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A Theoretical Study of Substituent Effects on Germanium−Phosphorus Triple Bonds

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To extend our knowledge of the germanium−phosphorus triple bond, the isomerization reactions of singlet XGeP (i.e., XGe≡P → TS → Ge═PX; X = H, Li, BeH, BH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, and Cl) were investigated using B3LYP and CCSD(T) calculations. It is found that electronegative and π-electron-donating substituents (X) can stabilize the XGe≡P triply bonded species in a kinetic sense, although germanium is less reluctant to form Ge═P doubly bonded than Ge≡P triply bonded compounds.

I. Introduction

Though multiple bonding plays a fundamental role in the chemistry of the second-row elements (such as carbon, nitrogen, and oxygen), complexes that exhibit multiple bonding to the heavier congeners of these elements are much less common.[1−10] For instance, even though much effort has been directed toward the study of multiple bonding to germanium, monomeric germaphosphenes with Ge═P double bonds are kinetically unstable due to the lack of stabilization by bulky groups. They have been frequently postulated as intermediates, mostly on the evidence of trapping experiments.[11,12] Only in the last 10 years have sufficiently stable germaphosphenes been stabilized to allow their analysis in the solid state and in solution.[13−21]

It is this fascinating experimental progress that has inspired this study. If compounds possessing a germanium−phosphorus double bond can be synthesized and stabilized, would it be possible to extend this to other molecular systems containing Ge≡P triple bonds? To the best of our knowledge, there have been no reports of the characterization of compounds with a Ge≡P triple bond. Indeed, to this date, no compounds of triply bonded germanium appear to have been isolated.[12,14] In particular, the reactive nature of these species makes it difficult to obtain quantitative data, e.g., energies and geometries, experimentally. Theory should provide helpful information in this regard, and it is now more practical to carry out systematic studies computationally. To gain insight into the extent of double and triple bonds in compounds of germanium with substituents, we have undertaken a theoretical investigation of the relative energies of the isomeric XGe≡P and Ge═PX structures and of the potential energy barriers separating them (i.e., X = H, Li, BeH, BH_2, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, and Cl). All of these species are presently unknown but appear to offer good prospects for experimental realization. Moreover, we shall use these computational results to predict what kind of molecules containing a Ge≡P triple bond are thermodynamically stable and are separated by significant barriers from their corresponding isomers, perhaps making both Ge≡P and Ge═P species synthetically accessible. Also, we shall provide accurate molecular parameters and spectroscopic data to guide experimental studies on these species.

II. Methodology

The geometries of all the species were fully optimized using the hybrid density functional method B3LYP/6-311++G(d,p).[22,23] All minima and transition states were verified by vibrational frequency analysis. The vibrational zero-point energy (ZPE) corrections determined at the B3LYP/6-311++G(d,p) level were also included, i.e., B3LYP/6-311++G(d,p) + ZPE (B3LYP/6-311++G(d,p)) (hereafter designed B3LYP). Further single-point CCSD(T) calculations were performed on all B3LYP optimized structures, i.e., CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) + ZPE (B3LYP/6-311++G(d,p)) (hereafter designed CCSD(T)).[24]

Density functional theory (DFT) and CCSD(T) calculations were performed on IBM 590 computers using the Gaussian 94 system of programs.[25]

III. Results and Discussion

Selected geometrical parameters calculated at the B3LYP level of theory for XGe≡P, Ge═PX, and the transition state connecting them are listed in Table 1. The calculated vibrational frequencies, rotational constants, and dipole moments of XGeP and its derivatives are collected in Table 2.

