RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 42215

Synthesis and characterization of 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one as an energetic material†

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Received 21st May 2014
Accepted 14th August 2014

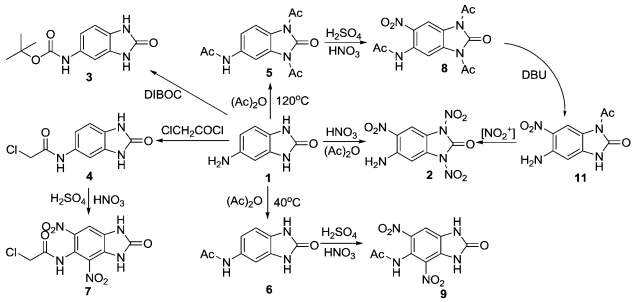
DOI: 10.1039/c4ra04796f

www.rsc.org/advances

Two synthetic routes for the preparation of 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2**) as an energetic material have been revealed. Direct nitration of 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) gave the trinitrated compound **2** in a poor yield of 11%; and similarly using **1** as starting material, **2** was obtained by *N*-protected reaction, nitration, deprotection and again nitration reaction with an overall-yield of 48%. All structures of **2** and relevant compounds were determined by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, MS and elemental analysis. Theoretical calculations showed that the detonation properties of compound **2** (D = 7.78 km s^{-1}, P = 27.05 GPa) were satisfactory, compared with 2,4,6-trinitrotoluene (TNT, D = 7.21 km s^{-1}, P = 22.49 GPa).

Introduction

Nowadays, the design and synthesis of new energetic compounds known as high-energy density materials (HEDMs) has been the focus. In the pursuit of new HEDMs, considerable efforts have been devoted to developing high-nitrogen heterocycles, and most energy derives from a combination of positive heats of formation and generation of large volumes of environmentally benign nitrogen gas under decomposition.[1–4] However, highly nitrated cages or ring heterocycles and carbocycles are also interesting as energetic materials because of the increased performance expected from the additional energy release (manifested in a higher heat of formation) upon opening of the strained cage or ring system during decomposition.[5–8]



Scheme 1

Nitroureas play an important role in the field of energetic materials, and the properties of nitrourea compounds suggest they would make excellent candidates as both insensitive and highly energetic materials. In general, both mono- and dinitrourea derivatives have attractive molecular densities, which has been attributed to the inherently high density of the urea framework. However, the dinitrourea explosives suffer from hydrolytic stability, and thus restricting their use; but the mono-nitrourea compounds are fairly stable to hydrolysis, mainly due to their intermolecular hydrogen bonding, and may be candidates as insensitive energetic materials.[9–11] The representative energetic compounds of nitroureas focus on alicyclic compounds, including 1,3,4,6-tetranitroglycouril (TNGU), 1,4-dinitroglycouril (DNGU), 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6), which have attractive densities and performances.[12–14] As too little research is available to synthesize aromatic nitroureas compounds, our interest focuses on combing the benzene ring with cyclic nitrourea to form fused ring compounds, which exhibit good thermochemical and physical properties.[15,16] In addition, these compounds may have the insensitivity and stability associated with alternating amino and nitro groups.

In our continuing effort to seek new energetic materials, here we present our attempts at designing and synthesizing new nitro derivatives using 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) as the primary material (Scheme 1).

Experimental

Caution

The titled compound is energetic material and tends explode under certain conditions. Proper protective measures (safety

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra04796f

glasses, face shields, leather coat, ear plugs and earthening equipment and person) should be taken during the synthesis, test and measurement processes, especially when these compounds are prepared on a larger scale.

Materials and instruments

The starting materials used in the present study were of AR grade and purchased from the trade without further purification. Melting point was measured on a X-4 melting point apparatus and was uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on Bruker Avance Spectrometer (TMS as an internal standard). Chemical shifts (δ) are reported in part per million (ppm). The coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analysis was carried out on Perkin-Elmer instrument.

Theoretical calculations were carried out by using the Gaussian 09 program suite.[17] The geometry optimization of the molecular structure and frequency analyses were carried out by using the B3LYP functional with the 6-31G** basis set. The optimized structure was characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The designed isodesmic reactions for the prediction of (ΔH_f^0 gas) are discussed in the ESI.†[18,19]

5-Amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2). (a) From **1**: 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (3.0 g, 20.1 mmol) was added slowly to a solution of fuming nitric acid (6 mL) and acetic anhydride (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 30 min, and poured into crushed ice, and then filtered, washed with water and dried to give 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2**) as a yellow solid (0.6 g, 11%); IR: 3073, 2246, 1732, 1603, 1560, 1510, 1440, 1370, 1324, 1238, 1210, 1116, 983, 824 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.59 (s, 2H), 8.55 (s, 1H), 8.14 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 154.59, 141.55, 138.60, 132.65, 112.70, 107.45, 98.65; anal. calcd for $C_7H_4N_6O_7$: C, 29.59; H, 1.42; N, 29.58; found: C, 29.51; H, 1.35; N, 29.50%.

