Herein we present the preparation and characterization of three new bispyrazolyl-based energetic compounds with great potential as explosive materials. The reaction of sodium 4-amino-3,5-dinitropyrazolide (5) with dimethyl iodide yielded bis(4-amino-3,5-dinitropyrazolyl)methane (6), which is a secondary explosive with high heat resistance \( T_{\text{det}} = 310 ^\circ \text{C} \). The oxidation of this compound afforded bis(3,4,5-trinitropyrazolyl)methane (7), which is a combined nitrogen-oxygen-rich secondary explosive with very high theoretical and estimated experimental detonation performance \( V_{\text{det}} (\text{theor}) = 9304 \text{ m/s} \) versus \( V_{\text{det}} (\text{exp}) = 9910 \text{ m/s} \) in the range of that of CL-20. Also, the thermal stability \( T_{\text{dec}} = 205 ^\circ \text{C} \) and sensitivities of 7 are auspicious. The reaction of 6 with in situ generated nitrous acid yielded the primary explosive bis(4-diazo-5-nitro-3-oxyopyrazolyl)methane (8), which showed superior properties to those of currently used diazodinitrophenol (DDNP).

"Safer, greener, stronger …" are the main keywords in the development of new explosives for civil but also military purposes. The new materials must meet many different requirements, for example, high performance, insensitivity toward accidental stimuli, stability, vulnerability, low solubility in water, hydrolytic stability, longevity, compatibility, and environmental safety.\(^1\) On the basis of their sensitivities or the time of their deflagration-to-detonation transition, explosives can be classified as secondary and primary explosives. Both groups are divided into subgroups depending on their application. For example, the mining and fracking industry uses heat-resistant explosives, such as hexanitrostilbene (Scheme 1), for deeper drill holes. In contrast, the military uses heat-resistant explosives, such as hexanitrostilbene (HNS), high explosives (hexanitrohexaazaisowurtzitane, CL-20), and primary explosives (DDNP, diazodinitrophenol).

In the current study, three different explosives, 6–8, belonging to the above-mentioned classes were found to show very promising performance and sensitivity characteristics. They are all based on methylene-bridged pyrazoles. Nitropyrazoles have been described as powerful energetic materials.\(^3\) Furthermore, ethylene-bridged pyrazoles, the synthesis of which is more trivial, have been described; however, they have been shown to have weaker performance values.\(^4\)

The present synthetic protocol has been optimized partly on the basis of previous studies. Pyrazole (1) was chlorinated to give 4-chloropyrazole (2) with chlorine generated in situ (NaClO/HCl; Scheme 2).\(^5\) The nitration of 2 was carried out by the use of a \( \text{H}_{2}\text{SO}_{4}/\text{HNO}_{3} \) (100%) mixture.\(^6\) The third step involved the reaction of 4-chloro-3,5-dinitropyrazole (3) with ammonia to give 4-amino-3,5-dinitropyrazole (4).\(^7\) followed by reaction with sodium hydroxide to yield sodium 4-amino-3,5-dinitropyrazolide (5) as a monohydrate salt.\(^8\) The sodium salt 5 was treated with diiodomethane to give bis(4-amino-3,5-dinitropyrazolyl)methane (6),\(^9\) which could be oxidized to bis(3,4,5-trinitropyrazolyl)methane (7) by stirring in a \( \text{H}_{2}\text{O}_{2} \) (50%) / \( \text{H}_{2}\text{SO}_{4} \) mixture. The final step to provide bis(4-diazo-5-nitro-3-oxyopyrazolyl)methane (8) was carried out by diazotation and the generation of \( \text{HNO}_{2} \) (NaNO\(_2 \) + \( \text{H}_{2}\text{SO}_{4} \)) at 0°C.

The solid-state structures of compounds 3 and 5–8 were determined by XRD. All compounds crystallize in common
Compounds 6–8 are valuable energetic materials with moderate sensitivities toward impact, friction, and electrostatic discharge. The measured sensitivity values (according to the German Bundesanstalt für Materialforschung und -prüfung (BAM)) are gathered in Table 1. The impact sensitivities (6: 11, 7: 41) are in the range of those of HNS and pentaerythritol tetroxide (PETN). Compound 8 is more sensitive (1.5 J) and should therefore be classified as a primary explosive. Positive enthalpies of formation were calculated for 6–8 (6: 205, 7: 379, 8: 497 kJ mol⁻¹; see the Supporting Information for details of the computations). With these values, several detonation parameters (Table 1) were calculated by using the EXPLO5 computer code.