As Table 1 shows, electronegative substituents (such as, C, N, P, O, S, F, and Cl) seem to strengthen the Ge≡P triple bond slightly, while electropositive substituents (i.e., Li, Be, and B) appear to lengthen the Ge≡P triple bond. On the other hand, in the case of the Ge═PX system, electronegative substitution weakens the Ge═P double bond, whereas electropositive substitution strengthens the Ge═P double bond. Moreover, it should be mentioned here that our calculated Ge═P bond length is in reasonable agreement with experimental findings (2.13 Å for Mes_2Ge═PAr) by Escudie and co-workers.[13]

The most striking feature in Table 1 is that in the DFT calculations, all the minimum-energy Ge═PX species are bent. This disagrees with the simple Walsh's rules that three-center species with 16 valence electrons should be linear in the ground

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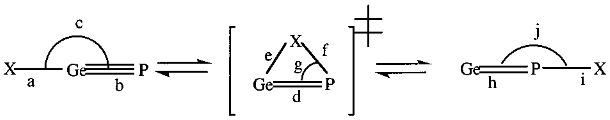
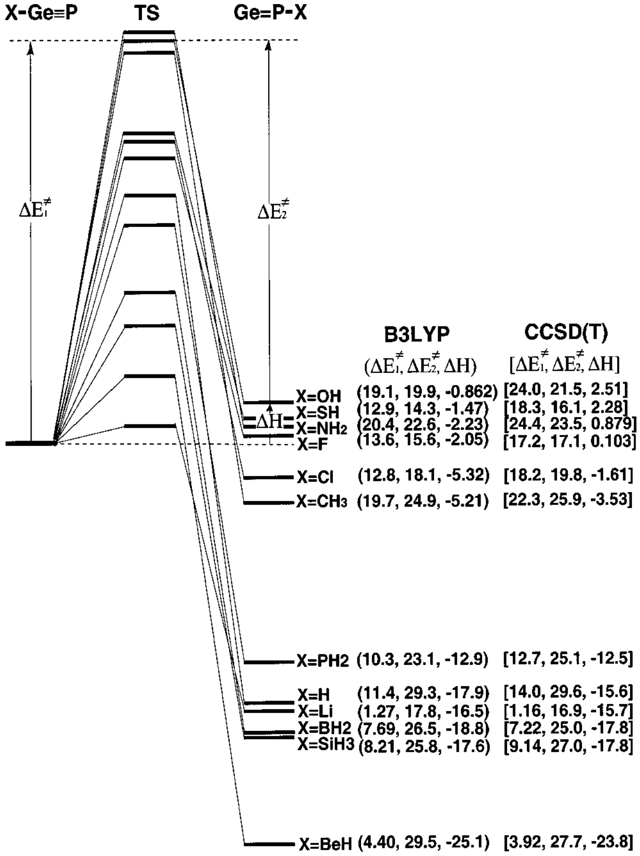
TABLE 1: Geometrical Parameters of Structures for Eq 1 at the B3LYP/6-311++G(d,p) Level of Theory (Distance in Å, Angles in deg)



(1)

X	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*
H	1.524	2.012	180.0	2.125	1.584	2.629	37.05	2.151	1.466	70.56
Li	2.413	2.047	180.0	2.057	2.408	4.035	27.57	2.108	2.293	83.45
BeH	2.155	2.029	180.0	2.061	2.163	3.507	34.82	2.135	2.001	87.41
BH_2	2.014	2.032	180.0	2.096	2.104	2.706	50.02	2.134	1.883	108.8
CH_3	1.961	2.017	180.0	2.137	2.116	2.992	45.01	2.160	1.933	83.06
SiH_3	2.391	2.023	179.5	2.092	2.457	3.475	44.24	2.178	2.251	77.68
NH_2	1.820	2.023	175.1	2.219	1.927	2.964	40.53	2.184	1.713	118.7
PH_2	2.336	2.024	172.1	2.119	2.441	3.446	44.53	2.169	2.276	78.99
OH	1.776	2.025	175.0	2.266	1.872	2.930	39.71	2.214	1.701	103.7
SH	2.219	2.025	175.6	2.174	2.331	3.283	45.14	2.178	2.163	109.4
F	1.750	2.026	179.9	2.286	1.828	2.943	38.40	2.200	1.789	70.41
Cl	2.146	2.025	180.0	2.262	2.210	3.319	42.68	2.202	2.265	69.82

SCHEME 1



state[25] (such as O═C═O). Though this rule seems to apply well to molecules containing light elements, a number of exceptions have been found for their heavier isoelectronic analogues.[27−29] The reason for this may be due to the fact that for the molecules consisting of heavier elements, contributions from electron correlation effects and electron repulsions interfere with the simple molecular orbital model, leading to a much more complex dependence of the molecular shape upon the number of filled valence orbitals.

