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Mendeleev Commun., 2010, **20**, 249–252
Mendeleev Communications

One-pot synthesis of 4,6,8-trinitro-4,5,7,8-tetrahydro-6*H*-furazano[3,4-*f*]-1,3,5-triazepine in ionic liquids

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DOI: 10.1016/j.mencom.2010.09.002

Nitration of 3,4-diaminofurazan with HNO_3, followed by condensation of the di(nitramine) intermediate with *N*,*N*-bis(hydroxymethyl)-*N*-nitroamine or *N*,*N*-bis(acetoxymethyl)-*N*-nitroamine in ionic liquids affords the title compound in good yield.

Cyclic nitramines constitute an important class of highly energetic materials whose synthesis and properties have been widely studied.[1] To investigate an effect of cycle size and number of nitro groups on energetic properties among nitramines, a vast variety of four-, five-, six-, seven-, and eight-membered N-nitrated azacyclanes (some examples are shown in Figure 1) were synthesized. Progress in the chemistry of such nitramines was the subject of comprehensive reviews.[2]

However, only few azole-fused N-nitrated azacyclanes have been described. The reported examples of these ring systems are furazano[3–5] and tetrazolo derivatives;[5,6] the most of them belonged to fused systems with six-membered azacyclanes.

The furazano[3,4-*f*]-1,3,5-triazepines represent rare types of energetic fused heterocycles.[7] The only two-step protocol for the synthesis of a furazano-fused seven-membered N-nitrated azacyclane, 4,6,8-trinitro-4,5,7,8-tetrahydro-6*H*-furazano[3,4-*f*]-1,3,5-triazepine **1**, reported so far, was prepared by the condensation of 3,4-diaminofurazan **2** with formaldehyde and potassium sulfamate followed by nitration of the condensation products (**3** and **4**) with HNO_3/Ac_2O, and final fractional crystallization (Scheme 1).[5] The overall (on two separate steps) yield of nitramine **1** was only 36%, since purification of the product **1** required a tedious separation from the by-products, the major one being RDX. Hence, a key challenge in its synthesis is to enhance selectivity of the three component construction of the triazepine ring.

In continuation of our interest in exploring safe approaches to energetic materials synthesis in ionic liquids,[8] a novel and effective one-pot strategy for the preparation of compound **1** involving two components construction of the triazepine ring was developed and is reported here. This approach consisted in

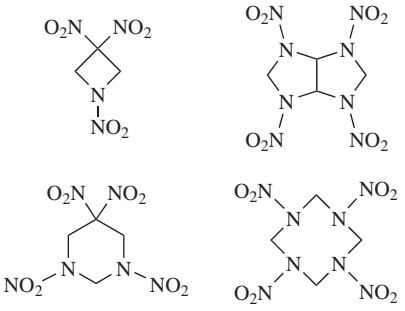
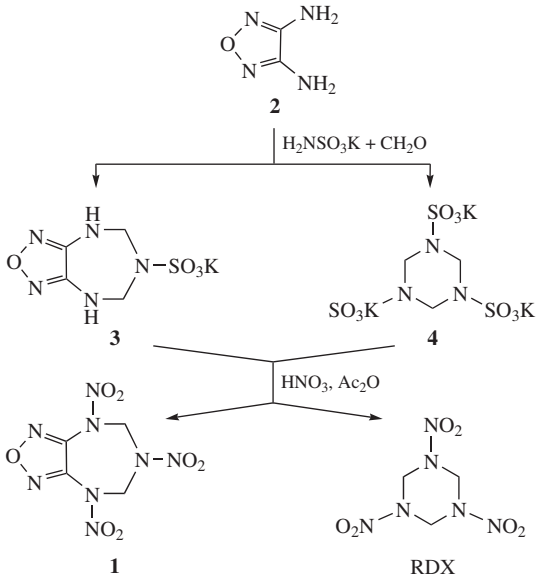


Figure 1 Cyclic nitramines.



Scheme 1

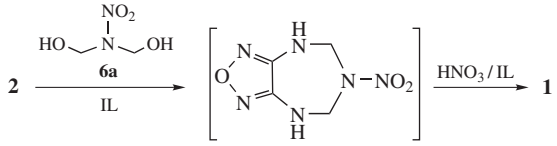
the generation of the 2-nitro-2-azaalkan-1-ol building blocks[9] followed by their Mannich-type condensation with appropriate nucleophilic reagents.

We reasoned that readily available 2-nitro-2-azapropane derivatives, namely *N*,*N*-bis(hydroxymethyl)-*N*-nitroamine **6a**[10] and *N*,*N*-bis(acetoxymethyl)-*N*-nitroamine **6b**,[11] can provide an access to 4,5,7,8-tetrahydro-6*H*-furazano[3,4-*f*]-1,3,5-triazepine skeleton.

