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## Research paper / Praca doświadczalna

# Study of interactions between nitrophenols and 1,1-diamino-2,2-dinitroethene Badanie oddziaływań nitrofenoli z 1,1-diamino-2,2-dinitroetenem

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**Abstract:** The results of a study of the interactions between mono-, di-, and trinitrophenols and 1,1-diamino-2,2-dinitroethylene (DADNE) are presented. Interaction studies were conducted ranging from 1:1 to 4:1 nitrophenol:DADNE, molar ratios. The interactions were studied using  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques for samples prepared in deuterated dimethyl sulfoxide (DMSO). It was observed that in the 2,4-dinitrophenol–DADNE system, at a 1:1 molar ratio, a hydroxyl proton transfer from the nitrophenol to the amino group of DADNE occurred. This effect was not observed in the 4-nitrophenol–DADNE system. The effects observed in the spectra of the 2,4,6-trinitrophenol–DADNE system do not indicate protonation of the DADNE  $-\text{NH}_2$  groups. The observed interactions probably result from the formation of coordination complexes, but this hypothesis needs further research.

**Streszczenie:** Przedstawiono wyniki badania oddziaływań pomiędzy mono-, di- i trinitro-fenolami a 1,1-diamino-2,2-dinitroetylenem (DADNE). Badania interakcji prowadzono przy stosunku molowym nitrofenol: DADNE od 1:1 do 4:1. Oddziaływania badano techniką  $^1\text{H}$  oraz  $^{13}\text{C}$  NMR dla próbek przygotowanych w deuterowanym DMSO. Zauważono, że w układzie 2,4-dinitrofenol – DADNE przy stosunku molowym 1:1 występuje przeniesienie protonu hydroksylowego z nitrofenolu na grupę aminową DADNE. Efektu tego nie zaobserwowano dla układu 4-nitrofenol DADNE. Efekty obserwowane na widmach w układzie 2,4,6-trinitrofenol-DADNE nie wskazują na protonowanie grup  $-\text{NH}_2$ . Obserwowane zmiany na widmach  $^1\text{H}$  NMR wynikają prawdopodobnie z powstawania kompleksów koordynacyjnych ale potwierdzenie tej hipotezy badań.

**Keywords:** 1,1-diamino-2,2-dinitroethene, 4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, nuclear magnetic resonance, interactions

**Słowa kluczowe:** 1,1-diamino-2,2-dinitroeten, 4-nitrofenol, 2,4-dinitrofenol, 2,4,6-trinitrofenol, magnetyczny rezonans jądrowy, oddziaływania

## Supplementary Material

Figures S1 to S7 of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 4-nitrophenol–DADNE, 2,4-dinitrophenol–DADNE and 2,4,6-trinitrophenol–DADNE, and Figure S8 of the  $^1\text{H}$  NMR spectra of the DADNE solution are available in the Supplementary Information (SI).

## 1. Background

Nitrophenols are a relatively well-known group of chemical compounds. The typical chemical reactivity of the nitro derivatives of phenols is well understood and described [1]. In the chemistry of explosives, the most important compound in this group is 2,4,6-trinitrophenol (picric acid, TNF, TNP). This compound readily forms salts with metals through proton exchange of the hydroxyl group [2]. Picric acid salts are explosive and, in the case of heavy metal salts, have a very high sensitivity to energy inputs such as impact or friction; their properties being typical of initiator explosives [1]. Di- and tri-nitrophenol ethers have been used as fusible explosive alternatives to 2,4,6-trinitrotoluene (TNT). The most widely used compound in this group is 2,4-dinitroanisole (DNAN) [3]. Many nitrophenols and their derivatives are soluble in water so their biological activity should be borne in mind. When applied to the skin, they cause inflammation and allergic response. 2,4-dinitrophenol (DNP) is classified as a phytotoxic agent. In the human body it causes decoupling of phosphorylation at the cellular level which leads to pathologically rapid weight loss [4].

