

Synthesis of the Ammonium Salt of 6-Amino-2-hydroxy-3,5-dinitropyrazine and a Comparison of Its Properties with Those of Ammonium 3,5-Diaminopicrate (ADAP)

Anthony J. BELLAMY*, Alessandro E. CONTINI and James PADFIELD

*Cranfield University, Defence Academy of the United Kingdom, Shrivenham,
Swindon SN6 8LA, UK*

Phone: +44 1793 785397

E-mail: A.J.Bellamy@cranfield.ac.uk

Peter GOLDING

AWE Aldermaston, Reading RG7 4PR, UK

Mary F. MAHON

Chemistry Department, University of Bath, Bath BA2 7AY, UK

Abstract: The ammonium salt of 6-amino-2-hydroxy-3,5-dinitropyrazine has been synthesised from 2,6-dimethoxy-3,5-dinitropyrazine and its properties [DSC, crystal structure, impact sensitiveness, thermochemical properties] are compared with the analogous benzene derivative, ammonium 3,5-diaminopicrate.

Keywords: LLM-105, 2,6-dialkoxy-3,5-dinitropyrazines, 6-amino-2-hydroxy-3,5-dinitropyrazine, ammonium 6-amino-3,5-dinitropyrazin-2-olate, ammonium 3,5-diaminopicrate, amination.

Introduction

During our study of a new route for the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) by amination of 1,3,5-trialkoxy-2,4,6-trinitrobenzenes we encountered the new explosive compound ammonium 3,5-diaminopicrate (ADAP) as a by-product [1-4]. This became the dominant product when 1,3,5-trimethoxy-2,4,6-trinitrobenzene was aminated at high temperature and was formed by attack of ammonia at the methyl carbon instead of the methoxy-bearing ring carbon, methylamine being liberated. This type of side reaction appears to be much less unimportant when the displaced alkoxy

group is ethoxy, and essentially non-existent with propoxy. ADAP may also be formed in a more quantitative manner by selective hydrolysis of 1,3,5-trimethoxy-2,4,6-trinitrobenzene to 1-hydroxy-3,5-dimethoxy-2,4,6-trinitrobenzene followed by amination (see Figure 1)[5].

Our further recent study of amination in a series of 2,6-alkoxy-3,5-dinitropyrazines (R = Me, Et, Pr; see Figure 2), as a route to LLM-105 (2,6-diamino-3,5-dinitropyrazine 1-oxide), has shown that attack by ammonia at the alkoxy carbon is unimportant in the pyrazine systems, even at elevated temperature, the product in all cases being pure 2,6-diamino-3,5-dinitropyrazine [6].

The product that would have been formed in the pyrazine series, if attack by ammonia had occurred at the alkoxy carbon, namely the ammonium salt of 6-amino-2-hydroxy-3,5-dinitropyrazine (I), has now been synthesised (see Figure 3) in a manner analogous to that for ADAP, and its properties compared with those of ADAP.

Results and Discussion

Partial hydrolysis of 2,6-dialkoxy-3,5-dinitropyrazines

Hydrolysis of the dialkoxy derivatives with Na_2CO_3 in aqueous CH_3CN was rather slow at ambient temperature, but was complete within 24h at 75°C . A general observation was that extraction of the Na salt of the resultant 2-alkoxy-6-hydroxy-3,5-dinitropyrazine into acetone- d_6 for product analysis by ^1H NMR became less efficient as the length of the alkyl chain decreased. At the same time, the solubility of the free hydroxyl derivative became more water soluble as the length of the alkyl chain decreased.

Amination of 6-alkoxy-2-hydroxy-3,5-dinitropyrazines

Amination of the 6-alkoxy-2-hydroxy-3,5-dinitropyrazines, or their Na^+ salts, was achieved by dissolution in liquid NH_3 at ambient temperature (7-8 bar) during several days. This served to displace the alkoxy group and gave the NH_4^+ salt of the generated 6-amino-2-hydroxy-3,5-dinitropyrazine.

The most efficient procedure for the synthesis of the NH_4^+ salt of 6-amino-2-hydroxy-3,5-dinitropyrazine was from the dimethoxydinitropyrazine without isolation of the intermediate Na^+ salt of 6-methoxy-2-hydroxy-3,5-dinitropyrazine. The dried mixture of the latter and excess Na_2CO_3 was aminated in liquid NH_3 and 6-amino-2-hydroxy-3,5-dinitropyrazine was isolated. The latter was then converted to the NH_4^+ salt and its structure was confirmed by single crystal XRD (see below).

DSC study of I and ADAP

It was observed that the DSC behaviour of I (recrystallised material) was dependent upon whether the sample pan was sealed or had a hole in the lid. With an unsealed pan, an endothermic peak (250°C) preceded two exothermic peaks (273°C and 324°C). However with a sealed pan there was no endotherm and only one exotherm (271°C). Similar behaviour was observed with ADAP (unrecrystallised). With an unsealed pan, an endothermic peak (263°C) preceded two exothermic peaks (282°C and 302°C). However with a sealed pan there was no endotherm and only one exotherm (303°C). These observations may be interpreted in the case of I as initial loss of NH_3 during the endotherm (250°C; TG mass loss 14%) in an unsealed pan, followed by exothermic decomposition of the surviving ammonium salt (273°C; TG no mass loss) and of the generated free hydroxypyrazine (324°C; TG mass loss 55%) as two separate exotherms. In the case of ADAP, loss of NH_3 during the endotherm (263°C; TG mass loss 13%) is followed by exothermic decomposition of the generated free diaminopicric acid (282°C; TG mass loss 60%) and of the surviving ammonium salt (302°C; TG no mass loss)[NB. The exothermic peak assignments for ADAP are in the reverse order to those for I]. In the sealed systems, no NH_3 is lost and the single exotherms represent decomposition of the original ammonium salts (271°C and 303°C respectively). The mass losses measured during the endotherms were, in both cases, larger than those expected for loss of NH_3 alone, and may involve loss of H_2O too. The decomposition of ADAP was reported earlier [3] as 275°C and that of 3,5-diaminopicric acid as 267°C [lit 276°C; 7]. Thus the reported value for the

decomposition of ADAP is probably the temperature of decomposition of the diaminopicric acid, NH_3 having been lost at a slightly lower temperature.

Crystal structure of I and ADAP

Whilst I crystallized as an *unhydrated* monoclinic form ($P2_1/c$), ADAP crystallized as a *hemi-hydrate* of orthorhombic form ($Pcan$). Thus a comparison of both the individual molecules and the overall morphology will be somewhat perturbed by this difference, but the effect on the individual molecular units is not expected to be a dominant one. The crystallographic parameters are shown in Table 1.

