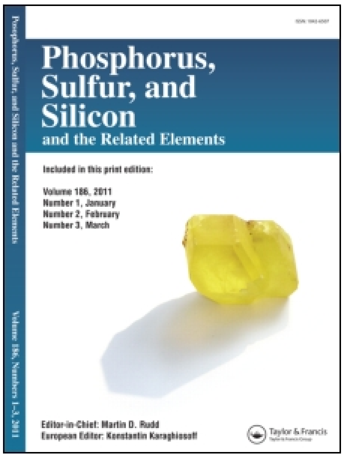

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Theoretical Study and Comparasion of Bent's Rule with Hardness and Polarizibility for SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 Molecules

Fatma Kandemirli[a]; Meral Hoscan[b]; Anatoly Dimoglo[c]; Seval Esen[b]
[a] Department of Chemistry, Kocaeli University, Izmit, Turkey [b] Department of Physics, Kocaeli University, Izmit, Turkey [c] Institute of Applied Physics, Academy of Sciences, Moldova

To cite this Article Kandemirli, Fatma , Hoscan, Meral , Dimoglo, Anatoly and Esen, Seval(2008) 'Theoretical Study and Comparasion of Bent's Rule with Hardness and Polarizibility for SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 Molecules', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 8, 1954 — 1967

To link to this Article: DOI: 10.1080/10426500701839577

URL: http://dx.doi.org/10.1080/10426500701839577

Phosphorus, Sulfur, and Silicon, 183:1954–1967, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701839577

Theoretical Study and Comparasion of Bent's Rule with Hardness and Polarizibility for SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 Molecules

Fatma Kandemirli,[1] Meral Hoscan,[2] Anatoly Dimoglo,[3] and Seval Esen[2]
[1]Department of Chemistry, Kocaeli University, Izmit, Turkey
[2]Department of Physics, Kocaeli University, Izmit, Turkey
[3]Institute of Applied Physics, Academy of Sciences, Moldova

Electronic parameters such as HOMO-LUMO energies, Mulliken charges, dipole moments for different isomers of SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 molecules have been carried out at the MP2 level of theory using 6-31G(d), 6-311G(d,p) basis sets by applying Gaussian 03 Revision B-04. Maximum hardness and minimum polarizability have been calculated to see the consistency with the Bent rule. According to Maximum Hardness Principles (MHP) and Minimum Polarizability Principles (MPP) most stable structure can be predicted if they have different isomers. We have investigated how bond orbitals change for studied molecules by natural bond orbital (NBO) analysis, as well. There is agreement between our results and experimentaql results on the dipole moments and structures of the phosphorus chlorofluorides obtained by IR and Raman vibrational data, NMR measurements and ^{35}Cl pure quadrupole resonance frequencies reported earlier by Holmes aand coworkers.

Keywords IR; maximum hardness; minimum polarizibility; MP2; NBO

INTRODUCTION

Bent's rule,[1,2,3,4] that is expressed as, atomic *s* character's tendency to concentrate in orbitals that are directed toward electropositive groups and atomic *p* character's tendency to concentrate in orbitals that are directed toward electronegative groups, has proved to be useful in explaining many aspects of the structural chemistry of organic and inorganic compounds,[5] accordance with the maximum hardness and minimum polarizibility principles.[6]

Received 13 August 2007; accepted 13 September 2007.

Address correspondence to Dr. F. Kandemirli, Department of Chemistry, Kocaeli University, Umuttepe Kocaeli, Turkey. E-mail: fkandemirli@yahoo.com

Grim et al.[7] have reported an apparent exception to Bent's rule, and, on the basis of this and other considerations, the Rule was modified in terms of orbital energy matching and overlap: "The *p* character tends to concentrate in orbitals with weak covalency (arising from either electronegativity or overlap considerations), and *s* character tends to concentrate in orbitals with strong covalency (matched electronegativities and good overlap)."[8]

MHP[9,10,11] and MPP[12] principles are among the most widely accepted electronic structure principles of chemical reactivity and validity for nontotally symmetric vibrations.[13]

The absolute hardness of a chemical species is given as following by

$$\eta = 1/2\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon} \tag{1}$$

where E is the electronic energy; N is the number of electrons; and υ is the external potential due to the nuclei. Absolute hardness is an important property, which measures both the stability and reactivity of a molecule.[14,15,16] In molecular orbital theory, e.g., Hartree-Fock theory or Huckel theory, it is given as following,

$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2. \tag{2}$$

Equation (2) is a good approximation as first emphasized by Pearson.[17] In this paper, we have taken Equation (2) as our working definition of hardness. If we make the usual diagram of the MOs of a molecule as a function of their energies, η is just half the energy gap between HOMO and LUMO.[7]

It has been suggested that the hardness is inversely proportional to the electric dipole polarizability (α). The electric dipole polarizability is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy.

$$\alpha = \left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \quad a, b = x, y, z$$

Its mean value is given in Equation (3):

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{xx} + \alpha_{zz}). \tag{3}$$

The DFT based reactivity descriptors hardness and polarizability are used as reactivity indices to predict the stability sequences of axial and equatorial isomers of SF_4, F_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 compounds using the maximum hardness and minimum polarizability principles (MHP and MPP) by Noorizadeh.[6] Huckel-type molecular orbital calculations were carried out. Stabilization of certain isomers occurs because of σ bonding and is not due to more favorable π bonding or d-orbital participation, although both are present to some extent.[18]

