Research Article

Propellants, Explosives, Pyrotechnics

doi.org/10.1002/prep.202100205

pep.wiley-vch.de

Synthesis, Characterization and Derivatives of Iso-Picramic Acid

Thomas M. Klapötke,[a] Jasmin T. Lechner,[a] and Jörg Stierstorfer*[a]

Abstract: Comparing the sensitive explosives DDNP (2-diazonium-4,6-dinitrophenolate) with iso-DDNP (para-DDNP, 4-diazonium-2,6-dinitrophenolate), it seems obvious that with increasing symmetry in the molecule, the energetic parameters also increase. This work therefore investigates whether the same trend can be applied for the isomers picramic acid (2-amino-4,6-dinitrophenol) and iso-picramic acid (para picramic acid, 4-amino-2,6-dinitrophenol). For this purpose, iso-picramic acid was synthesized and compared with the properties of picramic acid. In addition, selected ionic and other energetic derivatives such as 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol were synthesized. The compounds were extensively studied by XRD, IR, EA, DTA and TGA. Further, their sensitivities towards impact and friction were investigated and the energetic properties were computed using the EXPLO5 code.

Keywords: Nitrophenols · Energtic Materials · NMR spectroscopy · Isomers · Structure Elucidation

1 Introduction

The structures of energetic molecules are diverse, as are their uses. They reaches from covalent compounds like TNT (trinitrotoluene), over (mostly) ionic compounds like lead azide up to coordination compounds like BNCP (tetraamine-cis-bis(5-nitro-2*H*-tetrazolato) cobalt(III) perchlorate). On the other hand, it reaches from very small molecules like mercury fulminate to large molecules e.g. HNS (hexanitrostilbene). Beyond that, there are various applications in the military sector, such as in munitions, and in the civil sector, e.g. in the mining industry [1–7].

However, all energetic compounds have in common that, as the name suggests, there is a high energy release when used. This energy in the molecule is related based on their composition and constitution. An energetic material can be achieved through nitration of a carbon backbone, which combines a fuel (carbon) and an oxidizer (NO_2) in one molecule. A subgroup of these compounds are nitroaromatics where an aromatic ring, such as a benzene ring, constitutes the carbon backbone and nitro groups the oxidizing part. The most common nitroaromatics are shown in Figure 1 [6–9].

TNT, one of the most known and widely used representatives, is synthesized by nitration of toluene using mixed acid. It is used as a melt-castable explosive due to its melting point at around 80 °C [7,10]. Picric acid (PA) replaced black powder in almost all applications at the end of the 19th century [11,12]. It is synthesized similarly to trinitroresorcinol (TNR), also known as sytphnic acid. After initial disulfonation of phenol or resorcinol by sulfuric acid, nitric acid is used for nitration [13,14]. The lead salt of styphnic acid has application as a primary explosive e.g. in primer mixtures. Together with lead azide, it is the most commonly used primary explosive today [7,15]. However, there are problems with the decomposition products due to the use of the toxic heavy metal lead. For example, there is strong lead contamination on military training grounds or firing ranges [1]. Due to the problems with the heavy metal lead, there is a constant search for heavy metal-free primary explosives. One substitute that is used in some primer mixtures is the zwitterionic compound diazodinitrophenol

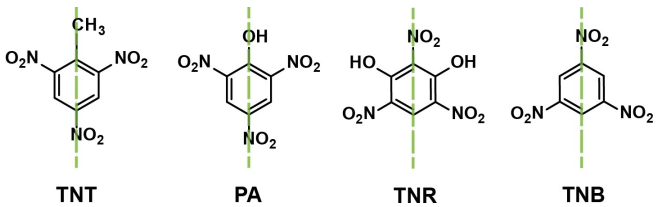


Figure 1. Molecular structure of 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (PA), 2,4,6-trinitroresorcinol (TNR), 1,3,5- trinitrobenzene (TNB). Dashed green lines indicate a symmetry element.

[a] *T. M. Klapötke, J. T. Lechner, J. Stierstorfer*
Department of Chemistry
Ludwig-Maximilian University of Munich
Butenandtstr. 5–13, 81377 Munich (Germany)
**e-mail: jstch@cup.uni-muenchen.de*
Homepage: http://www.hedm.cup.uni-muenchen.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.202100205

(DDNP). DDNP is synthesized by diazotization of picramic acid (PAM) [1,7,16]. Picramic acid can be synthesized by partial reduction of picric acid with sodium hydrogen sulfide or ammonium sulphide [12].