The molecular structures of I and ADAP are shown in Figures 4 and 5 respectively, and their respective unit cells are shown in Figure 6 and 7. ADAP has a crystal structure (Figure 7, crystal density 1.884 g cm^{-3}) not unlike that of TATB [8] i.e. the diaminopicate units lie in parallel planes (see Figure 7a), separation $\sim 3.2 \text{ \AA}$, with the NH_4 and H_2O units sandwiched between these parallel layers, but lying in vertical channels (see Figure 7b). The lattice is dominated by extensive H-bonding. By contrast the crystal structure of I (Figure 6, crystal density 1.807 g cm^{-3}) exhibits inclined adjacent anionic units with the NH_4 units lying at the intersection of the molecular planes.

Both structures exhibit very strong intramolecular H-bonding between adjacent NH_2 and NO_2 groups. I exhibits only one such [$\text{N}(3)\text{-H}(3\text{A})\dots\text{O}(2)$, 2.661 \AA], but ADAP exhibits four [$\text{N}(2)\text{-H}(2\text{A})\dots\text{O}(3)$, $\text{N}(2)\text{-H}(2\text{B})\dots\text{O}(4)$, $\text{N}(4)\text{-H}(4\text{B})\dots\text{O}(5)$, $\text{N}(4)\text{-H}(4\text{A})\dots\text{O}(6)$, $\text{N}\dots\text{O}$ distance 2.554 , 2.516 , 2.497 , 2.519 \AA respectively], all of which are stronger than that in I.

In I, one H atom [$\text{H}(5\text{A})$] of the NH_4^+ is strongly H-bonded to the formal anionic centre of the anion [$\text{O}(1)$, 2.803 \AA] and moderately to an O atom [$\text{O}(5)$, $\text{N}\dots\text{O}$ 2.965 \AA] in the adjacent NO_2 , whilst a second H atom [$\text{H}(5\text{C})$] of the NH_4^+ is strongly H-bonded to $\text{O}(1)$ of an adjacent anion [$\text{N}\dots\text{O}$ 2.882 \AA].

Likewise in ADAP, one H atom [$\text{H}(6\text{B})$] of the NH_4^+ is strongly H-bonded to the formal anionic centre of the anion [$\text{O}(1)$, $\text{N}\dots\text{O}$ 2.872 \AA] and moderately to an

O atom [O(2), N...O 2.916Å] in an adjacent NO₂, whilst a second H atom [H(6C)] is strongly H-bonded to O(1) of an adjacent anion [N...O 2.890Å] and a third [H(6A)] is strongly H-bonded to the O atom of a neighboring water [N...O 2.985Å]. One H atom of the H₂O is also strongly H-bonded to the formal anionic centre of the anion [O(1), O...O 2.893Å] and moderately to an O atom [O(7), O...O 2.293Å] in the other adjacent NO₂.

The rings and attached NH₂ groups in both I and ADAP are largely coplanar, but some NO₂ groups are twisted out of the plane. The most twisted NO₂ group in I (~10°) is that adjacent to the formal anionic centre of the anion [O(1)], and is probably caused by the H-bonding between H(5A) of the NH₄⁺ and O(5) of the NO₂ group. The other NO₂ group is twisted by ~5°. Likewise in ADAP, the most twisted NO₂ group (~25°) is that adjacent to the formal anionic centre of the anion [O(1)], and is again probably caused by the H-bonding between H(6B) of the NH₄⁺ and O(2) of the NO₂ group. This H-bond is stronger than the corresponding one in I and is probably the reason for the twist being greater. The other NO₂ group adjacent to the formal anionic centre is twisted by ~13° whilst the third NO₂ group is not twisted, being constrained by double H-bonding to its two adjacent NH₂ groups.

A full listing of crystallographic data e.g. bond lengths, bond angles, torsion angles and H-bonds, for both I and ADAP is available as Supplementary Information.

Impact sensitiveness and thermochemical properties of I and ADAP

The explosive and calorimetric data for I, ADAP and Explosive D (ammonium picrate) are shown in Table 2. The impact sensitiveness, as measured by the Rotter Impact test, indicated that I was significantly less sensitive (F of I = 124) than ADAP (F of I = 90)[F of I for RDX = 80]. The heat of formation, calculated from the bomb calorimetric combustion of I and ADAP, indicated that ADAP was less exothermically formed than I, and this is reflected in the calculated heats of explosion Q, ADAP evolving more heat than I. In addition, I is calculated to have a much lower Power Index (relative to picric acid) than ADAP.

Conclusions

The ammonium salt of 6-amino-2-hydroxy-3,5-dinitropyrazine (I) has been synthesised from 2,6-dimethoxy-3,5-dinitropyrazine and its properties [DSC, crystal structure, impact sensitiveness, thermochemical properties] are compared with the analogous benzene derivative, ammonium 3,5-diaminopicrate (ADAP). Apart from the lower impact sensitiveness of I relative to ADAP, I is judged in many respects to be inferior to ADAP as a potential explosive material.

Experimental

^1H and ^{13}C NMR spectra were run on a Bruker DPX250 instrument.

DSCs were run on ~1mg samples in aluminium pans at 10K/min.

CCDC xxxxxx contains the supplementary crystallographic data for ADAP monohydrate and CCDC xxxxxx contains the supplementary crystallographic data for I. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-366033; or deposit@ccdc.cam.ac.uk).

The calorimetric measurements of ADAP (6 replicate measurements) were carried out using a Gallenkamp 'Autobomb CBA-305' static adiabatic calorimeter, fitted with a Parr 1108-CI halogen-resistant twin-valve combustion bomb, with an internal volume of ~300 ml. The calorimetric measurements of I (5 replicate measurements) were carried out using a Parr 6200 static isoperibol bomb calorimeter fitted with a Parr 1109A semi-micro oxygen bomb with an internal volume of 22 ml.

The calorimeters were calibrated using Parr *thermochemical standard* grade (dry) benzoic acid with a quoted standard internal energy of combustion $\Delta_c U^\circ = -26454 \pm 3 \text{ Jg}^{-1}$. All calibrating and measuring experiments were performed under nitrogen-free oxygen of 99.95% certified purity (BOC Gases), at a nominal pressure of $3.0 \pm 0.1 \text{ MPa}$. Ignition of all samples was effected electrically.

Synthesis of 2,6-dialkoxy-3,5-dinitropyrazines

The 2,6-dialkoxy-3,5-dinitropyrazines (R = Me, Et, Pr) were synthesized as previously described [6]. Their purity was ascertained by HPLC and ^1H NMR spectroscopy.

