

## Substituent effect on the structural and electronic properties of P<sub>2</sub>(para-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> molecules: A computational investigation

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**Abstract:** Substituent effect on the structure and electronic properties of the P<sub>2</sub>(para-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> molecules (X=NH<sub>2</sub>, Me, H, F, Cl, CN, NO<sub>2</sub>) were studied at wB97XD/6-311G(d,p) level of theory. The substituent effect on the structural parameters and reactivity parameters (hardness, chemical potential and electrophilicity) was explored. Stability of the P(para-C<sub>6</sub>H<sub>4</sub>X) fragments were investigated in the singlet and triplet states for illustration of the P=P bond character. Electron donating groups (EDGs) and electron withdrawing groups (EWGs) effect on the stability of these different spin multiplicities of P(para-C<sub>6</sub>H<sub>4</sub>X) fragments were investigated. The P-C and P=P bonding situations in the studied molecules were examined via the natural bond orbital (NBO) studies.

**Keywords:** Diphosphenes, spin isomers, substituent effect, natural bond orbital (NBO).

### Introduction

Many investigations have been reported about heavier main group elements with low coordination numbers [1-11]. This considerable attention is due to their reactivity toward a various variety of chemical reagents and their exclusive electrochemical and photochemical properties [12-18]. One of these classes of molecules is diphosphenes. Diphosphenes have a P=P double bond in the molecule. low-lying P=P  $\pi^*$  orbital causes to increase the  $\pi$ -accepting character of the transition metal. Several diphosphene transition-metal complexes have been reported [19-23]. Also, other studies have been explored diphosphenes (HPPH) are potential candidates for use in chemical hydrogen storage systems [24].

Quantum chemical methods are useful tools for illustration of the substituent effects influence physical and chemical properties [25-45]. Quantitative substituent parameters have been considered to illustrate steric or polar effects of the substituent on molecular characteristics. For example, Hammett constant ( $\sigma_p$ ) is one of these parameters [46]. This parameter reflects the electronic effects of substituents on the rate constants and the equilibrium of a reacting molecule. In the present investigation, we explore the substituent influence on the structure and electronic properties of P<sub>2</sub>(para-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> (X=NH<sub>2</sub>, Me, H, F, Cl, CN, NO<sub>2</sub>) molecules at wB97XD/6-311G(d,p) level of theory.

### Computational Methods:

All calculations were conducted via the Gaussian 09 software package [47]. The standard 6-311G(d,p) basis

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set [48-50] and the w B97XD functional [51] were considered in the geometry optimization of the studied molecules.

Natural bond orbital (NBO) analysis[52]was done at wB97XD /6-311G(d,p) level of theory applying NBO 3.1 program [53]handled in Gaussian 09 package.

## Results and discussion

### Energetic aspects

$$\Delta E = -3.5679 \sigma_p + 35.531; \quad R^2 = 0.9279$$

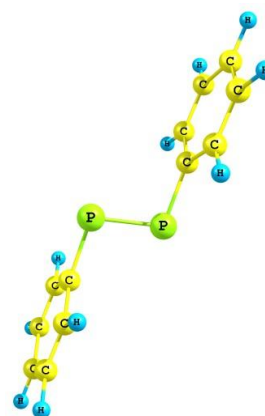
The calculated absolute energy and relative energy values of P(*para*-C<sub>6</sub>H<sub>4</sub>X) molecules (X=NH<sub>2</sub>, Me, H, F, Cl, CN, NO<sub>2</sub>) in the singlet and triplet states are gathered in Table 1. It can be found, triplet state is more stable spin isomer in compared to singletstate in the presence of the various substituents. The linear correlation between relative energy values of spine isomers and Hammett constants is:

**Table 1:** Absolute energy (a.u) and relative energy values of the P(*para*-C<sub>6</sub>H<sub>4</sub>X) molecules in the singlet and triplet states at the wB97XD/6-311G(d,p)level of theory.  $\sigma_p$  is Hammett constant of substituents.

