Analysis of Common Explosives in Different Solvents by Nuclear Magnetic Resonance Spectroscopy

Mateusz SZALA* and Leszek SZYMAŃCZYK

Military University of Technology,
Faculty of New Technologies and Chemistry,
2 Kaliskiego St., 00-908 Warsaw, Poland
E-mail: mszala@wat.edu.pl

Abstract: The results of systematic multinuclear NMR studies of 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5, 7-tetraazacyclooctane (HMX) and 3-nitro-1,2,4-triazol-5-one (NTO) are presented. For comparison of interactions between the analytes and the solvents, experiments in both deuterated DMSO and $CDCl_3$ (where possible) were performed. Complete assignment of the resonance signals for the compounds investigated are presented. Analysis of the high resolution NTO spectra leads to new conclusions about the different reactivities of the N-H protons. The results can be used for many analytical purposes, such as solvent matching for extracting traces of explosives, controlling the purity of various samples *etc*.

Keywords: NMR spectroscopy, common explosives, detection

1 Introduction

Analysis and detection of explosives is one of the most important matters for ensuring national and international security. There are many different instrumental methods for explosive detection which have been developed in the past, *i.e.* gas chromatography, ion mobility spectrometry, infrared spectroscopy, Raman spectroscopy, terahertz spectroscopy [1], nuclear quadrupole resonance [2] *etc*. In particular the rapid development of nuclear magnetic resonance spectroscopy (NMR) as an analytical technique has been observed [3, 4]. Nevertheless, this method is still relatively expensive and for routine experiments researchers tend to choose more traditional analytical methods.

Nuclear magnetic resonance spectroscopy is a powerful method for structural analysis and identification of organic compounds but there is a limited amount of published papers concerning the full analysis of explosives using this technique [5-12]. The use of superconducting magnets in NMR spectrometers allowed the sensitivity of detection for important diagnostic nuclei to be increased. Modern NMR spectrometers, operating at high magnetic fields, can detect resonance signals from low-sensitivity nuclei at natural abundance. NMR spectra of selected nuclei for common explosives have been published but only for selected solvents and the spectra were acquired in spectrometers using different configurations [13-17]. Yinon and Zitrin published an excellent book concerning the analysis and detection of explosives [18]. The ^{15}N isotope is present in all high-explosives and for this reason it is very important from an analytical point of view. The poor sensitivity of the ^{15}N isotope is due to its gyromagnetic ratio, a negative Nuclear Overhauser Effect (NOE), long relaxation times and a low natural abundance (0.364%) [19]. However, spectra with good resolution and intensities have been recorded on those samples which are readily soluble using many thousands of accumulated scans.

In this paper, we present the results of a systematic multinuclear NMR study of 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5, 7-tetraazacyclooctane (HMX) and 3-nitro-1,2,4-triazol-5-one (NTO). For comparison of the interaction between the analytes and the solvents we performed the experiments in both DMSO-d_6 and CDCl$_3$ (when that was possible).

2 Experimental

All chemicals were analytical grade. Deuterated solvents like chloroform and dimethylsulfoxide were purchased from Sigma-Aldrich. TNT, RDX and HMX were purchased from Nitro-Chem JSC (Poland). NTO was synthesized at the Military University of Technology.

NMR experiments were conducted on a Bruker AvanceIII HD 500 MHz spectrometer (field 11.7 T). [1]H and ^{13}C spectra were referenced to tetramethylsilane (TMS, δ 0.00 ppm) for protons and carbons respectively. [15]N chemical shifts were referenced to liquid ammonia. Spectra of all of the pure samples were measured at room temperature, with sweep widths of 15 (^{1}H), 300 (^{13}C) and 500 ppm (^{15}N), and the number of scans (1024-5000) depending on the sample. The spectra were acquired and processed using standard Bruker software (TopSpin 3.1.) [20].