Inspecting the structures of the nitroaromatics shown in Figure 1, it is noticeable that TNT, picric acid, styphnic acid and trinitrobenzene have a (nearly) axial symmetry. In Figure 1 the molecules are drawn one-dimensionally, but in reality the nitro groups are slightly twisted (at ~0 K, or in the rendering provided by an X-ray structure). Neglecting this fact, in the following discussion an axial symmetry is assumed for these molecules.

In DDNP and PAM, however, no axial symmetry can be found. The axially symmetric isomers, iso-DDNP and iso-PAM are also shown in Figure 2. Therefore the question arises, how the symmetrical isomers differ from the asymmetrical ones and if the symmetry might have an influence on the energetic character of these compounds. The symmetric isomer of DDNP was already synthesized by Preimesser *et al.* in 2015 and was recently reinvestigated by Wang *et al.* [17]. Comparing the densities of the two isomers, the density of the symmetrical isomer (1.79 g cm^{-3}) is higher than that one of DDNP (1.73 g cm^{-3}), as well as the heat of formation for isoDDNP (184.1 kJ mol^{-1}) is higher than that of DDNP (142.4 kJ mol^{-1}). When calculating energetic properties, the calculations mainly depends on the enthalpy of formation of the molecules and moreover on the density of the compounds. Therefore, slightly higher energetic parameters are obtained for iso-DDNP. Thus it is interesting, as shown in Figure 2, whether this trend is also visible for picramic acid and iso-picramic acid.

The energetic and molecular properties of picramic acid and its salts are also already described in the literature [12,18]. Iso-picramic acid, in contrast, is very poorly described in literature until now and its properties have not been investigated at all [19]. Therefore, in this work, the symmetric isomer of picramic acid was synthesized and the two isomers were compared with each other in terms of their properties. In addition salts of iPAM were synthesized and compared with the newly synthesized corresponding 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenolates.

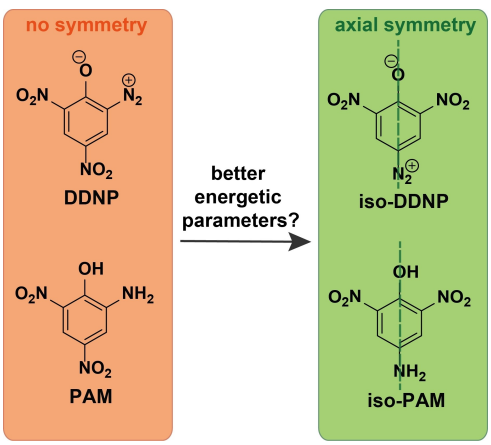


Figure 2. Figure illustrating the symmetric isomers of DDNP and PAM.

2 Experimental Section

Caution! *All investigated compounds are energetic materials and some of them show sensitivities towards various stimuli (e.g. elevated temperature). Although no hazards occurred, proper security precautions (safety glasses, face shield, earthed equipment and shoes, leather jacket, Kevlar sleeves, and earplugs) have to be worn while synthesizing and handling the described compounds.*

The synthesis of **1** and **2** was carried out according to a well working procedure released recently [20].

2.1 4-Acetamino-2,6-Dinitrophenol (1)

4-Acetaminophenol (15.0 g, 0.10 mol, 1.0 eq) was dissolved in concentrated sulfuric acid (96%, 75 mL) at 0 °C. A solution of ammonium nitrate (19.8 g, 0.25 mol, 2.5 eq) in sulfuric acid (96%, 30 mL) was slowly added while cooling to 0 °C. After stirring the reaction mixture for 5 hours at 0 °C it was quenched on ice (500 mL). The precipitation was filtered and washed with a small amount of cold water. 4-Acetamino-2,6-dinitrophenol (**1**, 19.5 g, 0.08 mol, 81%) was obtained as yellow powder. Crystals, suitable for X-Ray diffraction, could be obtained by recrystallization in ethanol.

DTA (5 °C min^{-1}) onset: 171 °C(endo.), 223 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.41 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 141.7, 139.5, 130.5, 120.0, 23.9; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3359 (m), 3175 (w), 3112 (w), 3076 (w), 1685 (m), 1646 (w), 1588 (m), 1551 (s), 1538 (vs), 1519 (s), 1467 (m), 1405 (m), 1364 (m), 1338 (s), 1316 (s), 1279 (s), 1249 (vs), 1147 (s), 1026 (m), 989 (w), 948 (w), 930 (w), 914 (s), 914 (s), 906 (s), 827 (m), 818 (s), 773 (m), 756 (w), 730 (s), 705 (w); EA ($C_8H_7N_3O_6$, 241.16): calcd: C 39.84, H 2.93, N 17.42%; found: C 39.91, H 2.96, N17.21%.

