# The Barrier to Internal Rotation in Monomethylphosphine: an *ab initio* LCAO–MO–SCF Study

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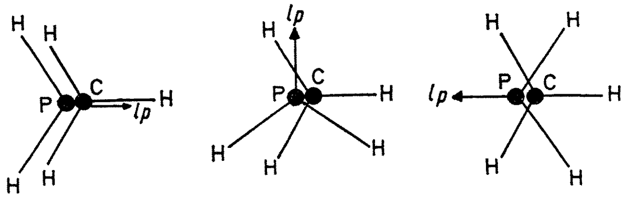
*Summary* Using two relatively small basis sets, non-empirical self-consistent-field calculations on three conformations of monomethylphosphine show that the relative stability of the three forms is as follows: staggered > semi-eclipsed > eclipsed; the calculated energy barrier between the semi-eclipsed and eclipsed forms agrees with the experimental value.

*Ab initio* RESULTS are needed as standards for further improvements in the semi-empirical methods of calculation for phosphorus compounds. Since methylphosphine is the simplest stable organophosphorus compound its wave function has been investigated, using the geometry obtained from microwave measurements[1] with P–H = 1·414, C–P = 1·863, C–H = 1·093 Å; ∠HPH = 93°23′, ∠CPH = 97°30′, ∠HCH = 109°45′; and $\epsilon$ = 2°0′; where $\epsilon$ is the angle between the methyl axis and the C–P bond. The microwave results[1] also showed the barrier to internal rotation to be 1·96 kcal mol$^{-1}$.

The *ab initio* LCAO–MO–SCF calculations using uncontracted Gaussian orbitals were carried out with the program MOSES,[2] using basis sets consisting of nine *s* and five *p* atom-optimized exponents (with and without an added *d* exponent) to describe the phosphorus, with five *s* and two *p* atom-optimized exponents to describe the carbon, and three *s* atom-optimized exponents to describe the hydrogen atoms. The program ATOM–SCF[3] was used to obtain the atom-optimized exponents. The exponent for the *d*-orbital resulted from molecular optimization in the phosphine[4] and phosphine oxide[5] molecules.

The three molecular geometries (I), (II), and (III) for which these calculations were carried out are shown in the projections (see Figure) of the molecule on to a plane perpendicular to the internal-rotation axis. The total SCF energies as well as the total electronic and the internuclear repulsion energies are presented in the Table.



eclipsed (I) semi-eclipsed (II) staggered (III)

FIGURE

The calculated rotational barrier for going from the staggered to the eclipsed form is 1·83 and 1·71 kcal mol$^{-1}$[†] for the (951/52/3) and (950/52/3) basis sets[‡] respectively, in agreement with the experimental value of 1·96 kcal mol$^{-1}$. Similarly the calculated barrier for going from the staggered to the semi-eclipsed form is 0·91 and 0·85 kcal mol$^{-1}$ for the two basis sets. On rotating the Me group, the eclipsed configuration repeats itself every 120°, the semi-eclipsed occurs twice in this process at 30 and 90°, while the staggered configuration occurs at 60°.

TABLE

*Energies in a.u. for the rotational conformations of monomethylphosphine*

| | Electronic | Nuclear | Total SCF |
|---|---|---|---|
| 95/52/3 GTO basis | | | |
| eclipsed .. .. | −441·0492 | +60·0274 | −381·0219 |
| semi-eclipsed .. | −441·0480 | +60·0247 | −381·0232 |
| staggered .. | −441·0467 | +60·0221 | −381·0246 |
| 951/52/3 GTO basis | | | |
| eclipsed .. .. | −441·1049 | +60·0274 | −381·0775 |
| semi-eclipsed .. | −441·1037 | +60·0247 | −381·0800 |
| staggered .. | −441·1025 | +60·0221 | −381·0804 |

Calculations[4,6,7] show that a 95 or 951 description for second row elements and a 52 description for first row elements with a 3 description for hydrogens is a fairly well balanced representation for a molecule containing these three types of atoms. Since the 3 basis set for hydrogen gives better valence-orbital energies than the basis sets used for phosphorus and carbon, we suggest that the errors in this rotational-barrier calculation will be due more to the limitations in the mathematical descriptions of the phosphorus and carbon than of the hydrogen atoms. A study[8] of methylamine, which is the rotational analogue of methylphosphine, in a (52/52/2) basis set also gave an energy barrier which agreed with the experimental value.[9] However, the equivalent calculated value for the methylamine barrier was larger than the experimental, whereas the reverse is true for our calculation on methylphosphine.

Calculations[10] on diphosphine show that the introduction of *d*-character to the phosphorus atom increases the calculated barrier and brings it closer to the experimental value. Calculated and experimental barriers have been reviewed and tabulated by Lowe.[11] According to an extension[13] of Gillispie's Rules,[12] the height of a rotational barrier should be larger when two rather than one lone pairs are involved. Thus, the diphosphine barrier is higher than the methylphosphine barrier.

Further details of these calculations with emphasis on the electronic structure of the P–C bond will be published shortly.

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[†] 1 au = 627·501 kcal mol$^{-1}$.

[‡] The notation (*abc*/*ef*/*g*) corresponds to the assignment *a* 1*s*, *b* 2*p*, *c* 3*d* Gaussian-type orbital exponents for the phosphorus, *e* 1*s* and *f* 2*p* for the carbon, and *g* 1*s* for each of the five hydrogen atoms.

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