a straight line. While stricter linearity might be expected for subsets of the correlated data, each representing a more restricted definition of a reaction series, the resulting loss in generality would more than offset any improvement in the correlation.

Inversion Centers of Group IVa and VIa Elements

Linear correlations exist between the calculated pyramidal inversion barriers of silyl anions and phosphines (Figure 3), sulfonium ions and phosphines (Figure 4), sulfoxides and methylphosphines (Figure 5),[11]

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[1] This work was supported by the National Science Foundation (GP-30257).

[2] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4854 (1968).

[3] R. D. Baechler and K. Mislow, *ibid.*, 92, 3090 (1970).

[4] J. D. Andose, J.-M. Lehn, K. Mislow, and J. Wagner, *ibid.*, 92, 4050 (1970).

[5] (a) R. D. Baechler and K. Mislow, *ibid.*, 92, 4758 (1970); (b) R. D. Baechler and K. Mislow, *ibid.*, 93, 773 (1971); (c) W. Egan and K. Mislow, *ibid.*, 93, 1805 (1971); (d) W. Egan, R. Tang, G. Zon, and K. Mislow, *ibid.*, 93, 6205 (1971); (e) R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *ibid.*, 94, 2859 (1972); (f) R. H. Bowman and K. Mislow, *ibid.*, 94, 2861 (1972).

[6] In two instances, lack of appropriate data required the comparison of similarly (rather than identically) substituted compounds. In Figure 1, for M = P, R = n-C_4H_9, and for M = As, R = C_2H_5.

[7] Other, more restricted definitions are possible; see below.

[8] In these earlier correlations, the reaction series were defined by maintaining invariant both the inverting center *and* two ligands. The third, variable, ligand was restricted to aryl groups which differed only in the identity of the meta or para substituent.

[9] (a) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 93, 6507 (1971); (b) J. D. Andose, A. Rauk, R. Tang, and K. Mislow, *Int. J. Sulfur Chem., Part A*, 1, 66 (1971).

(9c) Note Added in Proof. In light of a recent paper by J. R. Sabin, D. P. Santry, and K. Weiss (*J. Amer. Chem. Soc.*, 94, 6651 (1972)), we note that the results of all semiempirical calculations reported in the present and in the previous[9a,b] papers of this series are invariant with respect to rotation of the coordinate axes.

[10] Omitted from Figure 2 are systems bearing two or three second-row substituent ligands. There is evidence[9a] that the semiempirical scheme grossly overestimates the inversion barriers in amines incorporating such substituents.

[11] The correlation given in Figure 5 implies a more restricted definition of reaction series than employed in the other correlations.

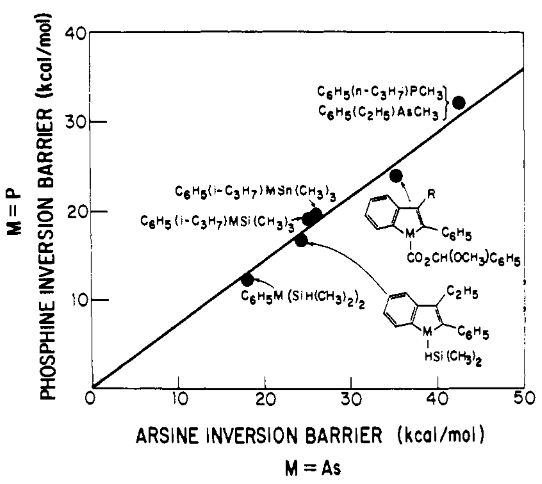

Figure 1.

