of M(BH$_4$)$_2$ giving origin to 2BH$_3$ + MH$_2$ is less unfavorable, on the basis of the values of Table III, with respect to the alternative one giving origin to BH$_3$ + H$_2$ + HMBH$_2$. This last molecule corresponds in all cases to a relative minimum on the energy hypersurface. In the Be case the decomposition into M + BH$_3$ is endothermic, while for the two heavier atoms it is exothermic. The correlation corrections to these energy differences modify the numerical values without altering the conclusions.

Conclusions

In the present paper we have examined the structures and the energetic properties of three metal borohydrides, Be(BH$_4$)$_2$, Mg(BH$_4$)$_2$, and Ca(BH$_4$)$_2$, at a comparable and fairly good degree of precision. Several conclusions may be drawn from these calculations.

The metal borohydride M(BH$_4$)$_2$ is in all the three case a stable compound, with a remarkable character of internal flexibility (politopy). There are many similarities among the three hydrides, as the similarity of the structures corresponding to the critical points indicate, but also noticeable differences. The beryllium borohydride exhibits a larger propensity for a smaller coordination number, while the Mg and Ca compounds have, under this viewpoint, a similar behavior. In passage from Be to Mg and Ca there is a progressive flattening of the portion of the potential energy hypersurface corresponding to stable structures of M(BH$_4$)$_2$.

Comparisons of the energetic results at the SCF and at the correlated levels show that correlation effects are important in each compound in assessing the general shape of the potential energy surface, as represented by the relative energies of the critical points under examination. These energetic effects are fairly well represented by the lowest level of the correlation theory, i.e. by MP2 calculations; the higher levels of the perturbation theory introduce only minor corrections. Electron correlation has less important effects on the geometrical parameters; we have performed checks only at the MP2 level, but what was said here above about the MPn (n = 2-4) energies at fixed geometry supports a generalization of this statement to the MP3 and MP4 levels. The correlation energy contribution, which, as we have said, depends on the geometry, may be easily modeled in terms of additive group contributions, with good precision, at every level of the Møller-Plesset theory. In addition these group contributions are relatively insensitive to the chemical nature of the metal atom. These characteristics confirm what was observed in a preceding occasion for other metal hydrides[1] and make it possible to utilize for future calculations on similar compounds a simpler computational procedure: a SCF calculation with a good basis set, followed by the use of correlation group contributions.

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Multiple Bonding in Perfluorodiphosphene (FPPF) and Perfluorodiphosphinylidene (PPF$_2$)

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Seven energy minima for the P$_2$F$_2$ system have been determined by means of ab initio self-consistent-field (SCF) and single- and double-excitation configuration interaction (CISD) analytic gradient methods using basis sets as large as triple-ζ plus double polarization (TZ2P). Detailed analyses of the bonding nature of these structures have been carried out, with an emphasis on the P-P bond. In particular, we find one structure corresponding to a planar PPF$_2$ configuration that contains a P-P triple bond, yielding a central phosphorus atom with a formal valence of 5. Our results indicate that this hypervalence is primarily the result of the ionic character of the P-F bonds, and the triple bond is comprised mainly of phosphorus s and p orbitals.

1. Introduction

Interest in polyphosphorus chemistry has risen steadily since 1950.[1] In particular, a large number of diphosphenes[2-4] have been synthesized since Yoshifuji and co-workers synthesized a true "phosphabenzene" in 1981.[5] Experimentally only diphosphenes with large substituent groups have been isolated, and most of these assume a planar trans configuration in the crystalline state with a PPX (X = C, N) angle of 102-109°.[2] The parent diphosphene, P$_2$H$_2$, has been observed experimentally via its mass spectrum in the pyrolysis of diphosphene, P$_2$H$_4$.[6-8] Both the singlet and triplet potential energy surfaces of P$_2$H$_2$ have been carefully studied by theoretical methods.[9-18] P$_2$H$_2$ is found to have a singlet trans bent ground state with a cis isomer only slightly higher in energy (3-4 kcal/mol) and a planar structure with H$_2$PP linkage about 25-30 kcal/mol higher than the trans isomer. On the triplet potential energy hypersurface, a skewed HPPH and a pyramidal H$_2$PP appear approximately 17 and 25 kcal/mol, respectively, above the singlet, *trans*-HPPH isomer. Although the effect of amino substituents was studied by Schoeller and Staemmler,[19] no one has yet considered the fluorine-substituted species P$_2$F$_2$. Experimentally, only its "parent" radicals PF[20-22] and PF$_2$[23,24] are

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known. The more electronegative fluorine atom is expected from Bent's rules[25] to decrease the FPP angles in the FPPF isomers and the FPF angle in the F_2PP isomers as well as to induce bond dipoles in the PF bonds, with negative charge shifted toward the fluorines. The effect of fluorine substitution on molecular properties, however, is often variable and difficult to predict. A good example is the C–C bond length in fluoroethenes, which first decreases and then increases with increasing fluorination.[26] Busch, Schoeller, Niecke, Nieger, and Westermann investigated the effect of electronegative substituents on unsymmetrically substituted diphosphenes both theoretically (HPPR) and experimentally ($R_\alpha P_\alpha P_\beta R_\beta$, R_α being an electronegative group) and found a decrease in the valence angle at the β-phosphorus. They attributed this effect to the importance of the close ion pair $(R_\beta P_\beta P_\alpha)^+R_\alpha^-$.[27]

In this paper, we report the results of ab initio self-consistent-field (SCF) and configuration interaction including single and double excitation (CISD) studies of the P_2F_2 molecule. We have located several stable structures and predicted their relative stabilities and spectroscopic properties. These results are compared to P_2H_2, which has been studied previously at comparable levels of theory.[14] As was done for P_2H_2, we have investigated three classes of structures. The first class has each phosphorus atom bonded to a fluorine and may be represented as FPPF. In the second class, both fluorine atoms are bonded to the same phosphorus, i.e., F_2PP. The third group has a dibridged linkage, $P(F_2)P$.

2. Theoretical Approach

We first located the stationary points for P_2F_2 and its parent radicals PF and PF_2 using analytical gradients[28-32] of the restricted self-consistent-field (SCF) method[33] in conjunction with a Huzinaga–Dunning–Hay[34-36] contracted double-ζ (DZ) Gaussian basis set. The contraction scheme is designated (9s5p/4s2p) for fluorine and (11s7p/6s4p) for phosphorus. The DZ SCF stationary points were characterized by analytic determination of the quadratic force constants and harmonic vibrational frequencies.[28,29,37] Infrared intensities were also evaluated.[38] We then repeated this SCF analysis using two larger basis sets, denoted DZP and TZ2P. The DZP basis set was obtained by augmenting the previously described DZ basis set with a set of six Cartesian d-like polarization functions on each of the atoms. The polarization function orbital exponents were $\alpha_d(P) = 0.5$ and $\alpha_d(F) = 1.0$. For the TZ2P basis set we used McLean and Chandler's[39] contraction scheme designated (12s9p2d/6s5p2d) for phosphorus and Dunning's[40] (10s6p2d/5s4p2d) contraction for fluorine. The polarization function orbital exponents for this basis set were $\alpha_d(P) = 1.0, 0.25$ and $\alpha_d(F) = 2.0, 0.5$.