Partial hydrolysis of 2,6-dialkoxy-3,5-dinitropyrazines to 6-alkoxy-2-hydroxy-3,5-dinitropyrazine

A. Using 2,6-dipropoxy-3,5-dinitropyrazine.

(i) The dipropoxy derivative (29mg, 0.05mmol) was dissolved in CH₃CN (1.0ml), Na₂CO₃ (10.6mg, 0.05mmol) dissolved in H₂O (0.2ml) was added and the reaction mixture was stirred at RT. The progress of the reaction was followed by evaporation of the solvent and analysis by ¹H NMR (acetone-d₆). The degree of conversion to the Na salt of 6-propoxy-2-hydroxy-3,5-dinitropyrazine was 20% after 20h, 43% after 3 days and 74% after 9 days.

(ii) The dipropoxy derivative (57mg, 0.10mmol) was dissolved in CH₃CN (2.0ml) and Na₂CO₃ (42mg, 0.20mmol) dissolved in H₂O (0.4ml) was added. The solution was heated at 75°C during 23h and then evaporated to dryness. Analysis by ¹H NMR (acetone-d₆) indicated complete conversion to the Na salt of 6-propoxy-2-hydroxy-3,5-dinitropyrazine. NMR (acetone-d₆) ¹H: 1.01 (t, 3.02H), 1.78 (m, 2.02H), 4.32ppm (t, 2.00H); ¹³C 10.8 (CH₃), 22.7 (CH₂), 69.6 (OCH₂), 125.1 (C-NO₂), 133.9 (C-NO₂), 157.2 (C-OPr), 160.5ppm (C-ONa).

About one third of the concentrated acetone-d₆ extract was dissolved in H₂O (1.0ml) and EtOAc (5.0ml) and then acidified with 1M HCl (5 drops). After extraction into the EtOAc phase, the latter was separated and washed with brine (3X1ml). At each washing the aqueous phase became yellow, whilst the organic phase was only slightly coloured. Evaporation of the solvent gave 6-propoxy-2-hydroxy-3,5-dinitropyrazine as a gum. NMR (acetone-d₆) ¹H: 1.02 (t, 3.04H), 1.84 (m, 2.07H), 4.49 (t, 2.00H), 9.09ppm (br s, 1.20H); ¹³C 10.5 (CH₃), 22.5 (CH₂), 72.2 (OCH₂), 130.8 (C-NO₂), 131.5 (C-NO₂), 156.2 (C-OPr), 157.3ppm (C-OH). The NMR solution was reconcentrated and dissolved in CH₃CN (1.0ml) and H₂O (0.2ml) containing Na₂CO₃ (42mg) by sonication and briefly heating at 75°C. After reconcentration and extraction with acetone-d₆, NMR analysis afforded the same spectrum as before acidification i.e. it had been converted back to the Na salt.

B. Using 2,6-diethoxy-3,5-dinitropyrazine.

The diethoxy derivative (28mg) was dissolved in CH₃CN (1.0ml) and Na₂CO₃ (24mg) dissolved in H₂O (0.2ml) was added. The solution was heated at 75°C during 24h and then evaporated to dryness. Analysis by ¹H NMR (acetone-d₆; only partially soluble – weak spectrum) indicated complete conversion to the Na salt of 6-ethoxy-2-hydroxy-3,5-dinitropyrazine. NMR (acetone-d₆) ¹H: 1.35 (t, 3.11H), 4.40ppm (t, 2.00H). The total residue was dissolved in H₂O (2.0ml) and EtOAc (5.0ml) and then acidified with 1M HCl (10 drops). After extraction into the EtOAc phase, the latter was separated and washed with brine (3X1ml). At each washing the aqueous phase became yellow, whilst the organic phase was only slightly coloured. Evaporation of the solvent gave the 6-ethoxy-2-hydroxy-3,5-dinitropyrazine as a gum. NMR (acetone-d₆) ¹H: 1.43 (t, 3.04H), 4.62 (t, 2.00H), 9.0ppm (br s, 1.20H); ¹³C 14.3 (CH₃), 67.0 (OCH₂), 130.6 (C-NO₂), 131.9 (C-NO₂), 156.1 (C-OEt), 157.1ppm (C-OH).

C. Using 2,6-dimethoxy-3,5-dinitropyrazine.

The dimethoxy derivative (28mg) was dissolved in CH₃CN (1.0ml) and Na₂CO₃ (27mg) dissolved in H₂O (0.2ml) was added. The solution was heated at 75°C during 24h and then evaporated to dryness. The total residue was dissolved in H₂O (2.0ml) and EtOAc (5.0ml) and then acidified with 1M HCl (10 drops). After extraction into the EtOAc phase, the latter was separated and washed with brine (3X1ml). At each washing the aqueous phase became yellow, whilst the organic phase was only slightly coloured. Evaporation of the solvent gave the 6-methoxy-2-hydroxy-3,5-dinitropyrazine as a gum which crystallised. NMR (acetone-d₆) ¹H: 4.17 (s, 3.00H), 8.02ppm (br s, 1.48H); ¹³C 57.2 (CH₃), 130.6 (C-NO₂), 132.0 (C-NO₂), 156.6 (C-OMe), 157.0ppm (C-OH).

Amination of 6-alkoxy-2-hydroxy-3,5-dinitropyrazine

A. Using 6-propoxy-2-hydroxy-3,5-dinitropyrazine

(i) 6-Propoxy-2-hydroxy-3,5-dinitropyrazine (40mg) was dissolved in CH₃CN (5ml) and NH₃ gas was passed over the solution during 3h. No solid separated but the solution turned yellow. Concentration gave a yellow solid (23mg) which was insoluble in acetone-d₆. NMR (DMSO-d₆) analysis indicated that it was the ammonium salt of 6-propoxy-2-hydroxy-3,5-dinitropyrazine; the propoxy group was still present. ¹H 0.98 (t, 2.78H), 1.72 (q, 1.87H), 4.33 (t, 2.00H), 7.36ppm (t, 3.96H).

(ii) The residue from (i) (18mg) was dissolved in liq NH₃ and sealed in a pressure vessel (7-8 bar at RT) during 22h. Evaporation of the NH₃ gave a yellow solid (11mg). NMR (DMSO-d₆) analysis indicated that the displacement of the propoxy group was incomplete. ¹H 0.98 (t, 3.00H), 1.72 (q, 2.00H), 4.24 (t, 2.57H), 6.65 (br s, 10.15H), 7.64 (br s, 3.25H), 8.01ppm (br s, 0.66H).

