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Computational Studies on Stable Triplet States of Heteroacetylenes and the Effects of Halogen Substituents

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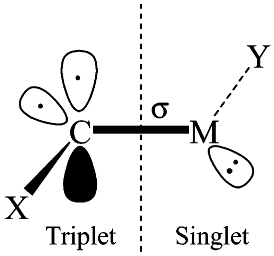
This paper describes theoretical studies of halogen-substituted heteroacetylenes (XC≡MY, M = Si and Ge; X, Y = H, Cl and F) performed at the QCISD(T)/6-311G**//QCISD/6-31G* level of theory. The electronegative halogen substituents destabilize the singlet state such that the triplet state tends to become favorable. The triplet state has the bifunctional electronic structure of a triplet carbene joined to a heavy singlet carbene. We found that the substituents effectively reduce the energy of the donor−acceptor interactions (E_{D-A}) between the two in-plane lone pairs of electrons of the singlet state; therefore, the remaining π bond is less favorable energetically than the triplet state with a σ bond. A related phenomenon occurs for the homonuclear heavy acetylenes in singlets in which the lead compound RPbPbR switches to a Pb−Pb σ bond from the π bonds observed for the lighter acetylenes.

Introduction

Many experimental and theoretical studies have been devoted to the chemistry of unsaturated compounds of the heavy group 14 elements, but very few compounds of the heteroacetylene (RC≡MR′) type (i.e., molecules containing a triple bond between a carbon atom and a heavier atom) have been synthesized and characterized,[1−5] presumably because of the high steric requirements and the reactivities of their polar C−M bonds. However, there have been several theoretical studies on these types of compounds, concerning the carbon−silicon triple bonded species.[6−12] Our interest here is the doubly substituted heteroacetylene series (XC≡MY, M = Si, and Ge; X, Y = H, Cl, and F). These species display a triplet ground-state electronic structure, which have a divalent state of their two central atoms, namely, a triplet carbene joined to a heavy singlet carbene, as indicated by structure **1**.



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This bifunctional state becomes increasingly more stable over the singlet state for heavier elements M and more-electronegative substituents X and Y. We have communicated previously our preliminary results on HC≡GeX systems;[13] we found, unexpectedly, that the triplet state is more stable than the singlet state for HC≡GeF and the former is also a global minimum on the triplet potential surface.[13] We report here a systematic study that we performed on the two series of the halogen-substituted heteroacetylenes (M = Si and Ge) with the goal of explaining why the triplet state is favored by halogen substituents and heavy atoms M. These results contradict our previous result that the triplet states of carbene analogues are destabilized by halogen substituents. The triplet has a planar structure. It can be rationalized as a bisubstituted triplet carbene with the push−pull substituents, X and MY. Note that MY is isoelectronic to the group 13 substituent M′HY (M′ = Al, Ga and Tl), an effective π acceptor (also a σ donor), whereas X behaves in an opposite way as a π donor and σ acceptor for X=Cl and F.

Our interest in these types of halogen-substituted compounds was inspired by the work of Schwarz, Apeloig, and co-workers,[1] who discovered that stabilization of the C≡Si triple bond can be achieved through the electronic effects of halogen substituents. The electronegative elements F and Cl can prevent HC≡SiX species from isomerizing to double-bonded silylidene compounds.

Calculation Methods

We performed full unconstrained optimization of the geometry and calculation of frequencies at the QCISD(T)/6-311G**//QCISD/6-31G* level. The frequency calculations show that all the singlet and triplet state of the molecules, which we study here, are minimum on the potential energy surface. The method we chose to use in this study resulted from a test performed on the HC≡GeH structure (Table 1). From the computed structural parameters of HC≡GeH, it is apparent that the results for the triplet state are less sensitive than are those for the singlet state with respect to the choice of theoretical method and basis set. The geometrical predictions of the bond angles at Ge (∠Ge) are poor for the singlet state at the MP2 and MP3 levels of theory, even with an improved basis set, but the B3LYP and QCISD results are in better agreement with the CCSD(T) and QCISD(T) predictions. When predicting the value of R_{C-Ge}, the B3LYP method displays its weakness with a ca. 0.03 Å deviation from the results obtained at the QCISD(T) and CCSD(T) levels; in contrast, the predicted value of R_{C-Ge} obtained using the QCISD method is in good agreement with the values determined at the QCISD(T) method with both basis sets. The predicted singlet−triplet energy gaps (ΔE_{S-T}) obtained at the

