

previous work on ammonium substituted cyclophane catalyst: I. Tabushi and Y. Kuroda, *Catalyst*, **16**, 78 (1974).

- (4) H. Meerwein, *Org. Syn.*, **46**, 120 (1966).
 (5) See ref 3b and the references cited therein for our modified preparation of I.
 (6) (a) Chloroacetates IV were chosen as the substrates in the present studies because the rates of spontaneous and catalyzed hydrolyses can be adequately compared under the condition. (b) The kinetics of the catalytic action of the heterocyclophane II in the hydrolyses of the ester substrates (IV) were analyzed, based on the following assumptions of hydrolysis mechanisms,



where the eq 2 refers to the Michaelis–Menten type hydrolysis of the substrate (S) to the product (P) catalyzed by C, and eq 3 refers to the uncatalyzed (spontaneous) hydrolysis. (c) R. L. VanEtten, J. F. Sebastian, G. A. Clowes, and M. L. Bender, *J. Am. Chem. Soc.*, **89**, 3242 (1967).

- (7) K_1 constant was determined from pH dependence and phosphate concentration dependence of the apparent K_m value.

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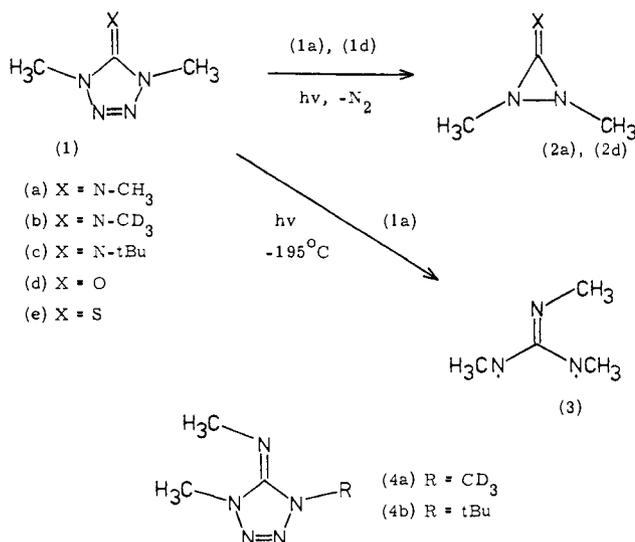
Tris(imino)methanes. An Electron Spin Resonance Identification of Nitrogen Analogues of Trimethylenemethane¹

Sir:

Increasing numbers of both experimental² and theoretical³ investigations center around trimethylenemethane. The triplet character of its ground state survives even rather severe perturbations by substituents.^{2b} In contrast, virtually nothing is known experimentally about the influence of heteroatoms in the trimethylenemethane skeleton. Thus, attempts to detect oxallyl, for which a triplet ground state has been predicted,⁴ by ESR spectroscopy during low temperature photolysis of 1,3-cyclobutanediones have met with failure.⁵ We report here the ESR spectra observed when the iminotetrazoline **1a** is irradiated at low temperatures. We assign the spectra to a nitrogen analogue of trimethylenemethane, i.e., the tris(imino)methane **3**.

In the search for heteronuclear analogues of trimethylenemethane the tetrazolines **1** were designed as precursors,

Scheme I



since they readily lose nitrogen on photolysis, **1a** and **1d** thereby affording the diaziridine derivatives **2a** and **2d**, respectively, Scheme I.⁶ When **1a**, at $-195^\circ C$ in a butyronitrile matrix⁷ degassed at 10^{-5} Torr, was irradiated inside the cavity of an ESR spectrometer,⁸ a centrosymmetrical four-line spectrum, centered at 3286 ± 10 G (Figure 1), was observed after only 30 s. The spectrum persisted after the irradiation had been terminated and lost about half of its intensity on warming to $-150^\circ C$. Under the same conditions, very similar, but less intense, ESR spectra appeared in methylcyclohexane, 2,2-dimethylbutane/*n*-pentane (73:27), hexafluorobenzene, and perfluoromethylcyclohexane.

