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Energetic Bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydro- and dichloroborates and Bis(5-nitro-2*H*-tetrazolyl)-, Bis(5-(trinitromethyl)-2*H*-tetrazolyl)-, and Bis(5-(fluorodinitromethyl)-2*H*-tetrazolyl)dihydroborate

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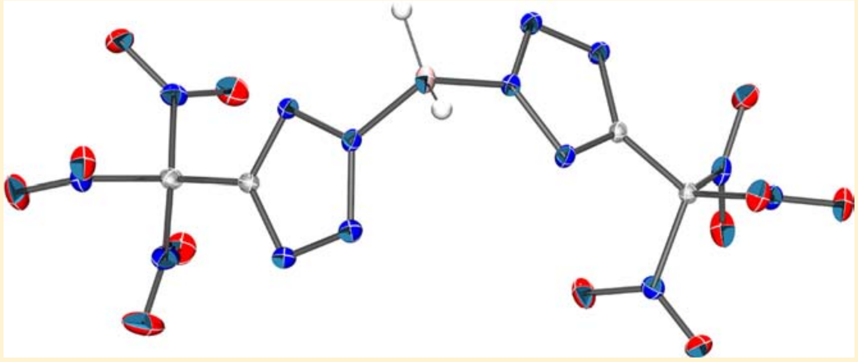
Supporting Information



ABSTRACT: Salts of bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydro- and dichloroborate and bis(5-nitro-2*H*-tetrazolyl)-, bis(5-trinitromethyl-2*H*-tetrazolyl)-, and bis(5-fluorodinitromethyl-2*H*-tetrazolyl)dihydroborate anions have been synthesized by the treatment of hydroborates or chloroborates with the corresponding nitroazoles or nitroazolates, respectively. Alkali-metal salts of these dihydroborates are energetic and can be shock-sensitive, while salts with larger organic cations, such as NMe_4^+, PPh_4^+, or $(Ph_3P)_2N^+$, are less sensitive. Poly(nitroazolyl)borates are promising candidates for a new class of environmentally benign energetic materials and high-oxygen carriers.

INTRODUCTION

The development of environmentally benign, nontoxic "green" energetic materials has received a great deal of attention in recent years.[1] 1,2,4-Triazoles and tetrazoles are readily accessible nitrogen-rich, energetic compounds whose usefulness as energetic materials can be further increased by the introduction of nitro functionalities. While poly(azolyl)borates derived from pyrazoles[2−21] and triazoles[22,23] are commonly used ligands in coordination and organometallic and bioinorganic chemistry, the chemistry of tetrazolylborates is much less developed. Although a series of tetrazolyldihydroborates such as bis(5-*H*-tetrazolyl)dihydroborate,[24−28] bis(5-aminotetrazolyl)dihydroborate,[29] bis(1-methyl-5-thiotetrazolyl)dihydroborate,[30] and tris(tetrazolyl)hydroborate[31] have been reported, these compounds did not contain the necessary oxidizing substituents for rendering them highly energetic materials. These shortcomings can be overcome by the introduction of nitro groups. Poly(dinitrotriazolyl)- and poly(nitrotetrazolyl)borates are expected to have high potential for green energetic materials applications because of their high nitrogen and oxygen contents. However, to the best of our knowledge, the syntheses and properties of polyazolylborates with nitro-group-containing azoles have not been explored so far.

EXPERIMENTAL SECTION

Caution! *Most compounds of this study are energetic materials that can explode under certain conditions (e.g., elevated temperatures, impact, friction, or electric discharge). Although no difficulties were encountered during the course of this work, appropriate safety precautions such as the use of shields or barricades in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves and suits made from leather and/or Kevlar) should be taken all of the time when handling these materials.* ***Ignoring safety precautions may lead to serious injuries!***

Materials and Apparatus. All reactions were carried out in Pyrex glass ampules that were closed by Teflon valves (Kontes or J. Young). Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glovebox. NMR spectra were recorded at 298 K on a Bruker AMX500 or a Varian VNMRS-600s spectrometer using a $(CD_3)_2CO$ or a CD_3CN solution in standard 5 mm glass tubes. Chemical shifts are given relative to neat tetramethylsilane (^1H and ^{13}C), $BF_3{\cdot}Et_2O$

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(^{11}B), neat CH_3NO_2 (^{14}N), $CFCl_3$ (^{19}F), or 85% H_3PO_4 (^{31}P). Raman spectra were recorded at ambient temperatures in Pyrex glass tubes in the range of 4000−80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrometer using a Nd:YAG laser at 1064 nm. IR spectra were recorded in the range 4000−400 cm^{-1} on a Midac, an M Series, or a Bruker Optics Alpha Fourier transform infrared spectrometer using KBr pellets. The pellets were prepared very carefully using an Econo mini-press (Barnes Engineering Co.). Differential thermal analysis (DTA) curves were recorded with a purge of dry nitrogen gas on an OZM Research DTA552-Ex instrument with *Meavy 2.2.0* software. The heating rate was 5 °C/min, and the sample size was 3−15 mg. The impact and friction sensitivity data were determined on OZM Research BAM Fall Hammer BFH-10 and OZM Research BAM Friction FSKM-10 apparatuses, respectively, through five individual measurements that were averaged. Both instruments were calibrated using RDX. The starting materials $LiBH_4$, $NaBH_4$, KBH_4, NMe_4BH_4, PPh_4Cl, and $(Ph_3P)_2NCl$ (all Aldrich) were used without further purification. Boron trichloride (Aldrich) was freshly purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. PPh_4BH_4 and $(Ph_3P)_2NBH_4$ were prepared according to literature procedures from $NaBH_4$ and PPh_4Cl or $(Ph_3P)_2NCl$, respectively.[32−34] Sodium 3,5-dinitro-1*H*-1,2,4-triazolate,[35] 3,5-dinitro-1*H*-1,2,4-triazole (HDNT), 5-nitrotetrazole (HNTz),[36] 5-(trinitromethyl)tetrazole (HTNTz),[37−39] and 5-(fluorodinitromethyl)tetrazole (HFDNTz)[40] were prepared according to literature procedures.

Preparation of Sodium Dihydroborates ***Na[1]–Na[4]***. Stoichiometric amounts of sodium borohydride (2.00 mmol) and the corresponding nitroazole (4.00 mmol) were loaded into a 100 mL glass ampule that was equipped with a Teflon-coated stir bar. The ampule was evacuated, and about 10 mL of anhydrous dimethoxyethane (DME) was condensed into the ampule at −196 °C. The ampule was closed, and the reaction mixture was allowed to warm to ambient temperature. After hydrogen-gas evolution had seized, the obtained pale-yellow to light-orange reaction mixture was stirred for 4 h at ambient temperature. The reaction mixture was cooled to −196 °C and the amount of evolved hydrogen determined by pressure and temperature in calibrated volume segments of a glass vacuum line.

