Does a Concerted Path Exist for the Head-to-Tail [$2\pi_s$ + $2\pi_s$] Cycloaddition of Silaethylene?

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The polarization of the double bond in the reactants is often supposed[1] to lead to a relaxation of the Woodward–Hoffman rules[2] which predict that [$2\pi_s + 2\pi_s$] cycloadditions are forbidden and occur via a multistep diradical mechanism. This relaxation of the usual rule has been recently suggested[3] for the head-to-tail [$2\pi_s + 2\pi_s$] cycloaddition of two silaethylene molecules where a concerted reaction pathway involving a "rhomboid" transition state with C_{2h} symmetry (see Figure 1b, parameters[3] in brackets) has been found at the SCF, CISD, and CCSD levels of theory using a double-ζ basis set augmented with d-type polarization functions on C and Si (DZ+d). In this communication we report CAS-SCF results which show that this reaction occurs via a multistep pathway similar to that found in a CAS-SCF/4-31G study of the cycloaddition of two ethylene molecules.[4] The CAS-SCF computations have been performed at the 3-21G* and DZ+d[6] levels using an active space of four orbitals and four electrons, in which one can represent the weakly avoided crossing region of this "forbidden" reaction correctly.

The CAS-SCF computations demonstrate that the C_{2h} rhomboid transition structure for the silaethylene dimerization shown in Figure 1b is not a special feature that arises because of the polar nature of the reactants of the reaction studied but rather is an artifact of the fact that CCSD with SCF orbitals cannot represent the very weakly avoided crossing region of the potential energy surface of this forbidden reaction correctly. (In fact, similar structure also exists for the ethylene + ethylene cycloaddition at the SCF/4-31G level.) The C_{2h} optimized CAS-SCF/3-21G* geometries are shown in Figure 1 together with a schematic cross section of the surface. A quasirectangular C_{2h} "supra–supra" structure (Figure 1a) was found to have two imaginary frequencies. (The extra negative direction of curvature points to a cisoid structure shown in Figure 2d.) As we have demonstrated previously, the C_{2h} rhomboid structure for the ethylene dimerization problem[7] can be shown to lie in the region of a singularity on the ground-state potential energy surface corresponding to a conical intersection[8] (i.e., a real crossing) between the ground and (π–π^*) doubly excited state. Remarkably, using the method reported in ref 9, a similar result is obtained for the silaethylene dimerization, and the C_{2h} CAS-SCF geometries for the two possible lowest energy points on the conical intersection are given in Figures 1b and 1c. Thus, for both reactions the only well-defined topological features of the ground-state potential energy surface with C_{2h} rhomboid structures are