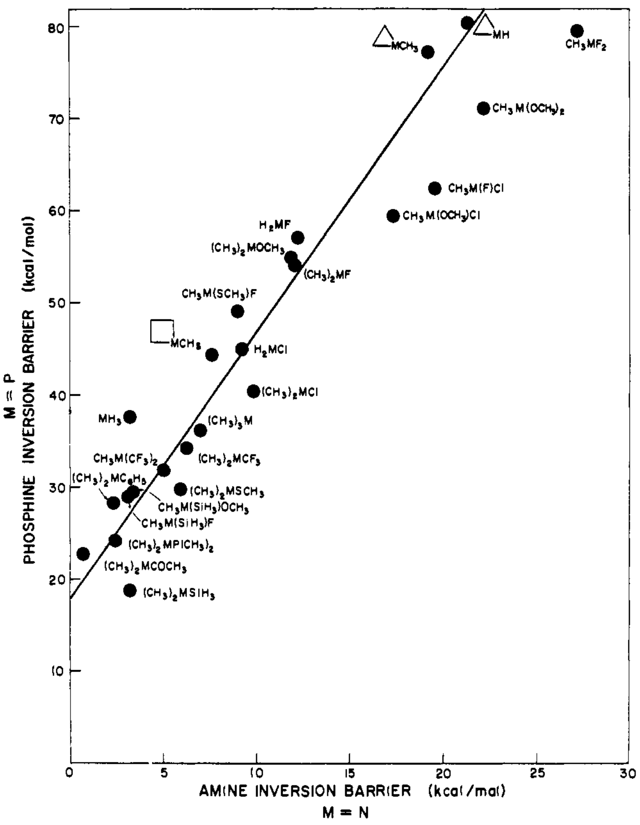

Figure 2.

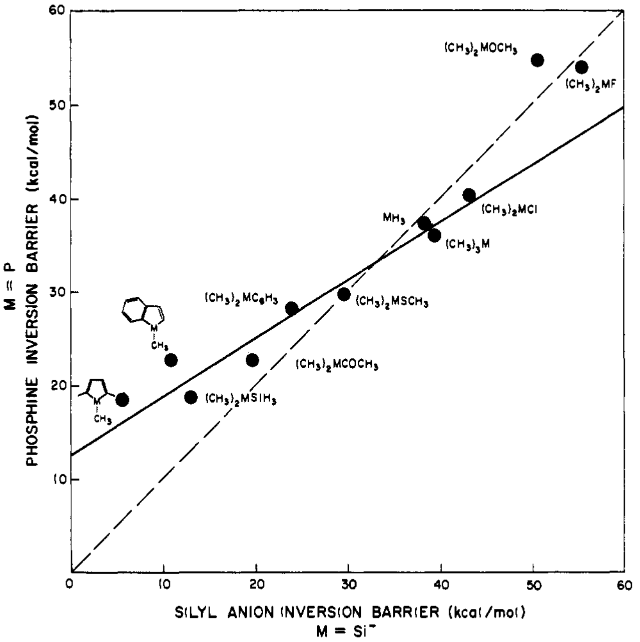

Figure 3.

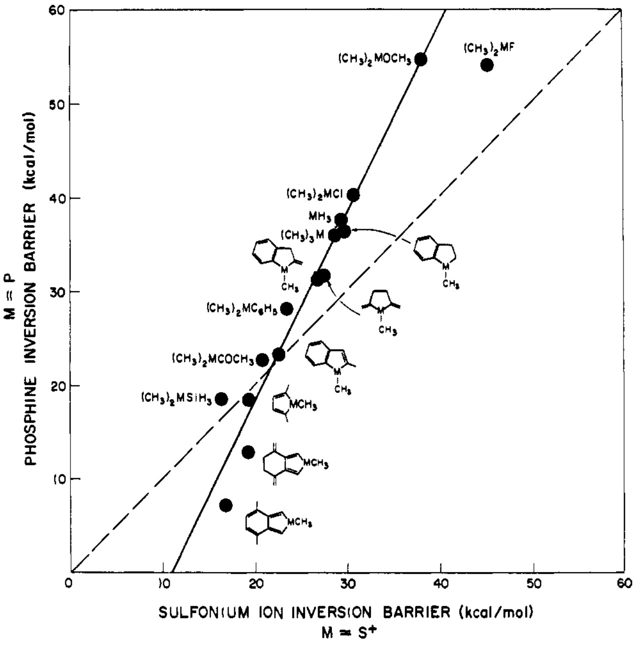

Figure 4.

carbanions and phosphines (Figure 6), and oxonium ions and phosphines (Figure 6).[12]

