

Semiempirical Calculation of Barriers to Pyramidal Inversion. Extension to the Third Row of the Periodic Table¹

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Abstract: Semiempirical calculations of barriers to pyramidal inversion at a third-row center, arsenic, are reported. The results are in satisfactory agreement with reported experimental values. Qualitative trends in the effect of substituents on the barrier magnitude are found to parallel those reported for inversion at nitrogen and phosphorus, as expected on the basis of previously established linear correlations of barriers to pyramidal inversion. As in the case of phospholes, the extraordinarily low barrier to pyramidal inversion in arsoles, as compared to simple arsines, is attributed to the cyclic nature of the 6π electron system, unambiguously pointing to extensive delocalization in the planar transition state to inversion.

Previous reports have described the application of a modified Pople CNDO/2 treatment to the calculation of barriers to pyramidal inversion in systems containing elements from the first and second rows of the periodic table.³ Using data derived by this method in conjunction with experimentally determined barriers to pyramidal inversion, the existence of linear free energy correlations of barriers to pyramidal inversion was deduced.⁴ The recent experimental determination of barriers to pyramidal inversion for a third-row inversion center, arsenic,⁵ provided the data necessary to test the feasibility of extending our earlier calculations to include third-row elements and to round out our studies in this area.⁶

Method

The starting point for the present calculations was the program CNINDO,⁷ as previously modified to permit calculations of barriers to pyramidal inversion.⁸ Additional modifications to the program required to permit its extension to the third row were minimal. As in previous work,³ d orbitals were omitted from the basis set. The principal modifications include (a) subroutine INTGRL, assignment of orbital exponents (MU)⁹ and core charges (CZ) to the elements of the third row, (b) subroutine COEFFT, expansion of Y and Z matrix elements to accommodate all quantum numbers up to $n = 4$, $l = 2$, $m = 2$,¹² and (c) subroutines HUCKOP and

HUCKCL, assignment of initial parameter values to ENEG and BETA0 arrays for nontransition elements of the third row (see below).

An initial, crude set of parameters (orbital electronegativities, χ_s and χ_p , and a bonding parameter, β° , for each element), required before any calculations could be undertaken, was obtained by a simple extrapolation based on the original (unmodified) parameters for the corresponding elements of the first and second rows.¹³ In the case of arsenic, optimization of the initial parameters followed the method used in our earlier studies.³ The orbital electronegativities, treated as a single dependent variable,¹⁴ together with the bonding parameter, represent two unknowns to be empirically evaluated. This was accomplished by adjustment of these parameters to yield calculated barriers of 25.0 and 17.7 kcal/mol for $C_6H_5As(SiH_3)CH_3$ and $C_6H_5As(SiH_3)_2$, respectively, to match corresponding experimental values.¹⁵ The parameters thus obtained are $\chi_s^{As} = 12.98$, $\chi_p^{As} = 4.81$, and $\beta^\circ_{As} = -17.80$.

A similar optimization of the empirical parameters for the elements germanium, selenium, and bromine was thwarted by the lack of reliable inversion barrier data for systems in which these elements form the inverting center. Trial calculations demonstrated that it is not feasible to base the parametrization of these elements on systems in which the element to be parametrized is a substituent rather than an inversion center, since the calculated barrier proves to be relatively insensitive to the choice of parameters for substituents but quite sensitive to the choice of parameters for the inverting center.

Results and Discussion

Using the optimized parameters, calculations were performed⁸ for a number of systems which undergo

(12) The Y and Z matrix elements are defined on pp 197 and 198, respectively, in Pople and Beveridge.¹¹

(13) For example

$$\chi_s^{As} = \chi_s^N + (\chi_s^P - \chi_s^N)(r_{As} - r_N)/(r_P - r_N) = 12.11$$

where r_i represents the covalent radius of atom i . Similar expressions were used to evaluate χ_p and β° .

(14) It was assumed that χ_s^{As} and χ_p^{As} may be varied by the same proportional amount in opposite directions.^{3a}

(15) Barriers to pyramidal inversion at arsenic of 25.1 and 17.7 kcal/mol are reported for isopropylphenyltrimethylsilylarsine and bis(dimethylsilyl)phenylarsine, respectively.^{5b}

(1) This work was supported by the National Science Foundation (GP-30257) and by the National Research Council of Canada.

