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Group IV Double Bonds: Shape Deformation and Substituent Effects

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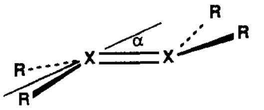
Abstract: A unified explanation of deformation and substituent effects is given for group IV double bonds. Results from experiments and previous theoretical work are correlated with ab initio calculations on electron withdrawal by substituents to determine the factors that govern geometry and bonding. Predictions are made and calculations carried out for a silyl substituent as a test of our hypotheses. In order to systematically investigate substituent effects we have adopted a nuclear charge perturbation approach. The GAUSSIAN set of ab initio electronic structure programs has been modified so that a continuous range of electron withdrawal is available.

The geometries of group IV double bonds have been much studied experimentally and theoretically because they demonstrate breakdown of the "classical double-bond rule" (whereby elements possessing a principal quantum number greater than 2 should not form p_π–p_π bonds) but also show a trend from planar to trans-bent as the element changes down the group.[1-17]



It is well-known that C=C double bonds are planar (except cases where other geometric demands make it impossible[4]). However, both planar[5,6] and trans-bent[6,7] Si=Si double bonds have been synthesized with substituents that have closely related steric effects, thereby indicating that the Si=Si bond is easily deformed. For Ge=Ge, both of the two known double bonded structures[8-10] are trans-bent, though their folding angles, α, are different. The only existing compound with a Sn=Sn double bond[9,11] is also trans-bent and possesses the largest observed α. Previous ab initio studies on the parent molecules, X_2H_4 where X = C, Si, Ge, and Sn, have been able to reproduce the known geometrical changes. Ethylene is planar at all calculational levels,[12] but the computed geometry of disilene depends strongly on basis functions and electron correlation.[13,14] The deformability of the Si=Si bond is also reflected in a flat potential energy surface as α is varied in disilene.[9] In contrast to disilene, the geometries of digermene and distannene are found to be independent of basis sets or the computational level employed.[9,15,16]

Several hypotheses have been proposed to explain these phenomena. Trinquier and Malrieu[17] assumed that a planar double bond is formed from two triplet fragments and that it is twice as strong as the two dative, banana-shaped bonds that can be formed in the trans-bend configuration. A planar double bond is preferred when half of its bond strength is larger than the energy required to prepare two fragments in triplet states (if their ground states are singlets). For disilene, digermene, and distannene this criterion is not satisfied, and thus they adopt a trans-bent conformation.[17] Goldberg et al.[9] employed an argument on the basis of the π–σ^* separation: As X descends the group, this separation decreases, thereby allowing more orbital mixing and energy lowering when the molecule distorts from planar D_{2h} to trans-bent C_{2h}. However, Teramae's explanation is based on the HOMO–LUMO separation trend.[13] He showed that disilene has some diradical character, and he proposed that digermene and distannene possess still more diradical character since their HOMO–LUMO separations are smaller than that of disilene. The trans-bent geometry of disilene, digermene, and distannene is thus attributed to their diradical nature. Krogh-Jespersen[14] noted that electronegative substituents increase the preference of Si for a tetrahedral environment. Thus, pyramidalization of sp^2-hybridized Si in disilene (which leads to trans-bending of the molecule) is facilitated by the electron-withdrawing effect of substituents.

Table I. Calculated Geometries of Digermene and Distannene[a]

X	method	X–X	X–H	∠HXH	α[b]
Ge	HF/ECP+21G[c]	2.307	1.538	109.0	38.1
	RHF/ECP+DZP[d]	2.302	1.550	111.1	34.4
	CI/ECP+DZP[d]	2.325			38.9
	RHF[e]	2.30		107	40
	exptl[f]	2.347			32
Sn	HF/ECP+21G[c]	2.702	1.735	108.1	41.0
	RHF[e]	2.71		105	46
	exptl[f]	2.768			41

[a] Bond lengths in angstroms, bond angle in degrees. [b] Folding angle. [c] This work (both RHF and UHF give the same results). [d] Reference 15. [e] Reference 9. (Although no explicit contraction scheme was reported, the basis is at least of double-ζ plus polarization quality.) [f] $CH(SiMe_3)_2$ substituted.[9]

