

# Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. III. Isocyanatoalkyl and Isothiocyanatoalkyl Radicals

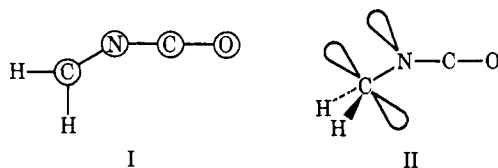
David E. Wood,\* Roger V. Lloyd, and William A. Lathan

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received December 3, 1970

**Abstract:** Several members of the previously unknown class of isocyanatoalkyl and isothiocyanatoalkyl radicals have been prepared and studied by epr by use of the adamantane matrix technique. Typical parameters for these radicals are exemplified by the results for isocyanatoethyl radical,  $\text{CH}_3\dot{\text{C}}\text{HNCO}$ , with  $a_{\text{H}^\alpha} = 21.1$ ,  $a_{\text{H}^\beta} = 21.1$ ,  $a_{\text{N}} = 4.2$  G, and  $g = 2.0026$ ; and for the sulfur analog,  $\text{CH}_3\dot{\text{C}}\text{HNCS}$ , with  $a_{\text{H}^\alpha} = 18.6$ ,  $a_{\text{H}^\beta} = 18.6$ ,  $a_{\text{N}} = 5.6$  G, and  $g = 2.0030$ . These radicals were obtained by the room-temperature X-irradiation of ethyl isocyanate and ethyl isothiocyanate trapped in adamantane. The corresponding radicals from propyl, isopropyl, butyl, and cyclopentyl isocyanates and isothiocyanates (except cyclopentyl isothiocyanate) were similarly obtained and their epr spectral parameters are reported herein. INDO and STO-3G calculations predict linear and bent planar structures, respectively, for the isocyanatomethyl radical, and the epr results are consistent with both structures or, as is more likely, with rapid interconversion. However, distortions from planarity are ruled out by lack of temperature dependencies of the  $\alpha$ -proton and nitrogen hyperfine splittings and by INDO calculations on the nonplanar forms.

The geometry of the isocyanate group in organic compounds of the general formula  $\text{RNCO}$  depends strongly on the nature of R. For example, methyl isocyanate and methyl isothiocyanate are nonlinear with CNC angles of  $125^\circ$  and  $142^\circ$ ,<sup>2</sup> respectively, while the corresponding silyl compounds are linear,<sup>3,4</sup> and phenyl isocyanate appears to have  $C_{2v}$  symmetry,<sup>5</sup> indicating a CNC angle of  $180^\circ$ . If the explanation for these structural differences is the existence of  $\pi$  bonding in the latter cases, an epr study of a  $\pi$  radical containing the isocyanate group could provide experimental support for this argument. Since the methyl radical is the simplest  $\pi$  radical known, a study of the isocyanate-substituted methyl radical would be desirable because of the ease of interpretation of the results.

If we consider the hypothetical formation of the isocyanatomethyl radical from methyl isocyanate by removal of a hydrogen atom, we can envision two distinct types of conjugation between the methyl radical so formed and the isocyanate group. In the first, the planar methyl radical could conjugate with the three-center  $\pi$  orbital of the isocyanate group to form a four-



center  $\pi$  orbital as shown in I. The result would be a planar but nonlinear radical retaining the CNC angle of methyl isocyanate since there is no "driving force" for

changing the angle. In the second case, the methyl radical could conjugate with the lone pair on nitrogen to form a two-center three-electron  $\pi$  bond as shown in II. This could result in a nonlinear and nonplanar geometry similar to that found for aminoalkyl radicals.<sup>6</sup> It is obviously difficult to choose between these alternatives for the structure and bonding in the isocyanatomethyl radical without some experimental evidence.

In this paper we wish to report that by use of the adamantane matrix technique,<sup>7</sup> five higher homologs of the isocyanatomethyl radical, and their sulfur analogs, have been prepared and studied by epr. To the best of our knowledge, no members of this class of free radical have previously been reported. In addition, we have calculated the geometry of the isocyanatomethyl radical by the INDO and STO-3G methods and have compared the hyperfine splitting constants calculated by the former method to the experimental values in order to elucidate the structure and bonding in these radicals.

## Experimental Section

The details of the sample preparation, X-irradiation, and computer program for fitting the experimental epr spectra have been described previously.<sup>6</sup> The Varian V-4547 variable-temperature accessory and general purpose rectangular TE<sub>012</sub> cavity with a previously calibrated copper-constantan thermocouple were used to obtain low-temperature spectra; the remainder of the epr spectrometer has been described previously.<sup>6</sup> All samples were X-irradiated at room temperature and the samples from isopropyl and cyclopentyl isothiocyanates were also X-irradiated at 77°K by immersion in a foam dewar filled with liquid nitrogen. The isocyanates and isothiocyanates, except as noted below, were obtained from Aldrich Chemical Co. and Eastman Organic Chemical Co. and were used as received.