(2) (a) Princeton University; (b) University of Calgary.

(3) (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).

(4) R. D. Baechler, J. D. Andose, J. Stackhouse, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 8060 (1972).

(5) (a) G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 291 (1972); (b) R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **94**, 2859 (1972); (c) R. H. Bowman and K. Mislow, *ibid.*, **94**, 2861 (1972).

(6) For a recent review, see K. Mislow, *Trans. N. Y. Acad. Sci.*, **35**, 227 (1973).

(7) P. A. Dobosh, program 141, Quantum Chemistry Program Exchange, Bloomington, Ind.

(8) For additional details on the method of calculation, see ref 3a.

(9) Orbital exponents were assigned on the basis of Slater's rules.¹⁰ Values for the effective nuclear charge were taken from the tabulation of Pople and Beveridge,¹¹ Table 1.5, p 29.

(10) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

pyramidal inversion at arsenic. Where comparisons are possible, the results agree satisfactorily with reported experimental values for systems of wide structural diversity (Table I). The ability of the present

Table I. Barriers to Pyramidal Inversion at Arsenic

Entry no.	Compound	Barrier (kcal/mol)		Ref
		Present work	Reported ^a	
1	Arsine	54.5		
2	Trimethylarsine	50.5		
3	Dimethylphenylarsine	43.8 ^b	42.4	j
4	Acetyldimethylarsine	37.4 ^b		
5	Silyldimethylarsine	30.0		
6	Disilyldimethylarsine	21.9		
7	Methylphenylsilylarsine	25.0 ^{b,c}	25.1	g
8	Disilylphenylarsine	17.7 ^{b,c}	17.7	g
9	Tetramethylborinoarsine	11.4 ^b		
10	Tetramethylaminoarsine	58.3 ^d		
11	Tetramethylphosphinoarsine	39.0 ^d		
12	Tetramethyldiarsine	34.3 ^d		
13	1,2-Dimethyl-1,2-diphenyldiarsine	32.0 ^{b,d}	27.0	h
14	Methyl dimethylarsinite	68.2 ^e		
15	Methyl dimethylthioarsinite	45.5 ^e		
16	Dimethylfluoroarsine	73.4		
17	Dimethylchloroarsine	56.7		
18	1-Methyl-2,5-dimethylenearsolane	49.5		
19	1-Methyl-2-methylenearsindoline	48.9		
20	Arsole	33.9		
21	1-Methylarsole	30.3		
22	1,2,5-Trimethylarsole	33.5		
23	1-Silylarsole	16.8		
24	1-Methylarsindole	38.2	35.2, 36.7	i
25	1-Silylarsindole	21.4	24.3	j
26	1-Methylisoarsindole	18.4		

^a All values refer to ΔG^\ddagger , except for **13**, whose barrier is reported as E_a . ^b A conformation was chosen which permitted maximum overlap of the lone electron pair of the inverting center with an adjacent $p\pi$ -orbital. ^c The parameters χ_a^{As} , χ_p^{As} , and β^{As} were adjusted to yield this calculated value. ^d A conformation was chosen in which the lone electron pair of the substituent was held orthogonal to the lone electron pair of the inverting center. ^e A conformation was chosen in which the lone electron pair on arsenic in **14** ($(CH_3)_2AsOCH_3$) and **15** ($(CH_3)_2AsSCH_3$) is eclipsed with the O-C and S-C bond, respectively. ^f Value reported for ethylmethylphenylarsine; see ref 5a. ^g See ref 15. ^h J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, **90**, 6401 (1968). See also ref 5b. ⁱ Values reported for 1-alkyl-2-phenyl-3-ethylarsindoles; see ref 5c and 21. ^j Value reported for 1-dimethylsilyl-2-phenyl-3-ethylarsindole; see ref 5c.

method to reproduce these values thus generates confidence in barriers calculated for systems for which matching experimental data are still lacking.