It is apparent from the brief outline above that geometry explanations for the hydrides, X_2H_4, X = C, Si, Ge, and Sn, are in conflict and that other research,[14] at least for the Si case, points to an important role for substituent electronegativity. In the present paper we have systematically studied the effect of sub-

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Table II. Data for Ethylene, 3-21G/OPT[a]

	Z_H					
	1.50	1.20	1.10	1.00[b]	0.95	0.80
C–C	1.300	1.302	1.307	1.315	1.320	1.336
C–H	1.055	1.055	1.062	1.074	1.081	1.106
∠HCH	112.0	114.8	115.6	116.2	116.4	116.9
α	0.00	0.01	0.01	0.00	0.00	0.04
q_C	0.044	–0.290	–0.368	–0.425	–0.446	–0.473
q_H	–0.022	0.145	0.184	0.213	0.223	0.237
$\Delta\epsilon$	0.595	0.580	0.573	0.567	0.563	0.552
ΔE_T	–2.297	–0.892	–0.442	0.00	0.219	0.866

[a] In this and the following tables, units and parameters are as follows: bond lengths, angstroms; angles, degrees; charges, electrons; energies, hartrees; α, folding angle of HXH formed by the HXH plane and X–X bond; $\Delta\epsilon$, HOMO–LUMO separation; ΔE_T, total energy difference. q_C, q_H, q_{Si}, etc., are Mulliken gross charges on the respective atoms. [b] $E_T = -77.600\,99$ au.

Table III. Data for Disilene, 3-21G/OPT

Z_H	0.85	0.90	0.95	0.98	1.00[a]	1.05
Si–Si	2.167	2.157	2.148	2.145	2.149	2.162
Si–H	1.512	1.499	1.487	1.481	1.477	1.470
∠HSiH	118.0	117.4	116.7	116.1	114.9	112.1
α	0.01	0.01	0.00	6.98	15.72	26.51
q_{Si}	–0.055	0.054	0.160	0.222	0.266	0.372
q_H	0.027	–0.027	–0.080	–0.110	–0.133	–0.186
$\Delta\epsilon$	0.310	0.313	0.316	0.318	0.316	0.312
ΔE_T	0.604	0.408	0.207	0.084	0.00	–0.214

[a] $E_T = -577.038\,62$ au.

Table IV. Data for Digermene, ECP+21G/OPT

	Z_H					
	0.80	0.90	0.95	0.98	1.00[a]	1.05
Ge–Ge	2.281	2.279	2.292	2.301	2.307	2.328
Ge–H	1.568	1.549	1.543	1.540	1.538	1.534
∠HGeH	118.9	114.7	111.7	110.0	109.0	106.3
α	0.05	23.95	32.07	35.89	38.07	43.06
q_{Ge}	–0.185	0.036	0.146	0.208	0.248	0.345
q_H	0.093	–0.018	–0.073	–0.104	–0.124	–0.173
$\Delta\epsilon$	0.286	0.289	0.289	0.289	0.289	0.289
ΔE_T	0.790	0.407	0.207	0.084	0.00	–0.214

[a] $E_T = -9.508\,39$ au.

Table V. Data for Distannene, ECP+21G/OPT

	Z_H					
	0.80	0.90	0.95	0.98	1.00[a]	1.05
Sn–Sn	2.655	2.664	2.680	2.693	2.702	2.728
Sn–H	1.772	1.751	1.743	1.738	1.735	1.729
∠HSnH	119.0	114.0	110.9	109.2	108.1	105.3
α	0.01	26.80	34.94	38.70	41.03	46.20
q_{Sn}	–0.282	–0.022	0.103	0.175	0.222	0.335
q_H	0.141	0.011	–0.051	–0.087	–0.111	–0.167
$\Delta\epsilon$	0.247	0.245	0.243	0.242	0.241	0.239
ΔE_T	0.768	0.399	0.203	0.082	0.00	0.212

[a] $E_T = -8.538\,24$ au.

