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Tuning of Electronic Structures of Poly(*p*-phenylenevinylene) Analogues of Phenyl, Thienyl, Furyl, and Pyrrolyl by Double-Bond Linkages of Group 14 and 15 Elements

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We investigated electronic structures of four sets of monomers and polymers comprising of phenyl rings and five-membered hetero(aromatic) moieties connected with double-bond −X═X− linkages (X = CH, SiH, GeH, N, P, As) by density functional theory, time-dependent density functional theory, and periodic boundary condition calculations with B3LYP functional. Electronic structures of poly(*p*-phenylenevinylene) (PPV) analogues are primarily dominated by central double-bond moieties. The introduction of ethylene homologues with group 14 and 15 elements was demonstrated to be a promising approach to modify electronic structures of conjugated oligomers and polymers. Excitation energies of monomers with double-bond linkages were reduced by around 13−50% with respect to corresponding dimers of phenyl, thienyl, furyl, and pyrrolyl rings. Similarly, band gaps of poly(*p*-phenylene) and polythiophene were decreased by 0.3−0.9 eV upon the insertion of double-bond linkages. Furthermore, excitation energies of monomers presented decreasing trends when descending through groups 14 and 15. For group 14 ethylene homologues, the decreasing trend in the lowest excitation energies was rationalized by a progressively favoring of $\pi-\sigma^*$ interactions as descending X = CH, SiH, and GeH. Increasing p contents of central bonds along X = N, P, and As accounted for geometry features and the lowest excitation energies of group 15 species. A decrease in the extent of electronic communications between aromatic rings and −X═X− linkages within higher congeners was also revealed.

1. Introduction

The π-conjugated oligomers and polymers containing double-bond linkages with semiconductivity have stimulated tremendous research interest both experimentally and theoretically.[1−3] The discovery that such conjugated polymers can be utilized as the light-emitting layer in an electroluminescent (EL) device has initiated explosive investigations to gain control of color and efficiency.[4,5] To obtain novel organic electronic devices, tuning of electronic structures of π-conjugated oligomers and polymers is a most appealing subject.

Some general principles have been widely recognized with respect to tuning of electronic properties of conjugated polymers so far. The commonly used strategies may follow three main threads. One is to maximize extent of π conjugation by sustaining planar backbones. For example, the scheme for rigidification of a π-conjugated system by partially or fully covalent bridging was efficient to reduce energy gaps of oligomers.[6−8] Another important factor of bond-length alternation in conjugated polymers was addressed nearly two decades ago.[9] Correlations between bond length alternations and band gaps of polymers have been extensively illustrated ever since.[10,11] Polymers with narrow band gaps normally exist concurrently with an increase of quinonoid character in a π-conjugated system.[11,12] The third theme is to refine electronic properties of oligomers and polymers by making various structural modifications on building blocks.[13−17] The synthesis of a highly conducting donor−acceptor complex between the tetrathiofulvalene and tetracyano-*p*-quinodimethane is a successful example of early attempts.[18]

Among various chemical modifications, insertion of vinylene linkages in π-conjugated systems has been demonstrated to be an effective strategy to modulate electronic properties.[3d,19] Some researchers thought vinylene linkage served as a "conjugated spacer" between aromatic units.[20,21] Therefore, the linkages effectively lowered torsion angles by reducing steric repulsion between consecutive rings. On the other hand, the presence of electronic communication between aromatic units and double-bond linkages was reflected by red shifts in UV−vis spectra.[22] Poly(*p*-phenylenevinylene) (PPV, **1a**) and its derivatives are the most successful representatives in this area. The past decade has witnessed rapid development of their applications in electronic devices.[23] Poly(2,5-thienylene vinylene) (PTV, **2a**) and its oligomers are newly emerging as promising candidates for molecular electronics.[24] PPV[25] and PTV[26] have lower optical gaps by about 0.3 eV compared with their counterparts, polyphenylene (PPP) and polythiophene (PT), without ethylene linkages.[27] Also, azo and diphosphene groups were used to construct some new conjugated oligomers with relatively low excitation energies.[22,28−30] Unlike their olefinic kin, however, electronic properties of compounds incorporating heavier main group atoms (such as Si, Ge, P, and As) have not been systematically investigated despite the tremendous progress in synthesizing various double-bond moieties.[31−36] Therefore, we carry out extensive studies on both monomers and polymers containing aromatic rings and double-bond linkages by density functional theory (DFT). We aim to answer the following two questions: (1) Are there some trends in variations of electronic structures of PPV analogues perturbed by double-bond linkages as descending group 14 and group 15? (2) What are similarities and differences in evolution trends of geometries and energy gaps between groups 14 and 15 species?

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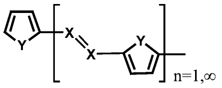


1	Y = -CH=CH-	**2**	Y = S	**3**	Y = O	**4**	Y = NH
1a	X=CH	**2a**	X=CH	**3a**	X=CH	**4a**	X=CH
1b	X=SiH	**2b**	X=SiH	**3b**	X=SiH	**4b**	X=SiH
1c	X=GeH	**2c**	X=GeH	**3c**	X=GeH	**4c**	X=GeH
1d	X=N	**2d**	X=N	**3d**	X=N	**4d**	X=N
1e	X=P	**2e**	X=P	**3e**	X=P	**4e**	X=P
1f	X=As	**2f**	X=As	**3f**	X=As	**4f**	X=As

Figure 1. The studied monomers and polymers with various double-bond linkages.

The compounds investigated are comprised of aromatic rings (R = phenyl, Ph, **1**; thienyl, Th, **2**; furyl, Fu, **3**; pyrrolyl, Py, **4**) linked by double bonds X=X (group 14, X = CH, SiH, GeH; group 15, X = N, P, As) as shown in Figure 1. Some interesting trends in tuning effects of linkages on geometries, the lowest excitation energies (E_{ex}), and band gaps (E_g) of **1**−**4** are observed in the present work. Because of the significance of oligomers for both theoretical and application interests,[24,37,38] we make emphasis on monomers to interpret effects of linkages. This paper is organized as follows. Computational details are briefly introduced in section 2. Discussions on optimized geometries, energy gaps between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), Δ_{H-L}, E_{ex} values of monomers **1**−**4**, and band gaps of related polymers are presented in section 3. Comprehensive understanding of group trends of geometries and E_{ex} is also given with the natural bond orbital (NBO) analysis. Finally, conclusions drawn from the present work are summarized in section 4.

2. Computational Details

Our calculations consisted of two parts: quantum chemistry computations on constituting monomers, and studies on polymers by introducing periodic boundary condition (PBC) as implemented in Gaussian 03.[39] The details of these two kinds of calculations are covered in the following subsections.

Electronic Structures of Monomers. The ground-state geometries of set **2** with various double-bond linkages were fully optimized using the B3LYP[40] functional at basis sets of 6-31G*, 6-31+G*, 6-31++G*, and 6-31++G**, respectively. Calculation results are given in Table S1 of Supporting Information, from which we find that the choice of basis sets had little influence on optimized geometries of **2** with the exceptions of **2c** and **2f**. For **2c** and **2f**, containing the third-row elements Ge and As, diffusion basis set was required due to relatively larger differences in calculated bond lengths of central double bonds, $R_{X=X}$, and trans-bent angles (fold angles), Θ,[41] between 6- 31G* and those diffusion basis sets such as 6-31+G* and 6-31++G*. In addition, the 6-31+G* basis set gave geometries almost identical to those obtained by higher basis sets, 6-31++G* and 6-31++G**; thus B3LYP/6-31+G* results were employed hereafter. The trans arrangements of aromatic rings and double bonds were found to be the most stable conformers for all studied monomers **1**−**4**.[42] Optimized geometries were characterized by harmonic frequency analysis as minima.

Although predicted excitation energies by the B3LYP functional as well as other exchange/correlation functionals were reported to be underestimated under some circumstances especially for long chains,[43−46] trends in experimental spectra were well reproduced by time-dependent DFT (TDDFT) calculations.[11,46−49] On the other hand, we are mainly interested in relative changes in E_{ex} values of monomers caused by different double-bond linkages. Thus, TDDFT calculations at the level of B3LYP/6-31+G* were performed to predict E_{ex} values of monomers **1**−**4**.