**Cyclopentyl Isocyanate.** Cyclopentyl isocyanate was prepared from cyclopentyl iodide (Chemical Procurement Laboratories) and silver cyanate (Fisher) by a method analogous to that of Sandler and Karo for allyl isocyanate.<sup>8</sup> Silver cyanate (0.30 mol, 45.0 g) was finely ground and slowly added to cyclopentyl iodide (0.2 mol, 40 g) in 40 ml of benzene. After the addition was completed, the mixture was refluxed for 3 hr. The product was then filtered, the

\* Address correspondence to this author at the Department of Chemistry, University of Connecticut, Storrs, Conn. 06268.

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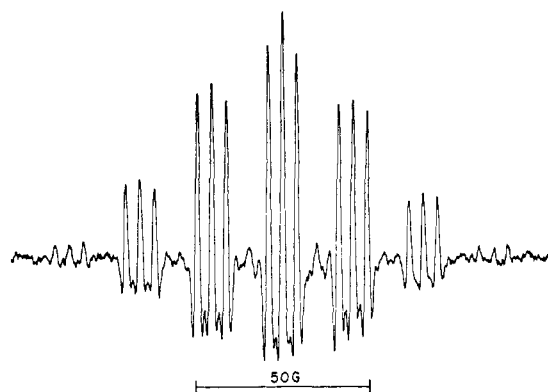


Figure 1. Second-derivative epr spectrum of the radical from isopropyl isocyanate.

filtrate was vacuum distilled, and a colorless distillate was collected [bp 61° (44 mm)]. (NOTE. This compound is a violent lachrymator.)

**Propyl, Isopropyl, and Cyclopentyl Isothiocyanates.** The alkyl isothiocyanates were prepared from the corresponding primary amines by the method of Moore and Crossley;<sup>9</sup> the preparation of propyl isothiocyanate is given in detail. A mixture of carbon disulfide (0.2 mol, 15 g) and sodium hydroxide (0.2 mol, 8 g, in 16 ml of H<sub>2</sub>O) was cooled to 10°. To this was added, with stirring, propylamine (Aldrich, 0.2 mol, 12 g, in 30 ml of H<sub>2</sub>O). The mixture was allowed to warm up to room temperature and methyl chloroformate (Eastman, 0.2 mol, 19 g) was added with stirring. The upper layer of the mixture was separated, dried over sodium sulfate, and vacuum distilled [bp 75° (40 mm)]. Analysis by high-resolution mass spectrometry confirmed propyl isothiocyanate. The other compounds were similarly prepared from isopropylamine (Fisher) and cyclopentylamine (Aldrich), and analyzed by mass spectrometry. Also, the former was shown by vpc to have ~0.3% isopropyl cyanide present as impurity.

The INDO method has been described previously<sup>10</sup> and has been used for a large systematic study of molecular geometries by Gordon and Pople.<sup>11</sup> The geometry optimization procedure used here is essentially that of Gordon and Pople, wherein the geometric parameters are varied in a stepwise fashion until the energy is minimized, each step involving optimization of the specified parameter using a three-point fit to a parabola. The initial grid size was 0.05 Å and 5° for bond lengths and bond angles, respectively, and was decreased to 0.01 Å and 2° for final scans. The procedure was continued until self-consistency was attained in both the geometry ( $\pm 0.002$  Å and  $\pm 0.2^\circ$ ) and energy ( $\pm 0.00001$  au). For radicals considered here, complete freedom was given to the geometry except that the NCO moiety was constrained to be linear. The application of INDO to the calculation of hyperfine coupling constants has been discussed previously.<sup>12</sup>

The *ab initio* STO-3G method of Hehre, Stewart, and Pople<sup>13</sup> has also been shown to be very successful in the prediction of molecular geometries.<sup>14</sup> The geometry optimization procedure used for STO-3G is the same as the above detailed method for INDO.

