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Article

Synthesis and Characterization of 4,5-Dicyano-2*H*-1,2,3-triazole and Its Sodium, Ammonium, and Guanidinium Salts

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In this contribution, the synthesis and structural characterization of the 4,5-dicyano-1,2,3-triazolate anion in its sodium, ammonium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium salts is reported. The synthesis of 4,5-dicyano-2*H*-triazole (**1**) was repeated as described in the literature (Johansson, P. et al. *Solid State Ionics* **2003**, *156*, 129) and spectroscopically characterized using ^{1}H, ^{13}C, and ^{15}N NMR, IR, and Raman spectroscopy, as well as differential scanning calorimetry (DSC) and mass spectrometry (DEI+). The molecular structure was determined for the first time using X-ray diffraction (**1**: monoclinic, $P2_1/c$, $a = 6.0162(6)$ Å, $b = 11.2171(10)$ Å, $c = 7.5625(7)$ Å, $\beta = 94.214(8)°$, $V = 508.97(8)$ Å^3, $Z = 4$). Compound **1** was deprotonated using Na_2CO_3 to form the corresponding sodium salt of the 4,5-dicyano-1,2,3-triazolate anion (**2**) as a monohydrate. This compound was also characterized using ^{13}C, ^{14}N, ^{15}N NMR, IR, and Raman spectroscopy, as well as single crystal X-ray diffraction (**2**: monoclinic, $P2_1/c$, $a = 3.6767(6)$ Å, $b = 20.469(4)$ Å, $c = 9.6223(13)$ Å, $\beta = 97.355(13)°$, $V = 718.2(2)$ Å^3, $Z = 4$). Reaction of **2** with AgNO$_3$ yielded silver 4,5-dicyano-1,2,3-triazolate (**3**) which was characterized using IR and Raman spectroscopy, as well as DSC, and was used to prepare the ammonium (**4**), guanidinium (**5**), aminoguanidinium (**6**), diaminoguanidinium (**7**), and triaminoguanidinium (**8**) salts of the 4,5-dicyano-1,2,3-triazolate anion in a metathetical reaction from the corresponding ammonium and guanidinium halides. All new compounds (**4**–**8**) were spectroscopically characterized (^{1}H and ^{13}C NMR, IR, Raman), the stabilities investigated using DSC, the mass spectra obtained using the FAB+ and FAB- methods and the solid state structures determined using single crystal X-ray diffraction: (**4**): orthorhombic, *Pnma*, $a = 6.5646(13)$ Å, $b = 7.5707(16)$ Å, $c = 13.303(3)$ Å, $V = 661.1(2)$ Å^3, $Z = 4$; (**5**): monoclinic, *Cc*, $a = 12.6000(11)$ Å, $b = 17.1138(15)$ Å, $c = 12.0952(9)$ Å, $\beta = 106.098(7)°$, $V = 2505.9(4)$ Å^3, $Z = 12$; (**6**): monoclinic, *Pa*, $a = 7.0921(9)$ Å, $b = 7.2893(9)$ Å, $c = 8.8671(11)$ Å, $\beta = 105.141(11)°$, $V = 442.48(10)$ Å^3, $Z = 2$; (**7**): monoclinic, *P2$_1$*, $a = 3.7727(4)$ Å, $b = 15.6832(17)$ Å, $c = 8.3416(10)$ Å, $\beta = 101.797(10)°$, $V = 483.13(9)$ Å^3, $Z = 2$; (**8**): monoclinic, *C2/c*, $a = 14.0789(14)$ Å, $b = 11.5790(11)$ Å, $c = 13.5840(14)$ Å, $\beta = 115.239(10)°$, $V = 2003.1(3)$ Å^3, $Z = 8$. The impact and friction sensitivities of compounds **4**–**8** were investigated using drop hammer and friction apparatus methods, and all compounds were found to be neither impact (> 30 J) nor friction sensitive (> 360 N). The detonation parameters of compounds **5**– **8** were computed using the EXPLO5 code.

Introduction

Energetic materials that derive their energy from a positive heat of formation rather than oxidation of the carbon backbone have recently attracted attention as gas generators or propellants.[1–21] High-nitrogen compounds which contain only the elements C, H, and N and which are free of both oxygen and metals are potentially useful as either gas generators or energetic materials which have a low flame temperature, to increase the impulse in gun or rocket propellants.[15]

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Nitrogen-containing five-membered heterocycles are traditional sources of energetic materials, since the N−N bonds in the ring are stabilized by pseudoaromatic electron delocalization and are therefore relatively insensitive. Therefore, stable nitrogen-rich salts can be formed when employing such rings. A result of this is that considerable attention is currently focused on azoles as new, future energetic materials, and in particular the tetrazole series.[20−26] Whereas the chemistry and application of nitrogen-rich tetrazole compounds as energetic materials has been extensively studied by us[1−11] and others,[12−19,27] the corresponding chemistry of the related triazole ring has only recently been the subject of systematic investigations.[28−36] Both 1,2,4-triazole and 1,2,3-triazoles have been reported previously in the literature, and both have positive heats of formation of 109 kJ mol^{-1} and 272 kJ mol^{-1} respectively.[37,38] Therefore, 1,2,3-triazole

based compounds are energetically of greater interest than 1,2,4-triazole derivatives. Energetic materials that are salts are often advantageous over non-ionic molecules, since the salts tend to exhibit lower vapor pressures (essentially eliminating the risk of exposure through inhalation)[29,39] and higher densities than their atomically similar neutral and non-

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ionic analogues.[28] The synthesis of 4,5-dicyano-1,2,3-triazole was reported as early as 1921 by E. Gryszkiewicz-Trochimowski[40a,d] by the diazotation of aminomalononitrile with "HNO₂". In the same work, some ionic species of the 4,5-dicyano-1,2,3-triazole, namely, the silver, potassium, ammonium, copper, and barium 4,5-dicyano-1,2,3-triazolate, characterized mainly by solubility and melting point. The publication of the calcium salt followed in 1924.[40e] The lithium salt was quite recently investigated by Johansson et al.[40b] and characterized using Raman spectroscopy. However, no experimentally determined structural data were presented, although the structure of the 4,5-dicyano-1,2,3-triazolate anion was computed in the gas phase.[40b] These authors were interested, however, in a different aspect of the chemistry of this species, namely, the relatively non-coordinating behavior of this anion for use in polymer electrolytes. To the best of our knowledge, there is no report in the literature concerning a structurally characterized salt containing the 4,5-dicyano-1,2,3-triazolate anion. Furthermore, only very few structurally characterized compounds containing the 4,5-dicyano-1,2,3-triazole ring can be found. Therefore, this prompted us to determine the molecular structure of the neutral compound **1** and to investigate its potential as possible precursor for the synthesis of ionic, nitrogen-rich 4,5-dicyano-1,2,3-triazolate salts. Consequently, a report on the preparation of the corresponding ammonium (**4**), guanidinium (**5**), aminoguanidinium (**6**), diaminoguanidinium (**7**), and triaminoguanidinium salts (**8**) of the 4,5-dicyano-1,2,3-triazolate anion is given in this paper.

Experimental Section

Materials. All chemical reagents and solvents of analytical grade were obtained from Sigma-Aldrich Fine Chemicals Inc. and used as supplied. Solvents were dried according to known procedures, freshly distilled, and stored under a nitrogen atmosphere.

General Procedure. The ^{1}H, ^{13}C, and ^{14}N/^{15}N NMR spectra were recorded in DMSO-d_6 using Multinuclear NMR. Spectra were recorded using a Jeol EX 400 FT-NMR spectrometer operating at 399.782 MHz (^{1}H), 100.525 MHz (^{13}C), and 28.889 MHz (^{14}N), a Jeol 400 eclipse FT-NMR spectrometer operating at 400.182 MHz (^{1}H), 100.626 MHz (^{13}C), 28.918 MHz (^{14}N) or a Jeol 270 FT-NMR spectrometer operating at 270.166 MHz (^{1}H), 67.933 MHz (^{13}C) and 27.376 MHz (^{15}N). Chemical shifts are given with respect to TMS (^{1}H, ^{13}C) and MeNO₂ (^{14}N) as external standards. Coupling constants are given in Hertz. Infrared (IR) spectra were recorded of the solids between KBr plates using a Perkin-Elmer Spectrum One FT-IR instrument between KBr plates at 25°C. Raman spectra were recorded using a Perkin Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported relative to the most intense peak and given in parenthesis. Elemental analyses were performed with a Netsch Simultanous Thermal Analyser STA 429. Melting points were determined by differential scanning calorimetry (DSC) (Perkin-Elmer Pyris 6 DSC, calibrated by standard pure Indium and Zinc). Measurements were performed at a heating rate of $\beta = 5$°C in closed Al-containers with a hole (1 μm) on the top for gas release

and a 0.003 × 3/16 in. disk was used to optimize good thermal contact between the sample and the container with a nitrogen flow of 20 mL/min. The reference sample was an Al container with air.

Synthesis of 4,5-Dicyano-2H-1,2,3-triazole (1). The synthesis of **1** was undertaken according to the literature procedure[40b] using the following scale: Diaminomaleodinitrile (10.81 g, 100.0 mmol) was dissolved in 125 mL of water and acidified with hydochloric acid (1M, 100 mL). At 0 °C sodium nitrite (6.89 g, 100.0 mmol) was added portion wise, while maintaining the reaction temperature below 4 °C. The reaction mixture was then allowed to warm up to room temperature and stirred for 1 h. After filtration the brownish solution was extracted five times with a total of 600 mL of diethylether. After removal of the solvent of the combined ether extracts under reduced pressure, a pale light brown solid was obtained. Yield of crude product = 10.6 g (89 %). Analytically pure **1** was obtained by subliming the crude product at 90°C under vacuum to yield white crystals suitable for single crystal X-ray diffraction. The white solid was used for the reported characterization.

Melting point = 148.8 °C. T_{dec} = 221.1 °C. IR (KBr, 25 °C, cm^{-1}) ν = 3258 (vs), 2839vw, 2263 (s), 1554 (vw), 1478 (m), 1382 (s), 1250 (w), 1228 (w), 1185 (w), 1131 (vs), 1090 (w), 999 (m), 792 (s) 627 (m), 521 (m), 465 (m). Raman (200 mW, 25 °C, cm^{-1}) ν = 3258 (6), 2263 (100), 2209 (2), 1486 (48), 1400 (3), 1381 (32), 1351 (2), 1299 (15), 1208 (24), 992 (9), 727 (3), 660 (19), 539 (6), 524 (12), 459 (12), 230 (2), 202 (2), 183 (3), 154 (6). ^{1}H NMR, δ(ppm): 7.63 (s, 1H, NH). ^{13}C NMR, δ(ppm): 111.7 (s,C₂N₃(CN)₂), 123.8 (s,-CN). ^{15}N NMR, δ(ppm): −108.6 (N2), −76.9 (N4, N5), −39.2 (N1, N3). MS (DEI+) C₄HN₅, calcd 119.10, found 119.1. C/H/N analysis: calcd (found) C 40.34 (40.34), H 0.85 (1.05), N 58.81 (59.10) %.

