enantiomeric selectivity occurs as well with cleavage. With Λ-Ru(TMP)$_3^{2+}$, twice the cleavage efficiency of the A-form polymer is observed in comparison with Δ-Ru(TMP)$_3^{2+}$.

In summary, Λ-Ru(TMP)$_3^{2+}$ has been shown to bind selectively to A-form polynucleotides and in the presence of light to cleave A-form polymers. This chiral probe should be useful to investigate DNA conformational heterogeneity in mapping sites in the A conformation along the helical strand. The role played by DNA secondary structures in protein recognition and in the expression of genetic information may be better understood by using this and other chiral complexes which are targeted specifically to different conformations.

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Tetramethyleneethane, a Ground-State Triplet

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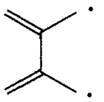
The question whether tetramethyleneethane[1] (I) is or is not a ground-state triplet is a central issue in understanding π-bonding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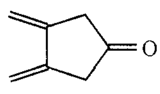

II

in conjugated hydrocarbons. Hund's first rule[2] suggests, as trimethylenemethane is,[3] that I should be a ground-state triplet. However, tetramethyleneethane (I) is an even, alternate, disjoint hydrocarbon.[4,5] In such molecules the nonbonding orbitals (or appropriate linear combination of them) are geographically isolated from each other and do not span common atoms.[4-7] Accordingly, the electron repulsion that provides the basis for Hund's rule is minimized and the singlet, according to this line of reasoning, can be the ground state.[4-7] This rationale has provided a means for understanding the contrasting multiplicities of ground-state trimethylenemethane[3]—triplet— and ground-state cyclobutadiene[7]—singlet. Tetramethyleneethane (I) is an important testing ground for these ideas.

Tetramethyleneethane (I), most probably in its singlet state, is a central intermediate in the dimerization of allene[8] as well as in the thermal rearrangement of 1,2-dimethylenecyclobutane.[9]

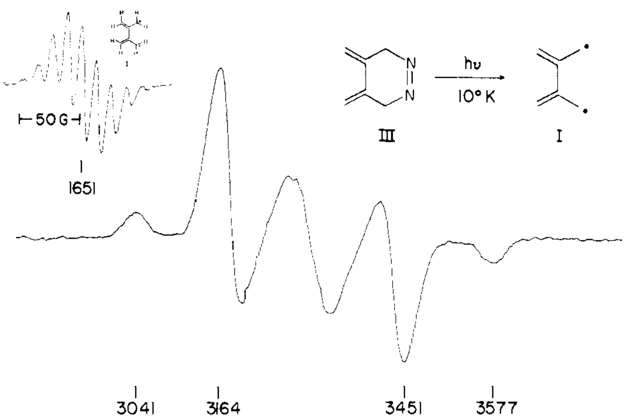
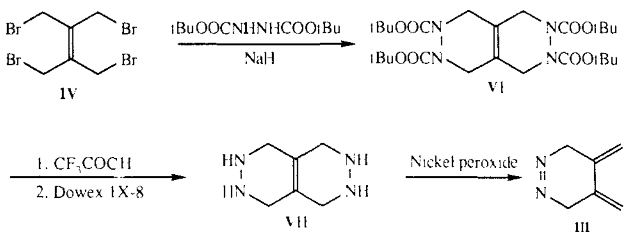


Figure 1. ESR spectrum of tetramethyleneethane (I) from irradiation of III at 265 nm and 10 K. Shown here are the $\Delta m = 1$ and (inset) $\Delta m = 2$ lines.

The triplet state of I was first observed[1] in 1970 following irradiation of the ketone II at 77 K. This experiment was not completely satisfactory because the diradical I is not stable in liquid nitrogen and continuous irradiation was required in order to observe the ESR spectrum of the triplet I. Under these circumstances, it was not possible to establish the multiplicity of the ground state of I. Following our experiments a tetramethyleneethane diradical incorporated into a six-membered ring was reported,[10] but in this experiment the nature of the ground state was also left unresolved.

We decided to explore the diradical I starting from the azo precursor III with the conviction that the structure of the diradical I would be more certain if it could be generated from two independent precursors. Temperatures below the boiling point of liquid nitrogen were used to prevent untimely decomposition of the diradical I. The synthetic strategy was important because at least one attempted synthesis of the azo compound III had not been successful.[11] This molecule contains the reactive s-cis diene system, which is highly susceptible to polymerization. Therefore, it is essential to keep the diene masked until the final step of the synthesis.

In our synthesis leading to III, the tetrabromide IV was treated with di-*tert*-butyl hydrazodicarboxylate (V) in the presence of sodium hydride yielding the double adduct VI.



Synthetic Scheme

The oxygen-sensitive dihydrazine VII was obtained upon removal of the *tert*-butyl groups and decarboxylation in trifluoroacetic acid followed by passage through a column of Dowex 1-X8 basic ion-exchange resin. Oxidation of VII with nickel peroxide in 1:2 carbon tetrachloride–chloroform-*d* at −78 °C yielded the azo diene III. The latter is very sensitive and too reactive to be isolated in the pure state; it must be kept cold and in solution. Even under these circumstances, however, good spectroscopic corroboration of its structure has been obtained. The proton NMR spectrum shows the two-proton exocyclic vinyl methylenes as singlets at δ 5.45 and 5.04 and a four-proton allylic methylene singlet at δ 4.68. The proton-coupled carbon-13 NMR spectrum

