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Ab Initio versus CNDO Barrier Calculations

II. P_2H_4 and P_2F_4

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Energy barrier curves to internal rotation in P_2H_4 and P_2F_4 have been studied by the *ab initio* SCF-LCAO-MO method in the gaussian approximation and by the CNDO method. For P_2H_4, two stable rotamers at 75° and 180° of equal energy and separated by a barrier of only 500 cal/mole are predicted, and the *cis* barrier computes to be 4.1 kcal/mole. A '*trans*-only' form of P_2F_4 is the theoretical structure with only an arrest in the barrier curve at the *gauche* position. The CNDO method does not produce reliable information concerning the number of stable rotamers, their precise configurations, or the heights of the barriers.

Die Kurven der Energiebarriere bei der inneren Rotation von P_2H_4 und P_2F_4 wurden nach der *ab initio* SCF-LCAO-MO-Methode mit einer Basis von Gaussfunktionen sowie nach der CNDO-Methode untersucht. Beim P_2H_4 ergeben sich zwei stabile Rotamere von gleicher Energie bei 75° und 180° und getrennt durch eine Barriere von nur 500 cal/mol; die cis-Barriere berechnet sich zu 4.1 kcal/mol. Eine reine trans-Form von P_2F_4 ist die theoretische Struktur mit nur einem Sattelpunkt in der Energiekurve bei der *gauche*-Position. Die CNDO-Methode liefert keine genügend genauen Anhaltspunkte zur Zahl der stabilen Rotameren, ihren genauen Konfigurationen oder zu den Höhen der Barrieren.

Les courbes d'énergie donnant les barrières de rotation interne ont été étudiées pour P_2H_4 et P_2F_4 par la méthode *ab-initio* SCF LCAO MO en base gaussienne et par la méthode CNDO. Pour P_2H_4 on prévoit deux rotamères stables de même énergie à 75° et 180° séparés par une barrière de 500 cal/mole seulement, la barrière *cis* calculée étant de 4,1 kcal/mole. La structure théorique de P_2F_4 est la forme «tout-trans» avec seulement un arrêt sur la courbe dans la position *gauche*. La méthode CNDO ne produit pas d'informations sûres en ce qui concerne les rotamères stables tant du point de vue de leurs configurations que de celui des barrières.

Introduction

In view of the apparent qualitative success of the semiempirical CNDO and INDO calculations in predicting the proper number of stable rotamers for hydrazine (N_2H_4) and tetrafluorohydrazine (N_2F_4) as reported in the previous paper [1], the results of similar *ab initio* SCF-LCGTO-MO energy barrier calculations on diphosphine (P_2H_4) and tetrafluorodiphosphine (P_2F_4) have been compared with the corresponding semiempirical CNDO calculations on these molecules.

Diphosphine, P_2H_4, is believed to have '*gauche*-only' structures in both the gaseous and liquid phases similar to those of hydrazine [2, 3], while in the solid phase it is supposed to exist in the *trans* configuration only [4]. A '*trans*-only' structure is also favored for liquid diphosphorus tetrafluoride, P_2F_4, on the basis of infrared and Raman data [5]. In all states studied, both P_2Cl_4 and P_2I_4 also apparently have '*trans*-only' structures [6, 7]. Unfortunately, structural parameters have not been reported for either P_2H_4 or P_2F_4, consequently we have had to estimate these quantities from standard bond distances and bond angles in conjunction with the known *x*-ray results on *trans* P_2I_4 [8]. Moderate variations in the assumed P–P bond distances in both P_2H_4 and P_2F_4 gave energy barrier curves very similar to those shown in our figures, but the value for minimum total energy was somewhat less for the CNDO than for the *ab initio* calculations. In the case of P_2H_4, minimum CNDO energy resulted when the P–P distance was 2.08 Å; minimum SCF energy was attained at a P–P distance of 2.23 Å. The values used for the geometrical parameters in the complete calculations are shown in Table 1.

