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Is Tetramethylene an Intermediate?

C. Doubleday, Jr.*§

Chemistry Department, Canisius College
Buffalo, New York 14208

R. N. Camp, H. F. King, J. W. McIver, Jr.,* D. Mullally,† and M. Page‡

Department of Chemistry, SUNY at Buffalo
Buffalo, New York 14214
Received April 25, 1983

We present computational evidence that singlet tetramethylene is an entropically bound intermediate. Our calculations suggest that it exists in an entropy-dominated free energy minimum *even though it lacks a potential energy minimum.*

Gas-phase pyrolysis results[1-6] indicate that tetramethylene derivatives are short-lived intermediates shared in common among several modes of generation (via diazenes,[3-5] cyclobutanes,[2] and olefin dimerizations[6]) and which undergo competitive cyclization, fragmentation to olefins, and loss of stereochemistry at the radical centers. This picture is largely supported by the seminal ab initio calculations of Segal.[7] Using a 15-configuration wave function and the STO-3G basis set,[8] he found that the gauche (**1**) and anti (**2**) conformers are both local minima on the singlet tetramethylene potential energy surface.[7] We have recently found[9] that the gauche minimum is an artifact of the STO-3G basis set. With a split-valence 3-21G basis set[10] and a two-configuration MCSCF wave function, only **2** survives as a local minimum.[9]

As Segal[7] has indicated, however, a two-configuration wave function gives a poor description of the fragmentation to two ethylenes. This is because of the additional unpairing of the electrons in the central C–C bond. We have thus reexamined the tetramethylene surface using 3-21G and a four-electron four-active-orbital CASSCF[11] wave function. This MCSCF wave function contains the 20 configurations corresponding to full CI with four electrons and four orbitals.

We find that **1** cyclizes and **2** fragments with no potential energy barrier. Extensive searches in other regions of our surface indicate that there are *no minima* in the biradical region of singlet tetramethylene. Two saddle points were located and characterized by force constant calculations, one for the cis–trans isomerization of cyclobutane and the other, 1.3 kcal/mol lower, for fragmentation to ethylenes.[12] Relative to cyclobutane as the zero of energy, the respective potential energies of two ethylenes and the fragmentation saddle point are 2.3 and 52.8 kcal/mol. Experimental $\Delta\Delta H_f°$ values[13] relative to cyclobutane are 18.8 and 61.8 kcal/mol, respectively. Our predicted absence of a biradical minimum is consistent with Doering's[13] recent thermochemical estimate of the depth of the tetramethylene enthalpy well of 2.0 ± 1.5 kcal/mol.

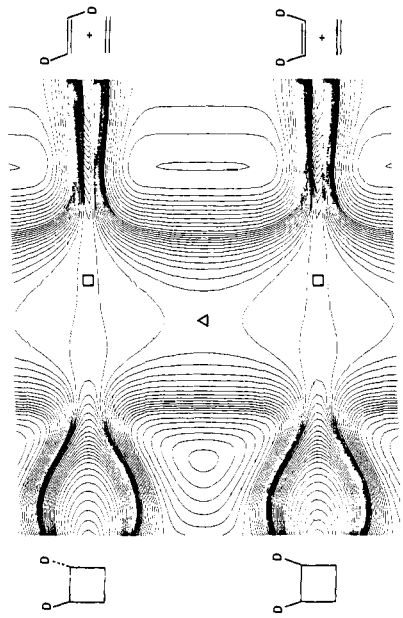

Figure 1. Contour plot of a projection of the full 30-D surface onto a 2-D subspace consisting of a CH_2 twist angle (vertical axis) and a distance parameter (horizontal axis). Squares and triangles mark the saddle points for fragmentation and cis–trans isomerization, respectively.

Our results (details to be reported later) yield a picture of tetramethylene as a broad, flat plateau region of the C_4H_8 potential surface. This is remarkably similar to Hoffmann's[14] extended Huckel results, which led to his twixtyl model. However, our results also show an additional feature that is crucial to a twixtyl-type model of a common intermediate. Along a reaction path proceeding from either saddle point toward a product, two effects occur: the potential energy is lowered and the loose modes (especially the internal rotations and terminal methylene wagging) become tighter. The tightening implies a decrease in entropy as the product starts to form. If the decrease in potential energy is not too great, the entropy reduction can give rise to a free energy barrier to product formation. In the language of canonical variational transition-state theory,[15] the transition state connecting tetramethylene with either product is shifted away from the saddle point to the point where the free energy is maximized along the reaction path. In this model tetramethylene exists as an entropy-locked species.

As a first step toward a rigorous examination of this hypothesis we have calculated an additional force constant matrix at a geometry (**3**) corresponding to incipient cyclization—a gauche conformation with the p orbitals pointing toward one another and a C_2 symmetry axis through the central C–C bond. The potential energy of **3** is 1.0 kcal/mol below the cis–trans saddle point. Nevertheless the free energy of **3**[16] is higher than the free energy at either saddle point. As expected, this is due to tightening the loose modes. Compared to the cis–trans saddle point, the free energy of **3** is higher by 4.1, 2.9, and 2.3 kcal/mol at 700, 500, and 300 K, respectively. This clearly supports the hypothesis of an entropy-dominated free energy minimum. However, these are preliminary conclusions and are by no means proven. We also point out that although the four-electron four-orbital CASSCF wave function is capable of an evenhanded description of the entire

†Graduate School Fellow 1982–1983.
‡Present address: Ballistic Research Laboratory, US Army Proving Ground, Abderdeen, MD 21005.
§Present address: Department of Chemistry, Columbia University, New York, NY 10027.

