ChemPlusChem
doi.org/10.1002/cplu.202000427

Comparison of Functionalized Lithium Dihydrobis(azolyl) borates with Their Corresponding Azolates as Environmentally Friendly Red Pyrotechnic Coloring Agents

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The recent awareness of the impact of strontium on health has stimulated research efforts on lithium-based red pyrotechnic colorants. We have previously shown lithium dihydrobis(azolyl) borates to be promising candidates due to their favorable adjustment to a reductive and low-temperature flame atmosphere. These compounds are assumed to be sufficiently stable only if the pK_a values of the heterocycles are between 5 and 20. Apart from their acidities, functionalization of 1*H*-tetrazole and 1*H*-pyrazole with nitro or amino groups, respectively, tailors the oxygen balances of the resulting Lewis acid base adducts to enhance the fuel-rich flame environment or to make them oxidizing agents. This work determines whether the lithium salts of dihydrobis(3-nitropyrazol-1-yl)borate and dihydrobis(5-aminotetrazol-1-yl)borate are suitable replacements for strontium-containing color imparters. Furthermore, the influence of potentially green-light-producing boron is evaluated by comparing the emissions of the lithium borates and the corresponding lithium azolates.

Introduction

When first concerns were expressed about the substitution of calcium by strontium in the human bone,[1] the search for other elements coloring a pyrotechnic flame red began. A quick survey of the literature on flame theory suggests that an astonishingly large number of elements is capable of emitting in the red region of the electromagnetic spectrum.[2] However, the radioactivity of radium as well as the high cost of the rare earth elements praseodymium, neodymium, samarium, yttrium, and scandium is prohibitive for their application.[2a] Red emissions from metastable copper(II) oxide were only observed as a marginal phenomenon in blue pyrotechnics,[2b] whereas the flame color of calcium has a dominant yellowish aspect.[2c] Lithium is well known for its production of carmine red light and is not currently considered toxic as demonstrated by its use in the treatment of mental diseases and LD50 values of 422–1165 mg kg^{-1} for oral administration of several compounds to different animal species.[3]

In contrast to all other elements mentioned above, in the case of lithium it is the metastable atomic species, which provokes two emission lines of high intensity at 671 and 610 nm.[2a,4] Regarding that chlorine donors have fallen into disrepute due to their combustion to highly carcinogenic polychlorinated aromatics,[4,5] this is a further advantage of lithium. The presence of chlorine is even considered to have an adverse effect on the light output of a lithium-containing pyrotechnic formulation.[2a] A fuel-rich flame atmosphere is suggested in order to convert incandescent lithium hydroxide back to gaseous atomic lithium and water vapor in the flame and thus to avoid paling of the flame color. Furthermore, the probability of higher energetic electron transitions leading to a blue shift of the dominant wavelength should be low, if cool flame temperatures are adjusted.[2a,6] Despite all this theoretical knowledge on lithium flame chemistry the selection of chlorine-free lithium-based pyrotechnic compositions is very narrow.[4,7] Additionally, a significant percentage of these show a burning behavior rather comparable to a strobe than to a flare,[7] which might be due to the strong tendency of lithium to attract water in some form.

The hygroscopicity of the lightest alkaline metal might be delimited by saltification of bulky molecules offering a large number of coordination sites. Bis(azolyl)borates, especially with 1*H*-pyrazole as substituent, are not only chelating ligands,[8] adjust a reductive environment and release high volumes of nitrogen to cool the flame,[9] but have extensively been investigated in the past.[8,10] A mechanism based on the principles of nucleophilic substitution was postulated for the reaction of the borohydride anion with an azole, whereby the nucleophilic heterocycle and electrophilic tetrahydroborate form a cyclic five-membered transition state and hydrogen leaves concertedly.[8] While previous studies proved lithium dihydrobis(1,2,4-triazol-1-yl)borate sesquihydrate to be a suitable red pyrotechnic color agent, their lack of stability renders the corresponding salts carrying 1*H*-pyrazole or 1*H*-tetrazole as ligands not useful for practical applications.[7b] Also the Lewis acid-base reaction toward lithium dihydrobis(tetrazol-1-yl)bo-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cplu.202000427

rate is accompanied by a highly exothermic formation of hydrogen and the dissociation of unconverted azole so that it bears a certain risk and affords unsatisfying yields. In regard of the acidities of the different substituents (1*H*-pyrazole: $pK_a = 20.4$,[11] 1*H*-1,2,4-triazole: $pK_a = 10.0$,[12] 1*H*-tetrazole: $pK_a = 4.9$) this means that a pK_a value higher than 5 and lower than 20 allows for convenient preparation and sufficient stability of the resulting dihydrobis(azolyl)borate (see Figure 1). By functionalization of the pyrazole or tetrazole rings with nitro or amino groups, respectively, their pK_a values are shifted into this range and additionally the oxygen balances of the compounds can be tuned toward oxidizers or fuels to reduce the number of components of a pyrotechnic mixture. This work concentrates on the lithium salts of dihydrobis(3-nitropyrazol-1-yl)borate (**3**, **4**) and dihydrobis(5-aminotetrazol-1-yl)borate (**6**, **7**), whereby particular attention is paid to dehydration.

Present boron may potentially form metastable green light-emitting boron dioxide in the flame even, if this process should require an oxygen-rich atmosphere to be observable.[13] Its influence on the color performance is evaluated by comparing the emissive properties of the lithium borates with those of the respective azolates (**5**, **8**).

