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

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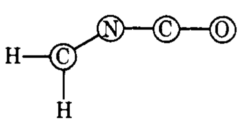
Abstract: Several members of the previously unknown class of isocyanatoalkyl and isothiocyanatoalkyl radicals have been prepared and studied by epr by use of the adamantane matrix technique. Typical parameters for these radicals are exemplified by the results for isocyanatoethyl radical, $CH_3\dot{C}HNCO$, with $a_H^\alpha = 21.1$, $a_H^\beta = 21.1$, $a_N = 4.2$ G, and $g = 2.0026$; and for the sulfur analog, $CH_3\dot{C}HNCS$, with $a_H^\alpha = 18.6$, $a_H^\beta = 18.6$, $a_N = 5.6$ 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 α-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 RNCO depends strongly on the nature of R. For example, methyl isocyanate and methyl isothiocyanate are nonlinear with CNC angles of 125[1] and 142°,[2] respectively, while the corresponding silyl compounds are linear,[3,4] and phenyl isocyanate appears to have C_{2v} symmetry,[5] indicating a CNC angle of 180°. If the explanation for these structural differences is the existence of π bonding in the latter cases, an epr study of a π radical containing the isocyanate group could provide experimental support for this argument. Since the methyl radical is the simplest π 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 π orbital of the isocyanate group to form a four-center π 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 π bond as shown in II. This could result in a nonlinear and nonplanar geometry similar to that found for aminoalkyl radicals.[6] It is obviously difficult to choose between these alternatives for the structure and bonding in the isocyanatomethyl radical without some experimental evidence.



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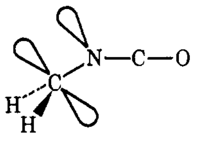

II

In this paper we wish to report that by use of the adamantane matrix technique,[7] 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.[6] The Varian V-4547 variable-temperature accessory and general purpose rectangular TE_{012} 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.[6] 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.[8] 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

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(1) E. H. Eyster, R. H. Gillette, and L. O. Brockway, *J. Amer. Chem. Soc.*, **62**, 3236 (1940).

(2) C. I. Beard and B. P. Dailey, *ibid.*, **71**, 927 (1949).

(3) E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 4844 (1962); M. C. L. Gerry, J. C. Thompson, and T. M. Sugden, *Nature (London)*, **211**, 846 (1966).

(4) D. R. Jenkins, R. Kewley, and T. M. Sugden, *Trans. Faraday Soc.*, **58**, 1284 (1962); E. A. V. Ebsworth, R. Mould, R. Taylor, G. R. Wilkinson, and L. A. Woodward, *ibid.*, **58**, 1069 (1962).

(5) C. V. Stephenson, W. C. Coburn, Jr., and W. S. Wilcox, *Spectrochim. Acta*, **17**, 933 (1961).

(6) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).

(7) D. E. Wood and R. V. Lloyd, *ibid.*, **52**, 3840 (1970).

(8) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Academic Press, New York, N. Y., 1968, p 309.

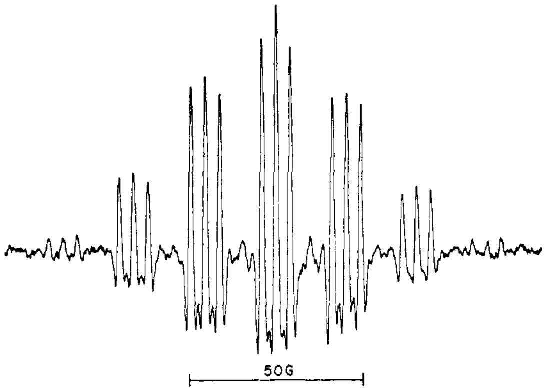

Figure 1. Second-derivative epr spectrum of the radical from isopropyl isocyanate.

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;[9] 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_2O) was cooled to 10°. To this was added, with stirring, propylamine (Aldrich, 0.2 mol, 12 g, in 30 ml of H_2O). 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[10] and has been used for a large systematic study of molecular geometries by Gordon and Pople.[11] 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 (±0.002 Å and ±0.2°) and energy (±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.[12]

The *ab initio* STO-3G method of Hehre, Stewart, and Pople[13] has also been shown to be very successful in the prediction of molecular geometries.[14] 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 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 isothiocyanatoalkyl 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.

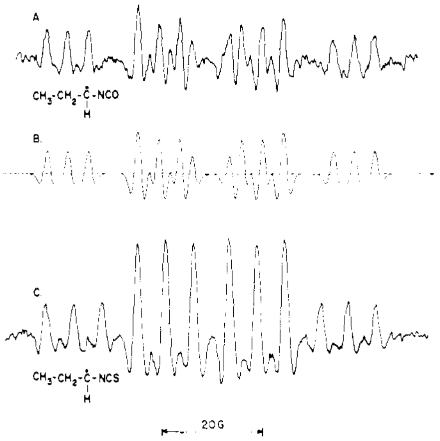

Figure 2. A. Second-derivative epr spectrum of the radical from *n*-propyl isocyanate. B. Computer simulation for (A). C. Second-derivative epr spectrum of the radical from *n*-propyl isothiocyanate.