To understand resultant trends concerning geometries and excitation energies on descending groups 14 and 15, the NBO method,[50] which is based on the natural population analysis, was employed to analyze bond orbital interactions, as implemented in Gaussian 03.[39] Stabilization energies of orbital interactions between donors (bonding orbitals, such as $\pi_{X=X}$ and σ_{X-X}, and lone-pair orbitals, n_x) and acceptors (antibonding orbitals, e.g., σ_{X-X}* and $\pi_{X=X}$*), occupancy numbers of orbitals, and s and p contents of hybridized orbitals are addressed in subsection 3.3. In addition, bond orders derived by NBO analysis, supplemented in Tables S2−S5 of Supporting Information, may offer chemists useful information on bond strength.

PBC Calculations on Polymers. Polymers of series **1** and **2** with one-dimensional periodic structures were studied by the PBC-DFT/B3LYP/6-31G* method, whose performance was recently validated by PPP, PT, polyfuran, and polypyrrole with an average deviation of no more than 0.1 eV relative to experimental optical gaps.[11b] Because of difficulties in convergence of PBC calculations with diffuse basis sets, all PBC-DFT computations were performed at the level of B3LYP/6-31G*, which was anticipated to give reasonable predictions on variation trends.

3. Results and Discussion

3.1. Trends in Excitation Energies and Band Gaps.

Table 1 collects calculation results of E_{ex} and Δ_{H-L} values of monomers **1**−**4** as well as band gaps of polymers **1**−**2** along with available experimental values for their derivatives. It can be found that TDDFT excitation energies and PBC-DFT band gaps are in good agreement with experimental spectra of derivatives of **1**−**4**.

Excitation Energies and HOMO−LUMO Gaps. As addressed in some literature,[20,51] the inclusion of double-bond linkages does reduce the lowest excitation energies of oligomers, as reflected by smaller values of excitation energies for **1**−**4** in comparison to those of biphenyl, bithiophene, bifuran, and bipyrrole, respectively. More interestingly, progressively decreasing trends in E_{ex} values of monomers **1**−**4** descending through both groups 14 and 15 are clearly illustrated in Figure 2. The excitation energy drops sharply from ethylenes (**1**−**4a**) through heavier analogues, Si species (**1**−**4b**), to Ge species (**1**−**4c**). Group 15 shows a similar decreasing trend in the lowest excitation energy from azo compounds through diphosphenes to diarsenes.

Little correlation is observed between excitation energies and aromaticities of aromatic rings connected by the same double bond. A sequence of **1** > **3** ≈ **4** > **2** in excitation energies is quite different from that in aromaticities of those isolated rings as characterized by negative nucleus-independent chemical shifts: **1** (benzene, −9.7 ppm) > **3** (furan, −12.3 ppm) > **2** (thiophene, −13.6 ppm) > **4** (pyrrole, −15.1 ppm).[52] This implies little influences exerted by aromatic moieties.

On the other hand, since the lowest dipole-allowed excitations of the studied monomers **1**−**4** assigned by our TDDFT calculations are mainly excitations from HOMOs to LUMOs,[53] similar trends in Δ_{H-L} as those in E_{ex} values can be expected here. In fact, Figure 3 indicates a good correlation between TDDFT excitation energies and Δ_{H-L} values for the whole set of 24 monomers studied in the present work (with a correlation coefficient of 0.98). Such a linear relationship between E_{ex} and Δ_{H-L} was also found in some other π-conjugated oligomers.[11a,46]

TABLE 1: HOMO−LUMO Gaps (Δ_{H-L}), the Lowest Excitation Energies (E_{ex}) of Monomers, and Band Gaps of Polymers Obtained by DFT and PBC-DFT Calculations, Respectively[a]

	properties of monomers			band gaps of polymers	
compd	Δ_{H-L}	E_{ex}[b]	exptl	calcd	exptl
*n*Ph	5.14	5.04		3.06,[c] 3.29,[d] 2.8[e]	3.40[f]
1a	4.05	3.85, 3.98[g]	3.91[h]	2.45, 2.27,[d] 3.09[g]	2.42−2.45,[i] 2.70[j]
1b	3.01	3.01		2.18	
1c	2.87	2.87		2.36	
1d	3.93	3.67	3.88[k]	2.33	
1e	3.27	3.29	3.33,[l] 3.16[h,m]	2.28	2.58[n]
1f	2.90	2.74	3.03−3.10[m]	2.63	
*n*Th	4.28	3.98		2.05[c]	2.0−2.2[o]
2a	3.56	3.45	3.44[p]	1.70	1.70−1.80[q]
2b	2.87	2.87		1.98	
2c	2.81	2.82		2.19	
2d	3.19	3.11		1.76, 0.98[r]	
2e	2.85	2.64		1.41	
2f	2.69	2.55		1.48	
*n*Fu	4.66	4.57		2.42[c]	2.35[s]
3a	3.72	3.71			1.76[t]
3b	2.83	2.89			
3c	2.75	2.80			
3d	3.29	3.40			
3e	2.84	2.79			
3f	2.69	2.62			
*n*Py	5.10	4.88		2.88[c]	2.85[u]
4a	3.76	3.70			
4b	2.85	2.84			
4c	2.72	2.69			
4d	3.17	3.21		1.12[r]	1.0[v]
4e	2.69	2.60			
4f	2.54	2.44			

[a] Experimental excitation energies and optical gaps are also given for comparison. All values are in units of eV. HOMO−LUMO gaps of monomers are calculated by B3LYP/6-31+G*. Excitation energies of monomers are obtained by TDDFT/B3LYP/6-31+G* calculations. Band gaps of polymers are calculated by PBC−B3LYP/6-31G* method. [b] The available experimental data are mostly obtained for derivatives instead of pristine monomers or polymers. [c] Reference 11b. [d] VEH method, ref 56d. [e] DFT/LMTOs basis functions (linear muffin-tin orbitals), ref 56a. [f] Reference 73. [g] PPV, VEH method; stilbene, INDO/S-CI, ref 57b. [h] λ_{max} of stilbene and the compound containing Mes*P═PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl) in $CHCl_3$, ref 74a. [i] The absorption edges of poly[2,5-bis(decyldimethylsilyl)-1,4-phenylenevinylene], ref 23c. [j] λ_{max} of poly(1,4-didodecyloxy-2,5-phenylene-vinylene-2',5'-phenylenevinylene), ref 75. [k] *trans*-Azobenzene, 3.88 eV; *cis*-azobenzene, 2.89 eV; ref 76. [l] λ_{max} of bis(disphosphene)DmpP═PAr$_4$C$_6$PDmp (Dmp = 2,6-Mes$_2$C$_6$H$_3$), ref 22. [m] 2,6-Trip$_2$H$_3$C$_6$P═PC$_6$H$_3$-2,6-Trip$_2$, 2,6-Mes$_2$H$_3$C$_6$As═AsC$_6$H$_3$-2,6-Mes$_2$, and 2,6-Trip$_2$H$_3$C$_6$As═AsC$_6$H$_3$-2,6-Trip$_2$, ref 31f. [n] The first polymer containing multiple bonds of heavier main group elements (P═P) with phenylenevinylene and 2, 5-dihexyloxybenzene repeat units; UV/vis spectra in $CHCl_3$; ref 74b. [o] Reference 3e. [p] Reference 77. [q] Reference 6e. [r] Extrapolated band gaps for polymers based on TDDFT-B3LYP/6-31+G* excitation energies of oligomers, ref 30. [s] Reference 78. [t] Reference 79. [u] Reference 80. [v] Reference 81.

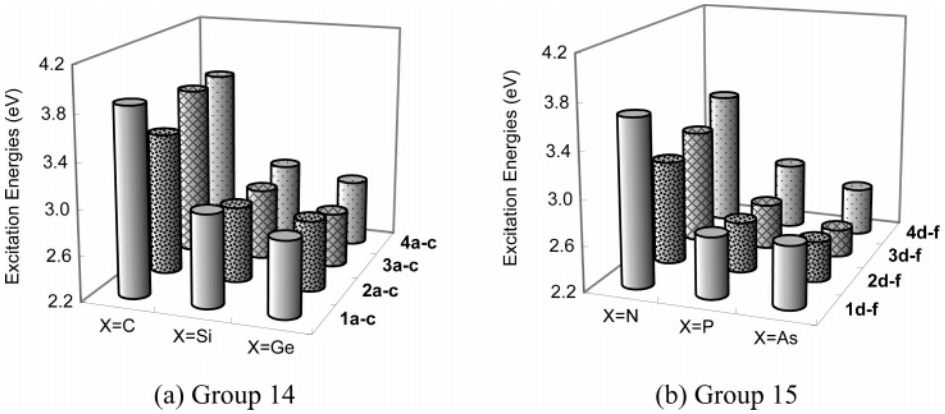
Figure 4 illustrates clearly sketches of evolution of frontier orbital levels for monomers **1**−**4**. In comparison to ethylene monomers (**1**−**4a**), when other double-bond linkages are inserted, LUMO levels are stabilized and HOMO levels exhibit less variation; thus lower HOMO−LUMO gaps are achieved (monomers **b**−**f**). It was recognized that the HOMO−LUMO gap decreases significantly from hydrides $CH_2{=}CH_2$ to $SiH_2{=}SiH_2$.[54] We notice the trend in Δ_{H-L} values of PPV analogues bears a resemblance to this case. Thus, electronic properties of series **1**−**4** depend mainly on central X═X units. This observation can also explain the similarity among four sets of monomers.

