

Figure 1. ESR spectrum of TMB⁺ in aqueous micellar solution of sodium dodecyl sulfate. (a) Spectrum recorded at 295 K at 9.5 GHz, (b) spectrum recorded at 77 K at 9.3 GHz, and (c) calculated stick diagram for the multiplet groups. Numbers given denote the relative intensities. In cases a and b the sample was irradiated at 295 K with 366 nm light.

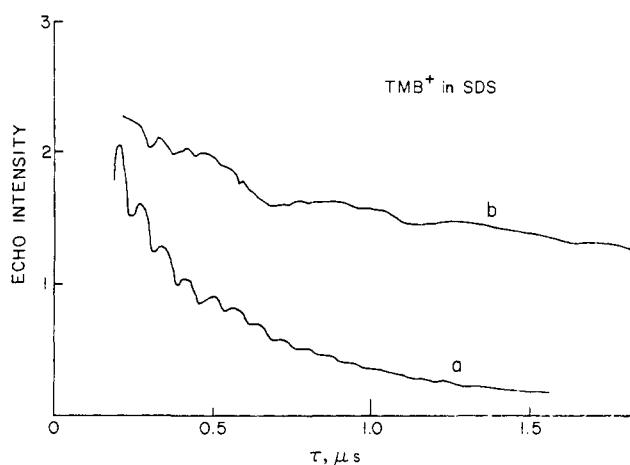


Figure 2. Two-pulse electron spin echo envelope of TMB⁺ in (a) SDS prepared in H₂O and (b) SDS prepared in D₂O. Spectra were recorded at 4.2 K.

The ESR spectrum of TMB⁺ in Figure 2a consists of 11 multiplets split by 4.8 G with a multiplet splitting of 0.85 G. We interpret the main splitting as due to nearly equivalent N and H(CH₃) hyperfine splitting as is the case for the structurally similar Wurster's blue cation.¹³ This would give 17 multiplets of which we observe only the central 11. Figure 1 shows that the observed and calculated intensities agree well with this model. The smaller multiplet splitting is attributed to ring-proton interactions.

Photoionization of TMB in benzene at 295 K or SDS aqueous solutions below the critical micelle concentration produces no observable ESR spectra, indicating that charge recombination is rapid in nonmicellar solutions. Thus the observation of TMB⁺ at 295 K after freezing and thawing the micelle solution and after irradiation at 4.2 and 77 K indicates that the micellar structure is retained in the frozen solution and upon thawing. If it were not, rapid charge recombination would remove the cation. This conclusion is further supported by the identity of the ESE modulation of TMB⁺ at 4.2 K for irradiations at 77 and 295 K. Electron microscope studies¹⁴ of spray frozen micellar solutions also indicate that micellar structure is retained in frozen solutions.

The modulation of the ESE decay envelope of TMB⁺ arises primarily from dipolar interaction between the unpaired electron and surrounding nuclei.¹⁵ The modulation period identifies the interacting nucleus, and the modulation depth is related to the

number and distance of the closest interacting nuclei. In Figure 2a the modulation period indicates that the interacting nuclei are protons on the alkyl chains of the surfactant molecules or on solvent water molecules. If the modulation arises from water protons, the proton modulation should be replaced by deuterium modulation when the micellar solution is prepared in D₂O. Deuterium and proton modulation are easily distinguished by the difference in their magnetic moments. Deuterium modulation is also more prominent, since the modulation depth increases with nuclear spin. In Figure 2b we observe both proton and deuterium modulation and that deuterium modulation arises at the expense of proton modulation. This suggests that the cation interacts with protons of both alkyl chains and solvent water. From the modulation depth the cation to water distance is 0.4–0.5 nm.