X	$\sigma_p$	E(singlet)	E(triplet)	$\Delta E$
NH <sub>2</sub>	-0.66	-628.2062	-628.2670	38.16
Me	-0.17	-612.1671	-612.2238	35.56
H	0.00	-572.8517	-572.9073	34.87
F	0.06	-672.0883	-672.1457	35.97
Cl	0.23	-1032.4574	-1032.5133	35.07
CN	0.66	-665.0816	-665.1346	33.26
NO <sub>2</sub>	0.78	-777.3440	-777.3960	32.63

### Structural parameters

Figure 1 presents optimized geometry of of P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> molecule. P-P and P-C bond lengths and C-P-P bond angles values of the P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> molecules are listed in Table 2. It can be found, there is minor variation of P-P and C-P bond distances and P-C-C bond angles with changes of X-groups. It can be seen, the longer P-P bond lengths in the presence of electron donating groups (EDGs)thanelectron withdrawing groups (EWGs). In contrast, there are shorter C-P bond lengths in presence of EDGs than EWGs.



**Figure 1:** The optimized geometry of of P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> molecule.

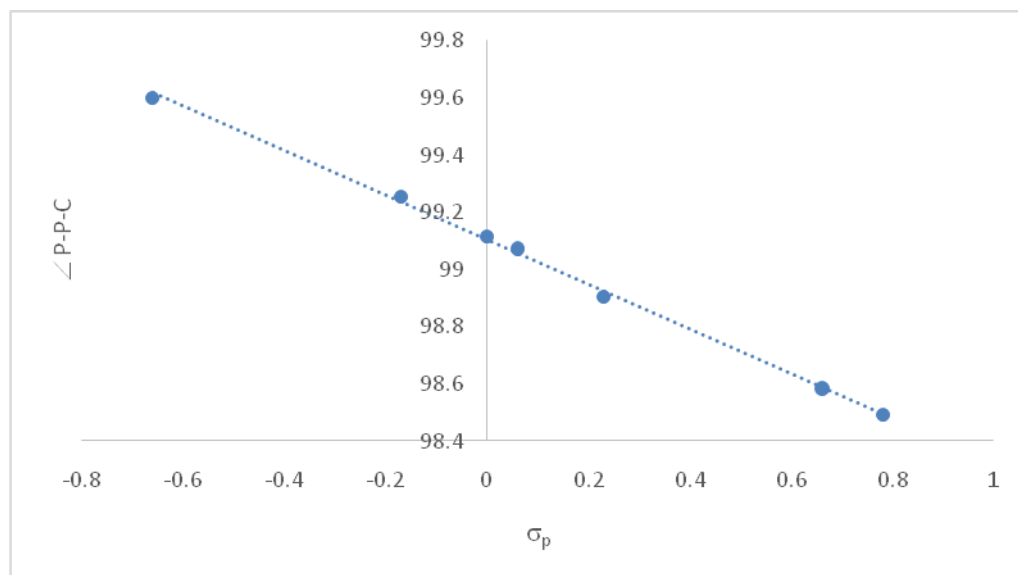
In other hand, P-C-C bond angles are larger in presence of EDGs than EWGs. There are good linear

relationships between these bond angles values and Hammett constants (Figure 2):

$$\angle \text{P-C-C} = -0.781\sigma_p + 99.104; \quad R^2 = 0.9983$$

**Table 2:** PP, CP bond distances (in pm) and CPP bond angle (in degree) values of the optimized  $P_2(\text{para-C}_6\text{H}_4\text{X})_2$  molecules at the wB97XD/6-311G(d,p) level of theory.

X	PP	$\angle \text{CPP}$	CP
NH <sub>2</sub>	202.01	99.60	184.00
Me	201.89	99.26	184.29
H	201.86	99.12	184.44
F	201.89	99.07	184.41
Cl	201.87	98.91	184.45
CN	201.84	98.58	184.57
NO <sub>2</sub>	201.81	98.49	184.59



**Figure 2:** The linear correlation between P-P-C bond angles values and Hammett constants in the  $P_2(\text{para-C}_6\text{H}_4\text{X})_2$  molecules.