In contradistinction to the group Va inversion centers, for which the credibility of the calculated inversion barriers is established by direct comparison with a large number of experimentally determined barriers representing a variety of structural types, the scarcity of experimental data for the inversion centers of groups IVa and VIa exludes the possibility of such verification at this time. In particular, no experimental data whatsoever exist which allow the quantitative estimation of barriers to pyramidal inversion for carbanions and silyl anions, uncomplicated by solvent and/or gegenion effects, and serious experimental difficulties due to such association phenomena are likely to impede their reliable determination.[13] Although limited experimental results are available for inversion of oxonium ions and sulfonium ions, these values were used in the parametrization of the semiempirical scheme,[9a] leaving no data for subsequent credibility tests. Finally, the available sulfoxide inversion barriers do not span a sufficient structural range to permit adequate verification of our semiempirical calculations for these compounds. Therefore, in the absence of experimental confirmation, we must express some reservation concerning the reliability of barrier calculations and de-

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[12] The dashed line in the figures corresponds to the identity line (*i.e.*, the line of slope unity and intercept zero).

[13] The parametrization of the CNDO/2 scheme for carbanions and silyl anions utilized barriers to inversion obtained by nonempirical calculations.[9a]

Table I. Slopes, Sensitivities, and Intercepts for Linear Correlations of Inversion Barriers

Inversion center	Row of periodic table	Correlations with phosphines: Slope[a] (sensitivity)[b]	Correlations with phosphines: Intercept,[a] kcal/mol	Correlations with amines: Slope[c]	Correlations with amines: Intercept,[c] kcal/mol
C (carbanions)[d]	1	6.8 (0.15)	~13	0.4	~1
N (amines)	1	2.9 (0.34)	18	1.0	0
O (oxonium ions)[d]	1	5.3 (0.19)	~9	0.5	~2
Si (silyl anions)	2	0.6 (1.7)	12	4.7	9
P (phosphines)	2	1.0 (1.0)	0	2.9	18
S (sulfonium ions)	2	2.0 (0.50)	−22	1.4	20
As (arsines)	3	0.7 (1.4)	0	4.0	25

[a] Inversion barriers for the designated inversion center are plotted on the abscissa with the corresponding phosphorus values on the ordinate. This corresponds to the linear relation, $E_{\text{inv}}{}^{\text{P}}$ = slope × $E_{\text{inv}}{}^{\text{M}}$ + intercept, where M represents any inversion center. [b] Sensitivity relative to phosphorus is defined as the reciprocal of the slope. [c] Inversion barriers for the designated inversion center are plotted on the ordinate with the corresponding nitrogen values on the abscissa, corresponding to the linear relation, $E_{\text{inv}}{}^{\text{M}}$ = slope × $E_{\text{inv}}{}^{\text{N}}$ + intercept. [d] Slopes and intercepts are somewhat uncertain (see ref 15).

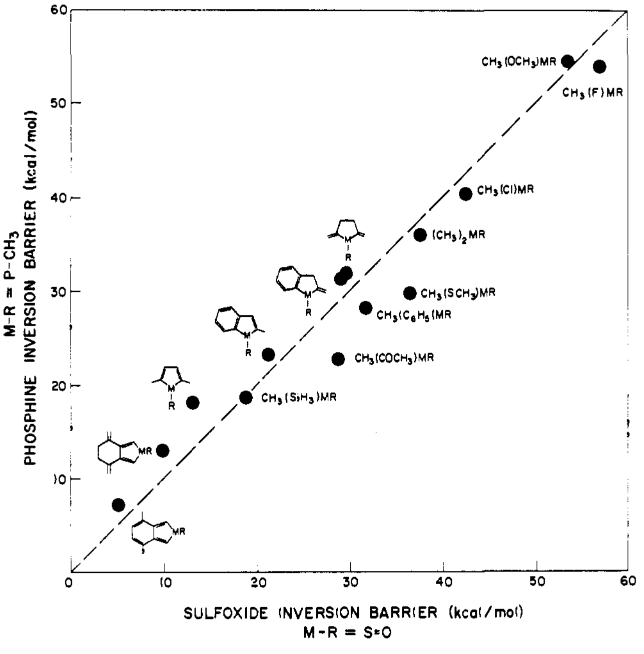

Figure 5.

rived correlations for group IVa and VIa inversion centers. Nevertheless, bearing these reservations in mind, we will proceed to discuss several consequences of these linear correlations. We believe that even though our comments are of necessity somewhat conjectural, their value may lie in helping to establish directions for future experimentation.

