



## Polynitrobenzenes Containing Alkoxy and Alkylenedioxy groups: Potential HEMs and Precursors of New Energetic Materials

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**Abstract:** Several di-, tri- and tetranitroderivatives of alkoxy-, dialkoxy-, trialkoxy- and cyclic alkylenedioxybenzene derivatives were synthesized by nitration of starting compounds under different conditions and their properties were compared to the already known 2,4,6-trinitroanisole and TNT. Synthesized trinitro- and tetranitrocompounds of alkoxy-/alkylenedioxybenzene (especially cyclic derivatives) may serve as useful precursors for the synthesis of numerous energetic derivatives. The highest melting point (286 °C) and calculated density (1.907 g/cm<sup>3</sup>) is marked for 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine (TNBD). Promising properties of the latter compound allow further exploration of this material as a potential thermostable HEM.

**Keywords:** polynitroderivatives, HEMs, synthesis, 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine (TNBD), reactions

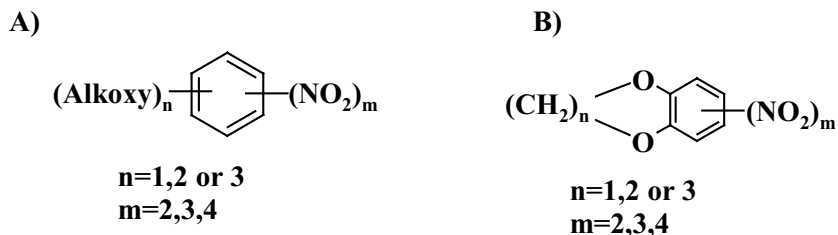
### Introduction

Aromatic polynitroderivatives belong to the most common high energy materials (HEMs) [1]. Many nitrocompounds from this class have been known as explosives and propellants since WWI or WWII and have had a wide range of civilian and military applications [2-5].

Modern high energy materials must fulfil several important requirements, such as insensitivity, thermostability, etc. [6].

The aim of this article is a brief exploration of the dinitro-, trinitro- and tetranitro- derivatives of alkoxy- or alkylenedioxybenzenes, which are

represented by the general formulas A and B respectively (Figure 1).



**Figure 1.** General formulae of alkoxy- (A) and alkylenedioxy- (B) benzene polynitroderivatives.

2,4,6-Trinitroanisole (TNA, 1-methoxy-2,4,6-trinitrobenzene) – is well known representative of this series and it is one of the safest, insensitive HEMs. The energetic properties of TNA are superior to TNT. Even the energetic properties of 2,4-dinitroanisole are similar to those of TNT. 2,4,6-Trinitrophenetole (1-ethoxy-2,4,6-trinitrobenzene) (m.p.78 °C) (A, alkyl=C<sub>2</sub>H<sub>5</sub>, m=3) has almost the same explosive properties as TNT. We have been unable to find any information on the energetic properties of other polynitroderivatives of these series. Literature analysis provides information only about one of these tetranitroderivatives - 2,3,4,6-tetranitroanisole, briefly described as a compound with a lead block expansion (Trauzl block test) value, superior to TNT (135%) [2].

The properties of the known polynitroderivatives of alkoxybenzenes are compared with those TNT in Table 1.

**Table 1.** The properties of known polynitroderivatives of alkoxybenzenes in comparison with those of TNT (all data cited in this table are taken from [18], with the exception of tetranitroanisole characteristics [2])