Apparently no previous *ab initio* computations of any type have been performed on either molecule, although semiempirical calculations have been reported for all of these molecules [9, 10], albeit in one case with the incredible conclusion that the *cis* configurations are more stable than the *trans* configurations in all such X_2Y_4 molecules.

The methods of calculation are essentially the same as those used previously [1]. Orbital exponents and contraction coefficients under the same small (7*s*, 3*p*) canonical basis set as before were obtained for the phosphorus atom by use of the computer program ATOM-SCF [11]. These values are displayed in Table 2.

Table 1. *Geometrical parameters used for* P_2H_4 *and* P_2F_4

Parameter	P_2H_4	P_2F_4	P_2I_4
P–P distance	2.20 Å	2.20 Å	2.212 Å
P–X distance	1.437 Å	1.535 Å	2.474 Å 2.477
XPX angle	93°	102°	102.18′
PPX angle	98°	96°	93° 56′ 93° 58′

Table 2. *Orbital exponents and contraction coefficients for phosphorus*[a]

s-type functions	*p*-type functions	*d*-type functions
1. 3543.636228	8. 18.575386	11. 0.45
2. 536.127007	9. 3.646498	
3. 121.572803	10. 0.268971	
4. 33.288729		
5. 6.723555		
6. 2.303495		
7. 0.204794		

$1s(P)$: $0.015106\,\chi_1 + 0.106675\,\chi_2 + 0.394480\,\chi_3 + 0.560759\,\chi_4$
$2s(P)$: $0.235149\,\chi_5 + 0.854946\,\chi_6$
$3s(P)$: $1.000000\,\chi_7$
$2p(P)$: $0.325554\,\chi_8 + 0.787068\,\chi_9$
$3p(P)$: $1.000000\,\chi_{10}$
$3d(P)$: $1.000000\,\chi_{11}$

[a] The $\chi_1, \chi_2, \ldots$ are the gaussian functions whose exponents are given above.

For P_2H_4 we again have a total of 44 gaussian orbitals, but now these are contracted to 22 orbital functions. The 96 gaussians employed for P_2F_4 were contracted to 38 orbital functions representing the 1*s*, 2*s*, 3*s*, $2p_x$, $2p_y$, $2p_z$, $3p_x$, $3p_y$, and $3p_z$ atomic orbitals on each of the two phosphorus atoms and the 1*s*, 2*s*, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals on each of the four fluorine atoms. The SCF energies and wavefunctions were computed at eight different values of the dihedral angles for each molecule. Only CNDO semiempirical calculations were performed on the P_2H_4 and P_2F_4 molecules since in our version of CNINDO the INDO program does not apply to second-row elements. However, *d*-orbitals on the phosphorus atoms are taken into account in these CNDO calculations.

Results and Discussion

P_2H_4. The *ab initio* calculations on P_2H_4, using the same basis set as for N_2H_4, generated the potential barrier curve shown in the middle of Fig. 1. The corresponding CNDO barrier curve for P_2H_4 is exhibited on the upper part of Fig. 1. Neither of these calculated energy barrier curves would predict a strictly '*gauche*-only' structure for P_2H_4. However, the *ab initio* result could certainly account for the experimental expectations because of the low barrier between the predicted *gauche* and *trans* configurations, and because of the general 'flatness' of