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B3LYP and QCISD levels are underestimated when compared with the QCISD(T) results. Therefore, a sensible strategy is to obtain the geometries using the QCISD method with the smaller basis set and then to calculate the energies of the optimized structures using the QCISD(T) method with larger basis set, denoted as QCISD(T)/6-311G**//QCISD/6-31G* in the last row. We used the Gaussian 03 program to perform all of the calculations reported in this paper.[14]

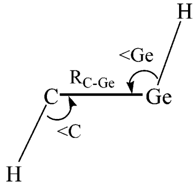
Results and Discussion

We performed structural optimizations at the QCISD/6-31G* level for the two series of heteroacetylene compounds (XC≡MY, M = Si and Ge) in both their singlet and triplet states. The structural parameters, the adiabatic values of ΔE_{S-T}, and spin density of triplet state compounds are presented in Table S1 in the Supporting Information. Figure 1 presents the most interesting quantities (the values of ΔE_{S-T}) for the two series. It is interesting to note that the more electronegative the substituents and the heavier the elements, the more stable the triplet state is relative to the corresponding singlet state, i.e., a more negative ΔE_{S-T}. For example, FC≡MF species (M = Si and Ge) have more-stable triplet ground states: $\Delta E_{S-T} = -1.6$ and -7.3 kcal/mol, respectively, at the QCISD(T) /6-311G** //QCISD/6-31G* level; in contrast, the corresponding HC≡MH species are all more stable in the singlet ground state: ΔE_{S-T} = 26.8 and 20.8 kcal/mol, respectively. For each series, the values of ΔE_{S-T} of the remaining substituted compounds lie between these two limits. The two sets of compounds display qualitatively similar behaviors: increasing both the electronegativity of atoms X and Y and the heaviness of atom M cause the value of ΔE_{S-T} to become more negative. These results appear to be rather counterintuitive in view of the fact that the values of ΔE_{S-T} of carbene analogues of the type XMY display the opposite behavior,[15−17] although these two cases cannot be related directly because the heteroacetylene possess two central atoms. In fact, the substituent effect on M is more effective than on C atom in lowing the value of ΔE_{S-T} as shown in Figure 1 and Table 2. Their difference can be understood in terms of substituent effect for a simple carbene. We have a situation in which the triplet state essentially localized at the carbon site, as shown by the spin density in Table 2 and the structure **1**. Therefore, the triplet can be viewed as a simple triplet carbene with the two substituents, X and MY. The X destabilizes the triplet carbene to a near extent as it does to the C≡M moiety in the singlet XC≡MY. In constrast, Y destabilizes the C≡M moiety in the singlet XC≡MY more than it does to the triplet state for a distant triplet carbene fragment. It gives rise to the results that X is less effective than Y in lowing the value of ΔE_{S-T}.

TABLE 1: Values of ΔE_{S-T} [a] (kcal/mol) and Structural Parameters[b] of Singlet and Triplet HC≡GeH Determined at Various Levels of Theory

		singlet state			triplet state		
theoretical method	ΔE_{S-T}	∠C	∠Ge	R_{C-Ge}	∠C	∠Ge	R_{C-Ge}
B3LYP/6-31G*	13.4	149.0	122.0	1.720	135.5	96.3	1.903
B3LYP/6-311G**	12.7	147.7	123.3	1.718	135.7	96.2	1.916
MP2/6-31G*	26.6	140.0	148.8	1.709	138.3	95.2	1.914
MP2/6-311G**	24.5	136.9	147.8	1.710	137.9	94.7	1.928
MP3/6-31G*	13.2	144.2	140.1	1.696	138.9	95.0	1.917
MP3/6-311G**	10.8	141.9	138.6	1.698	138.5	94.6	1.932
QCISD/6-31G*	18.7	149.7	121.0	1.751	136.2	96.4	1.914
QCISD/6-311G**	15.8	148.3	120.3	1.752	136.3	95.9	1.928
QCISD(T)/6-31G*	24.0	146.6	124.0	1.756	135.0	96.7	1.914
QCISD(T)/6-311G**	21.5	145.1	123.5	1.757	135.9	96.1	1.928
QCISD(T)/6-311G// QCISD/6-31G***	**21.4**	**149.7**	**121.0**	**1.751**	**136.2**	**96.4**	**1.914**

[a] $\Delta E_{S-T} = E_{Triplet} - E_{Singlet}$. [b] Units: *R*, Å; angle, degrees.