The very promising detonation velocity of 7 ($V_{det} = 9304$ m s⁻¹) was corroborated by the estimated detonation velocity determined in a LASEM experimental setup ($V_{det} = 9910 ± 310$ m s⁻¹). In LASEM, the laser-induced air shock velocity is measured by schlieren imaging and correlated to the laser-induced shock velocities of conventional energetic materials to estimate the detonation velocity of the tested energetic material (see the Supporting Information for a closer description of this method). The average measured characteristic laser-induced shock velocity for 7 is shown in Table 2 (along with 95% confidence intervals). The LASEM results suggest that 7 has a higher detonation velocity (at the theoretical maximum density) than CL-20, and the value is almost 600 m s⁻¹ higher than that predicted by EXPLO5 V6.01. However, LASEM is applied as a screening method, and the obtained data are not definitive, but only serve as an indicator of promising performance. Therefore, further testing will be performed to confirm the LASEM results.

The thermal stability of 6–8 at a heating rate of 5 °C min⁻¹ was investigated, and excellent decomposition values were found (6: 310, 7: 205, 8: 226 °C ($T_{de} = 194$ °C)). The decomposition temperature of 8 is lower than the value determined for 1,2-ethylenediamine(4-diazonium-3-nitro-1H-pyrazol-5-olate)[27] but still higher than that of DDNP (Table 1).

In summary, we have introduced three new methylene-bridged nitropyrazole derivatives with potential use as explosives for different applications. Bis(4-amino-3,5-dinitropyrazolyl)methane (6) is a secondary explosive with a high heat resistance ($T_{de} = 310$ °C), enhanced detonation parameters in comparison to those of HNS, and lower sensitivity to

**Figure 1.** Molecular structures of 6–8 with atom labels. Thermal ellipsoids represent the 50% probability level.
Table 1: Energetic properties and detonation parameters of 6–8 and comparison with state-of-the-art compounds.

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>HNS</th>
<th>7</th>
<th>RDX</th>
<th>CL-20</th>
<th>8</th>
<th>DDNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₇H₇N₃O₅</td>
<td>C₂H₂₅N₄O₂</td>
<td>C₂H₂₅N₄O₂</td>
<td>C₂H₂₅N₄O₂</td>
<td>C₂H₂₅N₄O₂</td>
<td>C₂H₂₅N₄O₂</td>
<td>C₂H₂₅N₄O₂</td>
</tr>
<tr>
<td>IS</td>
<td>11</td>
<td>5 (&lt;100 µm)</td>
<td>4</td>
<td>7.5</td>
<td>3</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>FS</td>
<td>&gt; 360</td>
<td>&gt; 360</td>
<td>144</td>
<td>120</td>
<td>96</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>ESD test</td>
<td>&gt; 1.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>Ω [%]</td>
<td>-40.20</td>
<td>-67.6</td>
<td>-11.48</td>
<td>-21.6</td>
<td>-11.0</td>
<td>-44.70</td>
<td>-60.92</td>
</tr>
<tr>
<td>T swore(°C)</td>
<td>310</td>
<td>320</td>
<td>205</td>
<td>210</td>
<td>195</td>
<td>194 (m.p.), 226 (dec.)</td>
<td>157 (dec.)</td>
</tr>
<tr>
<td>Density [g·cm⁻³]</td>
<td>1.802</td>
<td>1.745</td>
<td>1.934</td>
<td>1.806</td>
<td>2.035</td>
<td>1.732</td>
<td>1.719</td>
</tr>
<tr>
<td>ΔH°f [kJ·mol⁻¹]</td>
<td>205</td>
<td>78</td>
<td>379</td>
<td>86</td>
<td>365</td>
<td>497</td>
<td>139</td>
</tr>
</tbody>
</table>

