Contribution from the Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Molecular Orbital Study of PF_2CN and Its Inversion Barrier as Compared with PF_3

WILLIAM ROY HALL and HENDRIK F. HAMEKA*

Received December 28, 1972

We performed a semiempirical calculation on PF_2CN and also on PF_3. We found that PF_2CN has two stable configurations, namely, a cis and a trans configuration. The trans configuration is more stable than the cis configuration by about 1 kcal/mol and the two configurations are separated by an energy barrier of about 35 kcal/mol. We found that there is considerable interaction between the phosphorus 3d orbitals and the fluorine 2p orbitals and that the interaction between the phosphorus 3d orbital and the carbon and nitrogen 2p orbitals is much smaller. We calculated the molecular dipole moment for both the cis and the trans form and we found that both results agree with the experimental value.

1. Introduction

There has been much interest in the structure and bonding of substituted fluorophosphines.[1] In PF_2Cl,[1c] where all of the d orbitals of phosphorus are available for π bonding, the loss of electrons due to this π bonding can occur from both the fluorine p_x and p_y orbitals. This results in long PF bonds and a small FPF bond angle. In the cases of PF_2H[1a] and PF_3,[2] the bonds are smaller and the FPF bond angles are larger. In PF_2NH_2,[1b] there is $(p \rightarrow d)\pi$ interaction arising from the lone pair of electrons on the nitrogen with empty d orbitals of the phosphorus, and, in addition, there is $(p \rightarrow d)\pi$ interaction with the fluorines. Consequently, the PF bonds are longer and the FPF bond angle is smaller. (See Figure 1 for pertinent structures.)

Since $(p \rightarrow d)\pi$ interaction is present in other substituted fluorophosphines and affects the structures, we are interested in the effects it might produce in PF_2CN. From the ir and Raman spectra of PF_2CN, it was concluded[3] that the equilibrium configuration has either C_s or C_{2v} symmetry. The structure of PF_2CN was considered to be analogous to that of PF_3 but an X-ray study[4] of $P(CN)_3$ shows that the average PCN bond angle is not 180° but 171 ± 3°. Originally, this deviation from linearity was felt to be the result of the close packing in the crystal lattice;[5] however, this deviation from linearity was also found in a recent microwave study[6] of PF_2CN.

It has been known for some time that phosphorus exhibits weak to moderate but important d_π-p_π bonding in many compounds.[7,8] Hillier and Saunders recently performed an *ab initio* calculation[9] using STO with best-atom exponents, augmented by phosphorus 3d orbitals with an exponent of 1.4. They found that PH_3 and PF_3 both had a relatively large 3d population. The 3d orbitals of phosphorus participate in σ bonding with hydrogen in PH_3 and in both σ bonding and π bonding in PF_3. The major interaction in PF_3 was found to be $3d_\pi$-$2p_\pi$. Because our calculation is based on Pople's many-electron approximate SCF CNDO/2, we felt that a comparison with the more accurate *ab initio* calculation might be helpful. Therefore, we calculated PF_3 by the same CNDO/2 and compared the results with the *ab initio* calculation. We also compared the results for PF_2CN with PF_2. For the semiempirical CNDO/2 calculations, we used the computer program CNINDO.[10] The details and parametrization of this method have been fully discussed elsewhere.[11-14]

2. Results and Discussion

We examined many configurations of PF_2CN. The largest variation in total energy is caused either by changing the FPF bond angle which in turn affects the FPC bond angle or by changing the length of the PF bond. Varying the PCN bond angle causes the smallest change in total energy. The coordinates and molecular data for the equilibrium configurations are reported in Figure 2.

The bond energies that we obtained for *cis*- and *trans*-PF_2CN show that both are stable configurations having ground-state energies that differ by only 1 kcal mol^{-1}. However, it has been shown that CNDO/2 is more suitable for estimating molecular geometries, charge distributions, and dipole moments than ground-state energies; therefore, this result may be in error by as much as 5 kcal mol^{-1}. Yet, the result is interesting because the microwave study predicts a trans configuration as the stable ground state without considering the possibility of a cis configuration. It does not seem possible to differentiate between the two configurations by using dipole moment measurements. The theoretical values for μ are very close for the two configurations; both agree with the experimentally determined value of 2.39 D. The contributions to the dipole moment of the trans form are given in Table I. As can be seen, the inclusion of the 3d orbitals introduces a pd polarization in the opposite sense to the sp polarization. This increases the calculated moment to within 0.2 D of the observed moment. This inclusion of 3d orbitals serves to reduce the excessive polarity by allowing a back-donation of electrons by the fluorines into the phosphorus 3d orbitals. Along with this, there is a slight overlap of the phosphorus 3d orbital with the CN

---

[1] (a) R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968); (b) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *ibid.*, **93**, 6772 (1971); (c) A. H. Brittain, J. E. Smith, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 39 (1972); (d) R. L. Kuczkowski, H. W. Schiller, and R. W. Rudolph, *ibid.*, **10**, 2505 (1971).

