(b) Sterically hindered oximes give rise to derivatives of hydroxamic acids, which can account for type iii radicals. (c) Partly hindered oximes give mixtures of both types of compounds and, as expected for our bicyclic oximes I, III, V, VII, VIII, X, XI, and XII, nitroxides of both types i and iii appear.

Experimental Section

Oxidized Samples. The nitroxides were prepared in the sample tube by mixing the reagents (oxime and lead tetraacetate) in benzene at room temperature.

Irradiated Samples. A 500-Ci ^{60}Co γ-ray source was employed for the irradiation of powder samples of oximes. Dosages of the order of 5×10^5 to 2×10^6 rads were given. The irradiation, storage, and epr measurements were carried out at room temperature. To eliminate the virtual influence of oxygen, a series of samples was evacuated to 10^{-6} Torr and sealed off before irradiating. No differences have been noticed as compared with samples irradiated at air pressure. The epr spectra of the powder samples were recorded at different time intervals and the evolution of the spectra (Figure 2) was followed. The solution spectra are obtained by dissolving the samples in benzene.

Epr Spectra. All epr spectra were recorded on a JES-3B (Jeolco) spectrometer with 100-kHz field modulation using X- as well as K-band frequencies. The hfs constants and g factors were measured by comparison with potassium peroxylamine disulfonate ($a_N = 13.0$ G, $g = 2.0055$).

Identification of Some Final Products. (a) 9-Acetoxy-9-nitrosobicyclo[3.3.1]nonane (XX). The oxidation of I (which was available in adequate quantity) was carried out on a preparative scale by adding small portions of lead tetraacetate to a benzene solution of oxime, under continuous stirring at room temperature. A blue-green solution (A) was formed from which XX was separated after liquid–liquid, column chromatography and tlc fractionation. From the 12 compounds so isolated, XX was identified by its specific ir ($\nu_{C=O}$ 1750, $\nu_{C-C=O}$ 1250, and ν_{C-O} 1060 cm^{-1} for the acetoxy group and $\nu_{N=O}$ 1550 cm^{-1} for the nitroso group) and visible ($\lambda_{N=O}$ 680 nm) absorption bands. With the reaction mixtures of the other oximes, a similar visible absorption band is always found.

The following procedure leads to the isolation of XX. The solvent was removed from A and the fraction (B) soluble in petroleum ether (30–60°) at room temperature was extracted; B was then passed over a silica gel (BDH) column and the benzene eluate (C) was retained. C was chromatographed again on an alumina (Merck, according to Brockmann) column, the fraction (D) eluted by petroleum ether being then concentrated to a blue-green oil. This was separated by preparative tlc on chromatoplates coated with a 500-μ thick layer of silica gel H (Merck, according to Stahl) which were activated at 110° and developed with a 5:3.5:1:0.5 (v/v/v/v) mixture of petroleum ether–toluene–acetone–methanol.

(b) Bicyclo[3.3.1]nonan-9-one. This ketone was separated by tlc directly from the reaction mixture using the pure ketone as internal and external standard. The identity of the ketone was then checked by its ir and uv spectra.

(c) Nitrous Gases. Brown vapors were observed to evolve from the reaction mixture. A filter paper moistened with a sulfuric acid solution of diphenylbenzidine turned blue when held in these vapors. This reaction was attributed to the nitrous gases, as other oxidizing gaseous products are not expected.

Acknowledgments. The derivatives of bicyclo[3.3.1]nonane, bicyclo[4.2.1]nonane, and bicyclo[3.2.1]octane were kindly supplied by Professor M. Hartmann, and the tricyclo[7.3.1.0^{2,7}]tridecane derivatives by Professor N. Bărbulescu, to whom we are very grateful. In addition, we wish to thank Mrs. Simona Badilescu for the ir spectra.

Molecular-Beam Microwave Spectra of HNCO and DNCO

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Abstract: Deuteron quadrupole coupling in DNCO was obtained from splittings of the 1_{01} rotational state. The measured quadrupole coupling strength for the 1_{01} rotational state is $eqQ(1_{01}) = 53.6 \pm 0.2$ kHz, which leads to a value along the D–N bond $eqQ_{DN} = 345 \pm 2$ kHz. Hyperfine splittings were observed using a molecular-beam maser spectrometer with 6-kHz resolution. The nitrogen quadrupole coupling strengths were $eqQ(1_{01}) = 2123.0 \pm 1.0$ kHz for DNCO and $eqQ(1_{01}) = 2052.7 \pm 1.0$ kHz for HNCO. High-precision values for the line-center frequencies and spin–rotation constants are also reported.

