

rise to energy surfaces approaching each other and dipole surfaces going away from each other, in a similar manner as in one-end pyramidalized ethylene ( $\varphi = 40^\circ$ ) [5]. Maximum polarization is reached at  $\vartheta = 75^\circ$ . The spp parameter and  $\Delta E$  in propylene for  $\vartheta = 75^\circ$  are: spp = 0.15 D/deg,  $\Delta E = 28.6$  kcal/mol.

In butadiene the  $S_2$  and  $S_3$  states [6] develop their polar character more and more upon geometrical relaxation and reach their maximum  $\mu_z$  value at  $\vartheta = 90^\circ$  where energy surfaces reach their minimum. At this point we have: spp = 0.19 D/deg and  $\Delta E = 17$  kcal/mol. If variational energy  $E_v$  is considered [6] the energy gap between polar states and the spp parameter at  $\vartheta = 90^\circ$  are: spp = 0.25 D/deg and  $\Delta E = 14.6$  kcal/mol.

Collecting and ordering we have (spp in D/deg and  $\Delta E$  in kcal/mole):

ethylene ( $80^\circ, 10^\circ$ ):	spp = 1.4 ,	$\Delta E = 2.0$ ,
ethylene ( $80^\circ, 20^\circ$ ):	spp = 0.30 ,	$\Delta E = 5.6$ ,
butadiene ( $90^\circ$ ), <sub>v</sub> :	spp = 0.25 ,	$\Delta E_v = 14.6$ ,
butadiene ( $90^\circ$ ):	spp = 0.19 ,	$\Delta E = 17.0$ ,
ethylene ( $80^\circ, 40^\circ$ ):	spp = 0.16 ,	$\Delta E = 22.6$ ,
propylene ( $75^\circ$ ):	spp = 0.15 ,	$\Delta E = 28.6$ .

That is, (a) as  $\Delta E$  between zwitterionic states grows, spp decreases, (b) except in ethylene ( $80^\circ, 10^\circ$ ) polarization develops gradually and (c) maximum polarization is reached near or at the end of geometrical relaxation.

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## THE STRUCTURE OF THE SINGLET TETRAMETHYLENE DIRADICAL INTERMEDIATE

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Ab initio MC SCF geometry optimizations of the gauche and trans conformers of the singlet tetramethylene diradical have been carried out using MC SCF gradients with a minimal (STO-3G) and extended (4-31G) basis set. At both computational levels, it has been found that the tetramethylene diradical exists as a stable species in two different conformations, a gauche and a trans.

In this communication we report the results of ab initio MC SCF calculations on the structure of the tetramethylene diradical. The tetramethylene diradical is invoked as an intermediate in the pyrolysis of cyclobutanes to ethylenes [1]. Though this diradical has never been directly observed, the indirect evidence for its existence is impressive [1,2].

Useful information about the nature and structural properties of transient species can be obtained from ab initio calculations. However, the previous ab initio studies of the structure of the tetramethylene diradical have provided contradictory results. In particular, Segal [3] has found, with an SCF treatment at the minimal STO-3G [4] level followed by a 15-dimensional configuration interaction, two stable conformers of the tetramethylene diradical, corresponding to a

gauche and trans conformation. On the other hand, Doubleday et al. [5], with a two-configuration MC SCF wavefunction at the extended 3-21G level [6], have found that only the trans conformer is a minimum. Recently, Doubleday et al. [7] have extended these calculations with 20-configuration MC SCF computations. They find that the gauche conformer cyclizes and the trans fragments with no potential-energy barrier. Further, they find *no minima* in the biradical region of singlet tetramethylene.