It is documented[12] that 2-nitro-2-azaalkan-1-ols and their acetates can readily undergo condensation with amines and nitramines to form linear or cyclic 1,3-dinitramines under acidic conditions. On the other hand, the N-nitration of aminofurazan derivatives with acidic mixtures is also known.[13] An intriguing possibility is the use of a one-pot procedure combining the condensation and nitration steps in the synthesis of nitrated furazano[3,4-*f*]-1,3,5-triazepines.

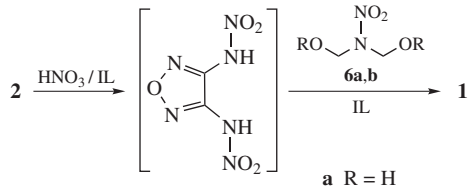
Ionic liquids (IL) have attracted much attention recently as nonflammable, noncorrosive, and nonvolatile media in organic synthesis,[14] in particular, the Mannich-type condensations[15] and aromatic C-nitration.[16] We reasoned that the combination of these two reactions, which takes advantage of the IL as a solvent and catalyst, can result in a highly effective and safe procedure for the preparation of cyclic nitramines.

Considering all factors, two approaches to the target triazepine **1** were attempted. We first envisioned a one-pot acid-catalyzed condensation/nitration procedure in IL (Scheme 2). Unfortunately, all attempts to form this bicyclic system from diamine **2** and alcohol **6a** under a variety of conditions {[emim]-[HSO_4], [bmim][CF_3SO_3] + H_2SO_4 (20:1), [bmim][PF_6] + H_2SO_4 (20:1)} gave complex mixtures of products (TLC control) from which, after nitration† with HNO_3/Ac_2O at 0 °C, compound **1** was isolated in a yield as low as 15–20%.



Scheme 2

In view of these results, another approach to nitramine **1** was developed which is outlined in Scheme 3. This involved nitration first of diamine **2** and then introduction of the intermediated nitramine into the triazepine ring closure.



Scheme 3

When a solution of diamine **2** in [emim][HSO_4]:[bmpyrr]-[CF_3SO_3] (1:1) was treated with 1 equiv. of 99% HNO_3 at 0 °C, followed by condensation of the resulting di(nitramine) intermediate **5** with alcohol **6a**, the cyclization product **1** was formed in 43% yield. The similar reaction with acetate **6b** produced compound **1** in a 54% yield. Further efforts were then focused on optimizing the reaction conditions, and these results are summarized in Online Supplementary Materials (Table 1). All mixed ILs gave comparable yields, however, less viscous liquids gave better conversion, and [emim][HSO_4]:[bmpyrr][CF_3SO_3] (1:2) showed to be optimal. We found that temperature is crucial and that the nitration must be carried out below 0 °C, otherwise decomposition of the IL occurs and the yield of the product drops. When the amount of HNO_3 is less than 1.2 equiv. the yield decreased, while the increase in this parameter does not change the yield. After screening a variety of conditions using 1.5 equiv. of diacetate **6b**, the 85% yield of the product **1** was achieved. This protocol‡ provides practical synthetic access to N-nitrated triazepine **1**. However, it is important to emphasize that ILs must be used dry to provide the yields achieved.

The examination of the recyclability of the mixed IL system [emim][HSO_4]:[bmpyrr][CF_3SO_3] (1:2) showed that the medium could be reused directly for a new cycle, after extraction of the product **1** with diethyl ether and removing violated impurities *in vacuo* at 80 °C. The experiments demonstrated that the IL system was recyclable for four runs with a slight drop in yields (87, 81, 79 and 72%, respectively).

The structure of compound **1** was established by X-ray crystallography. An asymmetric unit cell contains two independent molecules (A and A′).§ Structures of both molecules are rather similar, and general view of molecule A is depicted in Figure 2 (along with calculated molecular structure). The seven-membered ring adopts chair conformation so that atoms N(3), C(3), C(4), N(5) [N(3′), C(3′), C(4′), N(5′)] form central nearly planar fragment. Angles of these planes with two other planar fragments of each seven-membered cycle (of molecules A and A′) along with other meaningful geometry characteristics are given in Online Supplementary Materials (Table 2). In both independent molecules, in all N–NO_2 moieties amino-nitrogen atoms are not planar. All nitro groups deviate from corresponding C–N–C planes so that to come closer to each other. The deviation from planarity for central N–NO_2 fragment [at N(4), N(4′)] is more pronounced. In spite of isolated molecule can be characterized by C_s symmetry, in the crystal both molecules are found in general positions; their asymmetry can easily be seen from difference of O···O nonbonded intramolecular contacts between nitro groups: one nitro-nitro pair is stronger bound than another one. For molecule A′ this difference is more sizable. In addition, slightly shortened intramolecular contacts H(3A)···O(3) and H(4A)···O(6) are observed in both independent molecules and might correspond to weak C–H···O interaction (see Online Supplementary Materials, Table 3). Similar observation was made for RDX.[19] Intermole-