The infrared, Raman,[19]F NMR and ^{35}Cl pure nuclear quadrupole resonance spectra for PCl_4F, PCl_3F_2, PCl_2F_3, and $PClF_4$ were studied previously by Holmes and coworkers and it was found that the spectra of PCl_4F were interpreted in terms of C_{3v}, that of PCl_3F_2 is D_{3h}, that of PCl_2F_3 is C_{2v} and that of $PClF_4$ is C_{2v}.[19–22] Also, they studied atomic polarization, dielectric properties, and electric dipole moments of PCl_4F, PCl_3F_2, and PCl_2F_3.[19,23–24] Most of this experimental data was summarized in an Accounts of Chemical Research article by Holmes.[25] In this paper, SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, and PCl_2F_4 compounds have been selected. Further, both the hardness and the dipole polarizability for the isomer states have been calculated, and Mulliken charges, bond lengths and bond angles, and dipole moment have been calculated by using MP2 model and 6-31G(d), 6-311G(d,p) basis sets. The bond properties different isomers and IR spectra of stable isomers of $PCl_xF_{5\text{-}x}$ (x=1,4) by natural bond orbital (NBO) analysis were calculated, as well.

CALCULATION METHODS

Optimized structural geometries and energies were determined for all the above mentioned compounds by MP2 method using 6-31G(d) and 6-311G(d,p) basis sets, Vibrational frequencies were calculated for optimized structures without any scaling factor in order to check if there was a true minimum. For each structure zero-point energy (ZPE) correction had been taken into account in calculating the energies. All quantum chemical calculations were accomplished by program Gaussian 98.[26]

RESULTS AND DISCUSSION

We have studied SF_4, SF_4O, $PCl_xF_{5\text{-}x}$ (x=1,4) molecules. Different isomers of the optimized structures for studied molecules using MP2/6-31G(d) method are given in Figure 1.

SF_4 molecules have two isomers according to lone pairs are located axial and equatorial position. A lone pair of electrons is a pair of electrons in the valence shell of an atom that is not engaged in bonding. Lone pairs are important both structurally and chemically. They influence

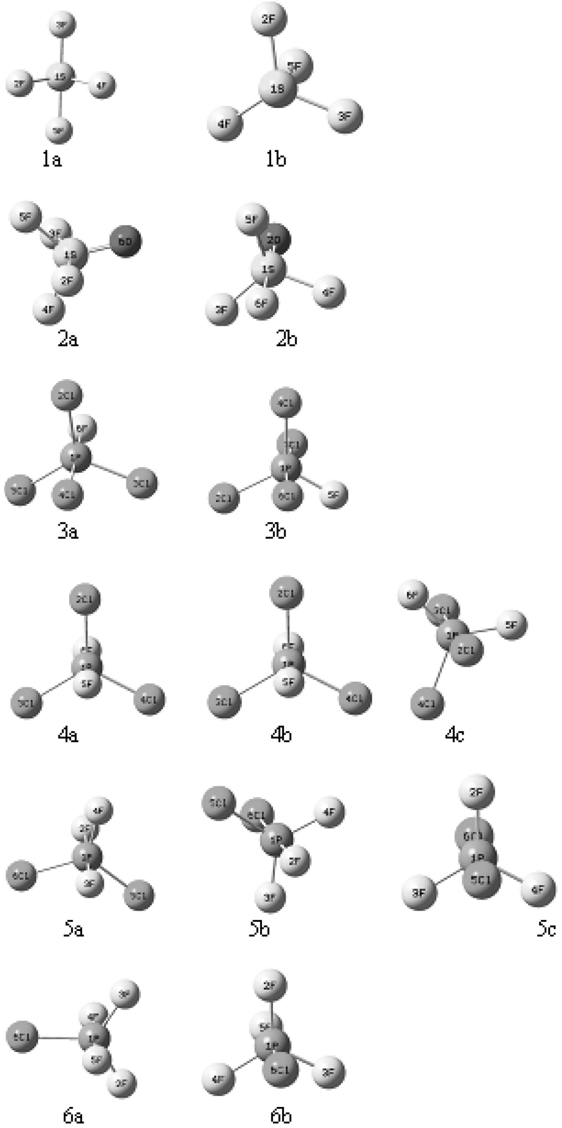

FIGURE 1 Optimized structure of different isomers of SF_4, SF_4O, PCl_4F, PCl_3F_2, PCl_2F_3, PCl_2F_4 molecules calculated with MP2/6-311G(d,p).

