

Figure 1. Absorption and corrected emission spectra of 1-[2-chlorophenyl]ethyl 9-anthroate (2): (1) Emission spectrum of chiral crystalline powder at 77 K, (2) emission spectrum of the racemic compound at 77 K, absorption (3) (300 K) and emission (4) (77 K) in ethanol (c 5×10^{-3} ; ϵ_{\max} 8×10^{-3} mol/l.).

the chiral enantiomer has a typical γ -type monomer emission, as demonstrated in Figure 1 for the 2-Cl derivative **2**, which indicates the validity of the suggested model.¹¹

We are also extending the method to additional systems and trying to engineer photodimerizable handles which will increase the probability of the racemic compounds crystallizing in α -type structures.

Beside the practical use of this approach for enantiomeric purification, this reaction might be of significance as a mode for possible routes for the amplification of optical activity under prebiotic conditions.¹²

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- This method may also be applicable to the rare chiral crystal that contains parallel pairs, the two molecules of which are not related to each other by crystallographic symmetry. This enantiomer yields dimers *RR* or *SS* which can be separated from the reaction mixture provided either the racemate is light-stable or it forms the meso dimer. The method is not applicable to systems for which the racemate undergoes spontaneous resolution, to systems where the two enantiomers form continuous solid solutions, such as in the case of the *sec*-butyl substituted molecules (see ref 2c and also M. Lahav, L. Leiserowitz, and L. Reitman, to be submitted for publication), or to systems where both the racemate compound and the enantiomer crystallize in the light-stable γ form.
- All new compounds have correct CH analyses as well as the expected NMR and mass spectra.
- E. Heller and G. M. J. Schmidt, *Isr. J. Chem.*, **9**, 449 (1971); M. D. Cohen, Z. Ludmer, J. M. Thomas, and J. O. Williams, *Proc. R. Soc. London*, **324**, 459 (1971); J. M. Thomas, *Philos. Trans. R. Soc., London*, **277**, 251-286 (1974), and references therein.
- In some examples anthracenes undergo nontopochemical reactions. This occurs more generally in structural defects. However these reactions are generally slow compared to the usual topochemical controlled reactions; see, for example: P. J. Desvergne, J. M. Thomas, J. O. Williams, and H. Boas-Laurent, *J. Chem. Soc., Perkin Trans. 2*, 363 (1974), and ref 6 and 8.
- M. D. Cohen, Z. Ludmer, and V. Yakhot, *Phys. Status Solidi B*, **67**, 51 (1975).
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- Whereas the irradiation of the racemic compounds of **2** and **3** yield cleanly the head-to-tail *meso*-dianthracenes, some racemic dimer could be isolated from the reaction mixture of the racemic compound **1**. The head-to-tail structures of the solid-state photodimer were established by reduction with LiAlH_4 to the centrosymmetric 9,9'-dihydroxy-methylenedianthracene (**4**).⁶ Its meso stereochemistry follows from the

observation that it differs from the racemic head-to-tail dimers (TLC, ir), independently synthesized by photodimerization of the chiral anthracenes **1**, **2**, and **3** in benzene solutions. The reduction of these dimers with LiAlH_4 also yields **4**.

- An analytical method for the determination of optical purity based on this difference of the fluorescence properties is presently being developed.
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The Ground Electronic State of Silaethylene. An Ab Initio Molecular Orbital Study of the Lower Electronic Manifold

Sir:

In the photochemical and thermal decompositions of silicon hydrides and alkylated silicon hydrides, the intervention of a variety of silicon free radicals and reactive intermediates has been demonstrated, largely on kinetic grounds.^{1a-d} In some instances a preference for the formation of a silaethylene structure, $\text{C}=\text{Si}$, has been shown to exist;^{1e-l} a clearly demonstrated case is the disproportionation reactions of silyl free radicals.² The value of the disproportionation to recombination rate constant of 0.046 obtained for the trimethylsilyl radical, for example, requires a rate increase in the order of 10^5 for the hydrogen-transfer reaction, $2(\text{CH}_3)_3\text{Si} \rightarrow (\text{CH}_3)_3\text{SiH} + (\text{CH}_3)_2\text{Si}=\text{CH}_2$, as compared with the case of the absence of a free spin on the silicon atom, such as in tetramethylsilane: $(\text{CH}_3)_3\text{Si} + (\text{CH}_3)_4\text{Si} \rightarrow (\text{CH}_3)_3\text{SiH} + \text{CH}_2\text{Si}(\text{CH}_3)_3$. This assistance must arise from the formation of either a singlet-state olefinic π -bond or a triplet-state 1,2-diradical in the resultant $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ moiety. The purpose of the present communication is to report the first ab initio type molecular orbital study addressed to the relative stability of singlet vs. triplet-state silaethylene and to show that the stability of the triplet 1,2-diradical is commensurate with the singlet π -bonded structure.