There is current controversy regarding micellar structure.¹⁶ To suggest a probable region of cation localization in frozen micellar solutions, we assume a spherical micelle with a polar exterior and nonpolar interior.^{17,18} For this model we suggest that TMB⁺ is located in a weakly polar region of alkyl groups adjacent to polar headgroups of the surfactant, since weak D₂O interactions are observed. Also, since identical ESE data are found for TMB⁺ produced at 295 K and then frozen as for TMB⁺ produced in frozen solution, it appears that TMB⁺ has not moved much relative to its precursor TMB.

If a more open micellar structure^{16,19} is assumed, the cation location becomes more uncertain. Further experiments concerning this with different length surfactants are under way.

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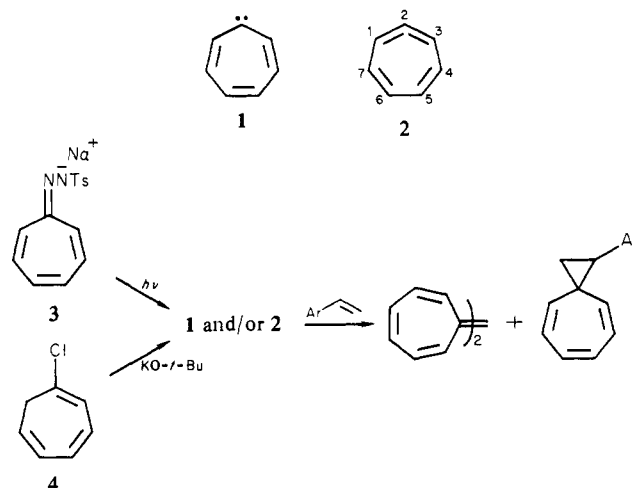
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The Cycloheptatrienylidene–Cycloheptatetraene Problem. A MNDO Investigation¹

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Cycloheptatrienylidene (**1**) is of prime importance to carbene chemistry, since it is a classical example of a carbocyclic, nucleophilic, aromatic carbene when in its lowest energy singlet state.



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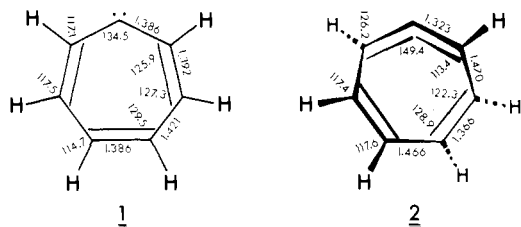


Figure 1. Optimized geometries of **1** (C_{2v}) and **2** (C_2). Units for angles and bond lengths are degrees and angstroms, respectively. The optimized dihedral angles for **2** are $C_1-C_2-C_3-C_4$ 23.98, $C_2-C_3-C_4-C_5$ -36.03, $C_1-C_2-C_3-H_3$ 210.08, $C_2-C_3-C_4-H_4$ 146.87, and $C_3-C_4-C_5-H_5$ 184.25°.

Table I. Calculated Properties for Geometrically Optimized **1** and **2**

compd	ΔH_f , kcal/mol	dipole moment, D	ionization potential, eV
1 (singlet)	114.4	4.03	7.39
2 (singlet)	91.5	0.83	8.57
1 (triplet) ^a	97.4	0.91	
2 (triplet) ^a			

^a Half-electron method. See reference 17.

The study of the intermediate generated from the thermolysis or photolysis of the sodium salt of tropono tosylhydrazone gave very solid evidence for **1**. The low reactivity,² nucleophilicity,^{2,3} and apparent singlet ground state⁴ of the intermediate were exactly the properties expected for **1**. The report that dehydrochlorination of 1-chloro-1,3,5-cycloheptatriene also gave heptafulvalene brought cycloheptatetraene (**2**) into the C_7H_6 picture.⁵ Studies by Jones and his co-workers began to unravel the **1**-**2** question. INDO calculations indicated that **2** was more stable than **1** by 14 kcal/mol.⁶ The report that the intermediate from **4** gave the same ρ value in its addition to substituted styrenes as the intermediate derived from **3** led to the conclusion that the same intermediate was responsible for the cyclopropanation reactions.⁷ There was additional evidence that the dehydrochlorination method resulted in the *initial* formation of **2**.⁸ The crucial questions which remain are do **1** and **2** exist in equilibrium with one another and does **1** or **2** give rise to the cycloaddition chemistry?