Results and Discussion

Synthesis

In general, bis(azolyl)borate salts are accessible by the Lewis acid-base reaction between borohydride and depending on its acidity at least two equivalents of the heterocycle under inert gas atmosphere, whereby hydrogen evolves.[7b,8a,10a,c] If such a reaction is carried out in solvent, the latter is distilled beforehand. A water-free reaction environment needs to be ensured due to the low resistance of tetrahydroborate to hydrolysis.

Procedures for both the potassium salts of dihydrobis(3-nitropyrazol-1-yl)borate[14] (**2**) and dihydrobis(5-aminotetrazol-1-yl)borate[15] have already been reported. The former is synthesized by thermal rearrangement of 1-*N*-nitropyrazole in anisole, addition of a stoichiometric amount of potassium borohydride at 80 °C and gradual heating of the resulting solution. However, 3-nitro-1*H*-pyrazole (**1**) has a mid-range pK_a value of 9.8[16] so that, given a reasonable solubility of this azole in the chosen solvent, the hydrogen formation upon encounter of the two starting materials was assumed to be relatively exothermic, especially at elevated temperature and thus reaction rate. Therefore, the reaction mixture was prepared under ice-cooling and was only heated, when the brisk hydrogen evolution had eased up. Apart from being safer, this approach also provides a higher degree of control over the stoichiometry of the reagents due to isolation of the ligand beforehand. Since acetonitrile has a lower boiling point than anisole and thus is more easily removable and since the acidity of **1** only slightly differs from that of 1*H*-1,2,4-triazole, our previously established synthesis protocol for potassium dihydrobis(1,2,4-triazol-1-yl)borate[7b] using this reaction medium was attempted to be transferred to the target compound. Indeed, refluxing a solution of potassium tetrahydroborate and two equivalents of **1** in acetonitrile for six days yielded **2** (see Scheme 1). Small impurities of boric acid or tetrahydroxyborate and of 3-nitropyrazolate, which might result from the hydrolysis of unconverted borohydride and the intermediate trihydro(3-nitropyrazol-1-yl)borate upon contact with moisture,[8a] can be removed by recrystallization from methanol and by washing with ethanol, respectively. In this way, the treatment with toxic *n*-hexane proposed by *Pellei* et al. is avoided. Even the yield achieved by this procedure of 69 % overcomes the literature value of 60 %.[14]

The metathesis reaction of the potassium precursor with lithium perchlorate leads to the corresponding lithium salt (**3**), which can be dehydrated at 100 °C over night. Interestingly, **2** as well as its anhydrous lithium analogue (**4**) change their color from yellowish or brownish, respectively, to green when exposed to air for one week. Nevertheless, no explanation for this behavior was found so far (see Supporting Information).

In the case of potassium dihydrobis(5-aminotetrazol-1-yl) borate a stoichiometric mixture of potassium borohydride and 5-amino-1*H*-tetrazole in acetonitrile is refluxed for four days (see Scheme 2). The literature also describes the acidification of the potassium salt by glacial acetic acid.[15] (5-amino-1*H*-

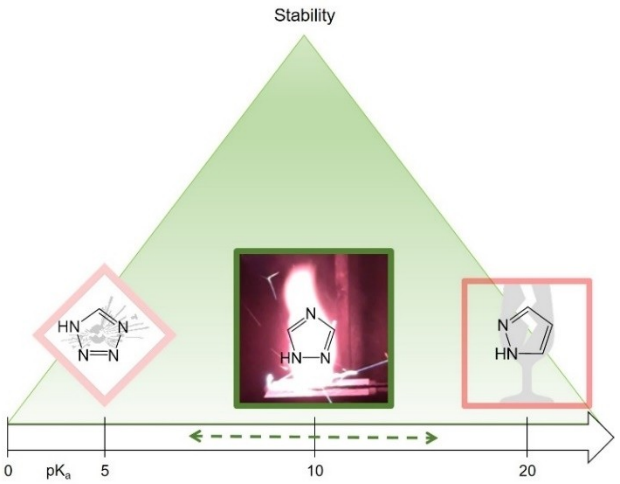
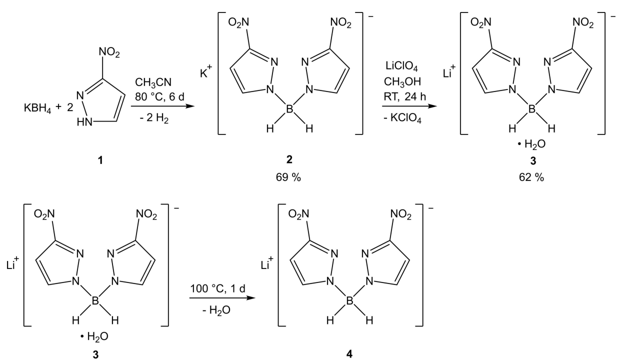
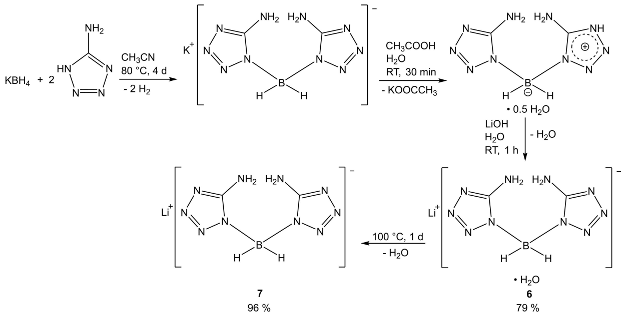


Figure 1. Stability of lithium dihydrobis(azolyl)borates as a function of the pK_a value of the ligands.



