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Synthesis and structure of 3,5-dinitro-*N*-(3,5-dinitrobenzoyl)benzamide

Igor K. Yakushchenko, Denis V. Korchagin, Alexander V. Chernyak and Sergei V. Chapyshev*

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 3588; e-mail: chap@icp.ac.ru

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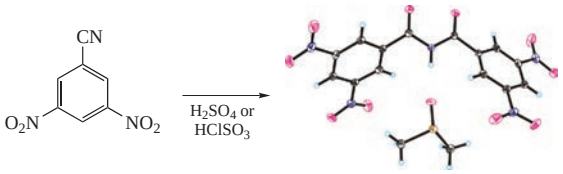
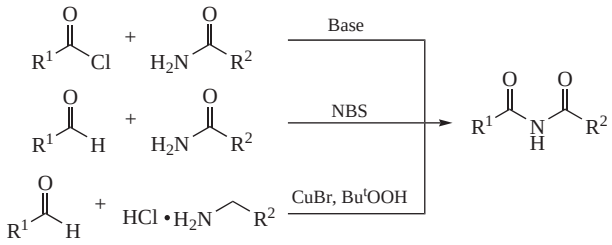
3,5-Dinitro-*N*-(3,5-dinitrobenzoyl)benzamide, the first representative of tetranitro-substituted imides, was obtained on dissolving 3,5-dinitrobenzonitrile in mineral acids and characterized with X-ray diffraction analysis and spectroscopic methods.

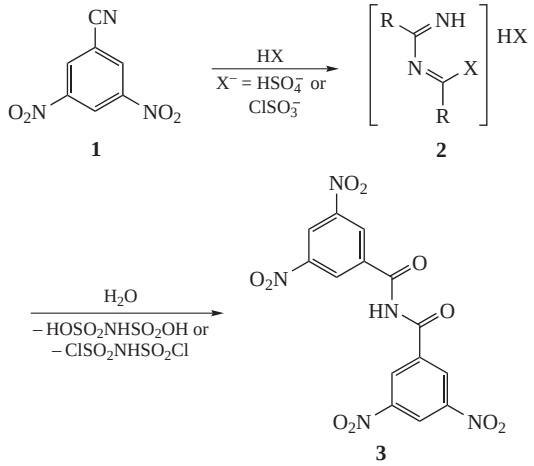


Imides are present in many natural products and bioactive molecules and play an important role for organic, inorganic, materials and pharmaceutical chemistry.[1] In the last years, much attention has been focused on the synthesis and investigations of nitro-substituted imides as precursors of polyimides possessing unique thermal and mechanical properties.[2] The most widely used method for the synthesis of imides is based on acylation of amides with acyl chlorides or anhydrides (Scheme 1).[3] Very recently, several new approaches to the synthesis of imides, involving the reactions of aldehydes with either amides or benzylamines in the presence of various oxidizers and catalysts, have been developed (Scheme 1).[4] In the present work, we report on the synthesis of 3,5-dinitro-*N*-(3,5-dinitrobenzoyl)benzamide **3** as the first representative of tetranitro-substituted imides that is formed in good yield just on dissolving 3,5-dinitrobenzonitrile **1** in mineral acids (Scheme 2).



Scheme 1

The reactions of nitrile **1** with concentrated sulfuric or chlorosulfonic acids were carried out either at room temperature or at moderate heating.† Previous studies have shown that most of aromatic and aliphatic nitriles were hydrolyzed into the corresponding amides upon the action of 100% H_2SO_4 at room temperature.[5] Thus, for instance, the acidic hydrolysis of *p*-nitrobenzonitrile gave *p*-nitrobenzamide in 47% yield. The only exception was the hydrolysis of chloroacetonitrile, leading to *N*-(chloroacetyl)chloroacetamide as a single product. We have found that a similar reaction also occurred with nitrile **1** to afford imide **3** in good yield. Similarly to recently described 4-nitro-*N*-(4-nitrobenzoyl)benzamide,[2(c)] imide **3** was obtained in the form of colorless prisms that melt at 285–286 °C. The structure of **3** was unambiguously confirmed by the data of analytical and spectroscopic studies† as well as by X-ray diffraction analysis‡ (Figure 1). According to the literature data,[5–7] the first step of the reaction is the acid-catalyzed dimerization of nitriles to adducts of amidines **2** with two molecules of a mineral acid. These adducts, depending on the structure of the starting nitriles and the reaction conditions, can further either add other molecules



