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Molecular Structures of P_2F_4 and $P_2(CF_3)_4$ by Gas-Phase Electron Diffraction[1]

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The principal structural parameters and uncertainties (2σ) for P_2F_4 are r_g(P–P) = 2.281 ± 0.006 Å, r_g(P–F) = 1.587 ± 0.003 Å, ∠PPF = 95.4 ± 0.3°, and ∠FPF = 99.1 ± 0.4°, and the rms libration about P–P is 16.7 ± 0.4°. Only trans conformers were observed. Gauche concentrations probably do not exceed 10% at room temperature. Corresponding values for $P_2(CF_3)_4$ were r_g(P–P) = 2.182 ± 0.016 Å, r_g(P–C) = 1.914 ± 0.004 Å, r_g(C–F) = 1.337 ± 0.002 Å, ∠CPC = 103.8 ± 0.8°, ∠PPC = 106.7 ± 0.7°, and ∠PCF = 110.4 ± 0.2°. Trans conformers predominated. Amplitudes of vibration were determined for both molecules. Structures of diphosphines provide no evidence for strong π delocalization across the P–P bond analogous to that found in aminophosphines. The longest P–P bond in diphosphines observed to date is that in P_2F_4, the molecule with the most electronegative ligands. The P–CF_3 bond is significantly longer than the P–CH_3 bond. Structural trends are in poor accord with VSEPR and semiempirical MO theories.

Introduction

The P–P bond in diphosphines has been the subject of many investigations. Several reviews have summarized the chemistry and structural features of compounds containing P–P linkages.[2–9] In diphosphines, the phosphorus atoms are joined by a σ bond, with each phosphorus bearing two substituent groups and an electron pair. It has been suggested that the unshared 3p electrons of one phosphorus are capable of overlap with the nominally unoccupied 3d orbitals of the second phosphorus in a pπ–dπ interaction.[2,3,10–12] Such behavior, if significant, might correlate with substituent electronegativity and be discernible in trends of P–P bond lengths and molecular geometries in a series of diphosphines. Structural investigations have been reported for several diphosphines with substituents of modest electronegativity and for F_2PPH_2.[13] It seemed worthwhile to examine diphosphines with substituents of particularly high electronegativity on both phosphorus atoms. Therefore we initiated studies of P_2F_4 and $P_2(CF_3)_4$. In addition, a study of the Lewis base properties of diphosphines was carried out to indicate the availability of the lone pairs. Results are reported elsewhere.[14,15]

Experimental Section

The preparation of P_2F_4 is described elsewhere.[16] Purity was checked by infrared spectroscopy, the principal impurities being PF_3 and PF_2HO. The sample of $P_2(CF_3)_4$ was donated by Professor R. G. Cavell and used as received. Mass spectral analysis indicated a purity of at least 98%.

Electron diffraction patterns were recorded using an electron diffraction apparatus equipped with an r^3 rotating sector.[17] The samples were introduced through a nickel nozzle having a throat approximately 0.7 mm long and 0.29 mm in diameter and the nozzle lip was 0.47 mm from the center of the electron beam. All diffraction patterns of $P_2(CF_3)_4$ and patterns of P_2F_4 taken at the 21-cm camera distance were recorded on 4 × 5 in. Kodak process plates; those of P_2F_4 at the 11-cm camera distance were recorded on Kodak electron image plates. Kodak anti-fog solution was added to the developer in the case of the electron image plates. Experimental conditions for recording of the diffraction patterns are given in Table I.

For P_2F_4, two plates at the 21-cm camera distance and four plates at the 11-cm distance were selected for analysis. For $P_2(CF_3)_4$, five 21-cm and four 11-cm plates were analyzed. Photographic densities were measured with an automatic recording microphotometer with digital output.[18] Readings were taken at $^1/_8$-mm intervals across the diameter of a spinning plate, and either the even or the odd set of $^1/_8$-mm readings was used in the structure determination.