Sensitivity to Substituent Effects

For a pair of reaction series, the comparison of the magnitudes of barrier changes with changes in substituent, as measured by the slope of the correlation line, provides an estimate of the relative sensitivities of the two series to structural modification. We define the *sensitivity* of an inversion center M to substituent effects, relative to phosphorus, as the reciprocal of the slope of the line correlating the barriers of $MR^1R^2R^3$ (abscissa) with the barriers of the corresponding phosphines $PR^1R^2R^3$ (ordinate).[14] It then follows, for example, that nitrogen and arsenic are approximately 0.34 and 1.4 times as sensitive, respectively, to a given structural change as is phosphorus. Table I summarizes the salient correlation characteristics for each inversion center.[15]

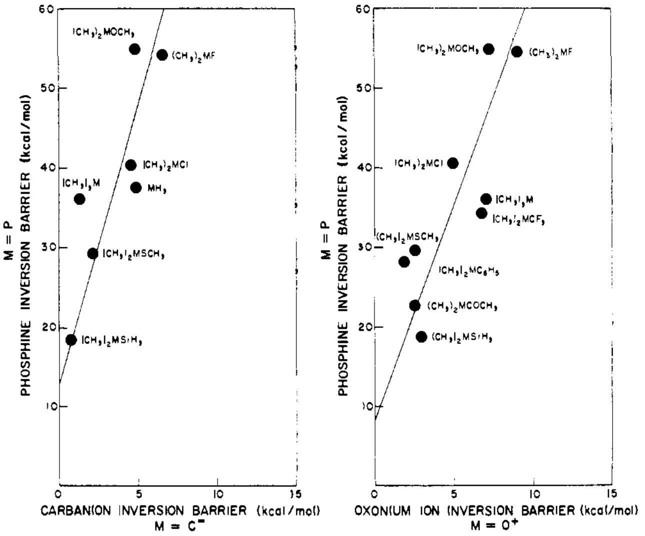

Figure 6.

Periodic trends in the sensitivities are revealed by inspection of Table I. The sensitivity to substituent effects within a group of the periodic table increases upon progressing from first- to second-row inversion centers. Within group Va there is an additional but small increase between the second- and third-row elements. Among the second-row inversion centers, the correlations suggest a marked decrease in sensitivity upon progressing from group IVa to VIa.[16]

Reversal Behavior

It may be noted that for a given set of substituents, the barrier to pyramidal inversion at arsenic always exceeds that to inversion at phosphorus, and that the barrier to inversion at phosphorus always exceeds

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(14) Because of the variety of structures for which amines are planar while the corresponding second-row systems remain pyramidal, phosphines were chosen instead of amines as a standard reaction series for the presentation of the inversion barrier correlations.

(15) Among the inversion centers examined thus far, carbon and oxygen appear to exhibit the lowest sensitivities to substituent effects: the calculated barriers, for a variety of systems bearing adjacent atoms as diverse in their effects on barrier heights as fluorine and silicon, span a range of merely *ca.* 5 kcal/mol. Given this small range, the approximate nature of the CNDO/2 calculations (*i.e.*, *ca.* ±3 kcal/mol), and the paucity of experimental data for such systems, the apparent trends in substituent effects, which deviate somewhat from those found for other inversion centers, are of dubious significance.