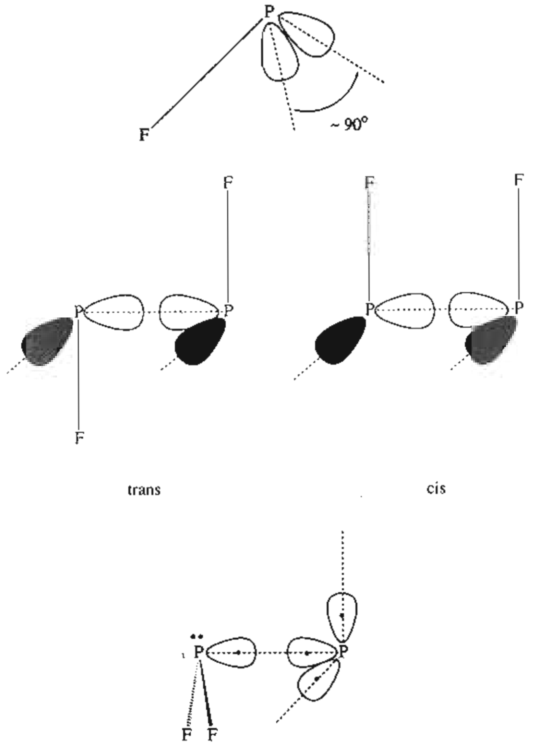

Figure 1. (a) Top: The two singly occupied orbitals of the radical PF. (b) Middle: Two interacting PF fragments oriented to form the trans and cis isomers of the FPPF molecule. (c) Bottom: PF_2 interacting with a phosphorus atom.

We would like to note at this point that the SCF frequencies are typically about 10% higher than experimentally determined frequencies due to the neglect of anharmonicity and other factors. We have chosen not to scale our frequencies (with the exception of the zero-point vibrational energy corrections, as noted below) since suitable scaling factors have not been determined. Breidung and Thiel[41] have determined scaling factors for the fluorophosphines at the SCF level using a 6-31G** basis set, which is similar to our DZP basis set. For example, for PF_3 they determined a scaling factor of 0.8281 for the PF stretching and 0.9195 for the FPF bending quadratic force constants.

The effect of electron correlation was evaluated by using the method of configuration interaction (CI).[42-44] Complete geometry optimizations were performed by using analytical derivative methods[28,29,45,46] and the DZP basis set. The DZP CI wave function included all single and double excitations from the SCF reference state (CISD). The four lowest lying occupied molecular orbitals (corresponding to the phosphorus and fluorine 1s-like molecular orbitals) and their four virtual orbital counterparts were excluded from the CI. The phosphorus 2s and 2p orbitals could also have been frozen, since they are also core orbitals, but we chose not to since they were significantly higher in energy than the 1s orbitals. Additionally, their virtual orbital counterparts were not appreciably higher in energy than the next lowest orbitals. The Hartree–Fock interacting spaces included 142 087, 142 087, 306 288, 308 350, 273 793, 142 989 and 71 235 configuration state functions for structures I–VII (see Figures 2–4), respectively. The CISD energies have been corrected to include the effects of unlinked quadruple excitations in an approximate manner by using Davidson's formula.[47] These corrected energies are designated CISD+Q.

For final energy comparisons, we have performed single-point TZ2P CISD energy determinations at the DZP CISD optimized geometries.

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Table I. Properties of the Radicals PF and PF_2, Predicted at Four Levels of Theory

		DZ SCF	DZP SCF	DZP CISD	TZ2P SCF	experiment
Total Energy (hartree)						
PF		−440.127 377	−440.171 123	−440.476 270	−440.213 179	
PF_2		−539.582 980	−539.689 273	−540.144 589	−539.741 819	
Bond Lengths (Å) and Bond Angles (deg)						
PF	r_e	1.702	1.597	1.622	1.578	1.590[a]
PF_2	r_e	1.679	1.581	1.602	1.563	1.579[b]
	θ_e	96.1	97.6	98.0	97.6	98.5[b]
Frequencies (cm^{-1}) and IR Intensities (km)						
PF	σ_g str	777 (119)	883 (169)		888 (171)	847[c]
PF_2	a_1 str	824 (130)	922 (168)		927 (162)	864[b]
	b_2 str	803 (163)	896 (224)		899 (212)	848[b]
	a_1 bend	338 (20)	394 (15)		407 (12)	365[b]
Net Charge (e) and Dipole Moment (D)						
PF	P	0.60	0.46	0.42	0.59	
	F	−0.60	−0.46	−0.42	−0.59	
	μ	2.72	1.46	1.47	1.05	
PF_2	P	0.92	0.89	0.83	1.17	
	F	−0.46	−0.44	−0.42	−0.59	
	μ	3.25	1.63	1.67	1.18	
Mulliken Valence						
PF	P	0.5	0.7	0.7	0.5	
	F	0.5	0.7	0.7	0.5	
PF_2	P	1.1	1.5	1.5	1.0	
	F	0.6	0.8	0.8	0.5	
Löwdin Valence						
PF	P	0.8	1.0	1.0	1.2	
	F	0.8	1.0	1.0	1.2	
PF_2	P	1.7	2.1	2.1	2.5	
	F	0.9	1.1	1.1	1.3	

[a] Reference 20. [b] Reference 24. The structural parameters here are r_0 and θ_0. [c] Reference 83.

As our "final predictions" of the relative energies, we have added the TZ2P SCF zero-point energy corrections (scaled by a factor of 0.9) to the TZ2P CISD relative energies.

3. Results

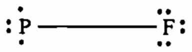
A. Structures and Properties of the "Parent" Radicals PF and PF_2.

Since FPPF and F_2PP can be considered as the products of the combination of two PF radicals and a PF_2 molecule with a P atom, we have also considered PF and PF_2 in our study. Although these molecules have already been considered theoretically,[48,49] it is important to use the same basis set and methodology when comparisons are made.

We first consider the combination of two PF molecules to form FPPF. PF has a $^3\Sigma^-$ ground state with an electron configuration given by

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^2$$

The Lewis electron dot structure[50,51] for this molecule looks like:



Hence, fluorine possesses a full octet, while a lone pair and two unpaired electrons are located on the phosphorus atom. According to VSEPR theory,[52] the P atom should exhibit sp^3 hybridization with the four hybrid orbitals directed at roughly tetrahedral angles toward the F, the lone pair, and the two unpaired electrons. Phosphorus, however, does not easily form sp hybrids.[53] Rather, phosphorus lone pairs are typically in orbitals of primarily 3s character, leaving the two unpaired electrons and the P–F bonding electrons in orbitals that are mostly of phosphorus 3p character (see Figure 1a). Hence two PF fragments can interact to form a central P–P double bond in either a cis or a trans fashion by forming σ and π bonds roughly perpendicular to the original PF molecular axis (Figure 1b).