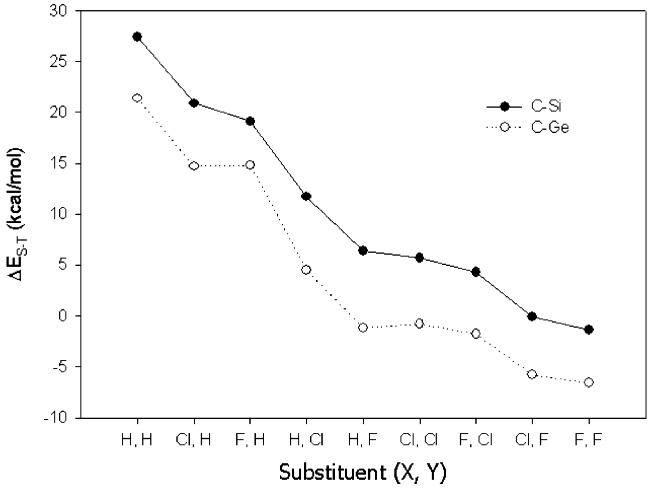


Figure 1. ΔE_{S-T} value ($E_{Triplet} - E_{Singlet}$) for the two series of XC≡MY (M = Si, and Ge) compounds with the QCISD(T)/6-311G**// QCISD/6-31G* level of theory.

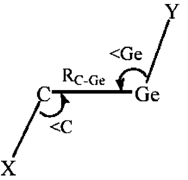
Because the general features of the two series are similar, we focused on obtaining results for the XC≡GeY series. We believe that our findings regarding the effects that the substituents have on the value of ΔE_{S-T} can be generalized readily to the silicon series of compounds.

A. Geometry of XC≡GeY. Table 2 lists the structural parameters (∠C and ∠Ge) and the spin densities (ρ(C) and ρ(Ge)) in addition to the values of ΔE_{S-T} with ZPVE correction of XC≡GeY species. It is interesting to note that the values of

TABLE 2: Values of ΔE_{S-T} ,[a] Structural Parameters[b] for Both Singlet and Triplet XC≡GeY (X, Y = H, Cl and F) and Spin Densities[c] (ρ) for Triplet States, Calculated at the QCISD(T)/6-311G//QCISD/6-31G* Level**

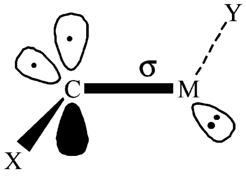
XC═GeY		singlet state			triplet state				
X	Y	ΔE_{S-T} [a]	∠C	∠Ge	R_{C-Ge}	∠C	∠Ge	R_{C-Ge}	ρ_C	ρ_{Ge}
H	H	21.4 (20.8)	149.7	121.0	1.751	136.2	96.4	1.914	2.01	0.04
H	Cl	4.5 (3.7)	137.4	124.6	1.768	140.0	99.0	1.923	2.05	0.03
H	F	−1.2 (−2.0)	134.3	122.5	1.780	143.9	98.1	1.931	2.07	0.04
Cl	H	14.7 (14.5)	155.9	106.6	1.780	132.2	92.9	1.936	1.82	0.12
Cl	Cl	−0.8 (−1.1)	147.1	112.5	1.808	131.6	97.2	1.949	1.84	0.09
Cl	F	−5.8 (−6.0)	144.6	111.2	1.826	132.0	96.4	1.956	1.85	0.10
F	H	14.8 (16.1)	156.1	99.8	1.798	125.2	91.0	1.966	1.73	0.23
F	Cl	−1.8 (−2.4)	146.0	109.1	1.833	122.9	96.2	1.973	1.74	0.20
F	F	−6.6 (−7.3)	143.8	107.6	1.851	123.6	94.9	1.976	1.74	0.20

[a] Adiabatic values of $\Delta E_{S-T} = E(\text{triplet}) - E(\text{singlet})$ in kcal/mol in parentheses are those obtained after ZPVE correction. [b] Units: *R*, Å; angle ∠, degrees.