Solutions of the pure explosives 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-

1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and 3-nitro-1,2,4-triazol-5-one (NTO) were prepared at room temperature. 0.1 g of each compound was placed in a glass vial with 1 cm^3 of CDCl$_3$ or DMSO-d$_6$ and mixed for 12 h in a mechanical shaker. The samples were left to stand for 2 h and the liquid phase was then removed by single-channel pipette and transferred to standard NMR tubes (5 mm).

3 Results and Discussion

All of the compounds tested are soluble in dimethylsulfoxide, so the recorded spectra in this solvent have good resolution and low noise in the proton, carbon and nitrogen channels. Despite the low solubility of the RDX, HMX and NTO in CDCl$_3$, good spectra in all channels were recorded only for TNT. Figures 1-12 show proton, carbon and nitrogen NMR spectra of the compounds tested in both solvents. The chemical shifts are shown in detail in Table 1.

3.1 NMR spectra of 2,4,6-trinitrotoluene

The ^{1}H NMR spectra of pure TNT are shown in Figure 1. The spectra in DMSO and CDCl$_3$ have the same form (two singlets), but the signals in DMSO are shifted to lower field. This phenomenon may be related to the dipole moments of the solvents (1.5 D for CHCl$_3$ and 4.1 D for DMSO, respectively [21]) and different intramolecular interactions between the analyte and the solvent molecules. The peak area ratios of the aromatic and aliphatic signals is 2:3 and fully corresponds to the known structure of TNT.

The ^{13}C and ^{15}N NMR spectra of TNT are shown in Figures 2 and 3, respectively. The spectra in the relevant channels are almost identical and the maximum differences between the chemical shifts of the appropriate carbon and nitrogen atoms are 0.8 and 3.3 ppm, respectively. TNT has three nitrogen atoms but the molecule is symmetric so in the ^{15}N spectrum only two signals are observed. This is in good accordance with chemical data about the different reactivities of nitro groups in trinitrotoluene [22].
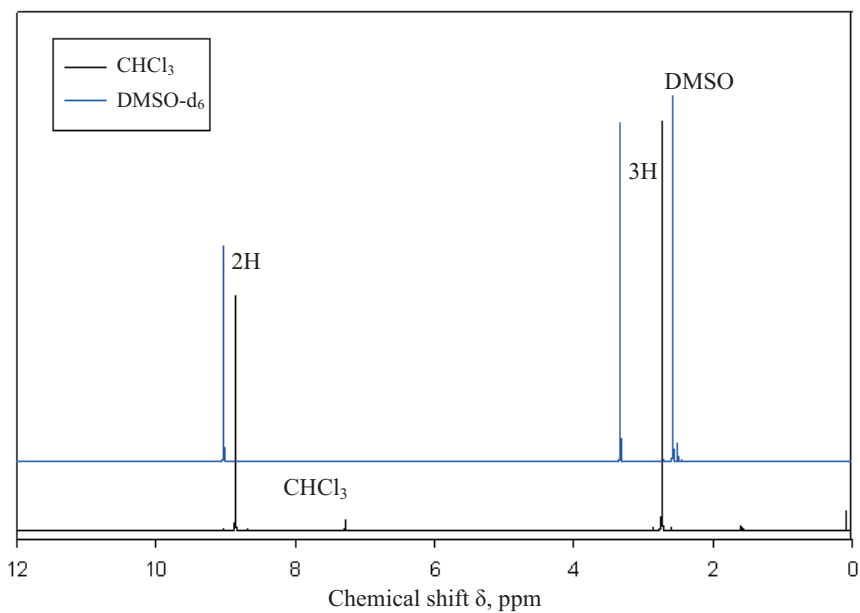
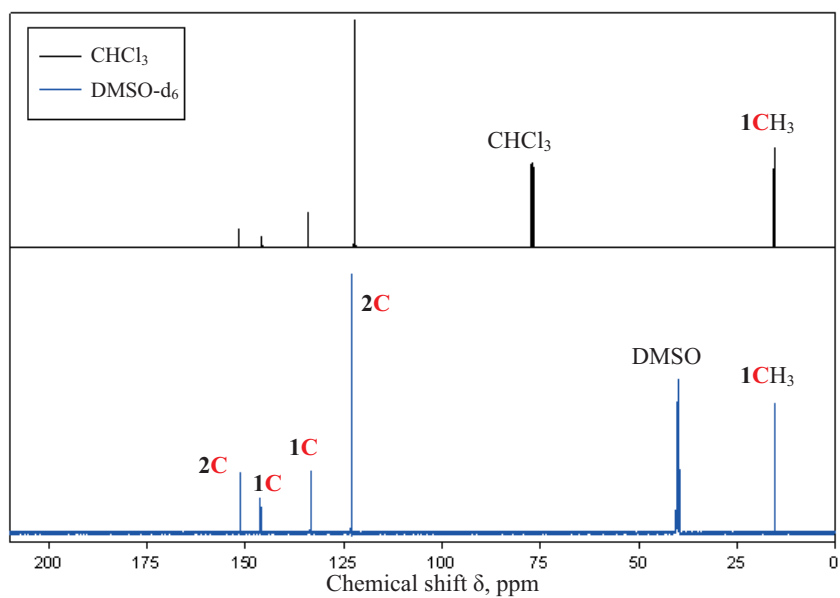**Figure 1.** ^{1}H NMR spectra of TNT in CDCl$_3$ and DMSO-d$_6$.