The structure of PF_2 can also be easily understood by using simple concepts. The phosphorus atom in its ^4S ground state has a set of paired (3s) electrons and three unpaired (3p) electrons. Two of the unpaired electrons can form PF σ bonds by interacting with the unpaired electrons on the two fluorine atoms. The resulting PF_2 molecule has two PF single bonds. The phosphorus atom also has a lone pair and one remaining unpaired electron. The electronic ground state is then $^2B_1$, with an electron configuration of

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1^2 4b_2^2 7a_1^2 2b_1^2 1a_2^2 5b_2^2 8a_1^2 3b_1$$

VSEPR theory predicts tetrahedral sp^3 hybrid orbitals to accommodate this valence configuration. The tetrahedron should be somewhat distorted due to the nonbonding electrons on phosphorus, leading to a bent FPF structure with a bond angle a few degrees less than the tetrahedral angle of 109.5°. (For example, the bond angle in NF_2 is 103°.[54]) As mentioned above, however, the difficulty of mixing phosphorus s and p valence orbitals leads to lone pairs with significantly more s character than expected. Therefore, the PF bonding orbitals (and the orbital containing the unpaired electron) are predicted to have more p character, resulting in a bending angle significantly less than 109.5°. In fact, the experimentally determined FPF bond angle is 98.5°.[24]

To form the PPF_2 molecule, the $^2B_1$ state of the PF_2 molecule may combine with a ^4S P atom. In doing this, one of the unpaired phosphorus electrons forms a P–P σ bond with the unpaired electron of the PF_2 fragment. From the above discussion, the anticipated geometry of PPF_2 is pyramidal about the internal

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Table II. Relative (kcal/mol) Energies of Structures I–VII, with the Second Entry in the CISD Columns Being the Davidson Corrected Energy (CISD+Q) and the Total Energy (hartrees) Given for the Trans Isomer (I)[a]

structure	DZ SCF	DZP SCF	DZP CISD	TZ2P SCF	TZ2P CISD	final predictions[b]
I (*trans*-FPPF)	0.0	0.0	0.0 0.0	0.0	0.0 0.0	0.0
II (*cis*–FPPF)	3.4	1.6	1.9 1.4	0.7	1.0 1.1	1.2
III (skewed FPPF)	−5.2	10.0	19.6 23.4	10.7	19.1 22.4	21.8
IV (pyramidal $^3A''$ PF_2)	−17.5	−6.8	5.1 9.7	−5.6	4.5 8.5	8.4
V (pyramidal $^1A_1$ PPF_2)	27.4	37.8	45.7 48.6	38.1	44.1 46.0	46.1
VI (planar PPF_2)	34.0	18.2	17.0 17.3	14.7	13.2 13.3	13.4
VII (dibridged $P(F_2)P$)	49.6	106.6	110.6 112.2	114.1	116.1 116.8	115.3

[a] Total energy (hartrees) of the trans structure: DZ SCF, −880.230 509; DZP SCF, −880.378 575; DZP CISD, −880.981 855; DZP CISD+Q, −881.060 233; TZ2P SCF, −880.468 132; TZ2P CISD, −881.151 838; TZ2P CISD+Q, −881.242 222. [b] Obtained by adding zero-point vibrational corrections to the result of the Davidson-corrected TZ2P CISD predictions in the previous column; see text.

Table III. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol, in Parentheses) for Structures I–VII Predicted at Three Levels of Theory

structure	description		DZ SCF	DZP SCF	TZ2P SCF
I (*trans*-FPPF)	a_g	PF sym str	760 (0)	864 (0)	868 (0)
	b_u	PF asym str	772 (255)	859 (388)	865 (382)
	a_g	PP stretch	611 (0)	731 (0)	716 (0)
	a_g	PPF sym bend	298 (0)	340 (0)	338 (0)
	a_u	FPPF torsion	199 (24)	220 (10)	221 (5)
	b_u	PPF asym bend	176 (16)	195 (13)	195 (9)
II (*cis*-FPPF)	a_1	PF sym str	818 (123)	924 (213)	928 (217)
	b_2	PF asym str	772 (95)	853 (150)	858 (144)
	a_1	PP stretch	559 (2)	672 (23)	653 (17)
	b_2	PPF asym bend	352 (16)	408 (16)	410 (19)
	a_2	FPPF torsion	211 (0)	243 (0)	247 (0)
	a_1	PPF sym bend	162 (5)	173 (5)	165 (4)
III (skewed FPPF)	a	PF sym str	772 (80)	871 (139)	876 (144)
	b	PF asym str	760 (177)	849 (221)	851 (212)
	a	PP stretch	373 (3)	483 (4)	457 (3)
	b	PPF asym bend	207 (15)	274 (16)	276 (14)
	a	PPF sym bend	185 (<1)	219 (2)	215 (1)
	a	FPPF torsion	64 (9)	107 (3)	111 (2)
IV (pyramidal $^3A''$ PPF_2)	a'	PF sym str	801 (158)	893 (211)	898 (202)
	a''	PF asym str	791 (138)	883 (192)	886 (173)
	a'	PP stretch	379 (10)	493 (25)	471 (30)
	a'	PF_2 scissors	336 (19)	403 (19)	415 (14)
	a'	PF_2 wag	217 (11)	274 (9)	271 (7)
	a''	PF_2 twist	183 (2)	226 (3)	222 (2)
V (pyramidal $^1A'PPF_2$)	a''	PF asym str	794 (159)	885 (218)	891 (193)
	a'	PF sym str	792 (160)	882 (193)	889 (176)
	a'	PP str	406 (14)	530 (40)	511 (49)
	a'	PF_2 scissors	328 (17)	397 (14)	406 (9)
	a''	PF_2 twist	263 (6)	310 (9)	307 (4)
	a'	PF_2 wag	211 (8)	261 (4)	263 (2)
VI (planar PPF_2)	a_1	PF sym str	905 (135)	1065 (309)	1067 (330)
	b_2	PF asym str	846 (130)	949 (130)	960 (153)
	a_1	PP stretch	512 (17)	678 (21)	679 (12)
	a_1	PF_2 scissors	334 (27)	431 (30)	444 (32)
	b_2	PF_2 rock	198 (5)	268 (4)	278 (2)
	b_1	PF_2 wag	151i (<1)	200 (1)	235 (<1)
VII (dibridged $P(F_2)P$)	a_g	ring breathe	526 (0)	566 (0)	557 (0)
	b_{3u}	ring def	502 (553)	518 (597)	510 (603)
	b_{2u}	ring def	398 (107)	475 (103)	474 (90)
	a_g	ring bend	379 (0)	387 (0)	394 (0)
	b_{1g}	ring def	211 (0)	131 (0)	112 (0)
	b_{1u}	ring pucker	119 (17)	71 (4)	36 (1)

phosphorus atom, and the PPF angle is expected to be roughly the same as the FPF angle of PF_2 (see Figure 1c). The ground electronic state should be of $^3A''$ symmetry.

Our results for the PF and PF_2 molecules are collected in Table I. As expected, the DZ basis set yields poor geometries, with the DZ SCF equilibrium bond lengths much too long. Addition of one set of polarization functions largely corrects this deficiency. This phenomenon has been described for the P_2H_2 system[10,11,14,15] and in fact is quite general.[55] Because of the known weakness

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(55) Schaefer, H. F. *Electronic Structure of Atoms and Molecules*; Addison-Wesley Publishing Co.: Reading, MA, 1972; pp 75–78.