As expected on the basis of established linear correlations of barriers to pyramidal inversion,⁴ the trends in the magnitudes of arsine inversion barriers closely parallel those reported for the corresponding nitrogen and phosphorus systems. In Figure 1, the experimentally based correlation between barriers to pyramidal inversion at arsenic and phosphorus⁴ is given by the solid line (data points indicated by open circles). Included in Figure 1 are calculated inversion barriers (solid circles) for identically substituted arsines (Table I) and phosphines.^{3a} By inspection, the solid circles approximately describe a straight line which is nearly parallel to and displaced by only *ca.* 3–4 kcal/mol from the experimental correlation line. This close agreement between the calculated and the experimental correlation provides an additional and critical test of our

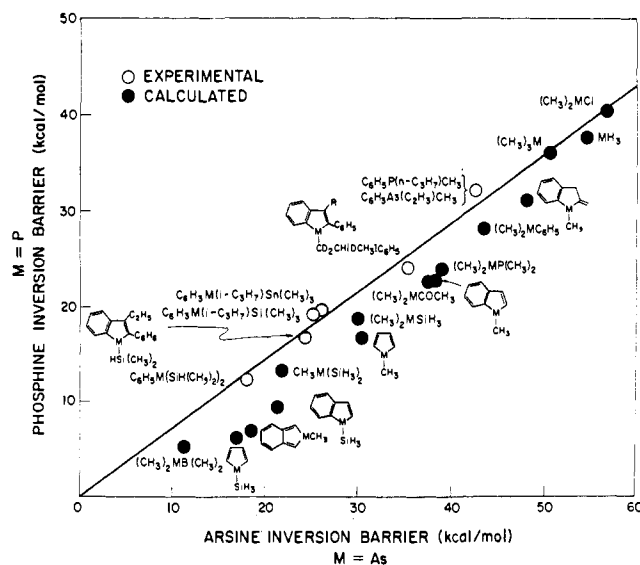
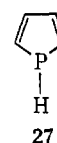
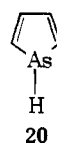


Figure 1.

approach. We conclude that the values calculated by use of the present semiempirical scheme are reliable to within a few kilocalories per mole over a large range of barrier heights (*ca.* 10–60 kcal/mol).

Of particular interest is an assessment of the inversion barrier for the parent compound, arsine. Previous estimates by Weston¹⁶ (35.0 kcal/mol) and by Miller and coworkers¹⁷ (34 and 30 kcal/mol), based on valence force-field calculations utilizing the Costain-Sutherland scheme, are considerably below our estimate of 54.5 kcal/mol (**1**, Table I). Similarly, the earlier calculations^{16,17} give a value of 29 kcal/mol for the inversion barrier of trimethylarsine, whereas we find a value of 50.5 kcal/mol (**2**, Table I). In view of the excellent agreement between our calculated value of 43.8 kcal/mol for dimethylphenylarsine (**3**, Table I) and the found value of 42.4 kcal/mol for ethylmethylphenylarsine,^{5a} we believe that there are grounds for accepting the higher value in each case. This conclusion is reinforced by information which may be deduced from the free energy correlation of Figure 1. Using a value of 36.7 kcal/mol for the inversion barrier of phosphine,¹⁸ it follows from the straight line correlation that the barrier for arsine is *ca.* 50 kcal/mol. The difference between the inversion barriers of arsine and phosphine is thus *ca.* 13–14 kcal/mol.

In that connection, and in context with the section immediately following, we note that our calculated values for the inversion barrier of arsole (**20**) and phosphole (**27**) (33.9 (Table I) and 19.1 kcal/mol,¹⁹ respec-



(16) R. E. Weston, Jr., *J. Amer. Chem. Soc.*, **76**, 2645 (1954).

(17) G. W. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967).

(18) Calculated by an extended *ab initio* LCAO-MO-SCF approach (J. M. Lehn and B. Munsch, *Mol. Phys.*, **23**, 91 (1972)). This result is in good agreement with the value of 35.6 kcal/mol found for a trialkylphosphine (R. D. Baechler and K. Mistow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970)).

(19) Calculated using the parameters and methods of ref 3a.