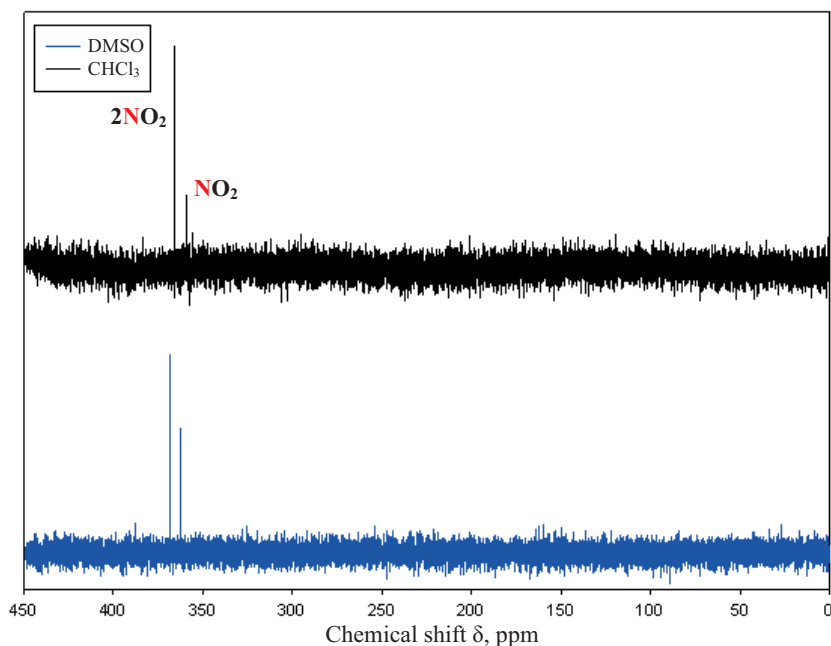**Figure 2.** ^{13}C NMR spectra of TNT in CDCl$_3$ and DMSO-d$_6$.

Figure 3. ^{15}N NMR spectra of TNT in $CDCl_3$ and DMSO-d_6.