## Results

**Epr Results.** Isotropic epr spectra were obtained over the temperature range 180–300°K from ethyl, propyl, isopropyl, butyl, and cyclopentyl isocyanates and propyl isothiocyanate which had been X-irradiated at room temperature in an adamantane matrix. Room-temperature spectra only were obtained from ethyl

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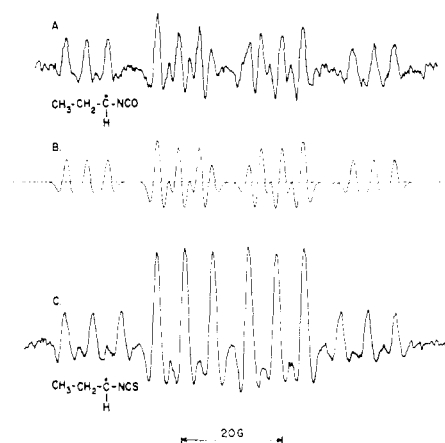



Figure 2. A. Second-derivative epr spectrum of the radical from *n*-propyl isocyanate. B. Computer simulation for (A). C. Second-derivative epr spectrum of the radical from *n*-propyl isothiocyanate.

and butyl isothiocyanates because of noticeably poorer S/N ratios in the case of their radicals. Isopropyl and cyclopentyl isothiocyanates when X-irradiated and observed at room temperature gave radicals identical with those obtained from the corresponding cyanides (e.g., isopropyl cyanide) X-irradiated in adamantane, probably due to small amounts of the cyanides present as impurities. Upon X-irradiation at 77°K and observation at room temperature, however, isopropyl isothiocyanate gave another radical which had spectral parameters similar to the other isothiocyanato-alkyl radicals and quite different from the cyanoalkyl radical. This second radical was studied at several different temperatures and is the one reported in this paper. Cyclopentyl isothiocyanate continued to give only the cyanoalkyl radical under these conditions.

The epr spectrum from isopropyl isocyanate shown in Figure 1 clearly displays the 1:6:15:20:15:6:1 septet of 1:1:1 triplets expected for six equivalent  $\beta$  protons split by a single <sup>14</sup>N nucleus, and the epr spectrum from cyclopentyl isocyanate consists of a 1:4:6:4:1 quintet of 1:1:1 triplets, showing the presence of four equivalent  $\beta$  protons. The hyperfine splittings could be measured directly from these spectra, but computer simulations were necessary for accurate analysis of the spectra from most of the other radicals. For example, the experimental epr spectrum of the radical from propyl isocyanate in Figure 2A is compared with its computer simulation in Figure 2B. The  $\alpha$ -proton hfs is found to be slightly larger than the  $\beta$ -proton hfs, resulting in considerable overlap of the lines. In contrast, the spectrum of the radical from propyl isothiocyanate, shown in Figure 2C, clearly results from accidentally equivalent  $\alpha$ - and  $\beta$ -proton hfs split by one nitrogen. Room-temperature epr spectral parameters for all the radicals are listed in Table I. Cyclohexyl isocyanate gave a spectrum almost certainly due to the expected isocyanatocyclohexyl radical, but the spectrum was characteristic of an intermediate rate of ring conformation interchange at room temperature and became anisotropic at lower temperatures. Therefore, the  $\beta$ -proton and <sup>14</sup>N hfs could not be obtained with as great accuracy as the other radicals and are not reported herein. The internal consistencies of the values in Table I indicate that the radicals obtained are

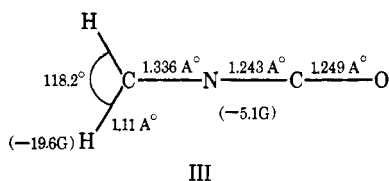
**Table I.** Epr Spectral Parameters of Isocyanatoalkyl and Isothiocyanatoalkyl Radicals in Adamantane at Room Temperature

Radical	Hyperfine splitting constants, G <sup>a</sup>				g value <sup>b</sup>
	$a_{\text{H}}^{\alpha}$	$a_{\text{H}}^{\beta}$	$a_{\text{N}}$		
CH <sub>3</sub> ĊHNCO	21.1	21.1	4.2		2.0026
CH <sub>3</sub> ĊHNCS	18.6	18.6	5.6		2.0030
CH <sub>3</sub> CH <sub>2</sub> ĊHNCO	20.4	18.1	4.1		2.0027
CH <sub>3</sub> CH <sub>2</sub> ĊHNCS	18.0	18.0	5.5		2.0033
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ĊHNCO	20.4	18.4	4.2		2.0029
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ĊHNCS	18.1	19.7	5.6		2.0031
CH <sub>3</sub> Ċ(CH <sub>3</sub> )NCO		20.3	4.1		2.0028
CH <sub>3</sub> Ċ(CH <sub>3</sub> )NCS		18.0 ± 0.2	5.9 ± 0.2		2.0029 <sup>c</sup>
		28.8	4.2		2.0028