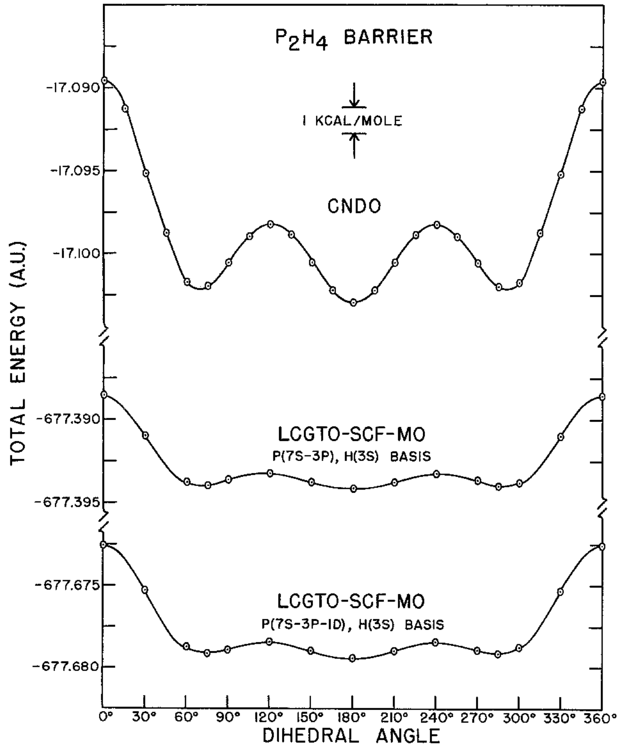

Fig. 1. Calculated energy barrier curves for P_2H_4

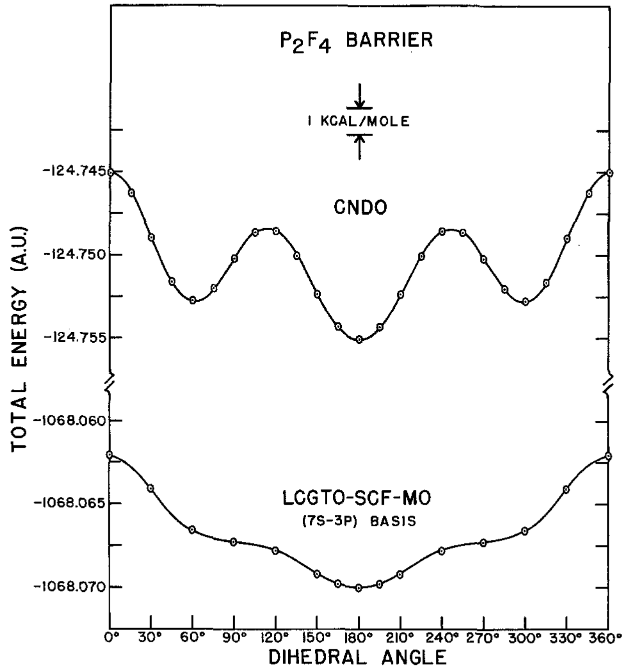

Fig. 2. Calculated energy barrier curves for P_2F_4

the barrier curve from 60° to 300°. The calculated values of the energies are given in Table 3, and the barrier heights are presented in Table 4. It is interesting here that the barriers calculated by the CNDO method are significantly larger than the *ab initio* barriers as well as being qualitatively different in shape. This is in contrast to the results for N_2H_4 where the CNDO barriers were considerably smaller than the *ab initio* barriers. However, the CNDO calculations here do take into account the *d*-orbitals on the two phosphorus atoms, whereas this first set of *ab initio* SCF calculations does not.

Using a new basis set for the phosphorus atoms obtained by adding to the canonical set a single gaussian function with orbital exponent equal to 0.45 for each of the six *d*-orbitals (one of which is redundant), produces the energy barrier curve shown at the bottom of Fig. 1. The corresponding energy terms are also tabulated in Table 3. It is apparent from these results that although the total energy is lowered considerably, the addition of *d*-orbitals to the phosphorus atom basis set in the manner used here, neither significantly alters the qualitative shape of the barrier curve nor notably modifies the heights of the barriers. This again corroborates the conjecture that the barrier potential curve is relatively unaffected by the size of the basis set [12], and thus gives some confidence in the reliability of our energy barrier curves.