Table VI. Data for Tetrafluoroethylene 3-21G/OPT

	Z_F			
	9.00[a]	9.05	9.08	9.15
C–C	1.293	1.291	1.290	1.289
C–F	1.330	1.330	1.330	1.331
∠FCF	113.2	112.9	112.7	112.4
α	0.00	0.00	0.01	0.00
q_C	0.714	0.753	0.775	0.826
q_F	–0.357	–0.376	–0.388	–0.413
$\Delta\epsilon$	0.592	0.596	0.598	0.603
ΔE_T	0.000	5.275	8.444	15.875

[a] $E_T = -470.855\,35$ au.

stituent electronegativity, and this leads to a unified explanation of geometry changes that brings out the interplay between the nature of the substituent and the position of X in group IV. Knowledge of the bonding pattern then makes possible predictions that can stimulate direct experimental tests. For example, silyl is a substituent group whose electronegativity is less than that of hydrogen, and we predict that it will give rise to more nearly classical, planar, double bonds. We have also carried out ab initio calculations for a silyl substituent on Si, Ge, and Sn double bonds, which supports our hypothesis.

Computational Methods and Results

Ab initio molecular orbital calculations were performed with GAUSSIAN 82.[18] The 3-21G basis set[19] was employed for carbon, silicon, and hydrogen, and effective core potentials (ECP) with the equivalent (3s3p)/[2s2p] basis[20] were used for germanium and tin. The geometries of all molecules were optimized by the Berny method, and C_{2h} symmetry was imposed unless otherwise specified.

Substituent electronegativity was studied by a perturbation approach wherein nuclear charges on specified atoms were increased or decreased by a small percent. Almost all of the substituent electronegativity effects were modeled by changing the nuclear charge of a hydrogen, Z_H, and it is significant to note that the optimized X–X bond lengths are quite insensitive to Z_H. Likewise, a given percent change in Z_H produces almost identical changes in the total energies irrespective of X. These two observations help greatly in establishing the credence of the method. To implement it, link 202 in GAUSSIAN 82 was modified so that any desired nuclear charge can be assigned.[21]

A principal purpose of the present research is to bring together the calculations of others, along with our own, to achieve a general and accurate description of group IV double bonds. We have not repeated Teramae's CASSCF 6-31G** disilene geometry calculation since our purpose is to explore the less correlation and basis set sensitive inductive effects associated with substituent electronegativity. The geometries of digermene and distannene are not strongly correlation and basis set dependent as seen from the collection of experimental and computational data given in Table I. Calculated geometries, Mulliken atomic charges,[22] HOMO–LUMO separations, and relative energies of ethylene, disilene, digermene, and distannene with different nuclear charge of hydrogen are listed in Table II–V, respectively.

Discussion

Table I demonstrates that for digermene and distannene different computational levels and different methods lead to very similar geometries. In particular, our RHF and UHF calculations give precisely the same results. This shows that digermene and distannene are stable singlets, contrary to Teramae's expectation.[13] Thus, the diradical character hypothesis is not adequate to explain the nonplanarity of these two molecules.

Table III shows that the geometry of disilene changes dramatically as the nuclear charge of hydrogen Z_H changes. Thus, increasing Z_H increases the folding angle of HSiH and transforms it from planar to trans-bent. This is accompanied by an increase in the negative charge of hydrogen and a decrease in the HSiH angle (pyramidalization of silicon), in line with Krogh-Jesperson's analysis.[14] However, this phenomenon cannot be rationalized by the HOMO–LUMO separation theory[23] as this separation is almost constant for both planar and trans-bent geometries (Table III). Similar observations apply to digermene and distannene (Tables IV and V).

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Table VII. Calculated Geometries[a] of $X_2(SiH_3)_4$

X	X=X	X—Si	∠SiXSi	α
Si	2.155	2.374	118.6	0.01
Ge	2.249	2.415	118.6	0.01
Sn	2.587	2.611	113.4	0.01

[a] C_s symmetry is imposed, the six heavy atoms are in C_{2h} symmetry, and silyl groups are in perfect tetrahedral environment with Si-H bond fixed at 1.46 Å.

