# An *ab initio* LCAO–MO–SCF Study of the Gauche, Staggered, and Eclipsed Forms of Diphosphine

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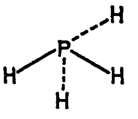
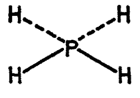
*Summary* Using three relatively small Gaussian basis sets, nonempirical self-consistent-field calculations on three conformations of diphosphine, $P_2H_4$, show that the relative stability of the three forms is the following: gauche > staggered > eclipsed.

BECAUSE of the current interest[1–3] in this molecule and because *ab initio* results are needed for further improvements in the semi-empirical methods of calculation for phosphorus compounds, the wavefunction of the diphosphine molecule was investigated, using the reasonable geometry suggested by Cowley and White[1] in which P–H = 1·42, P–P = 2·21 Å, ∠PPH = 100°, and ∠HPH = 92°. The SCF calculations were carried out with uncontracted sets of Gaussian-type orbitals using the program MOSES,† in which the initial eigenvectors were obtained from the procedure developed[4,5] by our group for converting from the usual chemists' localized-orbital description into an orthogonal, delocalized wavefunction. The program ATOM–SCF[6] was used to obtain optimized exponents for phosphorus on a (73) and (84) basis.‡ The exponent for the *d*-orbital resulted from molecular optimization in the phosphine molecule,[7] using the same *s* and *p* atom-optimized exponents as for diphosphine.

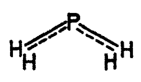
The three molecular geometries (I), (II), and (III) for which these calculations were carried out are shown in Newman projections about the P–P bond axis, with the respective symmetry group being given for each conformation. The total SCF energies as well as the total electronic and the internuclear-repulsion energies are shown in Table 1. Table 2 gives the binding energies, negative values of which are obtained by subtracting from the total SCF energy of the molecule the sum of the atomic SCF energies calculated from the same Gaussian basis set. The range in experimental binding energy is due to the use of the two values[8,9] reported for the heat of formation of diphosphine.



gauche ($C_2$)
(I)



staggered ($C_{2v}$)
(II)



eclipsed ($C_{2h}$)
(III)

The calculated rotational barrier for going from the gauche to the eclipsed form is 2·32, 2·57, and 2·17 kcal for the (84/2), (731/2), and (73/2) basis sets, respectively. Similarly, the calculated barrier for going from the gauche to the staggered form is 0·51, 0·49, and 0·66 kcal for these same three basis sets. Although for the phosphorus atom in both the (73) and (84) bases, the total SCF energy is considerably closer to the Hartree–Fock limiting energy than is the case with the hydrogen in the (2) basis, the opposite is true for the deviations of the valence-orbital energies from their Hartree–Foch values. Since the basis set used for the hydrogen gives better valence-orbital energies than do either of the basis sets used for the phosphorus, we speculate that the error in this calculation of the rotational barriers for diphosphine will be due more to the limitations in the mathematical description of the phosphorus atoms than of the hydrogen atoms. Thus, we

TABLE 1

*Energies in a.u. for the rotational conformations of diphosphine in several atomic bases*

| | Electronic | Nuclear | Total SCF |
|---|---|---|---|
| (73/2) Basis | | | |
| Gauche | −767·4209 | +88·6686 | −678·7523 |
| Staggered | −767·3277 | +88·5764 | −678·7513 |
| Eclipsed | −767·4373 | +88·6885 | −678·7488 |
| (731/2) Basis | | | |
| Gauche | −767·5855 | +88·6686 | −678·9169 |
| Staggered | −767·4926 | +88·5764 | −678·9162 |
| Eclipsed | −767·6013 | +88·6885 | −678·9128 |
| (84/2) Basis | | | |
| Gauche | −771·1536 | +88·6686 | −682·4850 |
| Staggered | −771·0606 | +88·5764 | −682·4842 |
| Eclipsed | −771·1698 | +88·6885 | −682.4813 |

TABLE 2

*Binding-energy calculations for diphosphine*

| | (73/2) | (731/2) | (84/2) |
|---|---|---|---|
| H atom in a.u. | −0·4807 | −0·4807 | −0·4807 |
| P atom in a.u. | −338·1905 | −338·2257[a] | −340·0926 |
| $P_2H_4$ mol. in a.u. | −678·7523 | −678·9169 | −682·4850 |
| SCF binding in a.u. .. | 0·4485 | 0·5427 | 0·3670 |
| SCF binding in ev .. | 12·2 | 14·8 | 10·0 |
| Exper. binding in ev .. | 15·1 — 15·3 | | |

[a] The value for the energy of the phosphorus atom in the (731) basis set is somewhat larger than in the (73) set because of the way the *d*-orbitals are handled. Instead of using five spherically harmonic *d*-orbitals in the molecular SCF calculations, we use the following six: $x^2$, $y^2$, $z^2$, $xy$, $xz$, and $yz$. This means that, upon conversion into the usual representation in terms of five *d*-orbitals, we have introduced an extra 3*s*-orbital. When this 3*s*-orbital was incorporated with the seven other *s*-orbitals and the three *p*-orbitals (with the orbital exponents being held the same as in the molecule) atom optimization of the coefficients led to the small increase in the energy of the phosphorus for the (731) as compared to the (73) basis.

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† This program was written by L. M. Sach and M. Geller and was modified by N. Winter, J. H. Letcher, L. C. Groenweghe, and H. Marsmann for use on a CDC computer (with *d*-orbitals being allowed).

‡ We have adapted the standard notation with (*abc*/*ef*) representing *a s*-orbitals, *b p*-orbitals, *c d*-orbitals, *etc.*, on the phosphorus atoms, and *e s*-orbitals, *f p*-orbitals, *etc.*, on the hydrogen atoms.

believe that varying the size of only the phosphorus basis set was a proper operation and that the gauche form is the most stable one of the three forms studied, with the staggered and eclipsed forms lying about 0·5 and 2·4 kcal above it in energy. A study[10] of the rotational conformations of the nitrogen analogue of diphosphine (hydrazine) in a small Gaussian basis set (52/2) gave energy barriers and the geometry of the stable conformation which agreed well with the values obtained from a (95/3) set of calculations.[11]

Using semi-empirical SCF approximations, two previous studies[1,2] have been made of the relative stabilities of the conformations of diphosphine. In one of these calculations,[2] using highly unrealistic geometry, it appeared that the eclipsed (*cis*) conformation is more stable than the staggered (*trans*). In the other paper,[1] the calculations suggested that the order of conformational stability is gauche > eclipsed (*cis*) > staggered (*trans*), using exactly the same molecular geometries as were employed in our work. As indicated above, our calculations led to the stability sequence of gauche > staggered > eclipsed. This sequence is the same as was obtained for hydrazine, and the gauche form appears to be the more stable one from vibrational spectroscopy.[12,13]

Further details of these calculations, with emphasis on the electronic structure of the P–P bond and the lone-pair electrons, will be published shortly.

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