

SYNTHESIS AND UNUSUAL NMR SPECTRA OF 4,4'-DINITRO-3,3'-BIFURAZANYL-4,4'-<sup>13</sup>C \*

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SUMMARY

The synthesis of 4,4'-dinitro-3,3'-bifurazanyl-4,4'-<sup>13</sup>C was accomplished starting with sodium cyanide-<sup>13</sup>C and dichloroglyoxime. The carbon-13 NMR spectrum of the product consists of a 1,1,1-triplet and the nitrogen-14 NMR spectrum contains a sharp doublet with the same coupling constant as the carbon-13 triplet.

Key Words: 4,4'-Dinitro-3,3'-bifurazanyl, Carbon-13, Nitrogen-14, NMR spectra.

INTRODUCTION

The synthesis of 4,4'-dinitro-3,3'-bifurazanyl (DNBF) was first reported in a communication from this Laboratory in 1968 (1). At that time, we did not obtain a carbon-13 NMR spectrum of the compound because we had no carbon-13 NMR facilities. Our recent interest in evaluating DNBF for certain explosives applications led us to the present study.

DISCUSSION

The natural abundance carbon-13 NMR spectrum of DNBF was found to consist of a well-defined triplet and a singlet (Table I), rather than two singlets as expected. In addition, the nitrogen-14 NMR spectrum contained a sharp singlet with a resonance half-height width of 12.2 Hz in the position expected for a nitro nitrogen. These results suggested that the nitro nitrogen-14, which has a spin of 1, was coupling with the carbon-13 to give the triplet. In order to observe splitting of the observed magnitude, both the carbon-13 and the nitrogen-14 must have very long relaxation times (2). In addition, the nitrogen-14 must have a very symmetrical environment to diminish

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Table I. NMR Spectral Data

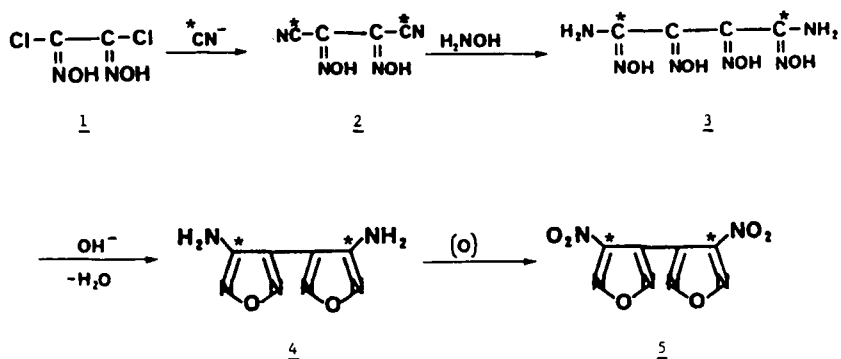
Compound	<sup>13</sup> C Chemical Shifts (ppm) <sup>a</sup>	<sup>14</sup> N Chemical Shifts (ppm) <sup>b</sup>	J <sub>C-N</sub> (Hz)	Solvent
Dicvanoqlyoxime	107.5 (s,CN) 127.4 (s,C=NOH)			DMSO-d <sub>6</sub>
Dicvano- <sup>13</sup> C <sub>2</sub> -qlyoxime	107.4 (s,CN)			DMSO-d <sub>6</sub>
1,4-Diamino-1,2,3,4-tetraoximinobutane	143.8 (s, 2,3-C) 147.3 (s, 1,4-C)			DMSO-d <sub>6</sub>
1,4-Diamino-1,2,3,4-tetraoximinobutane-1,4- <sup>13</sup> C	147.3 (s, 1,4-C)			DMSO-d <sub>6</sub>
4,4'-Diamino-3,3'-bifurazanyl	136.9 (s, 3,3'-C) 155.4 (s, 4,4'-C)			DMSO-d <sub>6</sub>
4,4'-Diamino-3,3'-bifurazanyl-4,4'- <sup>13</sup> C	155.4 (s, 4,4'-C)			DMSO-d <sub>6</sub>
4,4'-Dinitro-3,3'-bifurazanyl	137.0 (s, 3,3'-C) 158.8 (t, 4,4'-C)	344.6 (s, NO <sub>2</sub> )	19	CDC13
4,4'-Dinitro-3,3'-bifurazanyl-4,4'- <sup>13</sup> C	158.8 (t, 4,4'-C)	344.4 (d, NO <sub>2</sub> )	19	CDC13

<sup>a</sup>Relative to internal tetramethylsilane = 0.

<sup>b</sup>Relative to external liquid ammonia = 0.

the broadening of nitrogen-14 quadrupole coupling. If the observed splitting of the carbon-13 is the result of coupling with nitrogen-14, then the nitrogen-14 signal should be split by carbon-13 into a doublet with the same coupling constant. The only way to confirm or disprove this speculation was to prepare DNBF enriched with carbon-13 in the 4,4'-positions and obtain its nitrogen-14 NMR spectrum.