Table I. Experimental Conditions for Recording Diffraction Patterns

	P_2F_4		$P_2(CF_3)_4$	
Camera dist, cm	21.149	11.073	21.129	11.159
Reservoir temp, °C	Ambient	Ambient	−2	0
Vapor pressure, Torr	10–20	10–20	~20	~20
Exposure time, sec	4–5	5	2.2	5.5
Beam current, μA	0.32	0.37	0.46	0.46

Due to the extreme sensitivity of P_2F_4 to moisture, special attention was given to handling and monitoring for purity. The vacuum system was maintained at a pressure of 10^{-5} mm or better. All parts of the inlet system exposed to the atmosphere between runs were pumped down for a minimum of 4 hr. To avoid unnecessary decomposition in the liquid phase, the sample, stored in a Pyrex sample tube attached to a 300-ml Pyrex bulb, was maintained at −196° by a liquid nitrogen bath. Prior to a run, a small amount of P_2F_4 was expanded into the bulb connected to the nozzle by a stopcock. A gas-phase infrared cell was also attached to the bulb, and midway through a run a small amount of sample was expanded into the cell. The purity of the P_2F_4 was checked by infrared analysis at the end of a run, and if there was greater than approximately 5% impurity, the diffraction data were not used.

Analysis of Data

After recording the diffraction patterns, absorbances were measured by a digital microphotometer[18] and converted to exposures by the relation $E = A(1 + aA)$ where E is the exposure and A the corresponding absorbance and where a ranged from 0.05 to 0.10 for the various plates.

Exposures of the individual plates at a given camera distance were averaged and corrected for sector irregularities and extraneous scattering. Experimental intensities were leveled[19] using the elastic scattering factors of Strand and Bonham[20] and the inelastic scattering factors of Heisenberg[21] and Bewilogua.[22] For the 11-cm data of P_2F_4, an excessive rise in background intensity at large s necessitated a larger than normal extraneous scattering correction for the data at this camera distance to bring the background of the leveled intensity to a nearly horizontal line. The indices of resolution for P_2F_4 were 0.93 and 0.89 for the 21- and 11-cm camera distances, respectively, after correcting for extraneous scattering in the outer regions of the plates. The corresponding indices for $P_2(CF_3)_4$ were 1.06 and 1.01.

Reduced molecular intensities, $M(s)$, and radial distribution functions, $f(r)$, were calculated as described elsewhere.[19,23-30] A least-squares procedure which imposed geometric self-consistency on the internuclear distances was used with diagonal weight matrices to refine molecular intensities.[31,32] The elements of the weight matrix applied to $M(s)$ in the case of P_2F_4 were proportional to s^2. Elements for $P_2(CF_3)_4$ were calculated according to

$$W(s) = \{A - \exp[-\alpha(s - s_A)^2]\} \exp[-\beta(s - s_B)^2]$$

where A, α, s_A, β, and s_B were assigned the values 1.1, 0.64, 4.7, 0.017, and 6.3, respectively, for the 21-cm data and 1.1, 0.025, 9.4, 0.003, and 15.7 for the 11-cm data. Data from each camera distance were treated separately until the individual background functions were refined and there was good agreement between the molecular parameters obtained for each camera distance. A blended experimental intensity function was constructed by interpolating data from each camera distance to intervals of $\Delta s = \pi/10$ and then merging the data in the overlapping s region. The blended intensity function was treated by additional least-squares refinements. Radial distribution functions were calculated using a Degard damping factor of the form $\exp(-0.0015s^2)$. Atomic scattering factors used in the calculations were those of Cox and Bonham[33] and Tavard.[34] Anharmonicity constants[25,26] were taken to be 2.0 $Å^{-1}$ for all bond distances, 2.0 $Å^{-1}$ for nonbonded distances in P_2F_4, and 1.0 $Å^{-1}$ for nonbonded distances in $P_2(CF_3)_4$. No shrinkage corrections[35-37] were made for P_2F_4 but very rough corrections ranging from 0.001 to 0.002 Å for geminal distances and up to 0.005 Å for remote distances were made for $P_2(CF_3)_4$.

Calculated standard errors include the effects of random and scale factor errors.[17] Systematic errors for bond lengths and mean amplitudes of vibration were estimated to be 0.07% and 2%, respectively. A subjectively estimated "practical" uncertainty in the index of resolution (3%, greatly exceeding the least-squares result) is the principal systematic error in the mean amplitude of vibration.