3.2. NMR spectra of 1,3,5-trinitro-1,3,5-triazacyclohexane

The ^1H NMR spectra of pure RDX are shown in Figure 4. The six protons of RDX give one sharp singlet in the spectrum. Due to the poor solubility of RDX in $CDCl_3$, the peak intensity from the six protons is small relative to the residual solvent peak. A similar situation is also observed in the ^{13}C spectra (Figure 5). The three equivalent carbon atoms give one sharp resonance signal. The ^{15}N NMR spectrum shows two peaks which can be attributed to the amino nitrogen atoms in the ring and the nitro groups. The intensity differences are caused by the residual nitrogen-proton couplings.
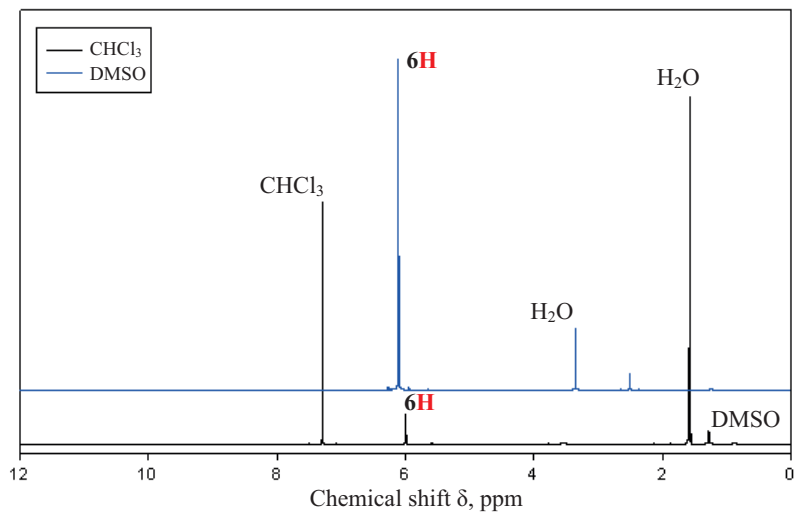
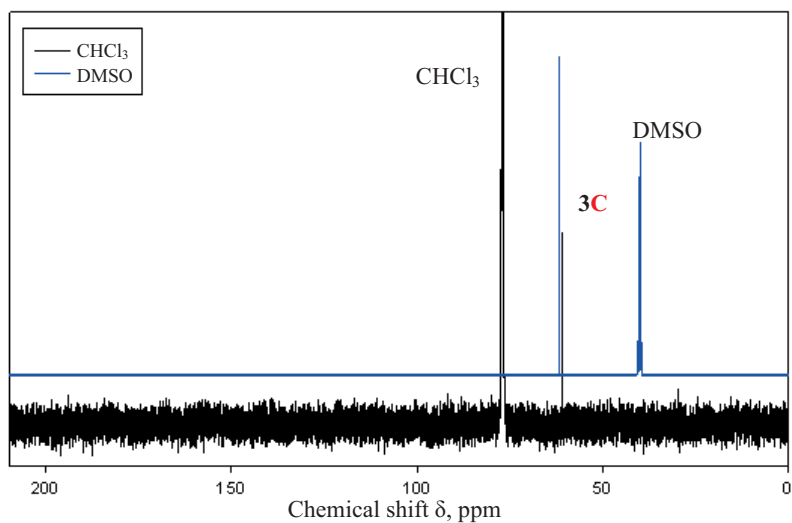**Figure 4.** ^1H NMR spectra of RDX in $CDCl_3$ and DMSO-d_6.