[2] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

[3] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966).

[4] K. Moritano, *Inorg. Chem.*, **8**, 867 (1969).

[5] F. A. Emerson and D. Britton, *Acta Crystallogr.*, **21**, 775 (1964).

[6] P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 1917 (1972).

[7] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

[8] D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

[9] I. H. Hillier and V. R. Saunders, *Chem. Commun.*, 316 (1970).

[10] The program CNINDO (P. A. Dobosh) received from the Quantum Chemistry Program Exchange (QCPE), Bloomington, Ind.

[11] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

[12] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

[13] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[14] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

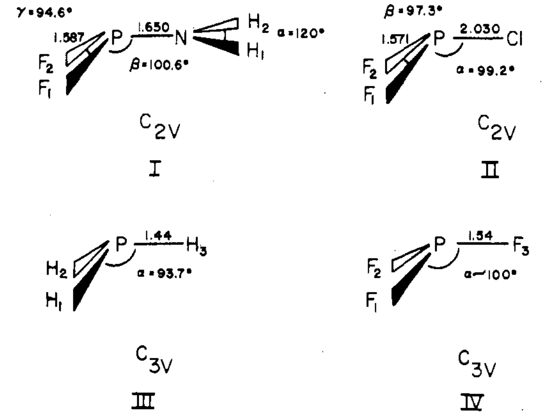

Figure 1.

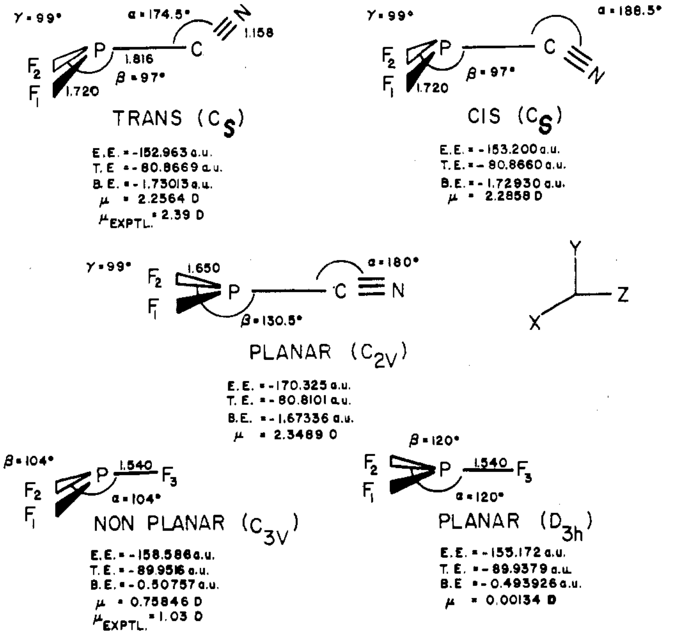

Figure 2.

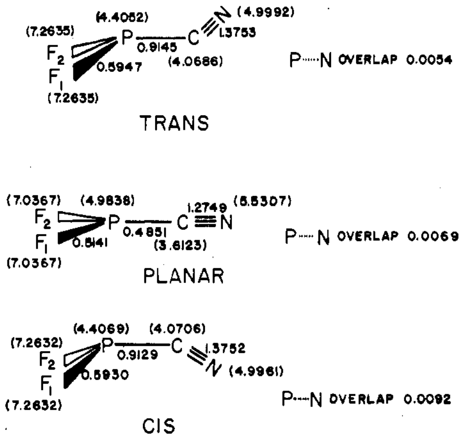

Figure 3.

triple bond. This overlap increases as the configuration changes from trans to cis as shown in Figure 3.

There has been much concern about the use of the d orbital and its orbital exponent. Fogleman and coworkers[15] found that calculated molecular properties are insensitive to the precise value of the orbital exponent for the 3d value over a moderage range centered between 1.4 and 1.7 for phosphorus-containing molecules. They found, however, that much smaller values produce extremely bad results for at least some of the computed molecular properties. Keeton and Santry[16] found that the 3d-orbital exponent can be approximated as 0.9 of the Slater 3s-orbital exponent. Since our exponent is not that much different from the Keeton-Santry approximation, we feel that our results will not be affected by our choice of the orbital exponent.