Table 2: Measured laser-induced air shock velocity and detonation velocity (D) estimated by LASEM, along with the theoretically predicted detonation velocity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser-induced shock velocity [m·s⁻¹]</th>
<th>D (estimated) [kms⁻¹]</th>
<th>D [EXPOS 6.01] [kms⁻¹]</th>
<th>D [TMD] [kms⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>849.54 ± 12.50</td>
<td>9.91 ± 0.31</td>
<td>9.304</td>
<td>–</td>
</tr>
<tr>
<td>RDX</td>
<td>806.83 ± 7.74</td>
<td>8.85 ± 0.19</td>
<td>8.834</td>
<td>8.833(178)</td>
</tr>
<tr>
<td>CL-20</td>
<td>835.41 ± 9.52</td>
<td>9.56 ± 0.24</td>
<td>9.673</td>
<td>9.57(210)</td>
</tr>
</tbody>
</table>

[a] TMD is maximum theoretical density.

Experimental Section

General methods, the preparation of 2–5, and more experimental data on 6–8 can be found in the Supporting Information.

Synthesis of 6: Sodium 3,5-dinitro-4-aminopyrazolylmethane (15 mL) was suspended in 25 mL ethyl acetate and diiodomethane (2.68 g, 805 µL, 10 mmol) was added. The mixture was stirred at 90°C for 16 h and then poured into water (100 mL). A little sodium thiosulfate solution is added to reduce the precipitated iodine until the suspension was a clean yellow color. The precipitated product was filtered, washed with a little water, and dried in air to give 6 (3.18 g, 89%) as yellow solid. DSC (5°C·min⁻¹); 310°C (dec.); 1H NMR (400 MHz, [D₈]DMSO, 25°C): δ = 7.29, 7.16 ppm; 13C NMR [1H] (400 MHz, [D₈]DMSO, 25°C): δ = 142.1, 131.7, 130.9, 67.2 ppm; 15N NMR (40.6 MHz, [D₈]DMSO): δ = –23.8 (s, NO₂); –29.3 (s, NO₂); –73.7 (t, J₈=2.7 Hz, N₈py-CH₃); –192.8 (t, J₈=1.1 Hz, N₈py); –314.1 ppm (t, J₈=93.7 Hz, N₈py); elemental analysis: calcd (%): for C₇H₇N₃O₅ (281.19): C: 60.92, H: 6.09, N: 33.09; found: C: 60.91, H: 6.10, N: 33.08.

Synthesis of 7: A solution of 6 (1.0 g, 280 mmol) in concentrated H₂SO₄ (5 mL) was added dropwise to a mixture of 50% H₂O₂ (7.5 mL) and H₂SO₄ (25 mL) at 0°C. The reaction mixture was stirred at 0°C for 3 h and then overnight at room temperature. Subsequently, the reaction mixture was poured onto iced water. Finally, the reaction mixture was isolated by filtration, washed with water, and dried in air to give 7 (1.0 g, 86%). DSC (5°C·min⁻¹): 205°C (dec.); 1H NMR ([D₈]acetone, 25°C): δ = 7.84 ppm; 13C-[1H] NMR ([D₈]DMSO, 25°C): δ = 144.2, 138.8, 123.8, 67.3 ppm; 15N NMR ([D₈]acetone, 25°C): δ = –29.1 (NO₂); –31.0 (NO₂); –33.5 (NO₂) ppm; elemental analysis: calcd (%): for C₂H₂₅N₄O₂ (418.15): C: 60.9, H: 6.84; 13C NMR (29.9 MHz, [D₈]DMSO): δ = –24.9 (NO₂), –139.9 ppm (N=N); 15N NMR (40.6 MHz, [D₈]DMSO): δ = –146.0 (N=N) ppm; –28.7 ppm (NO₂); –84.1 (t, J₅=2.8 Hz, N₅py-CH₃); –139.6 (N=N); –193.0 ppm (N₈py); elemental analysis: calcd (%): for CH₂₅N₄O₅ (522.15): C: 62.0, H: 0.63, N: 43.48; found: C: 62.03, H: 0.63, N: 43.46.
Acknowledgements

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