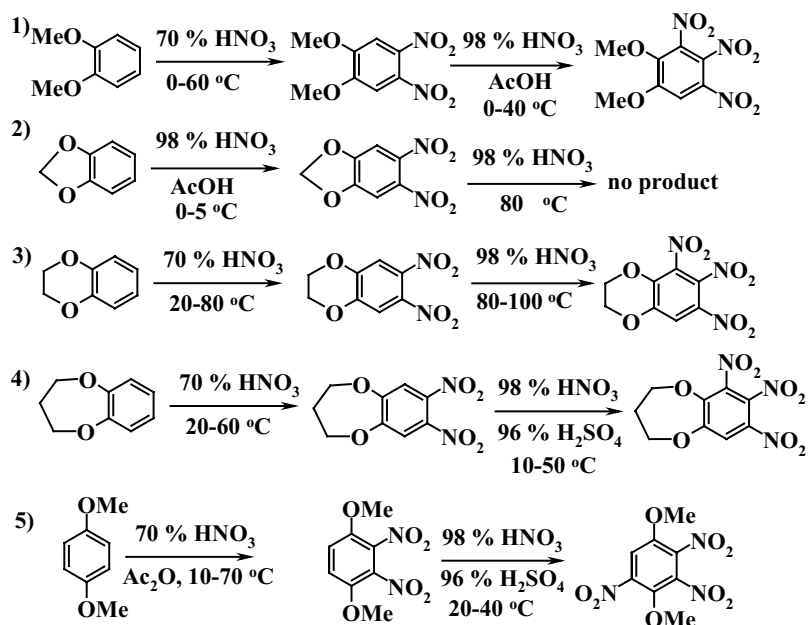
2,4-Dinitroanisole	2,4,6-Trinitroanisole	2,3,4,5-Tetranitroanisole	TNT
M.p.: 86.9 °C and 95 °C (two cryst. forms)	M.p. 68 °C	M.p. 139 °C	M.p. 80.8 °C
Lead block test – 295 cm <sup>3</sup> /10 g	Lead block test – 314 cm <sup>3</sup> /10g	Lead block test – 393- 414 cm <sup>3</sup> /10g [2]	Lead block test – 300 cm <sup>3</sup> /10g
Density – 1.61 g/cm <sup>3</sup>	Density – 1.61 g/cm <sup>3</sup>	-	Density – 1.654 g/cm <sup>3</sup>
VOD = 5620 m/s	VOD = 6800 m/s	-	VOD = 6900 m/s
	Impact sensitivity – 20 N/m	-	Impact sensitivity – 15 N/m

The properties of other derivatives from both these series have not been explored. In this article we will briefly describe the synthesis of the most promising tri- and tetranitrocompounds of these series and their potential as precursors for the synthesis of other energetic materials.

## Results and Discussion

### Synthesis of polynitroderivatives of alkoxy- and alkylendioxybenzenes

Dinitroderivatives of series A and B ( $m=2$ ) are widely known in organic chemistry and are also often utilized in our laboratory for the synthesis of different derivatives of O- and N-heterocycles. The synthetic route leading to dinitroderivatives is comparatively simple. In general, several methods of nitration were used, providing a good yields and purity of the corresponding dinitroderivatives (Scheme 1).

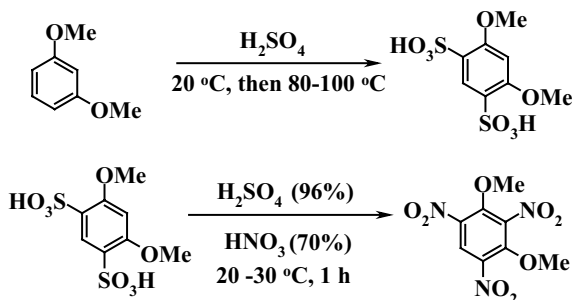


**Scheme 1.** Synthesis of dinitro- and trinitro- derivatives of alkoxy and alkylendioxybenzenes.

All nitration procedures resulted in good yields of the trinitroderivatives (Scheme 1) except for the trinitrocompound from 1,3-benzodioxole