Band Gaps of Polymers. The calculated band gaps of polymers **1**−**2** also fit reasonably well with available experimental data and documented theoretical values (Table 1). Band gaps of **1** and **2** are reduced by around 0.3−0.9 eV with respect to PPP and PT. Series **2** composing of thienylene units have lower band gaps than correspondents in series **1**. The difference between E_{ex} values of monomers and E_g values of polymers, $\Delta E_g = E_{ex} - E_g$, can be taken as a measure of delocalization extent or, more indirectly, conjugation length. Therefore, it is of interest to investigate variations of ΔE_g on descending groups 14 and 15, as drawn in Figure 5. The heavier X, the lower the value of ΔE_g is. This indicates less conjugation upon chain extension for heavier congeners. In other words, there exists an increasing tendency of localization of the excitation when going down the group. Moreover, Ge and As species have nonzero band gaps, although excitation energies of their monomers are much lower than those of Si and P analogues. When X becomes heavier, the extent of electron localization turns greater, leading to a singlet state with some amounts of diradical character. In this case, corresponding polymers exhibit nonzero band gaps of around ~1.48−2.63 eV due to Peiels instability. A latest theoretical investigation in our group predicted boron/thiophene cooligomers with strong diradical characters had band gaps of around 2.0 eV, in contrast to a vanishing band gap obtained by extrapolation of excitation energies of oligomers to an infinite limit.[11b] Studies on oligoacenes also predicted a nonzero band gap for polyacene as a result of Peiels instability.[55]

3.2. Different Geometries Between Groups 14 and 15 Species.

The above-mentioned trends in electronic properties are closely related with their geometrical features. Systems comprising of group 14 elements show different structural characteristics from dipnictenes. The difference in optimized geometries can be perceived from Figure 6 for monomers **1** and **2** as well as Figure S1 for series **3** and **4**. As expected, trans conformers of **1**−**4** are more stable than cis ones. To make easier comparisons of geometric structures for all the studied systems, some important structural parameters such as bond lengths of the X═X double bond, $R_{X{=}X}$, bond angles of C$_1$−X−X, ϕ, and trans-bent angles,[41] Θ, are summarized in Table 2. As characterized by smaller values of Θ, it is noteworthy that polymers have less deformation from planarity than monomers. In the following parts, we put emphasis on trends in geometries of monomers **1**−**4**.

It should be mentioned that experimental data correspond mostly to double-bond units protected by cumbersome substituted phenyl groups, i.e., derivatives of series **1**. As shown in Table 2, geometrical parameters, $R_{X{=}X}$, ϕ, and Θ of **1**−**4** obtained by B3LYP/6-31+G* calculations fit reasonably well with typical experimental values. Within a theoretical framework,[56] the relationship between geometries and electronic properties of PPV (**1a**) chains was extensively investigated by semiempirical Austin model 1 (AM1) and VEH methods.[57] Special theoretical attentions were paid to the preference of trans-bent geometries over coplanar geometries for heavier ethylene analogues, disilene (Si_2H_4) and digermene (Ge_2H_4).[54,58,59] MP2 calculations at 6-31G** and 6-311++G** levels were employed to investigate ground-state geometries of substituted disilenes, showing wide ranges of bond length $R_{Si{=}Si} = 2.19-2.41$ Å and trans-bent angle $\Theta = 17-55°$ depending on various substituents.[60,61] In the parent digermene, the bond length of 2.24−2.34 Å for Ge═Ge and a twisting geometry from planarity by 34−47° were also predicted by various methods such as SCF-



(a) Group 14 (b) Group 15

Figure 2. The trends in TDDFT/B3LYP/6-31+G* excitation energies of monomers **1**−**4** with double-bond linkages formed by (a) group 14 and (b) group 15 elements, respectively.

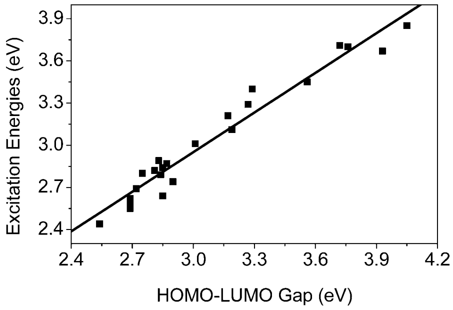


Figure 3. Correlation between the lowest excitation energies and HOMO−LUMO gaps of monomer **1**−**4** (B3LYP/6-31+G*).

DZP, MP2/3-21G, MCSCF/3-21G, and DFT/LDA with triple-ξ basis sets.[58,59] In addition, oligo(azothiophene) (**2d**) and oligo(azopyrrole) (**4d**) were studied at the same level as in the present work.[30] Phosphobenzene (**1e**) and diarsene compounds were also studied by DFT with the B3PW91 functional, with predicted geometries of $R_{\mathrm{P=P}} = 2.04$ Å, $\phi_{\mathrm{C-P-P}} = 99.6°$; $R_{\mathrm{As=As}} = 2.24$ Å, and $\phi_{\mathrm{C-As-As}} = 98.1°$.[63] It can be concluded that B3LYP/6-31+G* geometries of −X═X− linkages of **1**−**4** given in the present work are in good agreement with previous calculations. A systematic comparison regarding geometrical features between group 14 (**a**−**c**) and group 15 (**d**−**f**) compounds is made in the following subsections.

X═X Double-Bond Linkages. Since nonclassical multiple bonding models suggest pronounced character with nonbonding electron density at heavy main group elements,[31a] it is meaningful to survey the nature of central double bonds in **1**−**4** in terms of bond lengths and bond orders. Predicted values of $R_{\mathrm{X=X}}$ are found to be uniformly shorter than typical single bonds from optimized geometries in Table 2 and Tables S2−S5. For example, values of $R_{\mathrm{As=As}} = 2.26$−$2.27$ Å in **1**−**4f** are slightly smaller than those of 2.43−2.46 Å for typical As−As single bonds. [63] Furthermore, if taking the sum of covalent radii as a reference, we notice that optimized X═X bond lengths are slightly longer than sums of covalent double-bond radii and much shorter than those summed by covalent single-bond radii. The presence of double bonds in systems **1**−**4** is also demonstrated by Wiberg bond index (WBI)[64] and NLMO/NPA bond orders[65]. Both kinds of bond orders were obtained by NBO analysis with results given in Tables S2−S5 in Supporting Information. The relatively smaller bond orders with respect to nominal values of 2 reflect nonclassical double bonding.[31c,66] On the other hand, a different evolution trend is shown by two series of bond orders. WBI gives a decreasing sequence along C, Si, and Ge like **1a** (1.75) > **1b** (1.71) > **1c** (1.65). For parent hydrides, a decreasing trend in bond orders of hydrides Si_2H_4 (1.76), Ge_2H_4 (1.61), and Sn_2H_4 (1.46) was also reported according to Mayer's definition of bond orders.[67,68] NLMO/NPA bond orders present a different order, for instance, **1a** (1.89) < **1b** (1.93) < **1c** (1.95). In fact, a direct comparison of various bond orders may bring confusion because of their different definitions. WBI and Mayer's bond order use canonical molecular orbitals, while NLMO/NPA bond orders were