(b) From **11**: 1-acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**11**) (0.20 g, 0.8 mmol) was added very slowly to a solution of 20% N_2O_5/HNO_3 (1 g) and 2 mL of trifluoromethanesulfonic acid (TFMSAA) which was stirred at the ice bath. The reaction mixture was maintained stirring for 20 min, and poured into crushed ice, then filtered, washed with water and dried to give 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2**) as a yellow solid (0.18 g, 75%), whose ^{1}H NMR was identified with an authentic sample.

***tert*-Butyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-ylcarbamate (3).** To a stirred solution of 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (1.0 g, 6.7 mmol) in methanol (30 mL), dibutyldicarbonate (2.5 mL) was added dropwise at room temperature. The reaction mixture was evaporated after 30 min, and crystallized in methanol to give *tert*-butyl-2-oxo-2,3-dihydro-1*H*-benzo-[*d*]imidazol-5-ylcarbamate (**3**) as a pale pink solid (1.9 g, 96%), m.p. 245–247 °C (dec.); IR: 3344, 3125, 2984, 1694, 1643, 1512, 1474, 1388, 1291, 1235, 1211, 1163, 1053, 1024, 852 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.49 (s, 1H), 10.40 (s, 1H), 9.15 (s, 1H), 7.23 (s, 1H), 6.93 (d, J = 8.20 Hz, 1H), 6.77 (d, J = 8.20 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 155.00, 152.39, 132.59, 129.24, 124.24, 110.42, 107.63, 99.21, 78.10, 27.66; anal. calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86; found: C, 57.70; H, 6.16; N, 16.80%; MS (ESI) m/z: 250.02 (M + H).

2-Chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)-acetamide (4). To a stirred solution of 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (1.0 g, 6.7 mmol) in acetonitrile (30 mL), was added dropwise chloroacetyl chloride (1.5 mL) at room temperature, and maintained for 40 min. The reaction mixture was then filtered, washed with water, and dried to give 2-chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**4**) as a pale pink solid (1.36 g, 90%), m.p. >300 °C; IR: 3289, 2997, 1729, 1675, 1653, 1539, 1505, 1473, 1203, 1027, 845 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.60 (s, 1H), 10.55 (s, 1H), 10.18 (s, 1H), 7.45 (s, 1H), 7.02 (d, J = 8.30 Hz, 1H), 6.86 (d, J = 8.30 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 163.57, 154.97, 131.54, 129.18, 125.55, 111.51, 107.81, 100.28, 43.10; anal. calcd for $C_9H_8ClN_3O_2$: C, 47.91; H, 3.57; N, 18.62; found: C, 47.85; H, 3.48; N, 18.68%; MS (ESI) m/z: 225.96 227.97 = 3 : 1 (M + H).

***N*-(1,3-Diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)-acetamide (5).** 5-Amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (6.0 g, 40.3 mmol) was dissolved in 60 mL of acetic anhydride, the reaction mixture was heated to 120 °C and maintained three hours at this temperature, then the precipitate was cooled to 0 °C, filtered off, thoroughly washed with dichloromethane, then water, and dried to give *N*-(1,3-diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**5**) as a white solid (10.5 g, 95%), m.p. 248–250 °C (dec.); IR: 1762, 1703, 1485, 1431, 1360, 1313, 1243, 1179, 1011, 823 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.10 (s, 1H), 8.43 (s, 1H), 8.00 (d, J = 8.85 Hz, 1H), 7.56 (d, J = 8.85 Hz, 1H), 2.64 (s, 3H), 2.63 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.72, 169.46, 167.71, 150.39, 135.91, 126.18, 121.41, 114.67, 113.97, 105.47, 25.45, 25.27, 23.45; anal. calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27; found: C, 56.65; H, 4.71; N, 15.35%; MS (ESI) m/z: 297.95 (M + Na).

