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Notes

Substituent Effects on Shape Deformation and Energies of the Silicon and Germanium Double Bond

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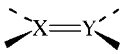
Summary: Substituent effects on the disubstituted heavier analogues of olefin $A_2X{=}YH_2$ (X, Y = Si, Ge; A = H, CH_3, NH_2, OH, F, and Cl) were investigated using density functional theory (B3LYP/6-311+G). Our theoretical findings suggest that the strength of the π-bond and the tendency to trans-bending are strongly related to the singlet−triplet energy gap (ΔE_{st}) of the corresponding disubstituted divalent species A_2X:. Namely, as ΔE_{st} becomes larger, the π-bond is weakened, the distortion increases, and the thermodynamic stability of the doubly bonded molecule is reduced. In this regard, heavier analogues of olefins with more electropositive substituents (or more bulky groups) will give rise to less distortion and possess greater thermodynamic stability, making them interesting goals for synthesis and isolation.*

Introduction

It is well known that the heavier analogues of olefins ($R_2X{=}YR_2$) do not exhibit classical planar geometry (**1**), but rather have a trans-bent structure (**2**), with pyramidalization of both XR_2 and YR_2 groups.[1] Indeed, these compounds, containing so-called "nonclassical double bonds", have been proven to be the preferred arrangements for disilene and digermene and are local minima on the potential energy surface for all of the heavier analogues of ethylene, from Si_2H_4 to Pb_2H_4.[2] Apparently, the heavier main group elements are pivotal atoms in this regard. It is therefore not surprising that these species have attracted wide interest not only because their unusual trans-bent geometries have given rise to several hypotheses explaining the nature of their bonding but also because of the controversy surrounding many of their properties. There is currently much discussion concerning these species in the literature. Interested readers can find excellent reviews in ref 1.



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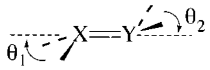

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The fact that various substituted heavy analogues of olefins possess differing deformations from planarity has also attracted some interest. Indeed, substituent effects on the structures and relative energies of doubly bonded compounds obviously deserves more attention. Several hypotheses have been proposed to explain these phenomena.[3−8] Although reports of calculations for a series of substituted disilenes have appeared,[9,10] the study of compounds containing double bonds to germanium is still in its infancy.[11] In particular, there seems to have been no systematic attempt to use theoretical calculations to study the intriguing structures of the doubly bonded species involving heavy heteronuclei. We thus present here the results of the first systematic density

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functional study of substituted heavier analogues of olefins, which shows that substituents can affect the double bond in different ways, causing remarkable changes in both the structures and the energies of $A_2X{=}YH_2$.

In this regard, a series of disubstituted homonulear ($A_2Si{=}SiH_2$ and $A_2Ge{=}GeH_2$) and heteronulear ($A_2Si{=}GeH_2$ and $A_2Ge{=}SiH_2$) doubly bonded species (A = H, CH_3, NH_2, OH, F, and Cl) were studied using density functional theory (DFT). We will show that the strength of the π-bond and the tendency to distort are closely related to the singlet−triplet gap (ΔE_{st}) of the corresponding disubstituted silene (A_2Si:) or germylene (A_2Ge:).

Methodology

All the geometries were fully optimized using the nonlocal hybrid density functional method at the B3LYP level.[12] The reason for using the B3LYP method is that it has been shown to be quite reliable both for geometries and energetics.[13] The 6-311+G* basis set has been used for all the elements studied in this work (denoted B3LYP/6-311+G*). The harmonic vibration frequency was also calculated to confirm the nature of the stationary points. The zero-point energy (ZPE) correction was also evaluated at the same level of theory.