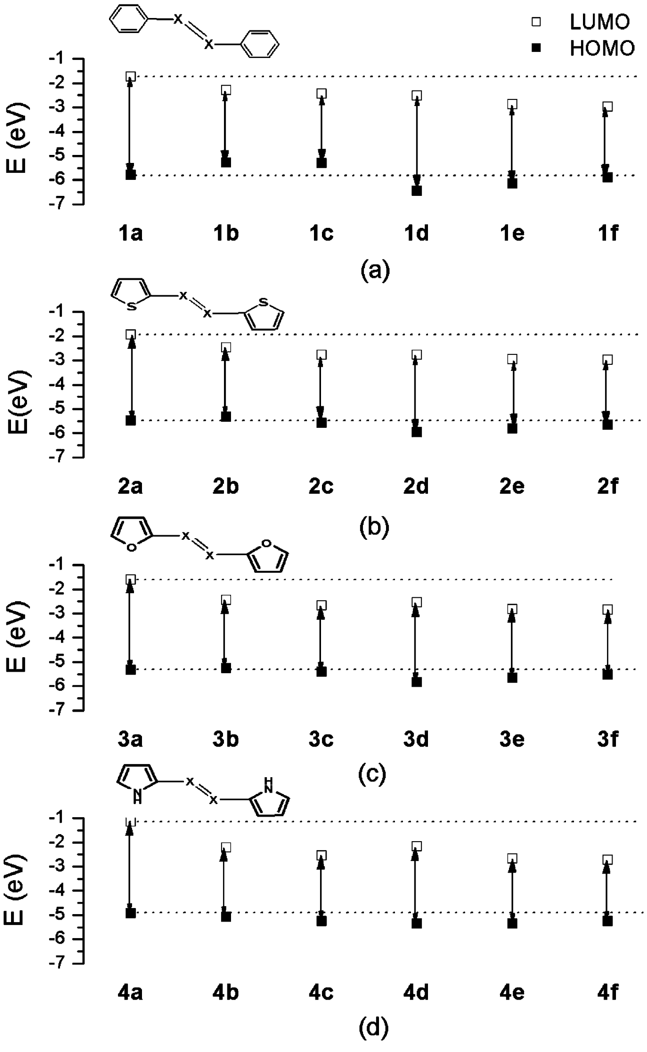


Figure 4. Sketches of evolutions of HOMO and LUMO levels of monomers (a) **1**, (b) **2**, (c) **3**, and (d) **4** with various double-bond linkages.

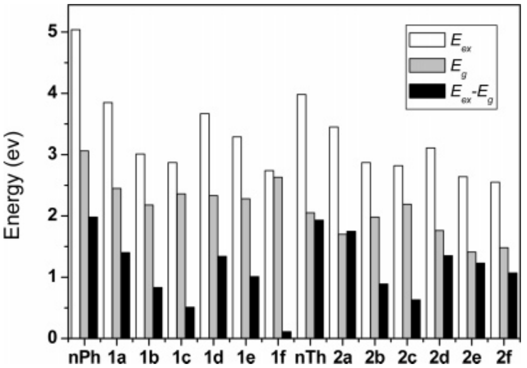


Figure 5. Excitation energies (E_{ex}) of monomers, band gaps (E_g) of polymers, and their differences ($E_{ex} - E_g$) in series **1** and **2**.

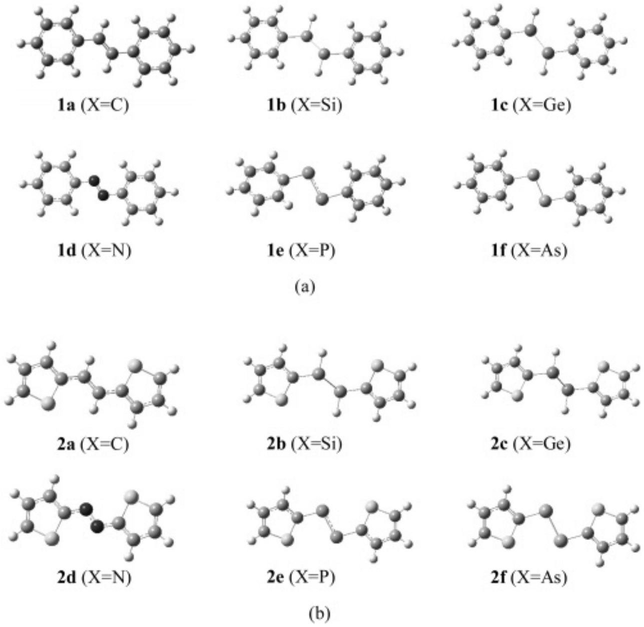


Figure 6. Optimized geometries of monomers (a) **1** and (b) **2**.

evaluated within the framework of localized molecular orbitals.[64,65] Therefore, researchers should be cautious when any conclusion is drawn from bond orders.

Of series **1**−**4**, little influence of hetero(aromatic) rings on bond lengths of X═X double bonds is observed. The only exception is that **1c** with phenyl (Ph) rings stands out for its more contracted bond length comparing to other digermenes (**2**−**4c**), which can be understood by strongest conjugation effects favored by the planar Ph−Ge═Ge−Ph backbone in **1c**.

Bond Alternations in Hetero(aromatic) Rings. The bond-length alternation parameter δ is frequently employed to investigate the extent of π conjugation. Here, we define the δ parameter as eq 1 with results collected in Table S6 of Supporting Information.

$$\delta = \frac{r_{C2-C3} - r_{C1-C2}}{(r_{C1-C2} + r_{C2-C3})/2} \qquad (1)$$

The magnitude of δ shows the extent of bond-length alternations within aromatic rings: if $\delta > 0$ (e.g., $\delta = 0.029$ in **2a**), aromatic character prevails; if it is close to zero, like $\delta = -0.005$ in **1c**, bond lengths are highly equalized; if $\delta < 0$ (e.g., $\delta = -0.010$ in **1e**), the molecule exhibits quinonoid character to some extent.

Values of δ do not change much with various central linkages. Series **1** composed of phenyl rings have the lowest values of δ among all the studied sets (Table S6), indicating the highest extent of electron delocalization within phenyl moieties. For series **2**−**4** containing five-membered hetero(aromatic) rings, δ increases in an order of **4 (Py)** < **2 (Th)** < **3 (Fu)**, which is in accord with increasing sequence in aromaticity (**Py** < **Th** < **Fu**).[52] Therefore, intrinsic properties of aromatic rings play an important role in determining the extent of electron delocalization. Enhancement of quinonoid characters is found in polymers to some extent with respect to monomers, as schematically shown in Chart 1.

Trans-Bent Geometries of Group 14 Compounds. To characterize trans-bent geometries of compounds containing group 14 double bonds, two important parameters, the bond angle of C1−X═X, ϕ, and the trans-bent angle, Θ, are examined (Table 2). First, bond angles ϕ decrease on descending group 14 (Figure 7). It has been recognized that heavier elements, Si (e.g., in **1b**) and Ge (**1c**), show less hybridization levels than C (**1a**) does. As a consequence, the nonbonding electron density is pronounced in heavier group 14 compounds, leading to an increase in lone-pair character and hence forcing ϕ to grow smaller.

Trans-bent angle Θ holds an important place when investigating geometries of heavier group 14 species. In contrast with coplanar ethylene species (**1**−**4a**) with $\Theta = 0$, trans-bent disilenes (**1**−**4b**) and digermenes (**1**−**4c**) are demonstrated to be trans-bent by nonzero Θ. In the case of disilenes, Θ ranges from around 37 to 46°. The Θ values of digermenes are in a range of 41−54°, with an exception of **1c** bearing only a slight twist by 4.1°. Two Ge atoms in **1c** lie in the same plane of phenyl rings, while H atoms attached to Ge atoms pointing out of the plane, resulting in a shorter Ge═Ge bond of 2.28 Å than other digermenes (**2**−**4c**).

Pyramidality, another critical factor to characterize geometries of heavier ethylene analogues of group 14 elements, was defined by a sum of angles at double-bond atoms as illustrated in Chart 2. The C═C-linked compounds (**1**−**4a**) are of ideal planarity with pyramidality of 360° at the central C atom (Table S7). Pyramidalities at the Si atom in **1**−**4b** range from 342 to 348°. The Ge species (**1**−**4c**) have even smaller values of ca. 333−345°. Clearly, decreasing values of pyramidality from **a** to **c** show growing preferences for trans-bent geometries on descending through group 14.

