Theoretical investigation on the structural and electronic properties of conjugated organophosphorus compounds

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ABSRACT

In this study, theoretical analysis on the geometries and electronic properties of various conjugated (phosphaalkene)s is reported in order to investigate the influence of the incorporation of phosphorus atom into the backbone of the compound. The theoretical ground-state geometry and electronic structure of the studied (p-phenylenephosphaalkene)s (PPP) are optimized by the hybrid density functional theory (DFT) method at the B3LYP level of theory with 6-31G basis set and compared with those of (p-phenylenevinylene) (PPV) and (p-phenylene nitrilomethylidyne) (PPN) and finally relate this values with synthetic Mesityl of phosphaalkene (DMPPP). The effects of the phosphorus atom and substituent incorporation on the geometries and electronic properties of the materials were discussed. The results of the of the study indicate how the electronic properties can be tuned by heavy phosphorus incorporation and side group substituent and suggests that organophosphorus compounds as good candidate for optoelectronic applications.

Key words: π-conjugated molecules; low coordinate phosphaalkene; Electronic property; DFT; low band gap

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INTRODUCTION

The research in the organic π-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 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. The replacement of carbon atoms in a conjugated backbone with different heteroatoms significantly changes their physical and chemical properties. The elements from group 13, group 14 and group 15 are most widely used for these purposes and to develop new conjugated organic materials. This work concentrates on the replacement of carbon atom with phosphorus atom at the backbone of the conjugated molecule. Phosphorus is a group 15 main group element and capable of exhibiting variable coordination numbers (number of atoms connected) ranging from 1 to 6. Among all possible coordination states, phosphorus has common coordination states of 3 and 5. The 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[6]. (p-phenylenephosphaalkene)s is an example of conjugated low coordinate organophosphorus compounds with a chemical structure of Ar-P=C(H)-Ar which is analogues to (p phenylenevinylene) (PPV), a luminescent organic macromolecule. Recently, these materials (PPV)

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found greater importance in various technological applications such as photovoltaic, nonlinear optics, organic light emitting diodes, data storage and in field effect transistors.[7] . The advantage of these materials is their unique electro-optical properties, tunable band gap, commercial viability and easy device fabrications.

We are particularly interested in the low coordinate organophosphorus compounds since chemical modifications of the structure allow a fine tuning of the optical and electrochemical properties of phosphorus-based ∂-conjugated systems. Starting from one Phosphorus Analogues of PPV, it is possible to readily access a family of derivatives with different physical characteristics and since the electronic properties of these compounds varied significantly with the arrangement and substituent attachment, 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 compounds would help to further develop other classes and novel low coordinate organophosphorus compounds for electronic applications.   In this article, the theoretical analysis on the geometries and electronic properties of conjugated low coordinate organophosphorus compound is reported.

EXPERIMENTAL SECTION

2. THEORETICAL METHODOLOGY

The computational method used to study the electronic properties of the polymers is the density functional theory (DFT). We use the Spartan 10 program package to run our calculations on intel®Core (TM) i3 CPU M350@2.27GHz computer with the Becke, three parameter, Lee-Yang- Parr (B3LYP) exchange- correlation method. In order to obtain an accurate description of the physical system, we used the large 6-31G* basis set for the electronic properties of the model compounds. It has been shown that B3LYP/6-31G* gives decent ground state structures of conjugated polymers.[10]. The molecules are built from the scratch as show in figure 1 below where 'Y' represent carbon, nitrogen and phosphorous.
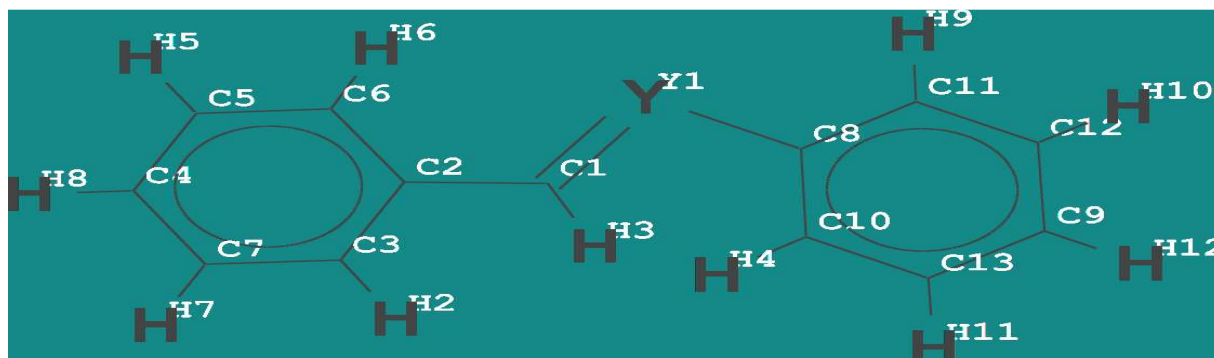