Synthesis of Sodium 4,5-Dicyano-1,2,3-triazolate Monohydrate (2). The synthesis of **2** was undertaken according to modification of the literature procedure for the Li salt[40b] using the following scale: To a solution of **1** (10.5 g, 89.0 mmol) in acetonitrile (100 mL) a slight excess of sodium carbonate (12.4 g, 116.0 mmol) was added. The mixture was stirred for 1 h and placed for 10 min into an ultrasonic bath. The solution was then centrifuged for 20 min (5000 rpm), and the resulting clear supernatant decanted and evaporated to dryness. The white solid obtained was dried under vacuum to yield **2** (11.5, 81%). Single crystals suitable for X-ray diffraction were obtained by allowing isohexane to slowly diffuse into a methanol solution of **2**.

IR (KBr, 25 °C, cm^{-1}) ν = 3757 (w), 3615 (w), 3381 (m), 2729 (w), 2573 (w), 2431 (w), 2251 (vs), 2114 (m), 1696 (w), 1512 (m), 1370 (s), 1290 (m), 1247 (m), 1178 (m), 1013 (w), 641 (m), 534 (m), 479 (m). Raman (200 mW, 25 °C, cm^{-1}) ν = 2260 (100), 1506 (44), 1382 (21), 1292 (16), 1183 (10), 1099 (31), 1086 (6), 1013 (11), 711 (8), 622 (15), 533 (24), 472 (14), 170 (11), 146 (21). ^{13}C NMR, δ/ppm: 114.5 (s, C₄N₅$^-$), 121.6 (s, C₄N₅$^-$). ^{14}N NMR, δ/ppm: 24 (s, $v_{1/2}$ = 760 Hz, N2), −19 (s, $v_{1/2}$ = 806 Hz, N1, N3), −116 (s, $v_{1/2}$ = 656 Hz, N4, N5). ^{15}N NMR, δ/ppm: −113.0 (N4, N5), −20.0 (N1, N3), 21.3 (N2). C/H/N analysis: calcd. (found) C 30.18 (30.30), H 1.27 (1.33), N 44.03 (44.25)%.

Synthesis of Silver 4,5-Dicyano-1,2,3-triazolate (3). Compound **2** (0.795 g, 5.0 mmol) was dissolved in water (15 mL) and reacted under stirring with a solution of silver nitrate (0.850 g, 5.0 mmol) in 10 mL of water. After 2 h stirring, the precipitated product was filtered off, washed with water, dried under vacuum and finally in the oven overnight at 50°C to yield a pale beige solid.

Melting point = 305 °C. $T_{dec.}$ = 386 °C. IR (KBr, 25 °C, cm^{-1}): ν = 2247 (s), 2159 (vw), 2131 (vw), 1520 (vw), 1503 (vw), 1421 (vw), 1408 (vw), 1377 (s), 1293 (w), 1283 (vw), 1242 (vw), 1234 (vw), 1190 (m), 1178 (m), 1113 (vw), 1097 (vw), 1086 (vw), 1029

(m), 710 (vw), 661 (vw), 649 (m), 635 (w), 528 (m), 516 (s), 470 (m). Raman (200 mW, 25 °C, cm^{-1}) ν = 2245 (100), 2194(5), 1522 (63), 1380 (25), 1292 (36), 1175 (17), 1095 (31), 1052 (15), 1030 (15), 708 (17), 662 (24), 518 (18), 475 (21), 166 (23). C/H/N analysis: calcd (found) C 21.26 (21.36), N 31.00 (31.32)%.

Synthesis of Ammonium 4,5-Dicyano-1,2,3-triazolate (4). A solution of ammonium bromide (0.196 g, 2.0 mmol) in methanol (5 mL) was reacted with 0.452 g (2.0 mmol) **3** and stirred for 1 h at room temperature. The yellowish solid precipitate (AgBr) was filtered off, and the remaining solution evaporated to dryness. Recrystallization from methanol/isohexane yielded crystalline material of **4** which was suitable for X-ray diffraction.

Melting with decomposition 194.8 °C. IR (KBr, 25 °C, cm^{-1}) ν = 3292 (m), 3167 (m), 3133 (m), 3014 (s), 2904 (w), 2881 (w), 2814 (w), 2484 (vw), 2393 (vw), 2248 (s), 2194 (vw), 2170 (vw), 1949 (vw), 1780 (vw), 1687 (m), 1473 (s), 1456 (s), 1421 (m), 1388 (m), 1296 (m), 1238 (w), 1189 (w), 1177 (m), 1118 (vw), 1095 (w), 988 (vw), 708 (vw), 658 (w), 640 (m), 522 (m), 480 (w). Raman (200 mW, 25°C, cm^{-1}) ν = 2245 (100), 2198 (7), 1701 (6), 1509 (73), 1492 (13), 1417 (8), 1390 (40), 1297 (26), 1178 (20), 1095 (47), 1015 (20), 715 (13), 659 (20), 523 (33), 481 (14), 470 (12), 223 (14), 163 (21). ^{1}H NMR, δ/ppm: 7.05 (4H, NH$_4^+$); ^{13}C NMR, δ/ppm: 114.4 (s, C$_4$N$_5^-$), 121.5 (s, C$_4$N$_5^-$). ^{14}N NMR, δ/ppm: 21 (s, $v_{1/2}$ = 676 Hz, N2), −12 (s, $v_{1/2}$ = 806 Hz, N1, N3), −112 (s, $v_{1/2}$ = 736 Hz, N4, N5), −359 (s, NH$_4^+$). C/H/N analysis: calcd (found) C 35.30 (35.03), H 2.96 (3.12), N 61.74 (61.11)%. MS (FAB+) NH$_4^+$, calcd 18.0, found 18.3. MS (FAB−) C$_4$N$_5^-$, calcd. 118.1, found 118.0.

Synthesis of Guanidinium 4,5-Dicyano-1,2,3-triazolate (5). A solution of guanidinium chloride (0.192 g, 2.0 mmol) in methanol (5 mL) was reacted with solid **3** (0.452 g, 2.0 mmol), and the reaction mixture was stirred for 1.5 h at room temperature. The white/grey, precipitate (AgCl) was filtered off, and the remaining clear solution was evaporated to dryness yielding a light off-white product (**5**). Recrystallization from methanol/isohexane yielded crystalline material of **5** which was suitable for X-ray diffraction.

Melting point = 135 °C. T$_{dec.}$ = 241 °C. IR (KBr, 25 °C, cm^{-1}) ν = 3494 (s), 3423 (s), 3349 (m), 3250 (m), 3180 (m), 3100 (m), 2478 (vw), 2235 (s), 2182 (w), 2158 (w), 1670 (vs), 1658 (vs), 1386 (s), 1295 (m), 1233 (w), 1184 (m), 1169 (m), 1123 (w), 1092 (w), 1004 (vw), 986 (vw), 765 (w), 717 (w), 655 (vw), 643 (m), 618 (m), 563 (vw), 539 (m), 521 (m) 482 (w), 465 (w). Raman (200 mW, 25 °C, cm^{-1}) ν = 3264 (3), 2238 (100), 2185 (3), 1652 (4), 1563 (6), 1502 (35), 1488 (16), 1416 (3), 1388 (19), 1297 (11), 1170 (8), 1093 (27), 1011 (38), 814 (3), 711 (8), 656 (14), 538 (14) 523 (19), 484 (8), 466 (9), 229 (5), 183 (6), 142 (9). ^{1}H NMR, δ/ppm: 6.87 (s, 6H, C(NH$_2$)$_3^+$). ^{13}C NMR, δ/ppm: 114.4 (s, C$_4$N$_5^-$), 121.5 (s, C$_4$N$_5^-$), 158.4 (s, C(NH$_2$)$_3^+$). ^{14}N NMR, δ/ppm: 23 (s, $v_{1/2}$ = 601 Hz, N2, C$_4$N$_5^-$), −19 (s, $v_{1/2}$ = 818 Hz, N1,N3 C$_4$N$_5^-$), −112 (s, $v_{1/2}$ = 825 Hz, N4, N5 C$_4$N$_5^-$). C/H/N analysis: calcd (found): C 33.71 (33.62), H 3.39 (3.37), N 62.90 (62.59)%. MS (FAB+) CH$_6$N$_3^+$, calcd 60.08, found 60.1. MS (FAB−) C$_4$N$_5^-$, calcd. 118.1, found 118.0.

Synthesis of Aminoguanidinium 4,5-Dicyano-1,2,3-triazolate (6). The reaction was carried out using the same general procedure as described above for the preparation of **5**. Aminoguanidinium bromide (0.31 g, 2.0 mmol) was used instead of guanidinium chloride.

Alternative Synthesis of Aminoguanidinium 4,5-Dicyano-1,2,3-triazolate (6). Analytically pure **6** could be prepared by the portion-wise addition of 0.357 g (3.0 mmol) of **1** to a stirred suspension of aminoguanidinium hydrogencarbonate (0.408 g, 3.0 mmol) in approximately 10 mL of CH$_3$CN at room temperature.

To this, 10 mL of distilled H$_2$O were then added, and the reaction mixture warmed up to 60°C until no further evolution of gas was observed. After the evolution of gas had stopped, the solvent was removed from the reaction mixture under reduced pressure at 40°C, and the residue dried overnight at 60°C in a crystallizing dish in the oven yielding an off-white crystalline solid, which was used for characterization.