† This was confirmed by a special experiment, amino group at the furazan ring can be easily converted to nitramine group by treatment with pure 99% nitric acid or its mixture with acetic anhydride in ILs. To get information about the effect of the IL structures on this N-nitration reaction, 3-amino-4-nitrofurazan **7**[17] was chosen as a model substrate, and its reactivity was analyzed in the presence of five ILs, namely, [emim]-[HSO_4], [bmim][X] (where X = PF_6^-, $MeSO_3^-$, $CF_3SO_3^-$, $CF_3CO_2^-$, and NTf_2^-), and [bmpyrr][CF_3SO_3] with addition of H_2SO_4. We found that the nitramine product, 3-nitramino-4-nitrofurazan **8**,[18] was formed in low yield when compound **7** in any IL was treated with a stoichiometric amount of 99% HNO_3 or HNO_3/Ac_2O at 0 °C. The ILs used are mobile liquids at room temperature, but at 0 °C they become very viscous. In order to decrease viscosity, we used mixtures of [emim][HSO_4]:[bmim]-[CF_3SO_3] (1:1) and [emim][HSO_4]:[bmpyrr][CF_3SO_3] (1:2) as solvent. In this case, with the use of 1.5 equiv. of HNO_3, the yields of compound **8** after 1 h at 0 °C were 86% and 94%, respectively. Efficient conversion to the product **8** in 85–90% yields also occurred when amine **7** was treated with a mixture of HNO_3/Ac_2O (1.5/1.5 equiv.) for 2 h in the medium of [C_2C_1im][HSO_4]:[bmpyrr][CF_3SO_3] (1:2) or [bmim][PF_6] + H_2SO_4 (20:1). The identity of product **8** was confirmed by NMR spectra, CHN analysis, mp, HRMS, and comparison with the literature data.[18]

‡ *General procedure.* A tree-necked round bottom flask equipped with a condenser, thermometer, magnetic stirring bar and rubber septa was charged with a mixture of [emim][HSO_4] (10 ml) and [bmpyrr][CF_3SO_3] (20 ml) under an inert atmosphere. Then diamine **2** (1 g, 10 mmol) was dissolved in the IL at 30 °C. The mixture was cooled to 0 °C, and 99% HNO_3 (1 ml, 24 mmol) was slowly added. After 1 h, diacetate **6b** (3.1 g, 15 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 8 h, and then extracted with diethyl ether (5×50 ml). The combined etheral phase was washed with $NaHCO_3$/water, dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by recrystallization to afford 2.34 g (85%) of compound **1** as a white solid; mp 150–151 °C (decomp.) [lit.,[5] mp 151 °C (decomp.)].

§ *Crystal data for* **1**: crystals of $(C_4H_4N_8O_7)_2$ are orthorhombic, space group *Pbca*: a = 11.9614(5), b = 13.8190(5) and c = 22.6601(9) Å, V = = 3745.6(3) Å^3, Z = 8, M = 276.15, d_{calc} = 1.959 g cm^{-3}, μ = 0.185 mm^{-1}, $F(000)$ = 2240, wR_2 = 0.1034, GOF = 1.013 for 6528 independent reflections with $2\theta < 62°$, R_1 = 0.0330 for 5526 reflections with $I > 2\sigma(I)$.

The single crystals of compound **1** suitable for X-ray diffraction study were obtained in the form of colourless prizms by slow evaporation of $CHCl_3$ solution at ambient temperature. Reflections for the compound **1** were collected on a SMART APEX2 diffractometer [λ(MoKα) = 0.71073 Å, graphite monochromator, ω-scans] at both 100 K and room temperature. The results at 100 K are more precise, therefore only low-temperature experimental data are discussed while room temperature data are given in supplementary. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. All the hydrogen atoms were placed in geometrically calculated positions and refined within riding model.