*$[Na(C_4H_{10}O_2)_3][BH_2(DNT)_2]$ (**Na[1]**, where DNT = 3,5-dinitro-1H-1,2,4-triazolyl):* 1.331 g; weight expected for 2.00 mmol, 1.223 g; H_2 evolved, 4.1 mmol; DTA decomposition onset, 150 °C. NMR (acetone-d_6, 298 K): ^{1}H, δ 3.27 (CH_3O), 3.46 (OCH_2), 3.8 (br, BH_2); ^{11}B, δ −6.1 (t, $^1J(^{11}B^1H)$ = 93.3 Hz); ^{13}C, δ 58.8 (CH_3O), 77.4 (OCH_2); ^{14}N, δ −27.3 ($\tau_{1/2}$ = 60 Hz, NO_2), −29.9 ($\tau_{1/2}$ = 60 Hz, NO_2), −70 ($\tau_{1/2}$ = 500 Hz, C_2N_3). Raman (100 mW): ν(rel intens) 3005 (1.3), 2990 (1.0), 2954 (2.7), 2933 (2.3), 2925 (2.3), 2909 (2.3), 2877 (1.5), 2858 (2.3), 2853 (2.1), 2836 (2.3), 2799 (0.6), 2795 (0.6), 2729 (0.4), 1558 (1.2), 1508 (0.6), 1477 (1.0), 1427 (10.0), 1379 (3.3), 1332 (1.0), 1318 (0.8), 1303 (0.4), 1287 (0.6), 1251 (0.4), 1199 (2.3), 1167 (0.4), 1156 (0.4), 1120 (0.8), 1105 (0.6), 1026 (1.7), 867 (1.2), 831 (1.3), 775 (0.6), 766 (0.4), 503 (0.4), 304 (0.6), 252 (0.4), 226 (0.6), 170 (1.2), 161 (1.0), 133 (1.5), 85 (3.7), 2464 (1.0), 2468 (0.8), 2473 (0.8), 2473 (0.8), 2494 (0.4), 338 (0.8), 356 (0.8), 362 (0.8), 367 (0.8) cm^{-1}. IR (KBr): ν 2997 vw, 2940 w, 2902 w, 2832 w, 2748 vw, 2498 m sh, 2479 m, 2158 w, 1570 vs, 1511 vs, 1474 w, 1458 w, 1420 m, 1373 m, 1328 s, 1320 s, 1247 w, 1192 m, 1150 m, 1122 m, 1106 m, 1086 s, 1031 w, 984 vw, 889 w, 854 s, 828 m, 771 w, 720 w, 652 m, 469 vw cm^{-1}.

*$[Na(C_4H_{10}O_2)_3][BH_2(NTz)_2]$ (**Na[2]**, where NTz = 5-nitro-2H-tetrazolyl):* 0.987 g; weight expected for 2.00 mmol, 1.048 g; H_2 evolved, 3.9 mmol; DTA decomposition onset, 169 °C (explosion). Raman (100 mW): ν(rel intens) 3006 (3.2), 2992 (3.2), 2953 (5.1), 2929 (4.8), 2904 (4.1), 2880 (3.0), 2852 (4.8), 2833 (4.8), 2725 (0.8), 2523 (1.1), 2467 (2.7), 1561 (1.6), 1465 (4.2), 1419 (10.0), 1383 (1.4), 1320 (3.2), 1291 (1.2), 1229 (0.9), 1222 (1.1), 1172 (1.4), 1152 (2.9), 1112 (1.2), 1072 (1.0), 1035 (4.4), 970 (0.8), 864 (1.9), 840 (1.6), 775 (1.3), 734 (2.5), 538 (1.0), 459 (1.0), 383 (1.6), 373 (1.4), 320 (1.3), 292 (1.7) cm^{-1}.

*$[Na(C_4H_{10}O_2)_3][BH_2(TNTz)_2]$ (**Na[3]**, where TNTz = 5-(trinitromethyl)-2H-tetrazolyl):* 1.621 g; weight expected for 2.00 mmol, 1.464 g; H_2 evolved, 3.8 mmol; DTA decomposition onset, 104 °C (explosion). Raman (100 mW): ν(rel intens) 3004 (3.9), 2955 (9.0), 2931 (7.8), 2904 (7.6), 2878 (4.8), 2853 (7.8), 2833 (7.6), 2727 (1.3), 2512 (1.2), 2469 (2.9), 1623 (1.9), 1611 (1.6), 1604 (1.6), 1465 (6.3), 1383 (2.6), 1369 (1.7), 1359 (1.8), 1352 (1.7), 1308 (2.0), 1300 (2.1), 1287 (2.6), 1249 (1.2), 1218 (1.0), 1182 (1.2), 1162 (1.2), 1156 (1.1), 1127 (1.4), 1118 (1.3), 1103 (0.9), 1056 (1.6), 1022 (1.2), 990 (4.3), 964 (2.9), 957 (2.8), 866 (3.5), 845 (10.0), 802 (1.0), 741 (0.7), 687 (0.8), 654 (0.9), 572 (0.7), 410 (2.6), 410 (2.6), 403 (2.8), 365 (6.5), 347 (7.0), 290 (1.5), 269 (1.5), 259 (1.5), 209 (2.5) cm^{-1}.

*$[Na(C_4H_{10}O_2)_3][BH_2(FDNTz)_2]$ (**Na[4]**, where FDNTz = 5-(fluorodinitromethyl)-2H-tetrazolyl):* 1.447 g; weight expected for 2.00 mmol, 1.356 g; H_2 evolved, 3.7 mmol; DTA decomposition onset, 148 °C (explosion).

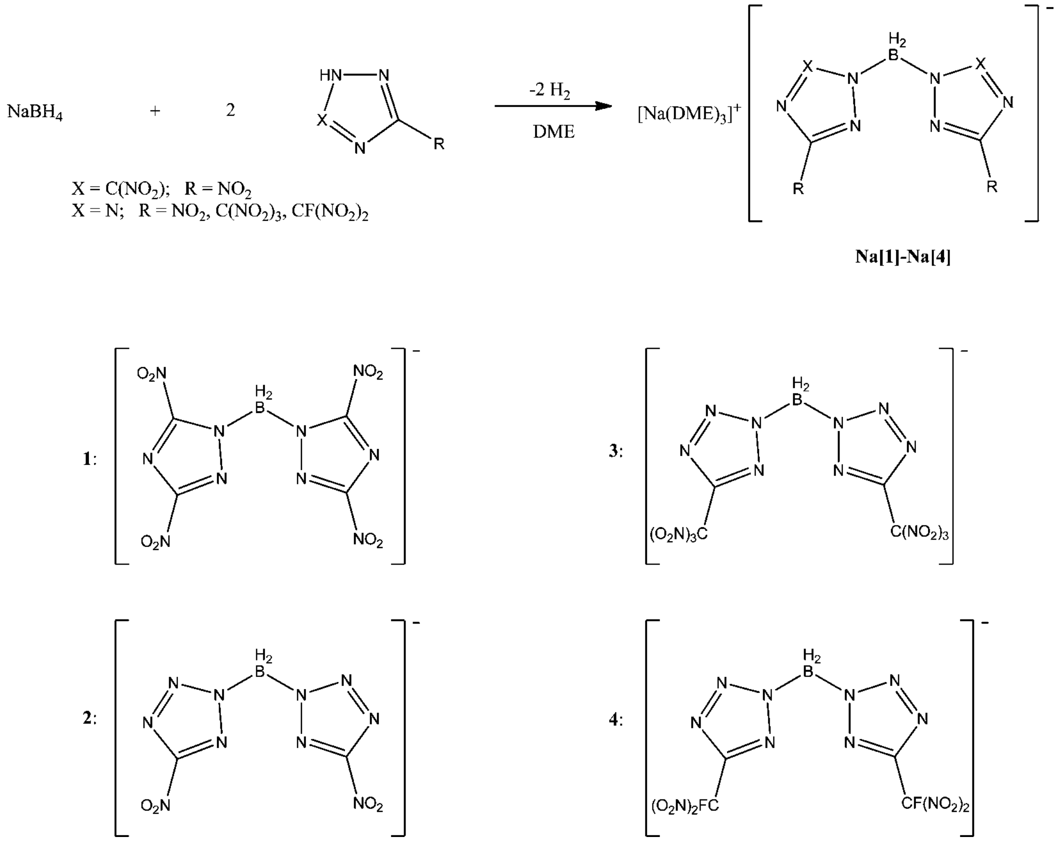
Preparation of the NMe_4^+, PPh_4^+, and $(Ph_3P)_2N^+$ Salts of Anions ***1–4***. A solution of NMe_4Cl, PPh_4Cl, or $(Ph_3P)_2NCl$ (1.10 mmol) in 30 mL of water and 10 mL of ethanol was added to a solution of the corresponding sodium bis(azolyl)dihydroborates **Na[1]–Na[4]** (1.00 mmol) in 20 mL of water. Immediately, an off-white to pale-yellow precipitate formed. The precipitated was filtered off, washed with water, and dried in air. Single crystals were obtained by recrystallization from acetone/water or acetonitrile/water solutions.