P_2F_4. The calculated energy barrier curves for P_2F_4 are shown in Fig. 2. The *ab initio* barrier curve is in accord with the expected '*trans*-only' structure, but again the curve is quite flat and the magnitude of the barrier considerably smaller than in the case of N_2F_4. The CNDO results are not in agreement with the experimental '*trans*-only' prognostication in that both *gauche* and *trans* configurations are predicted to be stable with the *trans* form somewhat more so by about 1.78 kcal/mole. The calculated CNDO barriers are also significantly higher than the *ab initio* barriers (cf. Table 4).

A ready comparison of all of our calculated *ab initio* and CNDO energy barrier curves may be made from Fig. 3. The *ab initio* calculations engender much larger barriers for the nitrogen-containing molecules than for the phosphorus molecules and they delineate the transition from the *gauche*-only structure through the *gauche* plus *trans* configurations to the *trans*-only case. In contrast, the semiempirical computations produce small barriers for the nitrogen compounds and large barriers for the phosphorus compounds. In addition, the CNDO method appears to favor the *gauche* plus *trans* structures for all of the molecules since there is even a hint of this in the case of N_2H_4 and there is no indication of approaching the *trans*-only structures in the phosphorus molecules.

Analyzing the barriers for the phosphorus molecules as before [1], we have plotted the attractive ($V_{att} = V_{ne}$) and repulsive ($V_{rep} = V_{nn} + V_{ee} + T$) components of the total energy ($E = T + V_{ne} + V_{nn} + V_{ee}$) as functions of the dihedral angles for P_2H_4 andP_2F_4 in Fig. 4. For P_2H_4, the *cis* barrier is repulsive dominant; the small barrier at a dihedral angle of 120° is slightly repulsive dominant from the *trans* position, but slightly attractive dominant from the *gauche* position, the difference between the two factors being very small in either case. In the case of P_2F_4, all barriers are repulsive dominant. Again it should be noted that the nuclear-nuclear potential repulsion terms do not reflect the barriers for either P_2H_4 or P_2F_4; only a monotonic dropping off of this potential energy component occurs as the dihedral angle changes from 0° to 180° but, of course, the magnitude of the change is much greater for P_2F_4.

Fig. 5 shows the total atomic populations, calculated from the *ab initio* wave functions of P_2H_4 and P_2F_4, as functions of the dihedral angles. The corresponding variations of the atomic charges as obtained from the CNDO wave functions are presented in Fig. 6. For P_2H_4, the gross atomic population curves calculated from wave functions obtained using either basis set, in a sense, reflect the *ab initio* potential barrier curves. The CNDO atomic charge variations in P_2H_4 reflect the semiempirical barrier curve, but the character of the variations is opposite to that in the *ab initio* curves. The gross atomic populations in P_2F_4 vary in such a way that they may be said to reflect the computed energy barrier curve in that as the molecule is rotated from the *cis* orientation to the *trans*, charge is transferred from the P-atoms to the attached F-atoms in a manner that imitates the barrier curve. For P_2F_4, the CNDO atomic charges on the P-atoms decrease with dihedral angle while the attached F-atoms gain electrons in the same fashion as the CNDO and INDO calculations prophesied for N_2F_4, but again these variations do not mirror the barrier curve.

The total overlap populations between atoms across the P–P bonds in P_2H_4 and P_2F_4 are shown in Fig. 7. In the case of P_2H_4, the sum of all the overlap populations across the P–P bond again well reflects the SCF energy barrier curve, although neither the PP′, PH′, nor HH′ overlap populations by themselves will do so. For P_2F_4, the sum of all the overlap populations athwart the P–P