Table I. Dipole Moment of *trans*-PF_2CN

	Component		
	x	y	z
Densities	0.00	2.80	0.09
sp	0.00	−1.97	1.03
pd	0.00	1.42	−1.01
Total	0.00	2.25	0.11

We computed the eigenvalues and eigenvectors (which may be obtained on request) for the three equilibrium configurations. From this information, we have determined the first and second ionization potential (Table II) by means of Koopmans' theorem,[17,18] *i.e.*

$$I_1 = E^+ - E_g = -\epsilon_{14}$$

$$I_2 = E^{2+} - E_g = -\epsilon_{13}$$

The ionization energies of the cis and trans forms are no more than 0.2 eV apart. From the ionization energies alone, it is difficult to ascertain which configuration has the strongest pull on its electrons since the theorem we used introduces an error of as much as 20% with respect to the experimental values when STO are used. The use of the CNDO/2 has no adverse effect on the accuracy of the calculated ionization potential, as shown by Sichel and Whitehead.[19]

With the conversion of either cis or trans to the planar form, there is a large charge shift for all the atoms involved. The phosphorus 3d charge is approximately the same in the cis and trans configurations, namely, 0.90 and 0.89, respectively, but in the planar configuration it is much lower, namely, 0.57. The total charge distribution for the three forms can be found in Figure 3. From this total charge distribution, we find that the inclusion of the 3d orbitals on the phosphorus strengthens the σ bonds and reduces the charge on the central atom by giving all the bonds a multiple-bond character; accompanied by a back-donation of charge from the surrounding atoms to the phosphorus, the d_π-p_π back-donation is calculated to be larger in both the cis and trans configurations than in the planar configuration. The orbitals that are most affected by bringing the PF_2CN into a planar configuration are the p_x and p_y orbitals of the nitrogen and carbon atoms. The change into the planar configuration is accompanied by an increase in the p_y charge densities of C, F, and P and by a decrease in the p_y density of N. The effect on the p_x orbitals is just the opposite. There is a decrease in the p_y charge density of C, F, and P and an increase in the p_y density of N.

In comparing the results of *trans*-PF_2CN with nonplanar PF_3, we find that the back-donation by fluorines is slightly less in *trans*-PF_2CN. In addition, the phosphorus charge in

---

[15] W. W. Fogleman, D. J. Miller, H. B. Jonassen, and L. C. Cusachs, *Inorg. Chem.*, 8, 1209 (1969).

[16] M. Keeton and D. P. Santry, *Chem. Phys. Lett.*, 7, 1056 (1970).

[17] T. A. Koopmans, *Physica (Utrecht)*, 1, 104 (1933).

[18] W. G. Laidlaw and F. W. Birss, *Theor. Chim. Acta*, 2, 181 (1964).

[19] J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, 11, 239 (1968).

Table II. Ionization Energies (eV)

Structures	I_1	I_2
PF_2CN (trans)	14.9	17.7
PF_2CN (planar)	11.3	13.6
PF_2CN (cis)	14.8	17.9

trans-PF_2CN is larger than in PF_3. This is due to the interaction with the CN triple bond.

In Table III, we have compared our CNDO results for PF_3 with the results of the *ab initio* calculation by Hillier and Saunders.[9] It may be seen that the atomic populations in the two calculations differ by as much as 20%. The dipole moment as calculated by CNDO/2 method is closer to the experimental value than the *ab initio* moment.

There is an appreciable π bonding involving the phosphorus 3p and 3d orbitals along with the fluorine $2p_\pi$ orbitals. The major interaction, in both cis and trans, is $(p \rightarrow p)\pi$ instead of $(p \rightarrow d)\pi$; however, in the planar form the reverse is true. There is also a slight interaction between the 3p and 3d orbitals of the phosphorus and the nitrogen orbitals. The total overlap populations were calculated by means of Kaufman's method[20] and are shown in Figure 3. The largest amount of 3d orbital overlap is with carbon and fluorine in the formation of σ molecular orbitals. The small overlap between phosphorus and nitrogen is due to both n–π interaction and d–π interaction which brings about the delocalization of CN_π system to include the phosphorus atom.