Melting point = 108 °C. T$_{dec}$ = 219 °C. IR (KBr, 25°C, cm^{-1}) ν = 3389 (s), 3337 (s), 3268 (s), 3159 (m), 3122 (m), 2923 (w), 2255 (s), 2234 (s), 1681 (s), 1661 (s), 1589 (m), 1387 (m), 1300 (m), 1186 (w), 1171 (w), 1103 (w), 1081 (w), 914 (s), 667 (m), 641 (m), 624 (w), 565 (w), 531 (m), 484 (w). Raman (200 mW, 25°C, cm^{-1}) ν = 3367 (6), 3343 (7), 3280 (6), 2257 (100), 2237 (82), 1665 (6), 1500 (35), 1486 (18), 1390 (23), 1302 (12), 1204 (6), 1172 (9), 1084 (36), 1006 (12), 963 (11), 710 (6), 663 (12), 533 (18), 530 (18), 486 (6), 470 (6), 207 (7), 195 (7), 148 (12). ^{1}H NMR, δ/ppm: 4.67 (s, (2H), H1, H2), 6.72 (s, (2H), H5, H6), 7.24 (s, (2H), H3, H4), 8.54 (s, (1H), H7). ^{13}C NMR, δ/ppm: 113.9 (s, C$_4$N$_5^-$), 121.0 (s, C$_4$N$_5^-$), 158.8 (s, C(NHNH$_2$)(NH$_2$)$_2^+$). ^{14}N NMR, δ/ppm: 25 (s, $v_{1/2}$ = 688 Hz, N2, C$_4$N$_5^-$), −18 (s, $v_{1/2}$ = 636 Hz, N1, N3, C$_4$N$_5^-$), −106 (s, $v_{1/2}$ = 606 Hz, N4, N5, C$_4$N$_5^-$), −322 (s, br, $v_{1/2}$ = 1515 Hz, C(NHNH$_2$)(NH$_2$)$_2^+$). C/H/N analysis: calcd (found) C 31.09 (31.34), H 3.65 (3.95), N 65.26 (65.89)%. MS (FAB+) CH$_7$N$_4^+$, calcd. 75.09, found 75.1. MS (FAB−) C$_4$N$_5^-$, calcd 118.1, found 118.0.

Synthesis of Diaminoguanidinium 4,5-Dicyano-1,2,3-triazolate (7). The reaction was carried out using the same general procedure as described above for the preparation of **5**. Diaminoguanidinium iodide (0.434 g, 2.0 mmol) was used instead of guanidinium chloride.

Melting point = 124 °C. T$_{dec.}$ = 228 °C. IR (KBr, 25 °C, cm^{-1}) ν = 3460 (s), 3374 (m), 3355 (m), 3241 (s), 3090 (s), 2240 (s), 1672 (s), 1501 (w), 1380 (m), 1362 (m), 1322 (w), 1288 (m), 1188 (w), 1171 (s), 1086 (w), 1055 (w), 961 (s), 946 (s), 762 (m), 707 (w), 680 (m), 651 (m), 639 (w), 524 (m), 477(w). Raman (200 mW, 25°C, cm^{-1}) ν = 3358 (5), 3295 (7), 2242 (100), 1636 (4), 1503 (17), 1483 (5), 1383 (11), 1290 (6), 1165 (5), 1088 (10), 1009 (5), 922 (7), 711 (3), 654 (6), 550 (5), 525 (8), 478 (4), 465 (5), 375 (2), 268 (4), 199 (2). ^{1}H NMR, δ/ppm: 4.55 (s, (4H), H1, H4), 7.10 (s, (2H), H5, H6), 8.51 (s, (2H), H7, H8). ^{13}C NMR, δ/ppm: 114.5 (s, C$_4$N$_5^-$), 121.5 (s, C$_4$N$_5^-$), 160.2 (s, C(NHNH$_2$)$_2$(NH$_2$)$^+$). ^{14}N NMR, δ/ppm: 19 (s, $v_{1/2}$ = 739 Hz, N2, C$_4$N$_5^-$), −19 (s, $v_{1/2}$ = 681 Hz, N1, N3, C$_4$N$_5^-$), −111 (s, $v_{1/2}$ = 622 Hz, N4, N5, C$_4$N$_5^-$). C/H/N analysis: calcd (found) C 28.85 (28.36), H 3.87 (3.93), N 67.28 (66.65)%. MS (FAB+) CH$_8$N$_5^+$, calcd 90.1, found 90.1. MS (FAB-) C$_4$N$_5^-$, calcd 118.1, found 118.0.

Synthesis of Triaminoguanidinium 4,5-Dicyano-1,2,3-triazolate (8). A clear solution of triaminoguanidinium bromide (0.370 g, 2.0 mmol) in water/methanol (5/1, 10 mL) was reacted with 0.452 g (2.0 mmol) of solid **3**. The reaction mixture was left stirring for 1.5 h, and the yellowish precipitate (AgBr) was filtered off. The remaining clear solution was evaporated to dryness, and the product dried under vacuum yielding a cream colored solid (**8**). Recrystallization from methanol/isohexane yielded crystals of compound **8** which were suitable for X-ray diffraction.

Melting point = 169°C. T$_{dec.}$ = 227 °C. IR (KBr, cm^{-1}) ν = 3355 (m), 3291 (s), 3209 (s), 3164 (m), 3107 (m), 3027 (m), 2246 (s), 2236 (s), 2121 (vw), 1681 (vs), 1612 (vw), 1566 (vw), 1503 (w), 1447 (vw), 1370 (m), 1349 (s), 1281 (m), 1184 (w), 1158 (w), 1135 (s), 1069 (w), 962 (s), 752 (w), 706 (w), 638 (m), 615 (m), 527 (w), 479 (w). Raman (200 mW, 25°C, cm^{-1}) ν = 3355 (5), 3348 (5), 3294 (6), 2247 (100), 2235 (80), 1681 (3), 1643 (2), 1504 (40), 1484 (4), 1373 (14), 1314 (1), 1283 (12), 1159 (6), 1072

(35), 1007 (6), 885 (6), 709 (5), 650 (8), 629 (4), 529 (8), 523 (6), 479 (6), 474 (6), 408 (4), 245 (3), 230 (3), 152 (5). ^{1}H NMR, δ/ppm: 4.48 (s, (6H), H1−H6), 8.58 (s, (3H), H7−H9). ^{13}C NMR, δ/ppm: 114.5 (s, $C_4N_5^-$), 121.5 (s, $C_4N_5^-$), 159.6 (s, $C(NHNH_2)_3^+$). ^{14}N NMR, δ/ppm: 20 (s, $v_{1/2}$ = 543 Hz, N2, $C_4N_5^-$), −20 (s, $v_{1/2}$ = 526 Hz, N1, N3, $C_4N_5^-$), −119 (s, $v_{1/2}$ = 730 Hz, N4, N5, $C_4N_5^-$). C/H/N analysis: calcd (found) C 26.91 (25.72), H 4.06 (4.15), N 69.03 (68.19) %. MS (FAB+) $CH_9N_6^+$, calcd 105.1, found 105.1. MS (FAB−) $C_4N_5^-$, calcd 118.1, found 118.0.

Results and Discussion

Synthesis and Characterization of 4,5-Dicyano-2*H*-1,2,3-triazole (1), Sodium 4,5-Dicyano-1,2,3-triazolate Hydrate (2), and Silver 4,5-Dicyano-1,2,3-triazolate (3). Compound **1**, 4,5-dicyano-2*H*-1,2,3-triazole was synthesized by the reaction of diaminomaleodinitrile in water with hydrochloric acid (1M) and sodium nitrite at 0 °C following the literature procedure (eq 1).[40b] After sublimation of the crude product, analytically pure **1** was obtained as a white crystalline powder.
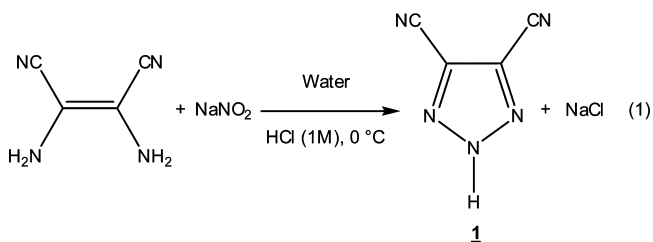
Compound **1** is air stable under ambient conditions and shows no sensitivity towards friction (> 360 N) or impact (> 30 J). The vibrational spectra (IR, Raman) of **1** show the presence of the N−H (3258 cm^{-1} (IR), 3258 cm^{-1} (Raman)) and C≡N (2263 cm^{-1} (IR), 2263 cm^{-1} (Raman)) groups. Other vibrations are difficult to unambiguously assign but suggest the presence of the triazole ring. In the ^{1}H NMR spectra compound **1** showed resonance at 7.63 ppm, which is in the expected N−H range. The ^{13}C NMR spectrum of **1** shows two signals with chemical shifts of 112.6 and 123.1 ppm which correspond to the triazole ring carbon atoms and the exocylic carbon atoms of the nitrile groups. However, since the chemical shifts of both are very similar, an assignment has not been made. Attempts to obtain a ^{14}N NMR spectrum of **1** in d^6-dmso showed only very broad peaks, and therefore a ^{15}N NMR spectrum of a highly concentrated solution of **1** in d^6-dmso was measured. In the ^{15}N NMR spectrum three signals are observed which correspond to the central ring N−H nitrogen atom (−108.6 ppm), the two equivalent ring nitrogen atoms (−39.2 ppm) and the two equivalent nitrile nitrogen atoms (−76.9 ppm). Compound **1** could be sublimed at relatively low temperature (90°C) under vacuum with cooling of the cold finger using dry-ice to yield white, crystalline **1** in good yields. The mass spectrum (DEI+) of **1** was readily obtained showing a peak corresponding to the molecular peak of **1**. Since **1** could be prepared on a multigram scale and also purified using the above mentioned method in significant quantities, salts of the 4,5-dicyano-1,2,3-triazolate anion could be conveniently