Fig. i Conjugated compound for theoretical analysis where 'Y'= carbon (C), Nitrogen (N) and phosphorous(P)
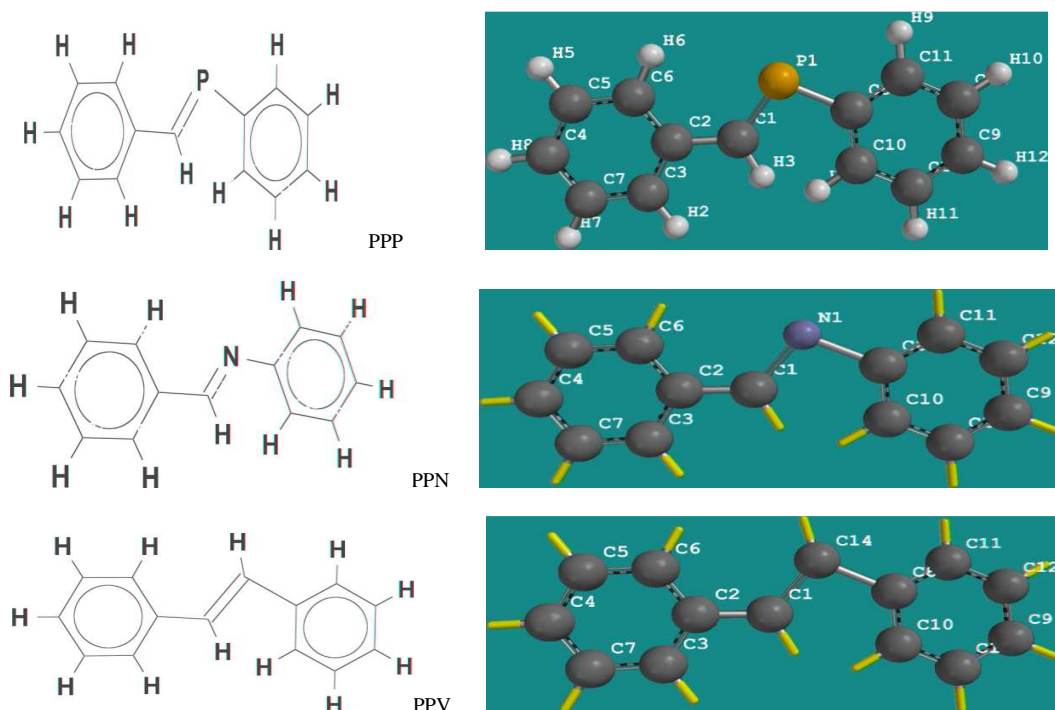
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Fig.ii Structure of the studied compounds   fig.iii optimized structures of the studied compounds

TABLE 1: Geometric parameters (bond length in Å) of studied compounds as obtained DFT/B3LYP/6-31G*

BOND LENGTH (Ο)	DMPPP EXP	DMPPP CAL	PPV CAL	PPN CAL	PPP CAL
C1-C2	1.461	1.465	1.466	1.468	1.460
C2-C3	1.409	1.396	1.409	1.406	1.412
C3=C7	1.393	1.385	1.391	1.390	1.389
C5-C6	1.393	1.382	1.394	1.394	1.393
C2=C6	1.411	1.394	1.408	1.403	1.410
C8=C11	1.414	1.417	1.409	1.405	1.406
C8-C10	1.414	1.400	1.408	1.406	1.406
C11-C12	1.403	1.397	1.391	1.392	1.394
C10=C13	1.403	1.406	1.394	1.394	1.395
C1=Y	1.691	1.666	1.349	1.281	1.695
Y-C8	1.860	1.838	1.466	1.406	1.840
C1-H3	1.089	0.951	1.089	1.101	1.090

DMPPP = Dimesityl P-Phenylenephosphaalkene, PPP = P-Phenylenephosphaalkene, PPV = P-Phenylenevinylene, PPN = P-phenylene nitrilomethylidyne. Exp = Experimental value. Cal = B3LYP/6-31G* calculated value

TABLE II. Theoretical electronic parameters showing the values of HOMO (eV), LUMO(eV), (Eg), (λ$_{max}$(nm)) and θ obtained by DFT/B3LYP/6-31G* of the studied molecules