(iii) The residue from (ii) was treated further with liq NH₃ (72h) and gave material (9mg) in which the propoxy group had been completely removed. ¹H 6.02 (br s, 0.15H), 7.33 (br s, 2.98H), 7.68 (br s, 2.00H), 8.02ppm (br s, 0.41H); ¹³C 120.3 (C-NO₂), 136.4 (C-NO₂), 153.5, 157.8, 162.4ppm. After addition of HCl (trace): ¹H 7.37 (t, 4.00H), 7.73 (br s, 0.43H), 8.01 (br s, 0.30H), 9.11ppm (br s, 1.42H); ¹³C 120.3 (C-NO₂), 136.4 (C-NO₂), 153.5, 157.8, 162.4ppm.

B. Using 2-hydroxy-6-methoxy-3,5-dinitropyrazine

The procedure was similar to that used for the synthesis of the NH₄⁺ salt of 3,5-diaminopicrate from 1,3,5-trimethoxy-2,4,6-trinitrobenzene [5].

(i) 2,6-Dimethoxy-3,5-dinitropyrazine (112mg) was hydrolysed to the Na salt of 2-hydroxy-6-methoxy-3,5-dinitropyrazine with Na₂CO₃ as above. After evaporation of the CH₃CN/H₂O and drying, the residue was dissolved in liq NH₃ (~40ml) and sealed in a pressure vessel (7-8 bar at RT) during 4 days. After evaporation of the NH₃, the residue was dissolved in H₂O (10ml) and acidified with 3M HCl (1.0ml). The precipitated yellow solid was filtered off,

washed with cold H₂O (2X) and dried to give 2-amino-6-hydroxy-3,5-dinitropyrazine (97mg). NMR (DMSO-d₆): ¹H 7.08 (t, 0.05H), 8.20 (s, 1.00H), 8.96ppm (s, 1.00H); ¹³C 119.7 (C-NO₂), 131.6 (C-NO₂), 148.9 (C), 150.0ppm (C). DSC (10K/min) endotherm onset 111.4°C, max 122.0°C (-34 Jg⁻¹), broad exotherm onset 276.5°C, maximum 301.4°C (+1164 Jg⁻¹).

(ii) The 6-amino-2-hydroxy-3,5-dinitropyrazine (94mg) from (i) was dissolved in liq NH₃ (~40ml) and sealed in a pressure vessel (7-8bar at RT) during 20h. Evaporation of the NH₃ gave the NH₄⁺ salt of 6-amino-2-hydroxy-3,5-dinitropyrazine (99mg) as a dark yellow solid which became darker on standing. NMR (DMSO-d₆): ¹H 7.08 (br s, 3.66H, NH₄⁺), 7.66ppm (s, 2.00H, NH₂); ¹³C 120.3 (C-NO₂), 136.5 (C-NO₂), 153.6, 157.8ppm; after adding a trace of HCl - ¹H 7.31 (t, 4.44H, NH₄⁺), 8.98 and 9.10ppm (2 s, 2.00H, NH₂); ¹³C 119.5 (C-NO₂), 131.4 (C-NO₂), 149.1, 149.2ppm. The NH₄⁺ salt of 3,5-diamino-picrate exhibits: ¹H 7.14 (t, 4.27H, NH₄⁺), 9.12ppm (s, 4.00H, NH₂); ¹³C 109.4, 120.4, 147.1, 163.3ppm. DSC (10K/min) broad endotherm onset 198.5°C, maximum 233.1°C (-145 Jg⁻¹), exotherm onset 251.5°C, maximum 256.3°C (+429.3 Jg⁻¹). TG step onset 236.1°C, inflection 243.2°C, mass loss 27.2%; step onset 282.0°C, inflection 291.8°C, mass loss 18.3%. Hammer test – negative.

(iii) Dimethoxydinitropyrazine (1.42g) was dissolved in CH₃CN (51ml) and Na₂CO₃ (1.37g) dissolved in H₂O (10ml) was added. The solution was heated at 75°C during 24h and then evaporated to dryness. Some solid had separated before concentration. The total residue was dispersed in liq NH₃ (~50ml) and sealed in a pressure vessel (7-8 bar at RT) during 4 days. After evaporation of the NH₃, the residue was dissolved in H₂O (110ml) and acidified with 3M HCl (13ml). The precipitated solid was filtered off, washed with cold H₂O (3X) and dried to give 6-amino-2-hydroxy-3,5-dinitropyrazine (1.06g, 85%). NMR (DMSO-d₆): ¹H 7.07 (minor t, overlapped with broad H₂O peak), 8.19 (br s, 1.00H), 8.85ppm (br s, 1.16H); ¹³C 119.7 (C-NO₂), 131.8 (C-NO₂), 149.0 (C), 150.2ppm (C).

The 6-amino-2-hydroxy-3,5-dinitropyrazine (1.01g) was dissolved in liq NH₃ (~40ml) and sealed in a pressure vessel (7-8bar at RT) during 22h. Evaporation of the NH₃ gave the NH₄⁺ salt of 6-amino-2-hydroxy-3,5-dinitropyrazine (1.04g, 95%) as a dark yellow solid. NMR (DMSO-d₆): ¹H 7.16 (br s, 3.66H, NH₄⁺), 7.57ppm (s, 2.00H, NH₂); ¹³C 120.4 (C-NO₂), 136.5 (C-NO₂), 153.6, 157.9ppm; after adding a trace of HCl - ¹H 7.31 (t, 4.44H, NH₄⁺), 8.98 and 9.10ppm (2s, 2.00H, NH₂); ¹³C 119.5 (C-NO₂), 131.4 (C-NO₂), 149.1, 149.2ppm. The NH₄⁺ salt of 3,5-diaminopicrate exhibits: ¹H 7.14 (t, 4.27H, NH₄⁺), 9.12ppm (s, 4.00H, NH₂); ¹³C 109.4, 120.4, 147.1, 163.3ppm.