Scheme 1. Synthesis of lithium dihydrobis(3-nitropyrazol-1-yl)borate (**4**).



Scheme 2. Synthesis of lithium dihydrobis(5-aminotetrazol-1-yl)borate (**7**).

tetrazole)dihydro(5-aminotetrazol-1-yl)borane hemihydrate in contrast to potential impurities such as residual boric acid or tetrahydroxyborate and unconsumed 5-amino-1*H*-tetrazole has a poor solubility in water. The saltification of the free acid with lithium hydroxide leads to lithium dihydrobis(5-aminotetrazol-1-yl)borate monohydrate (**6**) in satisfying purity and yield. The crystal water can be removed by drying at 100 °C over night. The water-free moiety (**7**) did not give any hints at ageing.

While lithium 5-aminotetrazolate[17] (**8**) and its tetrazolate analogue[18] are the only two water-free lithium salts known to literature, lithium 3-nitropyrazolate (**5**) has not been mentioned until now. The latter was prepared in 76% yield by the deprotonation of **1** by lithium hydroxide and subsequent drying at 100 °C over night. Nevertheless, this compound proved to be hygroscopic.

Crystal Structures

Crystalline material of **3** and **6** was obtained by evaporation of an ethanolic solution or of a hot solution of 2-propanol, respectively, before single crystals were prepared and the latter were analyzed by low-temperature X-ray diffraction. Both compounds crystallize in the monoclinic space group $P2_1/n$. The more carbon atoms in the unsubstituted heterocycle are replaced by smaller and heavier nitrogen, the higher the density seems to be (potassium dihydrobis(pyrazol-1-yl)borate: $\rho = 1.41\ \mathrm{g\,cm^{-3}}$ at 150 K;[8b] potassium dihydrobis(tetrazol-1-yl)borate: $\rho = 1.47\ \mathrm{g\,cm^{-3}}$ at 283–303 K[10c]). Nitro and amino substituents contribute approximately equally to a closer packing, since the oxygen atoms of nitro functionalities offer additional coordination sites for metal cations and amino groups push electron density into the ring and thus enhance its σ-donation toward metal centers (**2**: $\rho = 1.69\ \mathrm{g\,cm^{-3}}$ at 100 K,[14] potassium dihydrobis(5-aminotetrazol-1-yl)borate: $\rho = 1.70\ \mathrm{g\,cm^{-3}}$ at 296 K[15]). Therefore, the density of **6** of $1.60\ \mathrm{g\,cm^{-3}}$ at 113 K exceeds that of its 3-nitropyrazole analogue of $1.52\ \mathrm{g\,cm^{-3}}$ at 143 K. Additionally, the former forms a polymeric structure (see Figure 3) as opposed to the dimers of **3** (see Figure 2).

In both molecular units the bis(azolyl)borate anion has a half-boat conformation. In **3** the *cis*-oriented nitro groups are coplanar with the heterocycles, whereas the protons of the amino functionalities in the corresponding 5-aminotetrazole compound are in *trans* conformation and slightly bend out of the ring planes. While in **3** the lithium cation has a distorted octahedral coordination sphere of one oxygen and one nitrogen each of two adjacent anions and two water molecules, in **6** lithium is distortedly tetrahedrally coordinated by one nitrogen atom each of two neighboring dihydrobis(5-aminotetrazol-1-yl)borate units and by two water ligands. Interestingly, in both cases the lithium atoms of two monomers are connected by their two water molecules in a slightly distorted square planar manner.

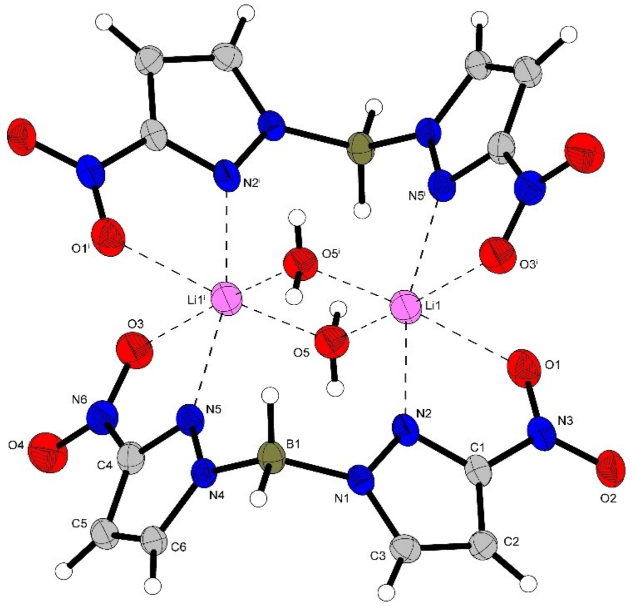


Figure 2. Dimer of lithium dihydrobis(3-nitropyrazol-1-yl)borate monohydrate (**3**). Selected bond lengths (Å): B1-H1A 1.035(14), B1-H1B 1.043(12), N1-B1 1.560(2), N4-B1 1.559(2), N5^{i}-Li1 2.157(3), O3^{i}-Li1 2.272(3), O1-Li1 2.229(3), N2-Li1 2.179(3), O5-Li1 2.044(3), O5^{i}-Li1 2.077(3); selected bond angles (°): H1A-B1-H1B 112.7(11), N1-B1-N4 109.66(11), O3^{i}-Li1-N5^{i} 73.51(9), O1-Li1-N5^{i} 94.52(11), O5-Li1-N5^{i} 98.63(14), O5^{i}-Li1-N5^{i} 94.04(13), O1-Li1-N2 74.22(11), O3^{i}-Li1-N2 93.10(12), O5^{i}-Li1-N2 95.53(12), O5-Li1-N2 94.12(12), O1-Li1-O3^{i} 80.50(9), O3^{i}-Li1-O5^{i} 93.43(12), O5-Li1-O5^{i} 90.42(10), O1-Li1-O5 97.08(13), O5-Li1-O5^{i} 90.42(10), Li1-O5-Li1^{i} 89.58(12); symmetry code: (i) 1−x, 1−y, 1−z.