prepared by deprotonating compound **1** with Na_2CO_3 to form sodium 4,5-dicyano-1,2,3-triazolate monohydrate (**2**) in good yields (eq 2), which could then be easily converted into the corresponding silver salt (**3**) (eq 3), which was suitable for metathesis reactions with metal-free salts containing nitrogen-rich cations.
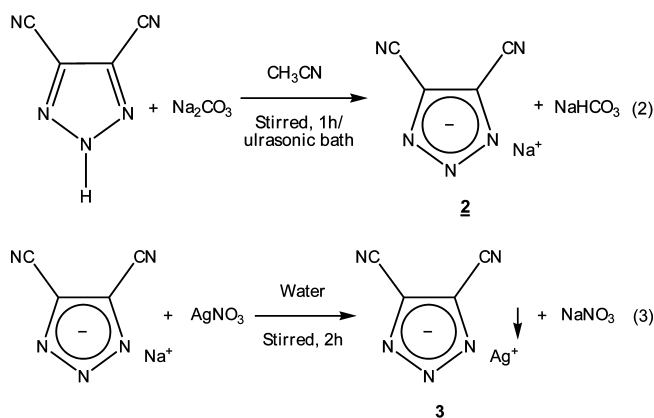
Compounds **2** and **3** were also useful starting materials since neither was shown to be friction (> 360 N) or impact (> 30 J) sensitive. Because of the low solubility of **3** in the organic solvents used, it was only characterized using IR and Raman spectroscopy, as well as elemental analysis and DSC. Compound **2**, however, was characterized using various techniques. The IR and Raman spectra of **2** and **3** show similar features such as the strong nitrile vibration in the Raman spectrum and a similar pattern of peaks in the ring vibration region between 450−1550 cm^{-1}. This characteristic pattern of ring vibrations is also observed for the nitrogen-rich salts **4**−**8**. However, the nitrile stretching vibration appears at slightly different wavenumbers (2263 cm^{-1} (**1**); 2260, 2253 cm^{-1} (**2**), and 2245 cm^{-1} (**3**) (Raman) 2263 cm^{-1} (**1**); 2251 cm^{-1} (**2**), and 2247 cm^{-1} (**3**) (IR)) in the vibrational spectra of compounds **1**− **3**. Notably absent from the IR and Raman spectra of **2** and **3** are the vibrations observed in **1** which were assigned to the N−H group (3258 cm^{-1}), suggesting that deprotonation has occurred. A comparison of the ^{13}C NMR of **1** and **2** shows little change in the positions of signals corresponding to the ring and nitrile carbon atoms following deprotonation. The ^{14}N NMR spectrum of **2** shows the presence of three resonances at 24, −19, and −116 ppm which correspond to the central ring nitrogen atom (N2), the two equivalent ring nitrogen atoms (N1, N3), and the nitrile group nitrogen atoms (N4, N5), respectively. Because of the high solubility of compound **2** in d^6-dmso, it was possible to obtain a ^{15}N NMR spectrum of this compound which showed much sharper resonances than the ^{14}N NMR at 21.3 (N2), −20.0 (N1, N3), and −113.0 ppm. These values show very good agreement with the calculated ^{14}N NMR chemical shifts for the DCT anion in the gas phase at the MPW1PW91/aug-cc-pVDZ level of theory (+21, −20 and −113). A comparison of the ^{15}N NMR spectra of compounds **1** and **2** shows that on deprotonation, the N1, N3 and N4, N5 signals (−20.0, −113.0 ppm in **2**; −39.2, −76.9 ppm in **1**) differ less than the values for the signals corresponding to the N2 nitrogen atom which is

considerably shifted from −108.6 ppm in **1** to 21.3 ppm in **2**. A comparison of the experimentally obtained (d[6]-dmso solution) ^{15}N NMR chemical shifts for **1** (−39.2, −108.6, −76.9 ppm) with the calculated (gas-phase) ^{14}N NMR chemical shifts (−36, −136, −76) at the MPW1PW91/aug-cc-pVDZ level of theory shows satisfactory agreement.

Synthesis and Characterization of Ammonium (4), Guanidinium (5), Aminoguanidinium (6), Diaminoguanidinium (7) and Triaminoguanidinium 4,5-Dicyano-1,2,3-triazolate (8). The synthesis of compounds **4**−**8** can be achieved in a convenient and straightforward route by the simple metathesis reactions of a halide salt of the corresponding nitrogen-rich cation with **3** in organic solvents at room temperature (eq 4). The reactions were carried out in methanol except for the preparation of **8**, where a methanol/water mixture was used because of the poor solubility of triaminoguanidinium bromide in methanol.
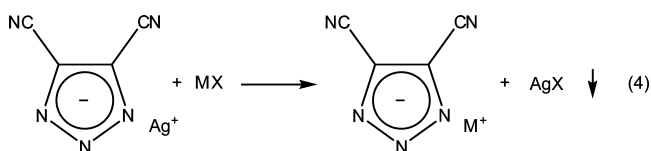
MX = NH$_4$Br, (H$_2$N)$_3$CCl, (H$_2$N)$_2$(H$_2$NNH)CBr, (H$_2$N)(H$_2$NNH)$_2$CCl, (H$_2$NNH)$_3$CBr

The sensitivity tests performed on compounds **4**−**8** showed that they are neither friction (> 360 N) nor impact (> 30 J) sensitive and were insensitive towards electric discharge. On substituting the sodium cation in the monohydrate **2**, for the metal-free cations in **4**−**8**, a large jump in the % nitrogen content (by weight) is observed. The theoretical percent nitrogen values increase from 61.7 % in **4** to 62.9 % in **5**, 65.3 % in **6**, 67.3 % in **7**, and 69.0 % in **8**, which contains the triaminoguandiainium cation.

In the vibrational (IR, Raman) spectra of **4**− **8**, the absorptions and peaks corresponding to the C≡N triple bond were clearly observed, with little variation in the values observed in changing the countercation, but a slight shift from the values observed for the neutral **1** (v(C≡N) = 2263 (IR), 2263 (Ra) cm^{-1} in **1**; 2248 (IR), 2249 (Ra) cm^{-1} in **4**; 2235 (IR), 2238 (Ra) cm^{-1} in **5**; 2255, 2234 (IR), 2257, 2237 (Ra) cm^{-1} in **6**; 2240 (IR), 2242 (Ra) cm^{-1} in **7**; 2246, 2236 (IR), 2247, 2235 (Ra) cm^{-1} in **8**). In addition, the characteristic peak pattern in the Raman spectrum corresponding to vibrations of the 4,5-dicyano-1,2,3-triazolate ring is observed in the spectra for all of the salts of the 4,5-dicyano-1,2,3-triazolate anion reported in this work (**2**−**8**).

For compounds **4**−**8** the ^{1}H NMR spectra were recorded which showed signals corresponding only to the different cations present. Whereas the ammonium salt **4** showed one resonance at 7.05 ppm corresponding to the NH$_4^+$ group, and **5** one resonance at 6.87 ppm corresponding to the C(NH$_2$)$_3^+$ cation, the ^{1}H NMR spectra of compounds **6**−**8** were more complicated as a result of the presence of both NH and NH$_2$ groups in the nitrogen-rich cations. The ^{1}H NMR spectrum of **6** showed four signals which were assigned as follows (atom numbering scheme used is given in Figure 1): δ = 4.67 (H1, H2), δ = 6.72 (H3, H4), δ =
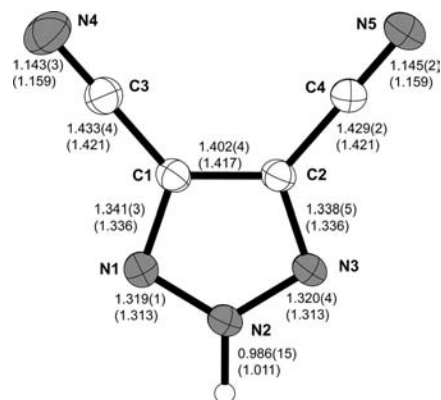
Figure 1. ORTEP representation of the molecular structure of **1** in the solid state determined using single crystal X-ray diffraction. Thermal ellipsoids are shown with 50 % probability. Bond lengths given in parenthesis (in Å) are the calculated (MPW1PW91/aug-cc-pVDZ level of theory) gas-phase values for comparison with the experimentally determined values for the crystalline state.
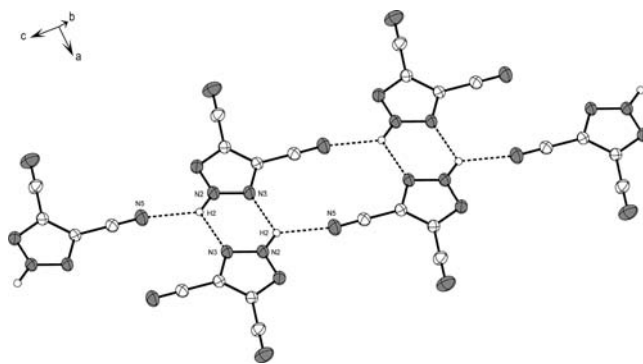
Figure 2. ORTEP representation showing selected intermolecular hydrogen bonds in **1** as determined using single crystal X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.

7.24 (H5, H6), and δ = 8.54 (H7) ppm. In the ^{1}H NMR spectrum of **7** three resonances corresponding to the eight hydrogen atoms in the diaminoguanidinium cation were observed, and the resonances can be assigned as follows: δ = 4.58 (H1, H2, H3, H4), δ = 7.14 (H5, H6), and δ = 8.55 (H7, H8) ppm. Finally, the ^{1}H NMR spectrum of **8** showed only two resonances at 4.48 and 8.58 ppm, corresponding to the three equivalent NH$_2$ and three equivalent NH groups (H7−N9), respectively.

In contrast to the ^{1}H NMR spectra, the ^{13}C NMR spectra of **4**−**8** are all very similar and show relatively little difference in the chemical shifts corresponding to the ring and nitrile groups of the C$_4$N$_5^-$ anion on swapping the cations. For compounds **4**−**8**, in the ^{13}C NMR spectra a signal was observed at 114 ± 1 ppm, and a second at 121 ± 1 ppm. In addition, **5**−**8** showed one additional signal in each ^{13}C NMR spectrum which corresponded to the central carbon atom of the guanidinium cations. The ^{14}N NMR spectra were recorded of **4**−**8** and showed three broad resonances corresponding to the 4,5-dicyano-1,2,3-triazolate anion at 20 ± 5 ppm, −15 ± 5 ppm, and −108 ± 5 ppm. Assignment of these signals was made by calculating the chemical shifts of the 4,5-dicyano-1,2,3-triazolate anion in the gas-phase at the MPW1PW91/aug-cc-pVDZ level of theory. A comparison of the average chemical shifts for **4**−**8** (22, −16 and −110 ppm) which were experimentally