All calculations were performed on an IBM590 in our laboratory, using the GAUSSIAN98 program.[14]

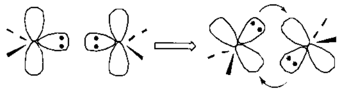
Results and Discussion

As suggested by Trinquier and Malrieu,[3] it is informative to view $R_2X{=}YR_2$ as consisting of R_2X: and R_2Y: units. Principally, two interaction modes (I and II) are possible, as shown in **3** and **4**. When the ground state of the divalent fragments are singlets ($\sigma^2\pi^0$), as for most silenes[15] and germylenes,[16] their bonding interaction will adopt mode I. Namely, not only is the central X−Y bond elongated to avoid repulsions, but also its structure is "trans-bent" to gain stabilization from electron transfer donor−acceptor bonds (denoted by arrows in **3**).[17] On the other hand, when the ground states of the divalent fragments are triplet ($\sigma^1\pi^1$), a planar double bond is formed from the two triplet fragments, as illustrated in **4.** This has also been suggested by Trinquier and Malrieu.[3] It therefore follows that the tendency of the doubly bonded molecule to distort from the planar should depend on the magnitude of singlet−triplet energy gap ($\Delta E_{st} = E_{triplet} - E_{singlet}$) of the corresponding divalent species.

Table 1. Singlet−Triplet Energy Gaps ($\Delta E_{st} = E_{triplet} - E_{singlet}$; in kcal/mol) of the Divalent Species of A_2Si and A_2Ge, and Relative Energies (kcal/mol) of the Planar and Trans-Bent Structures of $A_2X{=}YH_2$ at the B3LYP/6-311+G* Level of Theory (Including the ZPE Corrections)

	A = H	A = CH_3	A = NH_2	A = OH	A = F	A = Cl
$A_2Si{=}SiH_2$						
planar	0.772	1.24	12.5	11.6	12.2	7.62
trans-bent	0.0	0.0	0.0	0.0	0.0	0.0
ΔE_{st} for A_2Si	20.7	26.7	56.6	64.7	73.9	52.9
$A_2Ge{=}GeH_2$						
planar	4.83	6.10	24.5	22.6	26.0	20.2
trans-bent	0.0	0.0	0.0	0.0	0.0	0.0
ΔE_{st} for A_2Ge	27.5	31.5	59.2	72.3	83.5	63.6
$A_2Si{=}GeH_2$						
planar	2.28	3.31	20.4	18.3	18.3	12.4
trans-bent	0.0	0.0	0.0	0.0	0.0	0.0
ΔE_{st} for A_2Si	20.7	26.7	56.6	64.7	73.9	52.9
$A_2Ge{=}SiH_2$						
planar	2.28	3.07	17.6	18.1	18.9	14.1
trans-bent	0.0	0.0	0.0	0.0	0.0	0.0
ΔE_{st} for A_2Ge	27.5	31.5	59.2	72.3	83.5	63.6

(I)



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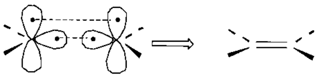

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To confirm the above prediction, we have calculated a series of disubstituted heavy analogues of olefins using the B3LYP level of theory. The singlet and triplet energy gaps (ΔE_{st}) and relative energies (ΔE) between trans-bent and planar structures are given in Table 1. As a result, we obtain the following correlations (units in kcal/mol; r^2 is the correction coefficient).

For $A_2Si{=}SiH_2$:

$$\Delta E = 0.245\Delta E_{st} - 4.439\ (r^2 = 0.912) \qquad (1)$$

For $A_2Si{=}GeH_2$:

$$\Delta E = 0.354\Delta E_{st} - 4.979\ (r^2 = 0.875) \qquad (2)$$

For $A_2Ge{=}SiH_2$:

$$\Delta E = 0.322\Delta E_{st} - 5.843\ (r^2 = 0.903) \qquad (3)$$

For $A_2Ge{=}GeH_2$:

$$\Delta E = 0.394\Delta E_{st} - 4.894\ (r^2 = 0.895) \qquad (4)$$

As one can see in eqs 1−4, there exists a linear correlation between ΔE_{st} and ΔE. That is to say, our model calculations provide strong evidence that the singlet−triplet gap (ΔE_{st}) in the divalent species plays a decisive role in determining the geometries of the doubly bonded molecules.