the shape of a molecule by exerting strong repulsive forces on the electron pairs in neighboring bonds and other lone pairs. Gillespies has suggested that a lone pair can be considered to be a “substituent” with an effective electronegativity of zero since the lone pair is under the complete control of a single nucleus.[27] SF_4O molecules have also two isomers according to oxygen atom are located axial and equatorial position. The calculated energies including the zero point energy, and$\varepsilon_{\mathrm{HOMO}}$, $\varepsilon_{\mathrm{LUMO}}$, and hardness and polarizability values for the isomers of SF_4, and SF_4O molecule are given in Table I, and the type of formed bond between the pair of atoms are summarized in Table II. Equatorial S-F NBO for 1a isomer is formed from an $sp^{6.63}d^{1.12}$ hybrid (11.44% s, 75.79% p, 12.78% d - character) on sulfur interacting with an $sp^{5.32}$ hybrid (15.79%) s, 84.08% p- character) on florur. Equatorial S-F bond is written as lineer combination of sulfur and oxygen atoms as $\psi_{S-F} = (0.490sp^{6.63}d^{1.12})_S + (0.872sp^{5.32})_F$. Bond energy of that is -1.17280 au. Axial S-F NBO bond for 1a isomer is consist of $sp^{8.60}d^{5.31}$ (6.70% s, 57.67% p, 35.62% d - character) sulfur orbitals and $sp^{6.18}$(13.92%) s, 86.00% p- character) florur orbitals $\psi_{S-F} = (0.402sp^{8.60}d^{5.31})_S + (0.915sp^{6.18})_F$ and its energy is -0.93360au. and axial Lone pair for 1a isomer consist of $sp^{0.46}$. The electronegativity of sulfur orbitals for equatorial position appears more than axial position, and the s character of S-F bond in equatorial positionda is more than that of in axial position. Equatorial S-F NBO bond for 1b isomer is formed from an $sp^{12.93}d^{3.11}$ hybrid (16.54%% s, 50.95% p, 32.51% d - character) on sulfur interacting with an $sp^{6.75}$ hybrid (14.75%) s, 85.15% p- character) on florur, and the S-F bond formed as a lineer combination of sulfur and oxygen atoms is written as. $\psi_{S-F} = (0.428sp^{12.93}d^{3.11})_S + (0.904sp^{6.75})_F$, and its energy is -0.97485au . Axial S-F bond for 1b isomer includes $sp^{3.96}d^{2.36}$ for S (13.65% *s*, 54.13% *p*, 32.22% *d* - character) atom and. $sp^{6.29}$ (13.70%) *s*, 86.17%) *p*- character) for F. Axial S-F NBO bond may be written as $(0.458sp^{3.96}d^{2.36})_S + (0.889sp^{6.29})_F$ and its energy is -1.07085 au. Lone pair for 1b isomer is $sp^{0.32}$.

According to the Bent rule, less electronegative substituent occupies the equatorial position. The calculated energies and hardness values of SF_4 show that 1A isomer has less energy than 2A isomer and therefore 1A isomer must be more stable, so the result is in accordance with Bent rule and the calculated energies with B3LYP method by Noorizadeh.[6] 1A isomer has less polarizability for basis sets so according to MPP 1A isomer must be more stable than 2A isomer. Hardness values calculated with 6-31G(d) basis set for 1A isomer are less than 2A isomer, this is not in accordance with Bent rule, but calculated with 6-311 G(d) basis set for 1A isomer is more stable than 2A isomer, the result is in accordance with Bent rule. The same result is also found in Noorizadeh paper,[6] and therefore, it is clear that for MHP calculations large basis sets are needed. The calculated energies including the zero point energy and MHP, and MPP show that 2A isomer is more stable for SF_4O molecule so they are in accordance with Bent rule.

TABLE I Calculated Energies with MP2, Including Zero-Point Energy, ε_{HOMO}, ε_{LUMO}, MHP and MPP

SF_4	E+ ZPE(au)	ε_{HOMO}(au)	ε_{LUMO}(au)	η	α_{XX}	α_{YY}	α_{ZZ}	$\pi\alpha\theta$	Symmetry
6-31G(d)									
1a	−795,979173	−0,32224	−0,08427	0,118985	26,918	21,659	16,759	21,77867	C_{2V}
2a	−795,946979	−0,30060	−0,06229	0,119155	26,267	26,267	18,415	23,64967	C_{3V}
6-311G(d,p)									
1a	−796,219888	−0,32520	−0,08405	0,120575	27,030	20,351	15,090	20,82367	
2a	−796,186127	−0,30517	−0,06854	0,118315	26,323	26,323	16,845	23,16367	
SF_4O									
6-31G(d)									
1b	−870,983885	−0,39139	−0,09122	0,150085	22,284	23,855	25,443	23,86067	C_{2V}
2b	−870,946217	−0,39121	−0,11326	0,138975	23,523	23,523	27,533	24,85967	C_{3V}
6-311G(d,p)									
1b	−871,254644	−0,39747	−0,08909	0,15419	20,816	22,770	24,278	22,62133	
2b	−871,217419	−0,39762	−0,11320	0,14221	22,234	22,234	26,612	23,69333	

TABLE II Calculated with MP2/6-311G(d,p) S-F NBO Bonds for SF_4 and SF_4O Molecules