Quadrupole coupling strengths, dipole moments, and molecular quadrupole moments provide detailed information about the electronic structure of molecules. For simple molecules, we can obtain precise values for these parameters using molecular-beam maser spectroscopy.

HNCO (isocyanic acid) is a slightly asymmetric top with a nearly linear configuration. Other similar molecules are HNCS (isothiocyanic acid), HN_3 (hydrogen azide), and, of recently determined structure,[1] HCNO (fulminic acid). The heavy atoms of all of these molecules are rigidly held in a straight line, and the hydrogen atom is displaced off this axis. The structure for HNCO was first determined by Jones, Shoolery, Shulman, and Yost.[2] The structure was obtained from infrared data by Reid and Herzberg.[3,4] Jones, *et al.*, determined the structure of the molecule from a combination of microwave transitions for HNCO and DNCO and the assumption that the atoms N, C, and O were in a straight line. A series of higher frequency transitions of HNCO and DNCO in the range 80–150 GHz were reported by Kewley, Sastry, and Winne-

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wisser.[5] Their data implied that the transition frequency for the $0_{00} \rightarrow 1_{01}$ transition for DNCO, reported by Jones, *et al.*, to be 20,394.7 MHz, actually occurred at 20,393.28 MHz. Our measurements have confirmed this.

The rotational constant about the *a* axis for these molecules is extraordinarily high (956,400 MHz for HNCO, 534,000 MHz for DNCO[5]). This gives rise to resolvable P-, R-, and Q-branch splittings in the infrared spectra. High-resolution far-infrared spectra and discussion of centrifugal distortion in HNCO and related molecules are given by Krakow, Lord, and Neely.[6] This also makes these molecules favorable for beam maser spectroscopy, since the partition function is nearly the same as for a linear molecule. Therefore, a large fraction of the molecules are in the lower *J* levels.

Splittings due to deuterium quadrupole coupling are relatively small, and very high resolution is required to observe them. The molecular-beam maser spectrometer provides significantly better resolution and accuracy than other techniques and so is well suited to these measurements. Other molecules whose rotational hyperfine spectra have been observed with the maser include NH_2D,[7] CF_3D,[8] and formic acid.[9] In these cases splittings arising from deuterium quadrupole coupling were completely resolved.

Experimental Section

HNCO was prepared by thermal dissociation of the trimer cyanuric acid. This was accomplished by refluxing the trimer in silicone oil and collecting the product on a trap at 77°K. The yield was low ($<10\%$), but other methods such as treating KNCO with sulfuric acid were less effective. In order to prepare DNCO the trimer was kept in refluxing D_2O overnight for two exchanges and dried by heating under vacuum.

The $1_{01} \rightarrow 0_{00}$ transitions in HNCO and DNCO were observed using a molecular-beam maser spectrometer. The spectrometer has been described previously.[10] Beam source pressure was near 20 Torr for these measurements and was maintained by controlling the temperature of the liquid sample.

All three transitions were observed in HNCO with high signal-to-noise ratio. The large splitting was caused by the nitrogen quadrupole coupling. No structure on these lines due to hydrogen spin-rotation or hydrogen-nitrogen spin-spin interactions was observed for HNCO. The resonance line width (fwhm) was 6 kHz. Two of the three transitions in DNCO showed clearly resolved splittings due to the deuterium quadrupole coupling. Recorder traces for the transition observed in DNCO are shown in Figure 1. The observed transition frequencies are listed in Table I.

Table I. Observed Transition Frequencies in HNCO and DNCO[a]

Molecule	F_1'	F'	Frequency
HNCO	0		21, 980, 545.34
	2		21, 981, 470.55
	1		21, 982, 085.35
DNCO	0		20, 392, 314.60
	2	3	30, 393, 270.18
	2	2	20, 393, 281.93
	1	1	20, 393, 901.83
	1	2	20, 393, 909.20
	1	0	20, 393, 921.63

[a] Frequencies are in kilohertz. Transitions are $1_{01} \rightarrow 0_{00}$ rotational transitions. F_1' is for the $J = 1$ state ($F_1 = 1$ for the 0_{00} state).

