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Organic salts of dinitromethane

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ABSTRACT

Seven new salts of dinitromethane (DNM) with organic bases were prepared by two different methods: either by neutralisation of dinitromethane solutions with appropriate base or by metathesis reactions between DNM sodium salt and a respective organic base salt. Crystal structures of formamidinium dinitromethanide, acetamidinium dinitromethanide and propionamidinium dinitromethanide and ^{1}H and ^{13}C chemical shifts of all compounds were determined. The new salts have been characterized in terms of their thermal stability.

1. Introduction

DNM and its salts, originally produced by cumbersome procedures,[1–4] had remained rather exotic compounds until the discovery of 5,5-dinitrobarbituric acid[5–7] and 2,2-dinitroethene-1,1-diamine;[8,9] both compounds easily hydrolysable in basic media to give inorganic salts of DNM in high yields and purity.[5–7,9]

These allowed us to use two different methods for the synthesis of dinitromethane salts with organic counter ions, which might be interesting energetic compounds.

Up to now, there was very limited information on such important properties of DNM salts as thermal stability, reactivity etc. For example, potassium and ammonium salts, having decomposition temperatures 220 °C and 105–110 °C, respectively, behave very different on storage.[3] As it was found in this work pure potassium and sodium salts can be kept for months at ambient temperature, while ammonium salt decomposes spontaneously with appreciable rate.

Only a few organic salts of dinitromethane were known before our work: fenylhydrazinium dinitromethanide,[1] piperidinium dinitromethanide,[10] tetraethylammonium dinitromethanide,[11] diethylamonium dinitromethanide,[12] guanidinium dinitromethanide[13] and 1-ethyl-3-methylimidazolinium dinitromethanide.[14] Guanidinium dinitromethanide was shown recently to be a thermally stable compound with surprisingly low sensitivity to mechanical stimuli.[13] This prompted us to extend the list of DNM salts and compare their chemical and thermal properties to decide if they can find some application in new energetic formulations, e.g., inflatable safety systems and pyrotechnics.

Moreover, non-centrosymmetric organic salts are of current interest because of their non-linear optical properties, in particular of second harmonic generation, which seems to be important in development of new hybrid materials for data storage and frequency modulation.[15] Extensive H-bonding and the presence of delocalized π-electrons, which causes so-called Y-aromaticity in groups such as $-NO_2$ and –CN, in the crystal lattice are one of the requirements in the search for suitable candidates in this field.[16]

2. Results and discussion

2.1. Synthesis

Two methods for the preparation of dinitromethane salts were used: extraction of dinitromethane from acidified aqueous solutions of potassium (sodium) DNM with organic solvents followed by neutralisation of dinitromethane with the appropriate base, and, alternatively, ion exchange of sodium dinitromethane, which has good solubility in water, with respective salts containing the necessary organic counter ion.

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$$CH_2(NO_2)_2 + BH^+CH_3COO^- \xrightarrow[MeOH]{EtOAc} BH^+CH(NO_2)_2^- + CH_3COOH$$

B = $CH(=NH){-}NH_2$ **(1)**, $CH_3(=NH){-}NH_2$ **(2)**, $CH_3CH_2C(=NH){-}NH_2$ **(3)**, $(NH_2NH)(NH_2)C{=}NH$ **(4)**

Scheme 1.

2.1.1. *Procedure A*

A solution of dinitromethane in ethyl acetate was mixed with a methanol solution of an organic base (free base or as an acetate, Schemes 1 and 2); after some time most of the salts precipitated. Only in the case of propionamidinium DNM, part of the solvent was removed by evaporation.

$$2\,CH_2(NO_2)_2 + B \xrightarrow[MeOH]{EtOAc} BH_2^+[CH(NO_2)_2^-]_2$$

B = $NH_2CH_2CH_2NH_2$ **(6)**, piperazine **(7)**

Scheme 2.

The precipitate of each salt formed was filtered off, washed with fresh ethyl acetate and dried.

2.1.2. *Procedure B*

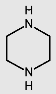
Water solutions of organic base hydrochloride and sodium salt of dinitromethane were mixed together (Scheme 3). The organic salts precipitated with varying yields depending on the solubility of the individual salt (Table 1).

$$Na^+CH(NO_2)_2^- + BH^+Cl^- \xrightarrow{H_2O} BH^+CH(NO_2)_2^- + NaCl$$

B = $CH_3(=NH){-}NH_2$ **(2)**, $(NHNH_2)_2C{=}NNH_2$ **(5)**, $(NH_2)_2C{=}NH$ **(9)**

Scheme 3.

Table 1
Synthesis of dinitromethane salts

Compound	Base (B)	Procedure	Yield (%)	Decomposition, DTA, onset (°C)
1	$HC(=NH){-}NH_2$	A	72	129
2	$CH_3C(=NH){-}NH_2$	A	79	153
		B	73	
3	$CH_3CH_2C(=NH){-}NH_2$	A	49	118
4	$(NH_2NH)C(=NH){-}NH_2$	A	40	104
5	$(NH_2NH)_2C(=NNH_2)$	B	36	131
6	$NH_2CH_2CH_2NH_2$	A	67	100
7		A	77	98
8[a]	$(NH_2)_2C{=}NH$	B	90[15]	173

[a] Added for comparison of thermal stability.

All new salts synthesized in this work were characterised by standard methods: elemental analysis, NMR, IR and UV spectra. Amidinium dinitromethanides were characterized by X-ray diffraction techniques using single crystals of the respective substances. They are all crystalline compounds with typical intense yellow coloration.

Yields and decomposition temperatures are summarized in Table 1; DTA thermograms of four salts are depicted in Figure 1. It is clearly seen that the thermal stability of the new compounds is strongly dependent on the type of the base in the given salt.

