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ESR of an Alkylalkoxyamino Radical Trapped in X-Irradiated Decanal Oxime O-Methyl Ether-Urea Inclusion Crystals*

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Recently there has been a good deal of interest in amino radicals of this type ($R-\dot{N}-R'$) have been produced by photolysis of tetrazines,¹ aziridine,² and azetidine,² and by x irradiation of pyrroline and nitrogen radicals in which the unpaired spin density is localized primarily in a nitrogen p orbital. Dialkyl-

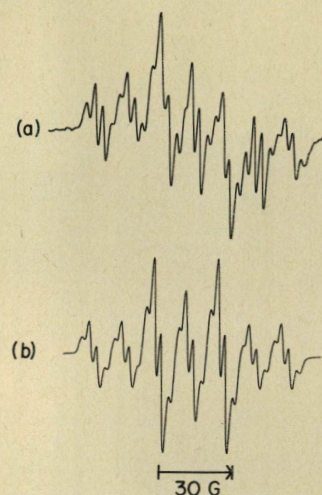


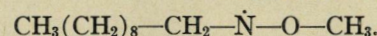
FIG. 1. Experimental (a) and computer simulated (b) ESR spectra of the uv-stable radical from decanal oxime O-methyl ether-urea inclusion crystals, recorded with the magnetic field approximately 45° from the crystalline z axis.

pyrrolidine trapped in an adamantane matrix.³ The purpose of this note is to report a new alkylalkoxy-amino radical formed by x-irradiating decanal oxime O-methyl ether, $\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{NOCH}_3$, oriented in a urea inclusion crystal. Oxime radicals have been widely studied both in solution⁴⁻⁶ and in single crystals⁷⁻⁹ and in most cases the stable radical is the iminoxy radical formed by removal of the -OH hydrogen atom. To our knowledge no x-ray produced oxime radicals have been reported in which the radical is formed by hydrogen addition to the carbon-nitrogen double bond. Urea is a convenient host for the otherwise transient species because all trapped molecules are magnetically equivalent, and the resulting radicals are stable for several days at room temperature.

Decanal oxime O-methyl ether was formed by reacting decyl aldehyde with methoxylamine hydrochloride in pyridine using standard methods.¹⁰ Experimental details concerning methods of crystal growth, x irradiation, and ESR measurements may be found elsewhere.¹¹ The crystals were x irradiated at 77°K , and spectra were recorded at room temperature. Spectral simulations were performed on a Varian 620/i computer. ESR spectra obtained immediately after x irradiation are complex and indicate the presence of more than one radical. However, after subjecting the inclusion crystal to uv light from a 110 W PEK mercury lamp for several hours, it was possible to isolate one of the radicals. (There was no indication of radical formation due to the uv light.) A second radical was partially isolated by heat treatment (three days at 50°C), but the resulting ESR spectra were too poorly resolved to make a positive identification. The first derivative ESR spectrum of the uv-stable radical from decanal oxime O-methyl ether obtained with the magnetic field oriented 45° to the crystalline z axis (needle axis) is shown in Fig. 1(a); Fig. 1(b)

is the spectral simulation. The spectra arise from two large isotropic and equivalent proton coupling constants, one anisotropic nitrogen coupling constant, and three small equivalent proton coupling constants, which are not completely resolved at all crystalline orientations. Coupling constants and g values (relative to DPPH: $g = 2.0036$)¹² for the uv-stable radical at the principal crystalline orientations are indicated in Table I. Similar results were obtained with heptanal oxime O-methyl ether trapped in urea and the O-methyl ethers of decanal oxime and heptanal oxime oriented in *trans-anti-trans-anti-trans*-perhydrotriphenylene inclusion crystals.

