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Synthesis and structure of 2,3,6,8,10,13,14-heptaaza-6,8,10-trinitro-4,12-dioxapentadeca-2,13-diene 2,14-bisoxide

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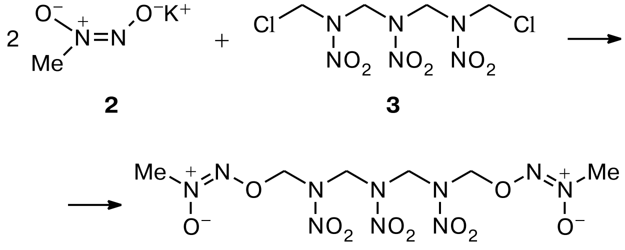
Alkylation of potassium salt of methylnitrosohydroxylamine with 1,7-dichloro-2,4,6-triaza-2,4,6-trinitroheptane afforded 2,3,6,8,10,13,14-heptaaza-6,8,10-trinitro-4,12-dioxapentadeca-2,13-diene 2,14-dioxide. The structure of the reaction product was established by X-ray diffraction analysis.

Key words: alkoxydiazene *N*-oxides, nitramines, 1,7-dichloro-2,4,6-triaza-2,4,6-trinitroheptane, potassium salt of methylnitrosohydroxylamine, 2,3,6,8,10,13,14-heptaaza-6,8,10-trinitro-4,12-dioxapentadeca-2,13-diene 2,14-dioxide, X-ray diffraction analysis, crystal structure.

The synthesis of acyclic and cyclic nitramines of the general formulas R—NNO_2—(CH_2—NNO_2)$_n$—NNO_2—R and (CH_2—NNO_2)$_n$, respectively, has long attracted the attention of researchers in the field of chemistry of energetic materials (explosives, blasting powders, and components of rocket propellants), which is being successfully developed.[1] In recent years, particular attention has been given to cage nitramines, because they combine a high enthalpy of formation, high density, and thermal stability. The preparation of hexanitrohexaazaisowurtzitane of composition $C_6H_6N_{12}O_{12}$, which has a density of 2.044 g cm^{-3} and an enthalpy of formation of 377.4 kJ mol^{-1} (861.3 kJ kg^{-1}), can be considered as an outstanding achievement in this field.[2] The synthesis of polyfunctional compounds containing not only the >N—NO_2 fragment but also other explosophoric groups (≡C—NO_2, >C(NO_2)$_2$, —C(NO_2)$_3$, —ONO_2, *etc.*) is another important field of the chemistry of nitramines, which has also long been in progress. Polyfunctional nitramines containing the alkoxydiazene *N*-oxide group, which is isomeric to the nitramine group but differs from the latter both in the geometry and electronic structure, are of particular interest. The introduction of the alkoxydiazene *N*-oxide group leads to an increase in the enthalpy of formation and gives promise that some important explosophoric characteristics may be improved. These compounds are also of interest from the viewpoint of the mutual effect of the alkoxydiazene *N*-oxide and nitramine groups.

In the present study, we synthesized 2,3,6,8,10,13,14-heptaaza-6,8,10-trinitro-4,12-dioxapentadeca-2,13-diene 2,14-bisoxide (**1**), which has previously been unknown. Compound **1** was prepared by alkylation of potassium salt of methylnitrosohydroxylamine (**2**)[3] with 1,7-dichloro-2,4,6-triaza-2,4,6-trinitroheptane (**3**).



Apparently, the low yield (13%) of compound **1** is associated with the formation of by-products of alkylation at another oxygen atom of anion **2**, *viz.*, *N*,*O*-dialkylnitrosohydroxylamines (*cf.* Refs 3 and 4), as well as with the side reaction of compound **3** with methanol. The melting point of compound **1** is much lower than that of its isomer containing five nitramine groups, *viz.*, 2,4,6,8,10-pentanitro-2,4,6,8,10-pentaazaundecane[1] (161 and 255 °C, respectively). It should be noted that the chemical shifts of the protons of the NCH_2N methylene groups are identical with those of the OCH_2N groups ($\delta = 5.90$, a narrow peak is observed even in the spectrum measured on an instrument operating at 500 MHz).