With the development of the chemistry of coordination compounds, interest in polynitrophenols has increased again due to their potential use as ligands. By the year 2025, hundreds of mono-, di- and trinitrophenol complexes had been described [5]. In 1998, the synthesis and basic properties of 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) were described [6] and, given its explosive properties, the compound quickly drew the interest of military research centres. Due to the presence of geminal amine groups, this compound shows an alkaline character but this is not typical of aliphatic primary amines [7]. An attempt was therefore made to study the interaction of DADNE with nitrophenols using nuclear magnetic resonance techniques to gain a better understanding of the interactions between the compounds at the molecular level.

## 2. Findings and discussion

Nitrophenols and DADNE of >99.5% purity were used for the study. Deuterated DMSO (99.9%D) was purchased from Merck. The NMR spectra were recorded using a pulse NMR method with a Bruker Avance III HD 500 MHz instrument [8]. The spectrometer's superconducting magnet generated an induction field of 11.7 T. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced as tetramethylsilane (TMS) standard. The spectra were recorded at 25 °C in standard 5 mm diameter tubes. A sample of 1 cm<sup>3</sup> DMSO of each solution was prepared for testing.

The study was conducted on solutions of 1,1-diamino-2,2-dinitroethene (DADNE) and the following nitrophenols: 4-nitrophenol (4-NF), 2,4-dinitrophenol (2,4-DNF) and 2,4,6-trinitrophenol (2,4,6-TNF). The molar ratio of the corresponding nitrophenol to DADNE was varied between 1:1 and 1:4. The results of the tests in the form of chemical shifts of the respective  $^1\text{H}$  and  $^{13}\text{C}$  nuclei are listed in Tables 1 to 3. The summaries of the proton and carbon spectra are shown in Figures S1 to S7 (see SI). Both spectra and tabulated summaries of chemical shifts are included. This was done to enable the reader to evaluate the changes in the spectra and possibly compare their results to those obtained in the discussed research cycle.

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR results for solutions containing 4-NF and DADNE

| Number | DADNE  |        | 4-NF   |        | $^1\text{H}$ [ppm]               | $^{13}\text{C}$ [ppm]                         |
|--------|--------|--------|--------|--------|----------------------------------|---|
|        | [g]    | [mol]  | [g]    | [mol]  |                                  |   |
| 1      | 0.0440 | 0.0003 | 0.0417 | 0.0003 | 6.91d; 8.08d; 8.70s <i>broad</i> | 116.2; 126.6; 128.8;<br>140.11; 158.0; 164.3  |
| 2      | 0.0880 | 0.0006 | 0.0417 | 0.0003 | 6.91d; 8.08d; 8.68s <i>broad</i> | 116.2; 126.5; 128.9;<br>140.0; 157.9; 164.3   |
| 3      | 0.1320 | 0.0009 | 0.0417 | 0.0003 | 6.89d; 8.06d; 8.68s <i>broad</i> | 116.2; 126.5; 129.1;<br>140.1; 157.8; 164.3   |
| 4      | 0.1760 | 0.0012 | 0.0417 | 0.0003 | 6.88d; 8.05d; 8.65s <i>broad</i> | 116.2; 126.5; 129.10;<br>140.06; 157.7; 164.3 |

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR results for solutions 2,4-DNF and DADNE

| Number | DADNE  |        | 2,4-DNF |        | $^1\text{H}$ [ppm]                | $^{13}\text{C}$ [ppm]  |
|--------|--------|--------|---------|--------|-----------------------------------|--|
|        | [g]    | [mol]  | [g]     | [mol]  |                                   |  |
| 5      | 0.0440 | 0.0003 | 0.0552  | 0.0003 | 7.24d; 8.32q; 8.64d; 8.72d        | 120.2; 122.3; 128.7;<br>129.8; 136.7; 138.7;<br>157.9; 158.1 |
| 6      | 0.0880 | 0.0006 | 0.0552  | 0.0003 | 5.39s; 7.23d; 8.29q; 8.62d; 8.70d | 120.2; 122.3; 128.8;<br>129.9; 136.6; 138.7;<br>158.0        |
| 7      | 0.1320 | 0.0009 | 0.0552  | 0.0003 | 4.97; 7.21d; 8.27q; 8.60d; 8.67d  | 120.3; 122.3; 129.1;<br>129.9; 136.4; 138.7;<br>157.6; 158.0 |
| 8      | 0.1760 | 0.0012 | 0.0552  | 0.0003 | 4.93s; 7.20d; 8.25q; 8.60d; 8.58  | 120.3; 122.3; 129.2;<br>129.9; 136.3; 138.7;<br>157.4; 158.1 |