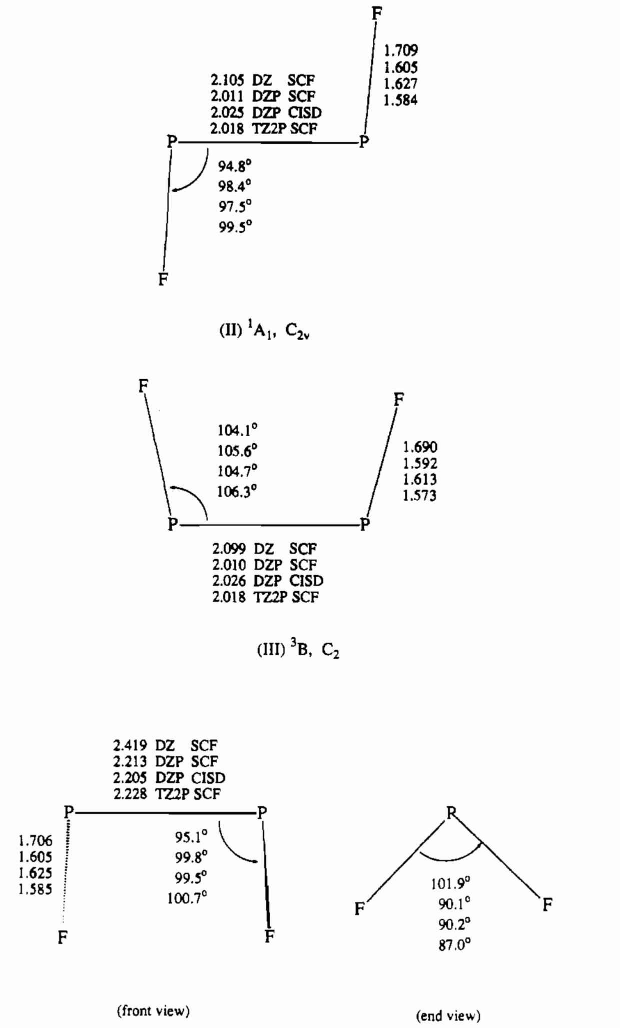


Figure 2. Theoretical prediction of the equilibrium geometries for FPPF structures. Bond distances are in Å and angles in deg.

of the DZ basis set, we will omit discussion of the DZ SCF results in the rest of the text, although these results are included in the tables and figures. Our DZP SCF, DZP CISD, and TZ2P SCF geometries agree well with the experimentally determined structures of PF$_2$ (r_e = 1.579 Å and θ_e = 98.5°[24]) and PF (r_e = 1.590 Å[20]).

B. Energy Minimia of FPPF. We have found three energy minima for the FPPF class of structures, namely, trans (I), cis (II), and skewed (III) conformations. The cis and trans isomers have closed-shell singlet electronic states (as predicted from the combination of two PF fragments) while the skewed isomer has a triplet electronic state. The relative energies of these structures are reported in Table II, and Table III contains the predicted harmonic vibrational frequencies and infrared intensities. Other molecular properties, such as dipole moment and charge distribution, are given in Table IV. Optimized geometries are depicted in Figure 2.

The trans (I) structure is the lowest in energy among the FPPF isomers at all levels of theory except DZ SCF. The planar configuration was predicted based on the electronic structure of the "parent" radical PF. A planar trans configuration is favored over a planar cis configuration due to the repulsive interaction of the partially negative fluorines in the cis orientation. The trans isomer has a ^1A_g ground electronic state arising from the electronic configuration

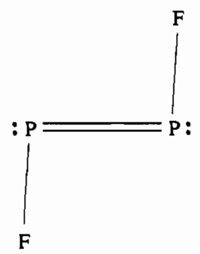
$$(\mathrm{core})6a_g^2 6b_u^2 7a_g^2 7b_u^2 8a_g^2 8b_u^2 2a_u^2 2b_g^2 9a_g^2 9b_u^2 10a_g^2 3a_u^2$$

The two highest occupied orbitals ($10a_g$ and $3a_u$) are substantially localized on the phosphorus atoms and are of σ- and π-bonding character, respectively. The $10a_g$ is weakly σ bonding between all of the atoms and has large lobes directed away from the P–P bond. Therefore it may be assigned as the n_+ (in-phase lone pair) orbital. The $10a_g$ and $3a_u$ orbitals are quite close in energy (ϵ = −0.3899 and −0.3581 au, respectively), and the lowest occupied molecular orbital (LUMO) is the P–P π^* ($3b_g$). This situation is analogous to *trans*-P$_2$H$_2$.

Table IV. Properties of Structures I–VII, Predicted by DZ SCF (First Row), DZP SCF (Second Row), DZP CISD (Third Row), and TZ2P SCF (Fourth Row) Levels of Theory

	I	II	III	IV	V	VI	VII
Dipole Moment (D)							
	0.0	3.83	3.09	3.43	3.38	2.41	0.0
	0.0	1.87	1.72	1.57	1.53	0.16	0.0
	0.0	1.98	1.77	1.66	1.61	0.14	0.0
	0.0	1.24	1.25	1.18	1.05	0.54	0.0
Net Charge (e)							
P$_1$	0.59	0.56	0.59	1.02	1.03	0.91	0.66
	0.47	0.45	0.46	0.89	0.89	0.87	0.55
	0.45	0.42	0.44	0.84	0.85	0.82	0.52
	0.59	0.59	0.59	1.18	1.20	1.17	0.56
P$_2$	0.59	0.56	0.59	0.14	0.13	0.11	0.66
	0.47	0.45	0.46	0.02	0.02	−0.09	0.55
	0.45	0.42	0.44	0.03	0.03	−0.08	0.52
	0.59	0.59	0.59	−0.01	−0.02	−0.03	0.56
F	−0.59	−0.56	−0.59	−0.58	−0.58	−0.51	−0.66
	−0.47	−0.45	−0.46	−0.46	−0.46	−0.39	−0.55
	−0.45	−0.42	−0.44	−0.44	−0.44	−0.37	−0.52
	−0.59	−0.59	−0.59	−0.59	−0.59	−0.57	−0.56
Mulliken Valence							
P$_1$	2.4	2.4	1.5	2.1	2.1	3.0	0.5
	2.7	2.7	1.7	2.5	2.6	4.1	0.6
	2.6	2.6	1.7	2.5	2.5	4.0	0.7
	2.6	2.6	1.6	2.2	2.2	3.9	0.6
P$_2$	2.4	2.4	1.5	1.0	1.0	2.0	0.5
	2.7	2.7	1.7	1.0	1.1	2.5	0.6
	2.6	2.6	1.7	1.0	1.0	2.4	0.7
	2.6	2.6	1.6	1.1	1.1	2.7	0.6
F	0.6	0.6	0.5	0.6	0.6	0.7	0.5
	0.7	0.8	0.7	0.8	0.8	0.9	0.6
	0.7	0.8	0.7	0.8	0.8	0.9	0.7
	0.5	0.5	0.5	0.5	0.5	0.6	0.6
Löwdin Valence							
P$_1$	2.9	3.0	1.9	2.7	2.8	3.8	1.0
	3.1	3.1	2.2	3.2	3.2	4.7	1.2
	3.0	3.0	2.1	3.1	3.1	4.5	1.2
	3.4	3.4	2.5	3.6	3.7	5.2	1.5
P$_2$	2.9	3.0	1.9	1.1	1.2	2.5	1.0
	3.1	3.1	2.2	1.2	1.3	2.8	1.2
	3.0	3.0	2.1	1.1	1.2	2.6	1.2
	3.4	3.4	2.5	1.3	1.4	2.9	1.5
F	0.9	0.9	0.9	0.9	0.9	1.0	1.0
	1.1	1.1	1.0	1.1	1.1	1.2	1.2
	1.1	1.1	1.0	1.1	1.1	1.2	1.2
	1.3	1.4	1.3	1.4	1.4	1.5	1.5