Scheme 1 shows the effects of various substituents on the relative stabilities of XGe≡P and GeP═X at the B3LYP and CCSD(T) levels of theory. From Scheme 1, it is apparent that the XGe≡P and Ge═PX energy differences (Δ*H*) are strongly dependent on the substituent X. For instance, when hydrogen is replaced by an electropositive substituent (such as Li, BeH, and BH_2), the energy of Ge═PX is much lower than that of the corresponding XGe≡P by 16, 24, and 18 kcal/mol for X = Li, BeH, and BH_2, respectively. By contrast, the energies of Ge═PCH_3 and Ge═PCl are slightly below the energies of H_3CGe≡P and ClGe≡P by 3.5 and 1.6 kcal/mol, respectively. In particular, our CCSD(T) calculations indicate that the most electronegative substituents can reverse the order of the relative stabilities of the triple-bonded and double-bonded XGeP species. However, the energy difference, Δ*H*, between them is quite small. For example, Ge═PF, Ge═PNH_2, Ge═POH, and Ge═PSH are calculated to be less stable than FGe≡P, H_2NGe≡P, HOGe≡P, and HSGe≡P only by 0.10, 0.88, 2.5, and 2.3 kcal/mol, respectively. As a result, our model calculations suggest that, when the substituent X is more electronegative than germanium, these XGe≡P and Ge═PX isomers are predicted to be nearly thermoneutral, with an exothermicity of less than 3 kcal/mol. This small energy difference between the triple-bonded and the double-bonded species is a general feature of germanium−phosphorus multiply bonded compounds with electronegative substituents and indicates that germanium is more reluctant to form Ge≡P triply bonded than Ge═P doubly bonded compounds.

The thermodynamic stability of XGe≡P relative to that of Ge═PX may be understood in terms of the Ge−X versus P−X bond energies. Namely, a strong Ge−X bond and a weak P−X bond can overturn the intrinsic preference of Ge═PX over XGe≡P. For instance, some available experimental bond dissociation energies (in kcal/mol) are as follows: Ge−F (116), P−F (105); Ge−O (158), P−O (143); Ge−Cl (103), Ge−H (77), P−H (71); Ge−S (132), P−S (106); Ge−Cl (103), P−Cl (69.1); Ge−C (110), P−C (123); Ge−Si (72), P−Si (87).[30] From these, it is evident that the relative order of bond dissociation energies between Ge−X and P−X bonds follow the same trend as the relative stability of XGeGe−P and Ge═PX species, as shown in Scheme 1.

Furthermore, according to Hammond's postulate,[31] exoergic reactions have transition-state geometries resembling the reactants, with the transition states becoming more like the products with decreasing exoergicity. For the predicted transition-state structures (see Table 1), our DFT calculations suggest that the Ge−P bond is stretched by 5.6%, 0.49%, 1.6%, 3.1%, 5.9%, 3.4%, 4.7%, 9.7%, 12%, 7.4%, 13%, and 12% for HGeP-TS, LiGeP-TS, HBeGeP-TS, H_2BGeP-TS, H_3CGeP-TS, H_3SiGeP-TS, H_2NGeP-TS, H_2PGeP-TS, HOGeP-TS, HSGeP-TS, FGeP-

TABLE 2: Calculated Harmonic Vibrational Frequencies (cm^{-1}), IR Intensities (KM/Mol) Rotational Constants (MHz), and Dipole Moments (Debye) of the Stationary Points in XGeP Isomerization Reactions (Eq 1) at the B3LYP/6-311++G(d,p) Level of Theory