Table 1. Crystal Data and Details of the Structure Determination for **1**, **2**, and **4−8**

parameter	HC$_4$N$_5$ (1)	NaC$_4$N$_5$·H$_2$O (2)	NH$_4$C$_4$N$_5$ (4)	C(NH$_2$)$_3$C$_4$N$_5$ (5)	C(NHNH$_2$)(NH$_2$)$_2$C$_4$N$_5$ (6)	C(NHNH$_2$)$_2$(NH$_2$)C$_4$N$_5$ (7)	C(NHNH$_2$)$_3$C$_4$N$_5$ (8)
formula	C$_4$ H N$_5$	C$_4$H$_2$N$_5$Na$_1$O$_1$	C$_4$N$_6$H$_4$	C$_5$ H$_6$ N$_8$	C$_5$ H$_7$ N$_9$	C$_5$ H$_8$ N$_{10}$	C$_5$ H$_9$ N$_{11}$
F. Wt. (g/mol)	119.10	159.10	136.12	178.18	193.20	208.21	223.23
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$Pnma$	Cc	Pa	$P2_1$	$C2/c$
size	0.06 × 0.05 × 0.06	0.08 × 0.06 × 0.01	0.05 × 0.04 × 0.05	0.06 × 0.05 × 0.03	0.06 × 0.05 × 0.02	0.07 × 0.06 × 0.04	0.05 × 0.04 × 0.04
a / Å	6.0162(6)	3.6767(6)	6.5646(13)	12.6000(11)	7.0921(9)	3.7727(4)	14.0789(14)
b / Å	11.2171(10)	20.469(4)	7.5707(16)	17.1138(15)	7.2893(9)	15.6832(17)	11.5790(11)
c / Å	7.5625(7)	9.6223(13)	13.303(3)	12.0952(9)	8.8671(11)	8.3416(10)	13.5840(14)
α / deg	90.00	90.00	90.0	90.0	90.0	90.0	90.0
β / deg	94.214(8)	97.355(13)	90.0	106.098(7)	105.141(11)	101.797(10)	115.239(10)
γ / deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0
V / Å^3	508.97(8)	718.2(2)	661.1(2)	2505.9(4)	442.48(10)	483.13(9)	2003.1(3)
Z	4	4	4	12	2	2	8
$\rho_{calc.}$ / g/cm^3	1.554	1.470	1.368	1.417	1.450	1.431	1.480
μ / mm^{-1}	0.114	0.181	0.107	0.104	0.108	0.107	0.111
$\lambda_{MoK\alpha}$ α / Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T / K	200	200	200	200	200	200	200
$F(000)$	240	350	304	1104	200	216	928
GooF	1.003	1.019	1.133	1.009	1.055	0.975	0.909
$R_1{}^a$ (obs)	0.0373	0.0376	0.0527	0.0487	0.0342	0.0459	0.0551
$wR_2{}^b$ (all data)	0.0957	0.1080	0.1420	0.1236	0.0879	0.1025	0.1174

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}, P = (F_o^2 - 2F_c^2)/3$.

Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) in 4,5-Dicyano-2H-1,2,3-triazole (**1**), with the 4,5-Dicyano-1,2,3-triazolate Anions in **2** and **4−8** Compared with the Calculated Structural Parameters of the C$_4$N$_5{}^-$ Optimized in C_{2v} Symmetry at the MPW1PW91/aug-cc-pVDZ Level of Theory^a

Parameter (d / Å; $\angle$ / deg)	(1)	(2)	(4)	(5)	(6)	(7)	(8)	calculated
N1−N2	1.319(1)	1.329(1)	1.336(1)	1.340(4)	1.340(5)	1.336(3)	1.342(4)	1.325
N2−N3	1.320(4)	1.329(2)	1.336(1)	1.340(6)	1.334(2)	1.346(6)	1.339(3)	1.325
N3−C2	1.338(5)	1.353(4)	1.349(2)	1.348(4)	1.350(9)	1.359(6)	1.351(4)	1.351
N1−C1	1.341(3)	1.349(2)	1.349(2)	1.340(6)	1.344(7)	1.380(8)	1.350(4)	1.351
C1−C3	1.433(4)	1.423(2)	1.421(2)	1.425(5)	1.421(8)	1.434(4)	1.424(4)	1.417
C2−C4	1.429(2)	1.423(3)	1.421(2)	1.428(7)	1.421(5)	1.450(8)	1.417(3)	1.417
C1−C2	1.402(4)	1.385(4)	1.386(2)	1.380(5)	1.391(2)	1.379(4)	1.383(4)	1.404
C3−N4	1.143(3)	1.140(2)	1.148(2)	1.149(5)	1.139(7)	1.146(4)	1.145(4)	1.164
C4−N5	1.145(2)	1.141(3)	1.148(2)	1.133(6)	1.144(4)	1.163(7)	1.147(3)	1.164
N2−H2	0.986(15)							
N1−N2−N3	116.92(8)	111.77(9)	111.62(7)	110.80(22)	112.18(14)	110.85(20)	111.06(21)	112.17
N2−N3−C2	103.07(8)	106.35(10)	106.4(1)	106.24(15)	105.99(14)	107.71(22)	106.59(18)	106.80
N2−N1−C1	103.13(8)	106.70(9)	106.4(1)	106.73(25)	106.01(14)	106.21(19)	106.73(20)	106.80
N3−C2−C1	108.59(8)	107.72(10)	107.79(11)	107.67(27)	107.78(14)	107.03(21)	107.95(23)	107.12
N1−C1−C2	108.28(8)	107.47(10)	107.79(11)	108.15(24)	108.04(13)	108.20(21)	107.68(20)	107.12
C3−C1−C2	131.05(9)	129.36(11)	128.03(12)	126.51(27)	126.94(15)	128.77(32)	128.77(25)	129.76
C4−C2−C1	130.58(9)	129.98(11)	128.03(12)	128.00(31)	127.02(14)	129.64(23)	129.43(21)	129.76
C1−C3−N4	179.24(11)	179.36(14)	176.66(15)	177.02(41)	176.06(20)	177.72(29)	177.73(29)	
C2−C4−N5	179.67(11)	178.79(13)	176.66(15)	176.19(39)	174.86(18)	178.46(27)	178.29(25)	

^{a} The numbering scheme used is illustrated in Figure 1.

Table 3. Comparison of Selected Hydrogen Bond Lengths (Å) and Angles (deg) between 4,5-Dicyano-1,2,3-triazole (**1**), and the 4,5-Dicyano-1,2,3-triazolate Anions in Salts **4−8** Containing the Nitrogen-Rich Cations^a

| (1)		(4)		(5)		(6)		(7)		(8)	
					d(D−A)/Å						
N2−N5	2.997(2)	N6−N5	3.02(3)	N7−N4	3.24(7)	N8−N5	3.14(2)	N6−N3	2.88(3)	N8−N1	2.91(7)
N2−N3	2.91(1)	N6−N4	3.02(3)	N7−N2	3.05(5)	N6−N4	3.00(2)			N6−N3	2.88(9)
		N6−N1	2.99(2)	N6−N3	2.91(5)	N7−N1	3.02(2)				
		N6−N3	2.99(2)			N6−N2	2.91(2)				
		N6−N2	2.91(2)			N7−N3	3.04(2)				
					$\angle$(D−H−A)/deg						
N2H2N5	135.3(1)	N6H1N4	123.7(6)	N7H7bN4	158.7(3)	N8H8N5	137.1(2)	N6H6aN3	166.1(2)	N8H8N1	149.8(2)
N2H2N3	122.3(1)	N6H1N5	123.7(6)	N7H7aN2	163.0(3)	N6H6aN4	166.7(2)			N6N6N3	156.0(2)
		N6H3N6	170.2(2)	N6H6bN3	158.4(3)	N7H7aN1	162.7(2)				
		N6H4N1	170.2(2)			N6H6bN2	170.0(2)				
		N6H2N2	172.5(2)			N7H7bN3	153.1(2)				

^{a} The numbering scheme used is illustrated in Figure 1 (for the anion without the hydrogen atom H2 located at N2) (D = hydrogen bond donor atom; A = hydrogen bond acceptor atom).

obtained in d^6-dmso solution, with the calculated (gas-phase) ^{14}N NMR chemical shifts (21, −20. −113) at MPW1PW91/

aug-cc-pVDZ level of theory shows very good agreement and were therefore assigned to the N2, N1/N3 and N4/N5
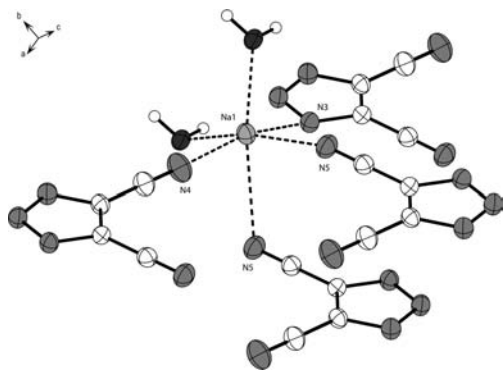
Figure 3. ORTEP representation showing the coordination environment of the sodium cations in **2** as determined using single crystal X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.
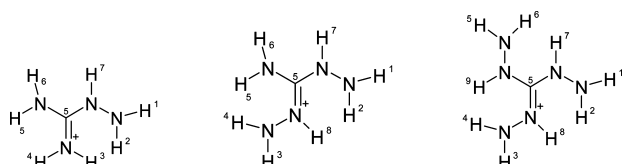
Figure 4. Labeling scheme used for the assignment of the ^{1}H NMR spectra in **6−8**.

atoms respectively (for labelling scheme see Figure 2). It is worthwhile to note that a satisfactory agreement between the experimentally obtained and calculated ^{15}N NMR chemical shifts for the neutral compound **1** was also observed using this method.