**Table 3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR results for solutions 2,4,6-TNF and DADNE

| Number | DADNE  |        | 2,4,6-TNF |        | $^1\text{H}$ [ppm]                         | $^{13}\text{C}$ [ppm]                       |
|--------|--------|--------|-----------|--------|--|---|
|        | [g]    | [mol]  | [g]       | [mol]  |  |   |
| 9      | 0.0440 | 0.0003 | 0.0687    | 0.0003 | 8.62s; 8.67s <i>broad</i> ; 11.27s; 11.41s | 125.7; 126.5; 158.7;<br>141.9; 158.1; 160.3 |
| 10     | 0.0880 | 0.0006 | 0.0687    | 0.0003 | 8.41s; 8.47s; 8.62s; 8.65s <i>broad</i>    | 125.9; 126.9; 128.9;<br>141.8; 157.9; 160.3 |
| 11     | 0.1320 | 0.0009 | 0.0687    | 0.0003 | 7.73s; 8.63s; 8.63s <i>broad</i>           | 126.0; 127.2; 129.1;<br>141.6; 157.6; 160.3 |
| 12     | 0.1760 | 0.0012 | 0.0687    | 0.0003 | 7.00s; 8.59s <i>broad</i> ; 8.64s          | 126.0; 127.5; 129.3;<br>141.5; 157.4; 160.4 |

By analysing the trend of changes in chemical shifts within the spectral summaries, it is possible to see primarily spectroscopic effects which exist with increases in analyte concentration. For the compounds studied herein, there is a clear tendency for the peak signal to shift towards higher fields [9]. Pure 2,4,6-TNF gave three resonance signals in DMSO: at 6.96, 8.14 and 11.10 ppm. The first two signals were from the protons of the aromatic ring and the last (extended) signal was from the hydroxyl proton.

In the spectra of the mixtures of 4-NF with DADNE, the hydroxyl proton signals of nitrophenol are practically invisible which is mainly due to the relatively high degree of dissociation (and exchange) of the hydroxyl proton in aprotic DMSO and the weak protonation of the DADNE amine groups. Only the protons of the nitrophenol ring are found, whose chemical shifts are described in Table 1 (specimen numbers 1 to 4). The lack of observed interactions along with the absence of nitrophenol hydroxyl group signals, indicates a chemical exchange in 4NF which did not result in interactions with DADNE amino groups.

Strong protonation of the  $\text{-NH}_2$  groups in DADNE is found in the spectra of mixtures with 2,4-DNF resulting in the emergence of two broad, overlapping signals (which are not doublets). Chemical shifts are described in Table 2 (specimen numbers 5 to 8). To better illustrate the effect, a typical spectrum for DADNE, protonated with dilute sulphuric acid(VI) ( $\text{H}_2\text{SO}_4$ ) is shown in Figure S8. The attachment of a proton to one amine group of DADNE results in the formation of an  $\text{NH}_3^+$  cation (in the molecule) and, as a result, two broad, overlapping signals are found on the spectrum. The strongest protonation in the DADNE-2,4-DNF system was observed at a molar ratio of 1:1 after which, as the ratio of DADNE increases, the effect becomes weaker (Figure S3). The protonation effect was also observed in changes in the intensity (and chemical shift) of the hydroxyl proton, which was present at around 5.0-5.5 ppm in the mixture with 2,4-DNF. At a molar ratio of DADNE to 2,4-DNF, a hydroxyl proton of 5 ppm (approx) could not be found due to the formation of the  $\text{NH}_3^+$  cation in the DADNE molecule.