species	frequencies (IR intensities)	rotational constants	dipole moments	species	frequencies (IR intensities)	rotational constants	dipole moments
HGe∞P	2136(34.4)	$A = 5441.94$	2.433	H$_2$NGe≡P	3631(48.6)	$A = 298402.00$	3.946
	589(0.1)			106(3.8)	3529(61.5)	$B = 2889.76$	
	284(16.5)				1564(29.6)	$C = 2871.45$	
HGeP-TS	1879, 476, 547i				861(0.4)		
Ge=PH	2134(30.5)	$A = 267853.78$	1.567		734(58.2)		
	515(17.8)	$B = 4952.39$			530(5.1)		
	411(31.7)	$C = 4862.49$			434(186.7)		
LiGe≡P	578(3.5)	$A = 3339.08$	10.46		115(1.7)		
	416(99.2)				92(4.9)		
	62(34.8)			H$_2$NGeP-TS	3599, 3491, 1567, 795,		
					630, 476, 355, 302, 309i		
LiGeP-TS	563, 412, 81i			Ge=PNH$_2$	3667(41.2)	$A = 27189.80$	2.285
Ge=PLi	513(30.3)	$A = 16982.61$	6.338		3565(43.6)	$B = 2514.19$	
	476(103.7)	$B = 4546.00$			1604(23.0)	$C = 2303.72$	
	125(20.3)	$C = 3586.06$			946(13.6)		
HBeGe≡P	2196(247.8)	$A = 3014.65$	2.394		823(99.6)		
	617(29.8)				394(26.2)		
	495(41.8)				313(231.7)		
	489(157.7)				277(8.9)		
	484(153.0)				124(3.4)		
	82(0.2)			H$_2$PGe≡P	2390(26.9)	$A = 113800.53$	3.532
HBeGeP-TS	2182, 571, 498, 471, 466,				2381(24.2)	$B = 1643.74$	
	106i				1100(17.6)	$C = 1643.18$	
Ge=PBeH	2160(245.9)	$A = 14825.12$	1.369		680(15.7)		
	648(71.6)	$B = 3984.18$			656(24.9)		
	531(102.7)	$C = 3140.25$			593(4.1)		
	529(110.0)				309(0.2)		
	473(0.2)				68(0.1)		
	135(4.5)				68(0.6)		
H$_2$BGe≡P	2729(44.4)	$A = 230681.43$	2.386	H$_2$PGeP-TS	2386, 2373, 1114, 640,		
	2615(82.9)	$B = 2885.05$			606, 475,280,150,145i		
	1133(80.7)	$C = 2849.41$		Ge=PPH$_2$	2343(68.0)	$A = 6976.53$	1.705
	862(39.5)				2138(34.8)	$B = 2657.57$	
	635(2.3)				1074(29.7)	$C = 1953.76$	
	615(26.7)				757(1.0)		
	502(16.5)				715(18.2)		
	98(0.0)				470(11)		
	78(0.0)				376(5.1)		
H$_2$BGeP-TS	2727, 2603, 1116, 843, 608,				266(5.3)		
	515, 470, 215, 208i				174(0.8)		
Ge=PBH$_2$	2677(70.3)	$A = 19326.59$	1.470	HOGe≡P	3820(185.6)	$A = 655440.67$	2.662
	2580(126.3)	$B = 2939.82$		174(0.8)	864(47.6)	$B = 2909.57$	
	1163(95.7)	$C = 2608.64$			708(160.9)	$C = 2896.71$	
	919(9.9)				517(7.8)		
	695(48.4)				101(11.3)		
	690(2.2)				91(2.1)		
	465(23.1)			HOGeP-TS	3811, 753, 544, 346, 144, 248i		
	104(0.2)			Ge=POH	3838(180.9)	$A = 21478.21$	0.0445
	90(8.2)				1027(97.7)	$B = 2742.44$	
H$_3$CGe≡P	3144(0.2)	$A = 157332.39$	4.073		719(189.7)	$C = 2431.92$	
	1451(11.5)	$B = 2785.32$			405(11.9)		
	1263(1.9)				219(149.4)		
	800(0.2)				97(1.4)		
	647(13.8)			HSGe≡P	2655(6.5)	$A = 266275.15$	2.627
	498(1.3)				722(16.2)	$B = 1750.05$	
	96(0.8)				591(16.7)	$C = 1738.62$	
H$_3$CGeP-TS	1462, 1441, 1189, 764, 729,		1.464		357(16.2)		
	461, 427, 114, 213i						
Ge=PCH$_3$	3132(1.3)	$A = 12279.88$			84(1.3)		
	3073(6.8)	$B = 3612.13$			62(0.2)		
	2915(17.7)	$C = 2841.61$		HSGeP-TS	2623, 686, 411, 317, 177, 140i		
	881(9.6)			Ge=PSH	2663(0.5)	$A = 14000.88$	0.6802
	1473(8.7)				812(0.9)	$B = 1658.89$	
	1440(4.2)				476(2.5)	$C = 1483.16$	
	1324(6.3)				378(37.0)		
	851(7.6)				134(34.9)		