Structurally, our theoretical predictions for *trans*-FPPF are qualitatively as expected. The P–P bond length (2.018 Å, TZ2P SCF) is comparable to the known P–P double bond lengths in substituted diphosphenes (2.004–2.034 Å),[2] and the PPF bond angle is typical of divalent phosphorus (≈95–100°). Thus the valence structure of *trans*-FPPF is well represented by the Lewis electron dot picture



where the phosphorus lone-pair orbitals are primarily of phosphorus 3s character.

The cis structure (II) may be thought of as a rotamer of the trans structure (I) where one of the PF bonds has been rotated around the PP bond by 180°. Energetically we find it to lie less than 4 kcal/mol above the trans isomer (I), with our "best guess" being 1.2 kcal/mol. Electron correlation does not appreciably affect this energy difference [ΔE(cis–trans) is 1.6 kcal/mol at the DZP SCF level and 1.4 kcal/mol at the DZP CISD+Q level], but improving the basis set from DZP to TZ2P decreases the relative energy by 0.9 kcal/mol with the SCF and CISD methods and 0.3 kcal/mol with the CISD+Q method. The cis electronic state is of $^1A_1$ symmetry, with the electron configuration

$$(\mathrm{core})6a_1^2 6b_2^2 7a_1^2 7b_2^2 8a_1^2 2b_1^2 9a_1^2 2a_2^2 8b_2^2 9b_2^2 10a_1^2 3b_1^2$$

The bonding character is essentially the same as in the trans configuration, and geometrically, the only major change is an opening in the FPP angle of about 7° as the negatively charged fluorines move away from each other. According to the Mulliken analysis (see Table 4) each fluorine atom has a net charge of about $-^1/_2|e|$.

The lowest skewed structure (III) is a ^3B state, with the electron configuration given by

$$(\mathrm{core})7a^2 7b^2 8a^2 8b^2 9a^2 9b^2 10a^2 10b^2 11a^2 11b^2 12a^2 12b 13a$$

This electron occupation correlates with a $\pi \rightarrow \pi^*$ excitation from either the trans (I) or cis (II) structure, and results in an unpaired electron on each phosphorus atom. Thus there is no P–P π bond in this structure. In fact, the P–P bond is about 0.2 Å longer than that for the other two FPPF isomers (I and II), which have double bonds, and it is similar to the experimentally determined P–P single bond in H_2PPH_2 (2.219 Å).[56] We find the FPP angle to be about 100° while the FPPF torsional angle is very close to 90°. The torsional angle can be rationalized by the fact that the unpaired electrons of the same spin which are localized on adjacent phosphorus centers can avoid each other by occupying perpendicular orbitals.

Although the SCF method predicts that the skewed ^3B structure (III) is about 10 kcal/mol higher in energy than the trans isomer, at the CISD+Q level of theory the energy difference is 23.4 kcal/mol with the DZP basis set and 22.4 kcal/mol with the TZ2P basis set (our "best guess") is 21.8 kcal/mol). Since the energy of the cis isomer relative to the trans did not change appreciably, electron correlation is seen to stabilize the doubly bonded isomers preferentially. This preferential stabilization of the doubly bonded isomers by the CISD method is expected since it introduces the $\pi^2 \rightarrow \pi^{*2}$ pair correlation energy of the π bond, which is not accounted for in the SCF wave function. In contrast, the correlation energy of the unpaired electrons of the twist isomer is much smaller. The ^3B state should have a singlet analogue, which may be reasonably low in energy.

C. Energy Minima of PPF_2. Structures in this group can be viewed as the conjunction of a PF_2 fragment with a phosphorus atom. On the basis of the above analysis of the electronic structure of PF_2, we qualitatively predicted that the lowest energy PPF_2 moiety should be a triplet pyramidal structure with the two unpaired electrons on the terminal P atom. In fact, three energy minima of the form PPF_2 were found in this work—namely, two pyramidal (IV and V) and one planar (VI). Their optimized geometries are shown schematically in Figure 3. Relative energies, harmonic vibrational frequencies, and other properties predicted by this work are collected in Tables II–IV, respectively.

The lowest energy PPF_2 structure is the pyramidal structure IV, a $^3A''$ state. The electron configuration of this state is given by

$$(\mathrm{core})10a'^2 4a''^2 11a'^2 12a'^2 5a''^2 13a'^2 14a'^2 6a''^2 7a''^2 15a'^2 16a'^2 8a'' 17a'$$

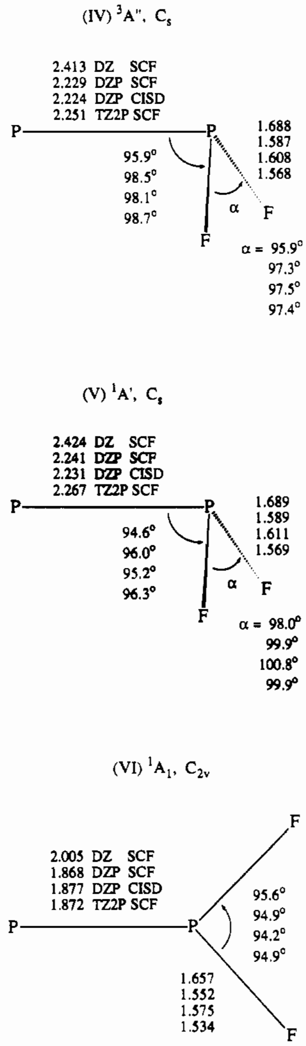


Figure 3. Theoretical prediction of the equilibrium geometries for PPF_2 structures. Bond distances are in Å and angles in deg.

From the molecular orbital analysis, the central P atom (hereafter designated P_1) has two σ bonds to fluorine, a σ bond to the terminal P atom (hereafter designated P_2), and a lone pair. The PPF angle is predicted to be about 98° while the FPF angle is 97° (nearly unchanged in comparison with the angle in PF_2). The PP bond length (2.229, 2.224, and 2.251 Å at the DZP SCF, DZP CISD, and TZ2P SCF levels of theory) is consistent with a single bond. We predict structure IV to be 8.4 kcal/mol above the lowest FPPF isomer (trans, I), although we note that the SCF method predicts IV to be 6–7 kcal/mol below I. The $^3A''$ state (IV) should have a singlet analogue, which may be reasonably low in energy.