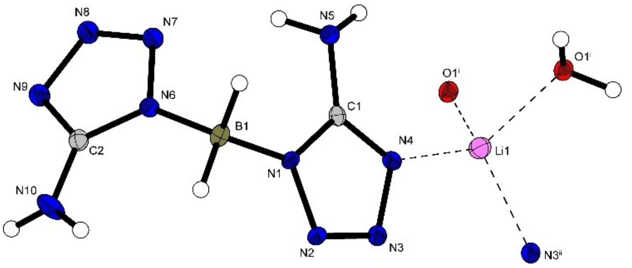


Figure 3. Advanced molecular unit of lithium dihydrobis(5-aminotetrazol-1-yl)borate monohydrate (**6**). Selected bond lengths (Å): B1-H1 A 1.121(19), B1-H1B 1.14(2), N1-B1 1.569(3), N6-B1 1.558(3), N3^{iii}-Li1 2.045(4), N4-Li1 2.018(4), O1^{i}-Li1 1.967(3), O1^{ii}-Li1 1.959(3); selected bond angles (°): H1A-B1-H1B 114.9(14), N1-B1-N6 108.50(17), N3^{iii}-Li1-N4 113.74(16), O1^{i}-Li1-N3^{iii} 107.29(16), O1^{ii}-Li1-N3^{iii} 109.17(16), O1^{i}-Li1-N4 114.30(17), O1^{i}-Li1-O1^{ii} 90.92(14), O1^{ii}-Li1-N4 118.88(17), Li1-O1^{i}-Li1^{i} 89.08(15); symmetry codes: (i) x, y, 1+z; (ii) −x, −y, 1−z; (iii) 1−x, −y, 2−z.

The B–N bond distances in **3** are very similar to those of the potassium representative[14] (B–H 1.102–1.140 Å, B–N 1.554–1.567 Å, H–B–H 114.6°, N–B–N 108.2°), whereas the B–H bonds are shorter, the protons on the boron center are more strongly and the nitrogen atoms less angled. The B–H bonds in **6** are elongated compared to the corresponding 3-nitropyrazole material, because the higher number of electron-withdrawing nitrogen atoms in the azole compensates for the amino ligands pushing electron density to the boron atom. The B–N bond distances as well as the N–B–N angle in **6** are almost identical to those determined for amino(2-(propan-2-ylidene)hydrazinyl) methaniminium dihydrobis(5-aminotetrazol-1-yl)borate (B–N 1.559–1.566 Å, N–B–N 108.5°).[10b]

Physico-Chemical Properties

Apart from being storable, a lithium-based red pyrotechnic formulation should at least be as safe as conventional mixtures.[19] Therefore, the thermal stabilities and resistances toward friction, impact and electrostatic discharge of the stable lithium salts **4**, **7**, and **8** were measured (see Figure 4 and Table 1).

Additionally, the oxygen balances of the latter were calculated in order to evaluate their capability of serving as oxidizers or fuels. The oxygen balance reflects, if the full burn of a compound with the sum formula $C_aH_bN_cO_d$ to CO_2, H_2O and N_2 produces or requires extra oxygen [Equation (1)].[20b]

$$\Omega_{CO2} = \frac{\left(d - 2a - \frac{b}{2}\right)}{M} \times 1600 \tag{1}$$

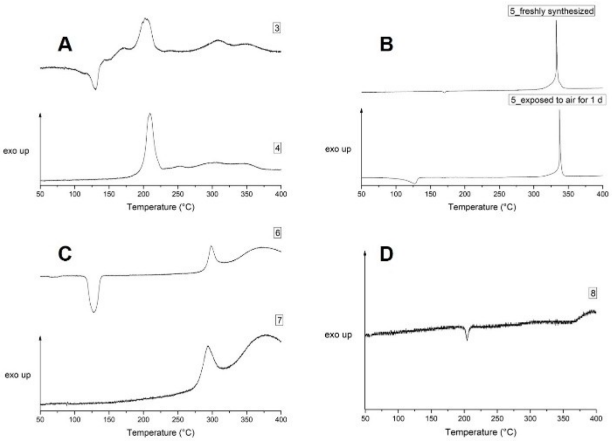


Figure 4. DTA plots from top to bottom of A – lithium dihydrobis(3-nitropyrazol-1-yl)borate (**3**, **4**) before and after drying, B – lithium 3-nitropyrazolate (**5**) after synthesis and exposure to air for one day, C – lithium dihydrobis(5-aminotetrazol-1-yl)borate (**6**, **7**) before and after drying, D – lithium 5-aminotetrazolate (**8**).