Table 3. *Calculated* SCF *energies for* P_2H_4 *and* P_2F_4

Dihedral angle	P_2H_4							P_2F_4			
	without *d*-orbitals on P-atoms				with *d*-orbitals on P-atoms						
	Total energy	V_{nn}	V_{ee}	$V_{ne}+T$	Total energy	V_{ee}	$V_{ne}+T$	Total energy	V_{nn}	V_{ee}	$V_{ne}+T$
0°	−677.38853	88.825623	349.21449	−1115.4286	−677.67261	349.20378	−1115.7020	−1068.0621	436.56164	854.32536	−2358.9491
30°	−677.39094	88.814850	349.18782	−1115.3936	−677.67530	349.17303	−1115.6632	−1068.0641	435.49616	853.20142	−2356.7617
60°	−677.39379	88.790987	349.15110	−1115.3359	−677.67874	349.12204	−1115.5918	−1068.0666	433.39689	851.03328	−2352.4968
75°	−677.39399	88.777558	349.14293	−1115.3145	−677.67915	349.10258	−1115.5593	—	—	—	—
90°	−677.39366	88.763577	349.13859	−1115.2958	−677.67891	349.08495	−1115.5274	−1068.0673	431.40215	849.03462	−2348.5041
120°	−677.39325	88.734739	349.12314	−1115.2511	−677.67839	349.04157	−1115.4547	−1068.0678	429.33406	846.94001	−2344.3419
150°	−677.39380	88.711075	349.09725	−1115.2021	−677.67894	348.99390	−1115.3839	−1068.0692	427.42582	844.95703	−2340.4520
165°	—	—	—	—	—	—	—	−1068.0698	426.84255	844.34411	−2339.2564
180°	−677.39417	88.701938	349.08463	−1115.1807	−677.67938	348.97306	−1115.3544	−1068.0700	426.63822	844.12879	−2338.8370

Table 4. *Calculated barriers to internal rotation in* P_2H_4 *and* P_2F_4*(kcal/mole)*

	P_2H_4			P_2F_4	
	CNDO	*ab initio* 7*s*−3*p*	*ab initio* 7*s*−3*p*−1*d*	CNDO	*ab initio*
cis-barrier	7.94	3.425	4.102	4.86	4.955
gauche-barriers	2.528	0.464	0.477	2.825	
	2.954	0.577	0.621	4.265	
stable forms	69°, 180°	72°, 180°	75°, 180°	60°, 180°	180°