Structure V is the result of forcing the two unpaired electrons of structure IV to doubly occupy the 17a′ orbital, yielding a $^1A'$ state. The two pyramidal PPF_2 isomers (IV and V) are quite similar in their structural and other properties, as can be seen in Figure 3 and Tables III and IV. Energetically, however, the singlet structure V is about 40 kcal/mol higher in energy than the triplet structure IV.

The most interesting of the PPF_2 stationary points is the planar singlet isomer, structure VI. It is a $^1A_1$ state with an electron configuration represented by

$$(\mathrm{core})8a_1^2 4b_2^2 9a_1^2 10a_1^2 5b_2^2 3b_1^2 11a_1^2 1a_2^2 6b_2^2 12a_1^2 4b_1^2 7b_2^2$$

This electron configuration arises by forcing the 8a″ orbital in structure IV to be doubly occupied. As several authors have pointed out for the related P_2H_2 system,[9,16,17] this conformer has the potential for a P–P triple bond. Our data suggest that there may indeed be a P–P triple bond. The P–P bond length (1.868, 1.877, and 1.872 Å at the DZP SCF, DZP CISD, and TZ2P SCF levels of theory) is 0.35–0.38 Å shorter than the single bond of

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structure IV and 0.14–0.15 Å shorter than the double bond of the trans structure (I). For comparison, we determined the equilibrium bond length of the triply bonded P_2 molecule at the TZ2P SCF level of theory. We obtained a bond length of 1.858 Å, only 0.014 Å shorter than the PPF_2 P–P bond. The Mulliken[57–59] and Löwdin[60,61] valences provide additional support for a P–P triple bond, although these analyses are not expected to give absolute numerical accuracy and therefore should be viewed cautiously. Certainly the valences are not expected to yield integral values as anticipated from a simplistic freshman chemistry bonding picture since bonds do not form in discrete units. Theoretically, a triple P–P bond in structure VI would yield a valence of 5 for P_1 and 3 for P_2. Both P atoms of structures I (trans) and II (cis) and atom P_1 of structures IV and V formally have a valence of 3, and we note that the predicted values are similar to those for atom P_2 of structure VI. Additionally, the ratio of the valence of P_1 and that of P_2 in structure VI is always nearly 5/3.

Further support for a P–P triple bond in structure VI is provided by the SCF harmonic vibrational frequencies. At first it may seem odd that the P–P stretch frequency (678 cm^{-1} for DZP SCF; 679 cm^{-1} for TZ2P SCF) is lower than that for the doubly bonded trans (I) isomer and only slightly greater than for the cis (II) isomer. A comparison can be made with the P_2 molecule. At the TZ2P SCF level of theory, we found it to have a harmonic vibrational frequency of 899 cm^{-1}. (Raghavachari, Haddon and Binkley[62] obtained a value of 908 cm^{-1} and the experimental frequency is 781 cm^{-1}.[63]) Because of mass effects and mixing of modes of the same symmetry, however, the harmonic vibrational frequencies are not a direct indicator of bond strength. Having both fluorines at one end of the molecule is expected to lower the P–P stretch frequency. Additionally, the potential energy distribution indicates that the P–P stretch mode of PPF_2 has significant contribution (≈25%) from the higher energy symmetric P–F stretch. This also would decrease the frequency of the P–P stretch. A comparison of the diagonal component of the quadratic force constants is perhaps a better indication of bond strength since this eliminates both the mode mixing and the mass effect. At the TZ2P level of theory, the force constant for the P–P stretch mode is 7.4 mdyn/Å for P_2, 5.1 mdyn/Å for planar PPF_2, and 4.2 mdyn/Å for *trans*-FPPF. If we accept P_2 and *trans*-FPPF as prototypical triple and double P–P bonds, the force constant for planar PPF_2 is 40% of the way from a double to a triple bond. This might suggest that the bond order of the P–P bond is perhaps 2.5 at the most. If bond length and valence are used as the criteria for bond strength, on the other hand, a bond order near 3 is certainly warranted. From this data, therefore, we can conclude that the P–P bond in planar PPF_2 is significantly more than a double bond, although we cannot absolutely say that it is a triple bond.

Since multiple bonds between higher main-group elements are typically relatively weak, it is not surprising that this isomer is higher in energy than the doubly bonded trans (I) and cis (II) structures, which are also singlets. Compared to the $^3A''$ structure IV, which is the most stable of the PPF_2 structures studied, structure VI is 25.0 and 20.3 kcal/mol higher in energy at the DZP SCF and TZ2P SCF level of theory. At the correlated DZP CISD+Q and TZ2P CISD+Q levels, however, this energy difference drops to 7.6 and 4.8 kcal/mol, respectively, which is expected due to the π-bonding character of structure VI. Because of the low-lying π^* orbitals, the $\pi^2 \rightarrow \pi^{*2}$ excitations afford considerable correlation energy to the multiply bonded isomers, I, II and VI. This can be seen in the CISD wavefunctions. While all of the isomers have a leading coefficient (c_0, corresponding to the SCF reference function) of ≈0.93, the isomers containing π bonds have a larger coefficient for the second most important configuration state function (c_1). The singly bonded structures have $c_1 \approx 0.03$–0.04 while the multiply bonded structures have $c_1 \approx 0.06$–0.07, corresponding to the $\pi^2 \rightarrow \pi^{*2}$ excitation. Our "best guess" for the energy of structure VI relative to trans I is 13.4 kcal/mol. It should also be noted that the pyramidal $^1A'$ structure (V) corresponds to a double excitation of structure VI ($4b_2^{\,2} \rightarrow 7b_1^{\,2}$).

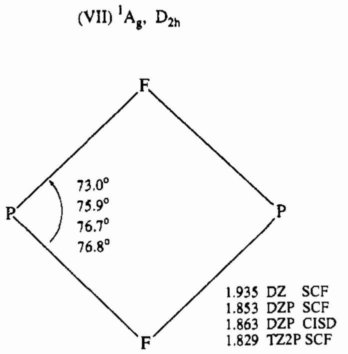

Figure 4. Theoretical prediction of the equilibrium geometry of planar dibridged $P(F_2)P$.

D. The Dibridged Structure. A doubly bridged structure (VII), shown in Figure 4, was located as well. It has a planar D_{2h} configuration and a $^1A_1$ electronic ground state, arising from the electron configuration

$$(\text{core})1b_{1u}^{\,2}5a_g^{\,2}3b_{2u}^{\,2}4b_{3u}^{\,2}6a_g^{\,2}2b_{1g}^{\,2}2b_{1u}^{\,2}1b_{3g}^{\,2}4b_{2u}^{\,2}7a_g^{\,2}5b_{3u}^{\,2}3b_{1u}^{\,2}$$

The long P–P separation (≈2.9 Å) indicates that there is no direct bonding between the phosphorus atoms. Vibrational frequency analysis indicates that this structure is indeed a local minimum on the singlet potential energy surface, although energetically it is not very favorable. It is more than 100 kcal/mol higher in energy than the low-lying isomers IV, I, and II. Preliminary investigation into open-shell states indicated that they are considerably (i.e., >50 kcal/mol) higher in energy than the closed-shell state. The high energy of the dibridged isomer for both P_2F_2 and P_2H_2 is in contrast to Si_2H_2,[84] where the global minimum is a nonplanar dibridged structure and a planar dibridged structure is a low-lying transition state.

