

## Nitrogen 14 detection of explosophores

D. McAteer & J. Akhavan

Nitrogen-14 ( $^{14}\text{N}$ ) quadrupolar nuclear magnetic resonance (NMR) spectroscopy was successfully used to detect and measure the chemical environment of various nitrogen nuclei located within the explosophore of many commonly studied explosives (Figure 1). The values are presented here as a resource for researchers in the field who may find use in this non-destructive and convenient analytical technique.

NMR spectroscopy is routinely used by chemists to determine the local chemical environment of nuclei within molecules. The information provided by NMR allows the elucidation of molecular structures particularly when

used in combination with analytical techniques such as mass spectrometry (MS). The advantages of NMR over many other techniques are the speed and ease with which analysis may be carried out, particularly in proton ( $^1\text{H}$ ) NMR, where information on an analyte material, which may be a mixture or a single compound, may be provided in a matter of minutes.

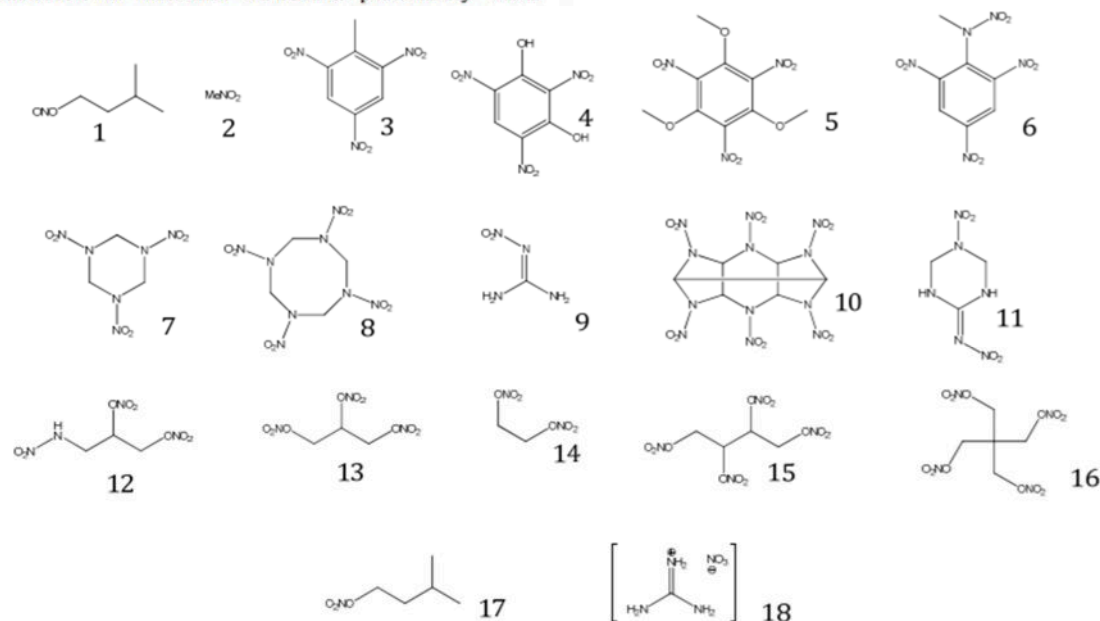


Figure 1: The explosives assessed in this communication

It has also become commonplace to study  $^{13}\text{C}$  nuclei in structures, although due to the lower natural abundance and decreased sensitivity these experiments can be time consuming. In an active chemistry department, the demand for NMR spectroscopy is such that these relatively time consuming experiments are programmed to run overnight when the instrument is free of the more time-efficient  $^1\text{H}$  experiments. As a result NMR experiments are commonly used when they are capable of providing significant structural information to a chemist in a practical timescale.