Moreover, preliminary observations show that on storage some salts (aminoguanidinium, triaminoguanidinium, formamidinium, ethylenediaminium and piperazinium dinitromethane) change colour significantly, thus indicating (some) chemical transformations.

The reasons for this are not yet understood and additional long-term stability tests are evidently necessary.

2.2. NMR

NMR data of the products **1**–**8** are summarized in Table 2. The ^1H and ^{13}C chemical shifts of $CH\ (NO_2)_2^-$ are 8.20–8.27 and 122.1–122.6, respectively, and these resonances are independent of cations. Relative proton integral intensity and the number of signals in bases determine the $CH\ (NO_2)_2^-$/base ratio undoubtedly.

Standard ^{13}C NMR spectra are measured with proton-noise decoupling and the consequence is that ALL ^{13}C signals are always SINGLETS. Odd (CH and/or CH_3) and even (C and/or CH_2) signals differ in APT, DEPT or INEPT spectra in positive or negative phases, however, all signals are again SINGLETS. In the proton-coupled ^{13}C NMR spectra (which are rarely used nowadays), an isolated methyl group gives a quartet (e.g., compound **2**), however, in an ethyl group each signal of the methyl quartet is split into a triplet with much smaller (ca. 130 vs ca. 7 Hz) carbon–proton coupling due to the presence of a methylene group in the neighbourhood (e.g., compound **3**). In this case, it is a quartet taking one-bond coupling into account only. I am convinced that my proposal is in line with customs used in presentations of ^{13}C NMR spectra in articles concerning structural elucidations where notation C, CH, CH_2, CH_3 is regularly used and clearly and undoubtedly describes the type of a signal.

2.3. X-ray crystallography of amidine salts

2.3.1. *Solid state study*

The structure of previously studied rather poor family of dinitromethane derivatives has been determined by XRD techniques for purely organic species as 1,1,4,4-tetranitrobutane-2,3-diol diacetate and tetranitrobutane-2,3,-diol,[17] 1,4-bis(dinitromethyl)cubane,[18] trinitromethanes: trinitromethane[19] and trinitromethane dioxane solvate;[20] ionic salts containing alkali metals: sodium dinitromethanide and potassium dinitromethanide,[21] rubidium and cesium dinitromethanide[22] and related ionic species as $Cs^+[HC(NO_2)(CN)]^-$, potassium dinitromethanide, $[EMI]^+[C(NO_2)(NO)(CN)]^-$, and $[Me_4N]^+[C(NO_2)(NO)(CN)]^-$.[14] To the best of our knowledge nobody was interested in such studies of ionic dinitromethanides containing an organic cation.

Compounds **1**–**3** have ionic structures with large separations between the CH group and the dinitromethanide and aminoinidium cation (see Figs. 2–4). All three compounds under a crystallographic investigation revealed 2D layered structures with significant hydrogen bridging network (see Figs. 5–7) which is in strong contrast to 3D networks found in compounds having alkali metals as a counter ions (sodium and potassium dinitromethanide,[21] rubidium and cesium dinitromethanide[22]). In the case of **1**, both the anionic and cationic part of the molecule lie in the same plane, in **2**, basic parts lie in neighbouring planes, as well as in **3**, where two independent molecules lie in a bit flexuous

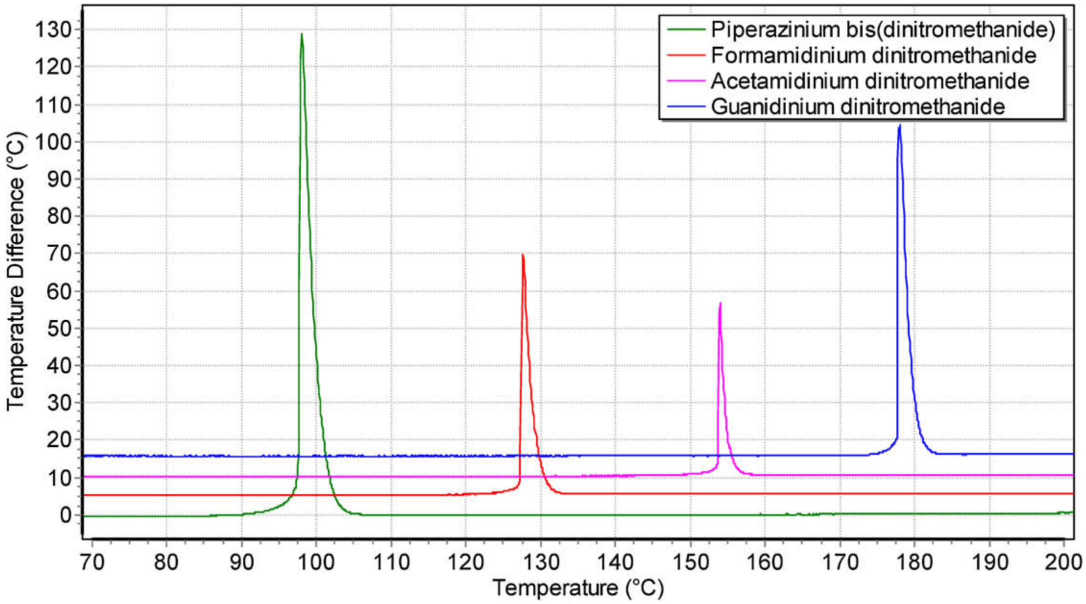


Figure 1. DTA thermograms for the new salts of dinitromethane.