Figure 5. ^{13}C NMR spectra of RDX in $CDCl_3$ and DMSO-d_6.
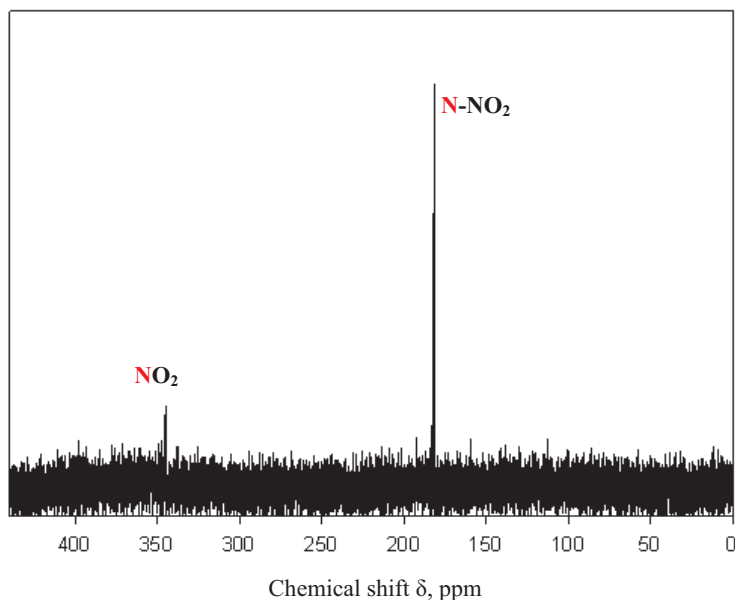
Figure 6. ^{15}N NMR spectra of RDX in DMSO-d_6.

3.3 NMR spectra of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane

The ^1H NMR spectra of HMX are shown in Figure 7. The spectra are very similar to those recorded for RDX, but the peak intensity for the eight protons is smaller because HMX is less soluble in CDCl$_3$ than RDX. Since the structures of both cyclic nitramines are similar, the chemical shifts of appropriate protons are very similar too. The differences in the chemical shifts of the corresponding carbon atoms (Figure 8) are small, but the high resolution NMR spectrometer used in these experiments (500 MHz) allowed simultaneous identification of RDX and HMX based on their carbon spectra. The ^{15}N spectrum of HMX is similar to that of RDX, and the peak for the nitro group nitrogens has the same chemical shift. The identification of HMX and RDX from their ^{15}N spectra is possible because the resonance signal from amino nitrogen atoms has a slightly different chemical shift. The very similar (or identical) ^{15}N chemical shifts of RDX and HMX confirmed that the analyzed molecules are homologous.
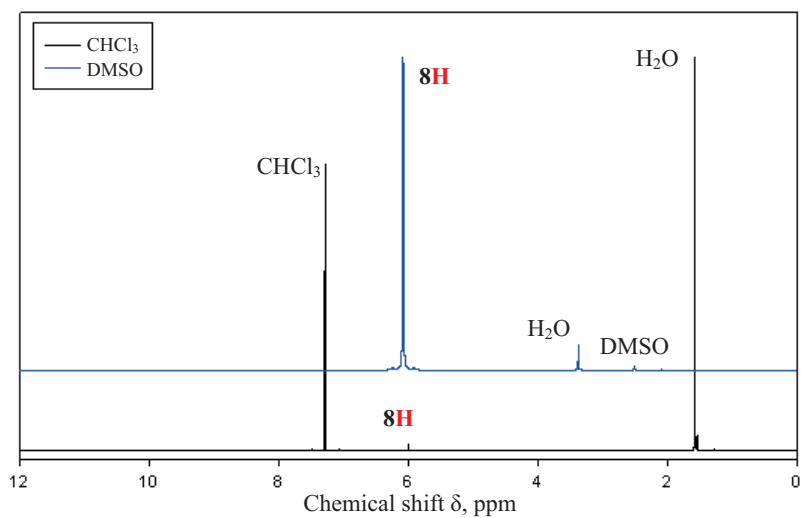
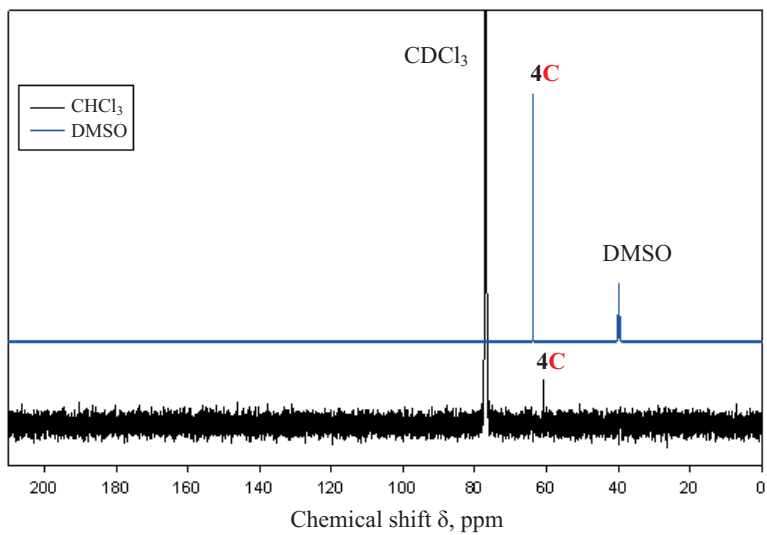**Figure 7.** ^{1}H NMR spectra of HMX in $CDCl_3$ and DMSO-d$_6$.