The MNDO semiempirical technique⁹ was used to assess the answers to these questions. The optimized geometries were obtained for singlet **1** (constrained to C_{2v} symmetry) and **2** (C_2 symmetry). The C-H bond lengths were kept at 1.1 Å. The C-C lengths, all bond angles, and, in the case of **2**, all dihedral angles were optimized. The structures are shown in Figure 1. Other calculated properties are given in Table I. The nonplanar **2** is found to be more stable than the planar **1** by about 23 kcal/mol.¹⁰

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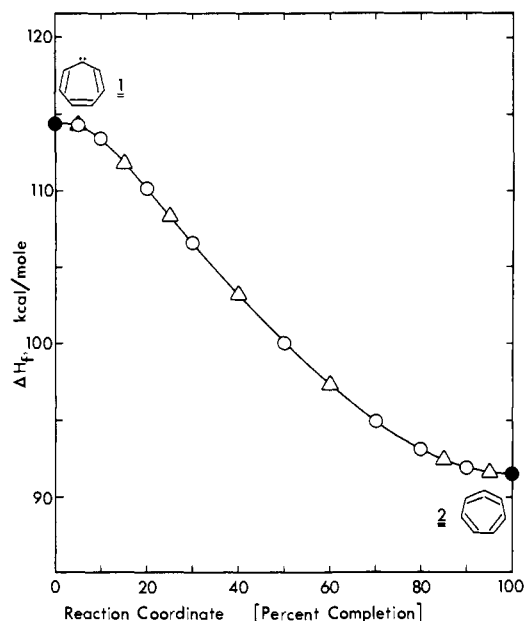


Figure 2. Heat of formation vs. percent completion (see text for definition). ●, optimized geometries for **1** (C_{2v}) and **2** (C_2); ○, reaction path in the direction **1** → **2**; Δ, reaction path in the direction **2** → **1**.

Structure **2** is very similar to that found by Dewar and Landman as the ultimate rearrangement product of phenylcarbene (MINDO/3).¹¹ If the MNDO heat of formation of **2** (91.5 kcal/mol) is contrasted with that calculated from group values¹² (74.9 kcal/mol), we can estimate a strain enthalpy of about 17 kcal/mol.

Although it now appears that **2** is much more stable than **1**, the existence of a significant isomerization barrier might allow the observation of some chemistry from **1**. Molecular orbital following¹³ considerations show that the **1** → **2** isomerization is allowed if the carbene electron pair is in the σ orbital (which is the highest occupied MO according to intuition and MNDO).

The simple reaction coordinate method does not provide a simple minimum energy reaction path (MERP) connecting **1** and **2**.¹⁴ For instance, when the $C_1-C_2-C_3-C_4$ dihedral angle of **2** is used as the reaction coordinate and is incremented from 23.98 (the optimized value in **2**) to 0° (while reoptimizing the remaining variables), the other dihedral angles change to produce a nearly planar system *except* the $C_1-C_2-C_3-H_3$ and $C_3-C_2-C_1-H_1$ dihedral angles which are finally 200.5°. Due to what must be very significant repulsions between H_3 (and H_1) and the σ carbene electron pair, H_1 and H_3 resist joining the other atoms in the plane. The ΔH_f for this structure is 109.6 kcal/mol. The use of other geometric variables as the reaction coordinate shows discontinuities which sometimes plague the reaction coordinate method.¹⁴

A more forceful approach gives valuable information. Using the dihedral angles and the C-C-C angle in **1**,¹⁵ one can develop

(10) (a) This difference is substantially greater than the previous INDO result (14 kcal/mol).⁶ Besides the difference in calculation methods, the present geometrical optimizations used fewer constraints. (b) There are other minor factors which could affect the relative stability or possible equilibrium distribution of **1** and **2**. For instance, the calculated dipole moment of **1** is much larger than that of **2**. In solution, the energy difference between **1** and **2** would be diminished. On the other hand, since **2** is a chiral intermediate, it would be additionally favored by a small entropy of mixing term ($R \ln 2$) when experimentally generated as a racemic mixture.