	1a		**1b**
$S_1-F_{2,4(eq)}$	$(0.490sp^{6.63}d^{1.12})_S+(0.872sp^{5.32})_F$	$S_1-F_{2,3,4(eq)}$	$(0.428sp^{12.93}d^{3.11})_S+(0.904sp^{6.75})_F$
$S_1-F_{3,5(ax)}$	$(0.402sp^{8.60}d^{5.31})_S+(0.915sp^{6.18})_F$	$S_1-F_{5(ax)}$	$(0.458sp^{3.96}d^{2.36})_S+(0.889sp^{6.29})_F$
Lone pair	$sp^{0.46}$	Lone pair	$sp^{0.32}$
	2a		**2b**
$S_1-F_{4,5(eq)}$	$(0.454sp^{3.08}d^{1.97})_S+(0.891sp^{5.77})_F$	$S_1-F_{3,4,5(eq)}$	$(0.439sp^{2.03}d^{2.09})_S+(0.899sp^{5.03})_F$
$S_1-F_{2,3(ax)}$	$(0.457sp^{2.59}d^{2.14})_S+(0.890sp^{5.36})_F$	$S_1-F_{6(ax)}$	$(0.452sp^{3.92}d^{2.78})_S+(0.892sp^{6.84})_F$
$S_1-O_{6(eq)}$	$(0.595sp^{1.85}d^{0.25})_S+(0.804sp^{3.20})_F$	$S_1-O_{2(ax)}$	$(0.572sp^{1.61}d^{0.71})_S+(0.820sp^{3.16})_F$

Bond length, bond angles and Mulliken charges for both SF_4, and SF_4O molecules are summarized in Table III. In $SF_{4,}$ the axial FSF angle is compressed moderately (−9.07°) from VSEPR effects from the lone pair. Viewed from VSEPR effects , the greater compression of the equatorial FSF angle (−17,74°) is surprising, since 90° interactions (lone pair-axial fluorine) are more intense than 120° interactions (lone pair-equatorial fluorine). The decrease in FSF, angle results in part from the added effect of Bent's rule: The lone pair attracts *s* character, leaving more *p* character and a smaller bond angle for the fluorine atoms. In SF_4O molecule the axial FSF angle is compressed moderately (−9.07°) from VSEPR effects from the lone pair (−7,14°). The greater electronegativity of oxygen makes the three equatorial substituents comparable and the deviations from ideality are small. In 2a isomers of

TABLE III Mulliken Charges and Geometric Parameters of Stable Isomers SF_4 and SF_4O Molecules

SF_4	6-31G(d)	6-311G(d,p)	SF_4O	6-31G(d)	6-311G(d,p)
Atoms no.	Bond lengths (Å)		Atoms no.	Bond lengths (Å)	
1S-2F	1.587	1.575079	1S-2F	1.626	1.629
1S-3F	1.665	1.676846	1S-4F	1.589	1.578
			1S-6O	1.438	1.422
	Bond angle (degree)			Bond angle (degree)	
2F-1S-5F	87.16	87.54753	2F-1S-5F	85.30	85.42
3F-1S-5F	170.93	172.18905	2F-1S-3F	162.95	163.49
2F-1S-4F	102.26	102.15752	4F-1S-5F	112.86	98.26
			5F-1S-6O	123.57	123.76
Atoms no.	Mulliken atomic charges(ē)			Mulliken atomic charges(ē)	
1S	1.457	1.378338	1S	1.646	1.553
2F	−0.312	−0.286497	3F	−0.343	−0.329
3F	−0.416	−0.402672	4F	−0.270	−0.252
			6O	−0.420	0.392
μ	0.9626	1.1134	μ	1.004	0.766

SF_4O molecule S-F equatorial bonds consist of s(16.54%), p(50.95%), and d (32.51%). When oxygen is placed instead of lone pair, the *s* character incread from 11.44 to 16.54% and *d* character increased 12.78 to 32.51%, too, but p character decreased from 75.79 to 50.95%. Because of decreasing *p* character more than increasing of *d* character in equatorial positon S-F bond for SF_4O molecule is longer than that of SF_4.

Pentacoordinated phosphorus compounds generally have a trigonal bipyramidal structure. Two geometric isomers are possible for compounds such as PCl_4F. In one isomer (C_{3v}) the fluorine atom occupies an axial site and in the other (C_{2v}) an equatorial site.There are three isomers for PCl_3F_2 and for PCl_2F_3. Two geometric isomers are possible for compounds such as $PClF_4$. In one isomer (C_{3v}) the chlorine atom occupies an axial site and in the other (C_{2v}) an equatorial site.

The calculated energies including the zero point energy, ε_{HOMO}, ε_{LUMO}, and hardness and polarizability values for the isomers of PCl_xF_{5-x} ($x = 1,4$) molecules were summarized in Table IV. From the Bent rule the following trends are expected for the stability of different isomers for PCl_xF_{5-x} ($x = 1,4$): The isomer (C_{3v}) in which the fluorine atom occupies an axial site is found to be the more stable for PCl_4F molecule, The isomer (D_{3h}) in which the chlorine atoms occupy an equatorial site, fluorine atoms occupy an axial site is found to be the more stable for PCl_3F_2 molecule. The isomer (C_{2V}) in which the two chlorine atoms and one fluorine atom occupy an equatorial site fluorine atoms occupy an axial site is found to be the more stable for PCl_2F_3 molecule. The isomer (C_{2v}) in which the chlorine atom occupies an equatorial site is found to be the more stable for $PClF_4$molecule that is 3a > 3b, 4a > 4b > 4c, 5a > 5b > 5c, and 6a > 6b for both basis sets the energies are in accordance with the Bent rule. Hardness values show the same trend for the stability of these isomers except PCl_3F_2 calculated with 6-31G(d) basis set and is in accordance with the Bent rule too. Large basis set is needed for MMP in accordance with the Bent rule. The theoretical data on the structures agree with the previously reported structural data obtained experimentally.