The respective values of the two lithium borates and the lithium azolate were determined assuming that lithium combusts to Li_2O[21] and boron to B_2O_3.[22] Although in moiety **4** the two heterocycles carry one nitro group each, its oxygen balance is even more highly negative than those of the other two compounds containing amino-functionalized azoles. This is because in materials **7** and **8** more carbon atoms in the ring are substituted by nitrogen. However, all three salts are thermally stable. While the impact sensitivity of **4** is in the range of a primary explosive,[20a] **7** as well as **8** are insensitive toward all tested ignition stimuli. This means that in contrast to the amination of the tetrazole units the nitration of the pyrazole rings only partially stabilizes the respective bis(azolyl)borate and that moieties **7** and **8** are worth considering application.

Pyrotechnic Formulations

In order to compare the emissive properties of 7 and 8 to a strontium-based coloring agent and amongst each other, drop-in formulations of a chlorine-free strontium-containing red pyrotechnic composition[9] were prepared (see Table 2) and spectrometrically analysed. Instead of strontium nitrate, its ammonium analogue was used as oxidizer. Magnesium is known to increase the flame temperature and to wash out the red flame color imparted by lithium due to its incandescent oxidation product[7a] so that the content of 7 or 8, respectively, with their highly negative oxygen balances was increased at the expense of the metallic fuel. Since these mixtures, especially that employing the azolate, were hygroscopic, the percentage of binder was raised. However, this only marginally curbed the hygroscopicity of the mixtures.

Both mixtures exhibit dominant wavelengths well below that of the control and also significantly weaker luminosities, which most probably originates from their reduced magnesium contents. Still, the spectral purities of A and B greatly exceed that of the reference despite their magnesium content. Although, in contrast to A, test composition B does not sustain combustion, the carmine color aspect of the flame is more dominant in this case (see Figure 5).

Table 1. Physico-chemical properties of lithium dihydrobis(3-nitropyrazol-1-yl)borate (**4**), lithium dihydrobis(5-aminotetrazol-1-yl)borate (**7**), and lithium 5-aminotetrazolate (**8**).

	ΩCO_2 [%][a]	T_{dec} (onset) [°C][b]	g.s. [μm][c]	FS [N][d]	IS [J][e]	ESD [J][f]
4	−72.16	200	100–500	144	2[g]	0.42
7	−59.61	280	100–500	> 360	> 40	> 1.5
8	−52.75	369	< 100	> 360	> 40	> 1.5

[a] Oxygen balance with respect to formation of CO_2, Li_2O, and B_2O_3. [b] Onset decomposition temperature observed as exothermic peak during differential thermal analysis using a heating rate of $\beta = 5\,^{\circ}C\,min^{-1}$. [c] Grain size. [d] Friction sensitivity. [e] Impact sensitivity. [f] Electrostatic discharge sensitivity. [g] The impact sensitivity of **4** was determined for a grain size < 100 μm.

Table 2. Composition of a chlorine-free strontium-based control[9] and of test formulations **A** and **B** containing lithium dihydrobis(5-aminotetrazol-1-yl) borate (**7**) or lithium 5-aminotetrazolate (**8**), respectively.

	$Sr(NO_3)_2$ [wt%]	NH_4NO_3 [wt%]	Mg 50/100 [wt%][a]	CH_3N_5 [wt%]	7 [wt%]	8 [wt%]	Epon 813/ Versamid 140 [wt%][b]
Control	48		33	12			7
A		48	12		30		10
B		48	12			30	10

[a] Magnesium with a mesh size 50/100 (300 μm > grain size > 150 μm). [b] Epon 813 and Versamid 140 in a weight percent ratio of 80:20.

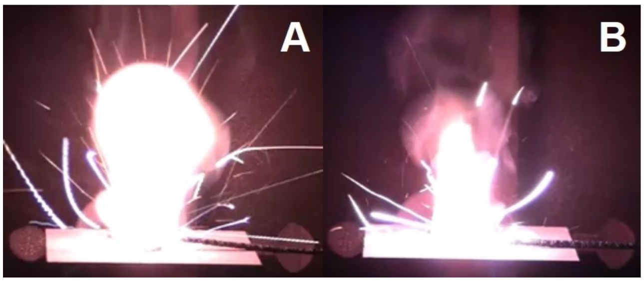


Figure 5. Combustion of test formulations A and B, respectively.

The slightly higher dominant wavelength of B compared to A according to Table 3 indeed suggests that lithium borate 7 forms metastable boron dioxide in the flame causing a blue shift of the value. In this context, the extremely high spectral purity of A is contradictory. Beyond the less efficient burn-down of B resulting in a longer burn time and a lower light output, the enhanced hygroscopicity of this formulation also shows in a strobe-like burning behavior.

Conclusion

The new lithium dihydrobis(azolyl)borates with 5-aminotetrazole or 3-nitropyrazole as ligands as well as their corresponding azolates were prepared, whereby the synthesis of potassium dihydrobis(3-nitropyrazol-1-yl)borate was improved in terms of safety and yield. In order to avoid an incontinuous burning behavior of pyrotechnic formulations employing these moieties as red colorants, the latter were dehydrated where necessary. The enhanced resistance of lithium dihydrobis(3-nitropyrazol-1-yl)borate to hydrolysis compared to its unnitrated analogue and the insensitiveness of lithium dihydrobis(5-aminotetrazol-1-yl) borate seem to support our theory that heterocycles with pK_a values higher than 5 and lower than 20 build stable lithium bis(azolyl)borates. However, lithium dihydrobis(3-nitropyrazol-1-yl) borate is very sensitive to impact and lithium 3-nitropyrazolate is hygroscopic so that only the other two salts were investigated further. Although the color purities of mixtures containing lithium dihydrobis(5-aminotetrazol-1-yl)borate or lithium 5-aminotetrazolate, respectively, do not support this theory, green light-emitting boron seems to cause a blue shift of the dominant wavelength.

