

# Pi-Conjugated Phosphole Derivatives: Promising Building Blocks for $\pi$ -Conjugated Organic Materials

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## Abstract

Pi-Conjugated organophosphorus derivatives have recently emerged as valuable building blocks for the tailoring of functional molecular materials. In order to guide the synthesis of novel materials with low band gaps, theoretical study on the geometries and electronic properties of new conjugated compounds based on low coordinate heterophosphole compounds were carried out. The theoretical ground-state geometries and the electronic structures of the studied molecules were obtained using the density functional theory (DFT) method at B3LYP level with 6-31G(d) basis set. The effects of the phosphorus and different heteroatom elements on the geometries and electronic properties of these materials were discussed. The results from this study show that conjugated molecules containing phosphorus atom gives better electronic properties compared to their organic counterparts that had been used in optoelectronic devices. Hence these compounds could be a good promising building blocks candidate for opto-electronic applications.

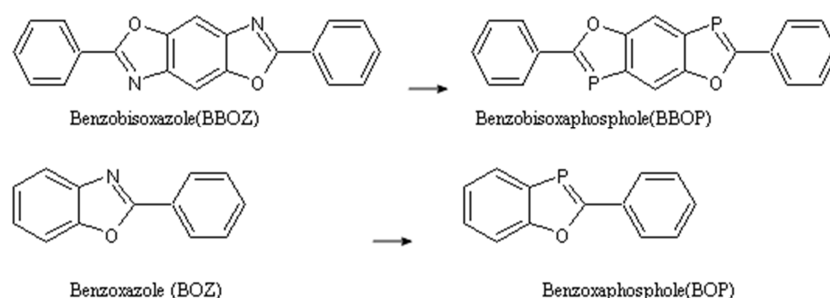
**Keywords:** Conjugated Compounds, Electronic Properties, Density Functional Theory, Opto-Electronic Device

## 1. INTRODUCTION

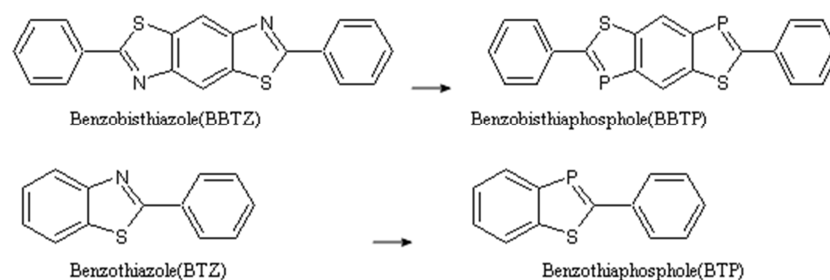
The research in the organic  $\pi$ -Conjugated molecules and polymers, has become of the most interesting area in field of chemistry, physics and materials science because of their specific properties which made them a promising materials for electronic and optoelectronic device technology [1]. Their properties have attracted great interest for their use in transparent conductors, photovoltaic cells, light emitting diodes, and semi-conductor layers in field effect transistors (FET) [2]. A key feature of these novel semiconductors materials is that manipulation of the chemical structures allows control of the optical band gap (3). Low band gap can afford intrinsic conductivity with enhanced nonlinear optical properties, and harvest more photon with long wavelength [4]. A fruitful approach involves the incorporation of heteroatomic moieties into the conjugated frameworks. In contrast to sulphur and nitrogen-based rings systems which have been widely exploited for decades, phosphorus- derivatives building blocks have only emerged in the late 1990s for the construction of  $\pi$ -conjugated materials [5]. The replacement of carbon atoms in a conjugated backbone with different heteroatoms significantly changes their physical and chemical properties [6]. The phosphorus compounds in the coordination states of 2 actually can mimic the unsaturated carbon chemistry due to their ability to exhibit low coordinate multiple bonds similar to that of alkenes and alkynes and also due to their isolobal analogy [7]. Benzoxaphosphole or benzothiaphosphole (sulfur instead of oxygen) is an example of conjugated low coordinate heterocyclic organophosphorus compounds which is analogues to benzoxazole or benzothiazole, a unique electro-optical properties, tunable band gap, commercial viability and easy device fabrications and luminescent organic macromolecule. Recently, these materials found greater importance in various technological applications [8].

