

Conformational Preferences in Methylsilane and Disilane. A Quantitative Non-Empirical Analysis of the Importance of the Hyperconjugative Interactions

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We have investigated the importance of the hyperconjugative interactions in determining the conformational preferences in methylsilane and disilane, and for comparative purposes also in ethane, using a procedure that provides quantitative information about the energy effects associated with orbital interactions. It is found that (1) these interactions are in all cases destabilizing and less destabilizing in the staggered conformation and that (2) in the absence of these interactions, in ethane the staggered conformer is still more stable, while in methylsilane and disilane the eclipsed conformer becomes more stable.

We have also investigated the effects of each type of orbital interaction in terms of a quantitative perturbational analysis.

Key words: Methylsilane – Disilane – Conformational preferences – Hyperconjugative interactions

1. Introduction

Wolfe *et al.* [1] have recently suggested a computational procedure that provides quantitative estimates, in the framework of SCF computations, of the energy effects associated with given orbital interactions. This procedure has been found to be particularly useful for analysing the effects of the interactions between π orbitals and in such cases we have suggested its implementation with the computation of the total energy of the system in the absence of the orbital interactions under examination [2]. In this way the effects of the orbital interactions can be discussed in terms of total energy differences, and therefore at a more accurate level than that used by Wolfe *et al.* [1] based on second order energy terms. In our approach the

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second order energy expressions are just used to provide information about the trends of the energy effects associated with each type of π interaction under examination.

In the present paper we report the results obtained in an application of such a computational procedure to investigate, at the *ab initio* SCF-MO level, the importance of the hyperconjugative interactions in determining the greater stability of the staggered conformation, relative to the eclipsed, of molecules of the H_3X-YH_3 type.

2. Computational Results

The molecules investigated in the present paper are methylsilane and disilane and, for comparative purpose, ethane. All SCF computations have been carried out with the Gaussian 70 series of programs [3] using in all cases an STO-3G basis set [4] with the exponents of the valence shells orbitals optimized in the various molecules [4]. It has, in fact, been found that the use of such an optimized STO-3G basis set provides, in the average, for these molecules, more accurate geometries and rotational barriers than those obtained with a standard STO-3G basis set [5]. Furthermore, all computations have been carried out at the corresponding fully optimized geometries [5].

Table 1. Total energies (a.u.) of the staggered and eclipsed conformations of ethane, methylsilane and disilane computed at the optimized geometries^a using an optimized STO-3G basis set, with (E_T) and without (E_T^0) π conjugation between the two interacting fragments

	Staggered	Eclipsed	Rotational barrier ^b	
			A^c	B^d
Ethane				
E_T	-78.31273	-78.30751	3.276	2.928
E_T^0	-78.36986	-78.36944	0.264	
$(E_T - E_T^0)^e$	35.849	38.861	3.012	
Methylsilane				
E_T	-326.56611	-326.56381	1.443	1.665
E_T^0	-326.58429	-326.58507	-0.489	
$(E_T - E_T^0)^e$	11.408	13.340	1.932	
Disilane				
E_T	-574.81144	-574.81005	0.872	~1.
E_T^0	-574.81690	-574.81712	-0.138	
$(E_T - E_T^0)^e$	3.426	4.436	1.010	

^a Values taken from Ref. [5] [Staggered (eclipsed) ethane: $r(C-C) = 1.5173 \text{ \AA}$ (1.5280 \AA), $r(C-H) = 1.0941 \text{ \AA}$ (1.0933 \AA), $HCH = 107.9^\circ$ (107.4 $^\circ$); staggered (eclipsed) methylsilane: $r(C-Si) = 1.8479 \text{ \AA}$ (1.8546 \AA), $r(Si-H) = 1.4869 \text{ \AA}$ (1.4871 \AA), $r(C-H) = 1.0973 \text{ \AA}$ (1.0968 \AA), $HCH = 107.7^\circ$ (107.5 $^\circ$), $HSiH = 107.7^\circ$ (107.4 $^\circ$); staggered (eclipsed) disilane: $r(Si-Si) = 2.272 \text{ \AA}$ (2.2775 \AA), $r(Si-H) = 1.494 \text{ \AA}$ (1.494 \AA), $HSiH = 107.5^\circ$ (107.5 $^\circ$)].

^b Rotational barrier = $E(\text{eclipsed}) - E(\text{staggered})$; values in kcal/mol.

^c Computed values.

^d Experimental values. See Ref. [6].

^e Values in kcal/mol.