*$NMe_4[BH_2(DNT)_2]$ (**TMA[1]**, where TMA = Tetramethylammonium):* DTA decomposition onset, 157 °C. NMR (CD_3CN, 298 K): ^{1}H, δ 3.20 (NCH_3), 3.9 (br, BH_2); ^{11}B, δ −6.2 (t, $^1J(^{11}B^1H)$ = 96.4 Hz); ^{13}C, δ 56.3 (t, $^1J(^{13}C^{14}N)$ = 4.2 Hz, NCH_3); ^{14}N, δ −22.6 ($\tau_{1/2}$ = 50 Hz, NO_2), −26.6 ($\tau_{1/2}$ = 50 Hz, NO_2), −29.6 ($\tau_{1/2}$ = 50 Hz, NO_2), −74 ($\tau_{1/2}$ = 350 Hz, C_2N_3), −337.3 ($\tau_{1/2}$ = 6 Hz, NCH_3). Raman (200 mW): ν(rel intens) 3043 (1.3), 2984 (2.1), 2958 (0.8), 2927 (1.4), 2896 (0.3), 2823 (0.5), 2530 (0.3), 2478 (0.7), 1558 (1.1), 1505 (0.4), 1449 (1.5), 1424 (10.0), 1393 (1.5), 1379 (2.4), 1371 (2.6), 1331 (0.8), 1314 (0.8), 1312 (0.7), 1198 (0.9), 1191 (1.1), 1180 (0.9), 1153 (0.3), 1115 (0.5), 1110 (0.4), 1102 (0.4), 1025 (0.9), 1003 (0.1), 954 (0.2), 830 (0.2), 771 (0.1), 766 (0.1), 755 (0.3), 498 (0.3), 473 (0.3), 455 (0.3), 369 (0.5), 355 (0.6), 336 (0.6), 299 (0.7), 259 (0.4), 223 (0.5), 174 (0.8), 151 (0.9), 96 (3.0), 92 (3.0), 85 (3.8) cm^{-1}. IR (KBr): ν 3040 vw, 2968 vw, 2925 vw, 2874 vw, 2867 vw, 2528 m, 2477 m, 1569 vs, 1545 s, 1507 s, 1485 vs, 1450 vw, 1417 m, 1379 m, 1332 s, 1315 m, 1301 m, 1287 w, 1198 w, 1190 m, 1180 m, 1153 m, 1110 m, 1039 w, 953 s, 898 w, 886 m, 850 s, 843 s, 827 s, 773 w, 770 w, 720 w, 694 vw, 654 m, 604 vw, 496 vw, 474 vw, 461 vw, 459 w, 456 w, 420 w, 404 w cm^{-1}.

*$[(Ph_3P)_2N][BH_2(DNT)_2]$ (**PPN[1]**, where PPN = Bis(triphenylphosphoranylidene)ammonium):* DTA decomposition onset, 178 °C. NMR (acetone-d_6, 298 K): ^{1}H, δ 3.9 (br, BH_2), 7.5−7.8 (C_6H_5P); ^{11}B, δ −6.1 (t, $^1J(^{11}B^1H)$ = 91.3 Hz); ^{13}C, δ 128.2 (d, $^1J(^{13}C^{31}P)$ = 107.0 Hz), 130.23, 130.28, 130.33, 133.11, 133.15, 133.20, 134.5 (PC_6H_5), 159.9 (CNO_2); ^{14}N, δ −27.8 ($\tau_{1/2}$ = 70 Hz, NO_2), −29.7 ($\tau_{1/2}$ = 50 Hz, NO_2), −89 ($\tau_{1/2}$ = 500 Hz, C_2N_3), −120 ($\tau_{1/2}$ = 500 Hz, C_2N_3); $^{31}P\{^1H\}$, δ 21.9 (PC_6H_5). Raman (200 mW): ν(rel intens) 3177 (0.4), 3149 (0.8), 3063 (10.0), 3028 (0.8), 3014 (1.2), 2995 (0.8), 2958 (0.4), 2511 (0.4), 2470 (0.8), 1591 (4.2), 1577 (1.5), 1567 (0.8), 1555 (0.8), 1529 (0.4), 1505 (0.4), 1483 (0.4), 1428 (6.5), 1390 (4.6), 1366 (2.7), 1343 (0.8), 1332 (0.8), 1321 (0.8), 1283 (0.4), 1198 (1.5), 1185 (1.2), 1165 (1.2), 1112 (2.7), 1100 (1.9), 1029 (3.5), 1002 (7.7), 830 (1.5), 775 (0.4), 767 (0.8), 725 (0.4), 665 (2.3), 618 (1.9), 547 (0.4), 540 (0.4), 528 (0.4), 498 (0.4), 476 (0.4), 462 (0.4), 442 (0.4), 430 (0.4), 397 (0.4), 359 (1.2), 336 (0.8), 319 (0.8), 282 (1.2), 266 (1.5), 257 (1.5), 242 (1.9), 233 (1.9), 201 (1.2), 178 (1.2), 161 (1.5), 93 (11.5) cm^{-1}. IR (KBr): ν 3080 vw, 3060 w, 2507 w, 2468 m, 1589 w, 1559 vs, 1535 m, 1504 s, 1482 m, 1439 s, 1417 w, 1407 w, 1375 w, 1365 w, 1320 s, 1313 s, 1303 s, 1288 s, 1270 m, 1184 w, 1161 w, 1150 w, 1116 vs, 1104 m, 1097 m, 1026 vw, 997 vw, 893 vw, 850 w, 839 vw, 825 w, 796 vw, 753 w, 745 w, 724 s, 693 s, 650 vw, 616 vw, 598 vw, 546 m, 534 s, 501 m, 457 vw cm^{-1}.