Table 2
^{1}H and ^{13}C NMR chemical shifts of compounds **1**–**7** in DMSO-d_6

Compound	Anion, $CH(NO_2)_2^-$		Cation, BH^+ or BH_2^{2+}	
	δ (^{1}H)	δ (^{13}C)[b]	δ (^{1}H)	δ (^{13}C)
1	8.24[a] (1H, s)	122.3	7.89 (1H, s, CH), 8.86 (4H, br s, 2×NH_x)	157.4 (CH)
2	8.27 (1H, s)	122.6	8.58 (4H, br s, 2×NH_2), 2.14 (3H, s, CH_3)	168.1 (C), 18.5 CH_3)
3	8.20 (1H, s)	122.2	8.71 (4H, br s, 2×NH_x), 2.40 (2H, q, CH_2), 1.20 (3H, t, CH_3)	172.0 (C), 25.7 (CH_2), 11.1 (CH_3)
4	8.23 (1H, s)	122.3	8.59 (1H, br s, NH), 7.29 (2H, br s), 6.76 (2H, br s), 4.73 (2H, br s) (all NH_2)	158.9 (C)
5	8.23 (1H, s)	122.3	8.63 (2H, br s, 2×NH),[c] 4.53 (4H, br s, 2×NH_2)[d]	159.2 (C)
6	8.27[e] (2H, s)	122.4	3.07 (4H, s, 2×CH_2), 7.75 (6H, br s, 2×NH_3)	36.8 (CH_2)
7	8.25 (2H, s)	122.4	3.31 (8H, s, 4×CH_2), 7.82 (4H, br s, NH_x)	40.7 (CH_2)

[a] $^1J(^{13}C, ^1H)$=218.0 Hz
[b] Typical half-width about 20–25 Hz.
[c] Two-fold relative integral intensity with respect to intensity of CH proton.
[d] Three-fold relative integral intensity with respect to intensity of CH proton.
[e] $^1J(^{13}C, ^1H)$=215.0 Hz.

planes. This arrangement is caused by the steric demand of the propionamidinium group also reflected in enlarged cavities within the plane and decrease of density. The supramolecular architecture of **1** in contrast to **2** and **3** reveals non-centrosymmetrical properties but the further study of non-linear optical properties is limited by its rather low stability.

3. Conclusions

- Two new synthetic methods for making organic salts of DNM have been developed. All organic salts of dinitromethane have very different chemical and thermal stability.
- To decide if the new products are suitable for practical application a more detailed research for thermal stability and compatibility is necessary.

4. Experimental

Caution. All poly nitro compounds are considered to be toxic and potentially explosive and should be handled with appropriate precautions. Free dinitromethane is unstable even at room temperature; potassium or sodium dinitromethanide may be sensitive to electric spark, friction and impact. Some described salts can also evolve gases during storage.

4.1. General

The Differential thermal analysis was carried out with thermal analyzer DTA 550Ex produced by OZM Research. The 50 mg samples were tested in open glass micro-test tubes in air. The heating range was 5 °C min^{-1}.

The IR spectra were measured by the KBr pellets technique on FTIR spectrometer Protége by Nicolet Corporation. The resolution was 2 cm^{-1} within a range of 4000–400 cm^{-1}.

UV spectra were taken on Helios gamma spectrometer by Thermo Electron. Cuvettes were made of quartz glass having 1 cm optical length were used. The resolution was 0.5 nm.

All salts were characterised by the typical UV absorption of the DNM anion at 363 nm (ε=20,000).[23] Procedure: 10 mg of the salt was weighed into a 100 mL flask, approximately 50 mL of distilled water was added, then 10 mL of 0.178 M of potassium hydroxide solution was added and finally water was added to 100 mL. The solution was diluted to obtain concentrations between 7×10^{-6} M and 1×10^{-4} M, and these solutions were directly added to the cells to perform the measurements at 363 nm, against a blank with distilled water.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C. The samples 1–7 were dissolved in hexadeuteriodimethyl sulfoxide and measured at laboratory temperature. The ^{1}H and ^{13}C chemical shifts were referenced to the central signal of the solvent (δ=2.55 (^{1}H). 39.6 (^{13}C)).

