



^1H , ^{13}C and ^{15}N Nuclear Magnetic Resonance Analysis of 3,3',4,4'-Diaminoazoxyfuran Obtained by Oxidation of 3,4-Diaminofuran with Peroxyformic Acid

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Abstract: The aim of this study was an extensive NMR analysis of 3,3',4,4'-diaminoazoxyfuran (DAAF) obtained by a new method that involves oxidation of 3,4-diaminofuran to DAAF using a $\text{H}_2\text{O}_2/\text{HCOOH}$ mixture. The raw product, after washing with water and drying, was min. 98% pure. We present proton, carbon and nitrogen NMR spectra of the prepared DAAF. Detailed analysis of the nitrogen spectrum gave interesting information about aromaticity of the substituted furazan rings.

Keywords: diaminoazoxyfuran, nuclear magnetic resonance, synthesis, peroxyformic acid

1 Introduction

One of the prospective explosives with reduced sensitivity to mechanical stimuli is 3,3'-diamino-4,4'-azoxyfuran (DAAF). This compound was first described in the former Soviet Union in 1981 [1]. Although, that was over 30 years ago, this compound is still of great interest and much research work has sought new methods for its synthesis. In DAAF, high detonation parameters (7.93 km/s, P_{CJ} 30.6 GPa) are combined with low sensitivity to mechanical stimuli (friction 360 N, impact >15 J) and a low critical diameter of detonation (<3.0 mm) [2]. Detailed studies of the detonation parameters were conducted by the Chavez group [3].

The only known starting substrate for DAAF synthesis is 3,4-diaminofurazan (DAF), which can be converted into DAAF using an oxidizing mixtures *e.g.* (1) $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ [1], (2) $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{S}_2\text{O}_8$ [2], (3) $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ [4]. The DAAF obtained by the Solodyk method [1] contains 3-6% impurities, such as its precursor DAF, 3-amino-4-nitrofurazan and 3-amino-4-nitrosfurazan [1]. In the Zelenin method [2] the byproduct is 3,3'-dinitro-4,4'-azoxyfurazan, which is sensitive to friction and impact. The last method, described by the Francois group [4], enables DAAF to be obtained in high yield (84%). The authors of this study [4] reported that they also obtained DAAF by using *m*-chloroperoxybenzoic acid (MCPBA), but did not provide details.

The structure of the DAAF molecule was confirmed by using ^1H and ^{13}C NMR spectroscopy [2, 4] and elemental compositions. However, to date a full NMR analysis of DAAF, especially ^{15}N NMR, has not been published.

The aim of the present study was a full analysis of DAAF by NMR techniques. The DAAF sample was prepared by a new method, wherein DAF was oxidized with a $\text{H}_2\text{O}_2/\text{HCOOH}$ mixture.

2 Results and Discussion

Caution! DAAF has low sensitivity to mechanical stimuli but the material is an explosive. Laboratories and personnel should be properly grounded and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast screens are necessary.

All chemicals were of analytical grade and were obtained from commercial sources (Avantor, Sigma-Aldrich). DAF was synthesized at the Military University of Technology by the Coburn method [5]. The NMR experiments were conducted using a Bruker AvanceIII HD 500 MHz spectrometer (field 11.7 T). ^1H and ^{13}C spectra were referenced to tetramethylsilane (TMS). The ^{15}N spectra were proton decoupled and chemical shifts were referenced to liquid ammonia. The spectra of all samples were measured at room temperature, with sweep widths of 15 ppm (^1H), 300 ppm (^{13}C) and 500 ppm (^{15}N), the number of scans depended on the tested nuclei (16 for ^1H , 1024 for ^{13}C and 5000 for ^{15}N). The spectra were acquired and processed using standard Bruker software (TopSpin 3.1). DTA measurements were conducted to determine the decomposition temperature of the product. They were carried out with a LabSYS apparatus (Setaram) in open Al_2O_3 crucibles (50 μL in volume) under an argon (99.999%) flow atmosphere (50 mL/min) at a constant heating rate (5 K/min) from 25 to 350 $^\circ\text{C}$ for samples of mass *ca.* 10 mg.

2.1 Oxidation of DAF with $\text{H}_2\text{O}_2/\text{HCOOH}$

A solution containing 95% formic acid (115 g) and 30% hydrogen peroxide (57 g) was prepared at room temperature. DAF (10.0 g) was then added portionwise and stirred for 24 h at ambient temperature. The orange solid product which precipitated from the solution was filtered off, washed with cold water and dried. The yield was 5.7 g (54%) of essentially pure DAAF. The synthetic scheme is presented in Figure 1. The melting point was 248 °C, purity 98% (HPLC, NMR). The NMR results are presented in Section 2.2.