*$[PPh_4][BH_2(NTz)_2]$ (**TPP[2]**, Where TPP = Tetraphenylphosphonium):* DTA decomposition onset, 168 °C; 276 mg. NMR (acetone-d_6, 298 K): ^{1}H, δ 4.1 (br q, $^1J(^1H^{11}B)$ = 115 Hz, BH_2), 7.8−8.1 (C_6H_5); ^{11}B, δ −5.5 (t, $^1J(^{11}B^1H)$ = 110.2 Hz); ^{13}C, δ 118.9 (d, $^1J(^{13}C^{31}P)$ = 90.5 Hz), 131.3 (d, $^2J(^{13}C^{31}P)$ = 13.2 Hz), 135.6 (d,

Scheme 1. Synthesis of Bis(nitroazolyl)dihydroborate Anions 1−4



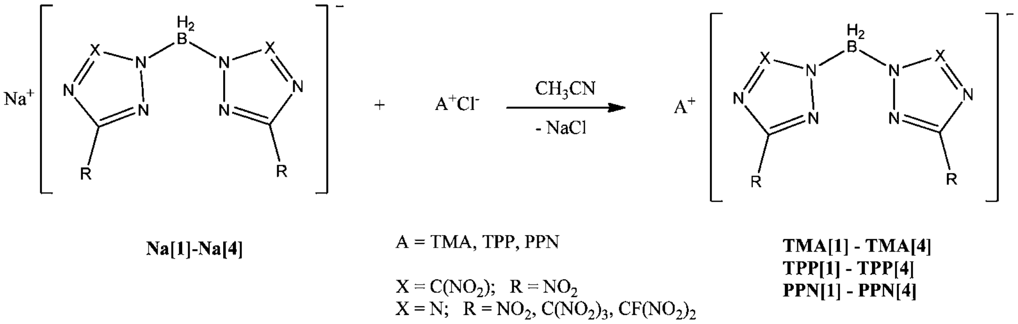
$^3J(^{13}C^{31}P)$ = 11.2 Hz), 136.3 (PC_6H_5); ^{14}N, δ −29.1 ($\tau_{1/2}$ = 50 Hz, NO_2), −67 ($\tau_{1/2}$ = 370 Hz, CN_4); $^{31}P\{^1H\}$, δ 23.9 (PC_6H_5). Raman (200 mW): ν(rel intens) 3175 (0.6), 3148 (0.7), 3067 (10.0), 3014 (0.7), 2998 (0.6), 2961 (0.5), 2530 (0.4), 2474 (1.0), 1589 (4.5), 1578 (1.7), 1551 (1.0), 1487 (0.4), 1461 (2.6), 1440 (0.6), 1414 (6.3), 1342 (0.3), 1317 (0.7), 1224 (0.5), 1190 (1.1), 1167 (1.2), 1150 (1.8), 1133 (0.7), 1112 (1.5), 1101 (2.6), 1068 (0.6), 1036 (4.5), 1029 (4.1), 1002 (9.1), 987 (0.6), 974 (0.6), 934 (0.3), 838 (0.8), 775 (0.5), 729 (0.5), 682 (1.8), 618 (1.8), 538 (0.4), 457 (0.4), 445 (0.4), 398 (0.3), 316 (0.6), 296 (1.1), 257 (2.8), 201 (2.6) cm^{-1}. IR (KBr): ν 3092 vw, 3063 w, 2959 vw, 2905 vw, 2511 w, 2470 w, 1609 vs, 1485 m, 1442 s, 1438 s, 1394 w, 1356 w, 1341 w, 1310 m, 1238 m, 1226 m, 1191 w, 1169 w, 1139 m, 1110 s, 1088 w, 1043 m, 1028 w, 998 m, 978 m, 857 vw, 835 s, 800 m, 753 m, 724 s, 690 s, 639 w, 616 vw, 591 vw, 527 vs, 463 vw cm^{-1}.

$[PPh_4][BH_2(TNTz)_2]$ **(TPP[3]):** DTA decomposition onset, 107 °C (explosion). NMR (acetone-d_6, 298 K): ^1H, δ 4.1 (br q, $^1J(^1H^{11}B)$ = 95 Hz, BH_2), 7.8−8.1 (C_6H_5); ^{11}B, δ −5.5 (t, $^1J(^{11}B^1H)$ = 90.5 Hz); ^{13}C, δ 118.9 (d, $^1J(^{13}C^{31}P)$ = 89.4 Hz), 131.3 (d, $^2J(^{13}C^{31}P)$ = 13.1 Hz), 135.6 (d, $^3J(^{13}C^{31}P)$ = 9.8 Hz), 136.3 (d, $^3J(^{13}C^{31}P)$ = 3.3 Hz, PC_6H_5); ^{14}N, δ −26.3 ($\tau_{1/2}$ = 40 Hz, NO_2), −32.6 ($\tau_{1/2}$ = 50 Hz, NO_2); $^{31}P\{^1H\}$, δ 23.8 (PC_6H_5). Raman (200 mW): ν(rel intens) 3174 (1.0), 3146 (1.0), 3073 (10.0), 3014 (1.0), 2964 (1.0), 2511 (1.0), 2471 (1.0), 1620 (1.0), 1589 (5.0), 1453 (1.0), 1417 (1.0), 1387 (1.0), 1377 (1.0), 1361 (1.0), 1343 (0.1), 1313 (1.0), 1286 (1.0), 1276 (0.9), 1245 (0.3), 1222 (0.3), 1191 (1.0), 1171 (1.0), 1113 (1.0), 1101 (2.0), 1059 (1.0), 1030 (4.0), 964 (1.0), 846 (2.0), 803 (0.4), 752 (0.3), 729 (0.5), 682 (2.0), 618 (1.0), 369 (1.0), 354 (2.0), 329 (1.0), 295 (1.0), 284 (1.0), 201 (2.0) cm^{-1}. IR (KBr): ν 3088 vw, 3058 w, 2510 m, 2470 m, 1618 vs, 1609 vs, 1597 vs, 1485 m, 1442 s, 1437 s, 1384 m, 1341 w, 1307 m, 1285 s, 1192 vw, 1171 w, 1139 m, 1110 s, 1046 s, 998 m, 988 m, 856 w, 843 s, 801 vs, 759 m, 753 s, 724 vs, 690 s, 657 w, 615 w, 607 vw, 527 vs, 461 w, 449 w cm^{-1}.