To obtain information on the structure of this radical at a more accurate computational level, we have performed MC SCF geometry optimizations of the gauche and trans conformers of the tetramethylene diradical using a minimal (STO-3G) and extended (4-31G) [8] basis set. In the present study we have selected for the valence space [9] the four  $\pi$  MOs associated with the two interacting ethylenes (two  $\pi$  and two  $\pi^*$  MOs). With this valence space the com-

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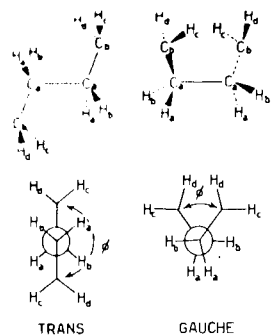


Fig. 1. Trans and gauche conformations of tetramethylene diradical intermediate.

plete CI has 20 configurations.

At both STO-3G and 4-31G levels, the geometry has been optimized in the complete space of internal coordinates using an MC SCF gradient procedure [10]. At both computational levels we have found a critical point for both the gauche and the trans conformer; the two conformers are shown in fig. 1. The computed geometrical parameters are shown in table 1 together

Table 1  
Geometrical parameters<sup>a)</sup> and total energies (au) of the gauche and trans tetramethylene minima

	Trans		Gauche	
	STO-3G	4-31G	STO-3G	4-31G
$r(C_a C_a)$	1.6072	1.6535	1.6058	1.6320
$r(C_a C_b)$	1.5070	1.4729	1.5092	1.4800
$r(C_a H_a)$	1.0880	1.0817	1.0885	1.0836
$r(C_a H_b)$	1.0880	1.0817	1.0882	1.0825
$r(C_b H_c)$	1.0835	1.0735	1.0829	1.0729
$r(C_b H_d)$	1.0835	1.0735	1.0827	1.0725
$\angle H_a C_a C_b$	110.41	111.71	109.58	110.28
$\angle H_b C_a C_b$	110.41	111.71	110.41	111.59
$\angle H_a C_a H_b$	108.70	108.38	107.80	107.77
$\angle H_c C_b C_a$	117.78	120.08	117.90	120.07
$\angle H_d C_b C_a$	117.78	120.08	118.51	120.76
$\angle H_a C_b H_c$	115.13	116.49	115.49	116.96
$\angle C_b C_a C_a$	111.90	111.88	113.96	114.14
$\phi$	180.00	180.00	71.12	75.40
$E_T$	-154.191957	-155.824393	-154.189480	-155.821312

<sup>a)</sup> Distances in Å and angles in deg.

with the related total energies.

The results at the two computational levels are very similar. In particular, the geometrical parameters show only minor differences and also the relative stability of the two minima is almost the same. At both levels, in fact, the trans minimum is found to be slightly more stable and the stabilization energy is 1.6 kcal/mol at STO-3G level and 1.9 kcal/mol at the 4-31G level. In further calculations (to be reported in more detail later) we have also been able to locate transition states for fragmentation from both the gauche and trans minima. However, in each case, the computed barriers to fragmentation are less than 1 kcal/mol and the optimized values of  $r(C_a C_a)$  are only about 0.1 Å longer than for the minima (at the 4-31G level).

It is apparent that our conclusion that the singlet tetramethylene diradical exists as a stable species in two different conformations depends upon the second-derivative matrix having all positive eigenvalues for both trans and gauche structures. In our (STO-3G) calculations, we have computed the second-derivative matrix by finite difference in the subspace consisting of  $r(C_a C_a)$ ,  $r(C_a C_b)$ ,  $\angle C_a C_b C_a$  and  $\phi$  (i.e. excluding the coordinates associated with the methylene groups). This computed second-derivative matrix was then updated numerically during the 4-31G geometry opti-

mizations. Diagonalization of this updated second-derivative matrix showed all positive eigenvalues for both conformers. As a final check, some second derivatives were recomputed numerically (4-31G). In the case of the gauche conformer, the same subspace of internal coordinates was used. For the trans, only the second derivative for  $r(C_a C_a)$  was recomputed.

The results of the numerical second-derivative computation, together with the fact that we have been able to locate transition states for fragmentation at both levels of computation confirm the previous results of Segal that the singlet tetramethylene diradical exists as a stable species in two different conformations.

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