The experimental spectral data of PCl_4F were best interpreted in terms of a C_{3v} structure in which the fluorine atom occupies an axial site; in PCl_3F_2 (D_{3H} point group) the fluorine atoms also assume axial positions; in $PC_{12}F_3$ data supports the C_{2v} structure.[19–22,25] The theoretical IR spectra results of stable isomers for the series of phosphorus(V) chloroflorides are given in Table V and it appears that theorical results are agreement with the experimental ones.

Bond length, bond angles. and Mulliken charges calculated with MP2 level and 6-31G(d) 6-311G(d,p) basis sets for PCl_xF_{5-x}: molecules are summarized in Table VI, and the NBO bond formed bond between the

TABLE IV Calculated Energies Including Zero-Point Energy , ε_{HOMO}, ε_{LUMO}, MHP and MPP

PCl_4F	E+ ZPE (au)	ε_{HOMO}(au)	ε_{LUMO}(au)	η	α_{XX}	α_{YY}	α_{ZZ}	$\pi\alpha\theta$	Symmetry
6-31G(d)									
3a	−2278,919668	−0,32789	−0,15509	0,0864	61,912	61,912	54,140	59,32133	C_{3V}
3b	−2278,911001	−0,32238	−0,15527	0,0835	69,200	61,041	44,705	58,31533	C_{2V}
6-311G(d,p)									
3a	−2279,117514	−0,32807	−0,15611	0,0859	62,200	62,200	56,954	60,45133	
3b	−2279,109731	−0,32249	−0,15569	0,0834	71,647	61,413	46,782	59,94733	
PCl_3F_2									
6-31G(d)									
4a	−1918,947538	−0,34649	−0,12217	0,11216	56,190	56,190	32,856	48,412	D_{3H}
4b	−1918,939530	−0,32928	−0,13698	0,09615	48,085	39,202	56,141	47,809	C_S
4c	−1918,932287	−0,32854	−0,13047	0,0990350	32,444	61,581	47,357	47,127	C_{2V}
6-311G(d)									
4a	−1919,170393	−0,34661	−0,12252	0,112045	55,723	55,723	34,217	48,55433	
4b	−1919,163419	−0,32936	−0,13702	0,09617	49,459	39,878	55,549	48,29533	
4c	−1919,156712	−0,32768	−0,13128	0,0982	33,447	63,069	48,019	48,17833	
PCl_2F_3									
6-31G(d)									
5a	−1558,967937	−0,34699	−0,10505	0,12097	50,571	28,746	33,864	37,727	C_{2V}
5b	−1558,961041	−0,33426	−0,11324	0,11051	39,375	44,565	28,169	37,36967	C_S
5c	−1558,954461	−0,34771	−0,10058	0,1235650	28,149	28,149	54,045	36,781	D_{3H}
6-311G(d,p)									
5a	−1559,217069	−0,34705	−0,10390	0,121575	49,493	28,772	33,584	37,283	
5b	−1559,210802	−0,33390	−0,11368	0,11011	39,048	45,061	27,902	37,337	
5c	−1559,204113	−0,34776	−0,09931	0,124225	28,440	28,440	54,670	37,18333	
$PClF_4$									
6-31G(d)									
6a	−1198,989693	−0,35215	−0,08060	0,135775	24,455	23,875	36,008	28,11267	C_{2V}
6b	−1198,983550	−0,35291	−0,08096	0,135975	23,845	23,845	35,933	27,87433	C_{3V}
6-311G(d)									
6a	−1199,264991	−0,35221	−0,07927	0,13647	23,563	22,764	35,022	27,11633	
6b	−1199,258514	−0,35265	0,07941	0,21603	23,013	23,013	35,390	27,13867	

TABLE V Fundamental Frequencies of PCl_xF_{5-x} (x=1,4)

	PCl_4F		PCl_3F_2		PCl_2F_3		$PClF_4$	
No	$Freq_{(exp)}$	$Freq_{(theor)}$[a]	$Freq_{(exp)}$	$Freq_{(theor)}$[a]	$Freq_{(exp)}$	$Freq_{(theor)}$[a]	$Freq_{(exp)}$	$Freq_{(theor)}$[b]
1	778	762	867	877	925	921	921	996
2	601	601	633	635	902	913	903	948
3	422	419	625	629	665	673	895	886
4	388	388	404	411	500	655	691	687
5	339	341	387	390	488	514	560	566
6	297	306	357	356	427	495	510	542
7	265	268	328	333	407	430	490	497
8	110	108	122	121	368	411	434	492
9	—	—	—	—	368	361	356	437
10	—	—	—	—	338	344	356	357
11	—	—	—	—	124	124	144	171
12	—	—	—	—	124	156	144	146

