

OPTIMIZED GEOMETRIES AND PYRAMIDAL INVERSION IN $\sigma^3\lambda^3$ -PHOSPHOLE: A BRIEF THEORETICAL TREATMENT

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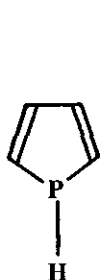
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Abstract - Optimized geometries and total energies for the pyramidal and planar conformations of $\sigma^3\lambda^3$ -phosphole have been calculated by *ab initio* methods using the 6-311G* basis set and the GAUSSIAN 86 series of programs. The inversion barrier is calculated to be 24.4 kcal/mol.

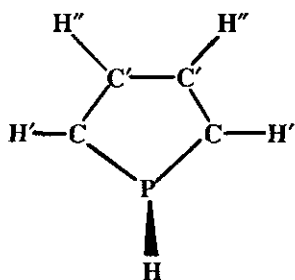
INTRODUCTION

$\sigma^3\lambda^3$ -Phosphole (1) and its derivatives are, at least superficially, similar to the common heterocyclopentadienes furan, pyrrole and thiophene but, while the latter have been known and studied for much of this century, the first monocyclic phosphole derivatives did not appear in the literature until 1959.¹ The parent compound was not reported until 1983² and was not fully characterized in pure form until 1987.³ Over the past three decades, however, the phosphole system has been studied extensively in terms of the synthetic challenge such molecules present, the unusual reactions into which they sometimes enter, and the electronic structure of the five-membered ring. Several in-depth reviews on these topics have appeared⁴ and it is not necessary here to comment further on the general chemistry of such systems. However, the driving force for many of the early studies in phosphole chemistry was the question of the electronic structure of the system. Thus, the non-bonding electron pair of the phosphorus atom apparently has the potential for delocalization into the ring (as occurs, for example, in thiophene and the cyclopentadienyl anion) to form a Hückel-type $6\pi e$ system although in order to do so, the inversion barrier

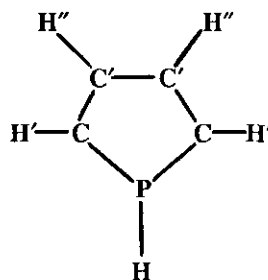
at the P atom must be overcome to give a planar system. As a result, numerous experimental and theoretical investigations of this aspect of phosphole chemistry have been published and summaries of the often mutually contradictory conclusions have appeared in the above-mentioned reviews.



1



2



3

In particular, ten theoretical treatments of phosphole derivatives have been published⁵⁻¹⁴ and several of these were prompted by experimental (nmr coalescence) measurements¹⁵ of an unusually low ($\Delta G_{25}^{\ddagger} \approx$ ca 16 kcal/mol compared with ca. 36-39 kcal/mol predicted¹⁵ for saturated derivatives of the system) inversion barrier in one heavily-substituted monocyclic phosphole. While these various theoretical studies produced conclusions which were frequently in conflict with one another and produced no conclusive evidence regarding the electronic structure of the system, it is not our intention to reopen the debate regarding the possible aromatic character of $\sigma^3\lambda^3$ -phospholes. Indeed, the present position is⁴ that phospholes are pyramidal¹⁶ species which are not significantly aromatic in the conventional sense, which react in the pyramidal conformation, and which normally react at the heteroatom unlike the more common heterocyclopentadienes pyrrole or thiophene where interaction of the non-bonding pair with the diene portion of the ring increases electron density at the ring carbon atoms. However, we wish to draw attention to the fact that the most recent theoretical treatment¹⁴ was published in 1976 and both theoretical approaches and computational techniques have improved dramatically in the intervening fifteen years. In this context, it is worth noting that Gilheany¹⁷ has recently carried out a highly detailed critical analysis of ab initio calculations on a variety of simple phosphines and two of the more important conclusions of this survey are that such calculations have only become useful since about 1980 and that the 3-21G and 3-21G* basis

sets are at the lower end of the adequacy scale for calculations on even very simple phosphines. Thus, a modern theoretical treatment of the much more complex cyclic phosphine (1) seems to be in order and we report, therefore, our results concerning optimized geometries and total energies for planar and pyramidal (1) together with the calculated value for the inversion barrier about the phosphorus atom. Also reported are the spatially integrated populations for all atoms in the pyramidal (2) and planar (3) conformations of $\sigma^3\lambda^3$ -phosphole which were found by utilizing Bader's theory of molecular structure.¹⁸

METHOD

The geometric parameters for the pyramidal (2) and planar (3) conformations of $\sigma^3\lambda^3$ -phosphole have been optimized at the 6-311G* *ab initio* level¹⁹ using the GAUSSIAN 86 series of programs.²⁰ The McLean and Chandler (6s5p) contraction for neutral phosphorus²¹ of the Huzinaga (12s9p) basis set²² was utilized rather than the programs default contraction for the anion since the phosphorus atom would be expected to be neutral or positively charged in such molecules. Polarization d-type function exponents of 0.626 for carbon (default) and 0.70 for phosphorus were used. The AIMPAC series of programs²³ was used to calculate the integrated charge on each atom.