### Molecular orbital analysis

The frontier orbital energy, HOMO-LUMO gap, hardness, electrophilicity and chemical potential values of the optimized  $P_2(\text{para-C}_6\text{H}_4\text{X})_2$  molecules geometry

are gathered in Table 3. These values show the increasing of the stability of frontier orbitals in the presence of EWGs. In contrast, the stability of frontier orbitals decreases in the presence of EDGs. There is

good linear relationship between frontier orbital energy values and Hammett constants:

$$E(\text{HOMO}) = -1.289 \sigma_p - 8.2661; \quad R^2 = 0.9902$$

$$E(\text{LUMO}) = -0.8145 \sigma_p - 1.1751; \quad R^2 = 0.9579$$

It can be found, the HOMO-LUMO gap, hardness and electrophilicity values are increased in the presence of EWGs. In contrast, these values are decreased in the presence of EDGs.

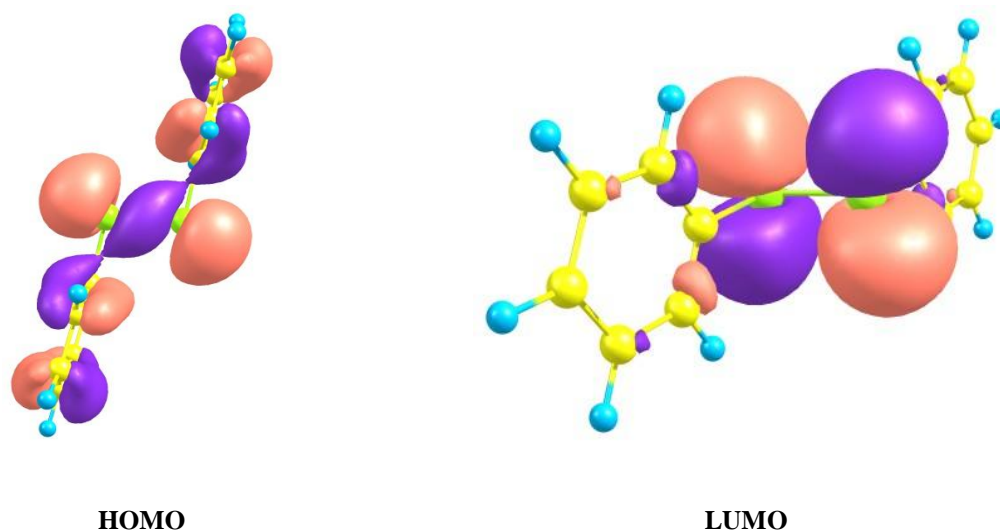
Variations of the chemical potential values in the presence of various substituents reveal that these values decrease in the presence of EWGs. In contrast,

electrophilicity values increase in the presence of EDGs. There are good linear relationships between chemical potential and electrophilicity values with Hammett constants:

$$\mu = -1.0517\sigma_p - 4.7206; \quad R^2 = 0.9964$$

$$\omega = 1.215\sigma_p + 3.1575; \quad R^2 = 0.9771$$

Figure 3 presents plots of HOMO and LUMO in the  $\text{P}_2(\text{para-C}_6\text{H}_5)_2$  molecule. It can be observed, there are  $\sigma$  and  $\pi^*$ -interaction between phosphorous atoms in this molecule.



**Figure 3:** Plots of HOMO and LUMO in the  $\text{P}_2(\text{para-C}_6\text{H}_5)_2$  molecule.

**Table 3:** Frontier orbital energy, HOMO-LUMO gap, hardness ( $\eta$ ), chemical potential ( $\mu$ ) and electrophilicity ( $\omega$ ) values (in eV) of the optimized  $\text{P}_2(\text{para-C}_6\text{H}_4\text{X})_2$  molecules at the wB97XD/6-311G(d,p) level of theory.