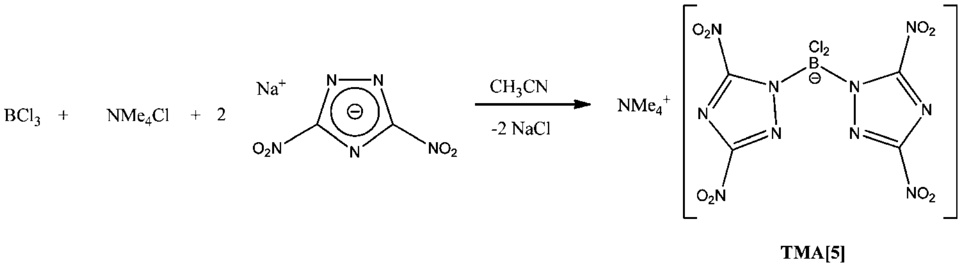
$[PPh_4][BH_2(FDNTz)_2]$ **(TPP[4]):** DTA decomposition onset, 152 °C (explosion). NMR (acetone-d_6, 298 K): ^1H, δ 4.2 (br q, $^1J(^1H^{11}B)$ = 98 Hz, BH_2), 7.8−8.1 (C_6H_5); ^{11}B, δ −5.8 (t, $^1J(^{11}B^1H)$ = 92.4 Hz); ^{13}C, δ 118.1 (br d, $^1J(^{13}C^{19}F)$ = 278 Hz, $CF(NO_2)_2$), 118.9 (d, $^1J(^{13}C^{31}P)$ = 89.7 Hz), 131.3 (d, $^2J(^{13}C^{31}P)$ = 13.2 Hz), 135.6 (d, $^3J(^{13}C^{31}P)$ = 10.0 Hz), 136.3 (d, $^3J(^{13}C^{31}P)$ = 3.2 Hz, PC_6H_5), 153.9 (d, $^2J(^{13}C^{19}F)$ = 24.8 Hz, CN_4); ^{14}N, δ −23.2 ($\tau_{1/2}$ = 50 Hz, NO_2), −24.9 ($\tau_{1/2}$ = 50 Hz, NO_2), −64 ($\tau_{1/2}$ = 400 Hz, CN_4); ^{19}F, δ −95.8 ($CF(NO_2)_2$); $^{31}P\{^1H\}$, δ 23.6 (PC_6H_5). Raman (200 mW): ν(rel intens) 3175 (0.7), 3147 (0.7), 3074 (9.6), 3015 (0.9), 2999 (0.9), 2964 (0.7), 2514 (0.7), 2474 (1.1), 1589 (6.2), 1579 (2.0), 1491 (1.6), 1445 (0.7), 1394 (0.7), 1361 (1.1), 1358 (1.1), 1354 (0.9), 1345 (0.9), 1316 (0.9), 1215 (0.9), 1193 (1.3), 1170 (1.6), 1110 (1.6), 1101 (2.7), 1056 (1.3), 1030 (5.3), 1003 (10.0), 985 (1.6), 971 (1.1), 944 (1.1), 837 (2.2), 803 (0.7), 757 (0.7), 727 (0.9), 682 (2.4), 618 (2.0), 550 (0.7), 424 (1.1), 369 (2.0), 331 (0.9), 286 (2.0), 253 (4.9), 202 (2.9), 182 (1.8) cm^{-1}. IR (KBr): ν 3093 vw, 3062 vw, 2902 vw, 2510 w, 2469 w, 1609 vs, 1485 m, 1442 s, 1438 s, 1393 w, 1358 w, 1341 w, 1310 m, 1233 m, 1228 m, 1192 m, 1169 m, 1139 m, 1110 s, 1088 m, 1043 m, 1028 w, 998 m, 978 m, 857 vw, 835 s, 800 s, 754 m, 724 s, 690 s, 667 m, 616 w, 528 vs cm^{-1}.

Preparation of $NMe_4BCl_2(DNT)_2$ **(TMA[5]).** A 25 mL glass ampule equipped with a Teflon-coated stir bar was charged with NMe_4Cl (0.110 g, 1.00 mmol) and sodium 3,5-dinitro-1*H*-1,2,4-triazolate (0.362 g, 2.00 mmol). The ampule was cooled to −196 °C, and acetonitrile (5 mL) and boron trichloride (0.117 g, 1.00 mmol) were condensed in on a vacuum line. The closed ampule was allowed to warm to ambient temperature. The milky mixture was stirred for 48 h. The precipitate was filtered off. The filtrate was cooled to −20 °C and the solvent slowly removed in a vacuum. **TMA[5]** was obtained as pale-yellow crystals (397 mg; weight expected for 1.00 mmol, 0.472 g). Raman (100 mW): ν(rel intens) 3044 (2.8), 2984 (4.8), 2960 (2.6), 2928 (2.9), 2896 (0.5), 2822 (1.2), 2775 (0.2), 1566 (1.2), 1513 (0.5), 1431 (10.0), 1404 (1.6), 1383 (5.8), 1334 (0.8), 1315 (2.9), 1182 (1.9), 1113 (1.4), 1024 (2.5), 951 (0.9), 917 (2.2), 853 (0.3), 832 (2.6), 815 (0.3), 773 (0.9), 764 (1.0), 755 (2.7), 656 (0.8), 516 (0.3), 480 (0.5), 457 (0.3), 392 (0.9), 370 (0.7), 352 (1.1), 322 (0.8), 309

Scheme 2. Conversion of the Sodium Salts into the Corresponding NMe_4^+, PPh_4^+, and $(Ph_3P)_2N^+$ Salts of the Bis(nitroazolyl)dihydroborates 1−4



Scheme 3. Synthesis of TMA[5]



(0.8), 248 (1.0), 214 (0.7), 171 (1.7), 115 (4.1), 606 (0.2), 1123 (0.4), 798 (0.2), 228 (0.6) cm^{-1}.

■ RESULTS AND DISCUSSION

The general strategy for the synthesis of azolylhydroborates involves the reaction of an alkali-metal borohydride with the corresponding azole. Such conversions are usually carried out with the molten azole and typically involve reaction temperatures in excess of 140 °C.[7] Substitution with NO_2 groups increases the acidity of an azole because of the strong electron-withdrawing effect of the nitro group. Because of their increased acidity, 3,5-dinitro-1*H*-1,2,4-triazole (HDNT), 5-nitro-2*H*-tetrazole (HNTz), 5-(trinitromethyl)-2*H*-tetrazole (HTNTz), and 5-(fluorodinitromethyl)-2*H*-tetrazole (HFDNTz) already react in solution at ambient temperature with alkali-metal borohydrides under evolution of hydrogen gas. The reaction of MBH_4 (M = Na, Li) with 2 equiv of HDNT, HNTz, HTNTz, and HFDNTz in DME at ambient temperature resulted in the formation of colorless to pale-yellow solutions of the corresponding bis(nitroazolyl)-dihydroborates **1**−**4** according to Scheme 1. The quantitative evolution of 2 equiv of hydrogen gas during these reactions was confirmed by *p*, *V*, and *T* measurements. After evaporation of the solvent in a vacuum, the DME adducts of the sodium dihydroborates **Na**[**1**]−**Na**[**4**] were isolated in quantitative yields as pale-yellow (nitrotetrazoles) to orange (dinitrotriazoles) solids. On one occasion, orange crystals of **Na1** were obtained when the solvent was removed from the reaction mixture very slowly in a vacuum at ambient temperature.