All calculations on silaethylene were carried out with s,p Gaussian-type functions contracted to a minimal (STO-4G) basis set³ using a version of the GAUSSIAN 70 program.⁴ The singlet closed-shell SCF problem was solved within the framework of Roothaan's restricted Hartree-Fock method, while the lowest triplet-state problem was solved using Pople's unrestricted Hartree-Fock method.

Four geometrically different structures of silaethylene were optimized starting from the recently published ab initio results on the study of the ir spectrum of silaethylene.⁵ These correspond to the absolute minima on the S_0 closed-shell singlet (I) and T_1 orbitally excited lowest triplet (II) conformational hypersurfaces as seen from the data presented in Figure 1 and Table I. The other two structures, III and IV, appear as transition states on the S_0 and T_1 conformational hypersurfaces, respectively. However, all four structures represent minima in the rotational cross sections associated with the cis-trans isomerization of silaethylene. These optimized points are shown as solid dots or solid triangles in the rotational cross sections of the S_0 and T_1 conformational hypersurfaces, Figure 1. The absolute minimum occurs at the skew position in the pyramidal T_1 state lying

Table I. Calculated State Energies in Hartree and Optimum Geometrical Parameters for S_0 and T_1 Silaethylene^a

θ , deg	Planar groups		Pyramidal groups	
	S_0	T_1	S_0	T_1
0 (180)	-327.233137* (I)	-327.189852	-327.217708	-327.226132
45 (135)	-327.192995	-327.198634	-327.182645	-327.230812
90	-327.092329	-327.206975* (IV)	-327.102640* (III)	-327.235380* (II)
Optimum geometries				
$r_{\text{Si-C}}$, Å	1.637	1.830	1.689	1.846
$r_{\text{Si-H}}$, Å	1.418	1.414	1.444	1.429
$r_{\text{C-H}}$, Å	1.073	1.081	1.065	1.0797
$\angle \text{HSiC}$	122.66	120.5	129.34	109.06
$\angle \text{HCSi}$	123.13	123.2	117.9	123.0
θ , deg	0	90	0	90
ϕ_{HSiH} , ^b deg	0	0	0	30
ϕ_{HCH} , ^c deg	0	0	14	0

^a An asterisk designates optimized values. ^b Angle of the H_2Si plane with the Si-C axis. ^c Angle of the H_2C plane with the C-Si axis.

Table II. Comparison of Various ab Initio Results for the S_0 and T_1 Energies of Ethylene and Silaethylene^a

	Total energy, hartrees		
	$\text{CH}_2=\text{CH}_2$		$\text{CH}_2=\text{SiH}_2$
	(4-31G)	(4G)	(4G)
Most stable triplet	-77.854796*	-77.572905	-327.235380
Most stable singlet	-77.922129*	-77.628078	-327.233137
$\Delta E = (E_{S_0} - E_{T_1})$, kcal/mol	-42.2	-34.6	+1.4

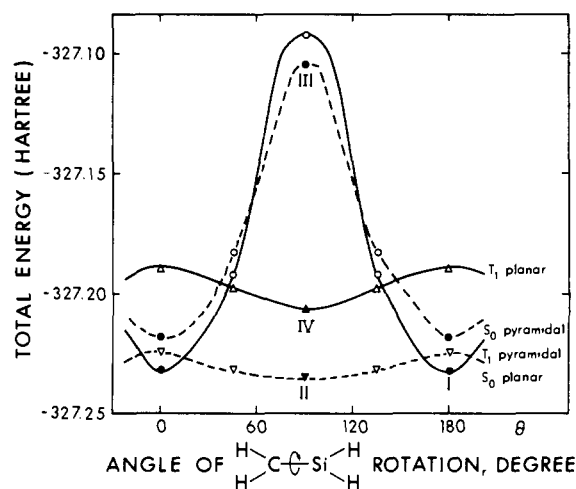
^a An asterisk designates the geometry optimization with the (4-31G) basis set resulting in the following geometrical parameters: (S_0) C-C 1.3202, C-H 1.0743, HCC 121.95°; (T_1) C-C 1.4610, C-H 1.0757, HCC 121.29°, HCCH 90.0°.

about 1.4 kcal/mol below the minimum in the planar S_0 surface. In the former the carbon atom is in an sp^2 hybrid state, the $\text{H}_2\text{C-Si}$ frame being planar, and the silicon atom is in an sp^3 hybrid state, the H_2Si plane at an angle of 150° to the Si-C axis.