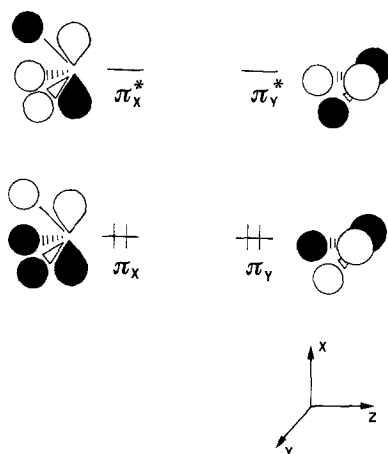


Fig. 1. Occupied and vacant π MO's of the $-\text{XH}_3$ fragment

The total energies computed with and without π orbital interactions for the staggered and eclipsed conformations of ethane, methylsilane and disilane, together with the corresponding rotational barriers, are listed in Table 1.

3. Quantitative Orbital Analysis

The π orbital interactions occurring in methylsilane between the $\text{H}_3\text{C}-$ and the $-\text{SiH}_3$ fragments and in disilane between the two $-\text{SiH}_3$ fragments are similar to those occurring in ethane between the two $-\text{CH}_3$ groups. Each $-\text{XH}_3$ fragment, in fact, has a degenerate pair of doubly occupied π MO's and a degenerate pair of vacant π MO's (see Fig. 1). The corresponding interaction diagrams are shown in Fig. 2.

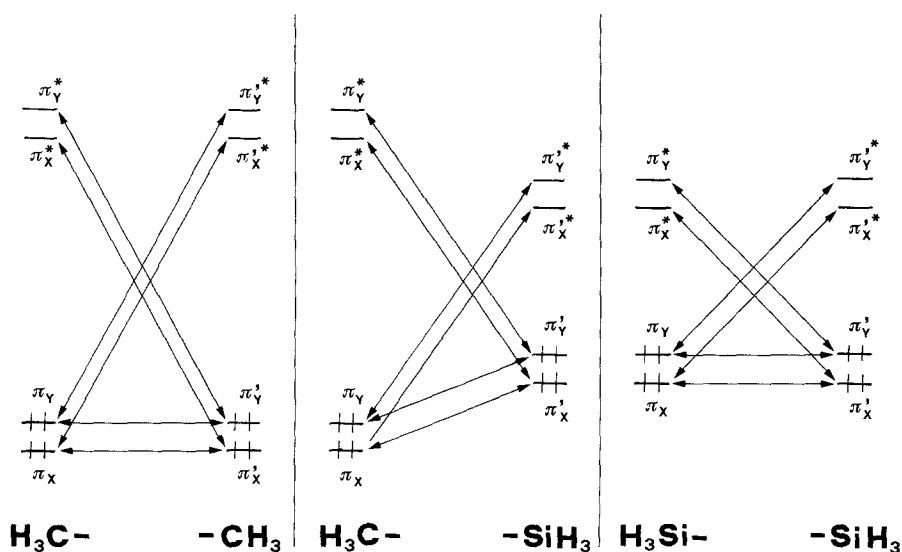


Fig. 2. Interactions diagrams for ethane, methylsilane and disilane

The π orbital interactions in ethane have already been discussed in the literature [7, 8]. In this case a qualitative analysis of the various stabilizing orbital interactions leads to the conclusion that the key orbital interactions controlling the conformational preference are those between the doubly occupied π MO's of one fragment and the empty π MO's of the other fragment. These interactions favor a preferential stabilization of the staggered geometry relative to the eclipsed because the non-bonded interactions between the hydrogen atoms favor the staggered geometry.

Wolfe *et al.* have already shown, using their quantitative approach, that these interactions actually operate in this way, but equally important are the destabilizing interactions between the doubly occupied MO's [1].

In the present paper we extend such type of quantitative orbital analysis to methylsilane and disilane. As already pointed out, in our approach we compute an estimate of the total energy of the system in the absence of the π interactions under examination, that allows us to assess the overall energy effect associated with the π orbital interactions under examination in terms of total energy differences. For comparative purposes, such procedure has been applied also to ethane.

We discuss first the various information provided by these energy values in the various cases. The values of the total energy computed in the absence of the π orbital interactions occurring between the two interacting fragments (E_T^0) are listed in Table 1 together with the energy differences ($E_T - E_T^0$), where E_T denotes the total energy of the system computed in the SCF computation.