[a]Griffiths et al.[21]; and [b]Holmes.[19]

pair of atoms are summarized in Table VII. Equatorial P-Cl NBO bond for PCl_4F, PCl_3F_2, PCl_2F_3, and $PClF_4$ as seen from the Table VII are $(0.601sp^{3.10}d^{0.67})_p + (0.799sp^{6.43})_{Cl}$ (20.97%% s, 64.93% p, 14.10% d – character on P atom), $(0.594sp^{3.13}d^{0.71})_P + (0.804sp^{6.25})_{Cl}$,(20.67%% s, 64.70% p, 14.63% d – character on P atom), $(0.589sp^{3.00}d^{0.69})_P + (0.808sp^{6.69})_{Cl}$, (21.31%% s, 63.92% p, 14.77% d – character on P atom), and $(0.589sp^{2.84}d^{0.70})_P + (0.812sp^{7.25})_{Cl}$.(2203%% s, 62.51% p, 15.46% d – character on P atom), respectively. It appears that in the bond formation, the polarization coefficient of P atom decreases, and the polarization coefficient of Cl atom increases in the series upon replacing chlorines with fluorines. p character of P atom in hybrid orbital decreases and s and d character of P atom in hybrid orbital increases. Axial P-Cl NBO bond is formed from $(0.535sp^{2.57}d^{1.77})_p + (0.845sp^{8.48})_{Cl}$. s, p, d characters on P atom are 18.72%, 48.18%, and 33.10%, respectively, and for axial P-Cl bond, they are 20.97%, 64.93%, and 14.10%, respectively.

Equatorial P-Cl bond length for PCl_4F, PCl_3F_2, PCl_2F_3, $PClF_4$ is 2.028, 2.016, 2.008, and 2.001 (Å), respectively. As the number of electronegative substituent increases P-Cl bond becomes stronger. Axial P-F bond length for PCl_4F, PCl_3F_2, PCl_2F_3, and $PClF_4$ is 1.624, 1.619, 1.569, and 1.563 (Å), respectively. As the number of electronegative increases axial P-F bond becomes shorter. 2Cl-1P-5Cl angle for PCl_4F is 119.96 and is 120.00 for PCl_3F_2. Theoretical dipole moments for PCl_4F, PCl_3F_2, PCl_2F_3, $PClF_4$ which are given in Table VIII are 0.1921, 0.0000, 0.70030, and 7190 Debye, respectively. The results of the dipole moments give the correct isomer and the theoretical calculations are in

TABLE VI Bond Length, Bond Angles, and Mulliken Charges for $PCl_xF_{5\text{-}x}$ (x=1,4)

PCl_4F	6-31G(d)	6-311G(d,p)	PCl_3F_2	6-31G(d)	6-311G(d,p)
Atoms No	Bond Lengths (Å)		Atoms No	Bond Lengths (Å)	
1P-2Cl	2.029	2.028	1P-2 Cl	2.018	2.016
1P-4 Cl	2.12	2.145	1P-5F	1.624	1.619
1P-6F	1.630	1.624			
	Bond Angle(degree)			Bond Angle(degree)	
2Cl-1P-5Cl	119.94	119.96	3Cl-1P-4Cl	120.00	120.00
5Cl-1P-4 Cl	91.43	91.19	3Cl-1P-6F	90.00	90.00
5Cl-1P -6F	88.57	88.81	5F-1P -6F	90.00	180.00
4Cl-1P -6F	180.00	180.00			
Atoms No	Mulliken Atomic Charges(ē)			Mulliken Atomic Charges(ē)	
1P	0.777	0.951			
2Cl	−0.062	−0.113	1P	1.050	1.186
4Cl	−0.210	−0.238	2Cl	−0.100	−0.143
6F	−0.379	−0.373	5F	−0.374325	−0.378
PCl_2F_3	6-31G(d)	6-311G(d,p)	$PClF_4$	6-31G(d)	6-311G(d,p)
Atoms No	Bond Lengths (Å)		Atoms No	Bond Lengths (Å)	
1P-2F	1.615	1.608	1P-2F	1.576	1.563
1P-4F	1.584	1.569	1P-4F	1.606	1.598
1P-5Cl	2.009	2.008	1P-6Cl	2.001	2.001
	Bond Angle(degree)			Bond Angle(degree)	
6Cl-1P-3F	90.50	90.46	6Cl-1P-3F	120.78	120.83
6Cl-1P-4F	119.14	119.37	6Cl-1P-4F	90.95	90.85
6Cl-1P-5Cl	121.72	121.27	3F-1P-4F	89.51	89.56
3F-1P-2F	177.97	178.14	4F-1P-5F	178.10	178.29
Atoms No	Mulliken Atomic Charges(ē)			Mulliken Atomic Charges(ē)	
1P	1.289	1.391	1P	1.489	1.562
2F	−0.371	−0.382	2F	−0.303	−0.318
4F	−0.294	−0.316	4F	−0.3682	−0.384
5Cl	−0.126	−0.155	6Cl	−0.147	−0.156

close agreement with the experimental gas phase values, also listed in Table VIII.[25]

In the series of $PCl_xF_{5\text{-}x}$ there is a lack of transmission of electron density to axial fluorine atoms as chlorine substitution increses. As a consuquence, a reduction in the positive charge at phosphorus occurs.[25] Mulliken charges of P atom for $PClF_4$, PCl_2F_3, PCl_3F_2, and PCl_4F are 1.562, 1.391, 1.186, and 0.951ē, respectively.