We are particularly interested in the low coordinate organophosphorus compounds since chemical modifications of their analogs allow a fine tuning of the optical and electrochemical properties of  $\pi$ -conjugated base systems. Starting from one heterocyclic Phosphorus Analogues of benzoxazole, (scheme 1), it is possible to readily access a family of derivatives with different physical characteristics and since the electronic properties of organic compounds varied significantly with the arrangement and substituent attachment [9], the knowledge of conformations and electronic structures will give a better understanding of the electronic and optical properties of these materials. Thus this theoretical calculation will provide a lot of useful information that will help in building up a good relationship between structures and properties of these materials. Also, a comprehensive understanding of the electronic structural properties of these low coordinate organophosphorus (scheme 2,3 and 4) compounds would help to further develop other classes and novel low coordinate organophosphorus compounds for electronic applications.

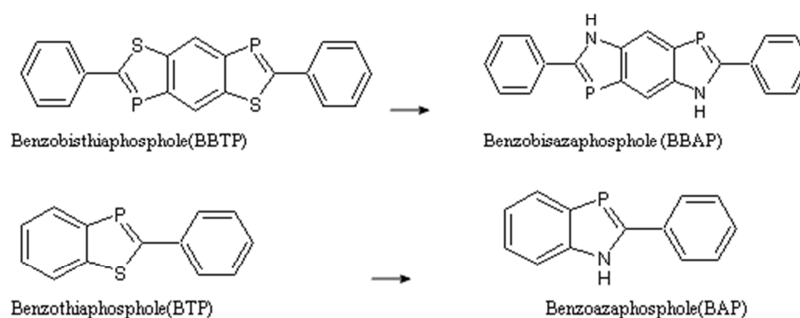




**Scheme 2. Oxazole structural modification to Oxaphosphole**



**Scheme 3. Thiazole structural modification to Thiaphosphole**



**Scheme 4. Benzothiaphosphole structural modification to Benzoazaphosphole**

**Scheme 4. Benzothiaphosphole structural modification to Benzoazaphosphole**

**TABLE 1:** Optimum geometry results (torsional angle  $\theta$  in ( $^{\circ}$ ) and bridge length  $L_B$  in ( $\text{\AA}$ ) and bond length alternation  $\delta_A$  in ( $\text{\AA}$ )) of the modeled compound calculated by DFT/B3LYP/6-31G\* level and HF/3-21G\* level

compounds	HF/3-21G			DFT/B3LYP/6-31G*		
	$L_B$	$\delta_A$	$\theta$ ( $^{\circ}$ )	$L_B$	$\delta_A$	$\theta$ ( $^{\circ}$ )
BBOZ	1.452	0.065	180.00	1.458	0.054	180.00
BOZ	1.453	0.066	179.99	1.459	0.053	179.92
BBTZ	1.469	0.081	179.97	1.468	0.064	179.59
BTZ	1.470	0.082	180.00	1.469	0.065	179.42
BBOP	1.462	0.071	180.00	1.460	0.052	180.00
BOP	1.462	0.071	179.93	1.461	0.053	178.92
BBTP	1.484	0.093	134.23	1.173	0.064	180.00
BTP	1.484	0.093	134.23	1.473	0.065	148.00
BBAP	1.475	0.084	140.38	1.468	0.061	152.25
BAP	1.475	0.084	140.18	1.475	0.084	140.18

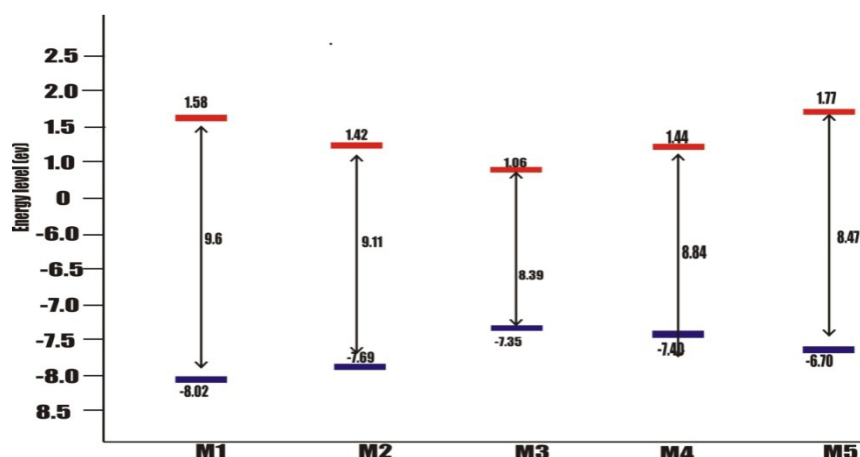
We perform full geometric optimization of all the studied compounds. The selected optimized structure parameters of the heterophospholes compounds calculated by semi-empirical and ab-initio methods are listed in table 1. To verify our theoretical calculations of geometry, experimental X-ray diffraction data for benzothiazole (BTZ) [7] was compared with the theoretical result of benzothiazole calculated in this work which is also similar to benzothiaphosphole, benzoxaphosphole and benzazaphosphole. The experimental result shows that the N=C, S-C intermolecular attraction distance and the inter bond length were 1.3150A, 1.764A and 1.463A respectively. Our theoretical calculations show that N=C and S-C distances and inter-bond distance were 1.279A, 1.769A and 1.469A from the HF method, while DFT values are 1.299A, 1.751A, 1.469A respectively. The comparison