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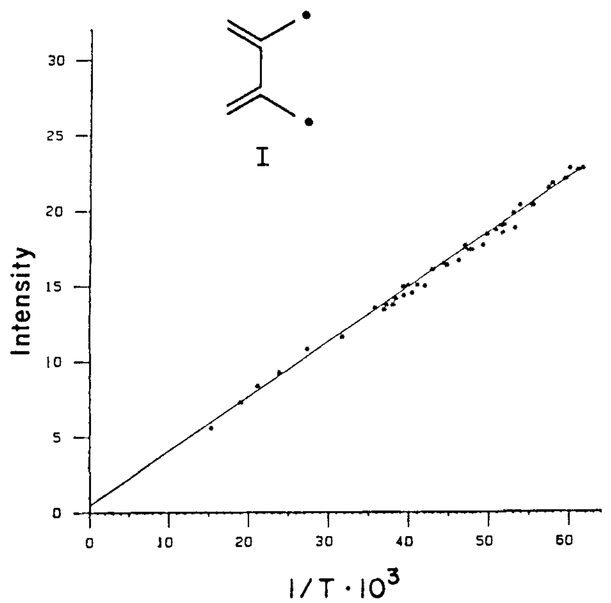
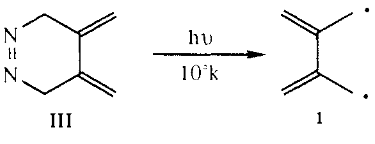


Figure 2. Curie–Weiss plot according to least-squares analysis (r = 0.997) of the signal intensity of the Δm = 2 line of tetramethyleneethane vs. the reciprocal absolute temperature. The temperature range was 16–65 K; the solvent was 2-methyltetrahydrofuran.

shows vinyl and allylic carbon triplets at δ 109 (J = 159 Hz) and δ 65 (J = 129 Hz) together with a quaternary carbon singlet at δ 133. Both spectra are free of extraneous peaks.

A solution of the azo diene III in a methyltetrahydrofuran glass was irradiated with a 1000-W dc xenon lamp using a Jarrell-Ash monochromator to control the wavelength of the light to ±25 nm. Irradiation at the wavelength expected for the azo chromophore (370–380 nm) yielded a very weak triplet ESR spectrum. The strong clean (and identical) spectrum shown in Figure 1 is the result of irradiating *at 265 nm!*[12] The triplet spectrum in Figure 1 has peaks at 3041, 3164, 3451, and 3577 G (microwave frequency 9.26 GHz) with zero-field parameters $|D/hc| = 0.025$ cm^{-1} and $|E/hc| < 0.001$ cm^{-1}. The appearance of the spectrum is identical with that observed earlier;[1] however, the D value is twice as large as that reported.[1] We believe that the earlier value was measured incorrectly. The new value is in better accord with theoretical estimates[1,13,14] and with the value reported for the cyclic analogue.[10] The Δm = 2 line (Figure 1, inset) was readily observed at 1651 G, and it exhibited the detailed hyperfine splitting pattern shown. The nine lines are in accord with expectation for a diradical bearing eight hydrogens, provided the inside and outside hydrogens of I are approximately magnetically equivalent.[15] This establishes the structure of the diradical I beyond question.



III 1

A Curie–Weiss law plot[16] of the intensity of the Δm = 2 line vs. $1/T$ over the range 16–65 K[17] gives the straight line (r = 0.997) shown in Figure 2. We conclude that *tetramethyleneethane is a ground-state triplet.*[18]

It has been suggested[4] that tetramethyleneethane (I) might not be the ideal test of theory if the two halves are canted 90° to one another. Indeed, if in the spectrum of Figure 1, the absence of splitting between the x and y lines is interpreted to mean that E = 0,[19] this would be consistent with a diradical I of D_{2d} symmetry.[20] The two ends of the system would then be isolated by geometric rather than orbital geographic circumstances but the electronic problem would be very closely related to that discussed above. The situation would still consist of two spatially isolated electrons and the question whether singlet or triplet is the preferred ground state in the absence of spatial overlap remains an important and relevant one. *Clearly, the triplet is preferred in the present instance.*

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[12] The same spectrum is observed in a methylcyclohexane glass.

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[15] Considering the close similarity in the a values of the inside and outside hydrogens on the allyl radical, this assumption seems to be reasonable. Strong support is also provided by the nine-line hyperfine splitting pattern (a_H = 7.17 G) of the tetramethyleneethane anion radical observed by: Bauld, N. L.; Stevenson, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3675.

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[17] A Rosemount Model 146MB platinum resistance thermometer immersed in the sample was used to measure the temperature during the Curie–Weiss law experiments. We estimate that the temperature was accurate to 0.02 K in these experiments.

[18] The Curie–Weiss plot is such that a linear plot would also be obtained if the singlet–triplet splitting were 10 cal/mol or less. So, it is also possible that the singlet and triplet are degenerate.

[19] Kindly suggested by Professor S. I. Weissman.

[20] The hyperfine splitting value in I is approximately 10.5 G, somewhat smaller than the 13–14 G of the allyl radical. This might argue for a more delocalized structure in which the two halves maintain some orbital overlap. At the SCF level [which yields calculated hyperfine splittings of 14 and −4.25 G for the allyl radical and 9.4 G for trimethylenemethane (expt.[21] 8.9 G)] the calculated hyperfine splitting for tetramethyleneethane I is 8.7 G.

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Silicon-Carbon Unsaturated Compounds. 22. The Formation and Reactions of a Nickelasilacyclobutene

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Although the formation of a metalasilacyclobutene has been proposed in the transition-metal-catalyzed reaction of silacyclopropenes with an acetylene,[2-4] no evidence for the existence of this intermediate has been obtained so far. Recently, we have found that the nickel-catalyzed reactions of 1-silacyclopropenes and phenylethynylpolysilanes with phenyl(trimethylsilyl)acetylene afford the products which can be best explained assuming the transient formation of nickel-containing reactive intermediates such as nickelasilacyclobutenes and silapropadiene–nickel complexes.[5,6] In this paper, we report that the stoichiometric reaction

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