CCDC 791221 and 791222 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

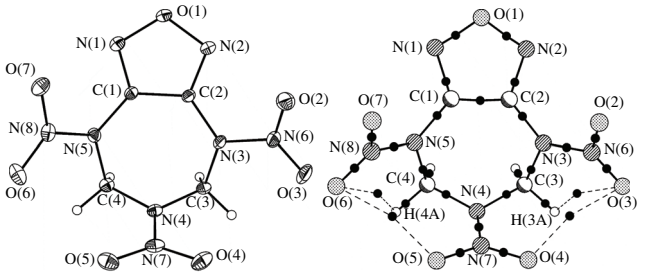


Figure 2 General view of compound **1**: ORTEP view of X-ray structure of unprimed molecule A (left) and M052X/aug-cc-pvdz optimized structure of isolated molecule (right). Bond critical points (3, –1) are given by solid circles.

cular non-bonded interactions can probably influence mutual orientation of nitro groups. For instance, well-known HMX, which has four N–NO_2 groups attached to more flexible eight-membered cycle, can exist in several polymorph forms[20,21] with different intra- and intermolecular interactions between nitro groups.

Nitro groups and furazan moiety of both independent molecules are involved in many nonbonding interactions. Among them there are two strongest O···O interactions (both of them are formed between two independent molecules) with interatomic separation to be significantly less than the sum of nonbonded radii.[22] The O(5)···O(7′) contact connects molecules into dimers which are additionally stabilized by several weaker interactions. Based on analysis of interatomic distances, interaction between molecules in this dimer is the strongest. This fact explains (at least partly) formation of two symmetrically independent molecules in the unit cell: such tight binding cannot be achieved by molecules related by any symmetry operation. The other short O(6)···O(5′) contact links molecules into the chains along axis *b* (Figure 3).

All the other interactions are formed by atoms separated by distances being at the boundary between normal and shortened ones that is usually observed in crystal structures involving furazan ring and nitro group.[23–25] Thus, nitro groups of A and A′ molecules differently participates in nonbonded interactions thereby leading to nonequivalent intramolecular O···O contacts between nitro groups.

In order to study preferable structure for isolated (gas phase) molecule we have carried out quantum chemical calculation using Gaussian03 program.[26] Based on our previous results on nitramino-furazans[13(*i*)] we chose M052X/aug-cc-pvdz level of approximation which was shown to better describe N–NO_2 moiety. As initial geometry, the X-ray one of less symmetric molecule A was utilized. As expected, geometry optimization leads to molecular structure of C_s symmetry. Topological analysis of the calculated electron density in terms of Bader's theory 'Atoms in Molecules'[27] (using AIMAll program[28]) has revealed that in isolated state, the molecular structure is stabilized by two intramolecular nonbonded O···O and two C–H···O interactions [see Tables 2 and 3 in Online Supplementary Materials and Figure 2 which shows all (3, –1) critical points]. Energies of O(3)···O(4), O(5)···O(6), H(3A)···O(3) and H(4A)···O(6) interactions (which are pairwise equal due to symmetry) estimated by the correlation of potential energy density in bond critical point and interaction energy[29,30] are equal to 2.64 and 5.96 kcal mol^{-1} for O···O and C–H···O contacts, respectively, and comparable to intermolecular ones. The results supported a conclusion that molecular asymmetry in the crystal structure is caused by a cooperative effect of several intermolecular interactions that lead to high density crystal packing (d_{calc} = 1.959 and 1.892 g cm^{-3} at 100 K and room temperature, respectively).

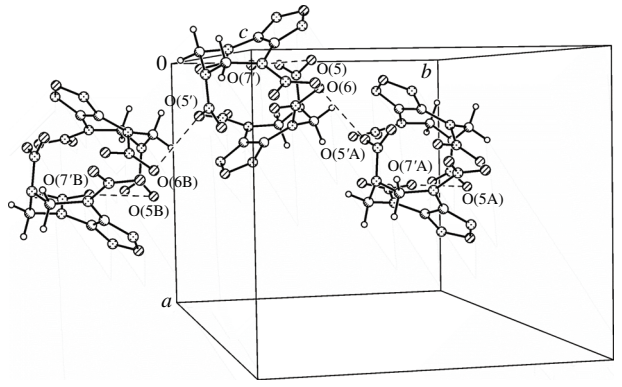


Figure 3 Crystal packing fragment of compound **1**: chain formed by O(6)···O(5′) and O(5)···O(7′) close contacts.

In summary, bicyclic nitramine **1**, whose molecule incorporates fused triazepine and furazan rings, was synthesized from 3,4-diaminofurazan **2** in a one-pot two-step procedure in IL in a good overall yield. Note that this is the first example of the IL utility for N-nitration reaction. Finally, we demonstrated that the ILs system can be readily reused in this process without any significant loss of efficiency.

We are grateful to Professor T. V. Timofeeva (New Mexico Highlands University) for providing us with computational time for the quantum chemical calculations. This work was supported in part by the Presidium of the Russian Academy of Sciences (programme 'Development of Methods for Synthesizing Chemical Compounds and Creating New Materials') and the Russian Foundation for Basic Research (grant no. 09-03-12230).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.09.002.

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Received: 2nd March 2010; Com. 10/3479