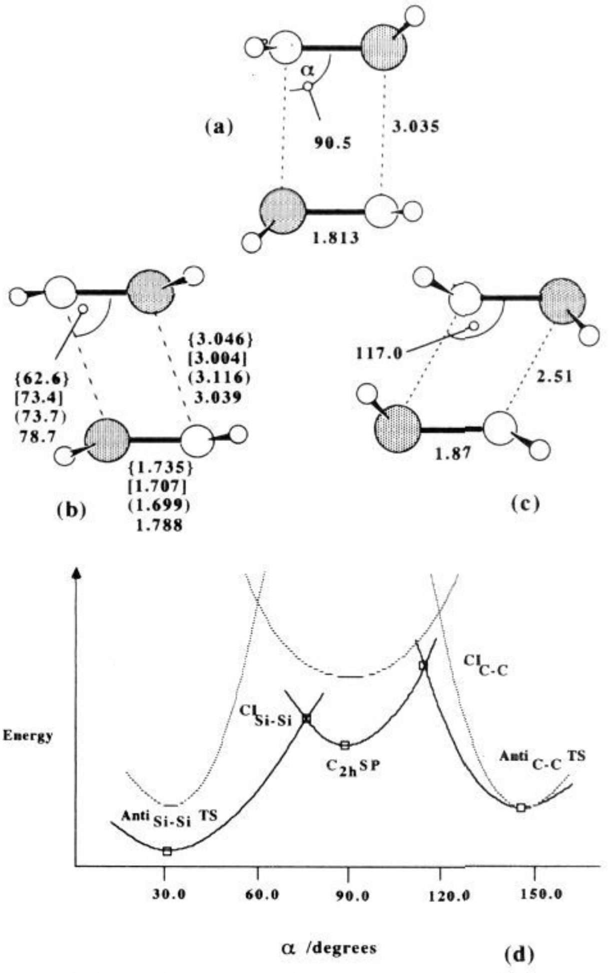

Figure 1. C_{2h} optimized geometries for the head-to-tail dimerization reaction of silaethylene (bond lengths are in angstroms and bond angles in degrees). (a) The $2\pi_s + 2\pi_s$ saddle point C_{2h}SP (CAS-SCF/3-21G*, two imaginary frequencies in full space). (b) Si–Si "rhomboid" structure (CI_{Si-Si}), which is a conical intersection at the CAS-SCF/3-21G* level and a transition state at SCF/3-21G* (parameters in brackets), at SCF/DZ+d (parameters[3] in square brackets), and at CCSD/DZ+d (parameters[3] in curly brackets) levels. (c) C–C "rhomboid" structure (CI_{C-C}), which is a conical intersection at the CAS-SCF/3-21G* level. (d) Schematic C_{2h} cross section of the potential energy surface for the dimerization of silaethylene along angle α (the corresponding cross section for the ethylene dimerization[7] is shown as a dashed line). The points labeled $Anti_{Si-Si}$ and $Anti_{C-C}$ correspond to the transition states leading to the head-to-head C_{2h} diradical structures found in ref 3.

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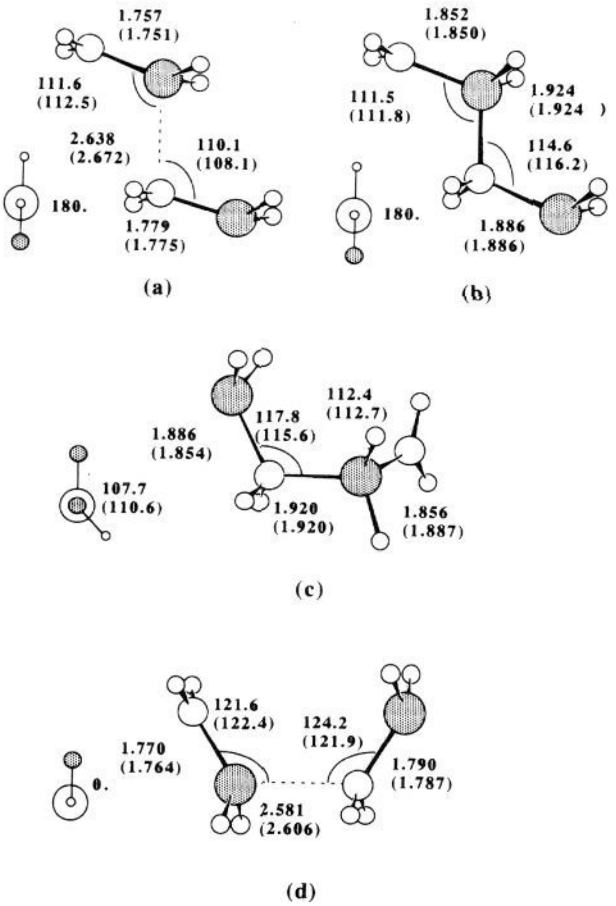

Figure 2. CAS-SCF/DZ+d and CAS-SCF/3-21G* (values in brackets) relevant geometrical parameters of the critical points found on the potential energy surface for the head-to-tail dimerization of silaethylene (bond lengths in angstroms and angles in degrees). (a) Anti transition state. (b) Anti minimum. (c) Gauche minimum. (d) Cis saddle point (two imaginary frequencies).

the conical intersections. Conventional CAS-SCF geometry optimization under C_{2h} symmetry constraint beginning in the region of C_{2h} rhomboid structures *collapses* to the C_{2h} anti diradicaloid transition structure indicated in Figure 1d or the "supra–supra" structure with two imaginary frequencies shown in Figure 1a.