Moreover, an analogous effect occurs in the pyramidalization angle θ of the doubly bonded olefins. According to the work of Malrieu and Trinquier,[3] there should exist a correlation between the degree of pyramidalization (θ) and ΔE_{st}, which is based on a qualitative valence bond (VB) and molecular orbital (MO) analysis. The

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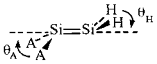
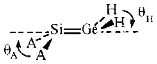
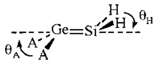
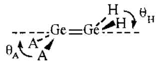
Table 2. Double Bond Distances (Å) and the Pyramidalization Angels (deg) of the Planar and Trans-Bent Structures of $A_2X{=}YH_2$ at the B3LYP/6-311+G* Level

	A = H	A = CH$_3$	A = NH$_2$	A = OH	A = F	A = Cl
						
$r_{Si\text{-}Si}$ (planar)	2.139	2.142	2.144	2.130	2.124	2.132
$r_{Si\text{-}Si}$ (trans-bent)	2.175	2.189	2.308	2.288	2.274	2.162
θ_A	32.01	24.22	14.92	21.58	29.02	31.35
θ_H	32.06	42.16	88.26	83.06	77.12	66.12
						
$r_{Si\text{-}Ge}$ (planar)	2.180	2.182	2.184	2.175	2.164	2.172
$r_{Si\text{-}Ge}$ (trans-bent)	2.239	2.261	2.397	2.385	2.356	2.332
θ_A	39.93	28.51	12.21	13.60	31.91	31.10
θ_H	38.04	52.10	94.13	93.80	84.55	73.65
						
$r_{Si\text{-}Ge}$ (planar)	2.180	2.186	2.192	2.186	2.177	2.181
$r_{Si\text{-}Ge}$ (trans-bent)	2.239	2.257	2.385	2.377	2.377	2.353
θ_A	38.04	28.01	24.52	20.09	32.40	34.76
θ_H	39.93	50.77	83.11	87.63	79.19	71.75
						
$r_{Ge\text{-}Ge}$ (planar)	2.224	2.230	2.234	2.232	2.225	2.228
$r_{Ge\text{-}Ge}$ (trans-bent)	2.307	2.337	2.483	2.475	2.467	2.440
θ_A	43.45	30.14	12.79	17.61	28.17	32.31
θ_H	43.72	59.55	94.64	92.94	86.03	78.09

calculated pyramidalization angles θ_H and θ_A (for definitions see Table 2) and the X═Y double bond distances for various substituted systems are all collected in Table 2. It can be shown that the pyramidalization angle θ_H of substituted $A_2X{=}YH_2$ correlates linearly with the ΔE_{st} of the disubstituted divalent species (A_2X:). The following are examples (units in deg; r^2 is the correction coefficient).

For $A_2Si{=}SiH_2$:

$$\theta_H = 0.987\Delta E_{st} + 16.19\ (r^2 = 0.832) \qquad (5)$$

For $A_2Si{=}GeH_2$:

$$\theta_H = 0.998\Delta E_{st} + 23.56\ (r^2 = 0.835) \qquad (6)$$

For $A_2Ge{=}SiH_2$:

$$\theta_H = 0.756\Delta E_{st} + 25.99\ (r^2 = 0.797) \qquad (7)$$

For $A_2Ge{=}GeH_2$:

$$\theta_H = 0.767\Delta E_{st} + 32.54\ (r^2 = 0.733) \qquad (8)$$

Again, these results are basically consistent with the predictions as discussed earlier. Namely, the larger the singlet–triplet energy gap of the divalent species, the more bent the geometry of the doubly bonded molecule.[18]

Besides these, Liang and Allen suggested that the geometries of disilenes are dictated by the electronegativity of the substituent.[7] That is to say, the more electronegative substitutents induce larger distortions. Apeloig and Karni proved that in addition to electronegativity the π-donor ability of the substituents is also important.[9a] In this work, we find that these predictions can be extended to other disubstituted systems. For instance, as can be seen in Table 2, for the aforementioned four kinds of systems our DFT calculations suggest that the double bond length of $A_2X{=}YH_2$ basically increases along the series A = H → CH_3 → NH_2 → OH → F, which is consistent with the electronegativity of the substituent A. Thus, both electronegative and π-donating substituents (such as F, OR, NR_2) should weaken X–Y (X, Y = Si, Ge) π-bonding. In brief, our DFT calculations have shown that the larger the singlet–triplet energy gap (ΔE_{st}) of the divalent species, the more favorable the interaction mode I, the larger the degree of pyramidalization (θ), and, in turn, the larger the energy difference between the planar and trans-bent structures.