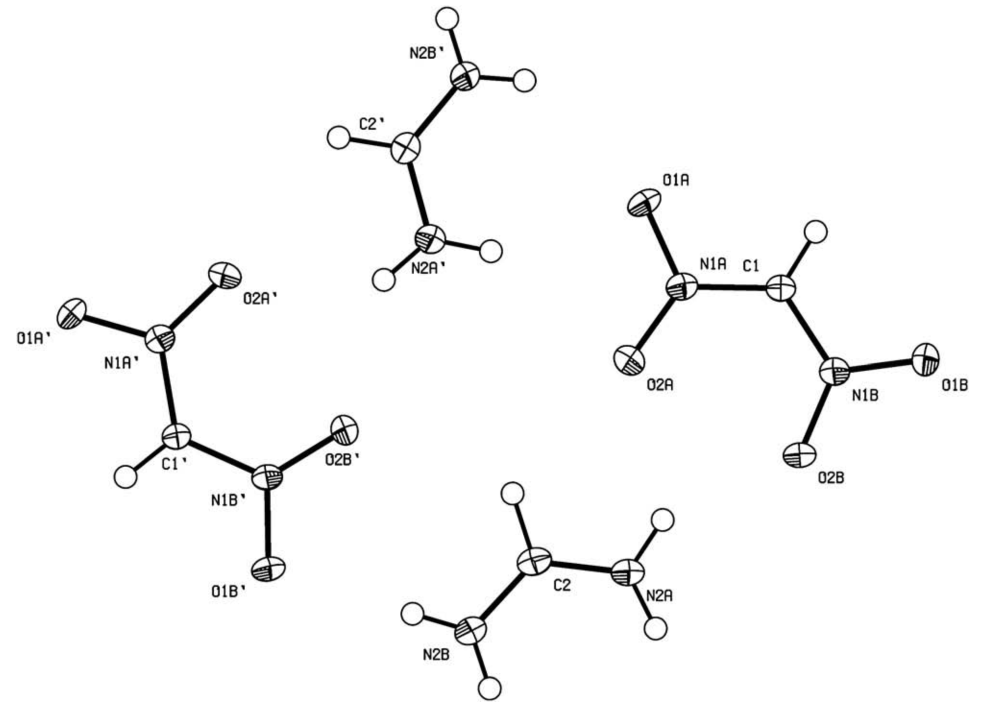


Figure 2. ORTEP view of compound **1** showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms), two independent molecules are present; selected bond lengths (Å) and angles (°): C1′ N1A′ 1.3545(18), C1′ N1B′ 1.3674(18), C1 N1A 1.3581(19), C1 N1B 1.3626(18), C2 N2A 1.294(2), C2 N2B 1.296(2), C2′ N2B′ 1.293(2), C2′ N2A′ 1.2987(19), O2B′ N1B′ 1.2449(16), N1A′ O2A′ 1.2482(16), N1A′ O1A′ 1.2619(16), O2B N1B 1.2450(16), N1B′ O1B′ 1.2613(15), O1B N1B 1.2612(17), N1A O2A 1.2431(16), N1A O1A 1.2644(16), N1A′ C1′ N1B′ 123.95(13), N1A C1 N1B 123.91(13), N2A C2 N2B 125.89(14), N2B′ C2′ N2A′ 125.41(14), O2A′ N1A′ O1A′ 119.80(12), O2A′ N1A′ C1′ 124.56(13), O1A′ N1A′ C1′ 115.63(12), O2B′ N1B′ O1B′ 120.65(12), O2B′ N1B′ C1′ 124.34(12), O1B′ N1B′ C1′ 115.01(12), O2B N1B O1B 120.41(12), O2B N1B C1 124.16(13), O1B N1B C1 115.43(12), O2A N1A O1A 120.10(12), O2A N1A C1 124.73(12), O1A N1A C1 115.17(12).

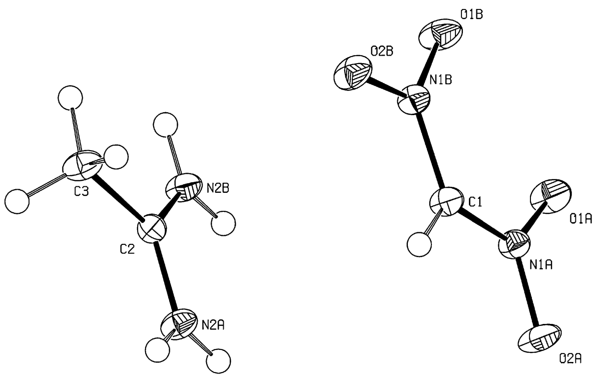


Figure 3. ORTEP view of compound **2** showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms); selected bond lengths (Å) and angles (°): O1A N1A 1.2462(19), O2B N1B 1.2564(19), O2A N1A 1.2608(19), N2A C2 1.314(2), N1A C1 1.361(2), N1B O1B 1.2497(19), N1B C1 1.363(2), N2B C2 1.310(2), C2 C3 1.490(2), O1A N1A O2A 120.71(14), O1A N1A C1 124.59(15), O2A N1A C1 114.70(14), O1B N1B O2B 120.19(14), O1B N1B C1 123.92(14), O2B N1B C1 115.90(14), N2B C2 N2A 121.11(15), N2B C2 C3 119.21(15), N2A C2 C3 119.68(15), N1A C1 N1B 124.06(15).

The X-ray data for colourless crystals of **1**–**3** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ=0.71073 Å), a graphite monochromator, and the φ and χ scan mode (Table 3). Data reductions were performed with DENZO-SMN.[24] The absorption was corrected by integration methods.[25] Structures were solved by direct methods (Sir92)[26] and refined by full matrix least-square based on F^2 (SHELXL97).[27] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)=1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H=0.96, and 0.97 Å for methyl, methylene and methine hydrogen atoms, respectively.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 684111–684113 for **1**–**3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

4.2. Ethyl acetate extracts of dinitromethane

Potassium dinitromethanide[5,6] (4.0 g, 27.8 mmol) was stirred in a mixture of 40 mL of water and 40 mL of ethyl acetate. Diluted sulfuric acid (5 mL aqueous solution containing 1.6 mL of 96% sulfuric acid) was added to obtain pH 1–2. Potassium dinitromethanide dissolved and stirring was continued for 10 min. The layers were separated and the aqueous phase was extracted with 40 mL of ethyl acetate. The combined ethyl acetate extracts were washed with water to obtain a neutral solution. The content of dinitromethane may be checked by UV analysis.[23]

4.3. Formamidinium dinitromethanide 1

Dinitromethane (3.00 g, 28.3 mmol) in 70 mL of ethyl acetate was added to a solution of formamidine acetate (2.94 g, 28.3 mmol; Aldrich, 99%) in methanol (160 mL). The mixture was stirred for 1 h, the yellow precipitate was filtered and washed with fresh ethyl acetate. Yield 3.0 g (72%), onset of decomposition at 129 °C (DTA).

IR (KBr): 3422, 3345, 3140 (NH), 1724 (NH), 1491, 1471, 1332 (NO_2), 1217, 1087, 1001, 783, 740.

Anal. Calcd for $C_2H_6N_4O_4$: C, 16.00; H, 4.03; N, 37.33. Found: C, 15.56; H, 4.22; N, 37.60.