Results for P_2F_4

Rotational Isomers. Four plausible conformations for P_2F_4 with a symmetry higher than C_1 are trans (C_{2h}), gauche (C_2), cis (C_{2v}), and semieclipsed (C_2). A comparison of the experimental radial distribution functions $f(r)$ with the theoretical functions from 2.4 to 5.0 Å is shown for each conformer in Figure 1, parts a–d. The independent geometric parameters used in these calculations are r_g(P–P) = 2.281 Å, r_g(P–F) = 1.587 Å, ∠PPF = 99.1°, and ∠FPF = 95.3°, where the dihedral angle, ϕ, is 0° for the cis configuration and 180° for the trans. Of the idealized, static conformations a–d, the agreement is best for trans.

The agreement between the experimental and theoretical $f(r)$ curves can be improved by one of several methods: skewing the trans model away from C_{2h} symmetry, inclusion of a torsional distribution about the P–P bond in the trans model, or using a mixture of trans and gauche rotamers. The effect of each of these approaches is to decrease the longer vicinal F···F distance (4.1 Å) and increase and/or decrease the two shorter vicinal F···F distances (3.3 Å) in the trans model but, as will be pointed out, the improvement due to inclusion of gauche seems to be merely a mathematical artifact. Each of these methods is discussed below.

If the dihedral angle in the trans model (model A) is allowed to vary from 180° along with the four other independent geometric parameters [r_g(P–F), r_g(P–P), ∠PPF, and ∠FPF] and all independent parameters are cycled to self-consistency by a least-squares analysis of the intensity, the dihedral angle refines to 169.5 ± 3.7°. The radial distribution function calculated from the new parameters represents the experimental radial distribution function satisfactorily. The independent parameters found for model A are, excluding the torsional angle, identical with those found for model B below.

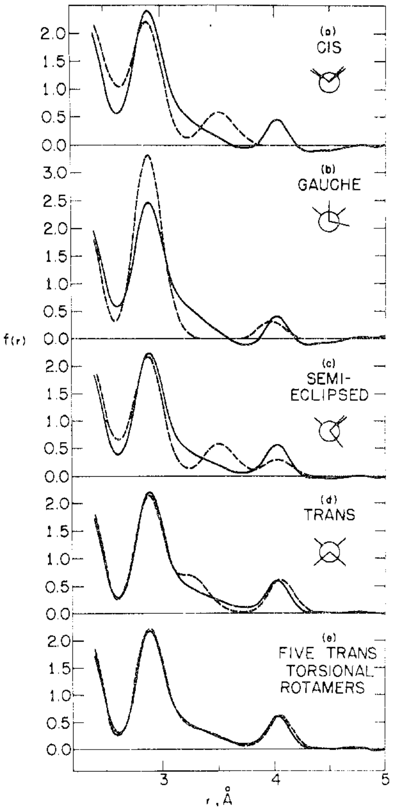

Figure 1. Experimental radial distribution function and radial distribution functions calculated for the possible rotational isomers of P_2F_4.

By taking the torsional libration about the P–P bond into account in a more realistic manner and optimizing the five independent geometric parameters [r_g(P–F), r_g(P–P), ∠PPF, ∠FPF, and root-mean-square torsional displacement] by least-squares analysis, the resultant fit (model B), shown in Figure 1e, is slightly better than that obtained for model A. Correspondingly, the standard deviation in leveled intensities [$\sigma(I)/I$] drops from 1.16 to 1.13 parts per thousand. The librational distribution was accounted for by adopting nine conformations (expressible in terms of five rotamers), identical except for their dihedral angles, which differ by integral values of a torsional increment parameter δ. The relative concentrations of the rotamers in model B were chosen to make the distributions in ϕ correspond to a gaussian distribution in torsional displacements from C_{2h} symmetry and to make increment δ correspond to 0.64 standard deviation. The independent parameters for model B, optimized by least-squares analysis, are given in Table II.