Scheme 2

† *Synthesis of imide* **3**. Method A. Concentrated sulfuric acid (3 ml) was added to nitrile **1** (1.93 g, 10 mmol), and the resulting mixture was heated at 60 °C for 15 min until complete dissolution of the nitrile, then the solution was cooled to room temperature and poured into 50 ml of water. The solid material was filtered off, washed with water, dried in air and recrystallized from ethanol. Imide **3** was obtained as a white solid in 86% yield; mp 285–286 °C (decomp.). IR (microcrystals, ν_{max}/cm^{-1}): 3264 (m, NH), 3099 (m) and 2887 (w, CH), 1730 (s, C=O), 1685 (w), 1629 (w), 1598 (w), 1552 (vs), 1539 (vs) and 1509 (vs, C=N, C=C), 1351 (vs, NO_2), 1292 (w), 1255 (m), 1244 (s), 1235 (s), 1162 (s), 1077 (w), 974 (w), 924 (m), 916 (m), 853 (w), 777 (m), 719 (s). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.84 (d, 4H, *J* 2.1 Hz), 8.97 (d, 2H, *J* 2.1 Hz), 14.30 (br. s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 122.0 (C-4), 128.8 (C-2 and C-6), 134.0 (C-1), 148.3 (C-3 and C-5), 163.9 (C=O). Found (%): C, 41.58; H, 1.86; N, 17.11. Calc. for $C_{14}H_7N_5O_{10}$ (%): C, 41.49; H, 1.74; N, 17.28.

Method B. Chlorosulfonic acid (3 ml) was added to nitrile **1** (1.93 g, 10 mmol), and the mixture was stirred at room temperature for two days, then the solution was poured into 100 ml of ice water. The solid material was filtered off, washed with water, dried in air and recrystallized from ethanol. Imide **3** was obtained as white solid in 72% yield.

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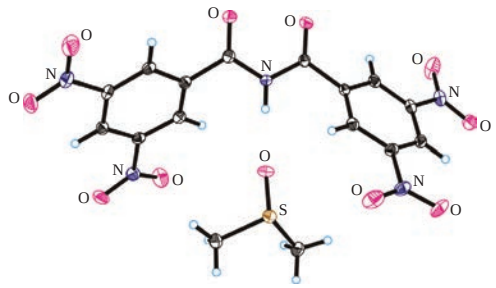

Figure 1 Molecular structure of imide **3**·DMSO solvate.

of nitriles to form trimers and polymers or undergo hydrolysis on treatment with water to form the corresponding amides and imides.[5–7] The synthesis of imide **3** is just the second example of successful preparation of any sort of imides and the first example of successful preparation of benzimides in the acid-catalysed dimerizations of nitriles.

Due to the presence of two nitro groups on the each aromatic ring, imide **3** has extraordinary high for imides melting point and may be of considerable interest as a starting material for preparation of polyimides possessing interesting thermal and mechanical properties.[2(c)] This imide is also characterized by a very acidic NH-function (δ 14.30 ppm) and may be of interest as highly efficient helating agent and biologically active compound.[1(a)] A simple and efficient method of synthesis of **3** from **1** also demonstrates that the acid-catalysed dimerizations of some nitriles may provide a fast and cheap access to some rather interesting imides.

‡ *Crystallographic data.* Crystals of **3**·DMSO solvate were grown up by slow evaporation of the solution of imide **3** in the mixture of DMSO, methanol and water (90 : 8 : 2). Crystals of **3**·DMSO ($C_{16}H_{13}N_5O_{11}S$, M = = 483.37) are monoclinic, space group $P2_1/c$ at 100.0(1) K: a = 12.2165(5), b = 14.5816(4) and c = 12.0930(5) Å, β = 114.979(5)°, V = 1952.7(1) Å^3, Z = 4, d_{calc} = 1.644 g cm^{-3}, μ(MoKα) = 0.242 cm^{-1}, F(000) = 992. Intensities of 10 466 reflections were measured with an Agilent XCalibur CCD diffractometer with EOS detector [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta < 58.14°$] and 5215 independent reflections (R_{int} = 0.0257) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation. Positions of hydrogen atoms were obtained from difference Fourier syntheses and refined with riding model constraints. The refinement converged to wR_2 = 0.1029 and GOF = 1.013 for all independent reflections [R_1 = 0.0417 was calculated for 3946 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL program.[8]

CCDC 1453469 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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