In evaluating the results obtained for the hypersurfaces of silaethylene, a comparison with the corresponding hypersurfaces of ethylene is useful. Since $\text{CH}_2=\text{CH}_2$ is a much simpler system than $\text{SiH}_2=\text{CH}_2$, the effect of using a minimal basis set on the relative stability of the S_0 and T_1 states was investigated on ethylene. Full geometry optimization was performed for the S_0 and T_1 states of ethylene using a split valence shell (4-31G) basis set.³ With these optimum geometries the S_0 and T_1 states of ethylene were then recalculated using a minimal (STO-4G) basis set.³ The calculated energy values are listed in Table II. A minimal basis set optimization of the pyramidal angle at the C centers in the triplet twisted ethylene, resulted in planar CH_2 moieties, in agreement with the (4-31G) results.

As is shown in Table II, the (STO-4G) energy difference between the S_0 and T_1 states of ethylene is of the same order and of the same sign as the (4-31G) calculated difference, and consequently it is reasonable to accept the (STO-4G) results on silaethylene as semiquantitatively correct.

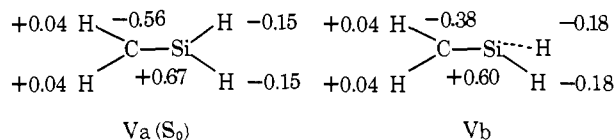
There is a significant difference between the two molecules with respect to the relative stability of the S_0 and T_1

**Figure 1.** Cross sections of the conformational hypersurfaces for S_0 and T_1 silaethylene.

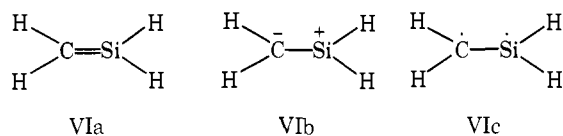
states as well as the geometry of the T_1 state, the Si center being pyramidal but all C centers planar.

Thus, the present results lead to the prediction that the ground state of silaethylene is triplet, but the lowest singlet state lies only 1.4 kcal/mol above it. These results are in line with the extreme reactivity of silaethylene, suggesting a diradical character. The calculated energy difference between the S_0 and T_1 states is not directly comparable to the experimental difference in stability because the correlation energy of the two states will be different, and this difference is not accounted for in the above calculations. Using a large basis set for a fully correlated wave function, the computed order of stability of the T_1 and S_0 states of silaethylene may be reversed, but it is clear that the splitting of the T_1 and S_0 energy levels is relatively small and the proximity of the two states should have a profound influence on the chemical reactivity of silaethylene.

A Mulliken population analysis carried out on the most stable conformation of the S_0 and T_1 state of silaethylene resulted in the charge distribution given by structures Va and Vb, respectively. The geometry of Va is that of I and the geometry of Vb is that of III in Table I and Figure 1.



Considering the three electronic structures



proposed earlier on the basis of reactivity of substituted silaethylenes, it is interesting to note that pair VIa, VIb is in agreement with the electron distribution of Va and the pair VIb, VIc with that of Vb. If indeed, the energy of the lowest singlet is close to that of the lowest triplet, as the present calculations indicate, then at room temperature both S_0 and T_1 are populated and as far as overall reactivity is concerned all three electronic structures proposed earlier⁶ are correct.