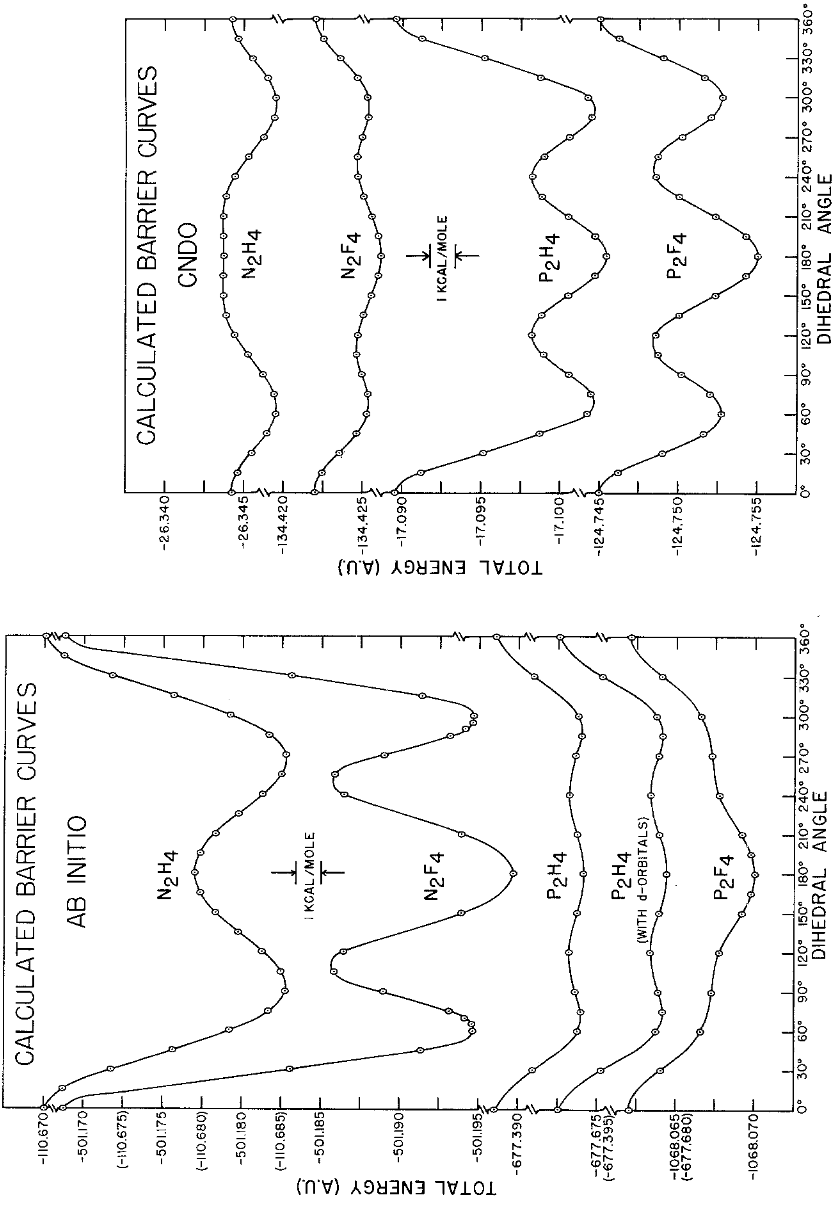

Fig. 3. SCF and CNDO energy barrier curves for N_2H_4, N_2F_4, P_2H_4, and P_2F_4

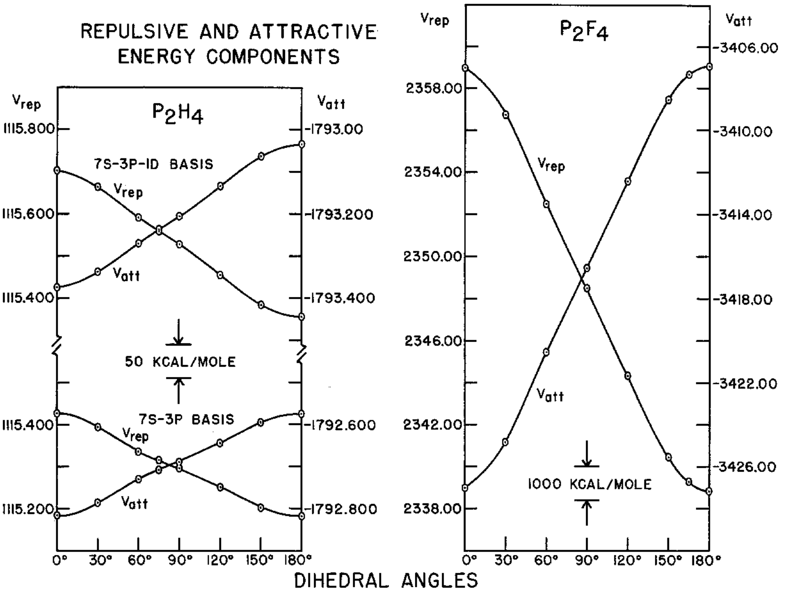

Fig. 4. Attractive and repulsive energy components *versus* dihedral angles for P_2H_4 and P_2F_4