Experimental Section

CAUTION! The reactions between potassium borohydride and azoles described herein, especially that with 3-nitro-1H-pyrazole, are exothermic and proceed with the release of high volumes of hydrogen gas. All reaction products are potentially explosive energetic materials, which are partly sensitive toward various ignition stimuli (e.g. heat, friction, impact or electrostatic discharge). Therefore, proper safety precautions (safety glasses, face shield, leather coat, earthed equipment and shoes, Kevlar gloves, Kevlar sleeves and ear protectors) have to be taken, when synthesizing and manipulating these compounds.

3-Nitro-1*H*-pyrazole (1):[23] 4.999 g 1-*N*-nitropyrazole (44 mmol) were thermally rearranged by heating a solution in 50 mL of benzonitrile at 180 °C for three hours. The colorless needles, which precipitated from solution upon cooling to 0 °C, were filtered off and dried at 100 °C overnight. This procedure afforded 3.564 g of the title compound (71 %).

IR (ATR): $\tilde{\nu} = 3142$(s), 3022(m), 2926(m), 2884(m), 2630(w), 1676(vw), 1556(s), 1511(s), 1483(s), 1438(m), 1423(m), 1379(vs), 1351(vs), 1286 (m), 1249(m), 1209(s), 1090(m), 1058(m), 1047(s), 990(s), 928(m), 903 (m), 862(m), 862(m), 820(vs), 794(s), 783(vs), 752(vs), 640(w), 613(m), 474(vw), 442(s) cm^{-1}. $^{14}N\{H\}$ NMR (DMSO-d_6, 25 °C): $\delta = -170.2$ (br s, *N*H), −18.8 (br s, *N*O_2) ppm. $^{13}C\{H\}$ NMR (DMSO-d_6, 25 °C): $\delta = 156.3$ (s, *C*-NO_2), 132.3 (s, *C*H), 101.8 (s, *C*H) ppm. $^{1}H\{/\}$ NMR (DMSO-d_6, 25 °C): $\delta = 13.94$ (br s, 1H, N*H*), 8.03 (d, 1H, C*H*), 7.03 (d, 1H, C*H*) ppm. EA ($C_3H_3N_3O_2$, 113.08): calcd. N 37.16, C 31.86, H 2.67 %; found N 37.29, C 31.73, H 2.62 %. DTA (5 °C min^{-1}): 176 (endothermic), 316 (endothermic) °C.

Table 3. Physico-chemical properties of the control and test formulations **A** and **B**.

	T_{dec}(onset) [°C][a]	FS [N][b]	IS [J][c]	ESD [J][d]	BT [s][e]	λ_d [nm][f]	Σ [%][g]	LI [cd][h]
Control	244	192	10	1	3	606	75	14083
A	218	>360	10	1	10	591	99	1002
B	204	>360	20	1	15[i]	593	87	763

[a] Onset decomposition temperature observed as exothermic peak during differential thermal analysis using a heating rate of $\beta = 5\,°C\,min^{-1}$. [b] Friction sensitivity. [c] Impact sensitivity. [d] Electrostatic discharge sensitivity. [e] Burn time. [f] Dominant wavelength. [g] Spectral purity. [h] Luminous intensity. [i] Burn time determined taking only one sample into account; all other combustion parameters were averaged over two measurements each.

Potassium dihydrobis(3-nitropyrazol-1-yl)borate (2): A reaction mixture consisting of 0.625 g potassium borohydride (12 mmol), 2.623 g **1** (23 mmol) and 3 mL of anhydrous acetonitrile was prepared under ice-cooling. When the release of hydrogen had eased up under stirring at room temperature, the suspension was refluxed for six days. The resulting solid was washed twice with approximately 5 mL of ethanol each and recrystallized from 44 mL of methanol, before the crystals were dried at 100 °C overnight. The product (2.201 g, 69 %) was obtained in the form of yellowish crystals.

IR (ATR): $\tilde{\nu} = 3146$(w), 3129(w), 2452(w), 2428(m), 2385(w), 2269(w), 1551(w), 1528(m), 1521(m), 1490(m), 1478(s), 1440(m), 1392(m), 1381(s), 1362(s), 1301(m), 1231(s), 1206(m), 1142(vs), 1055(s), 1006 (m), 989(m), 913(w), 913(w), 899(m), 886(w), 830(s), 822(m), 785(s), 754(vs), 728(m), 677(w), 662(m), 643(m), 616(m), 540(w), 451(w), 440 (w) cm^{-1}. ^{11}B{/} NMR (DMSO-d_6, 25 °C): $\delta = -5.5$ (br s, *B*H$_2$) ppm. ^{14}N {H} NMR (DMSO-d_6, 25 °C): $\delta = -19.3$ (br s, *N*O$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 156.6$ (s, *C*-NO$_2$), 137.1 (s, *C*H), 101.4 (s, *C*H) ppm. ^{1}H{/} NMR (DMSO-d_6, 25 °C): $\delta = 7.62$ (d, 2H, C*H*), 6.78 (d, 2H, C*H*), 3.61 (br s, 2H, B*H*$_2$) ppm. EA ($KBC_6H_6N_6O_4$, 276.06): calcd. N 30.44, C 26.11, H 2.19 %; found N 30.36, C 25.90, H 2.11 %. DTA (5 °C min^{-1}): 248 (exothermic) °C.