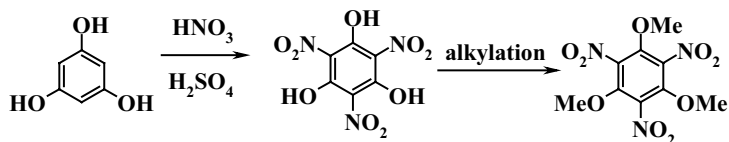
(Scheme 1, reaction 2). This fact can be explained by the increased sensitivity of methylenedioxy ring to the acidic medium. Although the direct route of nitration for the synthesis of tri- and tetranitro- methylenedioxy compounds is not possible, we are now planning the indirect synthesis of these derivatives by the alkylation of polynitrocatechols with  $\text{CH}_2\text{Br}_2/\text{K}_2\text{CO}_3$  in dimethylformamide. Nitration of 1,4-dimethoxybenzene (hydroquinone dimethyl ether) for the preparation of the dinitro compound was successful, but the yield of the trinitro derivative at the latest step was the lowest among the synthesized trinitro derivatives (14-33%, in several attempts), due to the parallel oxidative side-reactions, leading to destruction of the molecule.

For the nitration of 1,3-dimethoxybenzene (dimethyl ether of resorcinol) we successfully adopted the procedure described in [9]:



**Scheme 2.** Synthesis of 1,3-dimethoxy-2,4,6-trinitrobenzene by the two stage method.

1,3,5-Trimethoxy-2,4,6-trinitrobenzene (trinitro derivative of phloroglucinol trimethyl ether) has been obtained according to the convenient two-stage procedure of Bellamy et al. [10] (Scheme 3).

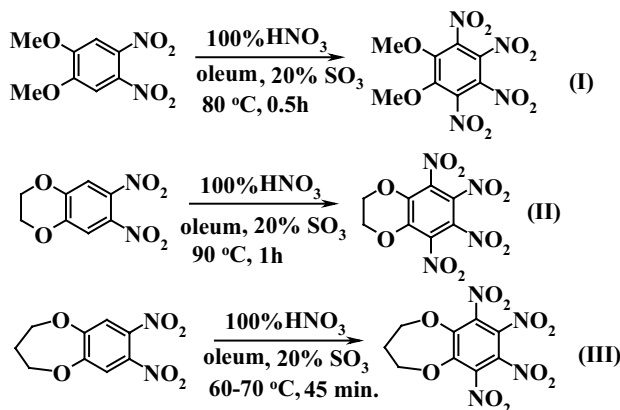


**Scheme 3.** Preparation of 1,3,5-trimethoxy-2,4,6-trinitrobenzene (trinitro derivative of phloroglucinol trimethyl ether).

Synthetic procedures for the preparation of the tetranitro derivatives of this series have been almost unexplored. There is only one old publication by Heertjes et al. (1941) concerning the successful synthesis of cyclic ethylenedioxy

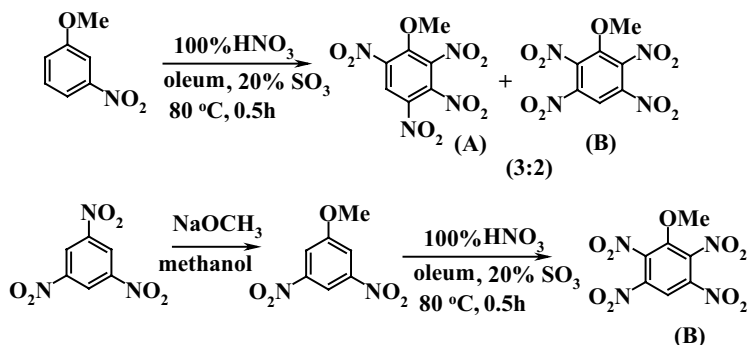
tetranitroderivative – 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine [7].

We have modified this published method replacing concentrated  $\text{H}_2\text{SO}_4$  in the concd. nitration mixture with oleum, containing 20%  $\text{SO}_3$ , and have used this procedure for the synthesis of other homologs – 6,7,8,9-tetranitro-3,4-dihydro-2*H*-1,5-benzodioxepine (propylenedioxytetranitrobenzene) and 1,2-dimethoxy-3,4,5,6-tetranitrobenzene (tetranitroveratrole) (I) (Scheme 4):