X	E(HOMO)	E(LUMO)	Gap	$\eta$	$\mu$	$\omega$
NH <sub>2</sub>	-7.33	-0.74	6.59	3.29	-4.03	2.47
Me	-8.10	-0.94	7.15	3.58	-4.52	2.86
H	-8.32	-1.04	7.28	3.64	-4.68	3.01
F	-8.42	-1.26	7.16	3.58	-4.84	3.28
Cl	-8.53	-1.38	7.15	3.58	-4.96	3.43
CN	-9.06	-1.77	7.30	3.65	-5.41	4.02
NO <sub>2</sub>	-9.25	-1.82	7.43	3.72	-5.54	4.13

## Natural bond analysis (NBO)

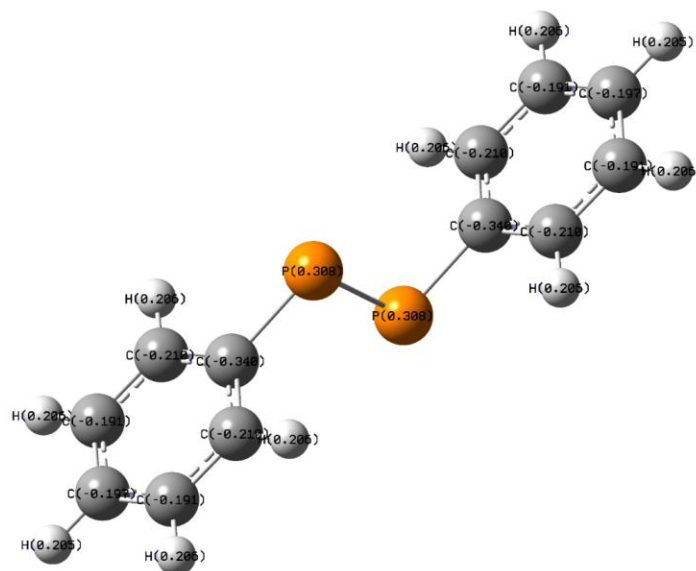
### Charge distribution

Figure 4 presents the atomic charge distribution from the natural population analysis (NPA) for the  $P_2(para-C_6H_5)_2$  molecule. Also, the atomic charges of P and C atoms bonded to Phosphorous atom ( $C_P$ ) in all molecules are listed in Table 4. These values show that the most positive charge on the P atoms. It can be found, the the calculated natural charge of P atom values are enhanced in the presence of EWGs. But,

these values are decreased in the presence of EDGs. There is a good correlation between the calculated natural charge of P atom and and Hammett constants:

$$Q(P) = 0.0169 \sigma_p + 0.3097; \quad R^2 = 0.978$$

On the other hand, the most negative charge is placed on the  $C_P$  atoms. It can be seen, the more negative  $Q(C_P)$  values in the presence of EDGs than EWGs.



**Figure 4:** Distribution of natural charges in the of  $P_2(para-C_6H_5)_2$  molecule.

**Table 4:** Calculated natural charges of P and  $C_P$  atoms in the optimized  $P_2(para-C_6H_4X)_2$  molecules at the wB97XD/6-311G(d,p) level of theory.

X	Q(P)	Q( $C_P$ )
NH <sub>2</sub>	0.3003	-0.3874
Me	0.3058	-0.3498
H	0.3077	-0.3398
F	0.3105	-0.3619
Cl	0.3141	-0.3454
CN	0.3214	-0.3200
NO <sub>2</sub>	0.3236	-0.3153

### Character of natural hybrid orbital (NHO)

The P–C bonds of  $P_2(para-C_6H_5)_2$  molecule are formed by the interaction between  $sp^{4.86}$  and  $sp^{2.74}$  orbitals centered on the P and the carbon atom

respectively. The occupancy of the electrons in this bond is 1.96236 electrons. These values of  $P_2(para-C_6H_4X)_2$  molecules are listed in Table 5. The polarization coefficients for the formation of the P–C

bond are 0.6046 and 0.7965 on the P and C<sub>p</sub> atoms, respectively. These values show a higher polarization through the carbon atom. This indicates a strong polarization directed toward the C atom. These values for the P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> molecules is listed in Table 5.