(16) No corresponding trend among the first-row elements is apparent.[15]

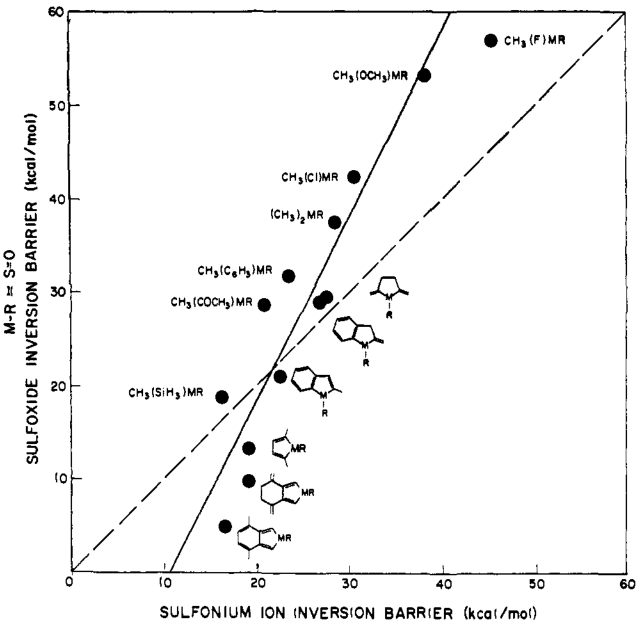

Figure 7.

that of the corresponding nitrogen system. In contrast, as revealed by examination of the linear correlations given in Figures 3 and 4, the relative ordering of inversion barriers for corresponding silyl anions and phosphines, or for sulfonium ions and phosphines, appears to depend upon the particular system in which the inversion center is incorporated. For example, the inverson barrier of trimethylphosphine, 36.0 kcal/mol, is calculated to be greater than that of trimethylsulfonium ion, 28.7 kcal/mol, but the order is reversed when comparing 1,3,6-trimethylisobenzophosphole, 7.2 kcal/mol, with 1,3,6-trimethylisobenzothiophenium ion, 16.6 kcal/mol.

The intersection of the correlation line with the identity line[12] (Figures 3 and 4) pinpoints the reversal in relative pyramidal stabilities. We designate such a point of intersection a *reversal point*, with corresponding energy E_{rev} given by

$$E_{\text{rev}} = b/(1 - m)$$

where b represents the intercept and m the slope of the correlation line.[17] The correlations of phosphines with silyl anions and with sulfonium ions appear to exhibit reversal behavior with reversal points at *ca.* 33 kcal/mol (Figure 3) and *ca.* 22 kcal/mol (Figure 4), respectively.

In a pairwise comparison of molecules belonging to two different reaction series, the ordering of barrier heights depends upon the relationship of the barrier magnitudes to E_{rev}. For barriers larger than E_{rev}, barriers belonging to members of the more sensitive series will exceed those of corresponding members of the less sensitive one. At E_{rev}, barriers in both series will be equal. Below E_{rev}, barriers within the less sensitive series will exceed those of the more sensitive one. *The potential existence of reversal points implies that any generalization assigning greater barrier magnitudes to all systems possessing one inversion center* ($MR^1R^2R^3$) *relative to corresponding systems possessing another inversion center* ($M'R^1R^2R^3$) *must be formulated with considerable caution.*[18]

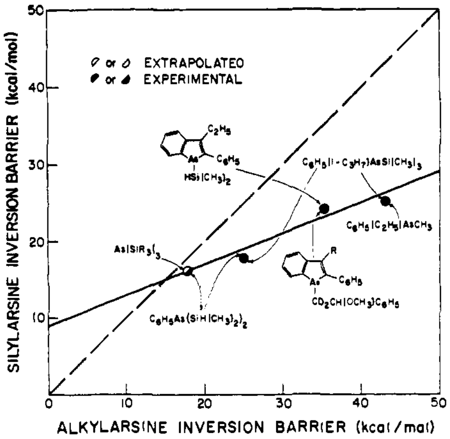

Figure 8.

The correlations which have been presented all involve the comparison of one inversion center with another. However, correlations of another type are also possible in which both of the reaction series possess the same inversion center.[19] For example, methylsulfonium ion inversion barriers may be correlated with those of sulfoxides (Figure 7). Here the reaction series are differentiated by the identity of one of the substituents at the inversion center rather than by the inversion center itself.[20]

The correlation line of Figure 7 intersects the identity line (dashed line) and reversal behavior is predicted for this correlation as well ($E_{\text{rev}} \simeq 22$ kcal/mol). For systems $R^1R^2S^+CH_3$ with inversion barriers above E_{rev}, the effect of replacing the methyl with an O^- substituent (giving R^1R^2SO) results in a barrier increase, whereas for systems with barriers below E_{rev} such a structural change is predicted to result in a barrier decrease.