Finally, if we define the X–Y bond energy of $A_2X{=}YH_2$ as the bond dissociation energy (ΔBDE) of $A_2X{=}YH_2$ to the corresponding singlet A_2X: and YH_2: fragments, then the computational results presented in this work can be rationalized on the basis of a configuration mixing model developed by Pross and Shaik.[19] According to this model, the X–Y bond energy of $A_2X{=}YH_2$ depends on the singlet–triplet splitting ($\sum\Delta E_{st}$) of both reactants A_2X: and H_2Y:. Namely, a smaller singlet–triplet splitting results in greater $A_2X{=}YH_2$ stabilization and, in turn, a larger exothermicity. Since the ΔE_{st} of reactant H_2Y: is a constant, a linear relationship between the X–Y bond energy (ΔBDE) and the singlet–triplet splitting of reactant A_2X: is therefore expected. In fact, this prediction is consistent with that of the model developed by Carter and Goddard[18] as well as Malrieu and Trinquier,[3] which allows a correlation between the singlet–triplet splitting of the divalent species and the bond dissociation energies of the doubly bonded compounds.

Again, our model calculations confirm the above prediction. For the B3LYP/6-311+G* calculations on the four kinds of systems studied here, a plot of ΔBDE vs ΔE_{st} is obtained; the best fit is as follows (units in kcal/mol; r^2 is the correction coefficient).

For $A_2Si{=}SiH_2$:

$$\Delta\text{BDE} = 0.597\Delta E_{st} - 79.44\ (r^2 = 0.975) \qquad (9)$$

For $A_2Si{=}GeH_2$:

$$\Delta\text{BDE} = 0.576\Delta E_{st} - 79.66\ (r^2 = 0.946) \qquad (10)$$

For $A_2Ge{=}SiH_2$:

$$\Delta\text{BDE} = 0.651\Delta E_{st} - 82.35\ (r^2 = 0.956) \qquad (11)$$

For $A_2Ge{=}GeH_2$:

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(18) It should be noted that this statement holds only if the singlet state is energetically below the triplet state. If the triplet would be lower than the singlet, this statement would not be true and the opposite relation would hold.

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$$\Delta \mathrm{BDE} = 0.515\Delta E_{\mathrm{st}} - 66.37\ (r^2 = 0.973) \quad (12)$$

Therefore, our B3LYP results suggest a decreasing trend in ΔE_{st} for F_2Si (73.9 kcal/mol) > $(OH)_2Si$ (64.7 kcal/mol) > $(NH_2)_2Si$ (56.6 kcal/mol) > Cl_2Si (52.9 kcal/mol) > $(CH_3)_2Si$ (26.7 kcal/mol) > H_2Si (20.7 kcal/mol), and F_2Ge (83.5 kcal/mol) > $(OH)_2Ge$ (72.3 kcal/mol) > Cl_2Ge (63.6 kcal/mol) > $(NH_2)_2Ge$ (59.2 kcal/mol) > $(CH_3)_2Ge$ (31.5 kcal/mol) > H_2Ge (27.5 kcal/mol), which is in excellent agreement with the trend in the bond dissociation energy for the four kinds of $A_2X{=}YH_2$ systems.

In summary, our theoretical investigations have shown that both shape deformations and bond dissociation energies of disubstituted heavier analogues of olefins ($A_2X{=}YH_2$) correlate linearly with the singlet−triplet splitting of the corresponding disubstituted divalent species (A_2X:). There are of course other factors (e.g., electronegativities, steric, bulk, etc.) that can change with substitution; however, we have shown that the singlet−triplet energy gap of the divalent species dominates the change in the geometries as well as the C=C bond energy. From our present analysis, we are confident in predicting that for the disubstituted olefin systems a more electronegative substituent will lead to a larger ΔE_{st} and, in turn, will decrease the strength of the π-bond and enlarge the degree of distortion from planarity. On the other hand, from our conclusions we predict that a more electropositive substituent will result in a smaller ΔE_{st} and will then increase the strength of the π-bond. Also, such a smaller singlet−triplet splitting can result in a relatively high thermodynamic stability of the doubly bonded molecule, making such a species synthetically accessible.

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