[c] Spin densities at the C and Ge atoms were calculated at the HF/6-311G**//QCISD/6-31G* level of theory.

∠Ge for the triplet states are rather small (they are in the range 91.0−99.0°), which suggests the characteristics of singlet germylenes. For comparison, the values of ∠Ge for singlet HGeY (Y = H, Cl and F) fall within the range 91.3−94.8° (112.7−119.3° for the corresponding triplet states). Furthermore, the values of ∠C are within the range 122.9−143.9°, which compare reasonably well with the values (120.9−132.1°) for the triplet carbenes HCX (X = H, Cl and F; 101.5−102.5° for the corresponding singlet carbenes). The spin is predominantly localized at the carbon atom with the spin density value close to 2.0. This finding reinforces the previous statement that the triplet state has a dicarbene-like electronic structure, with a singlet germylene joined to a triplet carbene (see structures **1** or **2**). This bifunctional electronic structure of the singlet germylene and triplet carbene also can be viewed as the bonding of quartet XC and doublet GeY fragments. Structure **2** depicts the compromised electronic structure of half an acetylene and half a heavy analogue; according to the CGMT model,[18−21] a linear acetylene XCCX can be perceived as consisting of two quartet XC fragments and a trans-bent heavy analogue YMMY can be perceived as consisting of two doublet MY fragments.[18−21] We note that the bonding between the carbon and germanium atoms is a σ bond in the triplet state. In comparison, in the singlet state, the XC and GeY fragments are connected by a covalent π bond in addition to an interfragmental n−p_π donor−acceptor interaction (E_{D-A}, as indicated by the two arrows), which has the planar structure similar to that of **3**.



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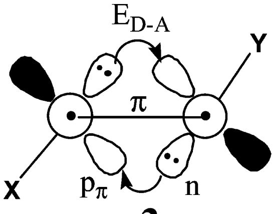

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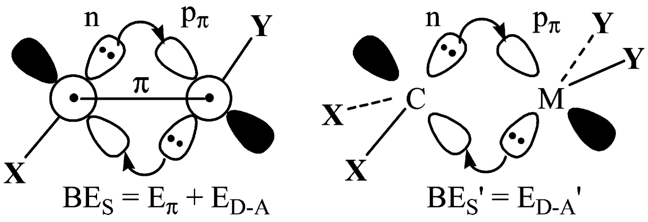
It appears that the geometries of singlet heteroacetylenes are sensitive to their substituents and to the level of theory (see Tables 1 and 2). We did not expect the bond angles to correlate with those of the free singlet carbenes and singlet germylenes because the covalent bond between the carbon and germanium atoms is a π bond rather than a σ bond. It is interesting to note that the electronic configuration in the triplet state differs from that of the singlet state by three electrons: a local n−p_π excitation at the carbon atom and a switch from a C−Ge π bond to a σ bond. The singlet state is formed through the bonding between the two doublet fragments XC and GeY, with a π bond oriented perpendicular to the molecular plane (structure **3**). We may also perceive the triplet state to be formed from the two doublet fragments in a different orientation: the two radical electrons lay orthogonal to one another: P_π at C and σ at Ge. Thus, C−Ge σ bond formation transforms the initial two radicals into a one-centered diradical localized on the carbon atom. As we mentioned earlier, the high-spin carbon atom can be also viewed as the result of direct σ bond formation between quartet XC and doublet GeY fragments. There is an avoided crossing between two configurations having the same A″ symmetry, i.e., the (doublet + doublet) and (quartet + doublet) fragments.

TABLE 3: Bonding Energies (kcal/mol) of the Singlet (BE_S) and Triplet (BE_T) XC≡GeY with Respect to the Corresponding Doublet SC and GeY Fragments Computed at the QCISD(T)/6-311G/QCISD/6-31G* Level of Theory**

X	Y	BE_S [a]	BE_T [a]	$\Sigma\Delta E_{DQ}$ [b]
H	H	99.2	77.8	52.7
H	Cl	78.9	74.4	85.8
H	F	75.0	76.2	99.4
Cl	H	71.3	56.7	91.1
Cl	Cl	51.6	52.4	124.2
Cl	F	48.4	54.1	137.8
F	H	58.7	43.8	118.1
F	Cl	38.3	40.1	151.2
F	F	35.5	42.0	164.8

[a] Bonding energy (BE) is defined as the energy difference between the state and the two doublet fragments (see Scheme 1). [b] $\Delta E_{DQ}(XC) + \Delta E_{DQ}(GeY) = \Sigma\Delta E_{DQ}$, the sum of the quartet-double energy gaps for the two fragments SC and GeY.