Group 15 Species with Shrinking ϕ Values. Different from characteristic trans-bent geometries of group 14 compounds, group 15 species adopt essentially coplanar geometries (with vanished Θ in Table 2) except for diphosphenes **1e** and **2e**. The most conspicuous structural feature in group 15 species is a rapidly shrinking ϕ value along the group, e.g., **2d** (X═N: 115.7°) > **2e** (X═P: 103.0°) > **2f** (X═As: 100.1°) (Figure 7). Apparently, chemical bonding of X═X units changes remarkably on descending through group 15.

3.3. Understanding of Tuning Effects by Linkages.

On the basis of the above discussions, a growing extent of trans bending for group 14 species and a rapid decline of ϕ of group 15 compounds are demonstrated by our calculations. NBO analysis is employed to further survey structure−property relationships.

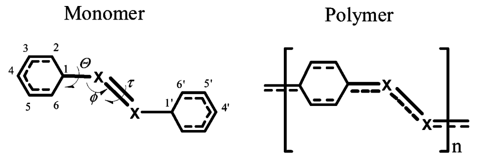
Trends in Orbital Interactions of Group 14 Species. Several models, including resonance structures, interaction of two carbonic fragments, $\pi-\sigma^*$ mixing, and banana bonds, etc., were proposed previously to qualitatively understand trans-bent geometries of heavier ethylene analogues.[31a,54] Of these models, $\pi_{X=X}-\sigma_{X-X}^*$ mixing can be revealed by interactions between electron-donating orbitals ($\pi_{X=X}$ or σ_{X-X}) and electron-accepting

TABLE 2: Optimized Geometries of Monomers and Polymers Obtained at Levels of B3LYP/6-31+G* and PBC−B3LYP/6-31G*, Respectively[a]

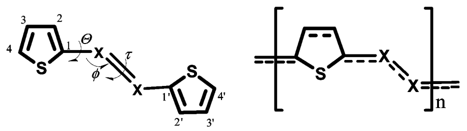
	$R_{X=X}$ (Å)		ϕ (deg)		Θ (deg)	
	monomer	polymer	monomer	polymer	monomer	polymer
			Phenyl-Containing Species (**1**)			
1a	1.35 (1.32−1.33[b,c])	1.35 (1.33−1.34[d,e])	127.2 (125−126[b,c])	127.2 (128[d])	0.3 (0−5[b,c])	0.0 (0[d])
1b	2.20 (2.14−2.29[f,g])	2.19	121.6 (118−125[h])	118.7	39.8 (0−34[g])	34.3
1c	2.28 (2.27−2.35[i,j,k])	2.29	117.5 (112−124[i,j,k])	118.4	4.1 (0−36[i,j,k])	53.8
1d	1.26 (1.24−1.27[c,l,m])	1.27	115.2 (114[l,m])	114.7	0.0 (0[m])	0.0
1e	2.06 (2.01−2.04[c,o,p,q])	2.06	102.3 (100−106[o,p,q])	102.1	30.2	28.5
1f	2.26 (2.22−2.28[q,r,s])	2.26	101.3 (94−100[q,r,s])	98.3	0.0	40.9
			Thienyl-Containing Species (**2**)			
2a	1.36	1.36	126.9	126.9	0.0	0.0
2b	2.22	2.22	120.5	120.4	42.4	40.0
2c	2.35	2.31	116.5	117.5	53.7	51.1
2d	1.27	1.37	115.7	113.8	0.0	0.0
2e	2.07	2.07	103.0	102.7	12.1	0.1
2f	2.26	2.27	100.7	100.1	0.0	0.1
			Furyl-Containing Species (**3**)			
3a	1.36		125.3		0.0	
3b	2.22		119.0		37.1	
3c	2.34		115.5		40.7	
3d	1.28		115.7		0.0	
3e	2.07		100.9		0.0	
3f	2.27		98.1		0.0	
			Pyrrolyl-Containing Species (**4**)			
4a	1.36		127.2		0.1	
4b	2.23		120.3		45.9	
4c	2.37		116.1		51.3	
4d	1.28	(1.28−1.29[t])	114.5		0.0	
4e	2.07		102.9		0.0	
4f	2.27		100.5		0.0	

[a] The documental experimental and calculated values of various compounds containing X═X double bonds are given in parentheses. [b] Reference 82. [c] The predicted values of HnX═XHn molecules at B3LYP/6-311G*, ref 83. [d] Reference 25. [e] *p*-Phenylenevinylene oligomers optimized at AM1 level, ref 84. [f] Reference 85. [g] Reference 86. [h] Tetrakis(2,6-diethylphenyl)disilene, ref 87. [i] (*Z*)-1,2-Bis(2,6-diisopropylphenyl)-1,2-dimesityldigermene, ref 88. [j] Ge_2R_4 [R═CH($SiMe_3$)$_2$], ref 89. [k] Tetrakis(trialkylsilyl)digermenes, ref 90. [l] *trans*-Azobenzene optimized at MP2/cc-pVTZ, ref 91. [m] *trans*-Azobenzene studied with gas electron diffraction method and data analysis made using MP2/6-31+G* constraints, ref 92. [o] DmpP═PAr$_4$C$_6$P═PDmp (Dmp = 2,6-Mes$_2$C$_6$H$_3$), ref 22. [p] Bis(2,4,6-tri-*tert*-butylpheny1)diphosphene, ref 67. [q] Phosphobenzene- and diarsene-containing compound calculated at DFT-B3PW91, ref 63. [r] (2,4,6-(*t*-Bu)$_3$C$_6$H$_2$)As═AsCH(SiMe$_3$)$_2$, ref 32b. [s] 2,6-Mes$_2$H$_3$C$_6$As═AsC$_6$H$_3$-2,6-Mes$_2$, ref 31f. [t] Poly(azopyrrole) calculated at TDDFT-B3LYP/6-31+G*, ref 30.

CHART 1: Schematic Structures of Monomers and Polymers of 1 and 2 (X = CH, SiH, GeH, N, P, As)



(a) PhX=XPh (**1**)



(b) ThX=XTh (**2**)

X=CH, SiH, GeH, N, P, As

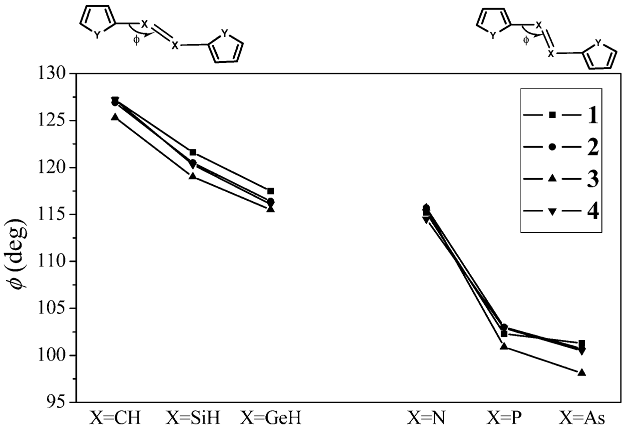


Figure 7. Trends in bond angles ϕ for monomers **1**−**4** with group 14 and 15 double-bond linkages.

orbitals (σ_{X-X}* or $\pi_{X=X}$*). Stabilization energies of these orbital interactions are collected in Table 3. For series **1**, progressively growing stabilization energies of $\pi_{X=X}\rightarrow\sigma_{X-X}$* interactions from C through Si to Ge species are shown in an order of **1a** (0.0 kcal/mol) < **1b** (8.16 kcal/mol) < **1c** (15.96 kcal/mol). Relatively weaker interactions of $\sigma_{X-X}\rightarrow\pi_{X=X}$* share a similar monotonically increasing trend. The orbital interactions are favored by small separations between electron-donating and -accepting orbitals if the phase property is satisfied. Here, when going down group 14, interacting $\pi_{X=X}$ and σ_{X-X}* orbitals are approaching with energy separation of **1a** (21.0 eV) > **1b** (12.1 eV) ≈ **1c** (12.6 eV), thus facilitating $\pi_{X=X}\rightarrow\sigma_{X-X}$* orbital interactions.