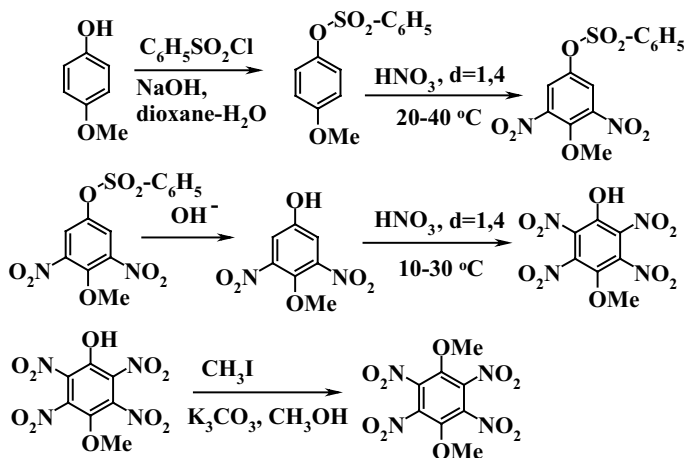
**Scheme 4.** Preparation of tetranitroderivatives.

This method was also successful in the synthesis of two different isomers of tetranitroanisole by nitration of *m*-nitroanisole and 3,5-dinitroanisole, according to (Scheme 5) (it is interesting, that the second reaction does not yield any traces of pentanitroanisole).



**Scheme 5.** Nitration of 3-nitroanisole and 3,5-dinitroanisole to form isomeric tetranitroderivatives.

The isomeric mixture resulting from the nitration of 3-nitroanisole was separated by several re-crystallizations and subsequent purification by vacuum-assisted chromatography on silicagel (isomer A m.p. 94 °C, isomer B – 151 °C). We have also attempted to adopt this procedure for the nitration of 2,3-dinitro-1,4-dimethoxybenzene and 2,3,5-trinitro-1,4-dimethoxybenzene to the tetranitroderivative, without success. Fortunately, literature analysis provides us another indirect method, using 4-methoxyphenol [3], which was applied efficiently (Scheme 6).



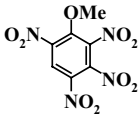
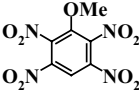
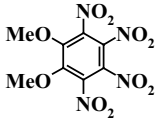
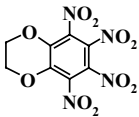
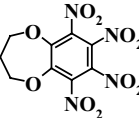
**Scheme 6.** The indirect synthesis of 1,4-dimethoxy-2,3,5,6-tetranitrobenzene (m.p.180 °C, from methanol).

The final stage of the Scheme 6 could also be utilized by analogy in our recently ongoing efforts to synthesize 2,3,4,5,6-pentanitroanisole from the already known pentanitrophenol.

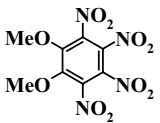
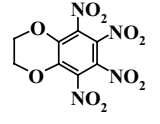
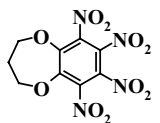
Evaluation of the properties of the most interesting alkoxy- and alkylendioxy- tetranitroderivatives

ACDLabs (Toronto) chemical software (version 4.6) has been used for the evaluation of density and spectral properties. Oxygen balance has been calculated by formula:  $OB = -1600/MW \cdot (2X + (Y/2) - Z)$ , where MW is the molecular weight of compound, X is the number of carbon atoms, Y is the number of hydrogen atoms and Z is the number of oxygen atoms [17]. The results obtained are presented in Table 2.

**Table 2.** Calculation of the properties of selected tetranitrocompounds

No.	Struct. formula	Molecular formula	MW	Calc. density g/cm <sup>3</sup>	Oxygen balance OB, %
1.		C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O <sub>9</sub>	288.13	1.791	-38.87
2.		C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O <sub>9</sub>	288.13	1.791	-38.87
4.		C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O <sub>10</sub>	318.16	1.721	-45.26
5.		C <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>10</sub>	316.14	1.907	-40.49
6.		C <sub>9</sub> H <sub>6</sub> N <sub>4</sub> O <sub>10</sub>	330.17	1.799	-53.31
7.	2,4,6-trinitroanisole	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>7</sub>	243.13	1.632 (1.610 - exp.)	-62.50
8.	TNT	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	227.13	1.648 (1.654 -exp.)	-73.97
9.	RDX	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	222.12	Not calc. (1.82 - exp.)	-21.61