The analysis of these results provide the following information:

- 1) in all cases the most stable conformer is found to be the staggered, in agreement with experimental evidence. Also the trend that the rotational barrier decreases with the replacement of a CH_3 group with a SiH_3 group is accurately reproduced at the computational level used in this paper;
- 2) the E_T^0 values are in all cases smaller than the corresponding E_T values. This means that in all cases investigated the overall energy effect associated with the π interactions occurring between the two $-\text{XH}_3$ fragments is destabilizing;
- 3) such a destabilization (compare the $(E_T - E_T^0)$ values in Table 1) is large in ethane and decreases going to methylsilane and to disilane. In all cases the overall energy effect is less destabilizing in the staggered conformation;
- 4) the rotational barrier in the absence of the π interactions is found to be very small in all cases. Furthermore, in the absence of the π interactions, the most stable conformer remains the staggered in ethane but becomes the eclipsed in methylsilane and disilane.

Details about the effect associated with each type of π interaction can be obtained in terms of the following second-order equations derived in the framework of OEMO theory [8]:

- a) the interaction of a doubly occupied MO, φ_i , with a vacant MO, φ_j , leads to a two-electron stabilization given by the following expression:

$$\Delta E_{ij}^2 = 2(H_{ij} - S_{ij}\epsilon_i)^2/(\epsilon_i - \epsilon_j) \quad (1)$$

where ϵ_i and ϵ_j are the energies of the two unperturbed MO's φ_i and φ_j , S_{ij} their overlap integral and H_{ij} their matrix element;

- b) the interaction of two doubly occupied MO's, φ_i and φ_j , leads to net four-electron destabilization given by the following expression:

$$\Delta E_{ij}^4 = 4(\epsilon_0 S_{ij}^2 - H_{ij} S_{ij})/(1 - S_{ij}^2) \quad (2)$$

where ϵ_0 is the mean of the energies of the φ_i and φ_j MO's before mixing.

Using the OEMO expressions (1) and (2) and the values of the matrix elements, overlap integrals and orbital energies computed with the procedure described before, we have obtained estimates of the two-electron stabilizations ΔE_{ij}^2 and four-electron destabilizations ΔE_{ij}^4 associated with the various interactions. The relevant data are listed in Table 2. For comparative purposes, we have carried out the quantitative analysis also for ethane, even if similar values were already reported by Wolfe *et al.* [1]. The latter values differ from those listed in Table 2 for ethane because those reported by Wolfe *et al.* were computed using a standard basis set, while those listed in Table 2 have been computed with an optimized basis set. The two sets of values are very similar and therefore also the corresponding

Table 2. Orbital energies (ϵ_i), matrix elements (H_{ij}), overlap integrals (S_{ij}), stabilization (ΔE_{ij}^2) and destabilization (ΔE_{ij}^4) energies computed at the optimized STO-3G level for the staggered and eclipsed conformations of ethane, methylsilane and disilane

	Ethane		Methylsilane		Disilane	
	Staggered	Eclipsed	Staggered	Eclipsed	Staggered	Eclipsed
ϵ_π	-0.5311	-0.5295	-0.5448	-0.5442	-0.4782	-0.4778
ϵ_π^*	0.6612	0.6625	0.6444	0.6451	0.4044	0.4051
$\epsilon_{\pi'}$	-0.5311	-0.5295	-0.4683	-0.4675	-0.4782	-0.4778
$\epsilon_{\pi'^*}$	0.6612	0.6625	0.4415	0.4415	0.4044	0.4051
$H_{\pi\pi'}$	-0.1186	-0.1203	-0.0691	-0.0720	-0.0404	-0.0430
$H_{\pi\pi'^*}$	-0.0709	-0.0602	-0.0919	-0.0856	-0.0463	-0.0418
$H_{\pi'\pi'^*}$	-0.0709	-0.0602	-0.0324	-0.0245	-0.0463	-0.0418
$S_{\pi\pi'}$	0.1157	0.1194	0.0742	0.0784	0.0482	0.0520
$S_{\pi\pi'^*}$	0.0691	0.0552	0.1062	0.0982	0.0632	0.0567
$S_{\pi'\pi'^*}$	0.0691	0.0552	0.0383	0.0266	0.0632	0.0567
$\Delta E_{\pi\pi'}^2$	-1.23	-1.01	-1.47	-1.32	-0.37	-0.31
$\Delta E_{\pi'\pi'^*}^2$	-1.23	-1.01	-0.24	-0.17	-0.37	-0.31
$\Delta E_{\pi\pi'}^4$	16.82	17.34	5.90	6.40	2.11	2.38
$\Delta E_{\pi\pi'}^2$	28.72	30.64	8.38	9.82	2.74	3.52
Δ^b		1.92		1.44		0.78

^a $\Delta E_T = 2(\Delta E_{\pi\pi'}^2 + \Delta E_{\pi'\pi'^*}^2 + \Delta E_{\pi\pi'}^4)$.