Series **2**−**4** have almost identical stabilization energies of $\pi\rightarrow\sigma$* (or $\sigma\rightarrow\pi$*) interactions. Occupancy numbers of electron-accepting orbitals of σ_{X-X}*($\pi_{X=X}$*) also accord nicely with growing trends (Table 3).[69] So, involvements of heavier elements in **1**−**4** increase electron delocalizations from donating orbitals ($\pi_{X=X}$) to accepting orbitals (σ_{X-X}*) to some extent. The $\pi-\sigma$* mixing stabilizes antibonding orbitals. Meanwhile, separations

CHART 2: Double-Bond Models for Systems with Linkages Formed by Group 14 Elements in (a) Coplanar and (b) Trans-Bent Geometries as Defined by Their Pyramidality

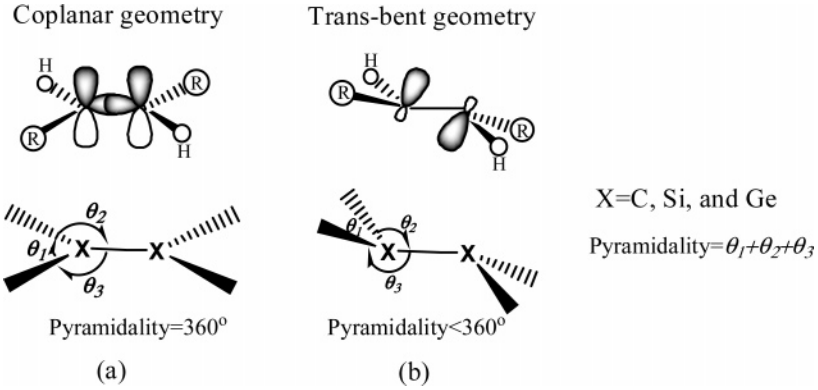
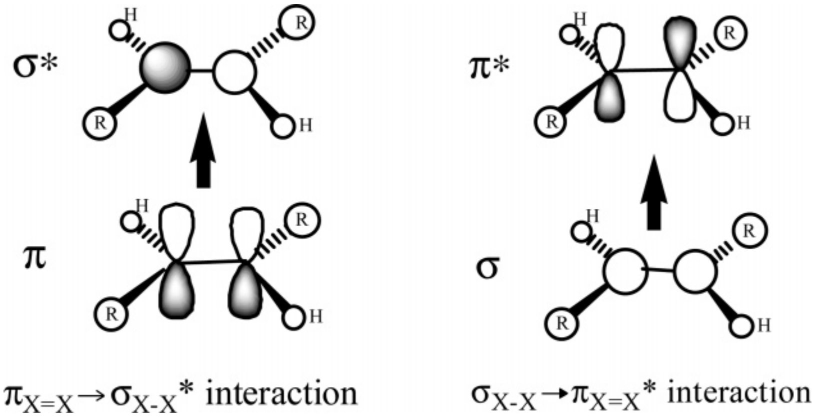


TABLE 3: Progressively Growing $\pi_{X=X}\rightarrow\sigma_{X-X}$* ($\sigma_{X-X}\rightarrow\pi_{X=X}$*) Interactions, Characterized by Increasing Stabilization Energies (in kcal/mol) and Occupancies of Acceptors, σ_{X-X}* ($\pi_{X=X}$*), as Descending Group 14 for Monomers 1−4 (NBO analysis at the level of B3LYP/6-31+G*)



	stabilization energies of $\pi_{X=X}\rightarrow\sigma_{X-X*}$ ($\sigma_{X-X}\rightarrow\pi_{X=X}$*)			occupancy of σ_{X-X}*($\pi_{X=X}$*)		
	X=C	X=Si	X=Ge	X=C	X=Si	X=Ge
1	0.0 (0.0)	8.16 (5.55)	15.96 (7.74)	0.015 (0.135)	0.045 (0.112)	0.056 (0.120)
2	0.0 (0.0)	8.21 (11.20)	18.55 (28.67)	0.013 (0.183)	0.059 (0.154)	0.110 (0.207)
3	0.0 (0.0)	8.92 (11.82)	16.83 (26.66)	0.012 (0.196)	0.061 (0.174)	0.101 (0.220)
4	0.0 (0.0)	9.34 (11.92)	19.34 (27.97)	0.012 (0.217)	0.071 (0.198)	0.119 (0.261)

TABLE 4: Increasing p Character of Hybridized Orbitals as Demonstrated by s and p Contents of Bonding σ and π Orbitals of X═X (σ_{X-X} and $\pi_{X=X}$), σ Orbitals of X−C (σ_{X-C}), and Lone Pair Orbitals of X (n_X) of 2d−f as Descending Group 15

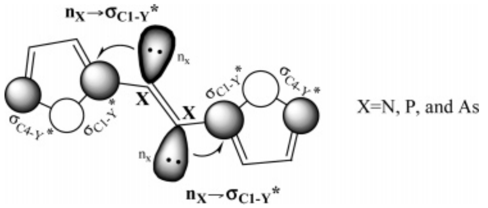
	σ_{X-X}		$\pi_{X=X}$		σ_{X-C}		n_X	
	s	p	s	p	s	p	s	p
2d X═N	29.6%	70.2%	0.0%	99.7%	34.5%	65.3%	35.9%	64.0%
2e X═P	17.8%	81.6%	0.3%	99.2%	17.7%	81.4%	68.2%	31.8%
2f X═As	13.8%	85.9%	0.0%	99.3%	14.1%	85.5%	75.4%	24.6%

between HOMOs and LUMOs become narrower and thus heavier ethylene analogues have lower excitation energies than ethylene derivatives.

Increasing p Components on Descending Group 15. The rapidly decreasing ϕ in geometries of dipnictenes is intuitively assumed to be caused by increasing p character on X.[70,71] Analysis on hybrid orbitals is thus conducted with results shown in Table 4. The p contents of σ_{X-X} orbitals increase from 70.2% (**2d**, X═N) to 81.6% (**2e**, X═P) and 85.9% (**2f**, X═As). The corresponding p contents of σ_{X-C1} orbital are 65.3% (**2d**), 81.4% (**2e**), and 85.5% (**2f**), respectively.

Similar to group 14 species, intraring interactions of group 15 compounds alter little with various double-bond linkages.

TABLE 5: Decreasing n→σ_{C1-Y}* Interactions as Descending Group 15 Are Reflected by Decreasing Stabilization Energies (in kcal/mol) and Occupancies of Acceptors (σ_{C1-Y}*) for Monomers 1−4 Containing Linkages of Group 15 Elements (NBO Analysis at B3LYP/6-31+G* Level of Theory)



	stabilization energies			occupancy of σ_{C1-Y}* (σ_{C4-Y}*)[a]		
	X═N	X═P	X═As	X═N	X═P	X═As
1	8.63	4.91	4.93	0.033 (0.016)	0.028 (0.016)	0.027 (0.016)
2	14.62	7.60	6.87	0.073 (0.018)	0.047 (0.020)	0.043 (0.021)
3	15.76	8.11	6.97	0.061 (0.015)	0.048 (0.020)	0.045 (0.021)
4	12.38	7.35	6.56	0.043 (0.012)	0.036 (0.016)	0.034 (0.017)

[a] Occupancies of σ_{C4-Y}* are given in parentheses for comparison.

Decreasing $n_x\rightarrow\sigma_{C1-Y}$* interactions shown in Table 5 imply weaker electron communications between rings and central atoms. Occupancy numbers of acceptors σ_{C1-Y}* fit well with dropping tendency of $n_x\rightarrow\sigma_{C1-Y}$* interactions.

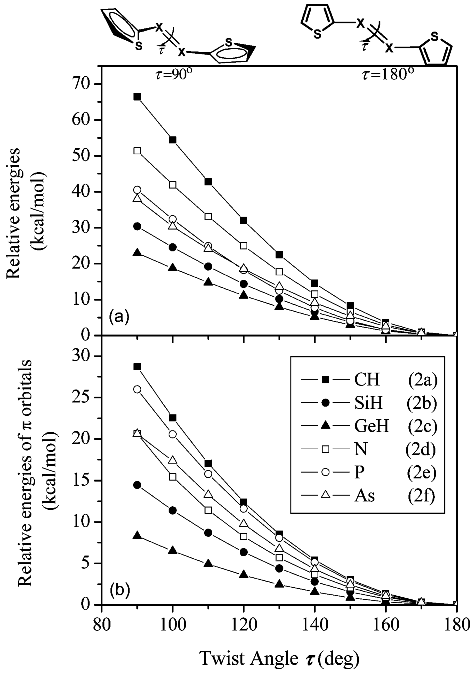


Figure 8. The monotonically decreasing trends in (a) relative energies of the whole systems and (b) π orbitals of **2** with twist angle τ changing from 90 to 180°. The total energies and π orbtial energies of $\tau = 180°$ are taken as the zero point.