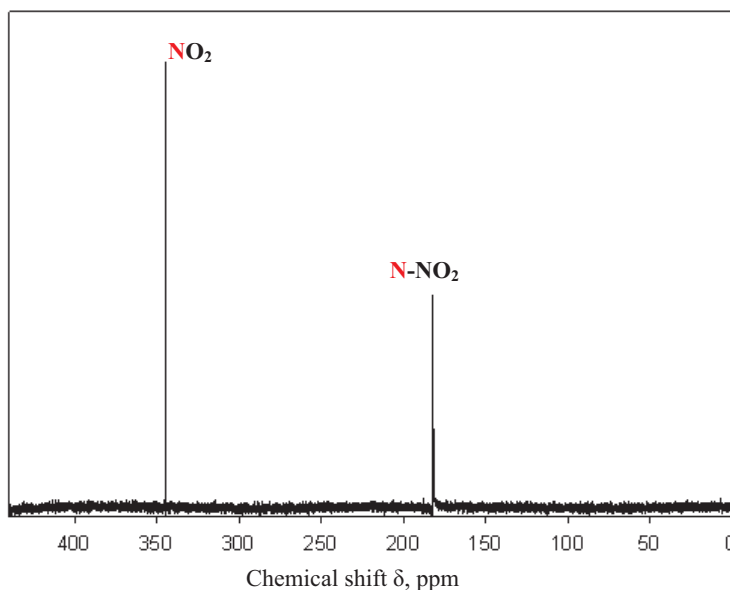**Figure 8.** ^{13}C NMR spectra of HMX in $CDCl_3$ and DMSO-d$_6$.

Figure 9. ^{15}N NMR spectra of HMX in DMSO-d_6.

3.4 NMR spectra of 3-nitro-1,2,4-triazol-5-one

The ^1H NMR spectra of NTO are shown in Figure 10. The amino protons give two peaks with different relative heights and different full-widths at half maximum height (FWHM). Broadening of the NMR lines of amino protons is characteristic and caused by intermediate rates of exchange. The structure of these signals undoubtedly indicates that one proton is more reactive than the other. NTO is practically non-hygroscopic but even traces of water present on the crystal surfaces can cause the N-H protons to dissociate in DMSO/H_2O solution. The integrals of the N-H signals are practically equal but integration was performed after signal deconvolution with TopSpin software. The ^1H spectrum fully confirms the chemical properties of the N-H protons in NTO as determined by other methods.