suggests the accuracy of the theoretical geometry of the model compound in the present study is good. Also heincke *et.al* reported the x – ray crystal structure data of benzoxaphosphole with P=C bond length and its P=C-P=C torsional angle given 1.712Å and 177.8Å respectively. Our theoretical calculations shows that P=C bond length and P=C-C=C torsional angle were 1.696Å and 179.48<sup>0</sup> respectively. The trend of the bond lengths and the dihedral angles of the geometries of the modelled compounds obtained from the DFT/B3LYP/6-31G\* and HF/3-21G basis set is similar. Thus the values of dihedral angles of BBTZ, BBOP and BBTP molecules from both DFT/B3LYP/6-31G\* or HF/3-2G level calculations is almost zero indicates that they exhibit planar conformations. On the other hand the 152.25<sup>0</sup> and 140.18<sup>0</sup> Value in dihedral angle makes BBAP twisted (schem 3). This is as a result of the repulsive force between the adjacent hydrogen atom of benzene and H-N-C of benzaphosphole (BBAP) hence a non coplanar conformation.

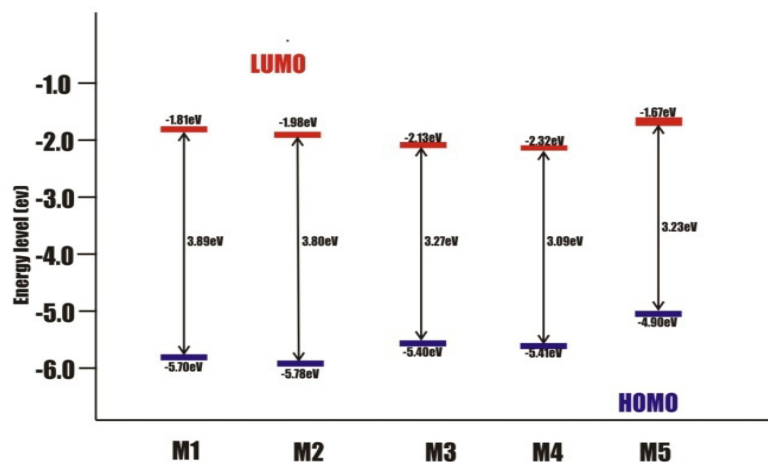
Table 2 and 3, list the theoretical electronic properties parameters ( $E_{HOMO}$ ,  $E_{LUMO}$ ,  $E_{GAP}$ ). The band gaps values calculated at DFT/B3LYP/6-31G\* for M1-M5 were in the range 3.09-3.89eV. The calculated parameters ( $E_{HOMO}$ ,  $E_{LUMO}$ ,  $E_{GAP}$ ) of M3, M4 and P5 are (-5.40, -2.13, 3.27)eV, (-5.41, -2.32, 3.00)eV and (-4.90, -1.67, 3.23)eV respectively. As compared with M2 (-5.78, -1.98, 3.80)eV and M1 (-5.70eV, -1.81eV and 3.89eV), when we substituted nitrogen with phosphorus atom, A systematic destabilization of the  $E_{HOMO}$  and  $E_{LUMO}$  levels and reduction of the E gap is observed.