4. Discussion

A. Hypervalency—d-Orbital Participation. There have been several models proposed to explain hypervalency. The traditional interpretation of hypervalent compounds of the second-row and higher row non-metals, such as PCl_5, SF_6, I_3^-, $SeCl_4$, and XeF_2, employs sp^3d and sp^3d^2 hybridization.[64–68] Other, nontraditional, models explain hypervalency without invoking d-orbital participation.[69–74] A common feature of these models is the requirement that the terminal atoms be electronegative. Most are related in that they propose the filling of nonbonding orbitals that are localized on the terminal atoms as well as filling the bonding molecular orbitals. Negative hyperconjugation[75] is a somewhat different picture that involves the delocalization of electrons into

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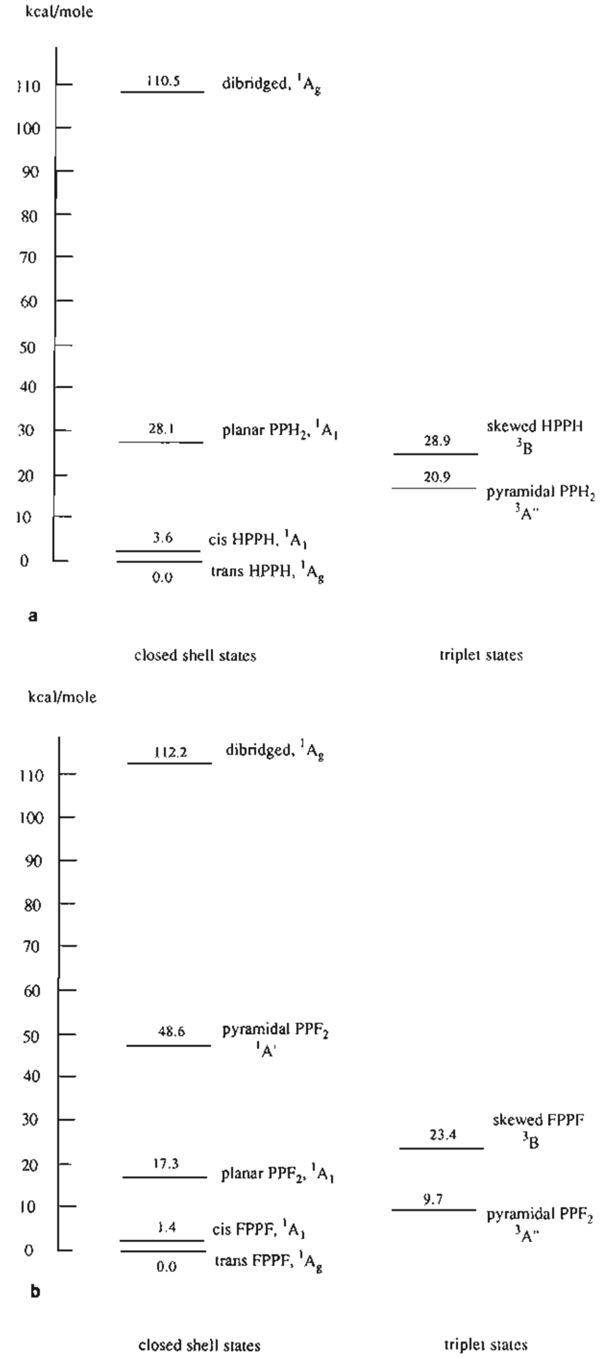
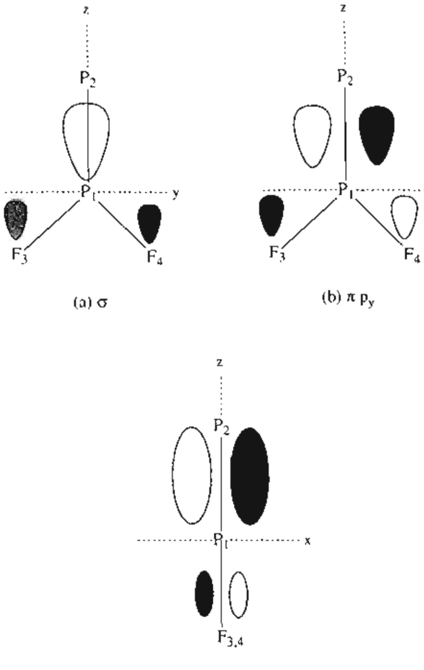


Figure 5. DZP CISD+Q relative energies for several isomers of (a) P_2H_2[14] and (b) P_2F_2 (this work).

vacant antibonding orbitals. This model has been used, for example, to explain the bond-shortening effect of the $-CF_3$ substituent.[76] A good example is the F_3CO^- ion,[77-80] which has a rather short C–O bond due to delocalization of oxygen lone-pair electrons into C–F σ^* orbitals.

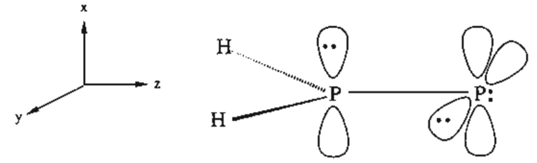
The planar PPF_2 $^1A_1$ structure (VI), if it indeed has a triple bond as we are suggesting, is hypervalent. The central phosphorus atom has a valence of 5. Previous discussion on the possible triple bond character of molecules analogous to structure VI has explained this hypervalent nature by invoking back-delocalization of the π lone pair on the terminal atom into the low-lying d_π orbital on the central phosphorous atom (traditional interpretation). For example, Schmidt and Gordon[16] describe a possible P–P triple bond in PPH_2 in the following way. They first consider only a σ framework



(a) σ (b) π p_y

(c) π p_x

Figure 6. DZP SCF orbitals involved in the P–P bond of structure VI: (a) σ; (b) π p_y; (c) π p_x.



where the central P has a lone pair of electrons in its p_x orbital. The terminal P has a lone pair in its σ orbital and a second lone pair in the p_y orbital. The electronic state shown above thus has a single P–P σ bond. The p_π lone pair on the central P atom can delocalize into the empty p_x orbital on the terminal P atom (out-of-plane delocalization), while the p_π lone pair on the terminal P atom can delocalize into the d_{yz} orbital on the central P (in-plane delocalization), thus yielding potentially two P–P π bonds for a total bond order of 3.