The room temperature ESR spectra of the decanal oxime O-methyl ether-urea crystals do not change with rotations of the laboratory magnetic field vector in the crystalline xy plane (i.e., the plane perpendicular to the needle axis) but are anisotropic with respect to rotations out of the xy plane. This behavior is typical of organic inclusion crystals.¹³ An estimate of the isotropic component a_0^{N} of the anisotropic nitrogen coupling constant can be obtained from the relation¹³ $a_0^{\text{N}} = \frac{1}{3}(2a_{xy}^{\text{N}} + a_z^{\text{N}})$, Eq. (1), where a_{xy}^{N} and a_z^{N} are the values of the nitrogen coupling constant measured with the magnetic field in the crystalline xy plane and parallel to the z axis, respectively. It is also useful to relate the measured g -value data to the isotropic g value g_0 which can be obtained to a good approximation¹³ from the relationship $g_0 = \frac{1}{3}(2g_{xy} + g_z)$, Eq. (2). Using Eq. (1), $a_0^{\text{N}} = 14.7$ G. Based on the anisotropic data of Table I and the derived isotropic values, we conclude that the uv-stable radical formed by x-irradiating decanal oxime O-methyl ether is



This assignment is supported by INDO¹⁴ calculations on the model $\text{CH}_3\text{—}\dot{\text{N}}\text{—O—CH}_3$ using as bond angles¹⁵: $\text{H—C—H} = 109.5^\circ$, $\text{C—N—O} = 117^\circ$, and $\text{N—O—C} = 111^\circ$, and bond lengths: $\text{C—H} = 1.12 \text{ \AA}$, $\text{C—N} = 1.39 \text{ \AA}$, $\text{N—O} = 1.41 \text{ \AA}$ and $\text{C—O} = 1.43 \text{ \AA}$. INDO yields an isotropic value of 12.5 G for a_0^{N} and approximately 1 G for the methoxy proton splitting.¹⁶ The calculated and experi-

TABLE I. Hyperfine coupling constants and g values for the radical $\text{CH}_3(\text{CH}_2)_8\text{—CH}_2\text{—}\dot{\text{N}}\text{—O—CH}_3$ at room temperature.^{a, b}

(1) $a_z^{\text{N}} = 4.0 \pm 0.5$ G	(1) $a_{xy}^{\text{N}} = 20.0 \pm 0.2$ G
(2) $a_z^{\text{H}} = 26.2 \pm 0.2$ G	(2) $a_{xy}^{\text{H}} = 26.0 \pm 0.2$ G
(3) $a_z^{\text{H}} = 4.0 \pm 0.1$ G	(3) $a_{xy}^{\text{H}} = 1.6 \pm 0.1$ G ^c
$g_z = 2.0074 \pm 0.0002$	$g_{xy} = 2.0036 \pm 0.0002$

^a The subscripts z and xy indicate the spectra recorded with the magnetic field in the crystalline z and xy directions.

^b The numbers in parentheses are the total number of species with a given coupling constant.

^c Resolved only for decanal oxime O-methyl ether trapped in deuterated urea.

mental results for a^{N} and $a_{\text{CH}_3}^{\text{H}}$ are thus in reasonably good agreement.

It is interesting to note that a_0^{N} for the uv-stable decanal oxime O-methyl ether radical is very nearly equal to the 12.5–14.8 G nitrogen splittings observed by Danen and Kensler for a series of dialkylamino radicals^{1,2} and also the 14.6 G reported by Wood *et al.* in pyrroline and pyrrolidine radicals.³ g -value data is available for the following dialkylamino radicals: pyrrolino and pyrrolidino ($g = 2.0046$),³ aziridino ($g = 2.0043$),² and azetidino ($g = 2.0045$);² these values are all similar to that obtained for the alkylalkoxy-amino radical from decanal oxime O-methyl ether (2.0049) using Eq. (2). Apparently the unpaired electron of the alkylalkoxyamino radical is largely localized on the nitrogen atom.

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¹⁶ Values of 44.1 and 0.6 G, respectively, were calculated by INDO for the two out-of-plane and one in-plane β protons of the methyl group bonded to nitrogen. The large β -proton splittings are those that would result if the two out-of-plane β protons were fixed with a dihedral angle of 30° between the axis of the nitrogen p orbital and the C-H bond. Large amplitude motion about the 30° position (as occurs in urea inclusion compounds¹³) tends to reduce the β -proton coupling constants substantially from these maximum values.