Finally, we also investigate evolution trend of molecules in series **2** when rotating central double bonds. Figure 8 presents variations of total energy and energy level of $\pi_{X=X}$ orbitals in series **2** with torsion angle τ ($C_1-X-X-C_{1'}$, shown in Chart 1) rotating from planar ($\tau = 180°$) to orthogonal geometries ($\tau = 90°$). Since relatively weaker π overlaps for heavier dipnictenes are normally associated with lower rotation barriers,[58] it is not surprising to observe that energy variations of P- and As-containing compounds have lower rotation barriers (**2e** and **2f** $\approx$ 40 kcal/mol) than the case in N species (**2d** ca. 51 kcal/mol). Meanwhile, profiles of relative π orbital energies appear a similar tendency. On the other hand, rotations exert less influence on the overlap even in orthogonal situations. A similar evolution tendency is observed for group 14 analogues (Figure 8).

4. Conclusion

The incorporation of alkene homologues formed by group 14 and 15 elements to aromatic rings presents interesting tuning effects on electronic structures. Through extensive calculations by DFT, TDDFT, and PBC-DFT methods with double-ξ basis sets, we reach conclusions as follows:

(1) Excitation energies of monomers **1**−**4** containing aromatic rings (phenyl, thienyl, furyl, and pyrrolyl) and double-bond linkages $-X{=}X-$ (X = CH, SiH, GeH, N, P, As) are reduced by around 13−50% with respect to corresponding dimers of phenyl, thienyl, furyl, and pyrrolyl rings. Furthermore, excitation energies of monomers show interesting periodic decreasing trends as descending through groups 14 and 15, respectively.

(2) Central double bonds primarily determine electronic structures of PPV analogues. Thus four sets of compounds show a consistent evolution trend.

(3) Group 14 species exhibit increasing trans-bent geometries and growing $\pi-\sigma^*$ mixing on descending the group. The increasing p character of hybridized orbitals of central bonds from N through P to As compounds are a main feature for group 15 species. Electronic communications between aromatic moieties and linkage units $-X{=}X-$ turn weaker for heavier group 14 and 15 congeners.

In summary, inherent properties of central linkages are prevailing factors to rationalize geometry preferences and excitation energies of monomers **1**−**4**. The last two decades have witnessed flourishing research on multiple bonding of main-group elements as well as organic optoelectronic materials. We envision the introduction of vinylene analogues in π-conjugated oligomers and polymers may afford an opportunity of exploring materials with novel electronic and optical properties.

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Supporting Information Available: Table S1 collecting geometry parameters of monomers **2** at various levels. Tables S2−S5 collecting geometry parameters of monomers and polymers **1**−**4** at B3LYP/6-31+G*. Table S6 collecting values of bond-length alternation parameter δ. Table S7 showing values of pyramidality of linkage atoms. Figure S1 showing optimized geometries of monomers **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons Ltd.: New York, 1997.

(2) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.

(3) For reviews, see: (a) Heeger, A. J. *Synth. Met.* **2002**, *125*, 23. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (c) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (d) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (e) Roncali, J. *Chem. Rev.* **1992**, *92*, 711 and references therein.

(4) The first report of electroluminescence in PPV: Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(5) (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (c) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884. (d) Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Jackson, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 10117. (e) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47. (f) Brédas, J. L.; Adant, C.; Tackx, P.; Persoonst, A. *Chem. Rev.* **1994**, *94*, 243.

(6) (a) Blanchard, P.; Riou, A.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 7107. (b) Blanchard, P.; Brisset, H.; Illien, B.; Riou A.; Roncali J. *J. Org. Chem.* **1997**, *62*, 2401. (b) Brisset, H.; Blanchard, P.; Illien, B.; Riou A.; Roncali J. *Chem. Commun*, **1997**, 569 (c) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846. (d) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1305. (e) Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E. H.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249.

(7) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.

(8) Choi, B.; Yamamoto, T. *Electrochem. Commun.* **2003**, *5*, 566−570.

(9) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808.

(10) (a) Vaschetto, M. E.; Springborg, M. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *460*, 141. (b) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 9714. (c) Miklos Kertesz, M.; Lee, Y. S. *J. Phys. Chem.* **1987**, *91*, 2690.

(11) (a) Zhang, G.; Ma, J.; Jiang, Y. *Macromolecules* **2003**, *36*, 2130. (b) Cao, H.; Ma, J.; Zhang, G.; Jiang, Y. *Macromolecules* **2005**, *38*, 1123.

(12) (a) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382. (b) Jenekhe, S. A. *Nature* **1986**, *322*, 345. (c) Lambert, T. M.;

Ferraris, J. P. *J. Chem. Soc.*, *Chem. Commun.* **1991**, 752. (d) Lorcy, D.; Cava, M. P. *Adv. Mater.* **1992**, *4*, 562. (e) Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *J. Chem. Soc.*, *Chem. Commun.* **1992**, 1672. (f) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem.* Soc., *Chem. Commun.* **1994**, 1305. (g) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791. (h) Hong, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1995**, *103*, 1871.

(13) Poly(3-alkylthiophenes), see, for example: (a) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc.*, *Chem. Commun.* **1986**, 1346. (b) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.

(14) Substituted PPVs and oligomers: (a) Brédas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 507. (b) Fahlman, M.; Lögdlund, M.; Stafström, S.; Salaneck, W. R.; Friend, R. H.; Burn, P. L.; Holmes, A. B.; Kaeriyama, K.; Sonoda, Y.; Lhost, O.; Meyers, F.; Brédas, J. L. *Macromolecules* **1995**, *28*, 1959. (c) Klärner, G.; Former, C.; Yan, X.; Richert, R.; Müllen, K. *Adv. Mater.* **1996**, *8*, 932. (d) Former, C.; Wagner, H.; Richert, R.; Neher, D.; Müllen, K. *Macromolecules* **1999**, *32*, 8551.

(15) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

(16) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119.

(17) Salzner, U.; Kızıtepe, T. *J. Org. Chem.* **1999**, *64*, 764.

(18) Ferraris, J.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

(19) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720.

(20) Frère, P.; Raimundo, J.; Blanchard, P.; Delaunay, J.; Richomme, P.; Sauvajol, J.; Garin, J.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 7254.

(21) Heun, S.; Bässler, H.; Müller, U.; Müllen, K. *J. Phys. Chem.* **1994**, *98*, 7355.

(22) Shah, S.; Concolino, T.; Rheingold, A. L.; Protasiewicz, J. D. *Inorg. Chem.* **2000**, *39*, 3860.

(23) See, for example, PPVs with alkoxyphenyl substituents: (a) Spiliopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* **2002**, *35*, 2149. Fluorenyl-substituted PPVs: (b) Lee, S. H.; Jang, B.; Tsutsui, T. *Macromolecules* **2002**, *35*, 1356. Silyl-substituted PPVs: (c) Chen, Z.-K.; Huang, W.; Wang, L.-H.; Kang, E.-T.; Chen, B. J.; Lee, C. S.; Lee, S. T. *Macromolecules* **2000**, *33*, 9015.

(24) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147 and references therein.

(25) Granier, T.; Thomas, E. L.; Gagnon, D. R.; Karasz, F. E. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2793.

(26) Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, A. *J. Chem. Soc.*, *Chem. Commun.* **1987**, *1448*.

(27) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303.

(28) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 6241.

(29) Huang, K.; Qiu, H.; Wan, M. *Macromolecules* **2002**, *35*, 8653.

(30) Zhu, Z.; Wang, Y.; Lu, Y. *Macromolecules* **2003**, *36*, 9585.

(31) (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463 and references therein. (b) Cui, C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 5062. (c) Stender, M.; Phillips, A. D. Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785. (d) Stanciu, C.; Richards, A. F.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 4106. (e) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667. (f) Twamley, B.; Chadwick D. Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

(32) (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389 and references therein. (b) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506. (c) Cowley, A. H.; Decken, A., Norman, N. C.; Krüger, C.; Lutz, F.; Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 3389. (d) Zilm, A. W.; Webb, G. G.; Cowley, A. H.; Pakulski, M.; Orendt, A. *J. Am. Chem. Soc*. **1988**, *110*, 2032.

(33) (a) Sekiguchi, A.; Lee, V. Y. *Chem. Rev.* **2003**, *103*, 1429. (b) Lee, V. Y.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758. (c) Lee, V. Y.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758. (d) Lee, V. Y.; Takanashi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2003**, *125*, 6012. (e) Sekiguchi, A.; Ishida, Y.; Fukaya, N.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 1158.