If a gauche rotamer with a dihedral angle of 50° is mixed with model A (or model B) and the six independent parameters [r_g(P–F), r_g(P–P), ∠PPF, ∠FPF, ϕ(trans) (or δ(torsional) for model B) and ϕ(gauche)] are refined by a least squares analysis, there is a significant deterioration in the agreement between the experimental and theoretical intensities. If the dihedral angle in the gauche rotamer is allowed to decrease to about 20°, the agreement between experimental and theoretical intensities improves slightly. Plots of the standard deviations of intensities obtained in least-squares analyses of model A and model B as a function of the gauche rotamer concentration display minima (1% lower than at 100% trans) at a composition of 90% trans and 10% gauche. However, the uncertainty in the composition at the minimum is estimated to be approximately 10%, and the *gauche* rotamer improves the standard deviation (and marginally, at that) only if it is

Table II. Derived Parameters for P_2F_4 and Specification of Model B

Parameters	r_g,[a] Å	l_g,[a] Å
P–F	1.587 ± 0.003	0.045 ± 0.002
P–P	2.281 ± 0.006	(0.060 ± 0.005)[b]
$F\cdots F_{gem}$	[2.415]	(0.060 ± 0.005)[b]
$P\cdots F$	[2.900]	0.110 ± 0.007
$F\cdots F_{trans}$	[4.081]	0.089 ± 0.018
∠PPF	95.4 ± 0.3°	
∠FPF	99.1 ± 0.4°	
Torsion incr δ	10.7 ± 3°	
Rms libration	16.7 ± 4°	
Indices of resolution	21-cm data 0.93 11-cm data 0.89	

Isomer	% compn	Dihedral angle (Φ), deg
1	25.0	180.0
2	41.4	180.0 – δ
3	22.6	180.0 – 2δ
4	8.6	180.0 – 3δ
5	2.4	180.0 – 4δ

[a] Uncertainties represent 2σ based on M_x^w for $r < 2.3$ Å and M_x^0 for $r > 2.3$ Å with uncertainties for amplitudes including systematic error of 0.02*l*. See L. S. Bartell and M. G. Anashkin, *J. Mol. Struc.*, 17, 193 (1973), for the meaning of M_x^w and M_x^0. The uncertainty in the P–P bond length does not include the uncertainty in composition which is believed to contribute an error less than that listed above. The amplitude of vibration for $F\cdots F_{gauche}$ is too uncertain to warrant listing. [b] The P–P and $F\cdots F_{gem}$ amplitudes were arbitrarily taken as equal.

allowed to correspond to an improbable structure. Therefore, it can be concluded that the trans composition is, within experimental error, 100% and that the minimum at 90% is devoid of physical significance.

It is possible to make a rough estimate of the barrier to internal rotation from the observed root-mean-square torsional displacement of 16.7 ± 4° according to equations published elsewhere.[38] If it is assumed that the potential energy of twist about the P–P bond can be expressed by the function $V_0(1 - \cos 3\theta)/2$ in the vicinity of the trans configuration, where V_0 is the rotational barrier and θ is a rotation measured from the trans position, and if the effective temperature of the expanding gas is taken as, say, 270°K, the implied barrier is in the range 0.9–2.5 kcal/mol.

Molecular Parameters. The values of the molecular parameters and estimated standard errors for model B are given in Table II. In all stages of the analysis it was assumed that the P–P distance, the bonded P–F distance, the PPF angle, and the FPF angle were common to all isomers (trans and gauche). In Table III are listed the elements of the correlation matrix. Experimental and calculated reduced molecular intensities and the radial distribution function for model B are given in Figures 2 and 3, respectively.

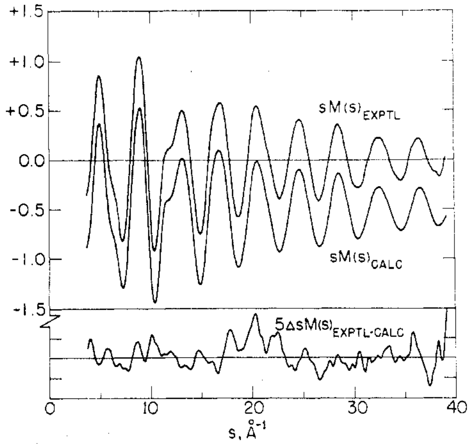

Figure 2. Experimental and calculated reduced molecular intensity functions for P_2F_4, model B.