**TABLE 2:** The theoretical electronic properties (HOMO, LUMO  $E_g$  and  $\lambda_{max}$ ) of the diphenyl-benzo(bis)hetrophosphole modeled compound calculated at HF/3-21 G\* and B3LYP/6-31G\* levels

compounds	HF/3-21G*				DFT/B3LYP/6-31G*			
	HOMO	LUMO	$E_{gap}$	$\lambda_{max}$	HOMO	LUMO	$E_{gap}$	$\lambda_{max}$
M1	-8.02	1.58	9.60	241.67	-5.70	-1.81	3.89	332.07
M2	-7.69	1.42	9.11	251.29	-5.78	-1.98	3.80	341.38
M3	-7.33	1.06	8.39	287.88	-5.40	-2.13	3.27	392.09
M4	-7.40	1.44	8.84	277.39	-5.41	-2.32	3.09	360.11, 421.92
M5	-6.70	1.77	8.47	275.98	-4.90	-1.67	3.23	330, 407



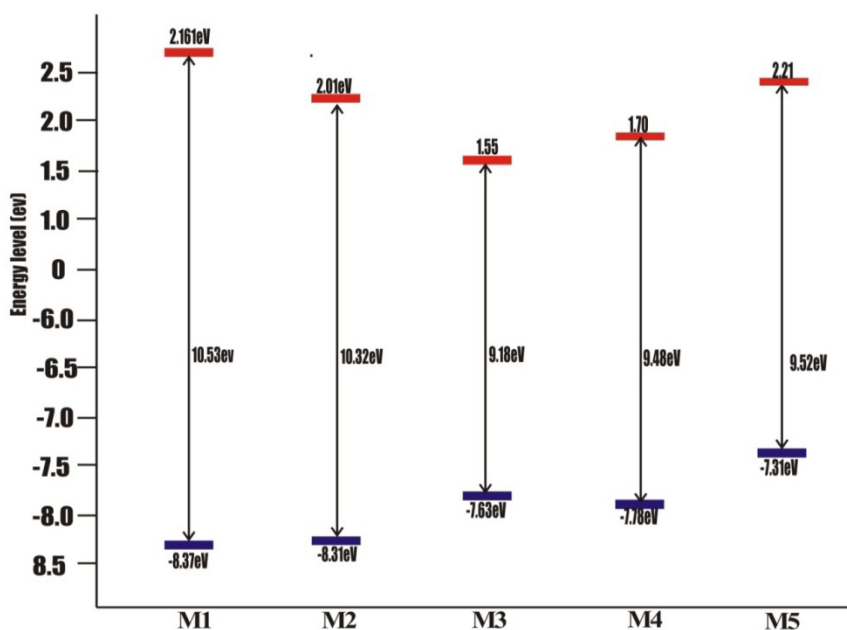
**Fig 1.** HOMO, LUMO energy levels and Band gap energy of the diphenyl- benzo(bis)hetrophosphole model compounds by HF/3-21G\* basis set M1= BBOZ, M2= BBTZ, M3= BBOP, M4= BBTP M5= BBAP



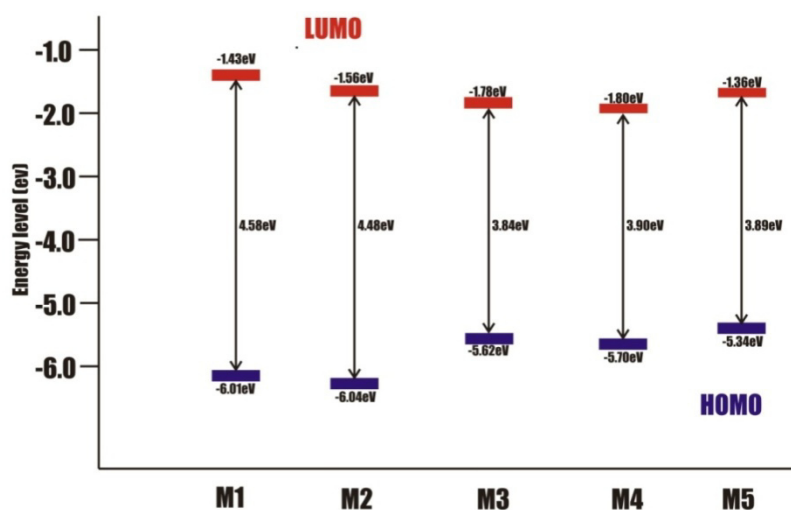
**Fig. 2:** HOMO, LUMO energy levels and Band gap energy of the diphenyl- benzo(bis)heterophosphole model compounds by DFT/B3LYP/6-31G\* basis set where, M1= BBOZ, M2= BBTZ, M3= BBOP, M4= BBTP M5= BBAP