Lithium dihydrobis(3-nitropyrazol-1-yl)borate monohydrate (3): The metathesis reaction between 0.998 g **2** (4 mmol) and 0.384 g lithium perchlorate (4 mmol) in 50 mL of methanol was allowed to proceed for 24 hours at room temperature. After potassium perchlorate had been filtered off, the solvent was removed from the filtrate *in vacuo*. Recrystallization of the residue from roughly 5 mL of ethyl acetate gave 0.583 g of a light brown powder (62 %).

IR (ATR): $\tilde{\nu} = 3608$(w), 3497(w), 3164(w), 3151(w), 3131(w), 2469(w), 2419(w), 1602(w), 1558(w), 1533(m), 1494(vs), 1456(w), 1447(w), 1392(m), 1359(vs), 1299(m), 1237(s), 1206(w), 1193(w), 1154(s), 1134 (vs), 1068(s), 1059(s), 1059(s), 1010(m), 1001(m), 987(w), 976(w), 882 (m), 828(s), 797(m), 786(s), 753(s), 723(m), 658(m), 639(w), 613(w), 548(w), 481(m), 453(m), 418(w) cm^{-1}. ^{7}Li{H} NMR (DMSO-d_6, 25 °C): $\delta = -1.0$ (s, *Li*) ppm. ^{11}B{/} NMR (DMSO-d_6, 25 °C): $\delta = -6.0$ (br s, *B*H$_2$) ppm. ^{14}N{H} NMR (DMSO-d_6, 25 °C): $\delta = -16.4$ (br s, *N*O$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 156.6$ (s, *C*-NO$_2$), 137.1 (s, *C*H), 101.4 (s, *C*H) ppm. ^{1}H{/} NMR (DMSO-d_6, 25 °C): $\delta = 7.62$ (d, 2H, C*H*), 6.78 (d, 2H, C*H*), 3.60 (br s, 2H, B*H*$_2$), 3.37 (br s, 2H, *H*$_2$O) ppm. EA ($LiBC_6H_8N_6O_5$, 261.92): calcd. N 32.09, C 27.52, H 3.08 %; found N 32.15, C 27.69, H 2.82 %. DTA (5 °C min^{-1}): 121 (endothermic), 189 (exothermic) °C.

Lithium dihydrobis(3-nitropyrazol-1-yl)borate (4): The target moiety (0.503 g, 93 %) was obtained by dehydration of **3** (0.583 g, 2 mmol) at 100 °C over night.

IR (ATR): $\tilde{\nu} = 3182$(vw), 3169(vw), 3149(w), 3126(w), 2480(w), 2421 (w), 1561(w), 1541(m), 1529(m), 1495(s), 1486(s), 1448(w), 1360(vs), 1299(w), 1231(s), 1187(w), 1179(m), 1168(m), 1159(m), 1151(s), 1136 (vs), 1124(vs), 1063(s), 1063(s), 1011(m), 982(w), 903(w), 884(w), 871 (w), 842(m), 827(s), 800(m), 787(s), 753(vs), 720(m), 710(m), 666(w), 656(m), 634(m), 622(w), 611(w), 550(w), 466(w), 450(w) cm^{-1}. ^{7}Li{H} NMR (DMSO-d_6, 25 °C): $\delta = -1.1$ (s, *Li*) ppm. ^{11}B{/} NMR (DMSO-d_6, 25 °C): $\delta = -6.0$ (br s, *B*H$_2$) ppm. ^{14}N{H} NMR (DMSO-d_6, 25 °C): $\delta = -18.8$ (br s, *N*O$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 156.6$ (s, *C*-NO$_2$), 137.1 (s, *C*H), 101.4 (s, *C*H) ppm. ^{1}H{/} NMR (DMSO-d_6, 25 °C): $\delta = 7.62$ (d, 2H, C*H*), 6.77 (d, 2H, C*H*), 3.60 (br s, 2H, B*H*$_2$) ppm. EA ($LiBC_6H_6N_6O_4$, 243.90): calcd. N 34.46, C 29.55, H 2.48 %; found N 34.22, C 29.12, H 2.49 %. DTA (5 °C min^{-1}): 200 (exothermic) °C. FS (100–500 μm): 144 N. IS (< 100 μm): 2 J. ESD (100–500 μm): 0.42 J.

Lithium 3-nitropyrazolate (5): A suspension of 1.000 g **1** (9 mmol) and 0.212 g lithium hydroxide (9 mmol) in roughly 13 mL of water was stirred at room temperature for one hour, before unreacted azole was filtered off and the solvent was removed from the filtrate *in vacuo*. Drying of the residue at 100 °C overnight gave 0.802 g of a yellow powder (76 %).