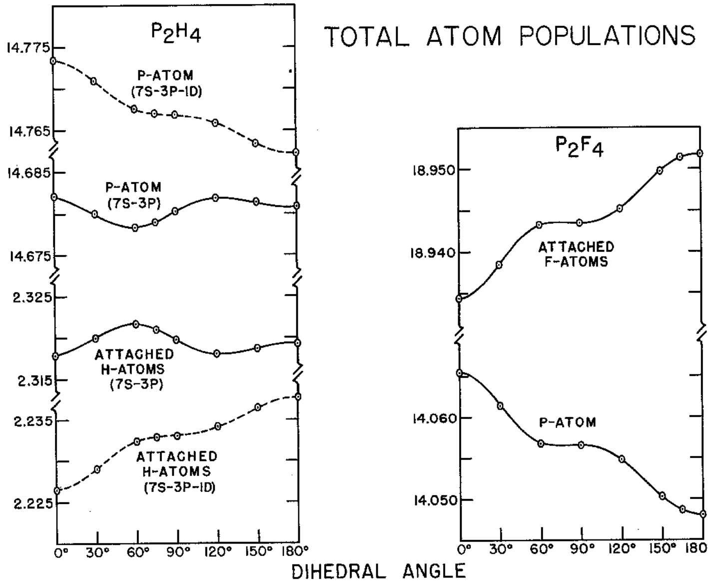

Fig. 5. SCF gross atomic populations as functions of the dihedral angles for P_2H_4 and P_2F_4

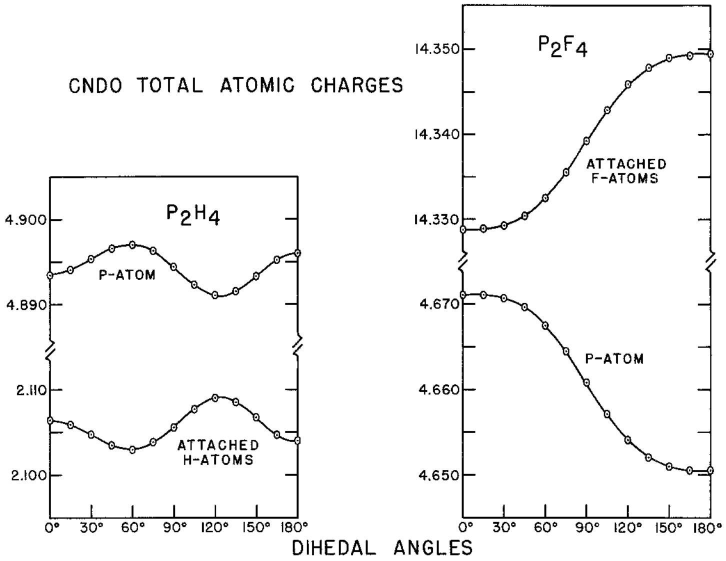

Fig. 6. CNDO total atomic charges as functions of the dihedral angles for P_2H_4 and P_2F_4

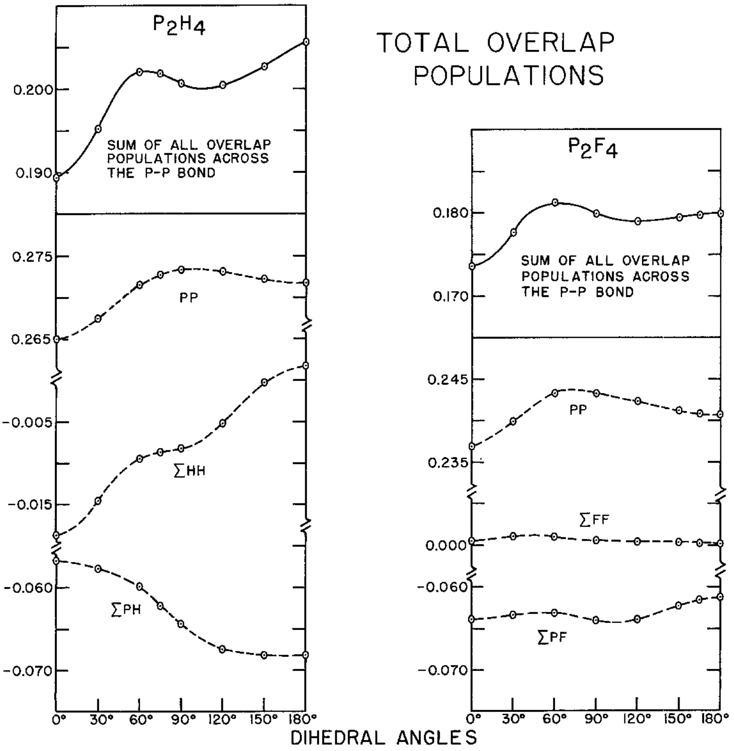

Fig. 7. SCF total overlap populations as functions of the dihedral angles for P_2H_4 and P_2F_4