***N*-(2-Oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (6).** 5-Amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (5.0 g, 33.56 mmol) was dissolved in 50 mL of acetic anhydride, the reaction mixture was heated to 40 °C and maintained four hours at this temperature, then the precipitate was cooled to 0 °C, filtered off, washed with dichloromethane, and then water, and dried to give *N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**6**) as a white solid (6.3 g, 98%), m.p. >300 °C; IR: 2989, 1719, 1651, 1621, 1539, 1501, 1364, 1273, 1254, 1203, 1157, 1029, 885 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.51 (s, 1H), 10.45 (s, 1H), 9.77 (s, 1H), 7.45 (s, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 167.18, 154.98, 132.52, 129.08, 124.86, 111.06, 107.65, 100.05, 23.40; anal. calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; found: C, 56.48; H, 4.67; N, 22.05%; MS (ESI) m/z: 214.02 (M + Na).

2-Chloro-*N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (7). 2-Chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**4**) (3.0 g, 13.3 mmol) was added slowly to a solution of fuming nitric acid (4 mL) and concentrated sulfuric

acid (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 40 min, and poured into crushed ice, and then filtered, washed with water and dried to give 2-chloro-*N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**7**) as a pale yellow solid (2.5 g, 60%); m.p. 300–302 °C (dec.); IR: 3332, 3231, 2989, 1742, 1688, 1614, 1514, 1403, 1352, 1293, 1187, 993 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 12.03 (s, 1H), 11.83 (s, 1H), 10.31 (s, 1H), 7.37 (s, 1H), 4.31 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 165.78, 154.86, 133.73, 132.36, 124.95, 123.66, 122.76, 109.99, 42.14; anal. calcd for $C_9H_6ClN_5O_6$: C, 34.25; H, 1.92; N, 22.19; found: C, 34.30; H, 1.85; N, 22.12%; MS (ESI) *m*/*z*: 313.84 : 315.83 = 3 : 1 (M − H).

***N*-(1,3-Diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (8).** *N*-(1,3-Diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**5**) (3.0 g, 10.9 mmol) was added slowly to a solution of fuming nitric acid (5 mL) and concentrated sulfuric acid (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 40 min, and poured into crushed ice, and then filtered, washed with water and dried to give *N*-(1,3-diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**) as a yellow solid (2.88 g, 83%), m.p. 208–210 °C; IR: 3356, 3304, 1733, 1712, 1671, 1608, 1494, 1367, 1317, 1278, 1165, 1100, 1067, 1003 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 10.41 (s, 1H), 8.59 (s, 1H), 8.42 (s, 1H), 2.67 (s, 3H), 2.66 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.74, 169.54, 167.98, 150.04, 137.65, 129.97, 128.89, 122.44, 110.08, 25.30, 25.07, 22.93; anal. calcd for $C_{13}H_{12}N_4O_6$: C, 48.75; H, 3.78; N, 17.49; found: C, 48.69; H, 3.70; N, 17.41%; MS (ESI) *m*/*z*: 342.94 (M + Na).

***N*-(4,6-Dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)-acetamide (9).** *N*-(2-Oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl) acetamide (**6**) (2.0 g, 10.5 mmol) was added slowly to a solution of fuming nitric acid (3 mL) and concentrated sulfuric acid (40 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 30 min, and poured into crushed ice, and then filtered, washed with water and dried to give *N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**9**) as a yellow solid (2.45 g, 83%), m.p. >300 °C; IR: 3346, 3242, 2989, 1738, 1678, 1604, 1547, 1510, 1476, 1410, 1296, 1246, 1176, 993 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 11.97 (s, 1H), 11.77 (s, 1H), 9.96 (s, 1H), 7.33 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.02, 154.88, 133.50, 132.22, 124.54, 122.76, 110.30, 22.39; anal. calcd for $C_9H_7N_5O_6$: C, 38.44; H, 2.51; N, 24.91; found: C, 38.38; H, 2.45; N, 24.99%; MS (ESI) *m*/*z*: 279.90 (M − H).

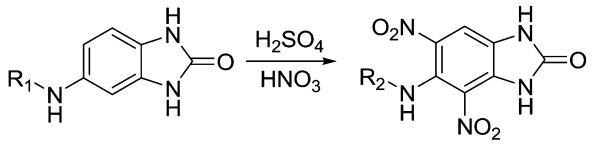
1-Acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (11). *N*-(1,3-Diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**) (0.5 g, 1.56 mmol) was dissolved in 20 mL of acetonitrile, and then 0.5 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene was added dropwise, the reaction mixture gradually turned into red. After 30 min, the reaction mixture was evaporated, and added 10 mL of water, the yellow solid was precipitated after standing for 25 min. the mixture was filtered, washed with water, and dried to give 1-acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**11**) (0.3 g, 81%); m.p. >300 °C; IR: 3463, 3332, 3066, 1719, 1698, 1646, 1614, 1557, 1488, 1369, 1316, 1274, 1173, 1065, 1018, 917 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 11.15 (s, 2H), 10.19 (s, 1H), 7.54 (s, 1H), 7.50 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 168.09, 155.12, 134.78, 133.81, 127.71, 125.67, 104.11, 103.04, 23.44; anal. calcd for $C_9H_8N_4O_4$: C, 45.77; H, 3.41; N, 23.72; found: C, 45.70; H, 3.35; N, 23.81%; MS (ESI) *m*/*z*: 234.92 (M − H).