X-ray Analyses. The X-ray crystallographic data for compounds **1**, **2**, and **4− 8** were collected on a XCalibur3 CCD diffractometer using graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved with SHELXS-97 and were refined by means of full-matrix least-sqare procedures using SHELXL-97[59] implemeted in the program package WinGX[60] and finally checked using Platon.[61]

Crystallographic data are summarized in Table 1. Selected bond length and angles are available in Table 2, and the labeling of the 4,5-dicyano-1,2,3-triazole frame is given in Figure 2 (see below). All non-hydrogen atoms were refined anisotropically. Further information on the crystal-structure determinations has been deposited with the Cambridge Crystallographic Data Centre[62] as supplementary publication nos. 702141 (**1**), 702142 (**2**), 702143 (**4**), 702144 (**5**), 702145 (**6**), 702146 (**7**), and 702147 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal Structures of 4,5-Dicyano-2H-1,2,3-triazole (1) and Sodium 4,5-Dicyano-1,2,3-triazolate Hydrate (2). 4,5-Dicyano-2H-1,2,3-triazole (**1**) crystallizes in the monoclinic space group $P2_1/c$ with four molecular moieties in the unit cell and a calculated density of 1.554 g cm^{-3}, which is low to be considered as being a possible useful

energetic material, and a cell volume of $V = 508.97(8)$ Å^3. In the neutral compound **1**, the C1−N1 and C2−N3 bond lengths were found to be much shorter (1.341(3) and 1.338(5) Å) than the average value for a C−N single bond (1.47 Å)[41] but significantly longer than a C═N double bond (1.22 Å), suggesting that some multiple bond character is present.[41] A similar trend is observed for the C1−C2 bond in **1** (1.402(4) Å), which is significantly shorter than a C−C single (1.54 Å) but longer than a C═C double bond (1.33 Å), [41] and the N1−N2 and N2−N3 bonds (1.319(5) and 1.320(4) Å, respectively), which are also significantly shorter than a N−N single bond (1.48 Å) but considerably longer than a N═N double bond (1.20 Å).[41] These findings support the presence of a delocalized π-system in the five-membered ring of compound **1**. The triazole ring is planar with the cyanogen groups and the hydrogen atom lying in the plane of the ring (Figure 2). The angles and bond lengths are therefore in good agreement with the expected values and also those calculated by Johansson.[40b]

The packing of the structure of **1** is characterized by two significant hydrogen bonds which are located between the N2 and N3 (donor and acceptor) and the N2 and N5 nitrogen atoms. Since we have only one donor center, we see a bifurcated hydrogen bonding scheme starting from N2 as the donor atom. The two hydrogen bonds show a distance of less than 3 Å (2.997(2) and 2.91(1) Å) from the donor to the acceptor atom. Both hydrogen bonds are within the sum of van der Waals radii for two nitrogen atoms ($r_{A(N)} + r_{D(N)} = 3.20$ Å) but are more of an electrostatic rather than a strongly directed nature because of the bond angles of 135.3(1) and 122.3(1)°, respectively (Table 3, Figure 3). The hydrogen bonding results in ordered rows in the structure formed by opposite lying HDCT moieties (Figure 3).

The sodium 4,5-dicyano-1,2,3-triazolate hydrate (**2**) crystallizes in the monoclinic space group $P2_1/c$ with four molecular moieties in the unit cell and a calculated density of 1.470 g cm^{-3} and a cell volume of $V = 718.2(2)$ Å^3. The 4,5-dicyano-1,2,3-triazolate anion in **2** shows a similar structure to that observed for the neutral compound **1**, the predominate difference being the absence of an N−H bond in **2** as a result of deprotonation. The C1−C2 bond length in **2** (1.385(4) Å) is shorter than the corresponding C1−C2 bond in **1** (1.402(4) Å), whereas the N1−N2 and N2−N3 bonds in the C$_4$N$_5$$^-$ anion in **2** are found to be essentially the same (1.329(1), 1.329(2) Å) as those observed in **1** (1.319(1), 1.320(4) Å). The C1−N1 and C2−N3 bonds in **2** (1.349(2), 1.353(4) Å, respectively) are slightly longer than the corresponding bond lengths in **1** (1.340(3) and 1.338(6) Å, respectively). There is some variation between the angles observed in **1** and **2**, namely the N1−N2−N3 angle is larger in **1** (116.92(8)°) than in **2** (111.77(9)°), whereas the N2−N3−C2 and N2−N1−C1 angles are smaller in **1** (103.07(8)°, 103.13(8)°), than in **2** (106.35(10) and 106.70(9)°).

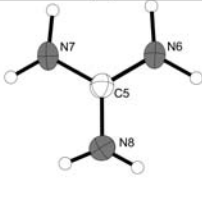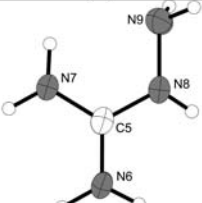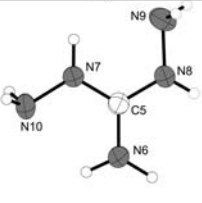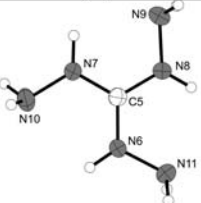(59) Sheldrick, G. M. *Shelxl-97*; University of Göttingen: Göttingen, Germany, 1994.
(60) Farrugia, L. J. *WinGX, J. Appl. Crystallogr.* **1999**, *32*, 837−838.
(61) Speck, A. L. *Platon*; Utrecht University: Utrecht, The Netherlands, 1999.

(62) Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center (CCDC). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: int.code (1223)336-033; E-mail for inquiry: filesrv@ccdc.cam.ac.uk; E-mail for deposition: deposit@ccdc.cam.ac.uk).

Table 4. Comparison of Selected Bond Length (Å) and Angles (deg) of the Nitrogen-Rich Guanidinium Cations in the 4,5-Dicyano-1,2,3-triazolate Salts **5−8**

Compound	(5)	(6)	(7)	(8)
d(C5–N8) / Å	1.34(5)	1.34(1)	1.35(4)	1.38(8)
d(C5–N7) / Å	1.31(6)	1.32(1)	1.33(3)	1.30(7)
d(C5–N6) / Å	1.33(6)	1.32(4)	1.34(8)	1.34(6)
d(N8–N9) / Å	--	1.41(4)	1.44(9)	1.38(8)
d(N7–N10) / Å	--	--	1.41(4)	1.41(8)
d(N6–N11) / Å	--	--	--	1.41(6)
∠(N7–C5–N8)/°	119.7(3)	118.8(1)	120.1(2)	115.4(5)
∠(N6–C5–N7)/°	120.7(3)	121.3(1)	121.0(2)	124.3(4)
∠(N8–C5–N6)/°	119.6(3)	120.0(1)	118.9(2)	120.3(5)
∠(C5–N8–N9)/°	--	118.6(1)	118.0(2)	115.5(5)
∠(C5–N7–N10)/°	--	--	117.5(2)	113.1(4)
∠(C5–N6–N11)/°	--	--	--	121.5(4)
∠(N9-N8-C5-N7)/°	--	4.8(2)	0.4(3)	2.9(8)
∠(N10-N7-C5-N6)/°	--	--	0.4(3)	5.2(8)
∠(N11-N6-C5-N8)/°	--	--	--	5.2(8)
∠(C5-N8-N7-N6)/°	0.0(3)	1.1(1)	0.4(2)	1.3(4)

The angles and bond lengths observed show no unexpected values and are in good agreement with the calculated values published by Johansson.[40b] The density of **2** is still very low (1.470 g cm^{-3}) and is lower than the density of the neutral compound **1**. The sodium cation shows a distorted octahedral environment, which is made up of the coordination of four $C_4N_5^-$ anions and two water molecules. Surprisingly, the interactions between the sodium cation and triazolate anion involve predominantly the nitrile nitrogen atoms (three contacts) and not the ring nitrogen atoms (one contact). The coordination sphere of the sodium cation in **2** is shown in Figure 4. Since this report is primarily concerned with metal-free C/H/N compounds and **2** was primarily of interest as a starting material for the preparation of **3**, the structure of **2** will not be discussed here in more detail.

Molecular Structures of Ammonium (4), Guanidinium (5), Aminoguanidinium (6), Diaminoguanidinium (7), and Triaminoguanidinium (8) 4,5-Dicyano-1,2,3-triazolate. The structures of compounds **4−8** in the crystalline state showed the presence of the 4,5-dicyano-1,2,3-triazolate anion in addition to the metal-free cation. A comparison of the structural parameters of the metal-free cations observed in **5− 8** with those of other guanidinium and related aminoguanidinium salts previously described in the literature[42] showed that no significant differences were observed in salts **5−8**.[42] A summary of selected structural parameters
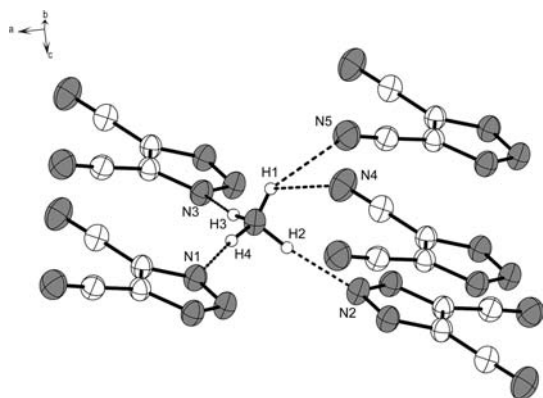
of the cations in **5−8** is given in Table 4. In addition, the structural parameters of the 4,5-dicyano-1,2,3-triazolate anion are summarized in Table 3 and show no significant differences in comparison with the structural parameters of the $C_4N_5^-$ anion described in **2**. Therefore, the structures of the $C_4N_5^-$ anions in **4−8** are not discussed here in more detail.

The calculated densities of the compounds are all in the same range, with the density for **4** being the lowest at 1.368 g cm^{-3} and 1.480 g cm^{-3} being the highest for **8**. If we only compare the guanidinium salts, we see less variation, with the density of **5** being the lowest at 1.417 g cm^{-3} of the four guanidinium compounds and **8** being the highest at 1.480 g cm^{-3}. Unfortunately, the densities are all low, in contrast to the high densities required for energetic materials.
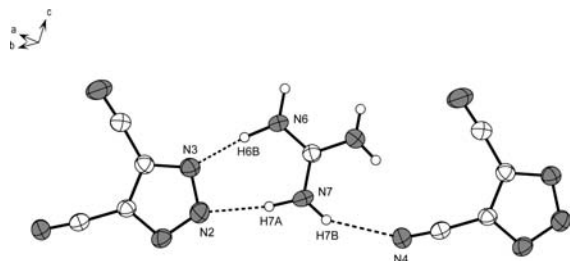
Compound **4** crystallizes in the orthorhombic space group *Pnma* with 4 molecular moieties in the unit cell, a density of 1.368 g cm^{-3} and a unit cell volume of $V = 661.1(2)$ Å^3. Because of the relatively high symmetry of the orthorhombic space group, we observe a very ordered structure. In the unit cell of **4**, the NH_4^+ cations are located between columns of 4,5-dicyano-1,2,3-triazolate anions, which are located as pairs with the nitrile groups pointing towards each other. In addition, the five-membered rings of the 4,5-dicyano-1,2,3-triazolate anions do not lie in one plane but are staggered