The four-line spectrum of Figure 1 can be assigned to the "parallel" (*z*) and "perpendicular" (*xy*) signals of randomly oriented triplet molecules having an axis of threefold or higher symmetry, i.e., $E/hc = \sim 0$ cm⁻¹.⁹ From $|D'| = 356 \pm 10$ G the zero-field splitting parameter is calculated as $|D/hc| = 0.033 \pm 0.001$ cm⁻¹. The half-field ($\Delta m = 2$) transition which is a criterion of triplets was observed at 1644 ± 10 G. It exhibited a hyperfine structure of at least nine equidistant lines separated by 11.7 ± 0.5 G. The absorption near the center of the four-line high-field spectrum was produced by monoradicals generated during the irradiation.

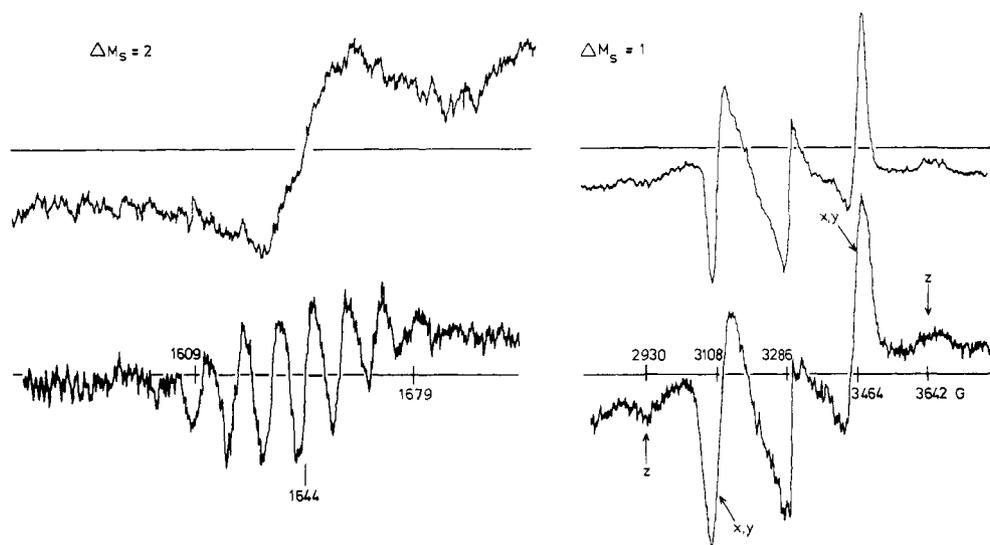
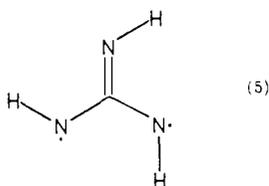


Figure 1. First derivative of the ESR absorption obtained during irradiation of the iminotetrazoline **1a** (lower trace) and the perdeuterated iminotetrazoline [D₃]-**1a**, respectively (upper trace), both in a butyronitrile matrix at $-195^\circ C$. Klystron frequency 9285 MHz, calculated from the resonance field of Fremy's salt.

Very slow cooling of pure molten iminotetrazoline **1a** in a sample tube during several weeks produced a clear (single?) crystal. Irradiation of this crystal at -195°C for 1 min produced two rather strong signals the appearance of which was very dependent upon the orientation of the sample in the magnetic field as expected. At an orientation which gave the most symmetrical hyperfine pattern, the low-field multiplet again consisted of at least nine equally spaced lines separated by 11.7 ± 0.5 G. The striking similarity of the single crystal spectrum to the $\Delta m = 2$ transition of randomly oriented triplets is already known from trimethylenemethane. Since the spectrum was centered at $\sim 3108 \pm 10$ G, it must correspond to alignment of the xy plane of the crystal with the magnetic field. Probably, the sample had crystallized with the z axis running the length of the tube similar to the precursor of trimethylenemethane, 3-methylenecyclobutanone.⁵

The assignment of the tris(imino)methane structure **3** to the species responsible for the ESR spectrum is based on the resemblance of the spectrum to that of trimethylenemethane ($|D/hc| = 0.025 \text{ cm}^{-1}$),^{2a} the size of the zero-field splitting parameter, and the changes, especially of the hyperfine pattern of the $\Delta m = 2$ transition, on deuteration of **1a**. In terms of a dipole approximation,⁹ the observed zero-field splitting parameter D/hc corresponds to an average separation of the unpaired electrons of 3.4 Å, in reasonable agreement with the proposed structure **3**. Introduction of one [D_3]methyl group as in **1b** and **4a** resulted in partial loss, and perdeuteration, as in [D_9]-**1a**, caused complete disappearance of the hyperfine structure of the $\Delta m = 2$ transition. Concomitantly, the expected sharpening of the xy lines was observed (Figure 1).