Figure 8 represents a linear correlation between the experimentally determined inversion barriers of similarly substituted alkylarsines and silylarsines. Figure 9 represents a similar correlation for alkylphosphines and silylphosphines.[21] These figures are noteworthy in that they provide experimental evidence which implies the potential existence of reversal behavior within the framework of pyramidal inversion. For example, Figure 8 suggests that for an alkylarsine with an inversion barrier below E_{rev} (14 kcal/mol), replacement of the alkyl ligand with a silyl ligand will induce an *increase* in barrier magnitude. *In general, the potential*

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(17) A positive value of E_{rev}, corresponding to an experimentally accessible value, results only under the conditions $b > 0$ for $m < 1$ or $b < 0$ for $m > 1$.

(18) Such reversal phenomena have yet to be experimentally verified. We note that all cases of reversal behavior indicated by the present correlations involve at least one group IVa or VIa inversion center, and that the existence of reversal points in these series should therefore be treated with some reservation (see above).

(19) The possible existence of such correlations has been discussed previously; see J. Stackhouse, R. D. Baechler, and K. Mislow, *Tetrahedron Lett.*, 3441 (1971).

(20) As in Figure 5, these reaction series are restricted, in the sense that only two ligands are permitted to vary.

(21) Such correlations have previously been used[5e] to estimate the inversion barriers for trisilylarsine and trisilylphosphine. Although the inversion barrier of an alkyldisilylarsine or alkyldisilylphosphine is strictly required for this extrapolation, the barrier for the phenyldisilylarsine or phenyldisilylphosphine is expected to provide a reasonably satisfactory estimate for this value.

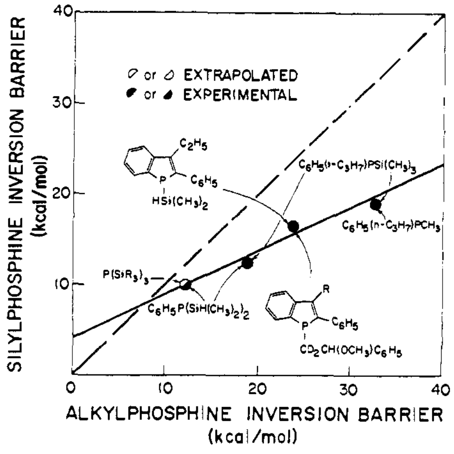


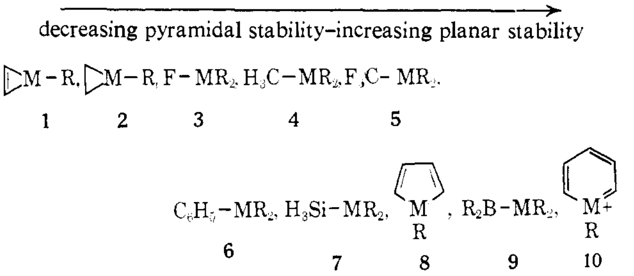
Figure 9.

existence of reversal points implies that for systems R^1R^2MX *the effect (barrier elevating or barrier depressing) of a given structural modification* ($X \rightarrow Y$) *may be dependent upon the remaining invariant ligands* (R^1 *and* R^2).

Planar Stability

If the barriers for each inversion center are plotted in relation to those of amines (as the abscissa),[14] the resulting intercepts (Table I) are seen to assume a special significance: they provide a quantitative indication of ranges of pyramidality and planarity for amines in relation to the other inversion centers. Qualitatively, three possible ranges of behavior may result upon variation of substituents: both the inversion center, M, and nitrogen may be pyramidal; M may remain pyramidal while nitrogen becomes planar in its ground state (*i.e.*, for systems with inversion barriers at M less than the intercept); or both M and nitrogen may be planar. Thus, for example, in the correlation between phosphines (ordinate) and amines (abscissa) the intercept of 18 kcal/mol implies that for phosphines with inversion barriers in excess of 18 kcal/mol, the corresponding amines are also pyramidal, with estimated barriers calculable from the slope (2.9) and intercept, whereas for phosphines with inversion barriers of less than 18 kcal/mol, including planar phosphines, the analogous amines are planar. Moreover, the positive intercept, which allows for the occurrence of corresponding structures with pyramidal phosphorus and planar nitrogen, simultaneously excludes the only remaining possibility, *i.e.*, pyramidal nitrogen and planar phosphorus.