In the field of energetic materials chemistry the most commonly assessed functional groups are those which impart an explosive or energetic property to the molecule in question. For instance, when considering the potential properties of nitroglycerine (1,2,3-propanetriyl trinitrate, NG, **13**, Figure 1) the chain of 3 aliphatic carbons is secondary in importance to the 3 nitrate ester functional groups which provide the oxygen required for complete combustion of the hydrogen and carbon present. Currently a chemist studying NG may use NMR to detect the chemical environment of the protons and of the carbons present in the structure. These may be compared to those observed for the starting material (typically glycerine) and any literature values for NG. However, a possible, although highly unlikely, contaminant to NG is the nitrite ester derivative. This would also affect the values given in the proton and carbon NMR spectra but an additional experiment capable of providing details on the chemical environment of the nuclei present within the explosophore itself would be a welcome additional technique.

The vast majority of common explosophores (see Table 1) contain nitrogen and/or oxygen and so any technique which is capable of detecting the NMR active nuclei of either element would provide additional information on the vast majority of explosives. The current method for detecting nitrogen nuclei utilises the naturally occurring isotope nitrogen-15 ( $^{15}\text{N}$ ).  $^{15}\text{N}$  NMR spectroscopy has been used in the past but is disadvantaged by the low natural abundance of the  $^{15}\text{N}$  isotope (0.37%) coupled with a low relative sensitivity ( $1.04 \times 10^{-3}$  in comparison with  $^1\text{H}$ ).<sup>1,2</sup>

Historically this has meant that researchers interested in nitrogen nuclei have relied upon time-consuming  $^{15}\text{N}$  experiments which require a high number of scans or use of isotopically labelled reagents which artificially increase the proportion of  $^{15}\text{N}$  present. While the latter option is relatively common it comes at great expense given the

cost of isotopically labelled reagents and is limited in scope due to the relatively small number of labelled materials commercially available.

Common Name	Semi-Structural Formula	Structure
Nitro	$-\text{NO}_2$	
Nitrate	$-\text{ONO}_2$	
Nitrite	$-\text{ONO}$	
Azide	$-\text{N}_3$	
Nitroso	$-\text{NO}$	
Nitramine	$-\text{NNO}_2$	
Nitrosoamine	$-\text{NNO}$	
Azo	$-\text{NN}-$	
Azoxy	$-\text{N}(\text{O})\text{N}-$	
Diazo	$-\text{NN}$	
Hydrazo	$-\text{N}(\text{H})(\text{H})\text{N}-$	

Table 1: A list of common explosophores

With the introduction of broadband or tuneable NMR probes, researchers are no longer limited to assessing a specific set of nuclei but rather a broad range of NMR active isotopes. Nitrogen-14 ( $^{14}\text{N}$ ) is one of these isotopes which are now within the capability of modern spectrometers.  $^{14}\text{N}$  is highly abundant in nature (99.63%) and has a comparable figure of relative sensitivity to  $^{15}\text{N}$  ( $1.01 \times 10^{-3}$  in comparison with  $^1\text{H}$ ).  $^{14}\text{N}$  differs with many traditionally NMR active nuclei in that it does not possess a net spin of  $1/2$  or  $3/2$  which is the classic prerequisite for NMR analysis. Instead the analysis of  $^{14}\text{N}$  is achieved due, exclusively, to the quadrupolar moment of the nuclei.<sup>2</sup>

All  $^{14}\text{N}$  NMR data was recorded using a Bruker Avance HD spectrometer operating at 9.4 T ( $\nu_0(^1\text{H}) = 400$  MHz) and equipped with a 5 mm broadband Bruker Smart probe. An anti-ringing ( $\pi/2-\tau-\pi/2-\tau-\pi/2$ ) sequence was employed with a 16 kHz excitation frequency and a relaxation time of 0.1 seconds was deemed sufficient. A minimum of 21600 transients were collected for each spectrum. The chemical shifts are quoted in parts per million (ppm) with reference tetramethylsilane (TMS) for  $^1\text{H}$  and nitromethane for  $^{14}\text{N}$  spectra.