The structure of compound **1** was established by X-ray diffraction analysis. In the triclinic crystals of **1**, the asymmetric molecules (Fig. 1) occupy general positions. Both $MeN^+(O^-)=NOCH_2$ groups are planar (the maximum deviation of the nonhydrogen atoms from the common plane is ±0.03 Å). The —N(O)=NO— fragments have *Z* configurations. The orbital couplings stabilizing the

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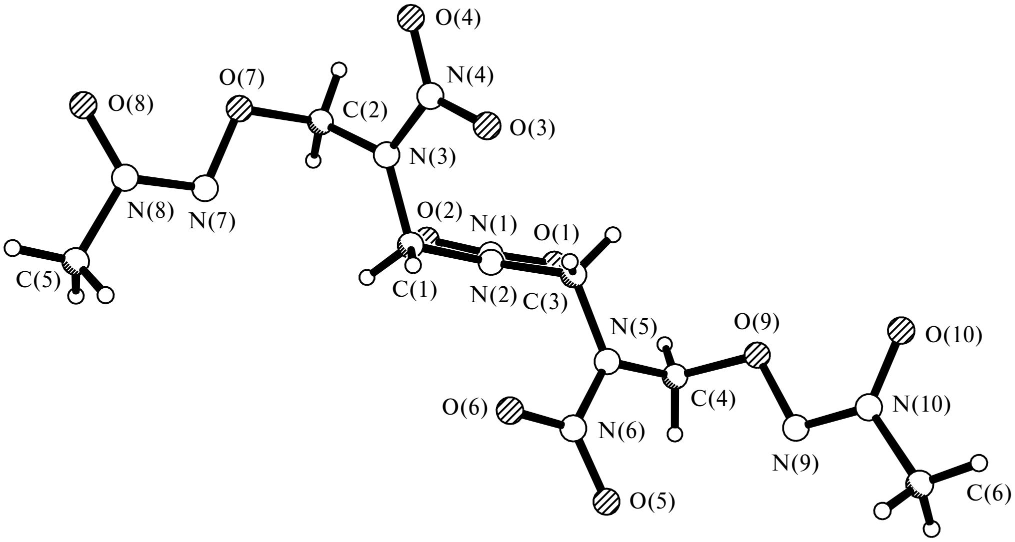

Fig. 1. Molecular structure of compound **1**.

Z configurations of the —N(O)=NO— fragments have been considered by us earlier.[5] All three nitramine fragments are also planar (the deviations of the atoms from the CNNOOC planes are no larger than ±0.02 Å). The geometry of the fragments (N—N, 1.36 Å; N—O, 1.23 Å; a planar configuration of the amino nitrogen atoms) provides evidence in favor of the possible p—π* orbital coupling between the lone electron pair of the amino nitrogen atom and the unoccupied orbital of the nitro group resulting in an increase in the charge density on the oxygen atoms of the nitro groups. The nitro groups in molecule **1** have higher charges than those in the molecules of other nitramines.[6] The mutual repulsion between the nitro groups of different molecules leads to a weakeing of the intermolecular O...O contacts. Apparently, this is the reason for the rather low density of compound **1** (d = 1.628 g cm^{-3}). For comparison, a mixture of di(methyl-NON-azoxy)dimethoxymethane[3] (d = 1.520 g cm^{-3}) and octogene[1] (d = 1.902 g cm^{-3}) (molar ratio is 4 : 3), which is identical in elemental and group composition to compound **1**, is much more dense (d = 1.718 g cm^{-3}, calculations according to an additive scheme).

Experimental

The ^{1}H NMR spectrum was recorded on a Bruker DRX-500 spectrometer. The mass spectrum was measured on an MX-1320 instrument.