MOLECULESS	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	$λ_{max}$ (nm)	$θ1(^0)$	$θ2(^0)$
PPV	-5.51	-1.36	4.14	367.71	0.01	0.06
PPN	-5.90	-1.55	4.35	370.86	1.53	39.42
PPP	-5.69	-2.02	3.67	401.99	5.70	36.22

E_{HOMO} = Energy of HOMO, E_{LUMO} = = Energy of LUMO, E_g = band gap energy, $λ_{max}$ = maximum absorption wave length, $θ$ = dihedral angle where $θ1 = C_3C_2C_1Y$, $θ2 = C_{11}C_8Y C_1$

RESULTS AND DISCUSSION

3.1. The influence of the linkage on the geometric and electronic structures
The geometric and electronic structure of   p-phenylenephosphaalkene) PPP are compared with those of (p-phenylene) (PPN) and (p-phenylene vinylene) (PPV) in order to study the influence of C=P linkage. For all

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molecules, geometrical parameters were obtained after total optimization by B3LYP/6-31G*.These parameters were justified by comparing their values with the experimental results reported in the literature [5]. The optimized geometries structures and data of PPP, PPV and PPN are shown in fig ii and table i and ii. The bond length of the C=N linkage in PPP and that of the C=C linkage in PPV are 1.692O and 1.349O respectively. Besides, the C-C bond length between the C=P linkage and the phenylene is 1.862O, while that between the C=C linkage and the phenylene of PPV is 1.466O. The longer bond length of C=P and C-P in PPP than those of C=C are due to the smaller electro-negativity of the phosphorous and carbon. However, a significant difference is shown on the dihedral angle (θ_1 and θ_2) between aromatic ring and linkage. The dihedral angles ($\theta1$ and $\theta2$) in PPV are almost zero but for PPN, both the dihedral angles $\theta1$ and $\theta2$ are 39.42^0 and 1.53^0 respectively and that of PPP are 5.70^0 and 36.22^0 respectively. The repulsive force between the adjacent hydrogen atoms on the C=P linkages and the N- phenylene of PPP result in a non –coplanar conformation. Both the differences of bond angles and dihedral angles of PPV and PPN are as a result of the distance between H_3 and H_4 of the molecules. The distance between H_3 and H_4 is much longer in PPV than that in PPN. Consequently, it results in a much smaller (and negligible) H-H repulsion force for PPV than that of PPN and that of PPP. This explains why PPV is coplanar but PPN and PPP are twisted and hence non-coplanar. This indicates that the nitrogen and phosphorous atom substitution significantly enhance the non-planarity of the PPN and PPP. Incorporation of a phosphaalkene (P=C) bond into a carbon based π-conjugated system results in the reduction of HOMO-LUMO energy levels. In a macromolecule these energy levels often known as valence band (VB) and conduction band (CB). The difference in the energy between these two bands is known band gap energy, which actually defines the overall electro-optical properties of the materials. The calculated electronic properties of the PPP and PPV and PPN are shown in table 3. The calculated (IP, EA, Eg) of PPP, PPN and PPV are (-5.69, -2.02, 3.67) eV, (-5.90, -1.55, 4.35) eV, and (-5.51, -1.36, 4.14)eV, respectively. These results obtained confirmed that the band gaps in conjugated molecules are governed by their chemical structures. The lowest band gap of PPP confirmed that the incorporation of phosphorous atom can greatly reduce the gap of materials used in semiconductor and opto-electronic devices despite its non-coplanar structure. The effect of the linkage between the phenylene rings on the electronics structures can be further illustrated by the Homo and Lumo energy levels of fig iv.
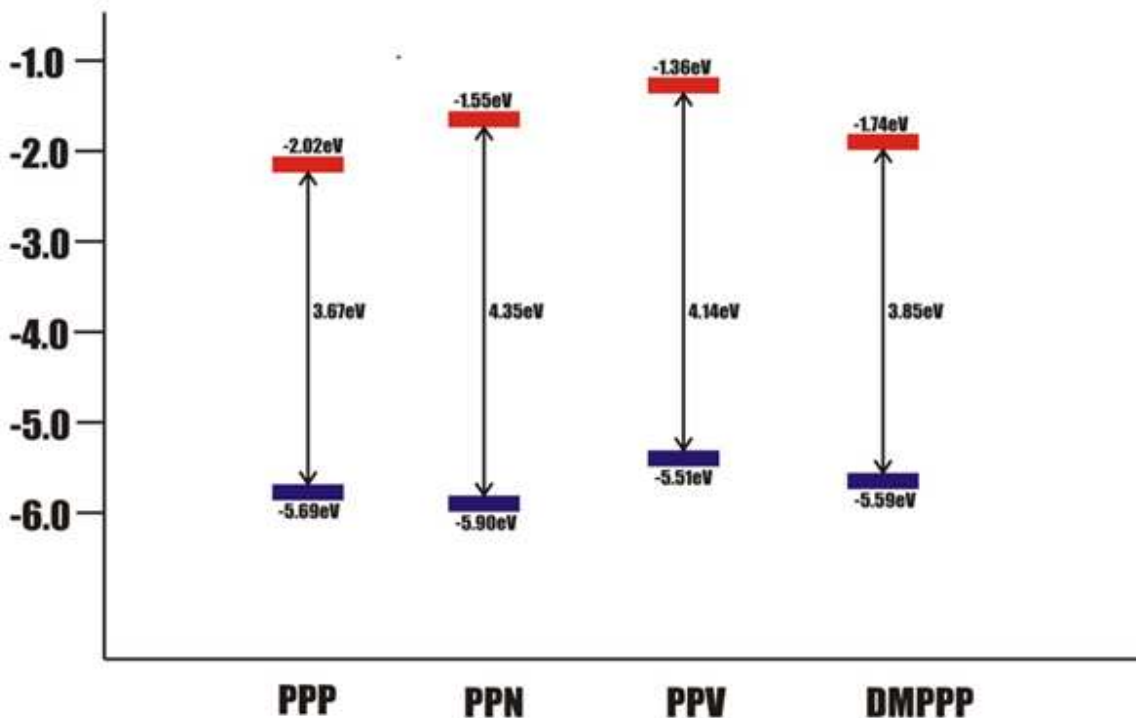