The crude salt (0.86g) was recrystallised by dissolving in water (17ml) at 100°C, filtering hot and cooling with stirring. The crystals were filtered off, washed twice with cold water and dried. Yield 0.67g. The FTIR spectrum and NMR spectra [(DMSO-d₆): ¹H 7.14 (br s, 4.34H, NH₄⁺), 7.59ppm (s, 2.00H, NH₂); ¹³C 120.5 (C-NO₂), 136.4 (C-NO₂), 153.6, 157.9ppm] were essentially the same as the unrecrystallised material, but the DSC and TG were somewhat different. DSC (10K/min) endotherm onset 217.1°C, max 249.7°C

(216 Jg⁻¹), exotherm onset 269.6°C, max 272.9 °C (388 Jg⁻¹), second exotherm onset 309.6°C, max 324.2°C (631 Jg⁻¹) [unrecrystallised material had: endotherm onset 198.5°C, maximum 233.1°C (-145 Jg⁻¹), exotherm onset 251.5°C, maximum 256.3°C (+429.3 Jg⁻¹). TG (10K/min) step onset 247.8°C, inflection 261.0°C, mass loss 14.3%; step onset 309.6°C, inflection 317.0°C, mass loss 54.7% [unrecrystallised material had: step onset 236.1°C, inflection 243.2°C, mass loss 27.2%; step onset 282.0°C, inflection 291.8°C, mass loss 18.3%]. The above DSC/TGs were run with open pans. When the DSC (recrystallised material) was run with a sealed pan, only one exothermic peak was observed, with no endotherm: onset 264.5°C, maximum 270.9°C (1558 Jg⁻¹).

Similar behaviour was observed with the ammonium salt of 3,5-diaminopicric acid (ADAP): DSC (10K/min) open pan – endotherm onset 237.8°C, maximum 263.4°C (92 Jg⁻¹), exotherm onset 278.0°C, maximum 282.2°C (460 Jg⁻¹), exotherm onset 293.3°C, maximum 302.3°C (222 Jg⁻¹; total exothermic peaks 1309 Jg⁻¹); sealed pan exothermic onset 294.3°C, maximum 302.6°C (1574 Jg⁻¹). TG (10K/min) mass loss 40-260°C 13%, step onset 266.7°C, inflection 285.2°C, mass loss 59.6% .

The crystals for single crystal XRD were from water.

Langlie test (10 shots) on the unrecrystallised ammonium salt of 6-amino-2-hydroxy-3,5-dinitropyrazine gave an F of I of 124. Langlie test (10 shots) on the recrystallised salt was essentially unchanged, with one spurious 'go' at 98.6cm; 'no-go' up to 157cm. For comparison, the ammonium salt of 3,5-diaminopicric acid (ADAP) had an F of I of ~90.

Acknowledgments

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References

- [1] Bellamy A.J., Golding P., Ward S.J., A new synthetic route to triaminotrinitrobenzene (TATB), *Insensitive Munitions & Energetic Materials Technology Symposium*, Bordeaux, France, Oct. 8-11, 2001, 2, 626-634.
- [2] Bellamy A.J., Golding P., Ward S.J., Synthesis of TATB and DATB from trihydroxybenzene and dihydroxybenzene by nitration, alkylation, and amination, GB 2355713 A (2001).
- [3] Bellamy A.J., Ward S.J., Golding P., A new synthetic route to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), *Propellants, Explosives, Pyrotechnics*, 2002, **27(2)**, 49-58.
- [4] Bellamy A.J., Golding P., Ward S.J., Amination of 1,3,5-trialkoxy-2,4,6-trinitrobenzene; formation of TATB vs. ADAP (ammonium 3,5-diaminopicrate), International Annual Conference of ICT (2002), 33rd (Energetic Materials), 1/1-1/10.
- [5] Bellamy A.J., Ward S.J., Golding P., Synthesis of ammonium diaminopicrate (ADAP), a new secondary explosive, *Propellants, Explosives, Pyrotechnics*, 2002, **27(2)**, 59-61.
- [6] Bellamy A.J., Golding P., A Study of the Synthesis and Amination of 2,6-Dialkoxy-3,5-dinitropyrazines, *Central European Journal of Energetic Materials*, 2008, **5**, 3-19.
- [7] Koppes W.M., Lawrence G.W., Sitzmann M.E., G.Adolph H.G., Reaction of 1,3,5-trifluorotrinitrobenzene with nucleophiles, *J.Chem.Soc.Perkin 1*, 1981, 1815-20.
- [8] Filippini G., Gavezzotti A., The crystal structure of 1,3,5-triamino-2,4,6-trinitrobenzene. Centrosymmetric or non-centrosymmetric? *Crystal Physics Letters*, 1994, **231(1)**, 86-92.
- [9] Rothstein L.R., Petersen P., Predicting high explosive detonation velocities from their composition and structure, *Propellants and Explosives*, 1979, **4**, 56-60.
- [10] Stull D.R., Westrum E.F., Sinke G.C., The Chemical Thermodynamics of Organic Compounds, John Wiley and Sons Inc., 1969.

Table 1. Crystallographic data for I and ADAP

	I	ADAP
Formula	$C_8H_{12}N_{12}O_{10}$	$C_6H_9N_6O_{7.50}$
Formula weight [g mol ⁻¹]	436.30	285.19
Temperature [K]	150(2)	
λ [Å]	0.71073	
Crystal system	Monoclinic	Orthorhombic
Space group	P2 ₁ /c	Pcan
Unit cell dimensions		
a [Å]	4.4640(1)	6.4470(0)
b [Å]	12.8890(2)	9.0540(2)
c [Å]	14.0350(3)	34.4430(7)
α [°]	90	90
β [°]	96.692(1)	90
γ [°]	90	90
Volume [Å ³]	802.02(3)	2010.48(7)
Z	2	8
ρ (calculated) [Mg/m ³]	1.807	1.884
μ [mm ⁻¹]	0.165	0.173
F(000)	448	1176
Crystal size [mm]	0.50 x 0.45 x 0.40	0.45 x 0.13 x 0.05
Theta range [°]	4.31 to 28.33	3.88 to 27.41
Reflections collected	15805	20492
Independent reflections	1978 [R(int) = 0.0303]	2279 [R(int) = 0.0792]
Reflections observed (>2 σ)	1739	1736
Data Completeness	0.994	0.991
Data/restraints/parameters	1978 / 6 / 161	2279 / 5 / 198
Goodness-of-fit on F ²	1.037	1.125
Final R indices [I>2 σ (I)]	R ₁ = 0.0325, wR ₂ = 0.0848	R ₁ = 0.0557, wR ₂ = 0.1563
R indices (all data)	R ₁ = 0.0383, wR ₂ = 0.0884	R ₁ = 0.0770, wR ₂ = 0.1678

Table 2. Thermochemical and calculated [9] detonation properties of I, ADAP and Explosive D (ammonium picrate)