(34) (a) Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 5498. (b) Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234. (c) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *177*, 78. (d) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489.

(35) (a) West, R.; Fink, M. J. *Science* **1981**, *214*, 1343. (b) Zilm, K. W.; Grant, D. M.; Michl, J.; Fink, M. J.; West, R. *Organometallics* **1983**, *2*, 193.

(36) (a) Weber, L. *Chem. Rev.* **1992**, *92*, 1839. (b) Driess, M.; Grützmacher, H. *Angew. Chem.*, *Int. Ed. Engl.* **1996**, *35*, 828.

(37) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Weinheim, Wiley-VCH: 1998.

(38) Hutten, P. F. V.; Krasnikov, V. V.; Hadziioannou, G. *Acc. Chem. Res.* **1999**, *32*, 257.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian Inc., Wallingford CT, 2004.

(40) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(41) The trans-bent angles Θ is defined as the angle between the R_2X planes and the X−X vector. Also it is the deviation of dihedral angle of C_2-C_1-X-X from 180° in the present study; cf.: Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig Y., Eds.; John Wiley & Sons: Ltd.: 2001; Volume 3, pp 396−397.

(42) The all-trans conformers of polymers calculated at PBC-DFT are more stable than trans-cis correspondents.

(43) De Oliveira, M. A.; Duarte, H. A.; Pernaut, J. M.; De Almeida, W. B. *J. Phys. Chem. A* **2000**, *104*, 8256.

(44) Hsu, C.; Hirata, S.; Head-Gordon, M. *J. Phys. Chem. A* **2001**, *105*, 451.

(45) Grozema, F. C.; van Duijnen, P. T.; Siebbeles, L. D. A.; Goossens, A.; de Leeuw, S. W. *J. Phys. Chem. B* **2004**, *108*, 16139.

(46) Ma, J.; Li, S.; Jiang, Y. *Macromolecules* **2002**, *35*, 1109.

(47) Yu, J. K.; Chen, W.; Yu, C. *J. Phys. Chem. A* **2003**, *107*, 4268.

(48) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Phys. Chem. A* **2002**, *106*, 10596.

(49) Hirata, S.; Head-Gordon, M.; Bartlett, R. J. *J. Chem. Phys.* **1999**, *111*, 10774.

(50) (a) Reed, E. A.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, E. A.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, E. A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(51) Berlin, A.; Zotti, G. *Synth. Met.* **1999**, *106*, 197.

(52) (a) Schleyer, P. von. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. van E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. von. R. *J. Org. Chem.* **2002**, *67*, 1333.

(53) One exception is phosphobenzene (monomer **1e**) whose first dipole allowed excitations is assigned to HOMO-1→LUMO.

(54) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.

(55) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416.

(56) Some examples of theoretical works on PPV and PTV: (a) Vaschetto, M. E.; Monkman, A. P.; Springborg, M. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *468*, 181. (b) Obrzut, J.; Karasz, F. E. *J. Chem. Phys.* **1987**, *87*, 2349. (c) Cornil, J.; Beljonne, D.; Friend, R. H.; Brédas, J. L. *Chem. Phys. Lett.* **1994**, *223*, 82. (d) Lögdlund, M.; Salaneck, W. R.; Meyers, F.; Brédas, J. L.; Arbuckle, G. A.; Friend, R. H.; Holmes, A. B.; Froyer, G. *Macromolecules* **1993**, *26*, 3815.

(57) (a) Brédas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 507. (b) Cornil, J.; Beljonne, D.; Friend, R. H.; Brédas, J. L. *Chem. Phys. Lett.* **1994**, *223*, 82. (c) Remmers, M.; Neher, D.; Grüner, J.; Friend, R. H.; Gelinck, G. H.; Warman, J. M.; Quattrocchi, C.; dos Santos, D. A.; Brédas, J. L. *Macromolecules* **1996**, *29*, 7432.

(58) (a) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559. (b) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057.

(59) (a) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Trinquier, G.; Malrieu, J. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (c) Trinquier, G.; Malrieu, J.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529.

(60) Takahashi, M.; Sakamoto, K. *Organometallics* **2002**, *21*, 4212.

(61) West, R.; Cavalieri, J. D.; Buffy, J. J.; Fry, C.; Zilm, K. W.; Duchamp, J. C.; Kira, M.; Iwamoto, T.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4972.

(62) The 6-311G** for P, 6-311G* for C, and 6-311G for C_6H_5: Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795.

(63) As−As single bond length: (a) Burns, J. H.; Waser J. *J. Am. Chem. Soc.* **1957**, *79*, 859. (b) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327. It is noteworthy that it is hard to find direct correlations between bond energies, bond lengths, and bond orders in heavier alkene homologues; see, for example: ref 31a.

(64) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(65) (a) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(66) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755.

(67) Lendvay, G. *Chem. Phys. Lett.* **1991**, *181*, 88.

(68) (a) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73. (b) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 477.

(69) The other interactions involved include $\pi_{X=X} \rightarrow \pi_{C1-C2}{}^*$ and back donations, $n_s \rightarrow \pi_{C1-C2}{}^*$ (lone pairs on S atoms donating to the antibonding bond), $n_s \rightarrow \pi_{C3-C4}{}^*$, and $\pi_{C1-C2} \rightarrow \pi_{C3-C4}{}^*$ as well as back donations. Most intraring interactions undergo minor changes with various linkages. But the stabilization energies of $\pi_{X=X} \rightarrow \pi_{C1-C2}{}^*$ decline sharply from **2a** (14.21 kcal/mol) to **2b** (5.93 kcal/mol) and **2c** (4.56 kcal/mol), indicating weaker interactions encountered between rings and linkages in Si and Ge species. Likewise, the back donations, $\pi_{C1-C2} \rightarrow \pi_{X=X}{}^*$, show identical trends and close values in stabilization energies.

(70) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

(71) For recent reviews on dipnictenes: (a) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773. (b) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, 453. (c) Tokitoh, N. *Pure Appl. Chem.* **1999**, *71*, 495. (d) Grutzmacher, H.; Fassler, T. F. *Chem.−Eur. J.* **2000**, *6*, 2317. (e) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73.

(72) West, R.; Cavalieri, J. D.; Buffy, J. J.; Fry, C.; Zilm, K. W.; Duchamp, J. C.; Kira, M.; Iwamoto, T.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4972.

(73) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.

(74) (a) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, 998. (b) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem.* Soc. **2004**, *126*, 2268.

(75) Okawa, H.; Wada, T.; Sasabe, H. *Synth. Met.* **1997**, *84*, 265.

(76) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.

(77) Jestin, I.; Frère, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150.

(78) Glenis, S.; Benz, M.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12519.

(79) Jen, K.-Y.; Jow, T. R.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1113.

(80) Kobayashi, M.; Chen, J.; Chung, T. C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.

(81) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A.; Casalbore-Miceli, G. *Synth. Met.* **1996**, *78*, 51.

(82) Finder, G. J.; Newton, M. G.; Allenger, N. L. *Acta Crystallogr., Sect. B* **1974**, *30*, 411.

(83) Galbraith, J. M.; Blank, E.; Shaik, S.; Hiberty, P. C. *Chem.−Eur. J.* **2000**, *6*, 2425.

(84) Cornil, J.; dos Santos, D. A.; Beljonne, D.; Brédas J. L. *J. Phys. Chem.* **1995**, *99*, 5604.

(85) Cotton, F. A.; Wilkinson, G.; Murrillo, G. A.; Bockmann, M. *Advanced Inorganic Chemistry;* John Wiley & Sons: 1999; pp 294−296.

(86) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig Y., Eds.; John Wiley & Sons, Ltd.: 2001; Volume 3, pp 391−424.

(87) Masamune, S.; Murakaml, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333.

(88) Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamme, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394.

(89) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

(90) Kira, M.; Iwamoto, T.; Maruyama, T.; Kabuto, C.; Sakurai, H. *Organometallics* **1996**, *15*, 3767.

(91) Fliegl, H.; Köhn, A.; Hättig, C.; Ahlrichs, R. *J. Am. Chem. Soc.* **2003**, *125*, 9821.

(92) Tsuji, T.; Takashima, H.; Takeuchi, H.; Egawa, T.; Konaka, S. *J. Phys. Chem. A* **2001**, *105*, 9347.