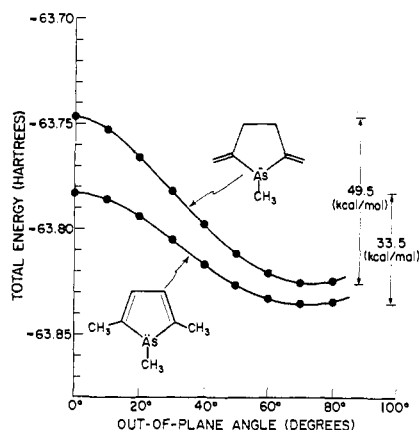


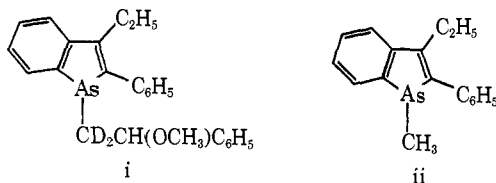
Figure 2.

tively) lead to a barrier *difference* of 14.8 kcal/mol. This result is substantially at variance with a recent report by Schweig and coworkers,²⁰ who calculated a corresponding energy difference of only 3.4 kcal/mol, using an extended CNDO/2 approach. These authors cited the "experimental" difference in barrier heights for arsine and phosphine as 2–7 kcal/mol, based on Weston's calculations;¹⁶ however, as was shown above, this difference is also underestimated. We conclude that the calculations of Schweig and coworkers²⁰ do not yield realistic estimates for inversion barrier differences between arsines and phosphines; by implication, values of inversion barriers calculated by their method are at least questionable.

Arsoles, Phospholes, and Aromaticity. The 30–34-kcal/mol barriers to pyramidal inversion calculated for arsole and some derivatives (20–22 in Table I) are lower by *ca.* 10–15 kcal/mol than those of simple arsines (*ca.* 45–55 kcal/mol for 1–3 in Table I). These results are in accord with expectations grounded in prior experimental work,²¹ which had led us to conclude that the electron pair on arsenic in arsindeoles, and in arsoles generally, is involved in cyclic (4p–2p) π delocalization (see below). Previously, similar reasoning, based on the observation that phosphorus inversion barriers in phospholes and phosphindeoles are markedly lower than those of standard cyclic and acyclic phosphines, had led us to a similar conclusion, *i.e.*, that the electron pair on phosphorus in phospholes and phosphindeoles is involved in cyclic (3p–2p) π delocalization.²³

(20) H. L. Hase, A. Schweig, H. Hahn, and J. Radloff, *Tetrahedron*, **29**, 469 (1973). See also H. L. Hase and A. Schweig, *Theor. Chim. Acta*, **31**, 215 (1973). Absolute inversion barrier magnitudes were not given.

(21) The barrier for arsindeole (i), 35.2 kcal/mol, was found²⁰ by following the rate of equilibration (at 151.1°) of a fraction enriched in one of the diastereomers. This result was confirmed²² by the observation that optically active arsindeole (ii) racemizes at 159.7° with $\Delta G^\ddagger = 36.7$ kcal/mol.



(22) A.-B. Hörnfeldt, unpublished results.

(23) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970); **93**, 6205 (1971).

Evidence that the low inversion barriers in arsoles are indeed uniquely associated with the *cyclic* nature of the 6 π electron system is found in a comparison (Table I) of the calculated inversion barrier, 33.5 kcal/mol, for 1,2,5-trimethylarsole (22), in which *cyclic* conjugation is possible, with that of the tautomeric 1-methyl-2,5-dimethylenearsolane (18, 49.5 kcal/mol), in which only *linear* conjugation is possible. The barrier lowering effect, 16.0 kcal/mol, is of comparable magnitude to the 13.3 kcal/mol effect found in a similar comparison of 1,2,5-trimethylphosphole and 1-methyl-2,5-dimethylene-phospholane.^{3a} Figure 2 shows the calculated energy of the two systems, 18 and 22, as a function of the out-of-plane angle²⁴ of the As–CH₃ bond with respect to the As(1)–C(2)–C(5) plane; a similar figure has previously been presented for the corresponding phosphorus systems.^{25,26}