IR (ATR): $\tilde{\nu} = 3152$(w), 3128(vw), 2568(vw), 2285(vw), 1559(vw), 1516 (m), 1510(m), 1488(s), 1437(w), 1423(m), 1364(m), 1329(vs), 1241(m), 1133(vs), 1108(vs), 1056(s), 1039(s), 1003(vs), 937(s), 897(w), 881(w), 825(s), 779(s), 779(s), 753(s), 613(m), 571(m), 503(m), 446(w), 414(w) cm^{-1}. ^{7}Li{H} NMR (DMSO-d_6, 25 °C): $\delta = -0.8$ (s, *Li*) ppm. ^{14}N{H} NMR (DMSO-d_6, 25 °C): $\delta = -14.2$ (br s, *N*O$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 157.4$ (s, *C*-NO$_2$), 138.1 (s, *C*H), 101.0 (s, *C*H) ppm. ^{1}H{/} NMR (DMSO-d_6, 25 °C): $\delta = 7.39$ (d, 1H, C*H*), 6.64 (d, 1H, C*H*) ppm. EA ($LiC_3H_2N_3O_2$, 119.01): calcd. N 35.31, C 30.27, H 1.70 %; found N 35.38, C 30.22, H 1.75 %. DTA (5 °C min^{-1}): 332 (exothermic) °C.

Lithium dihydrobis(5-aminotetrazol-1-yl)borate monohydrate (6):[15] 10 mL of anhydrous acetonitrile were added to 1.116 g potassium borohydride (21 mmol) and 3.518 g 5-amino-1*H*-tetrazole (41 mmol) and the reaction mixture was first left undisturbed and then stirred at room temperature, until the release of hydrogen had dropped. Subsequently, the Lewis acid-base reaction between the two starting materials was allowed to proceed for four days under reflux, whereby a precipitate was formed. The latter (4.561 g) was filtered off, suspended in roughly 9 mL of bidistilled water and acidified with the same volume of glacial acetic acid. After the suspension had been stirred at room temperature for 30 minutes, the resulting solid was filtered off and washed three times with approximately 9 mL of water each. Finally, the crude free acid (2.835 g) was suspended in roughly 50 mL water, neutralized with lithium hydroxide (0.358 g, 15 mmol) and the suspension was stirred at room temperature for one hour. Filtering off unreacted intermediate and removing the solvent from the filtrate *in vacuo* afforded 2.443 g of a white powder (79 %).

IR (ATR): $\tilde{\nu} = 3497$(w), 3399(m), 3365(w), 3334(m), 3195(w), 2784(w), 2484(m), 2420(m), 1610(s), 1552(s), 1488(m), 1462(m), 1308(m), 1221(w), 1173(w), 1151(m), 1117(vs), 1052(w), 1037(w), 1023(w), 904 (m), 876(w), 864(m), 864(m), 807(m), 774(m), 753(s), 728(s), 704(m), 637(vs), 505(w), 459(m), 438(m), 407(m) cm^{-1}. ^{7}Li{H} NMR (DMSO-d_6, 25 °C): $\delta = -1.0$ ppm. ^{11}B{/} NMR (DMSO-d_6, 25 °C): $\delta = -13.8$ (br s, *B*H$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 159.2$ (s, *C*-NH$_2$) ppm. ^{1}H {/} NMR (DMSO-d_6, 25 °C): $\delta = 5.60$ (br s, 4H, N*H*$_2$), 3.57 (br s, 2H, *H*$_2$O), 3.30 (br s, 2H, B*H*$_2$) ppm. EA ($LiBC_2H_8N_{10}O$, 205.91): calcd. N 68.02, C 11.67, H 3.91 %; found N 67.35, C 12.21, H 3.69 %. DTA (5 °C min^{-1}): 117 (endothermic), 290 (exothermic) °C.

Lithium dihydrobis(5-aminotetrazol-1-yl)borate (7): Drying 2.443 g **6** (12 mmol) at 100 °C overnight yielded 2.140 g of the water-free compound (96 %).

IR (ATR): $\tilde{\nu} = 3474$(w), 3442(w), 3409(w), 3379(m), 3291(w), 3213(w), 3169(w), 2457(w), 2417(w), 1621(vs), 1560(s), 1465(m), 1303(m), 1238(m), 1221(w), 1205(w), 1183(m), 1146(s), 1099(s), 1062(m), 1034 (w), 876(w), 780(m), 780(m), 762(w), 751(w), 674(m), 660(s), 631(m), 501(m), 460(w), 442(w), 431(w), 418(w) cm^{-1}. ^{7}Li{H} NMR (DMSO-d_6, 25 °C): $\delta = -1.0$ (s, *Li*) ppm. ^{11}B{/} NMR (DMSO-d_6, 25 °C): $\delta = -14.5$ (br s, *B*H$_2$) ppm. ^{13}C{H} NMR (DMSO-d_6, 25 °C): $\delta = 159.2$ (s, *C*-NH$_2$) ppm. ^{1}H{/} NMR (DMSO-d_6, 25 °C): $\delta = 5.60$ (br s, 4H, N*H*$_2$), 3.34 (br s, 2H, B*H*$_2$) ppm. EA ($LiBC_2H_6N_{10}$, 187.89): calcd. N 74.55, C 12.78, H 3.22 %; found N 73.64, C 13.06, H 2.87 %. DTA (5 °C min^{-1}): 280 (exothermic) °C. FS (100–500 μm): > 360 N. IS (100–500 μm): > 40 J. ESD (100–500 μm): > 1.5 J.

Deposition Number(s) 1998250 and 1998249 for compounds **3** and **6** and contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

For financial support of this work by Ludwig-Maximilian University (LMU), the Office of Naval Research (ONR) under grant no. ONR N00014-19-1-2078 and the Strategic Environmental Research and Development Program (SERDP) under contract no. W912HQ19C0033 are gratefully acknowledged. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: boron · heterocycles · lithium azolates · lithium bis (azolyl)borates · pyrotechnic colorants

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Manuscript received: June 2, 2020
Revised manuscript received: July 14, 2020
Accepted manuscript online: July 14, 2020