Theory

The Hamiltonian for the hyperfine structure of cyanic acid may be expressed as

$$H = H_Q(\mathrm{D}) + H_Q(\mathrm{N}) + H_{SR}(\mathrm{H}) + H_{SR}(\mathrm{N}) + H_{SS}(\mathrm{H,N}) \quad (1)$$

The coupling scheme for this description of the interaction energy is

$$\bar{F}_1 = \bar{I}_N + \bar{J} \qquad \bar{F} = \bar{F}_1 + \bar{I}$$

These terms are relatively standard and have been discussed previously.[7] The subscript SR refers to spin–rotation interaction and SS to spin–spin interaction. The quadrupole terms are defined explicitly below in order to avoid possible ambiguity in the definition of the coupling strength.

$H_Q(\mathrm{N})$ = nitrogen quadrupole interaction energy =

$$\frac{1}{4}(eq_JQ)_N[J(J+1)(2J+1)/(2J+3) \times (2J-1)]^{1/2}(-1)^{J+I_N+F_1}[(2I_N+1)(2I_N+3) \times (I_N+1)/I_N(2I_N-1)]^{1/2}\begin{bmatrix} F_1 & I_N & J \\ 2 & J & I_N \end{bmatrix} \quad (2)$$

$(eq_JQ)_N$ = strength of nitrogen quadrupole interaction.

$$q_J = \sum_g V_{gg}\langle J_g^2\rangle/J(J+1) \quad (3)$$

where the subscript *g* refers to one of the principal axes of inertia of the molecule (*a*, *b*, or *c*) and $\langle J_g^2\rangle$ is the average value of the square of the rotational angular momentum directed along that axis in a given rotational state. For a 1_{01} rotational state

$$\langle J_a^2\rangle = 0, \quad \langle J_b^2\rangle = \langle J_c^2\rangle = 1 \quad (4)$$

$$H_Q(\mathrm{D}) = \frac{1}{4}(eq_JQ)_D[J(J+1)(2J+1)/(2J+3) \times (2J-1)]^{1/2}(-1)^{J+I_H+I_N+F+2F}[(2F'+1) \times (2F+1)]^{1/2}\begin{bmatrix} J & F_1' & I_N \\ F_1 & J & 2 \end{bmatrix}\begin{bmatrix} F & I_H & F_1' \\ 2 & F & I_H \end{bmatrix}[(2I+1) \times (2I+3)(I+1)/I(2I-1)]^{1/2} \quad (5)$$

$(eq_JQ)_D$ = deuteron quadrupole interaction strength.

Owing to the presence of the large nitrogen nuclear quadrupole interaction, the coupling of the nitrogen spin to the molecular rotation is quite strong. Therefore the quantum number F_1 is a reasonably "good" quantum number, and the interaction energies are dominated by the diagonal matrix elements. The energies are therefore computed by treating the off-diagonal elements in F_1 as perturbations to the diagonal elements. Second-order terms are small (~0.1 kHz) but are included in the analysis. The same scheme was adopted in treating terms off diagonal in F_1 that involved the deuteron. Terms involving the hydrogen spin were not resolvable in the spectrum of HNCO, and the spectrum is adequately explained by the nitrogen quadrupole and nitrogen spin-rotation energies only. It was found necessary in the case of DNCO to include the nitrogen–deuteron spin–spin interaction $H_{ss}(\mathrm{N, D})$ calculated from the geometry of the molecule.

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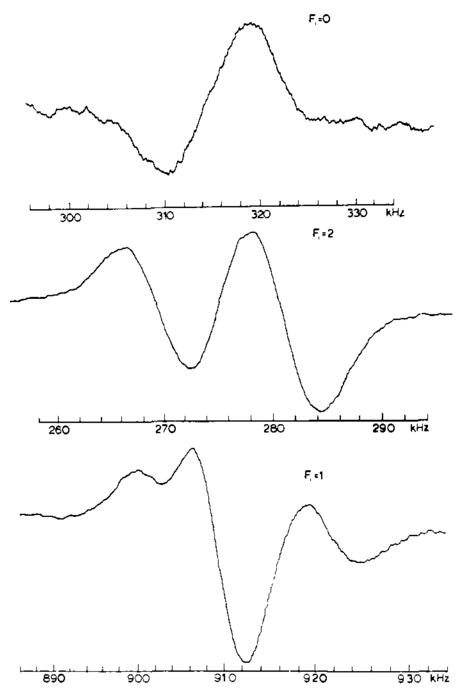

Figure 1. Recorder traces of the components of the $1_{01} \rightarrow 0_{00}$ transition in DNCO. Frequencies of $F_1 = 0$ components (upper trace) are relative to 20,392,000 kHz. Frequencies of $F_1 = 2$ components (middle trace) and $F_1 = 1$ components (lower trace) are relative to 20,393,000 kHz.