<sup>a</sup> Accuracy ±0.1 G except as noted. <sup>b</sup> Based on  $g_{\text{DPPH}} = 2.0036$ ; accuracy ±0.0002. <sup>c</sup> Accuracy ±0.0004.

the expected isocyanatoalkyl and isothiocyanatoalkyl radicals formed by removal of an  $\alpha$ -hydrogen atom. The hfs and  $g$  values of the radicals were independent of temperature with the exception of the radical from butyl isocyanate which exhibited a classic example of line-width alternation. This is demonstrated in Figure 3 where the "two-intensity" lines from the  $\beta$ -proton 1:2:1 triplet are seen to gradually broaden below room temperature, finally disappear, and then start to come back as two "one-intensity" lines which are the result of the  $\beta$ -proton inequivalence at the lowest temperatures. The average  $\beta$ -proton hfs in this radical has a linear temperature dependence over the range 200–300°K with a slope of  $-9.9 \times 10^{-3} \text{ G/}^\circ\text{K}$ .

**INDO Results.** Energy optimization by INDO of all the geometric parameters in the isocyanatomethyl radical results in a minimum energy for the structure of  $C_{2v}$  symmetry shown in III. Hyperfine coupling



constants calculated by INDO for  $^{14}\text{N}$  and  $^1\text{H}$  are given in parentheses. Calculated  $\pi$ -orbital (perpendicular to the plane of the radical) spin densities are listed in Table II. Spin densities in the other orbitals

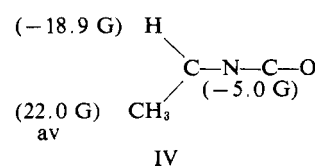
**Table II.** Calculated  $\pi$ -Orbital Spin Densities for Isocyanatoalkyl and Isothiocyanatoalkyl Radicals

Geometry used	Method of spin density calculation	Atom			
		C	N	C	O(S)
Structure III	INDO	0.75	-0.10	0.13	0.22
Structure V	STO-3G	0.88	-0.28	0.22	0.18
Structure V	INDO	0.81	-0.07	0.12	0.14
a	STO-3G	0.81	-0.34	0.29	(0.19)

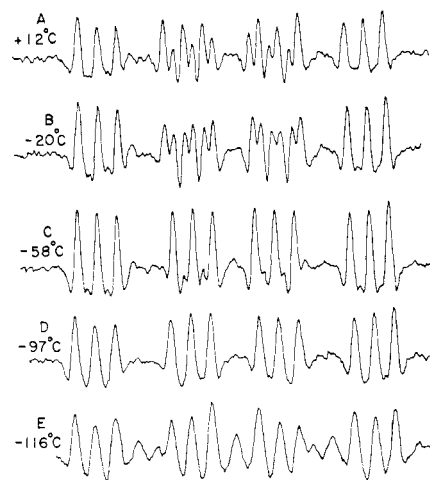
<sup>a</sup> The geometry used for CH<sub>2</sub>NCS was that of structure V, with the experimental CNC angle and CS bond distance from methyl isothiocyanate.

are smaller by an order of magnitude. The geometry III was then used for calculations of the hfs in isocyanatoethyl radical by replacement of one of the hydrogen atoms by a methyl group with standard geometry (C-C = 1.52 Å, C-H = 1.09 Å, and  $\angle\text{HCH} = 109^\circ 28'$ ). The hfs were calculated at intervals of  $30^\circ$

of the dihedral angle  $\theta$  measured between the methyl group C-H bond and the perpendicular to the plane of the radical. The hfs were then averaged over all  $\theta$  with the results given in IV. The calculated  $\alpha$ -proton and



nitrogen hfs are seen to be slightly reduced relative to the isocyanatomethyl radical as would be expected upon replacement of a proton with a methyl group. The calculated  $\beta$ -proton hfs were found to very closely follow the  $\cos^2 \theta$  relation which has previously been demonstrated for unsubstituted alkyl radicals.<sup>15</sup> For the

**Figure 3.** Temperature-dependent second-derivative epr spectra of the radical from *n*-butyl isocyanate.

parent methyl isocyanate, CH<sub>3</sub>NCO, INDO gave a minimum energy for a linear C-N-C-O structure, which is at variance with the experimental results.<sup>1</sup>

**STO-3G Results.** Energy optimization by STO-3G gave for the isocyanatomethyl radical the planar but nonlinear structure shown in V. INDO was used to calculate hyperfine coupling constants for this geometry since the STO-3G program does not include a hyperfine coupling routine. The results are shown in V in parentheses. The  $\pi$ -orbital spin densities obtained

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