The initial observations made were that  $^{14}\text{N}$  chemical shift values of explosives is broadly ordered with respect to their constituent explosophores (as shown in Table 2, Table 3).

Explosophore	$\delta_{\text{iso}}$ ( $^{14}\text{N}$ / ppm) Range
<b>Aliphatic Nitrite</b>	530
<b>Aliphatic Nitro</b>	336
<b>Ionic Nitrate</b>	334
<b>Nitroimine</b>	324 - 327
<b>Aromatic Nitro</b>	315 - 324
<b>Nitramine</b>	293 - 309
<b>Nitrate Ester</b>	288 - 298

Table 2: Chemical shift range of the explosophores tested

The nitroimine chemical shift values which were observed for NNHT and nitroguanidine (324 and 327 ppm respectively, shown in Table 3) are of particular interest in their variation from the closely related nitramine values which fall in the range 293 - 309 ppm.

Compound	$\delta_{\text{iso}}$ ( $^{14}\text{N}$ / ppm)	Assigned Explosophore
isoamyl nitrite ( <b>1</b> )	530	<b>Nitrite</b>
nitromethane ( <b>2</b> )	336	<b>Aliphatic Nitro</b>
2,4,6-trinitrotoluene (TNT) ( <b>3</b> )	317	<b>Aromatic Nitro</b>
TNT ( <b>3</b> )	324	<b>Aromatic Nitro</b>
styphnic acid ( <b>4</b> )	320	<b>Aromatic Nitro</b>
styphnic acid ( <b>4</b> )	315	<b>Aromatic Nitro</b>
1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTNB) ( <b>5</b> )	316	<b>Aromatic Nitro</b>
N-methyl-N,2,4,6-tetranitroaniline (Tetryl) ( <b>6</b> )	317	<b>Aromatic Nitro</b>
Tetryl ( <b>6</b> )	303	<b>Nitramine</b>
N,N',N''-trinitro-1,3,5-triazine (RDX) ( <b>7</b> )	303	<b>Nitramine</b>
N,N',N'',N'''-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) ( <b>8</b> )	301	<b>Nitramine</b>
nitroguanidine ( <b>9</b> )	327	<b>Nitroimine</b>
hexanitrohexaazaisowurtzitane (CL-20) ( <b>10</b> )	296	<b>Nitramine</b>
CL-20 ( <b>10</b> )	293	<b>Nitramine</b>
N-nitroiminohexahydro-1,3,5-triazine (NNHT) ( <b>11</b> )	324	<b>Nitroimine</b>
NNHT ( <b>11</b> )	309	<b>Nitramine</b>
N-nitro-1-amino-2,3-propanediyl dinitrate (NGN1) ( <b>12</b> ) <sup>3</sup>	310	<b>Nitramine*</b>
NGN1 ( <b>12</b> ) <sup>3</sup>	293	<b>Nitrate*</b>
NGN1 ( <b>12</b> ) <sup>3</sup>	291	<b>Nitrate*</b>
1,2,3-propanetriyl trinitrate (NG) ( <b>13</b> )	292	<b>Nitrate</b>
NG ( <b>13</b> )	290	<b>Nitrate</b>
1,2-ethanediyl dinitrate (EGDN) ( <b>14</b> )	294	<b>Nitrate</b>
1,2,3,4-erythritol tetranitrate (ETN) ( <b>15</b> )	292	<b>Nitrate</b>
ETN ( <b>15</b> )	288	<b>Nitrate</b>
pentaerythritol tetranitrate (PETN) ( <b>16</b> )	292	<b>Nitrate</b>
isoamyl nitrate ( <b>17</b> )	298	<b>Nitrate</b>
guanidine nitrate ( <b>18</b> )	334	<b>Ionic nitrate</b>

Table 3 : Chemical shifts (ppm) of the assessed explosives ( $^{14}\text{N}$  spectra previously reported by Klapötke et al.)<sup>3</sup> Full spectra are included in the supporting information.