The σ(P-P) and π(P-P) bonds of P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> molecule are formed by the interaction between sp<sup>5.06</sup>

and p<sup>1.00</sup> orbitals centered on the P atoms, respectively. The occupancy of the electrons in these bonds are 1.95008 and 1.97121 electrons, respectively.

**Table 5:** Occupancy and natural hybrid orbital (NHO) of (a) P-C and (b) P-P NBOs in the optimized P<sub>2</sub>(*para*-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> molecules at the wB97XD/6-311G(d,p) level of theory.

(a)				
X	occupancy	σ(P-C <sub>p</sub> )		
NH <sub>2</sub>	1.96262	0.6051 (sp <sup>4.77</sup> ) <sub>P</sub> + 0.7962 (sp <sup>2.66</sup> ) <sub>C</sub>		
Me	1.96246	0.6048 (sp <sup>4.83</sup> ) <sub>P</sub> + 0.7964 (sp <sup>2.72</sup> ) <sub>C</sub>		
H	1.96236	0.6046 (sp <sup>4.86</sup> ) <sub>P</sub> + 0.7965 (sp <sup>2.74</sup> ) <sub>C</sub>		
F	1.96193	0.6031 (sp <sup>4.89</sup> ) <sub>P</sub> + 0.7977 (sp <sup>2.69</sup> ) <sub>C</sub>		
Cl	1.96189	0.6026 (sp <sup>4.92</sup> ) <sub>P</sub> + 0.7980 (sp <sup>2.71</sup> ) <sub>C</sub>		
CN	1.96179	0.6017 (sp <sup>4.97</sup> ) <sub>P</sub> + 0.7987 (sp <sup>2.72</sup> ) <sub>C</sub>		
NO <sub>2</sub>	1.96172	0.6013 (sp <sup>4.99</sup> ) <sub>P</sub> + 0.7990 (sp <sup>2.73</sup> ) <sub>C</sub>		

(b)				
X	occupancy	σ(P-P)	occupancy	π(P-P)
NH <sub>2</sub>	1.95347	0.7071 (sp <sup>5.01</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.01</sup> ) <sub>P</sub>	1.97097	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
Me	1.95085	0.7071 (sp <sup>5.04</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.04</sup> ) <sub>P</sub>	1.97128	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
H	1.95008	0.7071 (sp <sup>5.06</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.06</sup> ) <sub>P</sub>	1.97121	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
F	1.95128	0.7071 (sp <sup>5.08</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.08</sup> ) <sub>P</sub>	1.97056	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
Cl	1.94958	0.7071 (sp <sup>5.10</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.10</sup> ) <sub>P</sub>	1.97052	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
CN	1.94609	0.7071 (sp <sup>5.17</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.17</sup> ) <sub>P</sub>	1.97014	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>
NO <sub>2</sub>	1.94535	0.7071 (sp <sup>5.18</sup> ) <sub>P</sub> + 0.7071 (sp <sup>5.18</sup> ) <sub>P</sub>	1.97015	0.7071 (p <sup>1.00</sup> ) <sub>P</sub> + 0.7071 (p <sup>1.00</sup> ) <sub>P</sub>

## Conclusion

Substituent influence on the structure and electronic properties of p<sub>2</sub>(*para*-C<sub>6</sub>H<sub>4</sub>X)<sub>2</sub> was illustrated at wB97XD/6-311G(d,p) level of theory. These

calculations revealed triplet state of P(*para*-C<sub>6</sub>H<sub>4</sub>X) fragment was more stable spin isomer than singlet state. P-C-C bond angles of the optimized molecules were larger in presence of EDGs than EWGs. It was found good linear relationships between these bond

angles values and Hammett constants. Also, molecular orbital analysis explored the increasing of the stability of frontier orbitals in the presence of EWGs. HOMO-LUMO gap, hardness and electrophilicity values were enhanced in the presence of EWGs. In contrast, these values are decreased in the presence of EDGs. NBO analysis results indicated the most positive and negative charges were placed on the P and C<sub>p</sub> atoms, respectively.

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