Analysis of Data

The interactions included in the Hamiltonian for the analysis of these data were the nitrogen quadrupole interaction (strength Q_N), the deuteron quadrupole interaction (strength Q_D), the nitrogen spin–rotation (C_N) interaction, the hydrogen spin–rotation interaction (C_H or C_D), and finally the hydrogen–nitrogen spin–spin interaction (D_{HN} or D_{DN}). The spin–spin interaction strength may be calculated from the geometry of the molecule, since electron-coupled terms are too small to be observed in this experiment (see ref 11). The remaining interaction strengths must be determined by fitting the observed transition frequencies. This was done in two steps. First, the splittings of each F_1 level of DNCO were analyzed to determine Q_D and C_D and the center frequency for that level; then the center frequencies were analyzed to find Q_N and C_N.

The observed splittings and the dependence of the splittings on Q_D (quadrupole coupling strength) and C_D (spin–rotation interaction strength) are listed in Table II. δ_{ss} is the contribution to that splitting due to the deuteron–nitrogen spin–spin interaction and δ_{OD} is the contribution to the splitting due to deuteron quadrupole coupling matrix elements off diagonal in F_1'. We note that the first and last entry have the same dependence on Q_D and C_D. When the δ terms are subtracted, the modified splittings are 11.80 and 11.81 kHz. This excellent agreement indicates that the measurements are quite accurate. The accuracy of the line positions is ~0.5 kHz, but we determine the splittings to much higher accuracy. The splittings listed in Table II are fit very well by the parameters listed in Table III.

Table II. Observed Splittings of F_1' States in DNCO Spectrum[a]

Splitting	F_1'	F_{upper}	F_{lower}	δ_{SS}	δ_{OD}	C^b (Q_D)	C^c (C_D)
12.43	1	0	2	0.71	−0.08	0.225	1.5
7.36	1	2	1	−0.48	0.31	0.15	−1.0
11.66	2	2	3	−0.07	−0.08	0.225	1.5

[a] Frequencies are in kilohertz. δ_{SS} and δ_{OD} are the contributions to that splitting from the deuteron–nitrogen spin–spin interaction and terms off diagonal in F_1'. [b] Dependence of the splitting on interaction strength Q_D. [c] Dependence of the splitting on interaction strength C_D.

Table III. Interaction Strength and the Centers Determined from Splittings in Table II and Analysis of F_1' Line Centers[a]

Parameter	Value
Q_D	53.6 ± 0.2
C_D	0.76 ± 0.1
F_1' = 2(line center)	20, 393, 272.88 ± 0.5
F_1' = 1(line center)	20, 393, 907.85 ± 0.5
Q_N(DNCO)	2, 123.0 ± 1.0
C_N(DNCO)	0.55 ± 0.2
Q_N(HNCO)	2052.7 ± 1.0
C_N(HNCO)	0.50 ± 0.2

[a] Values in kilohertz.

We now carry out the second step and determine the interaction strengths Q_N and C_N. The values of these are also listed in Table III. The difference in the values of the nitrogen quadrupole coupling strength arises when the principal inertial axes in DNCO are rotated by 1.5° from the principal inertial axes in HNCO. We need one more measurement on a different rotational state in order to completely determine the field-gradient tensor. There are three unknowns, two principal values of the field gradient tensor and the angle between principal inertial axes and principal axes of the field gradient (sum of the gradients = 0 due to Laplace's equation).

We may assume that the deuteron quadrupole coupling tensor is cylindrically symmetric about the D–N bond axis and obtain a value for the quadrupole coupling in this direction. The angle between the *a* axis and the D–N bond is 48° 37′ as determined from the structure, so the quadrupole coupling strength along the bond axis is 345 ± 2 kHz.

It is interesting to compare this figure to the H–N stretching force constant using the theory of Salem.[12] The value of *eq* determined from the quadrupole coupling is 8.26×10^5 dyn/cm. This value may be compared with the stretch constant *k* from infrared work. Venkateswarlu and Thirugnanasambandam[13] obtain an H–N stretch constant of 6.75×10^5 dyn/cm from a normal-coordinate analysis of the fundamental infrared transitions. A value of 6.90×10^5 dyn/cm was obtained by Thomas[14] from infrared work. It was noted previously[8] that *eq* from quadrupole coupling and the force constant *k* are in excellent agreement for NH_2D. In formic acid[8] the force constants were smaller than *eq* by about 20%.

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