1,7-Dichloro-2,4,6-triaza-2,4,6-trinitroheptane (3). Hydrogen chloride was bubbled through a suspension of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane[7] (10 g, 28.8 mmol) in dioxane (60 mL) with vigorous stirring for 15—30 min. The reaction mixture was stirred at 0 °C for 2 h and then at 20 °C for 5 h. The crystalline precipitate that formed was filtered off, washed with ether (50 mL), dried in air, and recrystallized from dichloroethane. The yield was 8.1 g (93%), m.p. 143—144 °C (*cf.* lit. data[2]: m.p. 144.5—145.5 °C).

2,3,6,8,10,13,14-Heptaaza-6,8,10-trinitro-4,12-dioxapentadeca-2,13-diene 2,14-bisoxide (1). A solution of compound **3** (1.57 g, 5.1 mmol) in anhydrous acetone (15 mL) was added in one portion to a solution of salt **2**[3] (1.27 g, 11.1 mmol) in anhydrous MeOH (15 mL) at ~20 °C. The resulting homogeneous solution was refluxed with stirring for 0.5 h, during which a precipitate of KCl formed. The reaction mixture was concentrated *in vacuo*, the temperature of the bath being maintained no higher than 40 °C. The residue was diluted with water (20 mL) and extracted with AcOEt (5×20 mL). The extract was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was subjected to flash chromatography on a dry column[8] packed with Silpearl silica gel (50 mL) with the use of a CH_2Cl_2—AcOEt mixture (from 1 : 1 to 1 : 3, v/v). The fraction with R_f 0.22 (Silufol, $CHCl_3$—AcOEt, 2 : 3, v/v) was concentrated *in vacuo* and the residue was recrystallized from an acetone—$CHCl_3$ mixture. The yield was 0.25 g (13%), m.p. 159—161 °C (melt slowly decomposed), d = 1.61 g cm^{-3} (flotation). ^{1}H NMR (DMSO-d$_6$), δ: 3.90 (s, 6 H, Me); 5.90 (s, 8 H, CH_2). MS, m/z (I_{rel} (%)): 302 $[M - MeN_2O_2]^+$ (1), 237 $[M - MeN_2O_2CH_2NNO_2]^+$ (21), 206 (2), 163 $[MeN_2O_2CH_2N(NO_2)CH_2]^+$ (35), 133 (29), 117 (10), 116 (6), 89 $[MeN_2O_2CH_2]^+$ (9), 87 (10), 75 (10) $[MeN_2O_2]^+$, 59 (33), 42 (100).

X-ray diffraction study of compound 1. Crystals of compound **1** suitable for X-ray diffraction analysis were prepared by slow evaporation of a solution of compound **1** in a mixture of acetone and $CHCl_3$ at ~20 °C. Compound **1** is virtually insoluble in pure $CHCl_3$. Single-crystal X-ray diffraction study of compound **1** was carried out on a four-circle KM-4 diffractometer (KUMA-Diffraction, Poland). The crystals of **1** are triclinic, M = 386.24, a = 10.829(10), b = 11.187(5), c = 7.412(2) Å, α = 76.57(4), β = 78.90(3), γ = 65.03(4)°, V = 787.36(7) Å^3, d = 1.628 g cm^{-3}, Mo-λKα = 0.710 Å, space group $P\bar{1}$, Z = 2, μ = 0.151 mm^{-1}.

A total of 3014 reflections were measured in the angle range 2θ ≤ 60.07° using the ω/2θ scan technique. The structure was solved by direct methods with the use of the SHELX-97 program package. The atomic coordinates were refined by the full-matrix least-squares method with anisotropic and isotropic thermal parameters for nonhydrogen and hydrogen atoms, respectively, using the SHELX-97 program package. The refinement converged to $R = 0.039$ for 1666 $F_0 > 4\sigma(F_0)$ and $R = 0.103$ for all 3014 reflections.

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