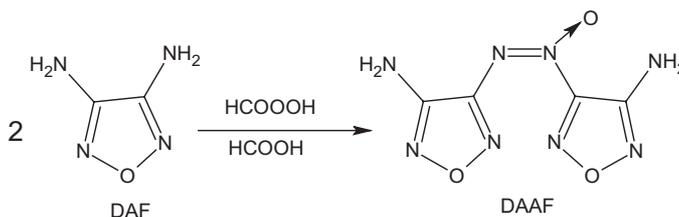


Figure 1. Synthetic scheme for obtaining DAAF from DAF by oxidation with peroxyformic acid.

2.2 NMR studies of DAAF obtained by the new method

^1H , ^{13}C and ^{15}N spectroscopy were applied to confirm the molecular structure of the DAAF obtained by the new method. Proton and carbon NMR spectra were identical to those for the same compound obtained by different methods. Depending on the synthetic method, it is possible to have different impurities. Additionally, the influence of molecular structure on the stability and appearance of the NMR spectra is discussed. The ^1H NMR spectrum (Figure 2) shows two sharp peaks, each of them originating from two hydrogens attached to the nitrogen atoms in the amino groups. The spectrum confirms that the DAAF molecule is unsymmetrical due to the presence of the azoxy group. The chemical shifts of the peaks were 6.69 and 6.95 ppm. The difference in chemical shift is over 0.3 ppm, which indicates that the amino groups are magnetically and chemically non-equivalent. This property may be exploited *e.g.* for the selective oxidation of one amino group during the synthesis of 3-amino-4-nitroazoxyfurazan [2]. In 3,4-diaminofurazan (DAF) the proton peak occurs at 5.8 ppm which means that in DAAF all protons are more deshielded than in DAF. The cause of this effect is the aromatic character of the furazan ring [6] and coupling between the ring and the azoxy bridge.

The proton NMR technique is very sensitive and four small peaks with relatively small intensities are observed at about 9.5 ppm. The compounds responsible for these signals remain unidentified, but we suspect they may be

due to hydroxyl protons from traces of formic acid. Typical impurities in DAAF, such as 3-amino-4-nitrofurazan (ANF) and 3-amino-4-nitrosfurazan (ANOF), give signals with very similar chemical shifts to DAAF itself, but are not visible in our product due to the low concentration.

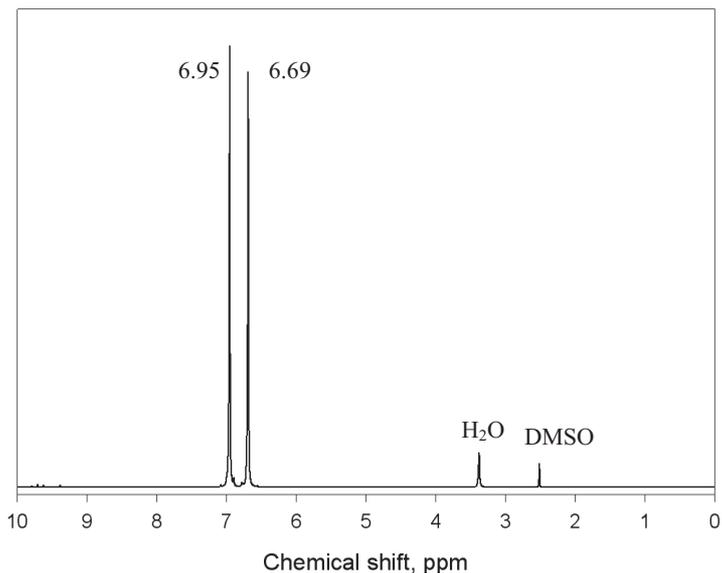


Figure 2. ^1H NMR spectrum of DAAF (DMSO-d_6).

The ^{13}C NMR spectrum (Figure 3) shows four peaks (148.3, 151.1, 152.5, 154.0 ppm), each representing one carbon atom in the furazan rings. Three peaks are of similar intensity and one is smaller. This effect is due to the relaxation time of the substituted carbon nucleus. It means that the carbon atom closest to the oxygen atom in the azoxy bridge has the longest relaxation time. The presence of four peaks from four carbon atoms in the DAAF molecule means that they are magnetically non-equivalent. The DAF carbon spectrum shows only one peak at 150.2 ppm. It is interesting that only one carbon in DAAF is slightly more shielded than the carbons in DAF. This phenomenon can be explained by a lack of axial symmetry in the molecule, causing a local increase in the electron density on one of the carbons.