The ^{13}C NMR spectra of NTO are shown in Figure 10. The location and number of signals corresponds well to the commonly accepted structure of NTO. The ^{15}N spectrum consists of four sharp peaks which indicate that each nitrogen nucleus exists in a different chemical environment. This information is in compliance with the results of the ^1H NMR analysis.
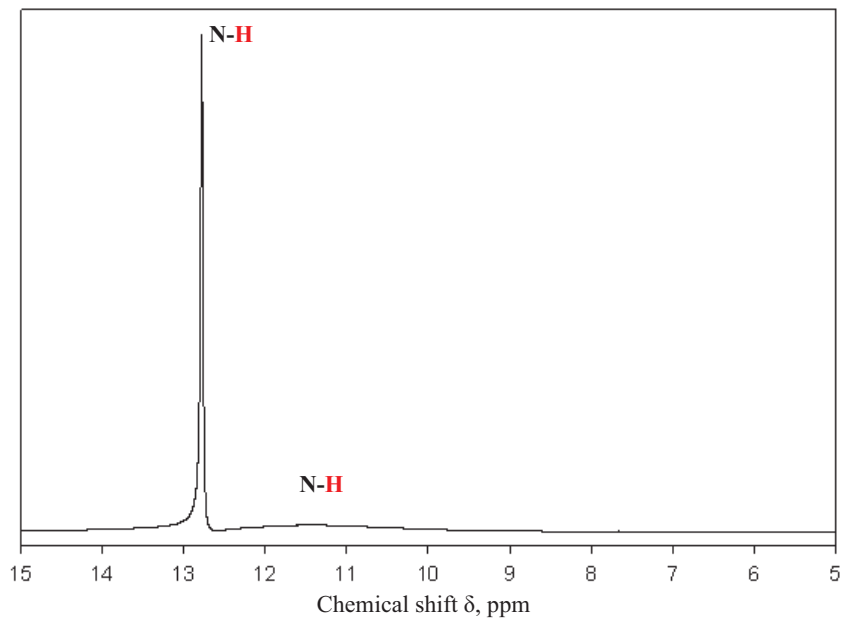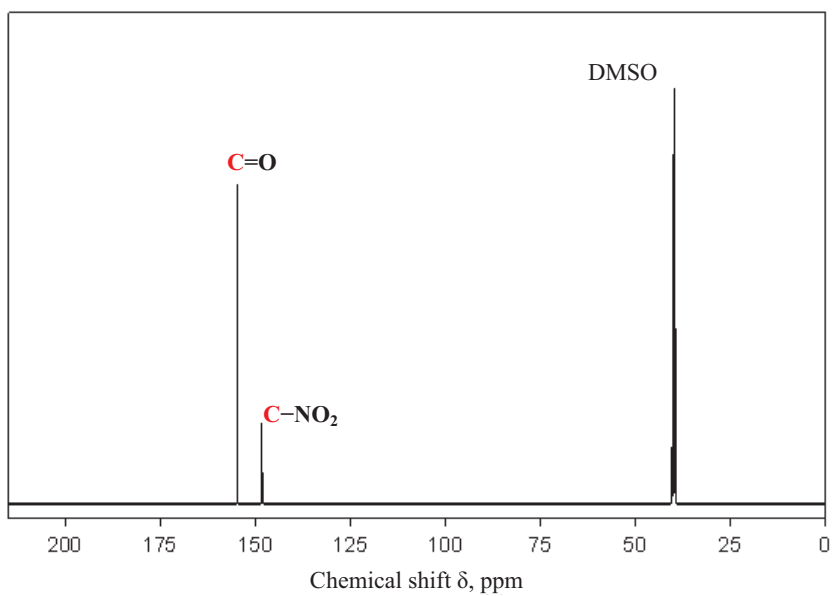
Figure 10. ^{1}H NMR spectra of NTO in DMSO-d$_6$.