As we previously remarked,⁶ the lowered inversion barriers found for arsoles and phospholes are a manifestation of Hückel aromaticity. These molecules are fully conjugated heterocycles possessing $4n + 2$ π -electrons capable of cyclic delocalization. However, it must be emphasized that it is in the nature of the determination of barrier heights that only the *difference* in ground and transition state energies is experimentally accessible. Evidently, the cyclic delocalization of the arsole and phosphole systems is more effective in the transition state (planar) than in the ground state (pyramidal), and the barrier lowering effect, and hence aromaticity, must thus in some manner be partitioned between these two states. A more quantitative statement is not warranted. Indeed, in the absence of reliable *ab initio* calculations, we cannot rule out the possibility that there is very little cyclic delocalization in the ground state,²⁹ so that, in essence, the full weight of delocalization, and hence of stabilization, resides in the *planar* conformation. In that respect, the criterion of inversion barrier lowering, which we have invoked as a gauge of aromaticity,⁶ differs crucially from those measurements which are concerned exclusively with the *pyramidal* conformation, *i.e.*, corresponding to the vibrational ground state.

In dwelling on this distinction, we have in mind the

(24) Throughout this paper, the "out-of-plane angle" is defined as zero for the coplanar arrangement (transition state of inversion).

(25) See Figure 4 in ref 6.

(26) These calculations also provide information on the ground state pyramidalities of arsoles and phospholes. In 22, the equilibrium out-of-plane angle²⁴ is calculated to be 74°, a value which is yet to be experimentally tested. In the analogous 1,2,5-trimethylphosphole, the value for this angle was calculated^{25,27} to be 69°, in excellent agreement with the value of 67° calculated from X-ray data reported for 1-benzylphosphole.²⁸ It is noteworthy that Schweig and coworkers²⁰ reported finding out-of-plane angles²⁴ of 85° for arsole and 88° for phosphole. However, in view of the questionable nature of their calculations (see above), it is doubtful that any significance should be attached to these values. Indeed, our calculations for arsole and for phosphole yield out-of-plane angles of 76 and 69°, respectively, values not significantly different from our calculated values for the corresponding methylated derivatives.

(27) R. Tang, Ph.D. Dissertation, Princeton University, Princeton, N. J., 1971.

(28) (a) P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Amer. Chem. Soc.*, **92**, 5779 (1970); (b) P. Coggon and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1888 (1973).

(29) We can rule out the possibility that there is *no* cyclic delocalization, since the 4p orbitals of arsenic are of the correct symmetry to overlap with the 2p orbitals of the diene system, and the value of the π overlap integral, $\int \chi_{4p}^{As} \cdot \chi_{2p}^C d\tau = 0.19$, is sufficiently large to allow these orbitals to interact (the carbon-carbon π overlap integral is 0.29).

continuing discussion³⁰ and controversy regarding the question of whether phosphole—and, by implication, arsole—may properly be regarded as an aromatic system akin to pyrrole and thiophene. Quin and coworkers,³¹ largely on the basis of nmr evidence, have felt justified in characterizing phosphole as heteroaromatic. The bond length parameters derived from an X-ray study of 1-benzylphosphole²⁸ are also consistent with cyclic π -electron delocalization, although an X-ray analysis of 1,2,5-triphenylphosphole³² seems to indicate "little if any electron delocalization." However, as has been noted elsewhere,^{28b} the attachment of three phenyl groups to the phosphole skeleton is likely to perturb the π -electron system of the latter quite significantly.

The single notable exception to the conclusions of the Duke group^{28,31} was recently voiced by Schweig, Märkl, Mathey, and coworkers,³³ who studied the photoelectron spectra of 1-phenyl- and 2,5-dimethyl-1-phenylphosphole, as well as of 2,5-dimethyl-1-phenylarsole. As a result of their studies, they concluded that "the lone pairs in the phospholes, and very probably also in the arsoles, take no part in a cyclic five-membered ring conjugation." According to these authors,³³ "phospholes and arsoles in their ground-state conformations consist of localized diene systems and lone pairs of heteroatom electrons. In this sense phospholes and arsoles are not aromatic." In thus furnishing what constitutes, according to these authors,³³ "direct proof of the non-aromaticity of phospholes and arsoles," a formidable challenge has been raised against the earlier conclusions based on nmr³¹ and X-ray²⁸ evidence, even if one chooses to disregard the less compelling non-spectroscopic evidence.³⁰