RESULTS AND DISCUSSION

The optimized geometric parameters for the pyramidal (2) and planar (3) conformations of $\sigma^3\lambda^3$ -phosphole are listed in Table 1 together with the respective total energies. Particularly noteworthy observations are that the P-C bond length decreases by 0.101 Å and the CPC bond angle increases by 8.7° upon proceeding from the pyramidal to the planar conformation. Also, the C-C' bond increases in length by 0.040 Å while the C'-C' bond decreases by 0.050 Å.

From the respective total energies listed for the two conformations in Table 1, the energy difference between the pyramidal and the planar conformation (the inversion barrier) is 0.038959 hartrees which is 24.4 kcal/mol.

While comparisons between the results summarized above and the various earlier calculations mentioned in the introduction would be pointless in view of the basis set inadequacies of those calculations, several useful

Table 1

Optimized Geometric Parameters and Total Energies for both
the Pyramidal (2) and Planar (3) Conformations of PC_4H_5 .^a

	Pyramidal	Planar
r(P-C)	1.817	1.716
r(C-C')	1.331	1.371
r(C'-C'')	1.473	1.423
r(P-H)	1.404	1.373
r(C-H')	1.074	1.070
r(C'-H'')	1.076	1.074
∠(HPC)	99.3	130.9
∠(PCC')	111.2	105.6
∠(PCH')	124.1	127.6
∠(CC'H'')	124.2	122.3
∠(CPC)	89.5	98.2
Energies	-495.105441	-495.066482

^aBond lengths in angstroms and angles in degrees. Energies in hartrees

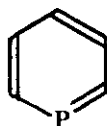
observations can be made. Before doing so, however, a brief discussion of the reliability of the results presented in Table 1 is in order.

In a very recent paper, Bachrach²⁴ reported optimized geometries (also calculated using GAUSSIAN 86) for fifteen compounds containing single, double, and triple P-C bonds. The adequacy of the basis set chosen (3-21G, 3-21G*, or 6-31G*) was determined (in part) by comparing the calculated with the experimentally measured geometries and it was found that the 6-31G* basis set is the smallest which will predict geometries in such molecules adequately. With this basis set, excellent agreement with experimentally determined geometries for compounds containing P-C single bonds (like 2) was obtained. However, it was

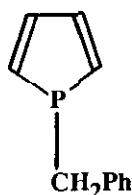
noted that as substitution upon the phosphorus atom increases, predicted bond lengths and bond angles tend to be slightly too large (by ca. 0.01 Å and 1°, respectively). Good agreement between calculated and experimental geometries was also obtained for compounds containing P-C multiple bonds including structures as complex as the aromatic molecule (4).

It seems likely then that the results reported for **2** and **3** in Table 1 and calculated using the larger 6-311G* basis set are reasonably reliable and comparisons with published experimental data are therefore in order.

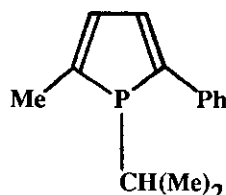
X-Ray crystal structures have been reported^{16,25-28} for four $\sigma^3\lambda^3$ -phosphole derivatives containing no additional fused rings and both bond lengths and bond angles vary considerably even over this small range of compounds. Thus, the intracyclic CPC angle varies from 89.2° to 91.8° according to the substitution



4



5



6

pattern on the ring and the P atom while intracyclic P-C bond lengths vary from 1.783 Å to 1.822 Å. Intracyclic C-C bond length variations are much smaller and the bond lengths observed are quite similar to those measured for other heterocyclopentadienes¹⁶ and, for that matter, butadiene itself.²⁶

The simplest phosphole for which a structure has been determined is 1-benzylphosphole (**5**) which has no ring substitution and only alkyl substitution upon the P atom. It seems reasonable then that this is the system with which the calculated parameters for **2**, listed in Table 1, should be compared. The P-C bond length calculated (Table 1) for **2** is 1.817 Å which is somewhat higher than that measured^{16,25} for **5** (1.783 Å) but is within the range measured for phospholes in general and noted above. The intracyclic CPC angles are, however, very similar with 90.7° measured for **5** and 89.5° calculated for **2**. Similarly, the PCC' angle calculated (111.2°) for **2** is very close to that measured (110°) for **5**. The greatest difference between the

calculated and observed geometries lies in the exocyclic bond angle at phosphorus where for **5** it is 106° while for **2** it is calculated to be only 99.3° . This, however, is not inconsistent with the known behavior of secondary and tertiary phosphines where CPC angles in acyclic tertiary phosphines are¹⁷ generally larger (97 - 103°) than HPC angles (95 - 96.5°) in secondary phosphines. This difference in the exocyclic bond angles might, at first sight, offer an explanation for the differences in the endocyclic P-C bond lengths since a smaller exocyclic bond angle could be taken to imply greater p character in the bonding orbitals. However, Gilheany has pointed out¹⁷ that such explanations do not survive close scrutiny.