Figure 5. ORTEP representation showing the unit cell of **4** along the *a*-axis, as determined using single crystal X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.
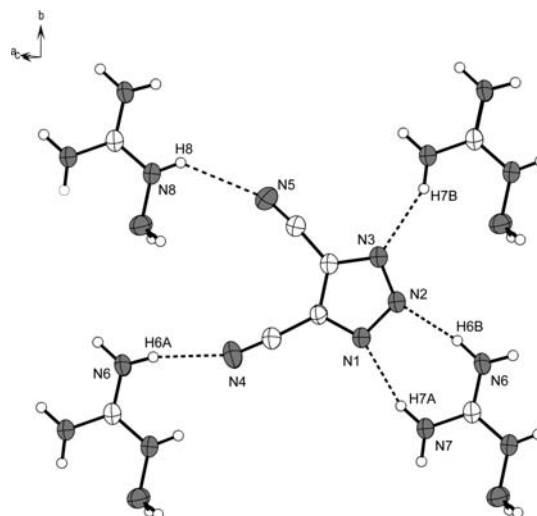

Figure 6. ORTEP representation showing selected hydrogen bonds between the NH_4^+ cation and $C_4N_5^-$ anion in **4**, as determined using X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.
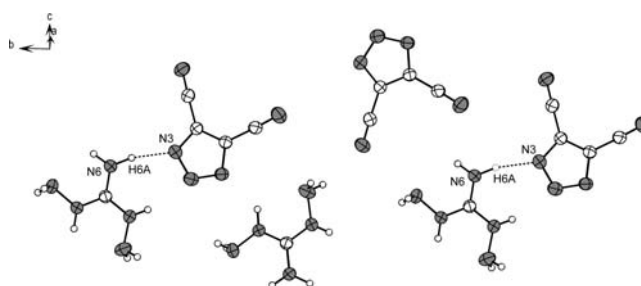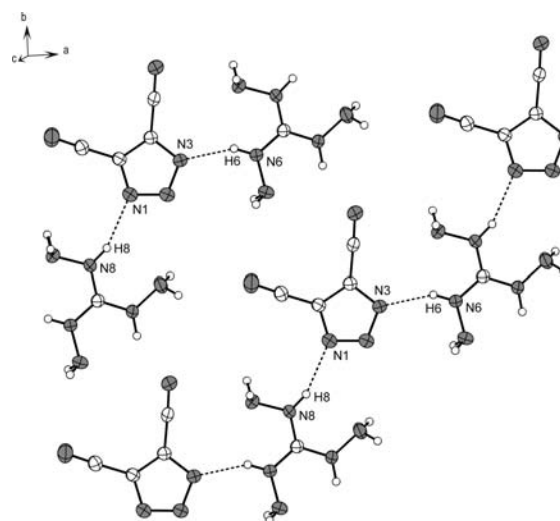

Figure 7. ORTEP representation showing selected hydrogen bonds between the guanidinium cation and $C_4N_5^-$ anion in **5**, as determined using X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.

with respect to one another. Furthermore, each row of the $C_4N_5^-$ anions present in the columns is composed of a stack of $C_4N_5^-$ anions from different layers (Figure 5).

Figure 8. ORTEP representation showing selected hydrogen bonds between the aminoguanidinium cation and $C_4N_5^-$ anion in **6**, as determined using X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.

Figure 9. ORTEP representation showing selected hydrogen bonds between the diaminoguanidinium cation and $C_4N_5^-$ anion in **7**, as determined using X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.

Figure 10. ORTEP representation showing selected hydrogen bonds between the triaminoguanidinium cation and $C_4N_5^-$ anion in **8**, as determined using X-ray diffraction. Thermal ellipsoids are shown with 50 % probability.

Each ammonium cation in **4** forms five significant hydrogen bonds with both the ring and nitrile nitrogen atoms of the surrounding 4,5-dicyano-1,2,3-triazolate anions. (Figure 6) Three of the hydrogen bonds observed involve the triazole ring nitrogen atoms (N1, N2, and N3), whereas the other occur with the two nitrogen atoms in the exocyclic

Table 5. Computational Results (MP2/aug-cc-pVDZ)

compound	formula	p.g	$-E$/a.u.	zpe/kcal mol^{-1}	NIMAG
ammonium	NH_4^+	T_d	56.739780	31.2	0
guanidinium	$C(NH_2)_3^+$	D_{3h}	205.218050	55.3	0
amino-guanidinium	$C(NH-NH_2)(NH_2)_2^+$	C_1	260.403398	66.2	0
diamino-guanidinium	$C(NH-NH_2)_2(NH_2)^+$	C_1	315.588401	77.5	0
triamino-guanidinium	$C(NH-NH_2)_3^+$	C_3	370.773187	100.8	0
dicyanotriazolate	$N_3C_2(CN)_2^-$	C_{2v}	425.137114	26.9	0
4,5-dicyano-2H-triazole	$HN_3C_2(CN)_2$	C_{2v}	425.633873	36.6	0
carbonmonoxide	CO	$C_{\infty v}$	113.054970	3.0	0
water	H_2O	C_{2v}	76.260910	13.4	0
dihydrogen	H_2	$D_{\infty h}$	1.156216	6.4	0
dinitrogen	N_2	$D_{\infty h}$	109.280650	3.1	0
carbondioxide	CO_2	$D_{\infty h}$	188.169700	7.1	0
dioxygen	O_2	$D_{\infty h}$	150.004290	2.0	0

nitrile groups (N4 and N5). However, the donor-acceptor distances are essentially the same. The donor-acceptor distances in the stronger hydrogen bonds involving the ring nitrogen atoms are just under 3.0 Å (2.99(2) Å, 2.91(2) Å) and are directed with D−H---A angles of 170.2(2) ° and 172.5(2)°. The slightly longer (3.02(3) Å) donor-acceptor distances in the hydrogen bonds between the ammonium cation and the nitrogen atoms of the exocyclic nitrile group of the $C_4N_5^-$ anion are more of an electrostatic nature with a bent D−H---A angle of 123.7(6)°. The hydrogen bonding towards the nitrile group shows a bifurcated character, which explains the electrostatic nature of the bonding, as well as the comparably small D−H---A angle of 123.7(6)°. The hydrogen bonds formed form a three dimensional network. The selected important hydrogen bonds discussed above are illustrated in Figure 6 and summarized in Table 3.

The cation used in the $C_4N_5^-$ salts was then changed from the tetrahedral NH_4^+ to the planar guanidinium cation. Guanidinium 4,5-dicyano-1,2,3-triazolate (**5**) crystallizes in the monoclinic space group Cc with 12 molecular moieties per unit cell, a calculated density of 1.417 g cm^{-3}, and a unit cell volume of $V = 2505.9(4)$ Å^3. The structure of **5** is strongly influenced by the formation of the hydrogen bonds between the guanidinium cation and the $C_4N_5^-$ anion. Three different hydrogen bonds form infinite rows which are packed in a co-planar manner. In **5**, one guanidinium cation forms three hydrogen bonds to two 4,5-dicyano1,2,3-triazolate anions which are at either side of the guanidinium cation within a row. However, only two of these bonds are below the sum of van der Waals radii for N−N donor-acceptor hydrogen bonds at 2.91(5) and 3.05(5) Å, respectively. The third hydrogen bond shows a donor acceptor distance of 3.237(7) Å which is longer than the sum of van der Waals radii ($r_{A(N)} + r_{D(N)} = 3.20$ Å).[43] All of these bonds are of a directed than only an electrostatic nature with D−H---A angles between 158° and 166° (Figure 7). No unexpected structural parameters were observed for the guanidinium cation (Table 4).

On introducing the aminoguanidinium cation instead of the guanidinium cation, the percentage nitrogen content by weight of **6** was increased relative to **5**; however, the density of **6** remained low (1.450 g cm^{-3}). Aminoguanidinium 4,5-dicyano-1,2,3-triazolate (**6**) crystallizes in the monoclinic space group Pa with two molecular moieties per unit cell, a calculated density of 1.450 g cm^{-3}, and a unit cell volume

of $V = 442.48(10)$ Å^3. The structure of **6** is relatively simple and consists of layers. Within these co-planar layers, four aminoguanidinium cations surround one 4,5-dicyano-1,2,3-triazolate anion and form five hydrogen bonds to each anion. Four of the hydrogen bonds shown in Figure 8 are within the range of the sum of the van der Waals radii ($r_{A(N)} + r_{D(N)} = 3.20$ Å),[43] and the D−H---A angles between are found in the range 152−170°. They are therefore again more of a directed rather than only of an electrostatic nature. However, the N8−H4---N5 hydrogen bond is relatively long (3.14(2) Å) and has an angle of only 137.1(2)°, which suggests that it should only be considered a very weak hydrogen bond. A list of selected hydrogen bonds found in **6**, is given in Table 3. Again, in **6**, the structural parameters for both the aminoguanidnium cation and 4,5-dicyano-1,2,3-triazolate anion are in good agreement with previously published structures,[40b,c] and the structures of compounds **2**, **4**, **5**, **7**, and **8** given in this work, respectively (Table 2), and therefore are not discussed here in more detail.

On addition of a further amino group to the cation, the diaminoguanidinium salt of the 4,5-dicyano-1,2,3-triazolate anion (**7**) could be prepared. Diaminoguanidinium 4,5-dicyano-1,2,3-triazolate (**7**) crystallizes in the monoclinic space group $P2_1$ with 2 molecular moieties per unit cell, a calculated density of 1.431 g cm^{-3}, and a unit cell volume of 483.13(9) Å^3. The calculated density of **7** (1.431 g cm^{-3}) is lower than that found for **6** (1.450 g cm^{-3}) but higher than that found for **5** (1.417 g cm^{-3}). As was observed in the structure of **6**, the structure of **7** is also built up of layers containing the diaminoguanidinium cations and 4,5-dicyano-1,2,3-triazolate anions. (Figure 9) In contrast to **6**, however, only one significant hydrogen bond was observed between the NH_2 group of the diaminoguanidinium cation and one ring nitrogen atom of a neighbouring $C_4N_5^-$ anion (Table 3). This hydrogen bond is relatively strong with a donor-acceptor distance of 2.88(3) Å and a N−H---N angle of 166.1(2)°.

The highest calculated density for the metal-free salts containing the 4,5-dicyano-1,2,3-triazolate anion discussed in this work was observed for compound **8**, which has a calculated density of 1.480 g cm^{-3}. Triaminoguanidinium 4,5-dicyano-1,2,3-triazolate (**8**) crystallizes in the monoclinic space group $C2/c$ with eight molecular moieties per unit cell, a calculated density of 1.480 g cm^{-3}, and a unit cell volume of $V = 2003.1(3)$ Å^3. As was observed for **6** and **7**, compound **8** also features a layer structure in the unit cell. The layers are again ordered in a co-planar fashion. Two strong hydrogen bonds are observed in the structure of **8** between two of the NH groups two triaminogiuanidinium cations and the N1 and N3 atoms of the nitrogen ring of one 4,5-dicyano-1,2,3-triazolate anions. Both hydrogen bonds show similar distances with 2.91(7) and 2.88(9) Å and non-linear angles of 149.8(2)° and 156.0(2)° (Table 3). One showing the corresponding hydrogen bonds is shown in Figure 10.