Thus, dichloroglyoxime (1) was treated with sodium cyanide-<sup>13</sup>C to give dicyano-<sup>13</sup>C<sub>2</sub>-glyoxime (2). Addition of hydroxylamine to 2 produced 1,4-diamino-1,2,3,4-tetraoximinobutane-1,4-<sup>13</sup>C (3), which was dehydrated to 4,4'-diamino-3,3'-bifurazanyl-4,4'-<sup>13</sup>C (4). Oxidation of 4 with peroxytrifluoroacetic acid gave 4,4'-dinitro-3,3'-bifurazanyl-4,4'-<sup>13</sup>C (5) (Scheme 1). The yields of the reactions shown in Scheme 1 were comparable to those reported for the unlabeled compounds (1).



Scheme 1

The carbon-13 NMR spectrum of 5 consists of the triplet and confirms the chemical shift assignments for the natural abundance spectrum in Table I. The nitrogen-14 NMR spectrum of 5 contains a sharp doublet with the same coupling constant as the carbon-13 triplet. These results prove that the nitrogen-14 of the nitro groups is coupled with the 4,4'-carbon-13 of 5. This is a very rare example of coupling between carbon-13 and nitrogen-14 that gives the cal-

culated bandshapes for a spin-1 nucleus coupled to a spin-1/2 nucleus for the case where both nuclei are relaxing very slowly (2). Nitrogen-14 quadrupole broadening must be drastically diminished in order for this phenomenon to be observed. A detailed discussion of this coupling is given in Reference 2.

#### EXPERIMENTAL

Dicyano- $^{13}\text{C}_2$ -Glyoxime. -- To a stirred solution of sodium cyanide- $^{13}\text{C}$  (90 atom%  $^{13}\text{C}$ , 94% sodium cyanide)(3.0 g., 0.054 mol) and sodium hydroxide (1.86 g., 0.046 mol) (the total amount of sodium hydroxide was 0.054 mol, 0.008 mol from the sodium cyanide- $^{13}\text{C}$ ) in water (50 ml) was added dichloroglyoxime (3) (4.20 g., 0.027 mol) in small portions below 10°C. After all the solid had dissolved, the solution was allowed to warm to 20°C, then it was acidified with ice cooling to pH2 with concentrated sulfuric acid. The resulting mixture was cooled to 0°C and the solid was collected by filtration, washed with ice water (10 ml), and dried to give 1.90 g (51%), mp 141°C dec. [lit. (4) mp 145°C dec. for the natural abundance compound].

1,4-Diamino-1,2,3,4-tetraoximinobutane-1,4- $^{13}\text{C}$ . -- To a solution of hydroxylamine hydrochloride (2.78 g., 0.04 mol) in water (10 ml) was added a solution of sodium hydroxide (1.60 g., 0.04 mol) in water (10 ml). Dicyano- $^{13}\text{C}_2$ -glyoxime (1.40 g., 0.01 mol) was added to the resulting solution and the mixture was heated at 50°C for 1.5 hours. Acetic acid (2.4 ml) was added and the mixture was cooled to 0°C. The product was collected by filtration, washed with water, and dried to yield 1.47 g (71%), mp 180°C dec. [lit. (4), mp 181-182°C dec. for the natural abundance compound].

4,4'-Diamino-3,3'-bifurazanyl-1,4- $^{13}\text{C}$ . -- To a solution of sodium hydroxide (0.53 g., 0.013 mol) in water (10 ml) was added 1,4-diamino-1,2,3,4-tetraoximinobutane-1,4- $^{13}\text{C}$  and the solution was heated at 165-170°C for one hour in a stainless steel autoclave. The vessel was cooled rapidly to 0°C in an ice bath, the pressure released, and the product was collected by filtration, washed with water, and dried to give 0.31 g (28%), mp 304°C dec. [lit. (1), mp 305°C dec. for the natural abundance compound].

4,4'-Dinitro-3,3'-bifurazanyl-4,4'-<sup>13</sup>C. -- To a slurry of 90% hydrogen peroxide (0.9 ml, 0.033 mol) in dichloromethane (20 ml) was added trifluoroacetic anhydride (5.0 ml, 0.035 mol) with stirring and ice cooling. After the exotherm had subsided, 4,4'-diamino-3,3'-bifurazanyl-4,4'-<sup>13</sup>C (0.31 g., 0.0018 mol) was added and the mixture was heated under reflux for 20 hours. The solution was cautiously extracted with saturated sodium carbonate solution until the aqueous extracts were basic to litmus. The organic layer was dried over magnesium sulfate, the solvent was evaporated on the rotary evaporator, and the residue was chromatographed over silica gel with chloroform/hexane (50/50) to yield 0.10 g (24%) of product that was pure according to thin layer chromatography. The compound melts at 85°C [lit. (1), mp 85°C for the natural abundance compound]. This compound is a sensitive explosive that should be handled with care.

NMR Spectra. -- The NMR spectral data for the carbon-13 labeled compounds and the corresponding natural abundance compounds are given in Table I. The spectra were determined with a JEOL FX90Q spectrometer.

#### ACKNOWLEDGMENTS

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