Splitting of both the supposed single-crystal spectrum and the $\Delta m = 2$ transition into at least nine lines proves that, as well as the nitrogen atoms, the protons are also involved in coupling. In general, the hydrogens of a methyl group attached to a nitrogen should have a coupling about twice as large as the nitrogen itself.¹⁰ A complete geometry optimization of **5** by INDO calculations produced a structure of C_{3h} symmetry having the parameters C-N = 1.357 Å, N-H = 1.073 Å, and $\angle\text{CNH} = 112.6^{\circ}$, and the coupling constants $a^{\text{N}} = 11.3$ and $a^{\text{H}} = -19.8$ G. Using the optimized geometry of **5** and sub-



stituting the optimized methyl group parameters obtained previously,¹¹ one obtains for **3** $a^{\text{N}} = 11.4$ and $a^{\text{H}} = 25 \pm 1$ G. Bending of the methyl groups out of the plane in order to account for possible steric interactions only slightly influenced the coupling constants. Thus, even at an assumed dihedral angle of 45° , the INDO calculation afforded $a^{\text{N}} = 10.9$ and $a^{\text{H}} = 25$ G. However, computer simulation of the ESR spectrum of **3** using $a^{\text{N}} = 11.7$ and $a^{\text{H}} = 23.4$ G did not give a satisfactory agreement with the observed spectra. Surprisingly, the computer-generated 16-line spectrum on the basis of $a^{\text{N}} = a^{\text{H}} = 11.7$ G, the inner eight lines of which represent >95% of its total intensity, did agree much better with the experimental spectra. For comparison, the INDO-optimized geometry of trimethylenemethane, which had yielded the expected planar D_{3h} structure and the parameters C-C = 1.395 Å,¹² C-H = 1.114 Å, and $\angle\text{HCH} = 112.2^{\circ}$, afforded a coupling constant $a^{\text{H}} = -18.9$ G. In view of the experimental value of $|a^{\text{H}}| = 9.17$ G,^{2a} the INDO approximation does not satisfactorily predict the value of a^{H} for trimethylenemethane, which may reflect exaggerated calculated couplings for the tris(imino)methane **3**.

When the *tert*-butyl substituted iminotetrazolines **1c** and **4b**, respectively, were irradiated in a butyronitrile matrix, the observed triplet ESR spectra closely resembled that of **3** but were of lower intensity. Irradiation of both **1d** and **1e** in hexafluorobenzene at -195°C produced only monoradicals.

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Energetics of the Thermal Polymerization of a Diacetylene Crystal

Sir:

There has been a great deal of interest recently in the solid-state polymerization of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS.¹ Interest in this particular diacetylene has two principal origins: (1) thermal polymerization of PTS yields quantitative conversion to a fully conjugated polymer single crystal and (2) the conversion vs. time curve (obtained by monomer extraction) is S shaped—a result of a dramatic autocatalytic effect observed at $\sim 10\%$ conversion to polymer.² The autocatalytic effect almost certainly has its origins in the strain energy associated with the formation of the polymer/monomer solid solution.^{1,3} However, a complete understanding of this effect requires a more detailed analysis of the energetics of the polymerization process as well as a reliable determination of the increase in polymerization rate in the autocatalytic region, i.e., a determination of $\gamma_{\text{max}}/\gamma_0$ where γ_0 is the polymerization rate at low conversion and γ_{max} is the maximum rate in the autocatalytic region. Monomer extraction measurements are not accurate enough to determine $\gamma_{\text{max}}/\gamma_0$, while recent spectroscopic work¹ has yielded only a lower limit, $\gamma_{\text{max}}/\gamma_0 > 10$.

In this communication, we present a preliminary report on the thermal polymerization of PTS studied by differential scanning calorimetry (DSC). We determine the heat of polymerization, ΔH_p , and discuss briefly the energetics and mechanism of diacetylene polymerization. We also present a