CHART 1



B. Values of E_{D-A} for Singlet XC≡GeY. The structure of **3** indicates that the bonding energy between the XC and GeY fragments in the singlet state has two components: E_{D-A} and E_π. In fact, we noted the E_{D-A} so defined has not only the dative type bonding from σ electrons but also an important contribution from the covalent type bonding especially for some electropositive substituents such as hydrogen. However, for the most discussions in this work, we do not need to distinguish the contributions from the two different types of bonding, we are concerned only with their sum. Table 3 shows the bonding energies of the singlet (BE_S) and triplet (BE_T) XC≡GeY with respect to the two doublet XC and GeY fragments. It is interesting to note the former covers a rather wide range of about 64 kcal/mol, from 99.2 kcal/mol for HC≡GeH to 35.5 kcal/mol for FC≡GeF, whereas those of BE_T cover a narrow range of 35 kcal/mol, which can be identified as σ bonding energies E_σ shown in structure **2**. Some rationalization of the variation in E_σ will be given later in this section. Let us focus on the results of BEs, which are a sum of E_{D-A} and E_π. Because the latter is expected to be weakly dependent on the substituent. Therefore, E_{D-A} is expected to be decreasing effectively as the electronegativity of the substituent increases. The nature of decreasing E_{D-A} may be shown also qualitatively in terms of a somewhat related doubly bonded series $X_2C{=}GeY_2$, which has a trans-bent structure. This series has only the E_{D-A} component without an E_π contribution (Chart 1).

In Table 4, the bonding energies of the two series are compared. The point of the interest is that the pattern in the reduction of the values of BE_S' (E_{D-A}') arising from the effect

TABLE 4: Bonding Energies (kcal/mol) of the Singlet XC≡GeY (BE_S) with Respect to Two Doublet Fragments Compared with Singlet $X_2C{=}GeY_2$ (BE_S') with Respect to Two Singlet Carbene-Like Fragments

X	Y	XC≡GeY BE_S	$X_2C{=}GeY_2$ BE_S'
H	H	99.2	104.9
H	Cl	78.9	72.4
H	F	75.0	62.9
Cl	H	71.3	64.2
Cl	Cl	51.6	31.2
Cl	F	48.4	21.3
F	H	58.7	39.4
F	Cl	38.3	7.4
F	F	35.5	6.4

of the substituent in $X_2C{=}GeY_2$ is qualitatively similar to the reduction of E_{D-A} ($BE_S = E_{D-A} + E_\pi$) in $XC{\equiv}XGeY$. E_π is reasonably assumed to be a constant nearly independent of the substituents. Our rationale on the reduction of E_{D-A} is that the electronegative substituents X and Y increase the interfragmental HOMO−LUMO energy gap, i.e., the energy difference between the vacant p_π orbital on one fragment and the occupied n orbital of the other. There are two pairs of in-plane (n, p_π) orbitals involved in the donor−acceptor bonding that contribute to the value of E_{D-A}. The effectiveness of such bonding can be correlated to the quantity $\Sigma\Delta E_{DQ}$, the sum of quartet-doublet energy gaps for the XC and GeY fragments, which can be rearranged as follows:

$$\Sigma\Delta E_{DQ} = \Delta E_{DQ}(XC) + \Delta E_{DQ}(GeY) \approx [\epsilon(p_\pi)_{XC} - \epsilon(n)_{XC}] + [\epsilon(p_\pi)_{GeY} - \epsilon(n)_{GeY}] = [\epsilon(p_\pi)_{XC} - \epsilon(n)_{GeY}] + [\epsilon(p_\pi)_{GeY} - \epsilon(n)_{XC}] \quad (1)$$