TABLE 2: (Continued)

species	frequencies (IR intensities)	rotational constants	dipole moments	species	frequencies (IR intensities)	rotational constants	dipole moments
$H_3SiGe\equiv P$	585(3.0)	$A = 84224.27$	3.731		80(1.4)		
104(0.0)	463(15.2)	$B = 1614.96$		$FGe\equiv P$	706(113.8)	$B = 2834.25$	0.0427
	254(0.4)				505(11.9)	$C = 2834.25$	
	104(0.0)				83(0.9)		
	2257(56.9)			FGeP-TS	559,332,186i		
	2234(64.2)			$Ge{=}PF$	576(67.7)	$A = 13421.44$	2.6958
	1411(40.6)				454(10.0)	$B = 3942.14$	
	941(40.7)				98(1.2)	$C = 3047.14$	
H_3SiGeP-TS	868(511.8)			ClGe∞P	591(31.2)	$B = 1760.89$	0.9918
$Ge{=}PSiH_3$	601(0.4)	$A = 6869.06$	1.283		371(42.7)	$C = 1760.89$	
	513(21.3)	$B = 2712.79$			71(0.1)		
	309(6.7)	$C = 1990.83$		ClGeP-TS	375,330,162i		
	63(0.0)			$Ge{=}PCl$	459(21.7)	$A = 6563.44$	2.041
	2257, 2248, 2230, 958, 940, 869, 532, 503, 497, 297, 63, 112i				362(26.4)	$B = 3101.38$	
	2236(88.7)				158(4.1)	$C = 2106.17$	
	2226(92.6)						
	1980(51.9)						
	964(71.0)						
	930(316.8)						
	896(22.7)						
	576(8.8)						
	550(34.5)						
	472(7.8)						
	353(7.4)						
	297(0.0)						
	106(3.8)						

TS, and ClGeP-TS, respectively, relative to its value in the corresponding XGeGe−P. All of these features strongly indicate that the transition structures for $XGe\equiv P$ with electropositive substituents take on a more reactant-like character than those with electronegative substituents. Consequently, one may anticipate a lower activation barrier and a larger exothermicity for the former than for the latter, which is confirmed by both B3LYP and CCSD(T) calculations, as shown in Scheme 1. Thus, our theoretical findings strongly support Hammond's postulate.

From Table 2, it is found that the dipole moments of both $XGe\equiv P$ and $Ge{=}PX$ are predicted to be quite large (1.0−10 D at B3LYP) except for the case of $FGe\equiv P$ (0.043 D at B3LYP). This implies that $FGe\equiv P$ itself is unlikely to be observed in some types of experiments, such as microwave spectroscopy. However, other experimental techniques, such as photoelectron spectroscopy, which do not have selection rules that depend on the dipole moment might detect it.

In conclusion, the present work predicts that the $XGe{=}P$ triple bond species lies at the minimum of the potential energy surface and can be strongly stabilized in a kinetic sense with a proper choice of substituents, even though germanium is more reluctant to form $XGe{=}P$ triply bonded than $Ge{=}P$ doubly bonded compounds. Nevertheless, our theoretical findings suggest that more electronegative and π-electron-donating substituents favor the $XGe{=}P$ triply bonded molecule, while electropositive substituents prefer the $Ge{=}PX$ doubly bonded species. As a result, the detection of such $Ge{=}P$ triply bonded species as a monomer should be achieved either in the low-pressure gas phase (e.g., as low as 10^{-4} Torr) or in a low-temperature matrix.

It is hoped that the theoretical interpretations of substituent effects will be of help in preparing fruitful precursors of the $Ge{=}P$ species.

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