2.2 Iso-Picramic Acid (4-Amino-2,6-Dinitrophenol) (2)

4-Acetamino-2,6-dinitrophenol (**1**, 19.5 g, 80.0 mmol, 1.0 eq) was dissolved in sulfuric acid (96%, 30 mL) at 0 °C. The mixture was heated up to 100 °C and kept at this temperature for one hour. After that, aqueous ammonia (25%, 100 mL) was added at ice cooling conditions. Then sulfuric acid (conc.) was added again until the reaction mixture reached a pH value of 5. The solution was extracted with toluene (3 × 300 mL), the combined organic phases were dried over magnesium sulfate and the solvent was removed *in vacuo*. After recrystallization from ethanol iso-picramic acid (**2**,

0.97 g, 0.005 mol, 6%) was obtained as golden yellow crystals suitable for X-Ray diffraction.

DTA (5 °C min^{-1}) onset: 158 °C (endo.), 183 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.43 (s, 2C*H*); ^{13}C NMR (101 MHz, DMSO) δ (ppm) = 140.3, 114.0; ^{14}N NMR (29 MHz, DMSO-d_6) δ −13; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3185 (w), 3162 (w), 3098 (w), 2789 (m), 2746 (m), 2518 (m), 2511 (m), 2446 (m), 1980 (m), 1935 (w), 1817 (w), 1620 (m), 1534 (m), 1499 (s), 1482 (vs), 1421 (s), 1364 (m), 1333 (s), 1253 (s), 1226 (s), 1190 (s), 1145 (m), 1120 (m), 1102 (m), 966 (m), 913 (m), 896 (s), 828 (s), 799 (s), 779 (vs); EA ($C_6H_5N_3O_5$, 199.12): calcd: C 36.49, H 2.53, N 21.10%; found: C 36.35, H 2,43, N 20.88%; BAM drophammer: > 40 J; friction tester: > 360 N; ESD: 500 mJ (at grain size < 100 μm).

2.3 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenol (3)

Iso-picramic acid (**2**, 500 mg, 2.50 mmol, 1.0 eq) was dissolved in triethyl orthoformate (3 mL) and sodium azide (195 mg, 3.00 mmol, 1.2 eq) was added to the reaction mixture. Over a period of 30 minutes, acetic acid (8 mL) was added dropwise and afterwards it was heated up to 90 °C for 12 hours. The solvent was removed *in vacuo* and the residue was then suspended in water (50 mL) again. After hydrochloric acid (2 M, 10 mL) was added, it was stirred at room temperature for 10 minutes and filtered. 2,6-Dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**, 377 mg, 1.50 mmol, 60%) was obtained as orange solid. Crystals, suitable for X-Ray diffraction, could be obtained by recrystallization in ethanol.

DTA (5 °C min^{-1}) onset: 175 °C (dec.);^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 11.26 (s, 1H), 10.07 (s, 1H), 8.73 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ (ppm) = 147.4, 142.2, 140.7, 123.5, 122.9; ^{14}N NMR (29 MHz, DMSO) δ (ppm) = −17; ^{15}N NMR (41 MHz, DMSO-d_6) δ (ppm) = 11.8 (d, J = 3.4 Hz), −15.5 (dd, J = 1.4 Hz), −19.4 (s), −51.8 (d, J = 12.1 Hz), −140.9 (dt, J = 9.3, 1.9 Hz); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3151 (w), 3089 (w), 3080 (w), 1843 (vw), 1820 (vw), 1790 (vw), 1720 (vw), 1645 (w), 1597 (w), 1561 (m), 1531 (vs), 1489 (s), 1455 (s), 1391 (m), 1373 (m), 1357 (s), 1318 (vs), 1291 (m), 1261 (vs), 1218 (s), 1162 (s), 1089 (s), 1077 (s), 1077(s), 1016 (s), 961(m), 922 (vs), 895 (s), 862 (s), 775 (s), 757 (m); EA ($C_7H_4N_6O_5$, 252.15): calcd: C 33.34, H 1.60, N 33.33%; found: C 33.21, H 1.49, N 32.70%; BAM drophammer: 30 J; friction tester: > 360 N; ESD: 380 mJ (at grain size < 100 μm).