Distribution of P3s character in overlap population calculated by MP2/6-31G(d,p) and Hückel theory[18] are summarized in Table IX. *s* character of phosphorus atom in P-Cl equatorial bonds is 20.97% and in axial bonds is 18.72% for PCl_4F, *s* character of phosphorus atom in P-F equatorial bonds is 20.08% and in axial bonds is 18.74% for PCl_2F_3,

TABLE VII P-F NBO and P-Cl NBO Calculated with MP2/6-311G(d,p) for $PCl_xF_{5\text{-}x}$ (x = 1,4)

3a		**3b**	
$P_1 - Cl_{2,3,5(eq)}$	$(0.601sp^{3.10}d^{0.67})_p + (0.799sp^{6.43})_{Cl}$	$P_1 - Cl_{2,4(eq)}$	$(0.605sp^{2.94}d^{0.57})_p + (0.796sp^{6.97})_{Cl}$
$P_1 - Cl_{4(ax)}$	$(0.535sp^{2.57}d^{1.77})_p + (0.845sp^{8.48})_{cL}$	$P_1 - Cl_{3,6(ax)}$	$(0.540sp^{2.87}d^{1.86})_P + (0.841sp^{7.57})_{Cl}$
$P_1 - F_{6(ax)}$	$(0.389sp^{2.82}d^{1.60})_p + (0.921sp^{2.70})_F$	$P_1 - F_{5(eq)}$	$(0.605sp^{3.07}d^{0.72})_P + (0.9106sp^{2.51})_F$
4a		**4b**	
$P_1 - Cl_{2,3,4(eq)}$	$(0.594sp^{3.13}d^{0.71})_P + (0.804sp^{6.25})_{Cl}$	$P_1 - Cl_{2,3(eq)}$	$(0.597sp^{2.98}d^{0.64})_P + (0.802sp^{6.86})_{Cl}$
$P_1 - F_{5(ax)}$	$(0.389sp^{2.62}d^{1.62})_P + (0.921sp^{2.79})_F$	$P_1 - Cl_{4(ax)}$	$(0.535sp^{2.63}d^{1.80})_P + (0.844sp^{8.25})_{Cl}$
4c		$P_1 - F_{6(eq)}$	$(0.417sp^{3.21}d^{0.72})_P + (0.908sp^{2.43})_F$
$P_1 - Cl_{4(eq)}$	$(0.602sp^{2.86}d^{0.53})_P + (0.798sp^{7.27})_{Cl}$	$P_1 - F_{5(ax)}$	$(0.390sp^{2.87}d^{1.65})_P + (0.921sp^{2.67})_{Fl}$
$P_1 - Cl_{2,3(ax)}$	$(0.540sp^{2.90}d^{1.88})_P + (0.842sp^{7.33})_{Cl}$		
$P_1 - F_{6(eq)}$	$(0.416sp^{3.02}d^{0.66})_P + (0.909sp^{2.61})_F$		
5a		**5b**	
$P_1 - Cl_{5,6(eq)}$	$(0.589sp^{3.00}d^{0.69})_P + (0.808sp^{6.69})_{Cl}$	$P_1 - Cl_{5(eq)}$	$(0.592sp^{2.83}d^{0.64})_P + (0.806sp^{7.34})_{Cl}$
$P_1 - F_{4(eq)}$	$(0.418sp^{3.27}d^{0.71})_P + (0.908sp^{2.37})_F$	$P_1 - F_{4(ax)}$	$(0.418sp^{3.13}d^{0.67})_P + (0.909sp^{8.12})_F$
$P_1 - F_{2,3(ax)}$	$(0.390sp^{2.67}d^{1.67})_P + (0.921sp^{2.79})_F$	$P_1 - Cl_{6(ax)}$	$(0.390sp^{2.90}d^{170})_P + (0.921sp^{2.67})_F$
5c		$P_1 - F_{2(ax)}$	$(0.534sp^{2.69}d^{1.83})_P + (0.845sp^{8.12})_{Cl}$
$P_1 - F_{2,3,4(eq)}$	$(0.417sp^{2.94}d^{0.61})_P + (0.909sp^{2.73})_F$		
$P_1 - Cl_{5,6(ax)}$	$(0.538sp^{2.92}d^{192})_P + (0.843sp^{7.20})_{Cl}$		
6a		**6b**	
$P_1 - Cl_{6(eq)}$	$(0.589sp^{2.84}d^{0.70})_P + (0.812sp^{7.25})_{Cl}$	$P_1 - F_{2,3,4(eq)}$	$(0.418sp^{2.99}d^{0.64})_P + (0.909sp^{2.75})_{Cl}$
$P_1 - F_{2,3(eq)}$	$(0.417sp^{3.17}d^{0.67})_P + (0.909sp^{2.54})_F$	$P_1 - Cl_{6(ax)}$	$(0.533sp^{2.74}d^{1.86})_P + (0.846sp^{8.01})_{Cl}$
$P_1 - F_{4,5(ax)}$	$(0.390sp^{2.72}d^{172})_P + (0.921sp^{2.81})_F$	$P_1 - F_{5(ax)}$	$(0.391sp^{2.96}d^{1.78})_P + (0.920sp^{2.70})_F$

s character of phosphorus atom in P-F equatorial bonds is 20.64% and in axial bonds is 18.38% for $PClF_4$ s character of phosphorus atom is greater in equatorial bonds than in axial bonds. s character of phosphorus atom in P-Cl equatorial bonds (%22.03) is greater than of that of P-F equatorial bonds (%20.64) for $PClF_4$. As it is explained in Van Der Voorn and Drago,[18] phosphorus 3s character is concentrated in bonds to the more electropositive substituent.