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a heavy-handed six-parameter combined reaction coordinate which can be termed the "percent completion" (Figure 2). It is seen that changing the dihedral angles and the C-C-C angle by 5% of their total changes in going from **1** to **2** (followed by reoptimizing the bond lengths and remaining angles) results in an immediate slight decrease in energy. Further changes (followed by reoptimization of the remaining variables) give a smooth decrease in energy until the allene **2** is reached. The same curve is generated if the optimized geometry of **2** is the starting point and the six parameters are changed until **1** is reached. While Figure 2 does not represent the MERP for **1** → **2** conversion, the actual MERP must be at least this favorable. Thus, according to MNDO, there is no barrier separating these structures, making **1** inaccessible to chemical interception. In this view, **1** could be very close to the transition state for the racemization of **2** and its enantiomer.¹⁶

It should be now recognized that the "aromatic" π electron delocalization does not provide overriding stability for singlet **1**. This is, of course, because π delocalization results in charge separation. In fact, MNDO calculations for triplet **1** (using the half-electron method) indicate the planar **1** is probably a ground-state triplet ($\Delta H_f = 97.4$ kcal/mol).¹⁷ The singlet allene **2** can successfully account for all of the chemistry previously ascribed to singlet **1**. The rearrangement chemistry can be attributed to singlet **2**.¹¹ If singlet **2** is considered as a conjugated tetraene whose termini share the same carbon (C₂), [$\pi_{2s} + \pi_{8s}$] cycloadditions giving cyclopropane products can be envisaged. Finally, nucleophilicity is also a property of strained allenes.¹⁸

While any semiempirical calculation can not be considered the final answer to any chemical system, this work shows the importance of considering nonplanar structures when considering the geometries and properties of carbocyclic, completely conjugated carbenes. The results of MNDO calculations for cyclopropenyldiene, cyclopentadienyldiene, and cyclononatetraenyldiene in their planar and nonplanar forms will be reported at a later time.

Note Added in Proof: The calculation of the MNDO-based vibrational force constant matrix and normal modes for **1** ("optimized" in a planar configuration but released from C_{2v} symmetry; ΔH_f still is 114.4 kcal/mol) has now been accomplished. The vibrational force constant matrix shows a *single negative eigenvalue* corresponding to a "frequency" of 428 cm⁻¹. Inspection of the normal mode vectors for this "vibration" shows the precise atomic movement necessary to convert **1** into **2**. Thus, according to MNDO, **1** is a transition state. We thank Professor M. J. S. Dewar for making this program available and Mr. J. Ritchey for discussions on its use.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The assistance of Professor R. J. Field and the University of Montana Computer Center in installing the MNDO program is greatly appreciated. Stimulating discussions with Professors W. M. Jones and J. D. Scott and Dr. J. O. Jarvie have been especially helpful and enjoyable.

(15) Assuming the presence of a C₂ axis of symmetry in **1** and **2** and using the numbering convention of **2**, specifying the C₁-C₂-C₃-C₄, C₂-C₃-C₄-C₅, H₃-C₃-C₂-C₁, H₄-C₄-C₃-C₂, and the H₅-C₅-C₄-C₃ dihedral angles will uniquely describe the planarity or nonplanarity of **1** and **2**.

(16) (a) The location of transition states on a multidimensional energy surface can be a difficult and time consuming process.¹⁴ McIver has shown that symmetrical transition states are unlikely (McIver, J. W., Jr. *Acc. Chem. Res.* 1974, 7, 72-77). A slight distortion of **1** could accommodate this point. (b) The structure **1** can only be energetically optimized if constrained to planarity.