For the pyramidal conformation (**2**) of $\sigma^3\lambda^3$ -phosphole then there is very good agreement between calculated geometric parameters and those measured for a variety of simple phosphole derivatives.

Considering now the planar conformation (**3**) and the inversion barrier, the level of the basis set used and the good agreement observed between calculated and observed geometric parameters for the pyramidal conformation noted above suggest that some confidence can be placed in the geometric parameters calculated for **3** and the calculated value of the inversion barrier. As noted earlier, the intracyclic P-C bond decreases in length significantly on proceeding from **2** to **3**, the C-C' bond increases by a small amount, and a decrease is observed for the C'-C' bond. The decrease in the P-C bond length can be explained, at least in part, by the fact that on proceeding from **2** to **3**, the geometry about the P atom changes from clearly pyramidal to approximately trigonal planar. This major change in geometry must lead to greater s character in the bonding orbitals and hence bond shortening although d orbital contributions to the bonding may have some effect also. Another factor to be considered is the possibility that the non-bonding pair of electrons on P, now in a predominantly 3p orbital, interacts to some extent with the π system of the ring giving some degree of delocalization which would also lead to a decrease in the length of the P-C bond. Some evidence that this may be the case is provided by the other calculated bond length changes within the ring upon proceeding from the pyramidal arrangement to the planar arrangement. Thus, as would be expected, the C-C' linkage increases significantly in length while the C'-C' bond decreases (Table 1) although these changes could also be due in part to ring angle changes in general caused by flattening of the arrangement about the phosphorus atom.

There are two further pieces of evidence which support the idea of some interaction of the phosphorus non-

bonding electron pair with the π system in the inversion transition state (3). Thus, the situation with respect to the intracyclic heteroatom-carbon bond length difference calculated for the pyramidal (2) and planar (3) conformations of $\sigma^3\lambda^3$ -phosphole is apparently quite similar to that which pertains for the planar molecule pyrrole where it has been noted²⁵ that the measured N-C bond length is significantly shorter (by 0.07 Å) than the sum of the appropriate single-bond covalent radii. Similar bond contractions have been noted also²⁵ for the related heterocyclopentadienes thiophene (0.07 Å) and furan (0.04 Å). More quantitative support for lone pair- π interaction in the planar conformation (3) of $\sigma^3\lambda^3$ -phosphole comes from calculations, carried out as part of the present study, of the total spatially integrated populations for each atom in both of the conformations of the phosphole molecule (Table 2). It is clear from Table 2 that the phosphorus atom loses almost 0.3 au of electronic charge upon proceeding from the pyramidal to the planar conformation. It appears, then, that electronic charge flows into the ring from the phosphorus atom, and the exocyclic hydrogen atom, to the neighboring carbon atoms during the pyramidal to planar transition.

Table 2
Total Integrated Populations^a

Atom	Pyramidal	Planar
P	13.2287	12.9398
C	6.7110	6.9427
C'	6.0344	5.9851
H	1.4788	1.4466
H'	0.9406	0.9210
H''	0.9569	0.9595

^aValues given in atomic units of electronic charge

The calculated value of 24.4 kcal/mol for the inversion barrier is also consistent with a small degree of delocalization in the planar state since, as noted elsewhere¹⁵ and earlier in this discussion, values of 36-

39 kcal/mol have been measured for saturated derivatives of **1** where ring size constraints upon the inversion process would be quite similar. That the value calculated is significantly higher than that observed¹⁵ (16 kcal/mol) for the heavily-substituted **6** is at first sight a little surprising but ring parameters and hence the inversion barrier would be expected to be quite sensitive to the size, the type, the location and the number of substituents upon the phosphole ring. In this connection, it is worth noting that fused ring derivatives of **1** have experimentally measured¹⁵ inversion barriers in the 24-26 kcal/mol range. The value calculated for **1** for this barrier therefore seems to be entirely reasonable.

CONCLUSION

The 6-311G* basis set is adequate for the calculation of optimized geometries for $\sigma^3\lambda^3$ -phosphole and the calculated geometric parameters for the pyramidal form agree well with those measured for several simple phosphole derivatives. The calculated value (24.4 kcal/mol) for the inversion barrier for $\sigma^3\lambda^3$ -phosphole is consistent with some degree of electron delocalization in the inversion transition state.

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