The sodium dihydroborate DME adducts **Na**[**1**]−**Na**[**4**] are energetic materials and, as such, should only be handled with great care, although no difficulties were encountered during the course of this work. The identity of the dihydroborates **Na**[**1**]−**Na**[**4**] was established by their vibrational and multinuclear NMR spectra and, in the case of **Na**[**1**], by its crystal structure. In addition, the sodium dihydroborates **Na**[**1**]−**Na**[**4**] were converted into the corresponding NMe_4^+, PPh_4^+, and $(Ph_3P)_2N^+$ salts of the anions **1**−**4** (Scheme 2), which were then characterized by their crystal structures. Because of the energetic and potential explosive nature of these compounds, no elemental analysis data were determined.

When $LiBH_4$ was reacted with 2 equiv of HDNT in diethyl ether and the solvent removed in a vacuum, the obtained pale-yellow lithium bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydroborate was found to be highly explosive and very sensitive to friction and mechanical impact. A small sample (~50 mg) of the compound that had been stored inside a drybox exploded violently without any provocation. Because of their high sensitivity, the synthesis and characterization of any lithium bis(dinitrotriazolyl)- and bis(nitrotetrazolyl)dihydroborate were not pursued any further.

When solutions of NMe_4Cl, PPh_4Cl, and $(Ph_3P)_2NCl$ in 10−25% ethanol in water were added to aqueous solutions of the sodium salts of the dihydroborates **1**−**4**, white precipitates of the corresponding tetramethylammonium salts **TMA**[**1**]−**TMA**[**4**], tetraphenylphosphonium salts **TPP**[**1**]−**TPP**[**4**], and bis(triphenylphosphine)iminium salts **PPN**[**1**]−**PPN**[**4**], respectively, formed (Scheme 2). Single crystals of **TMA**[**1**], **PPN**[**1**], **TPP**[**2**], **TPP**[**3**], and **TPP**[**4**] were obtained by recrystallization from acetone/water or acetonitrile/water.

The reaction of sodium 3,5-dinitro-1*H*-1,2,4-triazolate with BCl_3 and NMe_4Cl in acetonitrile was also explored as another way for introducing 3,5-dinitro-1*H*-1,2,4-triazolyl ligands into a borate anion (Scheme 3). When the reaction mixture was filtered after 48 h, followed by evaporation of the solvent from the filtrate, pale-yellow crystals of **TMA**[**5**] were obtained. The identity of the compound was established by its crystal structure.

The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra of the salts containing the anions **1**−**4** showed the expected resonances for DME, NMe_4^+, PPh_4^+, or $(Ph_3P)_2N^+$. In addition, the ^{11}B NMR spectra of the dihydroborate anions **1**−**4** showed broadened triplet resonances with $^{1}J(^{11}B^{1}H)$ coupling constants of 90−110 Hz, ranging from −6.2 to −5.5 ppm, which are similar to the

Table 1. Crystallographic Data and Structure Determination Details for Compounds **Na**[**1**], **TMA**[**1**], **PPN**[**1**], and **TMA**[**5**]

	Na[1]	TMA[1]	PPN[1]	TMA[5]
formula	$C_{16}H_{32}BN_{10}NaO_{14}$	$C_8H_{14}BN_{11}O_8$	$C_{40}H_{33}BN_{11}O_8P$	$C_{12}H_{12}BCl_2N_{11}O_8$
mol wt [g/mol]	622.31	403.11	867.52	472.00
temp [K]	100(2)	100(2)	100(2)	140(2)
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.1631(2)	11.4579(5)	9.9418(5)	7.4547(19)
b [Å]	12.6130(2)	12.0559(6)	12.6744(6)	10.322(3)
c [Å]	12.6791(2)	13.0552(6)	16.7980(8)	12.988(3)
α [deg]	110.9310(10)	85.815(2)	97.5665(7)	84.511(4)
β [deg]	105.0920(10)	86.127(2)	96.2596(7)	78.393(4)
γ [deg]	104.7700(10)	79.409(2)	90.1580(7)	77.534(4)
V [Å^3]	1485.24(4)	1765.24(14)	2053.12(17)	954.5(4)
Z	2	4	2	2
ρ_{calc} [g/cm^3]	1.392	1.517	1.403	1.642
μ [mm^{-1}]	0.132	0.132	0.174	0.406
F(000)	652	832	896	480
reflns collected	41074	10932	39853	5880
indep reflns	8675	7604	12196	4103
R_{int}	0.0453	0.0208	0.0253	0.0170
no. of param	414	529	567	292
R1 [$I > 2\sigma(I)$]	0.0324	0.0552	0.0344	0.0580
wR2 [$I > 2\sigma(I)$]	0.0866	0.1407	0.0875	0.1446
GOF	1.077	1.039	1.024	1.029