Just as the term *pyramidal stability* is defined as the resistance (in the form of an inversion barrier) of a pyramidal species to deformation toward planarity, so the term *planar stability* may be applied to the resistance (in the form of a negative inversion barrier) of a planar species to deformation away from planarity.[22] It is suggested that structural features which in pyramidal systems tend to lower the energy of the pyramidal relative to the planar form might also be expected to remain operative in planar systems. Accordingly, we propose that *the ordering of substituents according to their effectiveness in decreasing pyramidal stability may also be used to predict the effectiveness of these selfsame substituents toward increasing planar stability*. By way of illustration, the sequence, based on phosphine inversion barriers,[23,24] which is shown below, should be applicable to all inversion centers.



In the case of amines, this sequence could be used to predict a progressive increase in planar stability for systems **8–10**, all of which are calculated to be planar when M = nitrogen. Similarly, since the pyramidal stability at phosphorus has been shown[5e] to decrease upon progression from monosilyl to disilyl substitution and has been predicted[5e] to decrease even further upon incorporation of a third silyl ligand, an analogous sequence should be applicable to the corresponding amines. The monosilyl system is pyramidal[25] with a very small inversion barrier,[26] and the disilyl[27] and trisilyl[28] compounds are both planar; according to the above postulate, trisilylamine is expected to possess the greater planar stability.

Summary

The salient features embodied in the linear correlations discussed above may be conveniently summarized in the form of a nomograph (Figure 10).[29] The intersection of the correlation lines with an arbitrarily located vertical line (*e.g.*, the dashed line in Figure 10), parallel to the ordinate axis, provides barriers for identically substituted systems incorporating the various inversion centers. Consequently, a value for the inversion barrier of any one system incorporating a particular inversion center may be used to estimate barriers for all other centers bearing identical substituents. For example, the experimentally determined barrier for a monosilylphosphine (18.9 kcal/mol)[5a] may be used to estimate barriers of 27.0 kcal/mol for a monosilylarsine (experimental value,[5e] 25.1 kcal/mol) and

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[22] In our discussion of planar stability, we refrain from defining this concept in a quantitative fashion, since we believe that its chief usefulness resides in its qualitative applications.

[23] Values are reported in ref 9a, except for **1** (91 kcal/mol, by CNDO/2). These systems were selected because they span extremes in barrier magnitude between the pyramidal (**1**) and planar (**10**) termini, and because they exemplify the major structural effects likely to influence pyramidal and planar stabilities, *i.e.*, incorporation of the lone pair on the inversion center in an antiaromatic system (**1**), ring strain (**2**), ligand electronegativity (**3**, **4**, **7**), delocalization into adjacent antibonding orbitals (**5**), delocalization into an adjacent π system (**6**), delocalization into vacant p orbitals (**9**), and incorporation of the lone pair in an aromatic system (**8**, **10**).

[24] The depicted trend is strictly applicable only for systems in which the ligand R = alkyl, and a different sequence may well result for an invariant ligand of a different type, a possibility implied by the potential existence of reversal behavior.

[25] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, 6, 231 (1970).

[26] J.-M. Lehn and B. Munsch, *Chem. Commun.*, 994 (1970).

[27] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, 4, 215 (1969).

[28] K. Hedberg, *J. Amer. Chem. Soc.*, 77, 6491 (1955); B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 66, 2740 (1971).

[29] Correlations involving carbanions and oxonium ions have been omitted from Figure 10.[15]

0.3 kcal/mol for a monosilylamine (calculated value,[26] 0.7 kcal/mol). In general, the quantitative reliability of such estimates is limited by the approximate nature of the inversion barrier correlations, which reveal frequent deviations from linearity of several kilocalories per mole.