A ^{15}N NMR spectrum (Figure 4) shows eight peaks and each represents one nitrogen atom in the DAAF molecule. The nitrogen spectrum shown fully confirms the asymmetry of the azoxyfurazane skeleton. Two peaks with chemical shifts 45.0 and 48.9 ppm can be ascribed to the amino nitrogen atoms in positions 3 and 3'. This result is in good agreement with the proton spectrum obtained.

Figure 5 shows the ^{15}N NMR spectrum of DAF for comparison. The nitrogen atoms in the amino groups in DAAF are more deshielded than in DAF. The signals from the azoxy-bridge are visible in the downfield region of the spectrum as two singlets at 304.0 and 315.2 ppm [7]. The last four signals at 362.9; 378.3; 404.7 and 411.3 ppm can be assigned to the four nitrogen atoms in the furazan rings. All nitrogen atoms in the oxadiazole rings are more deshielded than those in DAF and this observation confirms that the nitrogen atoms in the azoxyfurazan structure are magnetically non-equivalent. The deshielding of the nitrogen and carbon atoms in the furazan rings is new circumstantial evidence for the aromatic character of the oxadiazole ring. This observation is in good agreement with the inferences of the Todres team [6] about the aromaticity of the furazan ring.

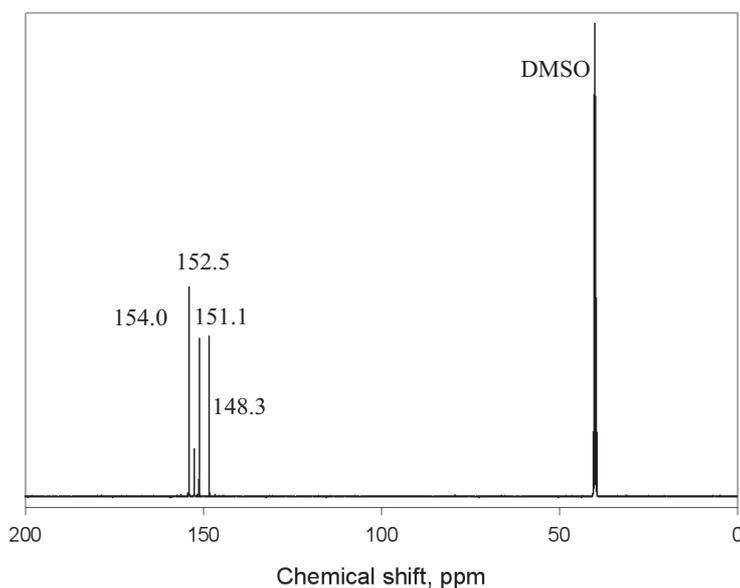


Figure 3. ^{13}C NMR spectrum of DAAF (DMSO-d_6).

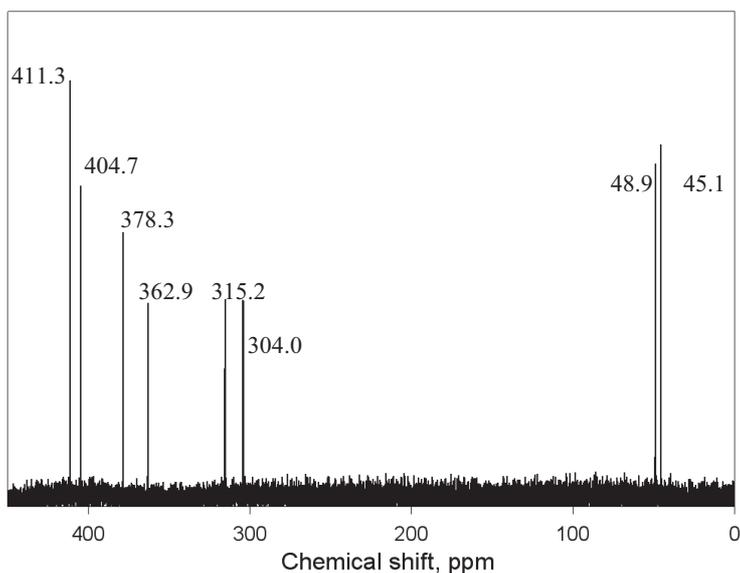


Figure 4. ^{15}N NMR spectrum of DAAF (DMSO-d_6).