^b $\Delta = \Delta E_T(\text{eclipsed}) - \Delta E_T(\text{staggered})$.

values of ΔE^2 and ΔE^4 are very similar, as well as the conclusions based on these values.

The points of interest are:

- 1) the energy effects described by the expressions (1) and (2) provide the larger contribution of the overall energy effect associated with these interactions, as it can be inferred from the comparison of the ΔE_T values in Table 2 with the $(E_T - E_T^0)$ values in Table 1. It is also important to point out that in all cases the trends of the ΔE_T values parallel those of the $(E_T - E_T^0)$ values;
- 2) in all cases the two-electron interactions are more stabilizing and the four-electron interactions less destabilizing in the staggered conformer;
- 3) the four-electron destabilization ΔE_{ij}^4 decreases along the series ethane, methylsilane, disilane because along this series both the ϵ_0 values and the matrix elements $H_{\pi\pi'}$ decrease;
- 4) in all cases the trend of the two-electron stabilization ΔE_{ij}^2 is matrix element controlled (i.e. the larger the absolute value of the matrix element the larger the stabilization energy). Therefore the energy effect associated with the stabilizing interaction $\pi - \pi'^*$ follows the trend:

$$-\Delta E^2(\text{Methylsilane}) > -\Delta E^2(\text{Ethane}) > -\Delta E^2(\text{Disilane})$$

while that associated with the stabilizing interaction $\pi' - \pi^*$ follows the trend:

$$-\Delta E^2(\text{Ethane}) > -\Delta E^2(\text{Disilane}) > -\Delta E^2(\text{Methylsilane})$$

- 5) in all cases the trend of the overlap integrals parallels that of the corresponding matrix elements. Therefore the trends of the various energy expressions can be pictorially rationalized in terms of overlap variations.

The present results provide also a rationalization of the decrease of the rotational barrier along the series ethane, methylsilane and disilane. This trend is caused by the fact that along this series the overlap between the hydrogens of the two interacting fragments decreases as a consequence of the lengthening of the X—Y bond. Consequently along this series the conformational preference of the non-bonded interactions between the hydrogen atoms becomes less pronounced and therefore the relative stabilization of the staggered conformation is reduced.

It is also interesting to point out that the rotational barriers computed on the basis of the second order expressions (1) and (2) are 1.94, 1.44 and 0.78 kcal/mole in ethane, methylsilane and disilane respectively, while the corresponding values in terms of total energies are 3.01, 1.93 and 1.01 kcal/mole. Therefore the trend of the rotational barriers computed in terms of second order energy effects is correct. However this result seems to suggest also that higher order energy contributions are significant for determining the correct order of magnitude of the rotational barrier in ethane, but much less so in methylsilane and particularly disilane.

References

1. Whangbo, M. H., Schlegel, H. B., Wolfe, S.: *J. Am. Chem. Soc.* **99**, 1296 (1977)
2. Bernardi, F., Bottoni, A., Epiotis, N. D., Guerra, M.: *J. Am. Chem. Soc.* **100**, 6018 (1978)
3. Hehre, W. J., Lathan, W. A., Ditchfield, R., Newton, M. D., Pople, J. A.: Gaussian 70, Quantum Chemistry Program Exchange No. 236, Indiana University, Bloomington, Indiana
4. Hehre, W. J., Stewart, R. F., Pople, J. A.: *J. Chem. Phys.* **51**, 2657 (1969)
5. Bernardi, F., Bottoni, A., Tonachini, G.: to be published
6. a) ethane: Weiss, S., Leroi, G. E.: *J. Chem. Phys.* **48**, 962 (1968); b) methylsilane: Herschbach, D. R.: *J. Chem. Phys.* **31**, 91 (1959); c) disilane: Cox, A. P., Varma, R.: *J. Chem. Phys.* **46**, 2007 (1967)
7. Hoffmann, R.: *J. Chem. Phys.* **43**, 1397 (1963); Lowe, J. P.: *J. Am. Chem. Soc.* **92**, 3799 (1970); Lowe, J. P.: *Science* **179**, 527 (1973)
8. Epiotis, N. D., Cherry, W., Shaik, S., Yates, R. L., Bernardi, F.: *Topics Curr. Chem.* **70** (1977)

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