(17) (a) The C₇-C₁-C₂ angle for triplet **1** is 145.6°. The C₁-C₂, C₂-C₃, C₃-C₄, and C₄-C₅ bond lengths are 1.356, 1.435, 1.374, and 1.450 Å, respectively. The C₁-C₂-C₃, C₂-C₃-C₄, C₃-C₄-C₅, H₂-C₂-C₁, H₃-C₃-C₂, and H₄-C₄-C₃ bond angles are 120.3, 126.2, 130.6, 120.3, 115.9, and 116.3°, respectively. (b) Geometric optimization of nonplanar triplet **2** (starting with the singlet **2** geometry) resulted in an essentially planar structure, whose dihedral angles differed from planarity by no more than 0.17°. This structure ($\Delta H_f = 97.4$ kcal/mol) was essentially the same as the triplet **1**. Although the energy surface was not completely searched, triplet **2** may not be an energy minimum.

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Minor and Trace Sterols in Marine Invertebrates. 23.¹ Xestospongesterol and Isoxestospongesterol—First Examples of Quadruple Biomethylation of the Sterol Side Chain

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The most characteristic difference between terrestrial and marine sterols resides in the side chain. The former contain side chains ranging from C₈ (e.g., cholesterol) to C₁₀ (e.g., sitosterol), while numerous marine sterols with C₁₁ side chains have recently been isolated³—i.e., products of *triple* biomethylation of an unsaturated precursor.⁴ Indeed, recent work suggests that sterols resulting from a hitherto unprecedented *quadruple* biomethylation sequence may also exist in nature: GC-MS analysis of the trimethylsilylated sterol fraction of a tunicate⁵ and a sponge⁶ suggested the presence of trace quantities of unknown sterols with C₁₂ side chains. We report now the isolation, structure elucidation, and synthesis of the first two members of this new class of biosynthetically intriguing marine sterols from two sponges, which are rich in sterols with C₁₁ side chains.

Our first choice was a Caribbean *Xestospongia* species, which has been shown⁷ to contain predominantly (71%) the C₃₀ sterol xestosterol (**1**) with a novel C₁₁ side chain. Capillary GC analysis⁸ indicated the presence of a trace sterol (0.01% of total sterols) with relative retention time 2.38 (cholesterol 1.00) which was separated (absolute MeOH) by reverse-phase HPLC (Whatman Partisil M9 10/50 ODS-2) to afford another new sterol, xestospongesterol, of M⁺ = 440.4013 (C₃₁H₅₂O). Assignment of structure **2** was based initially on mass spectrometric and proton NMR spectral analysis. Thus, its mass spectrum displayed the typical peaks⁹ (*m/z* 213, 231, 253, 271) of a Δ^5 -3 β -hydroxy sterol nucleus (N), while its two most intense ions were of mass 328 and 111. The former has been shown¹⁰ to be typical (McLafferty rearrangement) of Δ^{25} -unsaturated sterol side chains, but such sterols also display¹⁰ an intense *m/z* 314 peak (associated with electron-impact-induced rearrangement to a Δ^{24} isomer, which then undergoes its own diagnostic McLafferty rearrangement). The virtual absence of such an *m/z* 314 peak in the xestospongesterol (**2**) spectrum suggested the presence of a quaternary center at C-24, blocking rearrangement of the Δ^{25} double bond. The base peak at *m/z* 111 is then clearly due to fission at the highly labilized allylic C-24 quaternary center (see wavy line in **2**). Given this mass spectral interpretation and the presence of vinylic methyl and ethyl functions as deduced from the 360-MHz proton NMR spectrum (Table I), one could readily assign the biosynthetically unusual structure **2** (except for double-bond stereochemistry) to xestospongesterol.

Our second choice was the Indopacific sponge *Strongylophora*

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