Fig.iv.   Schematic representation of the effect of linkage between phenylene rings on the molecular orbitals and energy band gaps of PPP, PPN PPV and DMPP
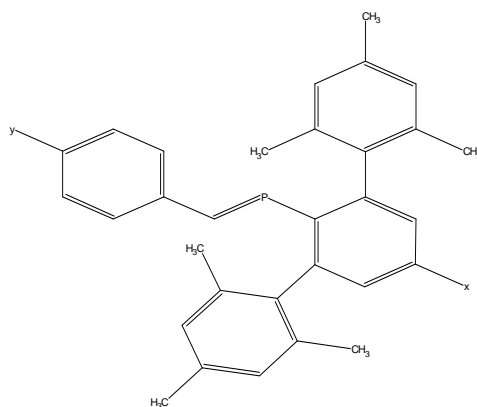
Fig.V. Conjugated compound for theoretical analysis of Dimesityl P-Phenylenephosphaalkene

TABLE III. Theoretical electronic parameters showing the effect of substitutions at the para positions of DMPPP obtained by DFT/B3LYP/6-31G*

MOLECULE	*SUB X*	*SUB Y*	$\theta1$ (^{0})	$\theta2$ (^{0})	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	$\lambda(nm)$ (shoulder)	λ (nm) exp
DMPPP1	H	H	0.00	92.34	-5.59	-1.74	3.85	342	331
DMPPP 2	Br	H	0.00	92.41	-5.72	-1.87	3.85	341	342
DMPPP3	H	Br	0.00	92.41	-5.71	-1.96	3.75	335	337
DMPPP4	Br	Br	0.00	93.12	-5.83	-2.09	3.74	336	345
DMPPP5	H	OCH	179.56	-89.04	-5.21	-1.53	3.68	333	-
DMPPP6	OCH	NO2	176.74	-99.20	-5.98	-2.64	3.34	340(439)	376(380)
DMPPP7	H	NO2	179.36	-96.34	-5.95	-2.59	3.36	339(430)	377

*SUB X = substituent at meta terphenyl, **SUB Y** = substituent at phenyl ring*

3.2. EFfect of substituent on phosphaalkenes

3.2.1. *The influence of the protecting group and bromine substitution on the geometry and electronic structure of the molecule*

Low coordinate phosphorus compounds had been successfully synthesized by using steric protecting groups, with this modification, phosphorus maintains its low coordination state (coordination number 2). Therefore it is necessary to investigate the effect of the protecting group and other substituent groups on the geometry and electronic structure of the phosphaalkene molecule.