Reversal points are indicated in Figure 10 by the intersection of any two correlation lines. In addition to the previously identified reversal points, reversal behavior is revealed in correlations between arsines and sulfonium ions ($E_{\text{rev}} = 17.1$ kcal/mol) and between silyl anions and sulfonium ions ($E_{\text{rev}} = 24.9$ kcal/mol).[18,30]

Figure 10 also indicates ranges of planarity and pyramidality. For example, in the case of amines, the figure may be divided by the dashed line into the two regions labeled "pyramidal nitrogen" and "planar nitrogen." That portion of each correlation line which extends into the latter region corresponds to barriers for systems whose nitrogen analogs are planar.[31] More generally, a similar division of the figure into planar and pyramidal regions may be envisioned for each inversion center, the corresponding dashed line originating from the point at which the correlation line for that particular center intersects the abscissa ($E_{\text{inv}} = 0$).

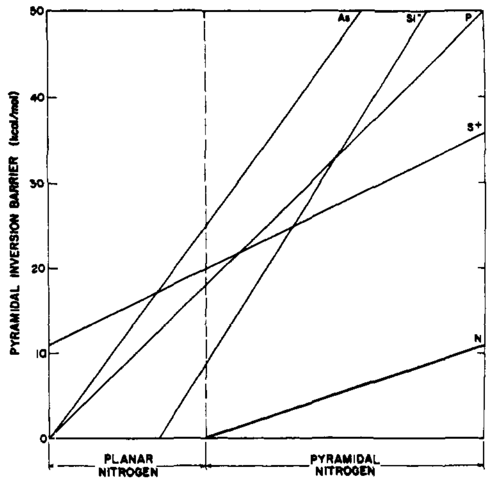

Figure 10.

The order in which the correlation lines intersect the abscissa is indicative of the order in which the respective inversion centers achieve planarity upon progression through a given series of substituents. We designate this order as the order of increasing *threshold pyramidal stability* (N < Si^- < P ~ As < S^+) of the inversion centers. In the absence of reversal points, this sequence would follow the order of relative sensitivities. However, assuming the actuality of the indicated reversal points,[18] sulfonium ions are predicted to possess the greatest threshold pyramidal stability although they exhibit the lowest sensitivity of the second- and third-row inversion centers.

[30] The phosphorus and arsenic correlation lines represent a special case in which a reversal point occurs at the abscissa ($E_{\text{inv}} = 0$).

[31] The energy values associated with the intersections of the correlation lines with the dashed line (Figure 10) correspond to the previously discussed intercepts (Table I) in correlations of the various inversion centers (ordinate) relative to amines (abscissa).

Electron Spin Resonance Study of the Conformational Stabilization of Allyl Radicals by Silicon, Germanium, Tin, and Sulfur Substituents. Barriers to Hindered Internal Rotation by Line-Shape Analysis

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Abstract: The esr spectra of a series of allyl radicals with β substituents consisting of heteroatoms such as Si, Ge, Sn, or S show a temperature-dependent variation of the hyperfine splitting constants and a pronounced selective line broadening due to hindered internal rotation about the C_3–C_4 bond. The rates of hindered internal rotation in these radicals are derived by a comparison of the experimental line shapes with those calculated using the density matrix equation of motion. These radicals exhibit a barrier to hindered internal rotation which increases with atomic number. The source of the stabilization of the radicals by (a) hyperconjugation between the π system and the carbon–metal bond and (b) p–d homoconjugation between the π system and the metal d orbitals is analyzed qualitatively, and it is concluded that both mechanisms are important.

The enhanced reactivity of allylsilanes to free-radical addition has been attributed to the stabilization of the intermediate organometallic radicals, and the electronic interactions involved have been discussed in terms of hyperconjugation (π–σ conjugation).[2] In

[1] (a) Contribution No. 2093, Chemistry Department, Indiana University. (b) Contribution No. 1936, Central Research Department, E. I. du Pont de Nemours & Co.

[2] (a) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, 34, 1764 (1969); (b) A. W. P. Jarvie and R. J. Rowley, *J. Chem. Soc. B*, 2439 (1971); (c) A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

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