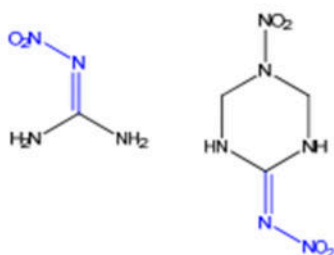


Figure 2: Nitroimine functional groups highlighted in nitroguanidine (9) and NNHT (11)

The nitro groups bonded to unsaturated nitrogen found in NNHT and nitroguanidine are classed as nitroimines and it is likely that the variation in chemical shift observed is due to the C-N double bond (see Figure 2). This suggests that the sensitivity of  $^{14}\text{N}$  NMR is sufficient to determine differences in chemical environments observed in similar compounds, which enhances its relevance as a technique. This sensitivity is particularly useful when the spectra of RDX and HMX are considered. RDX and HMX are commonly found together as the latter is a by-product formed during the synthesis of the former. It is not possible to differentiate the proton spectra of RDX and HMX but (as shown in Table 3) the  $^{14}\text{N}$  signals differ by 2ppm. This sensitivity is further emphasised by the comparison of the  $^{14}\text{N}$  spectra of the aliphatic nitrate esters, NG (13), and ETN (15). In both cases the 2h experiment was capable of differentiating between adjacent nitrate esters and allotting indicative but not definitive integral values. Particularly when the synthesis of NG is considered, the ability to detect and discriminate between nitration at the primary and secondary alcohol is highly desirable (see Figure 3).

An observed limitation of the technique is that detectable nitrogen nuclei seem to be limited to unhindered nuclei which are free to move in solution. Assessment of hindered moieties such as azo bonds, caged nitrogens (CL-20) and heterocyclic nitrogens (RDX, NNHT, etc) has proven unsuccessful using this acquisition parameter set. This may be a limitation observed across solution state quadrupolar NMR as the best results observed in this study have been recorded only in low viscosity solvents (dichloromethane, acetone), solubility in which has effectively become a selection criterion for this work.

The study illustrates the potential of using  $^{14}\text{N}$  direct observation NMR on many of the most commonly utilised

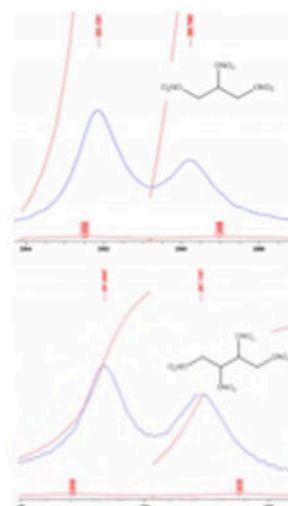


Figure 3: Expanded view of NG (13) and ETN (15) spectra

explosophores and the ease and speed with which  $^{14}\text{N}$  experiments may be run using modern spectrometers.

As a result, it is hoped that  $^{14}\text{N}$  NMR might be used more commonly as it has proved to be a highly sensitive and insightful technique which is particularly valid when assessing energetic materials.

#### Notes and references

† The net spin ( $I$ ) of a  $^{14}\text{N}$  nuclei is 1. In this case it is the non-symmetrical charge distribution which gives rise to quadrupolar moment. The quadrupolar moment is a function of the non-spherical distribution of charge at the  $^{14}\text{N}$  nuclei. This non-spherical distribution can interact with a magnetic field in much the same way as a spin-active nuclei such as  $^1\text{H}$  but it is essential that the deuterated solvent which is used to dissolve the sample allows maximum freedom to the nuclei to spin and tumble. Accordingly, this study has found that the best results in  $^{14}\text{N}$  NMR have been achieved when using low-viscosity solvents such as acetone and dichloromethane. These increase motion and therefore reduce the first and second order quadrupole moments, hence decreasing the intrinsic linewidth.

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McAteer, Daniel

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