For the mixture of DADNE with 2,4,6-TNF with a 1:1 ratio (Figure S5), the hydroxyl proton was seen as two broader signals with chemical shifts of 11.28 and 11.41 ppm. For the remaining DADNE/2,4,6-TNF molar ratios, hydroxyl signals with such a high chemical shift corresponding to a high degree of dissociation were not observed at all (Figure S5). Chemical shifts are described in Table 3 (specimen numbers 9 to 12). The appearance of two signals from 2,4,6-TNF hydroxyl protons may indicate the formation of 2,4,6-TNF complexes with DADNE and different stability constants. These complexes did not show sustained proton transfer to the amine group of DADNE because the signal of the  $\text{-NH}_2$  groups, at around 8.6 ppm, did not show the characteristic split described above. Increasing the DADNE:TNF molar ratio resulted in a 2,4,6-TNF hydroxyl signal at 8.4 ppm (2:1), 7.6 (3:1) and 7.0 (4:1). The shift of the 2,4,6-TNF hydroxyl signal towards higher fields indicates an increasingly strong shielding of the said proton with increasing concentration of DADNE in the solution.

2,4,6-TNF showed the highest degree of hydroxyl proton dissociation in the range of nitrophenols tested. The high degree of hydroxyl proton dissociation, for example, translates into 2,4,6-TNF reactivity and the formation of ionic salts with metals in a manner typical of acids. The expected effect of protonation of DADNE by 2,4,6-TNF was not found (Figures S5 to S7), so other types of interactions must have dominated in the system of interest. Complexes with different values of stability constants were most likely formed. Interactions of 2,4,6-TNF with the solvent itself should also be considered as such DMSO interactions have been the subject of many studies [10]. A better understanding of this effect requires additional research, as the formation of complexes is very often affected by the type of solvent used. DMSO was chosen for the NMR studies because it is aprotic and should not affect the interactions between the test components. In addition, DADNE shows low solubility in most typical organic solvents at ambient temperature [6].

The analysis of the  $^{13}\text{C}$  NMR spectra (Figures S2, S4 and S7) obtained for the test solutions, indirectly confirms the conclusions drawn from the analysis of the  $^1\text{H}$  NMR spectra. A slight shifting of the carbon signals resulting directly from increasing analyte concentrations, was found. For carbon nuclei, which are in atoms chemically bonded to atoms undergoing interactions associated with, for example, proton transfer, a stronger chemical shift of the signals of carbon atoms in the structure of the molecule was observed (Figure S4).

### 3. Conclusions

Based on analysis of the experimental material collected, the following conclusions can be made:

- ◆ The strongest intermolecular interactions were found in the mixture of DADNE with 2,4-DNF at a molar ratio of 1:1. A characteristic split in the proton signal of the amino groups was observed, which indicates direct protonation of the  $\text{-NH}_2$  group in DADNE with a hydroxyl proton from dinitrophenol. The spectroscopic parameters of the DADNE amine group signal indicate that an  $\text{NH}^{3+}$  cation was formed in the molecule.
- ◆ No interaction of DADNE with 4-nitrophenol was found at any of the molar ratios tested. The absence of nitrophenol proton hydroxyl signals on the spectrum indicates chemical exchange, the intensity of which was too low to trigger any protonation of the DADNE amino groups.
- ◆ The effects found in the spectra in the TNF–DADNE system did not indicate the protonation of  $\text{-NH}_2$  groups which was found in the 2,4-DNF–DADNE system. The observed interactions were probably caused by interactions of a coordinative nature, but confirmation of the hypothesis or indication of their character and stoichiometry, requires additional research.
- ◆ The analysis of signal structure changes in carbon  $^{13}\text{C}$  NMR spectra indirectly confirmed the conclusions drawn from the analysis of  $^1\text{H}$  NMR spectra. Signals of the carbon nuclei of chemically bonded atoms which underwent analyte interactions showed stronger changes in chemical shift which would result from a change in analyte concentration alone.
- ◆ Solid-phase X-ray analysis of DADNE revealed that the molecules of the compound formed quasi-polymeric chains bonded by hydrogen interactions between the oxygen atoms of the nitro groups and the hydrogen atoms of the amine groups [6]. So far, the presence of similar quasi-polymers in solution has not been confirmed. The formation of the interactions observed in the spectra of DADNE solutions with 2,4-DNF and 2,4,6-TNF probably requires a change in the total energy of the system which is greater than the energy of the interactions between the DADNE molecules. Estimating the value of the energy change of the system during complex formation requires calorimetric tests.

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