The only chemically relevant pathway for silaethylene dimerization at the CAS-SCF level of theory corresponds to an anti attack leading to an anti diradical intermediate. The optimized geometries of an anti transition state (anti TS) and an anti intermediate (anti M) obtained with 3-21G* and DZ+d basis sets are shown in Figures 2a and 2b. The intermediate can proceed to the ring-closure product via a gauche diradical intermediate (gauche M) shown in Figure 2c. There is no transition state for the formation of the gauche minimum. Rather, the only other critical point is a loose cisoid structure (Figure 2d) which has two imaginary frequencies. One of these corresponds to a rotation about the forming C–Si bond and the other to C–Si bond formation. (The frequencies were computed analytically at the 3-21G* level and checked numerically at the DZ+d level for the ani transition state.) Thus the gauche intermediate can be formed only by conformational isomerization from the anti intermediate (i.e., a slice through the potential energy surface along the rotational angle connecting the cisoid structure and the anti transition state has a minimum at the latter and a maximum at the former with a point of inflection at the position of a hypothetical gauche structure). The energetics are collected in Table I and show that the CAS-SCF energy of the rhomboid structure (C_{2h}) at the DZ+d (SCF geometry) lies some 8 kcal/mol above the energy of the anti transition state. The geometrical parameters found at the 3-21G* and DZ+d levels are similar.

Table I. Total (E_t) and Relative Energies (ΔE_t and $\Delta E_t'$) Computed with the DZ+d and the 3-21G* (values in parenthesis) Basis Set at the CAS-SCF Level for the Head-to-Tail Dimerization Reaction of Silaethylene

	E_t (au)	ΔE_t (kcal/mol)	$\Delta E_t'$ (kcal/mol)
anti M	–658.175 88	–18.92	0.00
	(–654.874 09)	(–23.22)	(0.00)
anti TS	–658.137 30	5.29	24.21
	(–654.832 55)	(2.84)	(26.06)
gauche M	–658.174 46	–18.02	0.90
	(–654.872 69)	(–22.34)	(0.88)
cis SP[a]	–658.131 57	8.89	27.81
	(–654.826 78)	(6.46)	(29.69)
C_{2h} TS[b]	–658.125 60	12.64	31.56
	(–654.823 09)	(8.78)	(32.00)
C_{2h} SP[a]	(654.797 56)	(24.80)	(48.02)
CI_{Si-Si}[c]	(–654.780 16[d])	(35.72)	(58.94)
CI_{C-C}[c]	(–654.739 53[d])	(61.5)	(84.7)
$anti_{Si-Si}$ TS	(654.835 50)	(0.99)	(24.22)
$anti_{C-C}$ TS	(–654.819 68)	(10.92)	(34.14)
reactants	–658.145 74	0.00	–18.92
	(–654.837 08)	(0.00)	(–23.22)

[a] Saddle point of index 2. [b] "Rhomboid" structure optimized at the SCF level. [c] Conical intersection point (see Figure 1). [d] CAS-SCF with state-averaged orbitals.

Thus, in contrast to the CCSD results, the CAS-SCF results support the existence of stepwise reaction pathways involving anti and gauche diradical intermediates and leading to formation of 1,3-disilacyclobutane. Furthermore, the potential energy surfaces for the dimerization of silaethylene and ethylene have very similar topologies. However, the silaethylene diradical intermediates are much lower in energy (relative to the reactants) and the activation energy for the dimerization is much smaller. In the ethylene dimerization reaction the activation energy is 51.3 kcal/mol and the fragmentation barrier is 0.4 kcal/mol at the 4-31G level.[4a] In the case of silaethylene the situation is almost opposite since the corresponding values at the DZ+d level are 5.3 and 26.1 kcal/mol, respectively (2.8 and 24.2 kcal/mol with the 3-21G* basis set). The activation energy for the dimerization of silaethylene is in good agreement with the experimental finding that this process occurs quite readily.[1] There is no experimental data supporting a stepwise mechanism for the silaethylene reaction. However, the ethylene reaction is known to be stepwise,[10] and in view of the similarities in the potential surface topology one can conclude that the mechanistic aspects of both reactions are similar.

In conclusion, the polarization of the double bond in silaethylene does not appear to alter the topology of the potential energy surface for [$2\pi_s + 2\pi_s$] cycloadditions established for ethylene dimerization,[7] and the reaction seems to occur via a multistep diradical mechanism.

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