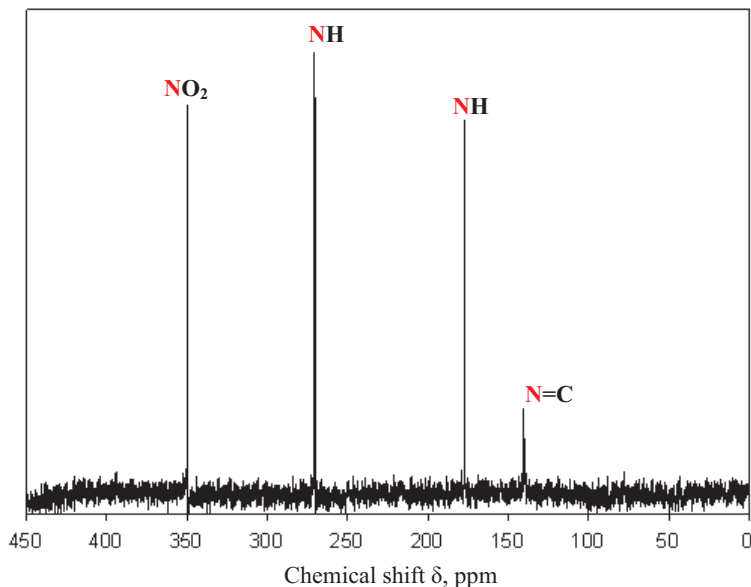**Figure 11.** ^{13}C NMR spectra of NTO in DMSO-d$_6$.

Figure 12. ^{15}N NMR spectra of NTO in DMSO-d_6.

3.5 Chemical shifts of ^1H, ^{13}C and ^{15}N nuclei in TNT, RDX, HMX and NTO

The chemical shifts for all of the tested nuclei obtained from the spectra presented are shown in Table 1. Unfortunately, due to the insufficient solubility of NTO in CDCl$_3$ and the too low sensitivity in the nitrogen channel for RDX and HMX, some spectra were not recorded. In all of the other systems tested spectra with very good resolution were recorded. The chemical shifts are presented with the maximum reliable resolution to allow for the accurate detection of these common explosives in proton, carbon and nitrogen NMR spectra. Information collected in Table 1 is in compliance with available literature data [5-17], but some spectra and some assignments are presented for the first time in this paper. The results can be used for many analytical purposes, such as solvent matching for extracting traces of explosives, checking the purity of various samples *etc*.

Table 1.   Spectral assignments for common explosives in CDCl$_3$ and DMSO-d$_6$

Sample	^{1}H, ppm		^{13}C, ppm		^{15}N, ppm	
	CDCl$_3$	DMSO-d$_6$	CDCl$_3$	DMSO-d$_6$	CDCl$_3$	DMSO-d$_6$
TNT	2.73 (3H); 8.86 (2H)	3.33 (3H); 9.03 (2H)	15.5; 122.2; 134.1; 145.8; 151.6	15.3; 123.0; 133.4; 146.1; 151.3	359.0; 365.7	362.3; 367.9
RDX	5.99 (6H)	6.10 (6H)	60.75	61.68	–	181.9; 345.0
HMX	5.99 (8H)	6.08 (8H)	60.80	63.80	–	182.2; 345.0
NTO	–	12.76 (1H); 11.43 (1H)	–	148.15; 154.62	–	140.7; 177.2; 270.4; 349.5

4 Conclusions

The observed differences in the chemical shifts in the various solvents have different values which depend on the chemical and physical properties of each solvent. The greatest influence on the chemical shift of the observed nuclei in solvents tested are polarity and possibly hydrogen bonding. The important factor influencing the chemical shift is the concentration of analyte in deuterated solvent. The identification of HMX and RDX from their ^{15}N spectra is possible because the peaks from the amino nitrogen atoms have similar but slightly different chemical shifts. The amino protons in NTO give two peaks with different intensities and FWHM. The structure of these signals undoubtedly indicates that one proton is more reactive than the other. The ^{15}N spectrum of nitrotriazolone consists of four sharp peaks, which indicates that each nitrogen nucleus exists in a different chemical environment. The quantitative and qualitative information obtained from these spectra can be used for many analytical purposes, such as solvent matching for extracting traces of explosives, controlling the purity of various samples, acidity evaluation of protons and many others.

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