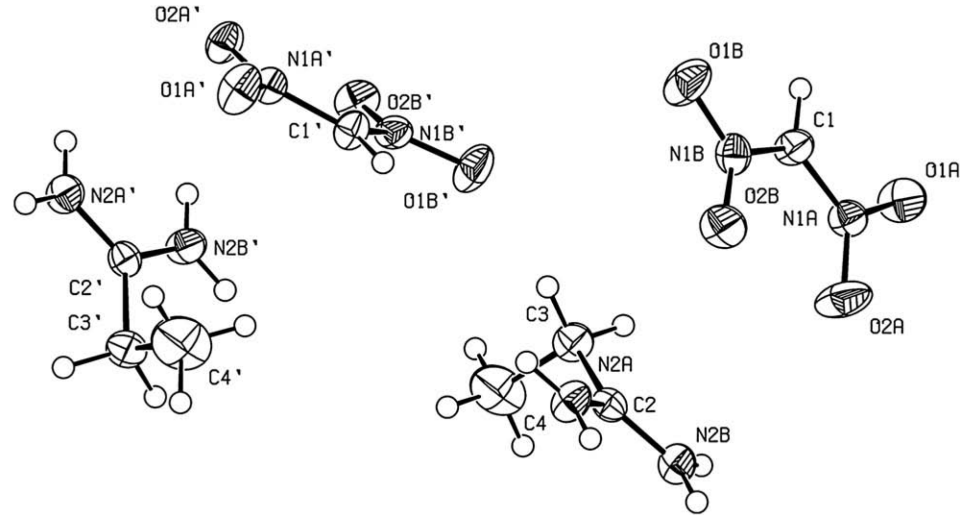


Figure 4. ORTEP view of one of two independent molecules of compound **3** showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms); selected bond lengths (Å) and angles (°): O2A′ N1A′ 1.242(3), N1A′ O1A′ 1.264(3), N1A′ C1′ 1.352(3), N1B′ O2B′ 1.247(3), N1B′ O1B′ 1.250(3), N1B′ C1′ 1.363(3), C2 N2A 1.304(3), C2 N2B 1.305(3), C2 C3 1.487(4), N2B′ C2′ 1.308(3), N1B O2B 1.244(3), N1B O1B 1.246(3), N1B C1 1.364(3), N1A O2A 1.244(3), N1A O1A 1.255(3), N1A C1 1.352(3), C3′ C4′ 1.503(4), C3 C4 1.503(4), O2A′ N1A′ O1A′ 119.9(2), O2A′ N1A′ C1′ 123.8(2), O1A′ N1A′ C1′ 116.2(2), O2B′ N1B′ O1B′ 119.8(2), O2B′ N1B′ C1′ 123.8(2), O1B′ N1B′ C1′ 116.4(2), N2A C2 N2B 121.2(2), N2A C2 C3 118.9(2), N2B C2 C3 119.8(2), O2B N1B O1B 120.4(2), O2B N1B C1 123.6(2), O1B N1B C1 116.0(2), O2A N1A O1A 120.1(2), O2A N1A C1 123.3(2), O1A N1A C1 116.5(2), N2A′ C2′ N2B′ 121.2(2), N2A′ C2′ C3′ 120.1(2), N2B′ C2′ C3′ 118.7(2), N1A C1 N1B 124.1(2), C2′ C3′ C4′ 112.8(2), C2 C3 C4 111.0(2).