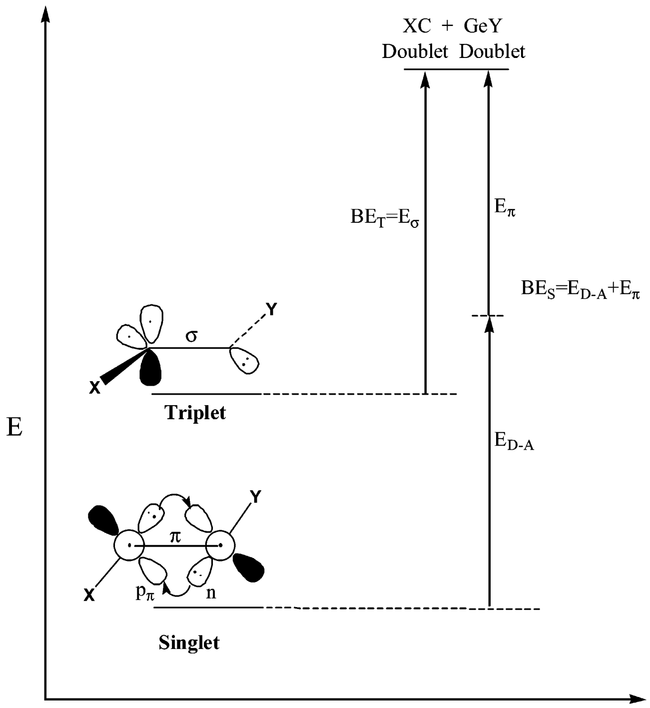
Thus, the value of $\Sigma\Delta E_{DQ}$ also is equal qualitatively to the sum of the two interfragmental (n, p_π) gaps related to the donor−acceptor interactions (see the last expression in eq 1). We note that the out-of-plane p_π orbital involved in the C−Ge π bond is independent of the donor−acceptor interaction in the molecular plane. For the doubly bonded compounds X_2CGeY_2, the previous discussion remains applicable, but with $\Sigma\Delta E_{DQ}$ replaced by $\Sigma\Delta E_{ST}$ for the X_2C and GeY_2 fragments, also, the n orbital of the sp hybrid orbital replaced by the sp^2 hybrid orbital.

Trinquier et al.[20,21] used the magnitude of $\Sigma\Delta E_{DQ}$ of the fragments in acetylene analogues as in comparison with the value of $E_{\sigma+1\pi}$ as a criterion for the transition from the covalent to dative bonding modes, with a corresponding change in the geometry from linear to trans-bent. Similarly, the value of $\Sigma\Delta E_{ST}$ also has been used as a criterion for the bent geometry of heavy olefins; this approach is known as the CGMT model.[18−21] In this paper, we propose another significance for this quantity in the regime of its large value. We consider that the magnitude of $\Sigma\Delta E_{DQ}$ also correlates with the strength of the dative interaction, the quantity E_{D-A}. As $\Sigma\Delta E_{DQ}$ increases, the corresponding value of E_{D-A} decreases. Therefore, two alternative interpretations of this former quantity allow one to use it in slightly different ways. In the original approach reported by Trinquier et al., the value of $\Sigma\Delta E_{DQ}$ represents the promotion energy required for the XC and GeY fragments to form a covalent triple bond. In contrast, our approach utilizes the fact that the quantity happens to be the sum of the interfragmental HOMO−LUMO gaps for the donor−acceptor interactions, as indicated in eq 1.

We are now in a position to interpret the situation when the triplet state is more stable than the singlet state. When the value of E_{D-A} of the singlet state is reduced effectively through the effect of the substituent, the singlet state will become higher in energy than the corresponding triplet state simply because the π bond of the singlet state is weaker than the σ bond of the triplet state. Therefore, it appears that the substituent does not stabilize the triplet directly; rather, it destabilizes the singlet by reducing the value of E_{D-A}, as indicated in Table 3. To summarize, the values of ΔE_{ST} becoming negative can be attributed to the decreasing strength of E_{D-A} in the singlet states and, thus, the remaining π bond is weaker than the σ bond of the triplet state.

In the column of BE_T of Table 3 and in Scheme 1, the bonding energies of the triplet state from the two doublet fragments are also defined as the strengths of the σ bond (E_σ).