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Crystal and Molecular Structure of a Novel Asymmetrical Neodymium-Cyclooctatetraene Compound, Cyclooctatetraenylbis(tetrahydrofuran)-neodymium(III) Bis(cyclooctatetraenyl)neodymate(III)

Sir:

In this communication we wish to report the preparation and crystal structure of a novel asymmetrical neodymium-cyclooctatetraene compound, $[\text{Nd}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_8)_2][\text{Nd}(\text{C}_8\text{H}_8)_2]$. Lanthanide metal atoms, prepared by high temperature vacuum evaporation,¹ were codeposited with cyclooctatetraene at -196°C . The reaction appeared to take place at -196°C to yield a new class of organolanthanides, $\text{Ln}_2(\text{COT})_3$, which show chemical and physical properties similar to the well-known compounds $\text{U}(\text{COT})_2$ and $\text{KLn}(\text{COT})_2$ prepared by Streitwieser et al.² The Nd mem-

Table I. Summary of Crystal Data

Molecular formula:	$[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$
Molecular weight:	745.13
Linear absorption coefficient, μ :	33.18 cm^{-1}
Observed density: ^a	1.75 g/cm^3
Calculated density:	1.71 g/cm^3
Crystal dimensions:	$0.3 \times 0.08 \times 0.08\text{ mm}$
Space group:	$P2_1/c$, monoclinic
Molecules/unit cell:	4
Cell constants:	$a = 16.664(3)$, $b = 12.778(3)$, $c = 14.347(4)\text{ \AA}$; $\beta = 108.90(2)^\circ$
Cell volume:	2894.74 \AA^3

^a Experimental density measurements were obtained by flotation measurements in $\text{CCl}_4\text{-CBr}_4$.

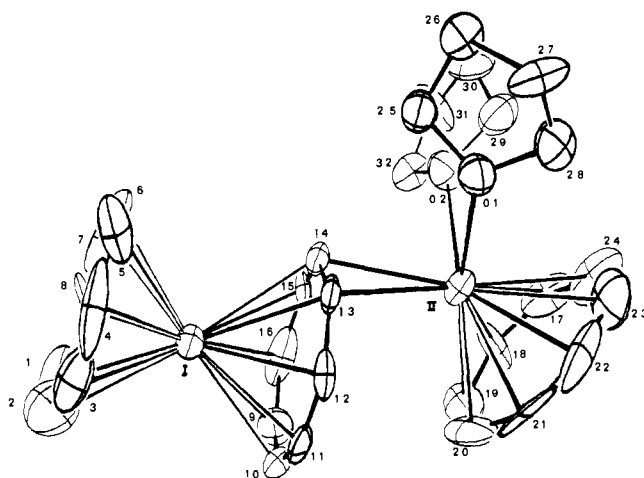


Figure 1. An ORTEP drawing of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ approximately along the C axis.

ber of this series was purified by Soxhlet extraction into THF. Bright green crystals of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ grew during the extraction.

Several crystals were sealed in thin-walled glass capillaries under a nitrogen atmosphere for x-ray diffraction analysis. The crystal chosen for study was mounted on a Syntex $P\bar{1}$ computer-controlled four-circle diffractometer. Data were measured out to $2\theta = 45^\circ$ using a θ - 2θ scan mode and monochromatic $\text{Mo K}\alpha$ radiation. Crystal data are shown in Table I. The structure was refined with full-matrix least-squares methods using 3351 independent and nonzero reflections. No absorption corrections were made. The structure was solved by MULTAN. Following an anisotropic least-squares fit on all 36 nonhydrogen atoms, refinement on the 1371 independent reflections with $F^2 > 3\sigma(F^2)$ is 3.30%. Positional parameters are presented in Table II.

The molecular structure consists of an anion-cation pair, $[\text{Nd}(\text{COT})_2]^-$ and $[\text{Nd}(\text{COT})(\text{THF})_2]^+$, as shown in Figure 1. The anion is composed of Nd_1 and COT rings 1 and 2. The carbons in ring 1 are numbered 1-8, while those in ring 2 are numbered 9-16. The cation is composed of Nd_{11} , COT ring 3, and two THF rings.

In rings 1, 2, and 3, the average bond distances are 1.384 (51), 1.419 (14), and 1.407 (25) \AA while the average angles are $134.79(2.25)$, $134.86(0.65)$, and $134.90(1.45)^\circ$, respectively. All the carbon atoms lie within 0.035, 0.048, and 0.026 \AA of the least-squares planes of their respective rings. These data demonstrate the ten π -electron aromatic nature of the COT^{2-} rings in this structure. The bond distances and interior angles of the THF rings agree well with those found in $[\text{Ce}(\text{COT})\text{Cl}2\text{THF}]_2$.³

The coordination sphere about Nd_1 consists of ring 1 with an average Nd-C distance of 2.660 (24) \AA and ring 2 with an average Nd-C distance of 2.787 (19) \AA . The coordina-