In sharp contrast to disilene, digermene, and distannene, ethylene remains planar when Z_H is increased to 1.5, even though the HCH angle has decreased and its hydrogen has become negatively charged (Table II). In order to confirm the results obtained from varying the hydrogen nuclear charge in ethylene, calculations on tetrafluoroethylene, C_2F_4, are carried out. C_2F_4 was chosen because fluorine is the most electronegative atom,[24] and thus C_2F_4 has the best chance to trans-fold if electron withdrawing does pyramidalize sp^2-hybridized carbons (in fact, it is thought to have a small force constant for the folding angle coordinate, α[17]). As it turns out, this molecule is also planar and remains so even though the electronegativity of fluorine is increased by increasing its effective nuclear charge (Table VI). The planarity of ethylene and tetrafluoroethylene is readily accounted for by the HOMO-LUMO separation argument.[23] Tables II-VI show that ethylene and tetrafluoroethylene have much bigger HOMO-LUMO gaps than the other three. Therefore, it is less favorable for them to bend since the orbital mixing would be much smaller.[25]

The analysis above suggests that what determines the geometry of a double bond is the degree of orbital mixing. Greater orbital mixing leads to pyramidalization or trans-bending of double bonds. The degree of mixing is determined by two factors: (1) the intrinsic π-σ^* gap of the double bond, which is related to the HOMO-LUMO separation of the molecule[23] (intrinsic because it is largely determined by its σ and π bond strength: stronger double bonds have larger π-σ^* gaps), and (2) electronegative substitution, which increases orbital mixing. Thus, for ethylene the intrinsic π-σ^* gap is so large that no substituent can increase the orbital mixing sufficiently to trans-bend the C=C bond (illustrated in tetrafluoroethylene). On the other hand, the π-σ^* gaps of disilene, digermene, and distannene are small enough to make orbital mixing possible. Consequently the electron-withdrawing effect becomes important in determining the degree of orbital mixing. This explains why their geometries depend on Z_H even though their HOMO-LUMO separations do not (Tables III-V).

It is interesting to note that these two factors compete when disilene is compared to digermene and distannene. On one hand hydrogen withdraws more charge in disilene than it does in digermene and distannene, reflecting the electronegativity differences between silicon, germanium, and tin.[24] This makes orbital mixing in disilene easier. On the other hand the HOMO-LUMO separation of disilene is larger than that of digermene and distannene (Tables III-V), making its orbital mixing more difficult. The fact that digermene and distannene are more trans-bent than disilene[26] indicates that the HOMO-LUMO separation differences prevail.

Our conclusion that the geometries of disilene, digermene, and distannene depend on the electronegativity of their substituents is tested with silyl as substituent. It is chosen because it is less electronegative than hydrogen[27] and thus may restore the planarity of these double bonds. Table VII shows that it is indeed the case. The calculated Si=Si and Si—Si bond lengths (2.16, 2.37 Å) agree very well with representative experimental values (2.14-2.16, 2.35-2.37 Å).[6,28] The Ge=Ge bond is 0.07 Å shorter than that in trans-bent configuration, in agreement with other calculations,[16] while the Sn=Sn bond is considerably shorter than that in bent geometry.

Finally, it should be noted that the planar Si=Si double bond commonly observed for large substituents probably arise from steric repulsion in the trans-bent geometry.[2] But in $Si_2(SiH_3)_4$, such repulsion does not exist since the shortest distance between two hydrogens of different silyl groups is 3.35 Å when the folding angle is 15° and the SiSiSi angle is 112°. For digermene and distannene no planar structures are known.

Conclusions

By using the nuclear charge as a perturbation in ab initio calculations, we have shown that the geometries of X=X (X = C, Si, Ge and Sn) double bonds are determined by both their intrinsic π-σ^* separation and substituent electronegativity. In the case of ethylene, the π-σ^* separation is so large that no substituent can trans-bend the C=C bond. On the other hand, disilene, digermene, and distannene have such small π-σ^* separations that substituent electronegativity determines their double-bond configuration. Thus, we predict that while their parent molecules are trans-bent, their silyl-substituted species will be planar. Calculations reported here support this prediction.

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Registry No. Digermene, 82323-93-1; distannene, 86041-63-6; ethylene, 74-85-1; disilene, 15435-77-5; tetrafluoroethylene, 116-14-3.

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