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 β protons split by a single ^{14}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 β 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 α-proton hfs is found to be slightly larger than the β-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 α- and β-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 β-proton and ^{14}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

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(9) M. L. Moore and F. S. Crossley, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 599.

(10) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

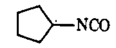
(11) M. S. Gordon and J. A. Pople, *ibid.*, 49, 4643 (1968).

(12) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

(13) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(14) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **52**, 4064 (1970).

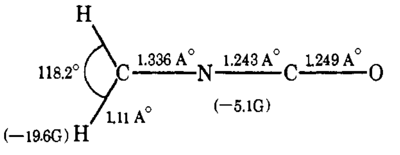
Table I. Epr Spectral Parameters of Isocyanatoalkyl and Isothiocyanatoalkyl Radicals in Adamantane at Room Temperature

Radical	Hyperfine splitting constants, G[a] a_H^α	a_H^β	a_N	g value[b]
$CH_3\dot{C}HNCO$	21.1	21.1	4.2	2.0026
$CH_3\dot{C}HNCS$	18.6	18.6	5.6	2.0030
$CH_3CH_2\dot{C}HNCO$	20.4	18.1	4.1	2.0027
$CH_3CH_2\dot{C}HNCS$	18.0	18.0	5.5	2.0033
$CH_3CH_2CH_2\dot{C}HNCO$	20.4	18.4	4.2	2.0029
$CH_3CH_2CH_2\dot{C}HNCS$	18.1	19.7	5.6	2.0031
$CH_3\dot{C}(CH_3)NCO$		20.3	4.1	2.0028
$CH_3\dot{C}(CH_3)NCS$		18.0 ± 0.2	5.9 ± 0.2	2.0029[c]
		28.8	4.2	2.0028

[a] Accuracy ±0.1 G except as noted. [b] Based on $g_{DPPH} = 2.0036$; accuracy ±0.0002. [c] Accuracy ±0.0004.

the expected isocyanatoalkyl and isothiocyanatoalkyl radicals formed by removal of an α-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 β-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 β-proton inequivalence at the lowest temperatures. The average β-proton hfs in this radical has a linear temperature dependence over the range 200–300°K with a slope of -9.9×10^{-3} G/°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}N and ^1H are given in parentheses. Calculated π-orbital (perpendicular to the plane of the radical) spin densities are listed in Table II. Spin densities in the other orbitals 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 ∠HCH = 109° 28′). The hfs were calculated at intervals of 30° of the dihedral angle θ measured between the methyl group C–H bond and the perpendicular to the plane of the radical. The hfs were then averaged over all θ with the results given in IV. The calculated α-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 β-proton hfs were found to very closely follow the $\cos^2 \theta$ relation which has previously been demonstrated for unsubstituted alkyl radicals.[15] For the parent methyl isocyanate, CH_3NCO, INDO gave a minimum energy for a linear C–N–C–O structure, which is at variance with the experimental results.[1]



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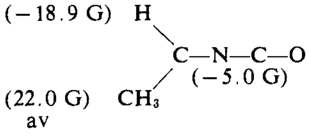

IV

Table II. Calculated π-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)

[a] The geometry used for CH_2NCS was that of structure V, with the experimental CNC angle and CS bond distance from methyl isothiocyanate.

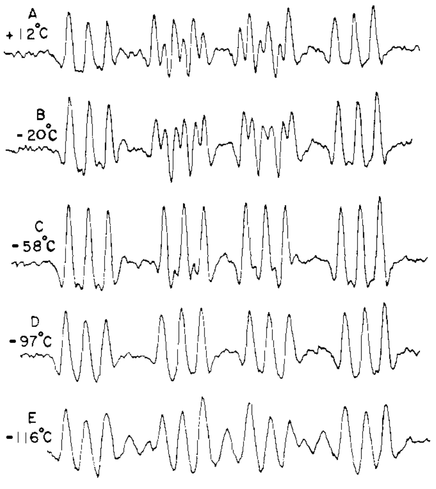

Figure 3. Temperature-dependent second-derivative epr spectra of the radical from *n*-butyl isocyanate.

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 π-orbital spin densities obtained

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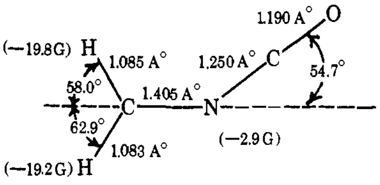
(15) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 37, 1326 (1962).



V

for this geometry by the two methods are also given in Table II. Finally, the barrier to interconversion of the -NCO group between its two equilibrium forms was calculated by STO-3G to be 3.2 kcal/mol, assuming a linear form for the intermediate. For the parent methyl isocyanate, STO-3G indicates a bent structure in accord with experiments,[1] although a complete minimization was not performed.