In an attempt to investigate the influence of the mesityl protecting group on the studied compound, phosphaalkene without the bulky mesityl protecting group (PPP) modeled above is compared with bulky mesityl protecting group (DMPPP). For the DMPPP, the B3LYP/6-31G* calculation predict that the dihedral angle are θ_1= 0.00^0 and θ_2=92.34^0. The large 92.34^0 dihedral angle of copolymer of DMPPP Compared with 36.32^0 of PPP suggest that the mesityl protecting group further increases the non-coplanar conformation of phosphaalkenes. This effect definitely, worsen the delocalization of π-electrons from the *meta*-terphenyl to phenylene These effect may explain the gap variation i.e the change in band gap of the modeled molecules from 3.67eV in PPP to 3.85eV in DMPPP (table iii). The bridged bond length (L_B) between carbon of terphenyl and phosphorous atom in DMPPP increases by 0.022Ọ when compare with corresponding PPP. This worsens the double-bond character due to their decrease π-electron delocalization. The dihedral angles of DMPPP6 from the x-ray diffraction result reported shows that the C=P plane twist 120.4^0 from the terphenyl [5] while our calculation shows 99.20^0 The correlation between the chemical structures of PPP based and $DMPPP_1$ based copolymers suggest that the protecting group has greatly increased band gap acyclic conjugated organophosporous. Thus the presence of these bulky groups breaks the π-conjugation and loses some planarity due to the steric constrains of the molecule.

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Moreover, Phosphaalkenes are relatively non polar compounds in the absence of strongly polarizing groups, owing to the very close electronegativity of carbon $((\chi)(C) = 2.5)$ and phosphorus $(\chi (P) = 2.1)$ [13]. The presence of different functional groups across the P=C unit can lead charge polarization which may increase the lowering of the band. Thus Systematic investigations of the impact of para-substituent to phosphaalkene groups have been made. In investigating the effect of substituent, the optimized structure and electronic prosperities of bromine substituted at the bulky steric hindered terphenyl were compared with those of substituted at the Para position of the less hindered phenyl ends. Bromine attached to the phenyl ring shows a reduction of 0.10eV in band gap when compared with DMPPP. However there is no significant difference in the band gap of bromo-terphenyl ring suggesting a steric hindrance as a result of the bulky protecting group.

The absorption wave length (λ_{max}) of the studied compounds in the gaseous phase is shown in Table iii. The peak of absorption wave length (λ_{max}) of PPP is about 329nm. λ_{max} for $DMPP_1$ is about 342nm. This value compared favorably with the experimental value of 334nm reported in literature [5] $DMPP_1$ exhibits a red shift of about 8nm in the UV region, when compared with λ_{max} of PPP. Therefore, we can say that the coupling of the protecting groups greatly affect the effective expansion of the light absorption range. The effect of bromine substitution on the absorption properties shows that, Bromine atom on either or both ends of $DMPPP_4$ induces a red shift on the UV-Vis spectra. The shifts are additive, and the shift is greater when substitution is present on the less-hindered phenyl unit. The presence of an electron withdrawing groups and accepting group on the less hindered phenyl ring possess greater influence on the π to π^* energy transition, thus leading to a greater red shift in the absorption spectra. Whereas the introduction of both electron donating methoxy group on the bulky mesityl ring and electron withdrawing group to the less hindered phenyl ring did not show a significant influence on the optical absorption when compare with electron withdrawing group attached to the less hindered phenyl ring. This indicates that the presence of a donor and withdrawing group attached to the bulky *meta*-terphenyl unit is not having sufficient influence on the π to π^* electronic transition. This can be due to the weak π-delocalization of π electrons from this ligand to the rest of the molecule in the phosphaalkene. The comparison suggests that the optical absorption property λ_{max} increases at the less hindered phenyl. Therefore conjugation of substituent at the less hindered phenyl will further enhance the lowering of band gap and absorption properties of phosphaalkenes.

CONCULSION

The replacement of carbon atom in a conjugated chemical backbone of stibene with phosphorus heteroatom significantly changes their physical and chemical properties through which, one can tune the overall electro-optical properties of a conjugated material. The decrease in the band gap reflected a red shift in the Uv-Vis absorption spectra of the concerned materials. Thus, these materials give better electro-optical properties that could be compared to their organic counterparts. The lower band gap will facilitate a good conducting material in electro-optical devices. Overall, the additive impact of the para-substituents can therefore make the polymeric material of phosphaalkene effective in applications of NLO materials that demand a high degree of polarization just the way they have been found in related alkenes. Moreover, considering the scarcity of NLO active phosphaalkenes, these studies provided the initial step to continue investigation on the effect of substituent on *meta*-terphenyl phosphaalkene. However, theoretical calculation of the synthetic phosphaalkene (DMPPP) reviled a break of π-conjugation and loses some planarity as a result of the bulky protecting (mesityl) group which also causes some steric constrains to the backbone of the compound. These effects may limit the use of this compound for other electro-optical devices. Hence there is a need to continue in the search for organic phosphaalkene that will not compromise with effective conjugation and planarity.

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