As it turns out, the P–P bond in $^1A_1$ PPH_2 appears to be slightly more than a double bond, having an out-of-plane π bond and only a small amount of in-plane delocalization. The P_2F_2 molecule, on the other hand, has a much shorter P–P bond (by 0.08 Å). The fact that the PF bonds in P_2F_2 are much more polar than the PH bonds in P_2H_2 and that only P_2F_2 exhibits hypervalency supports the nontraditional view of hypervalency for higher row non-metals. Additionally, the SCF wave functions for the $^1A_1$ PPF_2 structure VI in the present work shows that the role of the d orbitals of P_1 in the in-plane p_π bond is less significant than that of the p orbitals. According to the Mulliken gross orbital populations,[81,82] the central atom P_1 has a total d-orbital occupancy of 0.65 (primarily in d_{z^2} and d_{yz}) as compared to 0.10 for the terminal atom P_2. Although the d-orbital occupation on P_2 is significant, it is not large enough to alone account for the triple-bond character. To illustrate the bonding responsible for the P–P triple bond, the three molecular orbitals involved are shown schematically in Figure 6. These

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Table V. Comparison of P_2R_2 (R = H, F) Geometric Parameters (DZP SCF Results) with Bond Lengths in Å and Bond Angles in deg

structure	param	R = H[a]	R = F[b]
I (*trans*-RPPR)	r(PP)	2.004	2.011
^1A_g	β(RPP)	96.0	98.4
II (*cis*-RPPR)	r(PP)	2.010	2.010
$^1A_1$	β(RPP)	100.9	105.6
III (skewed RPPR)	r(PP)	2.209	2.213
^3B	β(RPP)	96.0	99.8
	τ(RPPR)	89.8	90.1
IV (pyramidal PPR_2)	r(PP)	2.218	2.229
$^3A''$	α(RPR)	95.4	97.3
	β(RPP)	97.6	98.5
VI (planar PPR_2)	r(PP)	1.943	1.868
$^1A_1$	α(RPR)	105.4	94.9
VII (dibridged $P(R_2)P$)	r(PP)	2.457	2.922
^1A_g	α(RPR)	71.0	75.9

[a] Reference 14. [b] This work.

illustrations show that the third bond arises primarily from in-plane p_π bonding between the phosphorus atoms. While it is true that this orbital is polarized toward the terminal phosphorus, significant delocalization is apparent.

The triple bond character of planar PPF_2 is perhaps most easily understood, however, from the negative hyperconjugation point of view. The p_y lone pair of P_2 can delocalize into the P–F σ^* orbital of the appropriate symmetry (b_2). This delocalization shortens the P–P bond and concentrates electron density on the electronegative fluorine atoms. The negative hyperconjugation becomes important for fluorine substituted molecules (as opposed to hydrogen substituents) because the large electronegativity of fluorine creates ionic bonds that have lower σ^* orbitals.

B. Comparison with P_2H_2. In a comparison of the present results of P_2F_2 with previous work on P_2H_2, the only significant qualitative change in either the singlet or triplet potential energy surface is the presence of a dibridged minimum for P_2F_2. Allen et al.[14] located a dibridged stationary point for P_2H_2, but at the DZP SCF level of theory, it had an imaginary vibrational frequency leading to a puckered ring form. Otherwise the singlet and triplet potential energy surfaces of the two molecules are quite similar. On the singlet potential energy surface, both molecules have *cis*- and *trans*-RPPR (R = H or F) isomers that are close in energy (both P_2H_2 and P_2F_2 prefer the trans form) and a planar PPR_2 structure higher in energy (28.1 kcal/mol for P_2H_2[14] and 17.3 kcal/mol for P_2F_2 relative to trans at DZP CISD+Q). For the triplet spin states, both molecules have a pyramidal PPR_2 and a skewed RPPR structure as the lowest two states, with the pyramidal isomer being lower in energy. For P_2H_2 the skewed isomer is 8.0 kcal/mol higher in energy[14] while for P_2F_2 it is 13.7 kcal/mol (DZP CISD+Q). Figure 5 illustrates the DZP CISD+Q relative energies of the isomers of P_2H_2 and P_2F_2 discussed in this paper.

The most significant effect of fluorine substitution is stabilization of the PPF_2 isomers with respect to the FPPF isomers. Planar PPH_2 and $^3A''$ pyramidal PPH_2 have energies relative to *trans*-HPPH of 28.1 and 20.9 kcal/mol (respectively; DZP CISD)[14] while the corresponding structures for P_2F_2 have relative energies of 17.3 and 9.7 kcal/mol (respectively; DZP CISD). Negative hyperconjugation, as discussed above with respect to the hypervalency of structure VI, can also be invoked to explain these energy changes. Similar factors come into play for structure IV, whose (p-type) unpaired electrons on the terminal phosphorus (P_2) can interact with the P–F antibonding orbitals. These interactions are "turned off" in the *cis*- and *trans*-FPPF structures, since the lone pairs are not oriented in positions allowing such delocalizations.

A smaller effect is the decreased relative energy of the skewed ^3B isomer, which has a relative energy of 28.9 kcal/mol for HPPH and 23.4 kcal/mol for FPPF. The π-type orbitals of fluorine, which are not available on hydrogen, are most likely responsible for this change. The skewed isomer represents a $\pi_{PP} \rightarrow \pi_{PP}^*$ excitation from the trans ground state. For *trans*-FPPF, both of these orbitals have significant π_{PF}^* character whereas the π and π^* orbitals of HPPH are located exclusively on the phosphorus atoms.

Because fluorine is more electronegative than hydrogen, Bent's rules[25] predict the PF bonds in P_2F_2 to have more p character than the PH bonds in P_2H_2. This would lead, for example, to smaller FPP angles in the FPPF structures. In Table V, we compare equivalent geometric parameters for the seven valence isomers of P_2F_2 and their P_2H_2 analogues (P_2H_2 data taken from ref 14). It is clear that structurally the P_2R_2 isomers are quite similar for R = H, F. The only large change is in the planar $^1A_1$ PPR_2 structure where $\alpha_{FPF} = 94.9°$ and $\alpha_{HPH} = 105.4°$—a 10° difference. Also, in the *cis*-FPPF structure (II), the FPP angle is about 5° larger than the equivalent HPP angle. Although this change contradicts Bent's rules, it is understandable due to the large dipolar character of the PF bonds. The usual geometric effects of fluorine substitution apparently are not observed in this case since the PH bonds already have a large amount of p character due to phosphorus's propensity for lone-pair orbitals with large s character.

Fluorine substitution also obviously gives rise to more ionic bonding in P_2F_2 that in P_2H_2. The large electronegativity differnce between phosphorus and fluorine leads to large charge separation in the various isomers of P_2F_2 (see Table IV for net charges). For all seven of the structures studied, each fluorine atom has about $^1/_2|e|$ charge while the two phosphorus atoms share a $+1|e|$ charge. This leads to ionic PF bonds and sizable dipole moments for the noncentrosymmetric isomers (the largest is 1.25 D at the TZ2P SCF level for the skewed structure, III).

5. Conclusions

We have located seven minima of P_2F_2—five singlet structures (I, II, V, VI, and VII) and two triplet structures (III and IV). Structures I (*trans*-FPPF) and IV (pyramidal PPF_2) are the global minima for the singlet and triplet potential energy surfaces, respectively. We have determined that structures III–V incorporate P–P single bonds and that structures I and II contain P–P double bonds. Structure VI may quite possibly have a P–P triple bond, although our findings do not consistently support this conclusion. The bond length and valence analysis argue strongly in favor of a triple bond, but the quadratic force constant indicates a bond order of perhaps 2.5. One might, however, give the most credence to the bond length, since it is the only one of the three criteria that is physically observable. The dibridged structure VII has no direct P–P bonding and is very high lying energetically. The triple-bond character in structure VI results in a hypervalent central phosphorus atom, a finding that has been interpreted by using ionic resonance structures and some d-orbital participation.

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