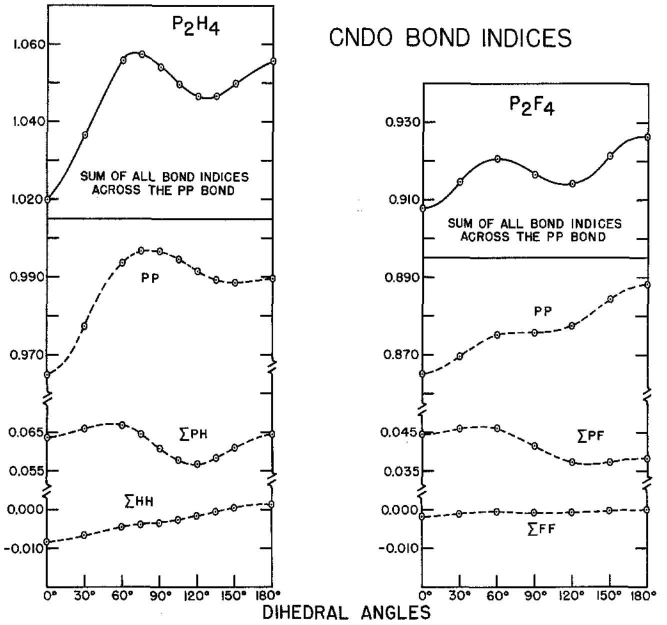

Fig. 8. CNDO total bond indices as functions of the dihedral angles for P_2H_4 and P_2F_4

bond best reflects the barrier curve, but now, in contrast to the N_2F_4 case, the FF′ interactions have little influence.

Fig. 8 gives the variations of the bond indices calculated from the CNDO functions. For P_2H_4, the sum of all bond indices across the PP bond reflects the CNDO barrier curve and this seems to result mainly from the PP bonding. In the case of P_2F_4, the sum of all the bond indices again closely follows the CNDO barrier curve and is very insensitive to the FF′ interactions.

Conclusions

Energy barrier curves for internal rotation about the single PP bonds in P_2H_4 and P_2F_4, as computed by the SCF method using a small basis of gaussian functions in the linear-combination-of-gaussian-type-orbital technique (SCF-LCGTO-MO), are completely compatible with the meagre experimental information available. Introduction of *d*-functions onto the P-atoms, within this theoretical framework, does not appreciably alter the barrier curve, so that some faith in the reliability of the results may be warranted. The magnitudes of the calculated barriers are significantly smaller than for the corresponding nitrogen compounds and this is exhibited by the decreased dependence of the overlap populations on dihedral angle as a consequence of the increased separations in the phosphorus compounds. The barriers are again best analyzed in terms of the sums of all the overlap populations across the PP bonds; these show maximum bonding at the orientations with minimum energies.

CNDO barrier curves for P_2H_4 and P_2F_4 are not accordant with the *ab initio* barrier curves nor with the experimental predictions. The CNDO barriers for these compounds are considerably larger than those for the corresponding nitrogen molecules and there seems to be a tendency for this method to predict stable *gauche* and stable *trans* configurations for all of these molecules. For the sort of molecules here considered, it does not appear that the CNDO procedure will yield reliable energy barrier curves for a phenomenon as subtle as internal rotation, neither in regard to the number of stable conformations, their exact configurations, nor the magnitudes of the barriers separating them.

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