Energetic Properties of 1 and 5−8. All calculations were carried out using the program package G03W.[44] The structure and frequency calculations were performed at the electron

Table 6. Lattice Energies, Lattice Enthalpies, Detonation Parameters, Energies, and Enthalpies of Formation for Compounds **1** and **5−8**

		(1)	(5)	(6)	(7)	(8)	8-AN $(0.2-0.8)^a$
V_M / nm^3		0.127	0.209	0.221	0.242	0.250	
U_L / kJ mol^{-1}			499.1	491.8	480.3	476.2	
ΔH_L / kJ mol^{-1}		79.3 (ΔH_{sub})	504.1	496.8	485.3	481.2	
$\Delta_f H°_{298}(s)$ / kJ mol^{-1}		+473.1	+398.3	+51β.4	+631.1	+795.0	
$\Delta_f U°_{298}$ / kJ mol^{-1}		+480.3	+415.6	+530.2	+653.4	+819.8	
M / g mol^{-1}		119.1	178.2	193.2	208.2	223.2	
$\Delta_f U°_{298}$ / J g^{-1}		+4032.7	+2332.2	+2744.3	+3138.3	+3672.9	
Oxygen balance	Ω / %	−114.2	−116.8	−111.8	−107.6	−103.9	−4.8
Heat of detonation / kJ kg^{-1}	Q_v	−4154.0	−2877.5	−3330.2	−3756.7	−4321.8	−3906.7
detonation temperature	$T_{ex.}$ / K	3318	2292	2514	2710	2958	2971
detonation pressure	P / kbar	143	130	159	171	210	247
detonation velocity	D / m s^{-1}	6377	6466	7054	7307	7919	8118
volume of detonation gases	V_0 / L kg^{-1}	519	680	710	738	759	970

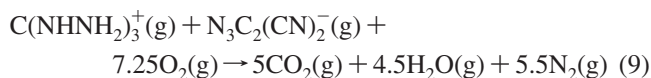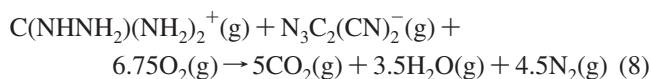^{a} Mixture of **8** (20%) and ammonium nitrate (80%), density = 1.672 g cm^{-3}.
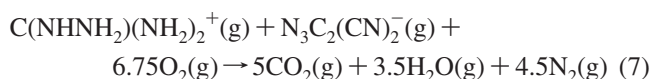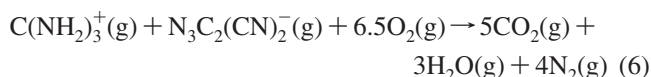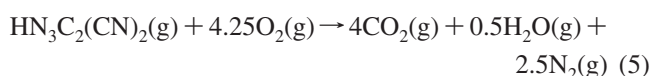
Table 7. Calculated Reaction Energies and Enthalpies for Equations 5−9

equation	$\Delta E^{el.}$/ kJ mol^{-1}	$\Delta_{rxn}H$ / kJ mol^{-1}	$\Delta_{comb}H$ / kJ mol^{-1}
5	−2253.2	−2248.1	−2168.8
6	−3596.6	−3596.3	−3092.2
7	−3817.9	−3822.0	−3325.2
8	−4040.2	−4052.1	−3566.8
9	−4263.0	−4332.8	−3851.6

correlated Møller-Plesset (MP) level of theory, truncated at second order (MP2).[45] For all H, C, N, and O atoms, an augmented correlation consistent polarized double-zeta basis set was used (aug-cc-pVDZ).[46] The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.02).[47] The computational results are summarized in Table 5.

For compounds **5−8** the lattice energies and lattice enthalpies were calculated according the Jenkins equations and are summarized in Table 6.[48−51] For compound **1** the enthalpy of sublimation was estimated according to the formula: ΔH_{sub} [J mol^{-1}] = 188T_m [K].

With the values given in Table 5 the $\Delta E^{el.}$ for eqs 5−9 were calculated and are summarized in Table 7.

$$HN_3C_2(CN)_2(g) + 4.25O_2(g) \rightarrow 4CO_2(g) + 0.5H_2O(g) + 2.5N_2(g) \quad (5)$$

$$C(NH_2)_3^+(g) + N_3C_2(CN)_2^-(g) + 6.5O_2(g) \rightarrow 5CO_2(g) + 3H_2O(g) + 4N_2(g) \quad (6)$$

$$C(NHNH_2)(NH_2)_2^+(g) + N_3C_2(CN)_2^-(g) + 6.75O_2(g) \rightarrow 5CO_2(g) + 3.5H_2O(g) + 4.5N_2(g) \quad (7)$$

$$C(NHNH_2)(NH_2)_2^+(g) + N_3C_2(CN)_2^-(g) + 6.75O_2(g) \rightarrow 5CO_2(g) + 3.5H_2O(g) + 4.5N_2(g) \quad (8)$$

$$C(NHNH_2)_3^+(g) + N_3C_2(CN)_2^-(g) + 7.25O_2(g) \rightarrow 5CO_2(g) + 4.5H_2O(g) + 5.5N_2(g) \quad (9)$$

The $\Delta E^{el.}$ values for eqs 5−9 (Table 7) were converted into the gas phase reaction enthalpy ($\Delta_{rxn}H$) after correction for the work term ($p\Delta V = \sum\nu_i RT$), the vibrational correction ($\Delta_{vib}U = \sum\nu_i(\text{zpe})_i$), the translational ($\Delta_{trans}U = \sum\nu_i(1.5)RT$), and rotational term ($\Delta_{rot}U = \sum\nu_i(F_i^{rot}/2)RT$).[52] With the help of the calculated lattice enthalpies (Table 6) the $\Delta_{rxn}H$ values

were now converted into combustion enthalpies $\Delta_{comb}H$ (Table 6).

With the known enthalpies of formation of carbon dioxide ($\Delta_f H°_{298}(CO_{2(g)}) = -393.7$ kJ mol^{-1})[53] and water ($\Delta_f H°_{298}(H_2O_{(g)}) = -241.8$ kJ mol^{-1})[53] the enthalpy of formation of solid compounds **1** and **5−8** can now be calculated (Table 6). The energies of formation ($\Delta_f U°_{298}$) can easily be obtained from the above calculated enthalpies of formation according to the following equation, with Δn being the change of moles of the gaseous components:[54]

$$\Delta_f U°_{298} = \Delta_f H°_{298} - \Delta nRT$$

The detonation parameters of compounds **1** and **5−8** were calculated using the EXPLO5 computer program.[47] The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker−Kistiakowsky−Wilson equation of state (BKW EOS) for gaseous detonation products and the Cowan−Fickett equation of state for solid carbon.[55−58] The calculation of the equilibrium composition of the detonation products is done by applying a modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations and X_i being the mol fraction of i-th gaseous product, k_i is the molar co-volume of the i-th gaseous product:[55−58]

$$pV/RT = 1 + xe^{\beta x} \qquad x = (\kappa\sum X_i k_i)/[V(T + \theta)]^{\alpha}$$
$$\alpha = 0.5, \quad \beta = 0.176, \quad \kappa = 14.71, \quad \theta = 6620$$

The detonation parameters of compounds **1** and **5−8** calculated with the EXPLO5 program using the experimentally determined densities (see Table 1) are summarized in Table 6.

The velocities of detonation and also the detonation pressures and detonation temperatures for compounds **1** and **5−7** are low compared to nitrogen rich salts of tetrazoles and triazoles (e.g. TAG AtNO2 or TAG DN). Compound **8** shows, despite its low density, the best detonation values of the prepared compounds with a VOD of over 8000 m s^{-1}, a detonation temperature of close to 3000 °K, and a detonation pressure of 210 kbar. These values are not as high as those for known secondary explosives like TNT or RDX, but lie within the range of other triaminoguanidinium salts. This

makes compound 8 the only potentially interesting compound for the further investigation for use as an energetic material.

Conclusions

From the experimental and theoretical study presented in this contribution the following conclusions can be drawn:

(i) 4,5-Dicyano-2*H*-1,2,3-triazole was prepared according to the literature in good yield and converted into various salts containing the 4,5-dicyano-1,2,3-triazolate anion.

(ii) Various salts containing the 4,5-dicyano-1,2,3-triazolate anion (Na^+, Ag^+, NH_4^+, guanidinium, amionoguanidinium, diaminoguanidinium, triaminoguanidinium) were synthesized and spectroscopically characterized for the first time.

(iii) The solid state structures of free 4,5-dicyano-2*H*-1,2,3-triazole, and six salts containing the 4,5-dicyano-1,2,3-triazolate anion (Na^+, NH_4^+, guanidinium, amionoguanidinium, diaminoguanidinium, triaminoguanidinium) were determined using single crystal X-ray diffraction.

(iv) The detonation parameters of the energetically most promising guanidinium salts (guanidinium, amionoguanidinium, diaminoguanidinium, triaminoguanidinium) were calculated, and the performance was predicted to increase from the guanidinium to the triaminoguanidinium salt.

(v) Because of the limited detonation abilities of compounds **1**, **5**, **6**, and **7**, relating the slow velocity of detonation and the low detonation pressure, the only compound of potential use as energetic material is compound **8** with a comparable VOD and detonation temperature to other triaminoguanidinium compounds.

(vi) To the best of our knowledge, compounds **2** and **4−8** are the first structurally characterized salts containing the binary 4,5-dicyano-1,2,3-triazolate ($C_4N_5^-$) anion to be reported.

Note Added in Proof: In addition to a single crystal structure of compound **1** we established by powder diffraction that the bulk material of **1** consisted exclusively of the monoclinic $P2_1/c$ phase, indicating that only the 2*H* isomer was formed.

Supporting Information Available: X-ray crystallographic files for HC_4N_5 (**1**), $Na[C_4N_5]\cdot H_2O$ (**2**), $[NH_4][C_4N_5]$ (**4**), $[(H_2N)_3C][C_4N_5]$ (**5**), $[(H_2N)_2(H_2NHN)C][C_4N_5]$ (**6**), $[(H_2N)(H_2NHN)_2C][C_4N_5]$ (**7**), $[(H_2NHN)_3C][C_4N_5]$ (**8**) are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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