Returning to our major theme: What conclusions concerning this point may be drawn from pyramidal inver-

(30) E. H. Braye and W. Hübel, *Chem. Ind. (London)*, 1250 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *J. Amer. Chem. Soc.*, **82**, 5099 (1960); E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961); D. A. Brown, *J. Chem. Soc.*, 929 (1962); A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *ibid.*, 2932 (1962); G. Märkl and R. Potthast, *Angew. Chem.*, **79**, 58 (1967); G. Märkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968); A. N. Hughes and S. Uaboonkul, *Tetrahedron*, **24**, 3437 (1968); K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 2560 (1970); A. N. Hughes and C. Sriyanavit, *J. Heterocycl. Chem.*, **7**, 1 (1970); D. Kilcast and C. Thomson, *Tetrahedron*, **27**, 5705 (1971); see also W. B. Farnham and K. Mislou, *J. Chem. Soc., Chem. Commun.*, 469 (1972).

(31) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969); L. D. Quin, S. G. Borieske, and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973); L. D. Quin, S. G. Borieske, and R. C. Stocks, *Org. Magn. Resonance*, **5**, 161 (1973).

(32) W. P. Ozbirn, R. A. Jacobson, and J. C. Clardy, *Chem. Commun.*, 1062 (1971).

(33) W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann, and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **12**, 145 (1973).

sion barrier measurements? Although, as we noted above, the possibility cannot be excluded that there is very little cyclic delocalization in the pyramidal ground state,²⁹ we do in fact consider this possibility extremely remote. The argument of Dewar and Rona,³⁴ that the lone electron pair on pyramidal nitrogen can conjugate effectively with an adjacent carbon 2p orbital (the resonance energy being about four-fifths that for the planar system), can be readily extended to phosphorus and arsenic analogs, with suitable modification of the quantitative aspects. Indeed, the results of nonempirical INDO calculations³⁵ on the planar and nonplanar conformations of arsole indicate a substantial amount of involvement of arsenic orbitals in two of the three highest occupied molecular orbitals, involvement in the third being excluded by the nodal structure of that molecular orbital. We thus find it inconceivable that the cyclic delocalization should be *exclusively* restricted to the planar conformation, and we maintain our originally stated position:⁶ The energy barrier lowering observed for phospholes²³ and arsoles^{5c} (present work) indicates $(3p-2p)\pi$ and $(4p-2p)\pi$ delocalization, respectively, which is at a maximum in the planar transition state to inversion. In brief, *our work unambiguously demonstrates heteroaromaticity in the planar conformation of phospholes and arsoles* and, on the assumption of ancillary arguments,³⁴ lends support to the contention^{28,31} that the pyramidal ground state of these systems partakes of cyclic delocalization as well.

What is here being emphasized is that the only point at issue is the *extent* of cyclic delocalization. Our work conclusively points to extensive delocalization in the planar conformation and, by implication, to less, but some, delocalization in the pyramidal state. The conflict between conclusions derived from direct evidence on delocalization in the ground state^{28,31,33} must therefore be regarded as still unsettled and, in the absence of universally agreed upon *quantitative* measures of aromaticity,³⁶ may remain unsettled in the future.

(34) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

(35) A. Rauk, unpublished results.

(36) Therein lies the nub of the problem: the term "aromatic" has no firmly defined meaning.³⁷ In an eloquent commentary on this point, Heilbronner has remarked³⁸ that "aromaticity is not an observable property, *i.e.*, it is not a quantity that can be measured."

(37) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972); see also J.-F. Labarre and F. Crasnier, *Fortschr. Chem. Forsch.*, **24**, 33 (1971).

(38) E. D. Bergmann and B. Pullman, Ed., "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," Israel Academy of Sciences, Jerusalem, 1971 (Jerusalem Symposium on Quantum Chemistry and Biochemistry, Vol. III), p 74 ff.