**TABLE 3.** The theoretical electronic properties (HOMO, LUMO and  $E_g$ ) of the phenyl- benzo-hetrophosphole modeled compound calculated at HF/3-21 G\* and B3LYP/6-31G\* levels

compounds	HF/3-21G*				DFT/B3LYP/6-31G*			
	HOMO	LUMO	$E_{gap}$	$\lambda_{max}$	HOMO	LUMO	$E_{gap}$	$\lambda_{max}$
M1	-8.37	2.16	10.53	218.71	-6.01	-1.43	4.58	278.00
M2	-8.31	2.01	10.32	227.83	-6.04	-1.58	4.46	293.80
M3	-7.63	1.55	9.18	267.79	-5.62	-1.78	3.84	315.67
M4	-7.78	1.70	9.48	254.69	-5.70	-1.80	3.90	302.16
M5	-7.31	2.21	-9.52	249.77	-5.34	-1.36	3.89	318.45



**Fig. 3:** HOMO, LUMO energy levels and Band gap energy of the phenyl- benzo-hetrophosphole model compounds by HF/3-21G\* basis set M1= BOZ, M2= BTZ, M3= BOP, M4= BTP M5= BAP



**Fig. 4.** HOMO, LUMO energy levels and Band gap energy of the phenyl- benzo-heterophosphole model compounds by DFT/B3LYP/6-31G\* basis set where M1= BOZ, M2= BTZ, M3= BOP, M4= BTP M5= BAP

The comparison of the HOMO and LUMO LEVEL of M1 M2 M3 M4 and M5 molecules revealed that M3 and M4 molecules have higher HOMO energy (lower ionization potential) and higher LUMO energy (lower electron affinity) than M1 and M2 molecules. The HOMO of M3 and M4 and m5 lies 0.39eV, 0.31eV and 0.37eV above M2 and 0.42eV, 0.34eV and 0.70eV above M1 respectively, showing a decrease of the HOMO upon incorporation of phosphorous atom. The LUMO level of M3 and M4 are 0.35eV and 0.37eV higher in energy than that of LUMO level of M1 and M2. However, LUMO of M1 and M2 lies 0.07eV and 0.32eV above that of BAP, showing a decrease in the electron affinity upon incorporation of nitrogen heteroatom and phosphorus atom.

The reported UV-Vis absorption spectra of terphenylphosphaalkene ( $\lambda_{max}$ :331 nm) and our theoretical calculated  $\lambda_{max}$  of the 2-phenyl-1,3- benzoxaphosphole scheme **5.3** ( $\lambda_{max}$ : 339 nm) were observed to have close  $\lambda_{max}$  for the UV-absorption spectra. However, a small red shift of ~ 9nm is observed in the case of 2-phenyl-1,3- benzoxaphosphole. This reflects clearly the electronic properties shown by the phosphaalkene should be very close to the properties of the benzo-bis(oxaphosphole) system.

The UV-vis absorption spectra for the synthesized benzo-bis(oxaphospholes) (scheme **3b**) and (scheme **3a**) showed very close absorption maximum ( $\lambda_{max}$ ) due to their close structural similarities. Interestingly, the presence of one more oxaphosphole unit and an extra phenyl ring did not showed any great shift in the absorption maxima ( $\lambda_{max}$ ) of benzo-bis(oxaphospholes) (scheme **3a**) compared to the simple benzoxaphosphole (scheme **3b**). The possible reason for this may be due to involvement of rotation of the aryl ring from the central benzo-bis(oxaphosphole) plane, resulting in a decrease in  $\pi$ - conjugation and thereby not influencing the  $\lambda_{max}$ .

## CONCLUSION

Replacing the nitrogen and oxygen atoms in  $\pi$ -extended 2,1,3-benzo[c]thiadiazoles (BTD) and benzo[c]oxazole by a phosphorous (heavy group 15 element) affords the materials with improved low bad gap (electronic) properties. The significantly lower reduction energy levels make the new heterophosphole compounds excellent candidates for application in  $\pi$ -conjugated organic materials. Actually related experimental works also confirmed the above computational results. This calculation procedure can be used as a model system for understanding the relationship between electronic properties and molecular structure and also can be employed to explore the potential opto-electronic device and their application. Presumably, the procedures of theoretical calculations can be employed to predict the electronic properties on the other materials, and further to design novel materials for organic materials.

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