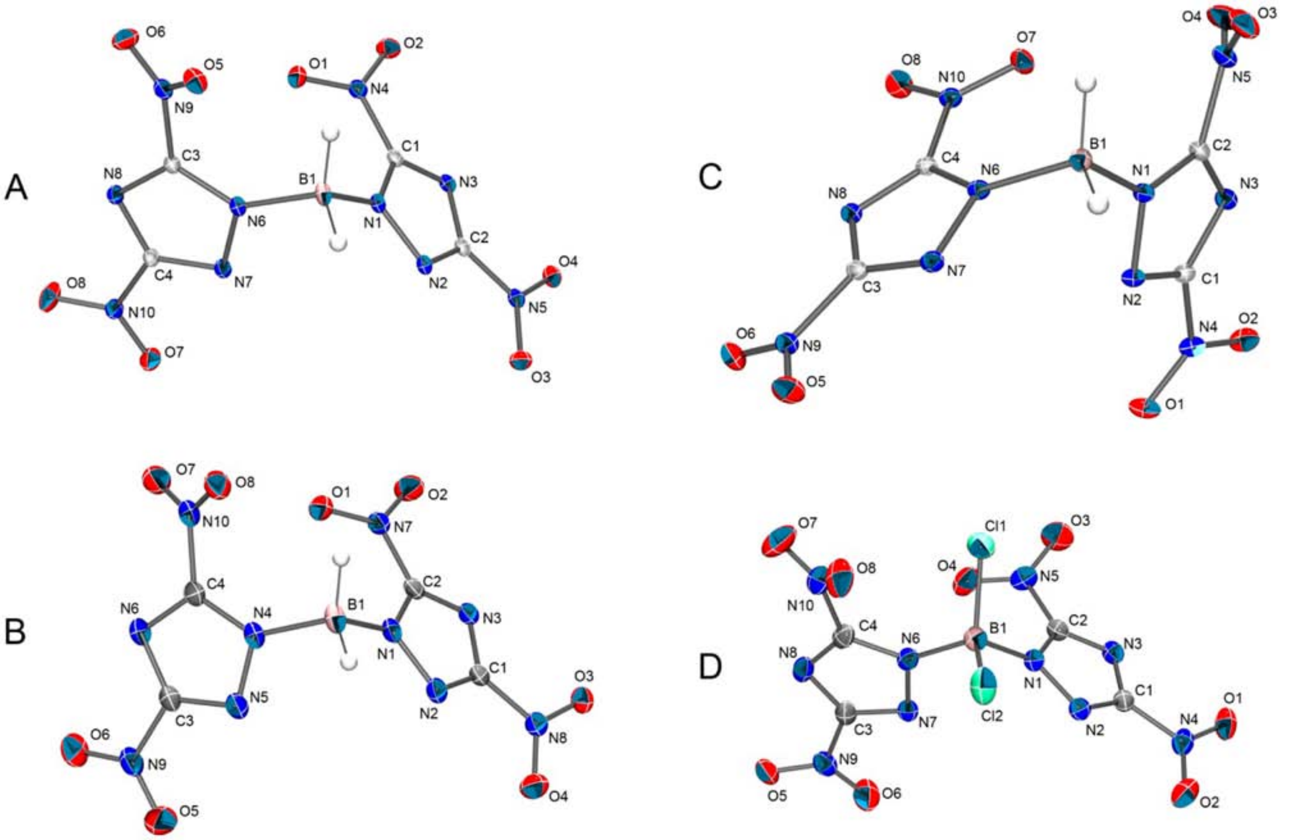


Figure 1. Crystal structures of the bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydro- and dichloroborate anions of **Na**[**1**] (A), **TMA**[**1**] (B), **PPN**[**1**] (C), and **TMA**[**5**] (D). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): **Na**[**1**], B1−N1 1.5756(12), B1−N6 1.5773(12), N1−B1−N6 106.74(7); **TMA**[**1**], B1−N1 1.586(3), B1−N4 1.577(3), N1−B1−N4 107.9(2); **PPN**[**1**], B1−N1 1.5717(16), B1−N6 1.5821(15), N1−B1−N6 104.49(8); **TMA**[**5**], B1−N1 1.574(4), B1−N6 1.550(4), B1−Cl1 1.827(4), B1−Cl2 1.818(3), N1−B1−N6 108.1(2), N1−B1−Cl1 107.1(2), N1−B1−Cl2 109.5(2), N6−B1−Cl1 110.9(2), N6−B1−Cl2 109.5(2).

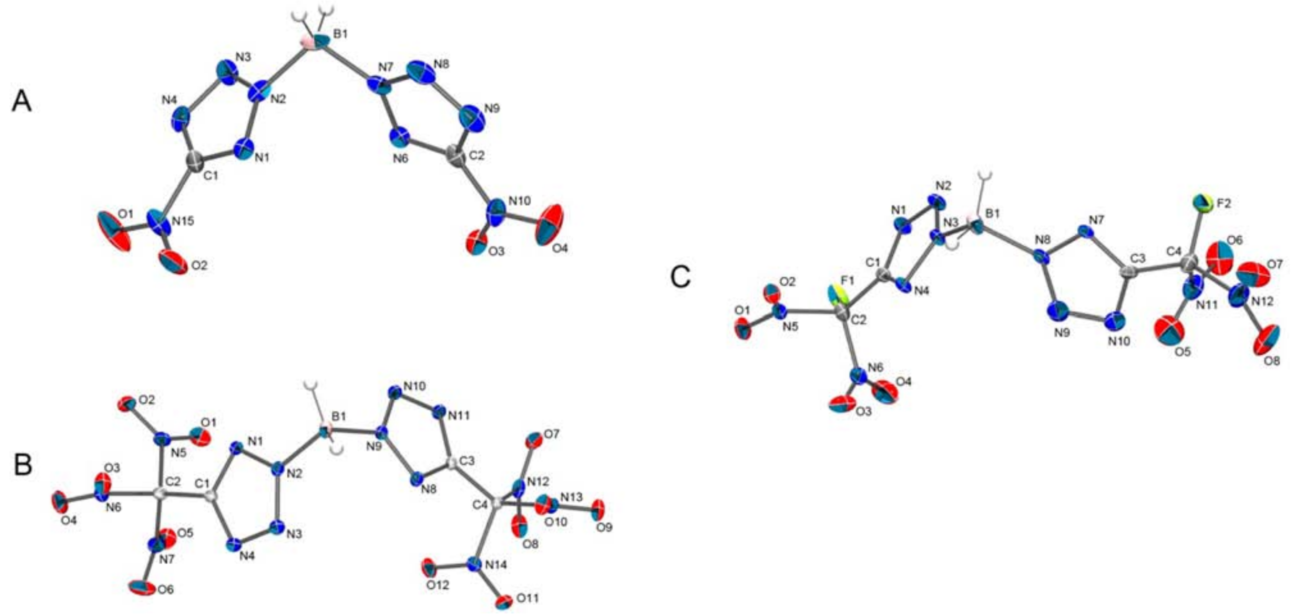


Figure 2. Crystal structures of the bis(tetrazolyl)dihydroborate anions in **TPP[2]** (A), **TPP[3]** (B), and **TPP[4]** (C). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): **TPP[2]**, B1–N2 1.560(2), B1–N7 1.559(2), N2–B1–N7 106.00(12); **TPP[3]**, B1–N2 1.575(2), B1–N9 1.573(2), N2–B1–N9 105.27(11); **TPP[4]**, B1–N3 1.572(3), B1–N8 1.626(8), N3–B1–N8 109.5(4).

values recently reported for potassium bis(tetrazolyl)-dihydroborate salts.[28] The ^{1}H chemical shifts of the BH_2 groups were observed in the range of 3.8–4.2 ppm. The vibrational spectra of the dihydroborate anions **1**–**4** showed two well isolated but somewhat broadened bands for the antisymmetric and symmetric BH_2 stretching vibrations at 2460–2480 and 2490–2530 cm^{-1}, respectively.

X-ray Crystal Structures. The crystal structures of the bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydroborate anions in **Na[1]**, **TMA[1]**, and **PPN[1]** and the dichloroborate anion in **TMA[5]** were determined. The relevant crystallographic data and parameters are summarized in Table 1, and the molecular structures of the bis(3,5-dinitro-1*H*-1,2,4-triazolyl)borate anions are depicted in Figure 1.

As expected for triazolylborates,[41] all compounds contain B–N bonds to the nitrogen atoms in the 2 position of the triazolyl groups. The compounds **Na[1]**, **TMA[1]**, **PPN[1]**, and **TMA[5]** crystallize in the triclinic space group $P\bar{1}$. The crystal structure of **Na[1]** consists of isolated $[Na(DME)_3]^+$ cation units and borate anions. Because of coordination with three DME molecules, the sodium atoms are well separated from the triazolylborate anions. The crystals of **TMA[1]**, **PPN[1]**, and **TMA[5]** contain well-separated cation and anion units. Selected bond lengths and angles of the bis(3,5-dinitro-1*H*-1,2,4-triazolyl)borates **Na[1]**, **TMA[1]**, **PPN[1]**, and **TMA[5]** are given in the caption of Figure 1. As expected, only small changes in the structure of the bis(dinitrotriazolyl)-dihydroborate anion **1** were observed between salts with $Na(DME)_3^+$, NMe_4^+, or $(Ph_3P)_2N^+$ counterions. The dihydroborate anion contains one short B–N bond of 1.572(2)–1.577(3) Å and a longer B–N bond of 1.577(1)–1.586(3) Å. The observed N–B–N bond angles vary between 104.49(8)° and 107.9(2)°. The replacement of the two hydrogen atoms of the borate anion with two chlorine atoms renders the B–N bonds more covalent. The observed B–N bond lengths are shortened to 1.550(4) and 1.574(4) Å, while the N–B–N bond angle remains virtually unchanged [108.1(2)°]. A full list of observed bond lengths and angles is given in the Supporting Information.