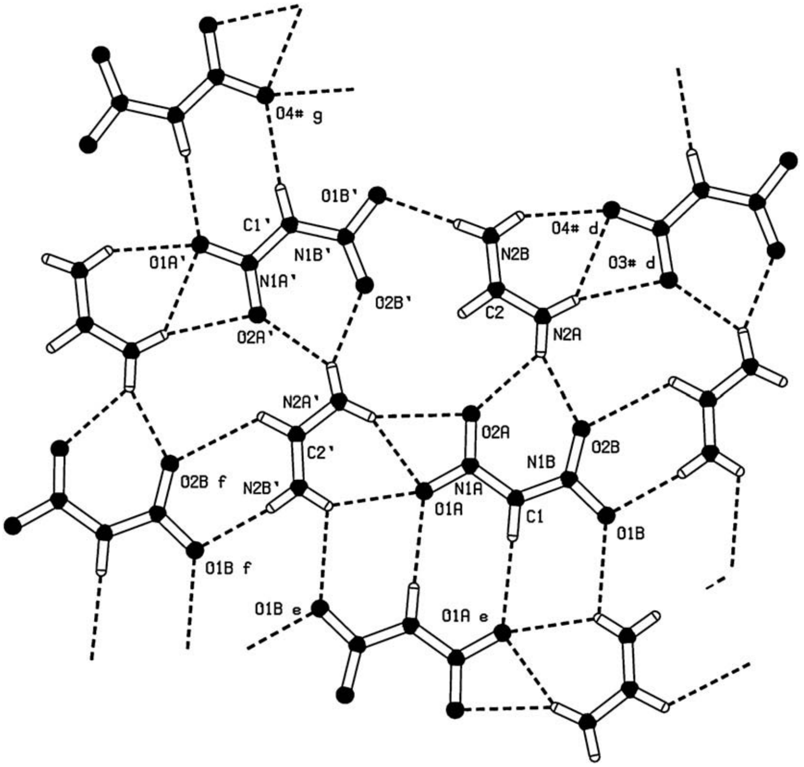


Figure 5. View of hydrogen bridging in **1**. Hydrogen bonds (D–H···A distances (Å), and angles (°)): N2A H2AA O2B 2.8640(18), 148.9, N2A H2AA O2A 2.9139(17), 134.4, N2A H2AB O2A′ 3.1640(16), 165.5, N2A H2AB O1A′ 3.0593(17), 138.9, N2A′ 2A′A O1A 2.9865(18), 151.1, N2A′ 2A′A O2A 3.2030(17), 152.8, N2A′ 2A′A N1A 3.5237(18), 176.1, N2A′ 2A′B O2B′ 2.8747(17), 144.0, N2A′ 2A′B O2A′ 2.8738(17), 135.0, N2B H2BA O1B′ 2.9095(17), 178.9, N2B H2BB O1A′ 2.9827(16), 148.9, N2B H2BB O1B′ 3.0706(17), 114.6, N2B′ 2B′A O1A 3.0192(17), 137.0, N2B′ 2B′A O1B 2.9938(17), 115.3.

4.4. Acetamidinium dinitromethanide 2

(A) Acetamidine acetate (4.50 g, 38.5 mmol) was dissolved in methanol (75 mL) and dinitromethane (4.08 g, 38.5 mmol) in 90 mL of ethyl acetate was added. The mixture was stirred for 1 h; the yellow precipitate was filtered and washed with fresh ethyl acetate.

Yield 5.0 g (79%), onset of decomposition at 153 °C (DTA).

IR (KBr): 3346, 3136 (NH), 2954, 2785 (CH_3), 1696, 1690 (NH), 1524, 1508, 1491, 1400 (NO_2), 1319, 1229, 1076, 997.

Anal. Calcd for $C_3H_8N_4O_4$: C, 21.96; H, 4.91; N, 34.13. Found C, 22.18; H, 4.79; N, 33.98.

(B) Acetamidine hydrochloride (1.90 g, 20.1 mmol) in water (3 mL) was added to a solution of sodium dinitromethanide[5,6] (2.60 g, 20.3 mmol) in water (14 mL) at 60 °C with stirring and the mixture was cooled to room temperature. The precipitate was

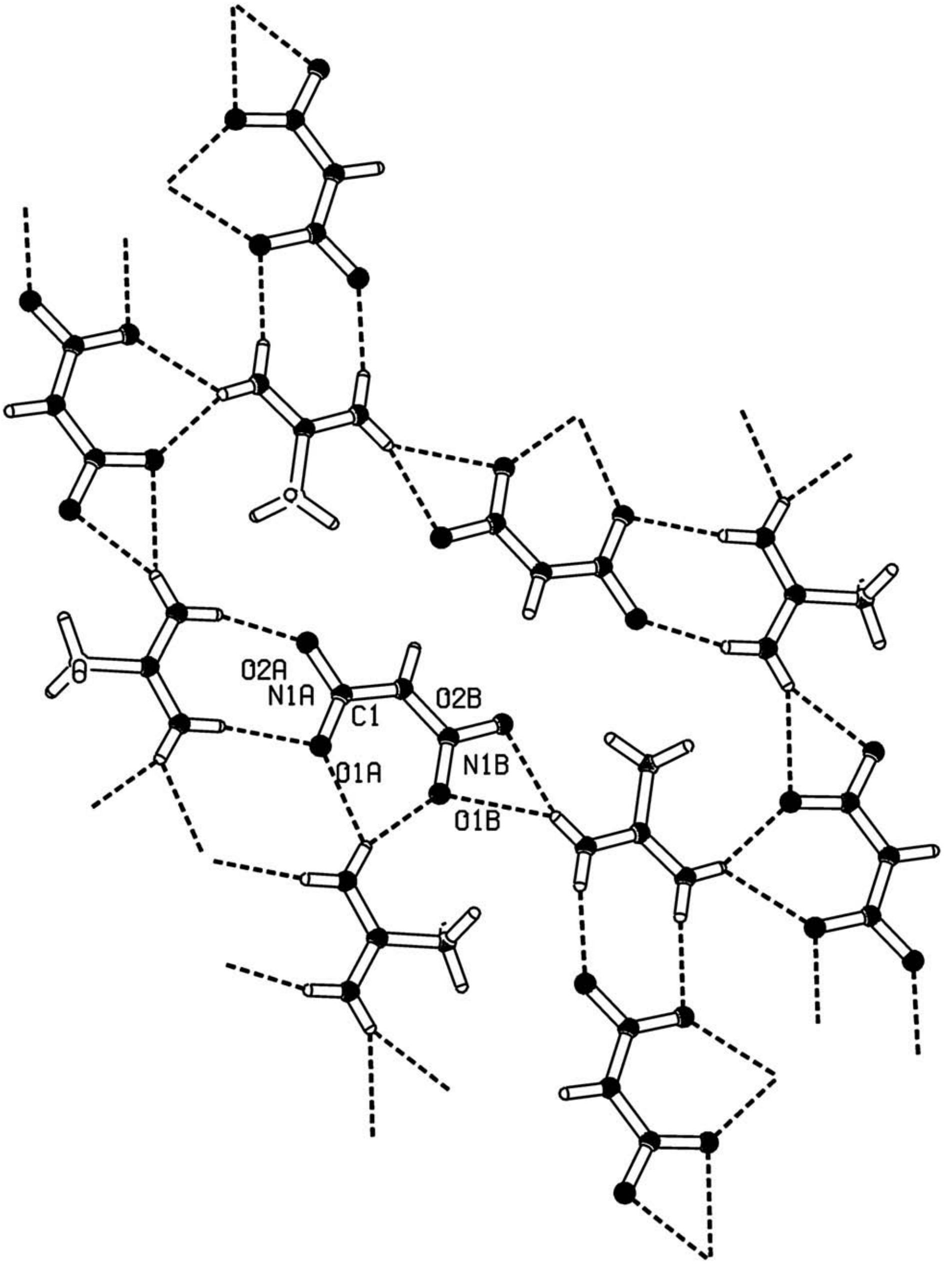


Figure 6. View of hydrogen bridging in **2**. Hydrogen bonds (D–H···A distances (Å), and angles (°)): N2A H2AA O1A 3.023(2), 171.6, N2A H2AB O1B 2.948(2), 154.9, N2A H2AB O1A 2.900(2), 128.4, N2B H2BA O2A 2.8904(19), 165.9, N2B H2BB O2B 3.019(2), 157.7, N2B H2BB O1B 3.257(2), 145.7.