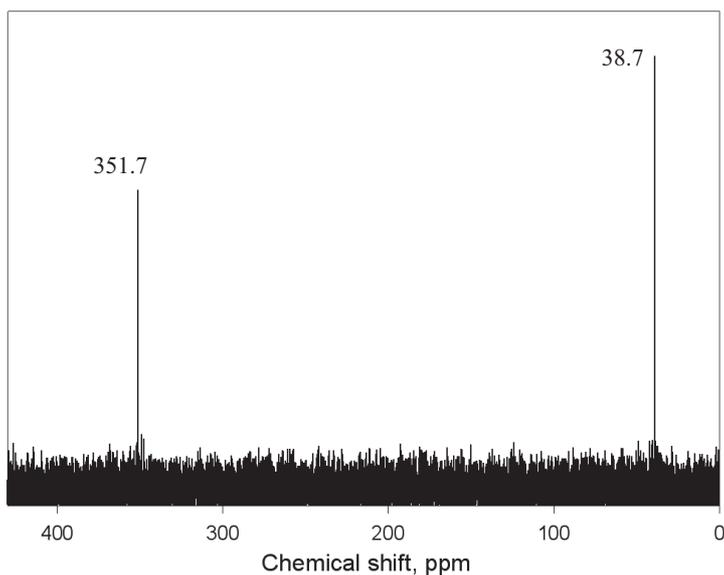


Figure 5. ^{15}N NMR spectrum of DAF (DMSO-d_6).

In the proton, carbon and nitrogen NMR spectra, there are no signals from the potential impurities of DAAF obtained by the Solodyuk method (*e.g.* 3-amino-4-

nitrofurazan, 3-amino-4-nitrofurazan). In our method the unreacted formic acid is removed by simple washing with water. Owing to the low boiling temperature, during drying any residue of formic acid evaporates. Since peroxyformic acid is a moderate oxidant there are no byproducts, or their concentrations are lower than observed when the other methods are used.

2.3 DTA analysis of the raw DAAF obtained by the new method

The raw sample of DAAF obtained by using the new method was subjected to DTA analysis (Figure 6). The DTA curve obtained shows only one exothermic peak with ONSET temperature at 238.5 °C and peak maximum at 246.6 °C. The peak can be assigned to the exothermic decomposition of DAAF. Additional signals from suspected and known impurities are not observed *i.e.* diaminofurazan (mp. 180 °C [5]), 3-nitroso-4-aminofurazan (79 °C [8]), 3-nitro-4-aminofurazan (125 °C [2]). Francois *et. al.* showed that for DAAF synthesized with Oxone, an endothermic peak assigned to the melting process was observed [4]. On the DTA curve of a sample of raw DAAF synthesized by our method, this endothermic peak was not observed. We suppose that this is due the small amounts (below 1%) of the compounds mentioned above. The characteristic endothermic peaks are not visible but early decomposition of DAAF suggests that some impurities might be present.

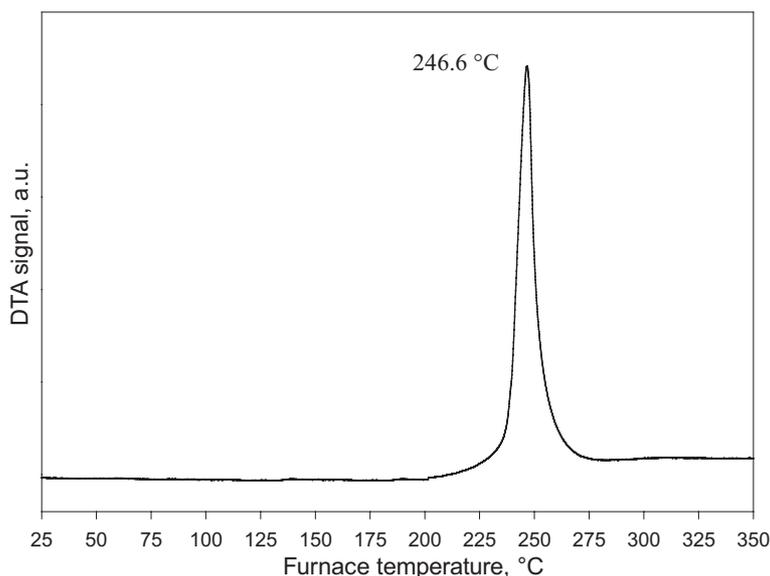


Figure 6. DTA curve of a raw sample of the DAAF obtained by the new method.

3 Conclusions

The synthesis of DAAF by oxidation DAF with $\text{H}_2\text{O}_2/\text{HCOOH}$ is a new and efficient method for producing an essentially pure product. The full NMR analysis shows that the DAAF obtained by the new method does not contain the impurities typical of other methods. The raw product contains small amounts of unidentified impurities which initiate the decomposition of DAAF. The unoptimized yield of DAAF for this method equals 54% and is satisfactory. The analysis of the NMR spectra of DAAF indicates that all nitrogen atoms in the oxadiazole rings in DAAF are more deshielded than in DAF and this observation confirms that the nitrogens in the azoxyfurazan structure are magnetically non-equivalent. Additionally, deshielding of the nitrogen and carbon atoms in the furazan rings is new circumstantial evidence for the aromatic character of the furazan ring.

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