**Table 3.** Comparison of calculated (ACDLabs) and experimental  $^{13}\text{C}$  NMR spectra for tetranitroderivatives

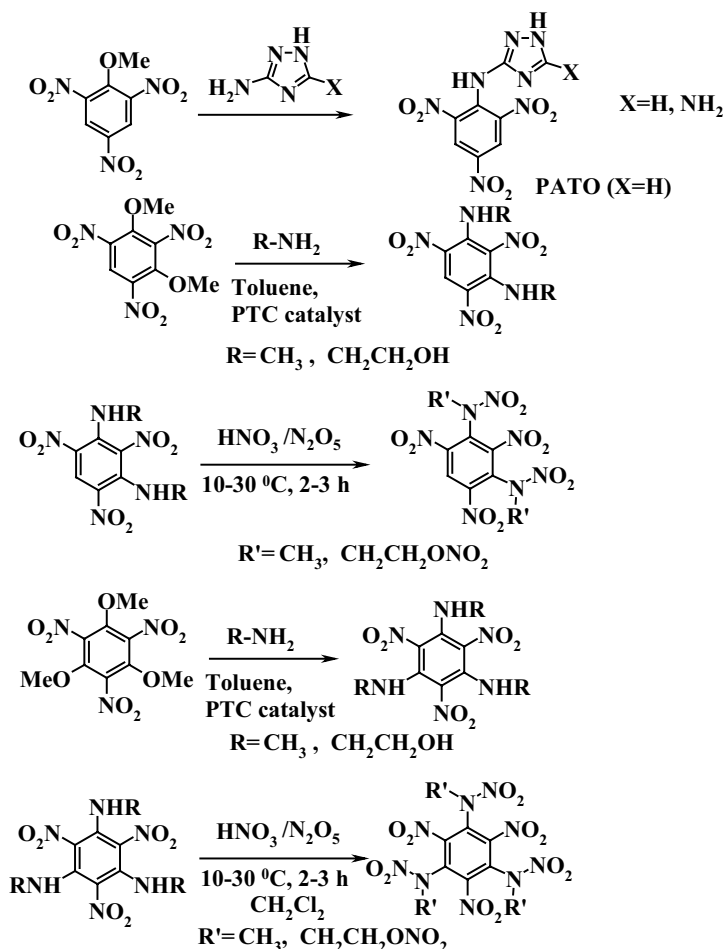
No.	Struct. formula and melting (decomp.) point	Calculated spectra, $\delta$ [ppm]	Experimental spectra, $\delta$ [ppm] (Freq. 75 MHz, DMSO- $d_6$ )
1.	 m.p. 168 °C (dec.)	135.91; 128.61; 126.23; 62.28.	138.76; 130.61; 119.32; 63.30.
2.	 m.p. 286 °C (deflagr.)	133.39; 128.65; 124.15; 65.71.	143.91; 132.43; 129.02; 66.31.
3.	 m.p. 184 °C (dec.)	131.53; 128.31; 126.33; 70.42; 23.83.	149.44; 137.07; 130.18; 73.83; 28.39.

5,6,7,8-Tetranitro-2,3-dihydro-1,4-benzodioxine, compound No. 5 (Table 3) is exceptionally thermostable and has a higher decomposition point (the sample deflagrates on heating with a flash after melting at 286 °C) than the other two tetranitroderivatives. According to the calculations, this derivative also has the highest density among all the compounds of this group – 1.907 g/cm<sup>3</sup>. It is interesting, that our sample of this substance does not undergo changes after more than 15 years storage at room temperature.

### Short description concerning the synthetic utilization of the synthesized polynitrocompounds in the synthesis of other energetic derivatives

The synthesized trinitro- and tetranitrocompounds of alkoxy-alkylenedioxybenzene (especially the cyclic derivatives) may serve as useful precursors for the synthesis of numerous energetic derivatives. Some principal reactions recently carried out in our laboratory [11-16] are shown in the following scheme (Scheme 7).