filtered off, wash with 8–10 mL water and dried. Yield 2.4 g (73%). The product possesses the same thermal and spectral properties as for product (A).

4.5. Propionamidinium dinitromethanide 3

Propionamidine acetate[†] (2.70 g, 20.7 mmol) in methanol (38 mL) was added to dinitromethane (2.20 g, 20.7 mmol) in 65 mL of ethyl acetate. The mixture became yellow, but no product precipitated during 1 h of stirring. Then the mixture was concentrated in vacuo at 40 °C to a final volume 10–20 mL and cooled to room temperature. Yellow crystals precipitated. Yield 1.8 g (49%), onset of decomposition at 118 °C (DTA).

IR (KBr): 3329, 3147 (NH), 2983, 2943, 2880, 2804 (CH_3, CH_2), 1688, 1685 (NH), 1487 (CH_3), 1465, 1462, 1302 (NO_2), 1319, 1229, 1076, 997. Anal. Calcd for $C_4H_{10}N_4O_4$: C, 26.97; H, 5.66; N, 31.45. Found: C, 26.75; H, 5.64; N, 31.06.

4.6. Aminoguanidinium dinitromethanide 4

Aminoguanidine bicarbonate (0.85 g, 6.2 mmol) and acetic acid (0.75 g, 12.5 mmol) were added to methanol (20 mL). The mixture was heated at 50 °C for 10–15 min, until gas evolution ceased. To this solution, dinitromethane (0.66 g, 6.2 mmol) in 20 mL of ethyl acetate was added. The colour turned to greenish-yellow and a solid precipitated. Yield 0.45 g (40%), onset of decomposition at 104 °C (DTA).

[†] Propionamidine acetate was prepared according to a general procedure for amidinium acetates, described in Ref. 28, mp 173–175 °C (ethanol); ^1H NMR (DMSO-d_6) δ 1.18, 1.71 s (2×CH_3), 2.34 s (CH_2), 3.6 br s (NH_2) ppm; ^{13}C NMR (DMSO-d_6) δ 11.2 (CH_3), 26.0 (CH_2), 172.8 ($C(NH_2)_2$), 176.7 (COO), 25.0 (CH_3).

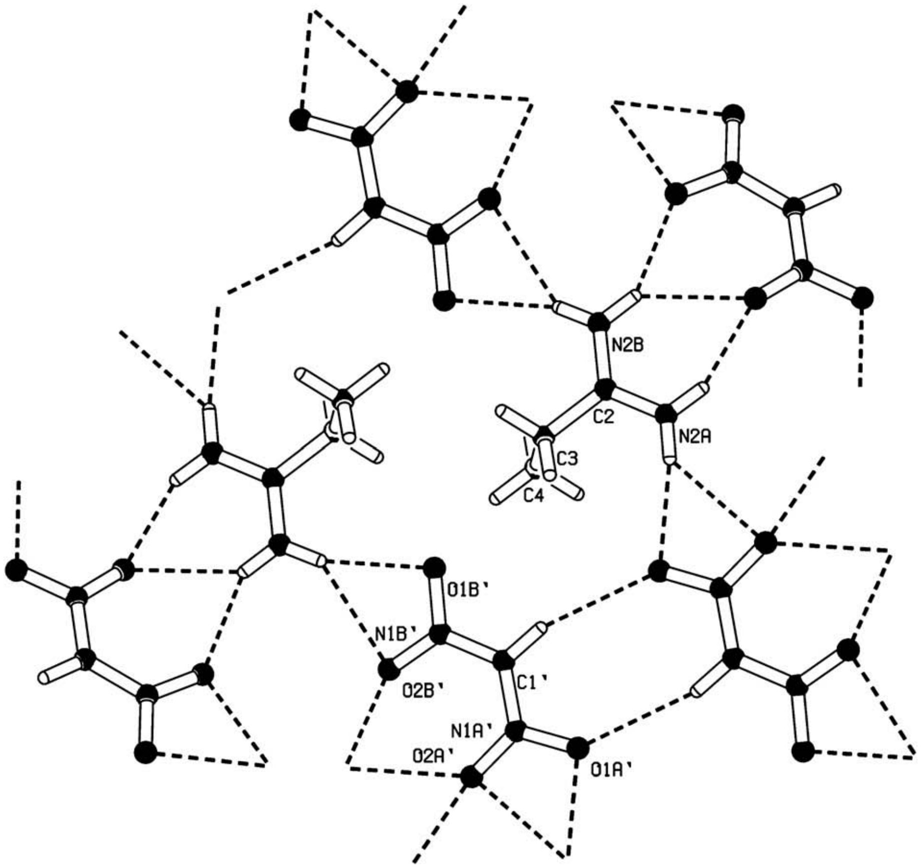


Figure 7. View of hydrogen bonding in **3**. Hydrogen bonds (D–H···A distances (Å), and angles (°)): N2B′ 2B′A O2A′ 2.921(3), 151.7, N2B′ 2B′B O1A 2.897(3), 171.2, N2A H2AB O1A′ 2.978(3), 162.2, N2A H2AB O2A′ 3.185(3), 137.3, N2A H2AB N1A′ 3.510(3), 161.8, N2A H2AA O2A 2.871(3), 149.6, N2B H2BA O2B 2.989(3), 142.5, N2B H2BA O2A 3.017(3), 141.7, N2B H2BB O1B′ 3.092(3), 162.7, N2B H2BB O2B′ 3.181(3), 142.4, N2A′ H2A′A O2B′ 2.929(3), 145.4, N2A′ H2A′B O2B 3.037(3), 148.3, N2A′ H2A′B O1B 3.232(3), 156.2, N2A′ H2A′A O2A′ 3.135(3), 141.1.