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region of interest, the small split valence basis set is rather limited. We believe, however, that the high-temperature thermochemistry will be dominated not by the small (~1 kcal) dips and humps in the diradical region but rather by the larger entropic effects. These should survive a better basis set.

The importance of entropy is illustrated in Figure 1, an idealized contour representation of the cis-trans isomerization and fragmentation processes that displays the qualitative features of our surface, though not itself the result of ab inito calculations. Both saddle points are located in the flat biradical plateau region of the surface. This is a region of high entropy associated with the loose modes. From the plateau region, a biradical can form products only by exiting through narrow channels, a restriction that reduces the entropy. The lower potential energy at the entrances to the product channels is more than offset by an increased zero-point energy and reduced entropy. A biradical in the plateau region is therefore trapped by entropic barriers.

There is reason to suspect that the model of an entropy-looked biradical intermediate is not limited to tetramethylene. In many cases, leaving the biradical region of a potential energy surface implies the formation of a new bond together with increasing hindrance to internal rotation. For larger open-chain biradicals in particular, the greater number of internal rotations suggests an even more pronounced entropic effect than in tetramethylene.

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Registry No. Tetramethylene, 287-23-0.

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Crystal and Molecular Structure of an *N*-Arylporphyrin Complex: Chloro(*N*-phenyl-5,10,15,20-tetraphenylporphinato)-zinc(II)

Debasish Kuila and David K. Lavallee*

Department of Chemistry
Hunter College of the City University of New York
New York, New York 10021

Cynthia K. Schauer and Oren P. Anderson*

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Received August 9, 1983

In 1885 Hoppe-Seyler reported that the addition of phenylhydrazine to red blood cells led to the formation of aggregated particles ("Heinz bodies") that resemble aggregates characteristic of malarial patients.[1] Recently, Ortiz de Montellano and others have found that *N*-phenylporphyrins are formed by the reaction of phenylhydrazine with hemoglobin or myoglobin under aerobic conditions in the presence of acid,[2] with formation of σ-phenylprotohemin[3] as an intermediate. The formation of other N-substituted porphyrins from biological sources has also been reported. A variety of *N*-alkylporphyrins are formed from the protoheme prosthetic groups of cytochrome P-450 enzymes in the liver of mice after their exposure to simple alkenes or to one of a number of drugs.[4] The isolation and identification of these porphyrins was a consequence of the fact that they inhibit heme biosynthesis and cause readily observable changes in the animals (the drugs had been used for several years to study heme biosynthesis disorders before the *N*-alkylporphyrins products were observed). Their effect on the heme biosynthetic pathway has been verified by direct administration of the *N*-alkylporphyrin to the animal.[5] In this first report of the molecular structure of an *N*-arylporphyrin complex, that of chloro(*N*-phenyl-5,10,15,20-tetraphenylporphinato)zinc(II), we will describe major structural features and compare parameters of the coordination site and the porphyrin ring topology with those of the corresponding *N*-methyl complex of zinc(II) and those of other *N*-methylporphyrin complexes.

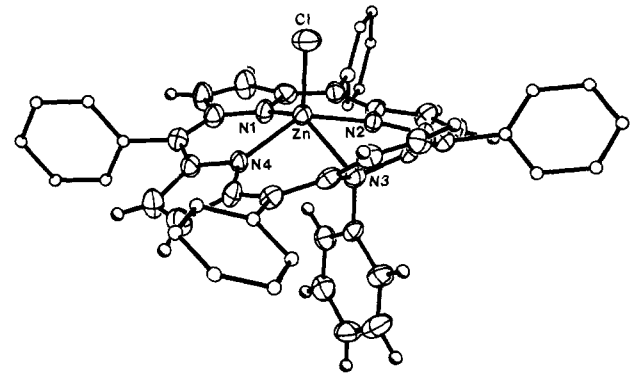

Figure 1. View of the Zn(*N*-Ph(TPP))Cl complex. Hydrogen atoms on the meso phenyl rings have been omitted for clarity, and the thermal ellipsoids that are shown are drawn at the 50% probability level. The complex is almost bilaterally symmetric about the plane of the *N*-phenyl ring.

The metal complexes of *N*-alkylporphyrins show striking similarities to one another. The molecular structures of *N*-methyl-5,10,15,20-tetraphenylporphyrin with Mn(II), Fe(II), Co(II), and Zn(II)[6] have differences that are predictable from bond lengths known from other metalloporphyrin structures[7] and the ionic radius of the particular metal ion.[6d] The highly similar visible absorption spectra of these complexes indicate a decrease in the sensitivity of the $\pi \rightarrow \pi^*$ electronic energy level difference to d subshell occupation in comparison with spectra of corresponding non-N-alkylated porphyrin complexes.[8] In like manner, complexes of *N*-methyldeuteroporphyrin IX dimethyl ester (*N*-CH_3(DP))[9] and *N*-methylprotoporphyrin IX dimethyl ester (*N*-CH_3(PP))[10] exhibit spectra that are more similar to one another than are those of complexes of deuteroporphyrin IX dimethyl ester and protoporphyrin IX dimethyl ester.

The coordination geometry and the topology of the porphyrin ring of chloro(*N*-(ethylacetoxy)octaethylporphinato)cobalt(II)[11]

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