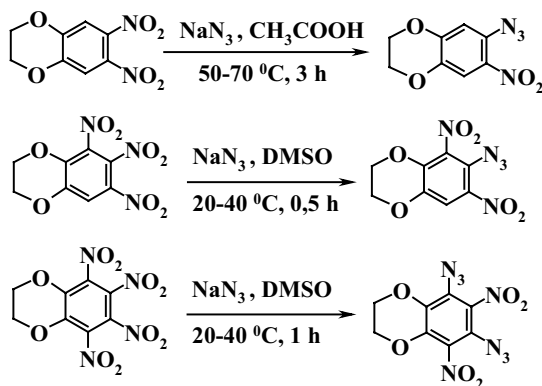


**Scheme 7.** The substitution reactions of an activated alkoxy group, which are useful for the synthesis of energetic derivatives.

The substitution of an alkoxy group by aminoheterocycles or aminoaliphatic reagents proceeds with a good yield of the amino/nitro derivatives [11]. This route is even more attractive for the production of PATO-type energetic compounds than the use of more deficient precursors containing activated halogens (PATO is a well-known thermally stable explosive – 3-picrylamino-1,2,4-triazole). On the other hand, aliphatic aminoderivatives from the first stage may further be nitrated yielding tetryl or pentryl type energetic substances [1, 8]. Traces of water or even some polar solvents must be avoided in these reactions, because they lead to contamination of the reaction products with by-products, containing

phenolic hydroxyl groups (alkoxy group changed to OH).

Another type of reaction is the replacement of the activated nitro group with azide as shown for nitroderivatives of 2,3-dihydro-1,4-benzodioxine (Scheme 8).



**Scheme 8.** Reactions of di-, tri- and tetranitroderivatives of 2,3-dihydro-1,4-benzodioxine utilizing the replacement of the nitro group by an azido group.

Replacement of the nitro group by azide leads to mono- or diazido-derivatives, analogues of picrylazide and pentanitrophenylazide (CL-16). The best solvent selected for this reaction is DMSO (and in some case – AcOH). A 2-phase system (dichloroethane/water) with a phase-transfer catalyst also provides good yields.

*(CAUTION: Azido-nitroderivatives are powerful explosives, sensitive to shock, friction, mechanical and thermal factors. Nitroaromatic azides are photosensitive to daylight and require careful work with these substances. During the heating, azides may decompose with deflagration or detonation. In one of our experiments a small dry sample of 5,7-diazo-6,8-dinitro-2,3-dihydro-1,4-benzodioxine (~ 100 mg) decomposed with deflagration and sound at 87-90 °C. However under appropriate conditions and in solution, at elevated temperatures (80-120 °C), the aromatic azido/nitro compounds mentioned here, smoothly undergo thermocyclisation with the release of nitrogen and formation of furoxan derivatives [16-17]).*

## Conclusions

This preliminary overview article demonstrates that, after appropriate synthetic modification, nitrated alkoxy- and alkylenedioxybenzene derivatives can produce potentially interesting energetic compounds – tetranitroderivatives.

The oxygen balance (OB) of the substances described in this paper varies from -53.31% for 6,7,8,9-tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (compound 6) to -38.87%, for both tetranitroanisole isomers (Table 2, compounds 1 and 2). The calculated density was highest for the 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine (compound 5) – 1.907 and lowest for 1,2-dimethoxy-3,4,5,6-tetranitrobenzene – 1.721 g/cm<sup>3</sup>. The highest melting point and decomposition temperature is marked also for compound (5) - 286 °C. These facts enable us to conclude that 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine (5) (TNBD) (OB=-40,48%) has promising properties and may be interesting for further exploration as a potential thermostable HEM. The substitution reactions of activated alkoxy and nitro groups can be utilized for the synthesis of derivatives of alkoxy-/alkylenedioxy polynitrocompounds as valuable precursors for the syntheses of other HEMs.

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