Table 3
Crystallographic data for **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_2H_6N_4O_4$	$C_3H_8N_4O_4$	$C_4H_{10}N_4O_4$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*−1	*C*2/c	*P*−1
a (Å)	3.5230(2)	8.2835(4)	8.5610(12)
b (Å)	9.4290(5)	12.3529(3)	9.5060(15)
c (Å)	18.0630(10)	13.6920(9)	10.6390(16)
α (°)	82.748(4)	90.00	89.225(10)
β (°)	86.694(5)	105.619(12)	70.741(15)
γ (°)	88.012(5)	90.00	83.065(15)
Z	4	8	4
V (Å^3)	594.01(6)	1349.30(14)	811.1(2)
D_c/g cm^{-3}	1.679	1.610	1.450
Crystal size (mm)	0.387×0.352×0.234	0.316×0.296×0.276	0.544×0.081 ×0.079
Crystal shape	Colourless block	Colourless block	Colourless needle
μ (mm^{-1})	0.158	0.146	0.129
F (000)	312	688	376
h; *k*; *l* range	−4, 4; −12, 12; −23, 23	−10, 10; −16, 13; −14, 17	−11, 11; −12, 12; −13, 13
θ range/°	2.18; 27.5	3.04; 27.5	2.03; 27.5
Reflections measured	10,164	4247	14,816
Independent (R_{int})[a]	2665 (0.0993)	1514 (0.0386)	3708 (0.0966)
Observed [$I>2\sigma(I)$]	2323	1275	2546
Parameters refined	181	100	217
Max/min $\Delta\rho$/e Å^{-3}	0.267/−0.367	0.438/−0.398	0.408/−0.331
GOF[b]	1.092	1.085	1.156
R[c]/wR[c]	0.0410/0.1045	0.0471/0.1212	0.0660/0.1354

[a] $R_{int}=\Sigma|F_o^2-F_{o,mean}^2|/\Sigma F_o^2$.

[b] $GOF=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{diffrs}-N_{params})]^{1/2}$ for all data.

[c] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for observed data, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

IR (KBr): 3459, 3391, 3354 (NH), 2875 (CH), 1670, 1613 (NH), 1559, 1362, 1300 (NO_2), 1206, 1052, 997, 783, 736.

Anal. Calcd for $C_2H_8N_6O_4$: C, 13.34; H, 4.48; N, 46.66. Found: C, 12.87; H, 4.91; N, 46.53.

4.7. Triaminoguanidinium dinitromethanide 5

Triaminoguanidinium hydrochloride[29] (0.87 g, 6.2 mmol) in water (5 mL) was added to solution of sodium dinitromethanide (1.15 g, 9.0 mmol) in water (5 mL) at 45 °C and the mixture was cooled to 15 °C. The precipitate was filtered off, washed with ethanol and crystallized from methanol/water. Yield 0.7 g (35.5%), onset of decomposition at 131 °C (DTA).

IR (KBr): 3366, 3340, 3212, 3140 (NH), 1694 (NH), 1447, 1414, 1386, 1291 (NO_2), 1238, 1127, 992, 779, 739, 539.

Anal. Calcd for $C_2H_{10}N_8O_4$: C, 11.43; H, 4.80; N, 53.31. Found: C, 11.79; H, 4.77; N, 53.31.

4.8. Ethylenediamonium bis(dinitromethanide) 6

Dinitromethane (3.00 g, 28.3 mmol) in 70 mL of ethyl acetate was added to ethylenediamine (1.67 g, 27.8 mmol) in methanol (10 mL). The mixture was stirred for 1 h; the yellow precipitate was filtered and washed with fresh ethyl acetate. Yield 3.1 g (67%), onset of decomposition at 100 °C (DTA).

IR (KBr): 3450, 3445, 3250 (NH), 2940, 2890 (CH_2), 1630 (NH), 1491, 1526, 1362 (NO_2), 1188, 1156, 998, 740.

Anal. Calcd for $C_4H_{12}N_6O_8$: C, 17.65; H, 4.44; N, 30.88. Found: C, 17.40; H, 4.79; N, 30.76.

4.9. Piperazinium bis(dinitromethanide) 7

Piperazine (0.30 g, 3.5 mmol) in methanol (4 mL) was added to a solution of dinitromethane (0.74 g, 7.0 mmol) in 30 mL of ethyl acetate. The mixture was stirred for 1 h; the yellow precipitate was filtered and washed with fresh ethyl acetate. Yield 0.8 g (77%), onset of decomposition at 98 °C (DTA).

IR (KBr): 3136, 3058 (NH), 2850, 2760 (CH_2), 2448, 1587 (NH), 1498, 1335 (NO_2), 1294, 1218, 1186, 1078, 998.

Anal. Calcd for $C_6H_{14}N_6O_8$: C, 24.17; H, 4.73; N, 28.18. Found: C, 24.21; H, 4.97; N, 28.36.

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