Results and discussion

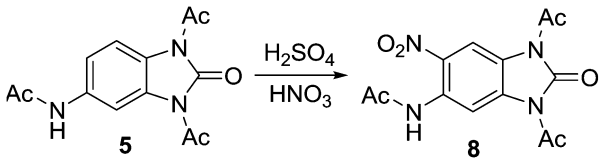
An investigation of the new amino and nitro substituted 1*H*-benzo[*d*]imidazol-2(3*H*)-one as energetic material is now undertaken. With a view to synthesize *N*,*C*-nitrobenzimidazolones, we examined nitration reaction of compound 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) with fuming nitric acid/acetic anhydride at a temperature of 10 °C, and no compound was obtained, but an important product 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2**) was synthesized at a lower temperature of the ice bath with a too low yield of 11%, which was possibly due to the unstable primary amino group in the benzene ring under strongly oxidizing conditions (Scheme 1). Other nitrating reagents including metal nitrate like cupric nitrate, fuming nitric acid/concentrated sulfuric acid, concentrated sulfuric acid/potassium nitrate, and even nitrogen pentoxide/fuming nitric acid were tried to react with compound **1**, but all resulted in compound **2** in a low yield. Thus, it was proposed to synthesize compound **2** or its derivatives through multistep strategy, including *N*-protection and succedent deprotection–nitration reaction.

An efficient and economical technology for the anchoring of 1*H*-benzo[*d*]imidazol-2(3*H*)-one derivatives *via* the protection of the amino group was investigated. Dibutyldicarbonate (DIBOC), chloroacetyl chloride, and acetic anhydride were chosen to give corresponding *N*-substituted intermediates *tert*-butyl 2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-ylcarbamate (**3**), 2-chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**4**), *N*-(1,3-diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**5**), and *N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)-acetamide (**6**), respectively. Compounds **4**, **5** and **6** are poorly soluble in organic solvents, as compared to compound **3**, and they could be brought into further nitration without additional purification.

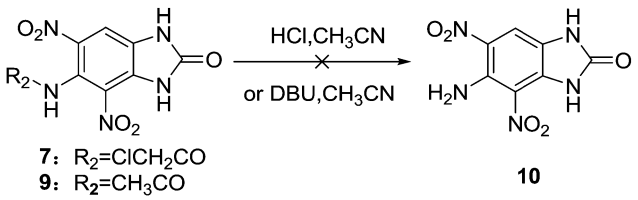
Subsequent nitration of compound **3** was the first attempt, but in no case could any sign of the nitration product be detected, even at the ice bath. However, nitration of **4**, **5** and **6** gave mono- or di-*C*-nitro derivatives, without *N*-nitro derivatives or removal of *N*-protected groups. The nitration of **4** and **6** with excess nitric acid in concentrated sulfuric acid at the ice bath gave *C*-dinitro derivatives 2-chloro-*N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**7**) and *N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**9**), respectively (Scheme 2). And nitration of **5** gave mono-*C*-nitro derivative *N*-(1,3-diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**) (Scheme 3). Owing to the decrease of aromatic ring electron density, caused by three acetyl groups attached to the benzene ring of compound **5** indirectly, di-*C*-nitro reactions are unlikely to happen. Further nitration of **4**, **5** and **6** with a variety of nitrating agents, such as concentrated sulfuric acid/fuming nitric acid, fuming nitric



Scheme 2



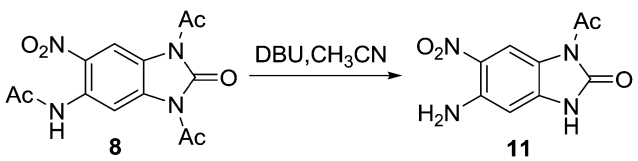
Scheme 3



Scheme 4

acid/acetic anhydride, fuming nitric acid/fuming sulfuric acid, trifluoroacetic anhydride/fuming nitric acid showed the same results. So it is likely that the synthesis of compound **2** involved a multi-step reaction sequence in which compound **1** was *N*-protected, nitrated, deprotected and renitrated.