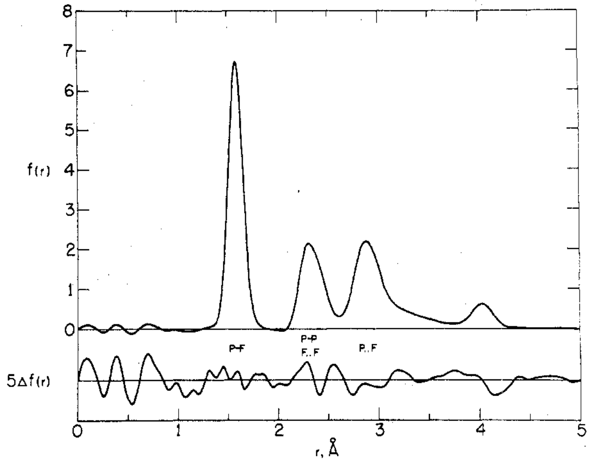

Figure 3. Experimental radial distribution function for P_2F_4, model B.

Because of the rather large value found for the P–P length and because of the poor resolution of the P–P and the geminal F···F distances which might lead to a significant error in the P–P bond length, a serious effort was made to find alternative solutions with shorter P–P bond lengths. No other least-squares minima were discovered with intensity residuals less than a factor of 4 larger than those for our reported solution. Effects of possible contamination by PF_3 were investigated and found to lead to an error of less than 0.01 Å.

Results for $P_2(CF_3)_4$

This molecule was not examined in as exhaustive detail as its simpler analog P_2F_4. A gauche structure was appreciably poorer in representing the intensities than a trans structure. The presence of gauche conformers could not be ruled out,

Table III. Matrix of Correlation Coefficients[a] for P_2F_4, Model B, Five Trans Torsional Rotamers[b]

	r(P–F)	r(P–P)	∠PPF	∠FPF	δ(torsional)	l(P–F)	l-(P–P, $F\cdots F_{gem}$)	l-($P\cdots F$)	l-($F\cdots F_{vic}$, short)	l-($F\cdots F_{vic}$, long)	R
r(P–F)	1.0	–0.01	–0.80	–0.23	0.006	–0.03	–0.01	0.02	0.04	–0.006	0.03
r(P–P)		1.0	–0.56	0.33	–0.09	–0.001	0.04	–0.02	0.03	0.03	–0.07
∠PPF			1.0	–0.04	0.21	0.007	–0.02	0.05	0.09	–0.07	0.02
∠FPF				1.0	–0.04	0.02	–0.15	–0.02	0.07	0.01	0.10
δ(torsional)					1.0	–0.009	0.01	0.30	0.05	–0.03	–0.05
l(P–F)						1.0	–0.05	0.02	0.06	0.00	0.66
l(P–P, $F\cdots F_{gem}$)							1.0	–0.05	–0.11	0.00	0.17
l($P\cdots F$)								1.0	0.38	–0.09	0.23
l($F\cdots F_{vic}$, short)									1.0	–0.05	0.05
l($F\cdots F_{vic}$, long)										1.0	0.09
R, index of resolution											1.0

[a] Matrix elements given by $\rho_{ij} = B_{ij}^{-1}/(B_{ii}^{-1}B_{jj}^{-1})^{1/2}$ where the notation corresponds to that of O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 27, 1311 (1957). [b] For a description of the molecular model, see text.

Table IV. Derived Parameters for $P_2(CF_3)_4$ [b]

Parameters	r_g,[a] Å	l_g,[a] Å
P–P	2.182 ± 0.016	0.074 ± 0.019
P–C	1.914 ± 0.004	0.051 ± 0.008
C–F	1.337 ± 0.002	0.048 ± 0.004
∠CPC	103.8 ± 0.8°	
∠PPC	106.7 ± 0.7°	
∠PCF	110.4 ± 0.2°	
CF_3 torsion τ	32.9 ± 2°	
Mean displacement about P–P from trans	16.6 ± 3°	
Indices of resolution	21-cm data 1.06 11-cm data 1.01	

[a] Uncertainties represent very crude estimates of 2σ derived subjectively. [b] For sense of torsional displacements see text.