SCHEME 1 [a]



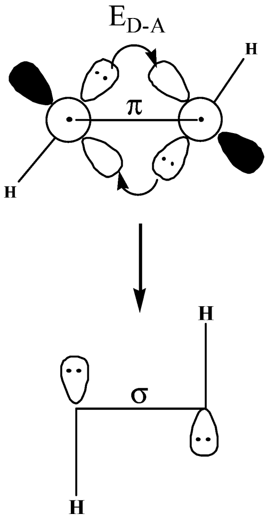
[a] The bonding energy of singlet $XC{\equiv}GeY$ (BE_S) equals $E_\pi + E_{D-A}$; that of the triplet state equals E_σ (BE_T) from the two doublet fragments with an avoided crossing with the (quartet + doublet) fragments (see text).

The values are, however, quite inconsistent. Interestingly, the values are dependent only on the substituent X and can be grouped into ranges of ca. 70, 50, and 40 kcal/mol for X = H, Cl and F, respectively. We believe the values are results of a nearly constant value of E_σ superimposed by a destabilization, caused by substituent X, of the energy of the out-of-plane p_π orbital of the carbon atom. Thus, we estimated the latter quantity from the values of ΔE_{S-T} of the carbene series $XCGeH_3$,[42] where X = H, Cl, and F; their triplet states model the local environments of the carbon atoms in the parent triplet compounds. The differences in ΔE_{ST} between the X = Cl and F compounds, relative to that when X = H, represent the destabilization of p_π. We expected these values to correlate to the reductions of BE_T for X = Cl and F relative to that of X = H. We found that the values of ΔE_{S-T} for the $XCGeH_3$ compounds were −18.7, −7.5, and −4.3 kcal/mol with the corresponding relative values of 0.0, 11.2, and 14.4 kcal/mol, for X = H, Cl, and F, respectively. These values explain, at least qualitatively, why BE_T is not a constant but instead decreases upon increasing the electronegativity of X. We expect that a more quantitative account of BE_T demands the consideration of the avoided crossing between the (doublet+doublet) and (quartet+doublet) fragmental states.

C. *σ* Bonds in Heavy Acetylenes. We may generalize the idea in Scheme 1 to a related bonding pattern for the heavy-acetylene series $HM{\equiv}MH$, where M = C, Si, Ge, Sn, and Pb.[23−41] When one goes down the group, there is a substantial reduction in the value of E_{D-A}, as indicated by the increase in ΔE_{DQ} in Scheme 2. We have taken the experimental and calculated values of $\Sigma\Delta E_{DQ}$ for $HM{\equiv}MH$ compounds (M = C, Si, Ge, Sn, and Pb) from ref 31.

The last member of the series, $HPb{\equiv}PbH$, switches from a π to a σ bond, whereas the lighter ones adopt π bonds and have two donor−acceptor interactions. Following the approach taken by Frenking et al.,[31] we consider two alternative singlet

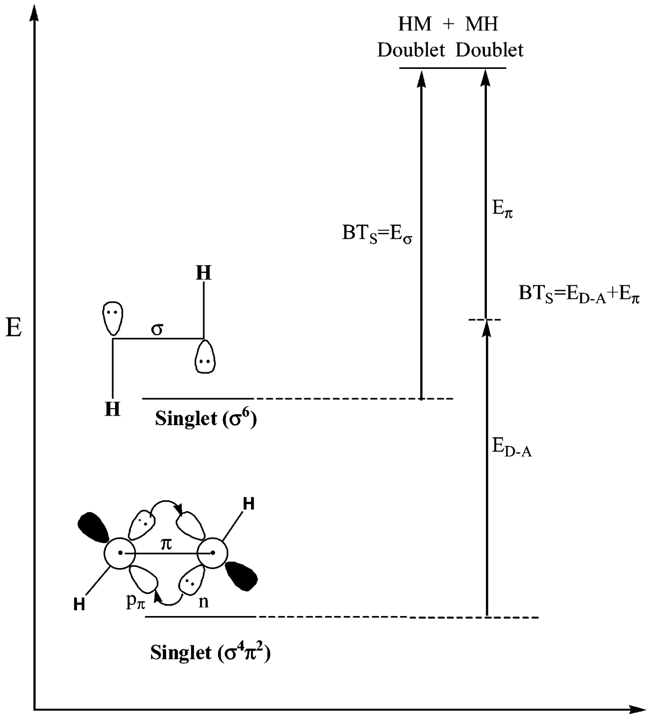
SCHEME 2 [a]



	$\Sigma\Delta E_{D\text{-}Q}$ **(kcal/mol)**
CH	33.4
SiH	72.8
GeH	95.6
SnH	89.0
PbH	100.6