Property	I	ADAP	Explosive D*
Density (gcm^{-3} ; XRD)	1.807	1.884	1.717
Detonation velocity (ms^{-1})	8270	7770	7400 (7360**)
Detonation pressure (kbar)	316	269	234
Oxygen balance (%)	-44.0	-52.2	-52.0
Nitrogen (%)	38.5	30.4	22.8
$\Delta U_c^\circ (\text{Jg}^{-1})$	-9664 \pm 16	-11730 \pm 190	-
$\Delta H_c^\circ (\text{Jg}^{-1})$	-9619 \pm 16	-11690 \pm 190	-
$\Delta H_f^\circ (\text{Jg}^{-1})$	-1527 \pm 16	-1042 \pm 190	-1571 [10]
Heat of explosion Q (Jg^{-1}) [*]	-2812 \pm 16	-3661 \pm 190	-3160
Volume of gas (dm^3g^{-1}) [*]	0.821	0.811	0.819
Power Index (%; vs PA)	85.5 \pm 0.5	110 \pm 6	96
Figure of Insensitiveness	124	90	-

* Ammonium picrate

** Experimental (~0.5% from calculated value)

^{*} Using modified Kistiakowsky-Wilson rules

Figure 1. Synthesis of ammonium 3,5-diaminopicrate (ADAP)

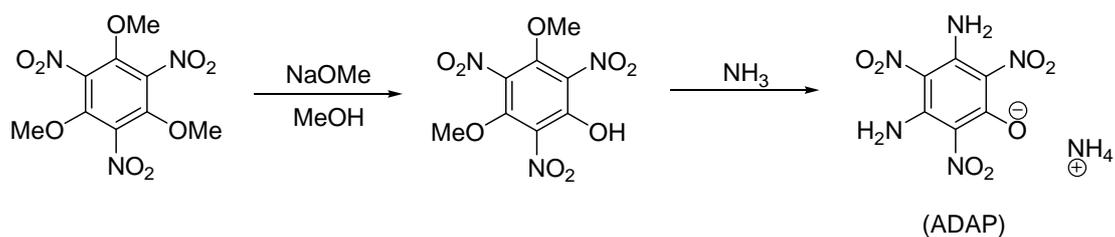
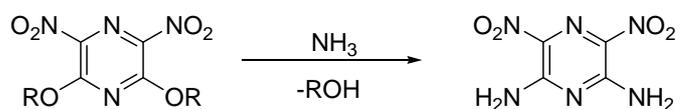


Figure 2. Amination of 2,6-dialkoxy-3,5-dinitropyrazine



R = Me, Et, Pr

Figure 3. Synthesis of the ammonium salt of 6-amino-2-hydroxy-3,5-dinitropyrazine (I)



Figure 4. Single molecule structure of I.

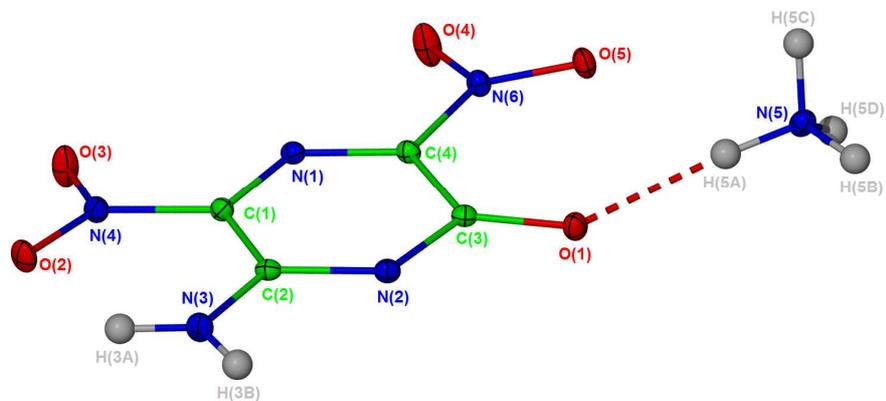


Figure 5. Single molecule structure of ADAP.

h04awe3

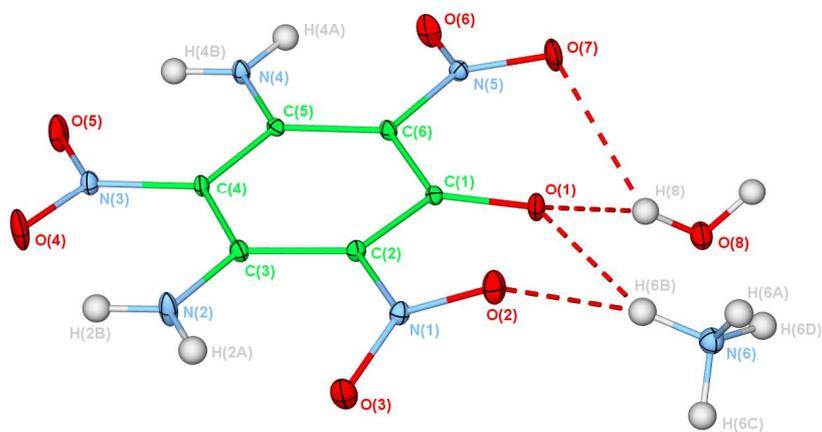


Figure 6. Unit cell of I.

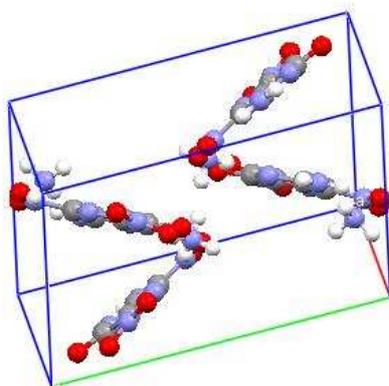
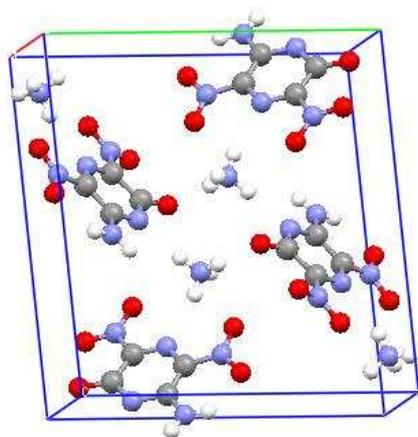
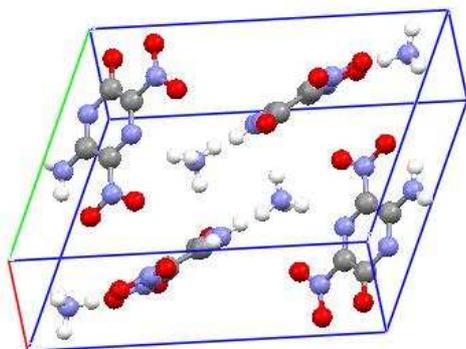
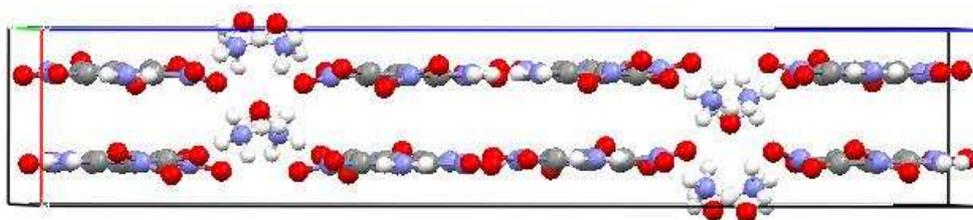
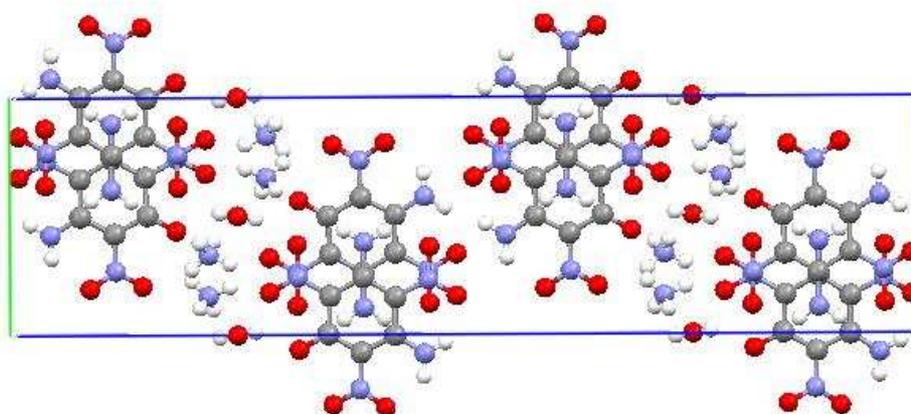