however. The fit with a trans model was improved significantly when the structure was twisted slightly away from C_{2h} symmetry to a configuration analogous to that of model A for P_2F_4. No distribution analogous to that of model B was tried. Structural parameters for the model A refinement are listed in Table IV. In deriving these parameters the following constraints were imposed. (1) All P–C bond lengths were made equal as were all PPC bond angles. (2) The CF_3 groups were given local C_{3v} symmetry with the symmetry axes coincident with the associated C–P bonds. (3) The CF_3 groups were all assigned the same magnitude of torsion angles, τ, with τ expressing the deviation of each trans F–C–P–P dihedral angle from 180°. The assumption was made that, viewing along the CF_3 axes from C to P, the torsions were clockwise for CF_3 groups bonded to one phosphorus and counterclockwise for groups bonded to the other.

The standard deviation of the fit of intensities was 2.1 parts per thousand of the total leveled intensity when the nonoptimum weighting specified in the foregoing was adopted. A weighting proportional to s^2 would have given a somewhat lower standard deviation.

The twist from $\phi = 180°$ is about 60% greater than that found for P_2F_4 which may indicate an increase in the rms torsional libration amplitude of a similar magnitude and a corresponding reduction in the torsional force constant by a factor of 2 or 3. In view of the simplifications and the molecular complexity, however, this conclusion is speculative.

The reduced molecular intensity function is shown in Figure 4. Approximate values for many amplitudes of vibration besides those listed in Table IV were found. They are included in the supplementary material.

Discussion

One of the stronger motivations for studying the present molecules was to examine the evidence for delocalization of electrons across the P–P bond. Delocalization of the lone pairs is strongly indicated in the analogous aminophosphines. X-Ray structural studies of $(CH_3)_2NPF_2$[39] and its B_4H_8 adduct[40] show a short P–N bond and a planar P–N–C_2 skeleton which bisects the F–P–F angle. A microwave investigation reveals an analogous structure for gaseous H_2NPF_2.[41] A gas-phase electron diffraction study of $(CH_3)_2NPF_2$ discloses a short P–N bond but a not quite planar P–N–C_2 skeleton.[42] It is natural to conclude from the P–N bond lengths, the near-planarity of the bonds about nitrogen, and the conformation about the P–N bond that $p\pi$–$d\pi$ bonding is appreciable in the aminophosphines.

For diphosphines, neither gas- nor solid-phase structure determinations have so far revealed the planar configurations around the phosphorus atoms which would be indicative of π bonding. Structure determinations show that diphosphine conformations can be trans, gauche, or a mixture of the two. Infrared–Raman vibrational studies on $P_2(CH_3)_4$ indicate that the structure for the solid phase is trans but that the liquid is a trans–gauche mixture.[43] A gas-phase electron diffraction study of the molecule was interpreted in terms of a "skewed" trans conformation.[44] On the basis of vibrational studies, it was concluded that conformational differences also exist between the liquid,[45,46] solid,[47] and gas[48] phases of P_2H_4. A microwave study shows that gaseous H_2PPF_2 has a trans configuration.[13] Vibrational spectroscopic data[49,50] and an *ab initio* MO calculation[51] favor the trans configuration for P_2F_4 although one particular set of semiempirical SCF and extended Hückel MO calculations suggested the order of conformational stability in P_2F_4 is gauche > cis > trans.[52] A vibrational study of $P_2(CF_3)_4$, undertaken after the present study was completed, confirmed that the molecule exists mainly in the trans form but indicated that a 30% population of gauche may exist.[53] A study of the photoelectron spectrum of $P_2(CF_3)_4$[54] suggested a somewhat lower gauche concentration of perhaps 10%. Some rules of thumb for predicting conformation stabilities are discussed by Durig, *et al.*[53]

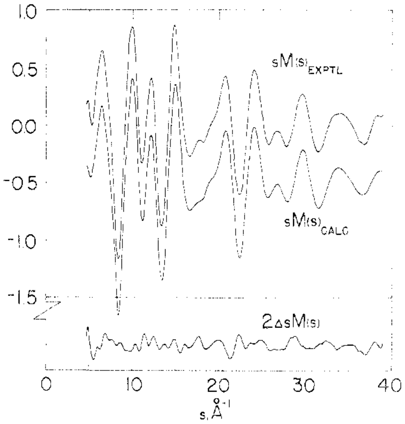

Figure 4. Experimental and calculated reduced intensity functions for $P_2(CF_3)_4$.