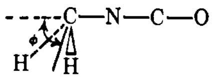
Discussion

Both the INDO and STO-3G geometries yield hyperfine splitting constants in very good agreement with those experimentally observed in the isocyanatoalkyl radicals. The INDO geometry has C_{2v} symmetry, but the parent methyl isocyanate is also calculated to be linear by this method. In contrast, the STO-3G calculations yield nonlinear geometries for both radical and parent molecule, although both methods predict isocyanatomethyl to be a π radical, as shown by the π-orbital spin densities listed in Table II. The disagreement in geometries is somewhat surprising, since the two methods have previously been shown to give the same geometry for the CH_2NH_2 radical.[6] Since STO-3G gives the correct geometry for methyl isocyanate, and since it is an *ab initio* method requiring no empirical assumptions, we believe that the nonlinear structure for the isocyanatomethyl radical is a more reliable prediction.

The facts that the α-proton and nitrogen hfs are nearly the same for all of the radicals in each of the two groups studied and that these hfs have virtually no temperature dependence show that the structure of the radicals is not seriously affected by the nature of the alkyl groups bonded to the α carbon and suggest that the simplest radicals (isocyanatomethyl and isothiocyanatomethyl) represent good models for each series. The epr results alone do not indicate any deviation from C_{2v} symmetry for any of the radicals. For example, the methyl groups in each of the isopropyl radicals and the β protons in the isocyanatocyclopentyl radical are equivalent within the experimental resolution (~0.2 G), which would *initially* appear to eliminate the possibility of structure I. The latter equivalence also eliminates structure II for the isocyanatoalkyl radicals since this deviation from planarity would lead to two pairs of equivalent β protons unless the radical were rapidly inverting between two equilibrium positions (*i.e.*, had time-averaged C_{2v} symmetry). The isocyanatobutyl radical does, however, show a β-proton temperature dependence, with inequivalent β protons at sufficiently low temperatures, probably because the size limitation of the "cage" in the adamantane matrix forces the radical to fold into a particular conformation.

Comparison of the calculated α-proton and nitrogen hfs given in III and V for the two different planar geometries of CH_2NCO shows that the in-plane distortion of the C–N–C–O axis from linearity has essentially no effect on the $a_H{}^\alpha$, and the values for a_N both differ from the experimental values by less than the ~2-G accuracy expected from INDO.[10] Probably the higher homologs of isocyanatomethyl would be even less affected. Thus, a definite choice between structures III and V cannot be made by epr alone.

However, the possibility of nonplanarity at the α carbon, as in structure VI, can be eliminated as follows. The variation of $a_H{}^\alpha$ in isocyanatomethyl with the degree of nonplanarity, ϕ, of the α protons was calculated by INDO to be -20 to $+4$ G over the range of ϕ from 0 to 60°, where ϕ is defined as the angle between the HCH bisector and the linear C–N–C–O axis. Because of the large dependence of $a_H{}^\alpha$ on ϕ, we can estimate that the maximum deviation from planarity consistent with our experimental results is $<10°$. Since this represents a conservative upper limit to nonplanarity at the α carbon, we have little doubt that the actual degree of nonplanarity is essentially zero.



VI

As can be seen by comparison of each isocyanatoalkyl radical with its sulfur analog in Table I, the effect of the substitution of sulfur for oxygen is to decrease $a_H{}^\alpha$ and increase a_N and the g value. The increase in g value is to be expected because of the considerably larger spin–orbit coupling constant for sulfur than for oxygen.[16] The observed differences in hfs indicate a shift of spin density away from the α carbon toward the sulfur end of the radical. Comparisons of the spin densities calculated by STO-3G for CH_2NCO and CH_2NCS which are listed in Table II show that the expected changes in spin density are adequately reproduced. Qualitatively, these results reflect the fact that oxygen is more electronegative than sulfur. This effect of an electronegative substituent repelling spin density has been noted before in the azabenzyl radicals.[17]

Conclusion

Theoretical calculations of the isocyanatomethyl radical by the INDO and STO-G3 methods indicate that it is a planar π radical. Epr studies of the isocyanatoalkyl and isothiocyanatoalkyl radicals are consistent with such a structure. The possibility that the radicals are nonplanar is definitely eliminated, but it is likely that rapid interconversion occurs between two equivalent planar forms with CNC angles of less than 180°. The α-proton and nitrogen hfs in the sulfur radicals *vs.* those in their oxygen analogs show the effects to be expected due to the higher spin–orbit coupling constant and lower electronegativity of sulfur compared with oxygen.

Acknowledgments. The authors take great pleasure in thanking Professor D. W. Pratt for suggesting that we try our adamantane technique on isocyanates, Professor John A. Pople for several interesting discussions, and Dr. Warren J. Hehre for his assistance with some of the calculations. This research was partially funded by NSF Grant No. GP9338.

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(16) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 138.

(17) R. V. Lloyd and D. E. Wood, *Mol. Phys.*, **20**, 735 (1971).