Figure 7. Unit cell of ADAP (a: along the bc-plane; b: along the a-axis).

(a)



(b)



Supplementary Information

Table S1. Bond lengths, bond angles, torsion angles and H-bonds for I.

Bond lengths [Å]			
C-O ⁻			
O(1)-C(3)	1.2498(13)		
C-N and C-C (ring)			
N(1)-C(4)	1.3068(14)	N(1)-C(1)	1.3200(14)
N(2)-C(2)	1.3362(14)	N(2)-C(3)	1.3579(14)
C(1)-C(2)	1.4417(15)	C(3)-C(4)	1.4621(15)
C-N (nitro)			
N(4)-C(1)	1.4449(14)	N(6)-C(4)	1.4608(13)
N-O (nitro)			
O(2)-N(4)	1.2421(12)	O(3)-N(4)	1.2236(13)
O(4)-N(6)	1.2358(13)	O(5)-N(6)	1.2229(12)
C-N (amino)			
N(3)-C(2)	1.3313(14)		
N-H (amino)			
N(3)-H(3A)	0.891(13)	N(3)-H(3B)	0.870(14)
N-H (ammonium)			
N(5)-H(5A)	0.925(14)	N(5)-H(5B)	0.921(14)
N(5)-H(5C)	0.908(14)	N(5)-H(5D)	0.904(14)
Bond angles [°]			
C-N-C (ring)			
C(4)-N(1)-C(1)	118.63(9)	C(2)-N(2)-C(3)	121.97(9)
C-C-N (ring)			
N(1)-C(1)-C(2)	121.82(10)	N(1)-C(4)-C(3)	123.26(10)
N(2)-C(2)-C(1)	118.36(9)	N(2)-C(3)-C(4)	115.75(9)
N-C-N / C-C-N (nitro)			
N(1)-C(1)-N(4)	114.89(9)	N(1)-C(4)-N(6)	114.54(9)
C(2)-C(1)-N(4)	123.27(9)	N(6)-C(4)-C(3)	122.18(9)
N-C-N / C-C-N (amino)			
N(3)-C(2)-N(2)	117.62(10)	N(3)-C(2)-C(1)	124.00(10)
N-C-O ⁻ / C-C-O ⁻			
O(1)-C(3)-N(2)	119.15(10)	O(1)-C(3)-C(4)	125.07(10)
O-N-O (nitro)			
O(3)-N(4)-O(2)	122.74(10)	O(5)-N(6)-O(4)	122.74(9)
C-N-O (nitro)			

O(2)-N(4)-C(1)	117.70(9)	O(3)-N(4)-C(1)	119.56(9)
O(4)-N(6)-C(4)	118.22(9)	O(5)-N(6)-C(4)	119.00(9)
C-N-H / H-N-H (amino)			
C(2)-N(3)-H(3A)	120.5(10)	C(2)-N(3)-H(3B)	116.5(11)
H(3A)-N(3)-H(3B)	123.0(15)		
H-N-H (ammonium)			
H(5A)-N(5)-H(5B)	112.4(15)	H(5A)-N(5)-H(5C)	107.9(15)
H(5B)-N(5)-H(5C)	110.0(15)	H(5A)-N(5)-H(5D)	111.4(15)
H(5B)-N(5)-H(5D)	108.7(15)	H(5C)-N(5)-H(5D)	106.2(16)
Torsion angles [°]			
ring-nitro			
N(1)-C(1)-N(4)-O(2)	175.60	N(1)-C(1)-N(4)-O(3)	-4.76
C(2)-C(1)-N(4)-O(2)	-5.73	C(2)-C(1)-N(4)-O(3)	173.90
N(1)-C(4)-N(6)-O(4)	7.99	N(1)-C(4)-N(6)-O(5)	-169.57
C(3)-C(4)-N(6)-O(4)	-170.39	C(3)-C(4)-N(6)-O(5)	12.05
ring-amino			
N(2)-C(2)-N(3)-H(3A)	180	N(2)-C(2)-N(3)-H(3B)	2
C(1)-C(2)-N(3)-H(3A)	2	C(1)-C(2)-N(3)-H(3B)	-176
internal ring			
C(2)-C(1)-N(1)-C(4)	-0.79	N(1)-C(1)-C(2)-N(2)	3.06
C(1)-C(2)-N(2)-C(3)	-1.06	C(4)-C(3)-N(2)-C(2)	-2.64
N(2)-C(3)-C(4)-N(1)	5.09	C(3)-C(4)-N(1)-C(1)	-3.32
external-ring (amine)			
N(3)-C(2)-N(2)-C(3)	-179.50	N(1)-C(1)-C(2)-N(3)	-178.60
external-ring (nitro)			
N(4)-C(1)-C(2)-N(2)	-175.51	N(4)-C(1)-N(1)-C(4)	177.89
N(6)-C(4)-N(1)-C(1)	178.31	N(2)-C(3)-C(4)-N(6)	-176.66
external-ring (C-O)			
O(1)-C(3)-N(2)-C(2)	175.38	O(1)-C(3)-C(4)-N(1)	-172.79
intra-substituent			
O(1)-C(3)-C(4)-N(6)	5.45	N(4)-C(1)-C(2)-N(3)	2.83
H-bonds [Å]			
N(3)-H(3A)...O(2)	2.661	N(5)-H(5A)...O(1)	2.820
N(5)-H(5A)...O(5)	2.965	N(5)-H(5C)...O(1)'	2.882

Table S2. Bond lengths, bond angles, torsion angles and H-bonds for ADAP.