One might expect the length of the P–P bond in diphosphines (or polyphosphines) to indicate the extent of any higher order bonding therein. This distance, however, does not deviate greatly from the single-bond value of 2.22 Å, listed by Pauling.[55] The P–P separations in three distinctively different compounds, P (black), $P_2Et_2S_2$ (acyclic), and $(PCF_3)_4$ (cyclic), are 2.224 ± 0.002 Å,[56] 2.220 ± 0.010 Å,[57] and 2.213 ± 0.005 Å,[58] respectively. The P–P bond length is also fairly insensitive to changes in oxidation state and substituents.[2] Compared with the analogous disulfides, S_2X_2, where the S–S bond length does appear to decrease with increased substituent electronegativity,[59] it seems that the P–P bond length is not a simple function of electronegativity of the substituent groups. For example, the P–P bond lengths in $P_2(CH_3)_4$ [2.192 ± 0.018 Å][44] and P_2H_4 [2.216 ± 0.005 Å][60] are about the same as that in $P_2(CF_3)_4$ [2.182 ± 0.016 Å], and the most electronegative substituent, fluorine, is associated with one of the longest P–P bonds observed to date [2.281 ± 0.006 Å]. This contradicts a prediction based on trends in disulfides, S_2X_2, that the P–P bond in P_2F_4 should be in the vicinity of 2.05–2.09 Å.[44] Tables of other P–P bond lengths and conformations in various diphosphines and hydrazines are included in the supplementary material and in a doctoral dissertation.[14] Of the various diphosphines studied to date, F_2PPH_2[13] is perhaps the best candidate for π delocalization across the P–P bond. Neither for this molecule nor for the other diphosphines do the conformations or bond lengths provide support for strong $p\pi$–$d\pi$ bonding.

The popular VSEPR theory of Gillespie and Nyholm has been strikingly successful in accounting for structures and stereochemistries of many molecules including phosphorus compounds involving fluorine and carbon ligands.[61,62] According to VSEPR theory, the lengths of bonds and angles between bonds adjacent to electronegative atoms or groups tend to be smaller, the higher the electronegativity. In the P_2X_4 series $P_2(CH_3)_4$,[44] $P_2(CF_3)_4$, and P_2F_4, conformity with this rule is not conspicuous. Consider the trends ∠XPX = 99.6, 103.8, 99.1° and ∠PPX = 101.1, 106.7, 95.4°. For a given type of angle the deviation of the CF_3 derivative from the trend may be a steric effect. This neither accounts for the angle FPF exceeding angle PPF nor does it account for the rather large 0.055 Å *increase* in P–C bond length when CH_3 groups are replaced by CF_3 groups.[63] The enormously more crowded molecule $N_2(CF_3)_4$ has quite normal N–C bond lengths.[64] Finally, as mentioned in the foregoing, when ligand electronegativity is increased, the P–P bond length does not follow the simple VSEPR trend obeyed, apparently, by its close relative the S–S bond.[59] Semiempirical MO calculations[52] for P_2H_4 and P_2F_4 imply P–P bond lengths in accord with VSEPR theory but *ab initio* MO calculations,[51] on the contrary, are consistent with experiment. Since the VSEPR and semiempirical MO models often yield good answers for structural trends, it would be helpful to understand the most important factors contributing to their failures.

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Registry No. P_2F_4, 13824-74-3; $P_2(CF_3)_4$, 2714-60-5.

Supplementary Material Available. Supplementary material including the leveled intensities $I_0(s)$ and background intensity function $I_B(s)$ for P_2F_4 and $P_2(CF_3)_4$, approximate values for the many different amplitudes of vibration of atom pairs in $P_2(CF_3)_4$ and assumed shrinkage corrections in the analysis, a compilation of P–P bond lengths, and a table on conformations in various diphosphines and hydrazines will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40531A.

References and Notes

(1) Presented in part at the Fourth Austin Symposium on Gas-Phase Molecular Structure, Austin, Tex., Feb 28, 1972; see Abstract M17.
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