TABLE VIII Dipole Moment Calculated with MP2/6-311G(d,p) for $PCl_xF_{5\text{-}x}$ (x = 1,4)

		μ theoretical		
	$\mu_{\text{experimental}^1}$	a	b	c
PCl_4F	0.21 ± 0.01	0.144	1.19	—
PCl_3F_2	0.00 ± 0.06	0.000	1.02	1.24
PCl_2F_3	0.68 ± 0.02	0.877	1.04	0.00
$PClF_4$	0.78	0.719	0.10	—

[1] Holmes.[25]

TABLE IX 3s% Character per P-X Bonds Calculated with MP2/6-311G(d,p)

	Axial P-F		Equatorial P-F		Axial P-Cl		Equatorial P-Cl	
	Hückel[a]	NBO	Hückel[a]	NBO	Hückel[a]	NBO	Hückel[a]	NBO
PCl_4F	13.4	18.43	—	—	14.6	18.72	24	20.97
PCl_3F_2	14.5	19.07	—	—	—	—	23.6	20.67
PCl_2F_3	16.5	18.74	18.4	20.08	—	—	24.3	21.31
$PClF_4$	18.4	18.38	19.1	20.64	—	—	25	22.03

[a] Van Der Voorn and Drago.[18]

CONCLUSIONS

Energy, dipole moment, and IR spectra results are a reliable parameter for predicting the stability order of different isomers of studied molecules and it is independed on the selected basis sets. it has been seen that large basis sets are needed for MHP, and MPP in consistent with stability and Bent rule. The hybrid type of formed NBO bond between the pair of atoms are calculated. Equatorial and axial bonds are formed with *s*, *p*, and *d* orbitals but in equatorial bonds *s*, *p* character on P is more than axial bonds for *d* character the inverse is true.

REFERENCES

[1] H. A. Bent, *J. Chem. Educ.*, **37,** 616 (1960).
[2] H. A. Bent, *J. Chem. Phys.*, **33,** 1258 (1959)
[3] H. A. Bent, *J. Chem. Phys.*, **33,** 1260 (1960).
[4] H. A. Bent, *Chem. Rec.*, **61,** 275 (1961).
[5] J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, (Harper & Row, New York and San Francisco, 1978). 2nd ed., pp. 145–147, 206, 227.
[6] S. Noorizadeh, *Journal of Molecular Structure*: *THEOCHEM,* **713,** 27–32 (2005).
[7] R. G. Pearson*, Proc. Natl. Acad. Sci.* U.S.A., **83,** 8440–8441(1986).
[8] J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, (Harper & Row, New York and San Francisco, 1978). 2nd ed., pp. 146.
[9] R. G. Pearson, *J. Chem. Educ.*, **64,** 561 (1987).
[10] R. G. Pearson, *J. Chem. Educ.*, **76,** 267 (1999).
[11] R. G. Pearson, *Chemical Hardness*, (Wiley-VCH, Oxford, 1997).
[12] P. K Chattaraj and S. Sengupta, *J. Phys. Chem.,* **100,** 16126 (1996).
[13] M. Torrent-Sucarrat, J. M. Luis, M. Duran, and M. Sola, *J. Am. Chem. Soc.,* **123,** 7951–7952 (2001).
[14] R. G. Pearson*, Hard and Soft Acids and Bases* (Dowden, Hutchinson, and Ross, Stroudsburg, PA, 1973).
[15] R. G. Pearson, *J. Chem. Educ.,* **64,** 561–567 (1987).
[16] R. G. Pearson, *J. Org. Chem.,* **54,** 1423–1430 (1989).
[17] R. G. Pearson, *Proc. Nut/. Acad. Sci. U.S.A.,* **8,** 8440–8441. (1986),

[18] P. C. Van Der Voorn and R. S. Drago, *Journal of the American Chemical Society 1,* **88,** 14–20 (1966).

[19] R. R. Holmes, *J. Chem Phys.,* **46** (10), 3718–3723 (1967).

[20] R. R. Holmes, R. P. Carter Jr. , and G. E. Peterson, *Inorg Chem.*, **3** (12), 1748–1754 (1964).

[21] J. E. Griffiths, R. P. Carter Jr., and R. R. Holmes, *J. Chem Phys*., **41,** 863–875 (1964)

[22] R. P. Carter Jr., and R. R. Holmes, *Inorg Chem.,* **4** (5), 738–739 (1965).

[23] R. R. Holmes and R. P. Carter Jr., *J. Chem Phys*., **43** (1), 1645–1646 (1965).

[24] R. R. Holmes and R. P. Carter Jr., *J. Chem Phys*., **43** (5), 1650–1657 (1965).

[25] R. R. Holmes, *Accounts of Chemical Research.,* **5,** 296–303 (1972).

[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Akatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *GAUSSIAN 03* (Gaussian Inc., Pittsburgh PA, 2003), Revision B. 04.

[27] R. J. Gillespie, *Molecular Geometry* (Van - Nostrand - Reinhold: London, 1972) pp 55–56.