The *C*-dinitro derivatives **7** and **9** were difficult to generate the deprotected derivative **10** by treatment with concentrated hydrochloric acid or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile (Scheme 4). To our delight, the triacetyl compound **8** is easy to convert into mono-acetyl derivative 1-acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**11**) in the presence of DBU (Scheme 5). The nitrolysis of the final acetyl group of compound **11** proved to be very difficult. Several nitrolysis reagents were tried including fuming nitric acid/acetic anhydride, fuming nitric acid/concentrated sulfuric acid, concentrated sulfuric acid/potassium nitrate, nitrogen pentoxide/fuming nitric acid, but all resulted in recovery of the starting material. The development of the powerful nitration reagent, trifluoromethanesulfonic acid anhydride (TFMSAA)/nitrogen pentoxide/fuming nitric acid, allowed the nitrolysis



Scheme 5

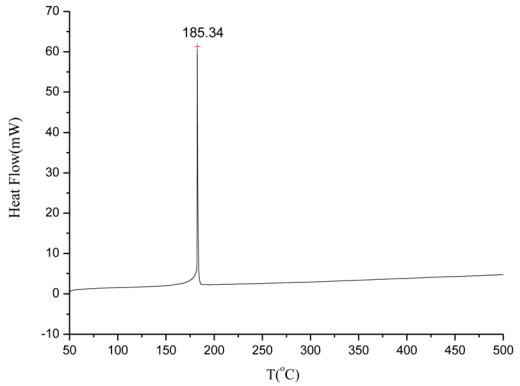


Fig. 1 The DSC curve of compound **2**.

of the final acetyl group to give 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]-imidazol-2(3*H*)-one (**2**). Thus, using **1** as a starting material, **2** was obtained by *N*-protected reaction, nitration, deprotection and again nitration reaction with an overall-yield of 48%.

In order to investigate the thermal behavior of compound **2**, the DSC curve (with a linear heating rate of 10 °C min^{-1} in N_2 gas flowing at a rate of 20 mL min^{-1}) is shown in Fig. 1. The DSC curve of compound **2** exhibits clearly an exothermic decomposition reaction with peak maximum at 185.34 °C and energy evolved during the decomposition reaction is 888 J g^{-1}. Thus, compound **2** has a lower thermal stability comparing with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), whose melting point is 350 °C.[20]

Detonation velocity (*D*) and detonation pressure (*P*) are the most important targets of scaling the detonation characteristics of energetic materials. For the explosives with CHNO elements, the Kamlet–Jacobs empirical equations[21,22] was used to determine these parameters.

Kamlet–Jacobs empirical equations:

$$D = 1.01(NM^{0.5}Q^{0.5})^{0.5}(1 + 1.30\rho_o) \quad (1)$$

$$P = 1.55\rho_o{}^2NM^{0.5}Q^{0.5} \quad (2)$$

where *D* is detonation velocity in km s^{-1}, *P* is detonation pressure in GPa, *N* is moles of gaseous detonation products per gram of explosives, *M* is the average molecular weights of gaseous products, *Q* is the energy of explosion in J g^{-1} of explosive and ρ_o is the crystal density in g cm^{-3}. *N*, *M* and *Q* are determined according to the largest exothermic principle, *i.e.*, for the explosives with CHNO elements, all the N atom converts into N_2, the O atom forms H_2O with H atom first and the remainder forms CO_2 with C atom. The remainder of C atom will exist in solid state if O atom does not satisfy full oxidation of C atom. The remainder of O atom will exist in O_2 if O atom is superfluous.

Density (ρ), Oxygen balance (OB), detonation velocity (*D*) and detonation pressure (*P*) are of the most important four factors in determining the performance of energetic compounds. The density of compound **2** was 1.83 g cm^{-3}, which was mainly attributed to the inherently high density of the urea framework.

Oxygen balance is a measure of how much oxygen is required for complete combustion of hydrogen to water and carbon to carbon dioxide. A positive or negative oxygen balance signifies that there is an excess of or a deficiency of oxygen in the molecule for complete combustion. And compound **2** ($D = 7.78$ km s^{-1}, $P = 27.05$ GPa, OB $= -50.70\%$) exhibits better detonation performance than 2,4,6-trinitrotoluene (TNT, $D = 7.21$ km s^{-1}, $P = 22.49$ GPa, OB $= -74\%$ (ref. 23)).

Conclusions

The present investigation demonstrates the synthesis of some new nitro derivatives for 5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one namely, 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2**), 2-chloro-*N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**7**), *N*-(1,3-diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**), *N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**9**), 1-acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**11**). The newly synthesized compounds have been characterized by elemental and spectral analysis data. The compound **2** has been evaluated for thermal and some detonation performances.

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