We decided to compare our overlap calculations of PF_3 with the *ab initio* results.[9] The two sets of results agree reasonably well with each other (Table III). In comparing the overlap of PF_3 with that of PF_2CN, we find that substitution of a CN for F increases the $3p_\pi$–$2p_\pi$ P–F overlap by more than a factor of 2 and that it decreases the $3d_\pi$–$2p_\pi$ P–F overlap by about one-third.

3. Stereochemistry of PF_2CN as Compared with PF_3

There are two stereochemical processes (conformation changes) which are possible: (1) phosphorus pyramidal inversion and (2) rotation about the P–C bond. The CNDO/2 method does not predict rotational barriers in medium-size molecules with reasonable accuracy so that we decided to investigate the first of these two processes only.

Many calculations of inversion barriers of phosphines have been reported in the literature.[21-26] There are four effects that can change the magnitude of the barrier;[25] these effects are conjugative, electrostatic, inductive, and steric in nature. We calculated a barrier of 35.6 kcal mol^{-1} for *trans*-PF_2CN and a barrier of 35.0 kcal mol^{-1} for *cis*-PF_2CN. It is difficult to assess how reliable these values are since the possible error in the energy is of the order of 5 kcal mol^{-1}. Nevertheless, our calculation predicts that the two isomers are both stable, differing by a small energy difference. The two effects which are predominant in PF_2CN are the inductive and conjugative effects. The conjugative effect lowers the barrier to interconversion. The electron-withdrawing power of the fluorines decreases the rate of inversion because of the tendency to increase the s character of the unshared electron pair on the phosphorus. In the planar transition state, these electrons must reside in a p or d orbital in order to lower the barrier. We found that the highest occupied MO of PF_2CN is mainly localized on the P atom in the cis and trans isomers, but not as much as in the case of PF_3 which has a barrier of 45 kcal mol^{-1}. Nevertheless, the unshared electron pair is almost pure p with only very little d character. This lowers the barrier to inversion.

Table III. Comparison of CNDO/2 and *ab Initio* Calculation of PF_3

	CNDO/2	*Ab initio*	Exptl
μ, D	0.76	1.44	1.03
IP, eV	15.44	−12.69	12.31
Atomic population			
P(3s)	1.76	1.51	
P(3p)	1.45	1.89	
P(3d)	1.17	0.71	
F(2s)	1.84	1.90	
F(2p)	5.34	5.42	
P atomic charge	0.62	0.89	
F atomic charge	−0.21	−0.32	

4. Conclusion

Our calculation shows that the greatest effect on the total molecular energy is due to changing the PF bond length or varying the FPF bond angle. We also found that PF_2CN could exist in two stereoisomeric forms of about the same stability, the trans form more stable than the cis form by only 1 kcal; however, we have some reservations about this conclusion because of the limited accuracy of the theoretical energy values. Qualitatively, the result may be explained by noting that a change in the PCN bond angle has negligible effect on the total energy as compared to changes in the FPF or FPC bond angles.

We also found that $(p \rightarrow p)\pi$ interaction is greater in *cis*- and *trans*-PF_2CN than the $(p \rightarrow d)\pi$ interaction. In the planar configuration the relative magnitudes of these interactions are just the opposite. This results in a shortening of the PF bond length in the planar configuration. There is also an interaction between the P $3p_\pi$ orbital and the CN $2p_\pi$ system which is responsible for the PCN bond angle.

We found that the inversion barriers for both *cis*- and *trans*-PF_2CN are quite close, namely, 35.0 and 35.6 kcal mol^{-1}, but it should be realized that the accuracy of the results may not be good enough to draw any decisive conclusions from them.

Registry No. PF_2CN, 14118-40-2; PF_3, 7783-55-3.

Acknowledgment. We wish to thank Dr. B. B. Wayland and G. Mayer for helpful discussions and Dr. E. Thornton for the use of his copy of the QCPE program CNINDO. Research was supported by the Advanced Research Projects Agency and by the National Science Foundation, through Grant GH-33633.

---

(20) J. J. Kaufman, *Int. J. Quantum Chem.*, 205 (1971).

(21) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 9, 400 (1970).

(22) J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969).

(23) P. Jordan, *J. Chem. Phys.*, 41, 1442 (1964).

(24) G. W. Koeppl, P. S. Sagatys, G. S. Krishnaturthy, and S. I. Miller, *J. Amer. Chem. Soc.*, 89, 3396 (1967).

(25) F. A. L. Anet. R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 89, 359 (1967).

(26) W. Egan and K. Mislow, *J. Amer. Chem. Soc.*, 93, 1805 (1971).