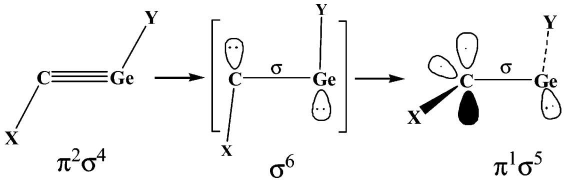
[a] Heavy acetylenes (HM≡MH, M = Si, Ge, Sn, and Pb) possess trans-bent structure with ΣE_{DQ} much greater than for HC≡CH and BE=E_π + E_{D-A}. For the HPbPbH compound, the metal−metal bond exhibits σ bonding and an HPbPb bending angle close to 90° due to the significant ΣE_{DQ} and a smaller E_{D-A} for the trans-bent structure.

SCHEME 3



electronic configurations for HPbPbH. One is trans-bent structure having energy contributions E_{D-A} and E_π; the other, which has ∠PbPbH of nearly 90.0°, has a bonding energy E_σ. These two configurations allow informative energy decomposition analyses to be performed.[31] Because E_{D-A} is rather weak for large values of $\Sigma\Delta E_{DQ}$, the remaining contribution of E_π is less favorable than that of E_σ in the second electronic configuration. Power and Frenking described the switch from the former's $\sigma^4\pi^2$ configuration to the latter's σ^6 configuration along the ∠PbPbH coordinate.[31,37] We may use the diagram in Scheme 3, which is closely related to that in Scheme 1, to indicate this concept qualitatively. In this case, there are two competing configurations for the ground singlet state, rather than a competition between triplet and singlet states. It is noteworthy that the σ bond in the second configuration (σ^6) would exclude the contribution of the donor−acceptor interaction, E_{D-A}, whereas in the first configuration the π bond can coexist with E_{D-A}. Therefore, the bonding situations in the two singlet configurations of HPb−PbH do indeed closely resemble those of the triplet and singlet states, respectively, of XC≡GeY.

Considering this second singlet configuration, σ^6, for the XCGeY compound sheds further light on the stability of its triplet state. If we start with the singlet configuration $\pi^2\sigma^4$, the electronegative substituents X and Y would reduce the energy gap between the $\pi^2\sigma^4$ and σ^6 configurations (the first step in eq 2). For the σ^6 configuration, a local n−p_π excitation at the carbon atom results in the desired triplet state (the second step of eq 2). Actually, this excitation could be energetically favorable because, as mentioned previously, the value of ΔE_{ST} for the carbene FC−GeH$_3$ is −4.3 kcal/mol. We utilized the singlet and triplet states of the carbene to model the local environments of the carbon atom in the singlet (σ^6) and triplet ($\pi^1\sigma^5$) states, respectively, both having a C−Ge σ bond. We may also view the stability of the triplet state from a more elementary prospect. When the two configurations, $\pi^2\sigma^4$ and σ^6, are degenerate as a result of a substituent effect (i.e., with their HOMOs and LUMOs interchangeable), we expect the open-shell structure of $\pi^1\sigma^5$ to be the ground state.



(2)

Conclusion

Our major conclusions from this study are the following:

(1) The electronegative halogen substituents X and Y effectively reduce the in-plane donor−acceptor interaction energy, E_{D-A}, for singlet XC≡MY This situation results in a corresponding configuration $\pi^2\sigma^4$, being nearly degenerate with the singlet configuration σ^6. Therefore, the open-shell triplet having the configuration $\pi^1\sigma^5$ becomes the ground state. The two singly occupied orbitals, π and σ, are localized on the carbon atom, which exhibits a localized triplet carbene structure.

(2) The reduction of the value of E_{D-A}, which leads to the π to σ switch, is a useful factor for understanding why HPb−PbH, the last member of heavy acetylene series (HM≡MH, M = Si, Ge, Sn, and Pb), has a Pb−Pb σ bond rather than a π bond. The reduction in the value of E_{D-A} is due to the nature of the heavier atom, rather than to a substituent effect, as indicated by the increases in the values of ΔE_{DQ} of the HM fragments.

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Supporting Information Available: Detail energy and structure parameters of two series XC≡XY (M = Si and Ge; X, Y = H, Cl and F) at the QCISD(T)/6-311G**//QCISD/6-31G* level were provided in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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