Bond lengths [Å]			
C-O			
O(1)-C(1)	1.257(2)		
C-C (ring)			
C(1)-C(2)	1.439(3)	C(1)-C(6)	1.458(3)
C(2)-C(3)	1.436(3)	C(5)-C(6)	1.438(3)
C(3)-C(4)	1.450(3)	C(4)-C(5)	1.444(3)
C-N (nitro)			
N(1)-C(2)	1.421(3)	N(3)-C(4)	1.419(2)
N(5)-C(6)	1.408(2)		
N-O (nitro)			
O(2)-N(1)	1.250(2)	O(3)-N(1)	1.246(2)
O(4)-N(3)	1.235(2)	O(5)-N(3)	1.254(2)
O(6)-N(5)	1.253(2)	O(7)-N(5)	1.253(2)
C-N (amino)			
N(2)-C(3)	1.319(3)	N(4)-C(5)	1.324(3)
Bond angles [°]			
C-C-C (ring)			
C(2)-C(1)-C(6)	116.00(17)	C(3)-C(2)-C(1)	123.62(19)
C(2)-C(3)-C(4)	117.78(18)	C(5)-C(4)-C(3)	121.39(18)
C(6)-C(5)-C(4)	118.14(18)	C(5)-C(6)-C(1)	122.78(17)
C-C-N (nitro)			
N(1)-C(2)-C(1)	117.09(17)	N(1)-C(2)-C(3)	119.28(17)
N(3)-C(4)-C(3)	119.03(18)	N(3)-C(4)-C(5)	119.58(18)
N(5)-C(6)-C(1)	117.59(17)	N(5)-C(6)-C(5)	119.63(18)
C-C-N (amino)			
N(2)-C(3)-C(2)	121.00(19)	N(2)-C(3)-C(4)	121.22(19)
N(4)-C(5)-C(4)	120.92(17)	N(4)-C(5)-C(6)	120.93(17)
C-C-O			
O(1)-C(1)-C(2)	122.31(18)	O(1)-C(1)-C(6)	121.62(18)
O-N-O (nitro)			
O(3)-N(1)-O(2)	119.29(17)	O(4)-N(3)-O(5)	118.03(17)
O(6)-N(5)-O(7)	117.92(17)		
C-N-O (nitro)			
O(2)-N(1)-C(2)	120.13(16)	O(3)-N(1)-C(2)	120.55(16)
O(4)-N(3)-C(4)	121.59(18)	O(5)-N(3)-C(4)	120.38(17)
O(6)-N(5)-C(6)	121.13(17)	O(7)-N(5)-C(6)	120.92(18)
Torsion angles [°]			

ring-nitro			
C(1)-C(2)-N(1)-O(2)	-25.28	C(1)-C(2)-N(1)-O(3)	156.67
C(3)-C(2)-N(1)-O(2)	156.20	C(3)-C(2)-N(1)-O(3)	-21.84
C(3)-C(4)-N(3)-O(4)	-3.33	C(3)-C(4)-N(3)-O(5)	177.10
C(5)-C(4)-N(3)-O(4)	177.34	C(5)-C(4)-N(3)-O(5)	-2.23
C(1)-C(6)-N(5)-O(6)	-167.69	C(1)-C(6)-N(5)-O(7)	14.15
C(5)-C(6)-N(5)-O(6)	11.89	C(5)-C(6)-N(5)-O(7)	-166.27
ring-amino			
C(2)-C(3)-N(2)-H(2A)	0	C(2)-C(3)-N(2)-H(2B)	180
C(4)-C(3)-N(2)-H(2A)	179	C(4)-C(3)-N(2)-H(2B)	-1
C(4)-C(5)-N(4)-H(4A)	-179	C(4)-C(5)-N(4)-H(4B)	1
C(6)-C(5)-N(4)-H(4A)	0	C(6)-C(5)-N(4)-H(4B)	-180
internal ring			
C(6)-C(1)-C(2)-C(3)	-6.09	C(1)-C(2)-C(3)-C(4)	4.29
C(2)-C(3)-C(4)-C(5)	-1.84	C(3)-C(4)-C(5)-C(6)	1.56
C(4)-C(5)-C(6)-C(1)	-3.63	C(2)-C(1)-C(6)-C(5)	5.72
external-ring (amine)			
C(1)-C(2)-C(3)-N(2)	176.80	N(2)-C(3)-C(4)-C(5)	179.25
C(3)-C(4)-C(5)-N(4)	179.65	N(4)-C(5)-C(6)-C(1)	177.59
external-ring (nitro)			
C(6)-C(1)-C(2)-N(1)	175.47	N(1)-C(2)-C(3)-C(4)	-177.30
C(2)-C(3)-C(4)-N(3)	178.85	N(3)-C(4)-C(5)-C(6)	-179.13
C(4)-C(5)-C(6)-N(5)	176.81	C(2)-C(1)-C(6)-N(5)	-174.71
external-ring (C-O)			
O(1)-C(1)-C(2)-C(3)	170.80	O(1)-C(1)-C(6)-C(5)	-171.19
intra-substituent			
O(1)-C(1)-C(2)-N(1)	-7.64	O(1)-C(1)-C(6)-N(5)	8.38
N(1)-C(2)-C(3)-N(2)	1.61	N(2)-C(3)-C(4)-N(3)	-0.06
N(3)-C(4)-C(5)-N(4)	-0.35	N(4)-C(5)-C(6)-N(5)	-1.97
H-bonds [Å]			
N(2)-H(2A)...O(3)	2.554	N(2)-H(2B)...O(4)	2.516
N(4)-H(4B)...O(5)	2.497	N(4)-H(4A)...O(6)	2.519
N(6)-H(6B)...O(1)	2.872	N(6)-H(6B)...O(2)	2.916
N(6)-H(6A)...O(8)'	2.984	N(6)-H(6C)...O(1)'	2.890
O(8)-H(8)...O(1)	2.893	O(8)-H(8)...O(7)	2.982