Compound **TPP[2]** crystallizes in the monoclinic space group $P2_1/c$, while compounds **TPP[3]** and **TPP[4]** crystallize in the triclinic space group $P\bar{1}$. The structures of the different bis(tetrazolyl)dihydroborate anions in the crystal structures of compounds **TPP[2]**–**TPP[4]** are depicted in Figure 2, and the relevant crystallographic data and parameters are summarized in Table 2.

It is worth noting that all three bis(tetrazolyl)dihydroborate anions contain B–N bonds to the nitrogen atom in the 2 position of the tetrazolyl ligand. This is in contrast to common tetrazolylborates such as bis(5*H*-tetrazolyl)dihydroborate,[24] (5-aminotetrazolyl)dihydroborate,[29] and bis(5-methyltetrazolate)-dihydroborate,[28] which contain B–N bonds to the nitrogen atom in the 1 position of the five-membered ring. The obtained crystal structures of **TPP[2]** and **TPP[4]** suffer from a positional disorder in one of the two tetrazolyl ligands of the anion. In both cases, it was possible to model the disorder as a superposition of two different orientations (ratio 60:40 in both cases) of the five-membered ring and its substituents.

Stability of the Compounds. The thermal stabilities of the dihydroborates **Na[1]**–**Na[4]**, **TMA[1]**, **PPN[1]**, and **TPP[2]**–**TPP[4]** were determined using DTA scans with a heating rate of 5 °C/min. The results of these scans are summarized in Table 3. While the compounds **Na[1]**, **TMA[1]**, and **PPN[1]** with bis(3,5-dinitro-1*H*-1,2,4-triazolyl)-dihydroborate anions showed smooth decompositions in the DTA scans at temperatures of 150 °C and above, all investigated bis(nitrotetrazolyl)dihydroborates exploded upon heating. The bis(5-trinitromethyltetrazolyl)dihydroborate anion **2** is the thermally least stable anion among the investigated tetrazolylborates with an explosion temperature of 104–107 °C. The replacement of a nitro group of the trinitromethyl moiety by a fluorine atom increases the thermal stability. The explosion temperature of the resulting bis[5-(fluorodinitromethyl)tetrazolyl]dihydroborate anion **4** was

Table 2. Crystallographic Data and Structure Determination Details for Compounds **TPP[2]**−**TPP[4]**

	TPP[2]	**TPP[3]**	**TPP[4]**
formula	$C_{26}H_{22}BN_{10}O_4P$	$C_{28}H_{22}BN_{14}O_{12}P$	$C_{28}H_{22}BF_2N_{12}O_8P$
mol wt [g/mol]	580.31	788.38	734.36
temp [K]	100(2)	100(2)	100(2)
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	22.1054(10)	11.0434(7)	11.1504(6)
b [Å]	10.5458(5)	12.7349(8)	12.2645(6)
c [Å]	23.8276(11)	13.7231(9)	13.5087(7)
α [deg]	90	109.7350(10)	109.3580(10)
β [deg]	97.5540(10)	97.9540(10)	99.4140(10)
γ [deg]	90	102.8410(10)	101.5770(10)
V [Å^3]	5506.5(4)	1722.62(19)	1653.72(15)
Z	8	2	2
ρ_{calc} [g/cm^3]	1.400	1.520	1.475
μ [mm^{-1}]	0.153	0.164	0.163
F(000)	2400	808	752
reflns collected	129956	40440	40373
indep reflns	16662	10098	9869
R_{int}	0.0535	0.0268	0.0216
no. of param	828	513	517
R1 [$I > 2\sigma(I)$]	0.0412	0.0414	0.0580
wR2 [$I > 2\sigma(I)$]	0.0973	0.1066	0.1561
GOF	1.018	1.023	1.042

Table 3. Sensitivity Data of Compounds **Na[1]**−**Na[4]** and **TPP[2]**−**TPP[4]**

compound	T_{dec} [°C]	$T_{explosion}$ [°C]	impact sensitivity[a] [J]	friction sensitivity[b] [N]
Na[1]	150		19	>360
TMA[1]	157		36	>360
PPN[1]	178		>100	>360
Na[2]		169	8.0	16
TPP[2]		168	25	40
Na[3]		104	1.0	12
TPP[3]		107	1.5	40
Na[4]		148	2.5	16
TPP[4]		152	2.8	64

[a] The impact sensitivity of RDX was found as 7.0 J on the instrument used. [b] The friction sensitivity of RDX was found as 160 N on the instrument used.

determined as 148−152 °C. The bis(5-nitrotetrazolyl)-dihydroborates **Na[4]** and **TPP[4]** showed the highest thermal stabilities with explosion temperatures of 168−169 °C. A comparison of the explosion temperatures of compounds **Na[2]**/**TPP[2]**, **Na[3]**/**TPP[3]**, and **Na[4]**/**TPP[4]** indicates that the nature of the cation has only a marginal influence on the thermal stability of the nitrotetrazolyldihydroborates.

The impact and friction sensitivities of the dihydroborates **Na[1]**−**Na[4]**, **TMA[1]**, **PPN[1]**, and **TPP[2]**−**TPP[4]** were determined using a BAM Fall Hammer and a BAM Friction Tester, respectively. The determined impact and friction sensitivities of the dihydroborates **Na[1]**−**Na[4]**, **TMA[1]**, **PPN[1]**, and **TPP[2]**−**TPP[4]** are summarized in Table 3 and show a trend similar the one observed for the thermal stabilities.

■ CONCLUSION

Poly(nitroazolyl)borates are promising candidates for a new class of environmentally benign energetic materials. The bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydro- and dichloroborate and bis(5-nitro-2*H*-tetrazolyl)-, bis(5-trinitromethyl-2*H*-tetrazolyl)-, and bis(5-fluorodinitromethyl-2*H*-tetrazolyl)-dihydroborate anions have been synthesized and structurally characterized. Salts of these dihydroborates with $[Na(DME)_3]^+$ counterions are energetic. The tetrazolyldihydroborate compounds are friction- and impact-sensitive and explode upon heating. Salts with larger organic cations such as NMe_4^+, PPh_4^+, or $(Ph_3P)_2N^+$ are less sensitive. The present work demonstrates the general concept of synthesizing polyazolylborates containing highly oxidized nitroazolyl ligands by the treatment of boronhydrides and -chlorides with the corresponding nitroazoles and sodium nitroazolates, respectively. The application of this concept for the synthesis of higher substituted borates such as tris(nitroazolyl)hydroborates and tetrakis(nitroazolyl)-borates is currently being studied in our laboratories and will be the subject of a forthcoming publication.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, Figures S1−S28, and Tables S1−S52. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through the contributions of all authors.

Notes

The authors declare no competing financial interest.

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