2.4 4-(5*H*-Tetrazol-1-yl)Phenol (3 a)

4-Aminophenol (546 mg, 5.0 mmol, 1 eq) was suspended in triethyl orthoformate (2 mL, 1.8 g, 12.0 mmol, 2.4 eq). Then, sodium azide (488 mg, 7.5 mmol, 1.5 eq) was added followed by the dropwise addition of glacial acetic acid (12 mL). The reaction mixture was refluxed at 100 °C for 5 hours. After slowly cooling to room temperature the resulting precipitation was filtered. The residue was suspended in a mixture of ethanol (25 mL) and water (5 mL). After stirring the suspension for 10 minutes hydrochloric acid (2 M, 5 mL) was added and the mixture was left over night for crystallization. The solid was filtered and washed with a small amount of cold water to yield 4-(5*H*-tetrazol-1-yl)phenol (**3 a**, 318 mg, 2.0 mmol, 40%) as colorless crystals suitable for X-Ray diffraction.

DTA (5 °C min^{-1}) onset: 209 °C (dec.), 270 °C(endo.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 10.12 (s, 1H), 9.90 (s, 1H), 7.71–7.63 (m, 2H), 7.02–6.93 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) = 158.6, 142.1, 125.6, 123.1, 116.2; IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3119 (m), 2837 (w), 2704 (w), 2603 (w), 2495 (w), 1886 (w), 1780 (vw), 1602 (m), 1519 (s), 1480 (m), 1469 (m), 1401 (m), 1374 (m), 1318 (w), 1268 (m), 1237 (s), 1209 (s), 1170 (s), 1110 (w), 1088 (s), 1043 (m), 1014 (m), 1000 (m), 972 (m), 952 (w), 894 (m), 830 (vs), 814 (m), 720 (s), 674 (s); EA ($C_7H_6N_4O$, 162.15): calcd: C 51.85, H 3.73, N 34.55%; found: C 51.54, H 3.83, N 34.59%.

2.5 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenol (3) (Alternative Synthesis)

Under ice cooling conditions, fuming nitric acid (3 mL) was added slowly to concentrated sulfuric acid (6 mL). 4-(1*H*-tetrazol)phenol (**3 a**, 300 mg, 1.85 mmol) was added to the mixture at 0 °C and after complete addition the mixture was allowed to warm up to room temperature and was further stirred for 1 h at this temperature. Then the reaction mixture was quenched on ice water (25 mL) and the precipitate was filtered. 2,6-Dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**, 307 mg, 1.22 mmol, 66%) was obtained as orange crystals suitable for X-Ray diffraction.

EA ($C_7H_4N_6O_5$, 252.15): calcd: C 33.34, H 1.60, N 33.33%; found: C 33.14, H 1.69, N 33.17%.

The synthesis of the following ionic compounds are described in the SI.

2.6 Sodium Iso-Picramate·H_2O (4)

DTA (5 °C min^{-1}) onset: 270 °C (dec.), 139 °C (endo.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3589 (m), 3403 (s), 3139 (m), 1636 (s), 1562 (s), 1550 (vs), 1510 (s), 1475 (m), 1437 (s), 1413 (m), 1336 (vs), 1288 (s), 1251 (vs), 1215 (vs), 1176 (m), 1101 (m), 1079 (s), 1021 (m), 979 (w), 907 (s), 885 (w), 782 (s), 714 (m); EA ($C_6H_6N_3NaO_6$, 239.12): calcd: C 30.14, H 2.53, N 17.57%; found: C 30.10, H 2.46, N17.63%; BAM drophammer: > 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.7 Potassium Iso-Picramate (5)

DTA (5 °C min^{-1}) onset: 270 °C (dec.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3439 (m), 3362 (m), 3221 (w), 3081 (w), 2886 (w), 2723 (w), 1768 (vw), 1650 (m), 1621 (m), 1539 (s), 1520 (vs), 1436 (s), 1420

(s), 1375 (w), 1325 (s), 1292 (w), 1253 (m), 1175 (vs), 1147 (vs), 1119 (vs), 991 (s), 902 (s), 873 (s), 822 (s), 796 (s), 779 (vs), 757 (m), 715 (m), 704 (m), 673 (s), 635 (m), 615 (m); EA ($C_6H_4KN_3O_5$, 237.21): calcd: C 30.38, H 1.70, N 17.71 %; found: C 30.42, H 1.72, N 17.75 %; BAM drophammer: 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.8 Barium Iso-Picramate · 1.5 H_2O (6)

DTA (5 °C min^{-1}) onset: 277 °C (dec.), 175 °C(endo.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3406 (m), 3316 (w), 3301 (w), 3202 (w), 3085 (vw), 2881 (vw), 1635 (w), 1524 (s), 1503 (s), 1490 (s), 1427 (m), 1375 (w), 1334 (s), 1236 (vs), 1152 (m), 1100 (w), 985 (w), 915 (s), 898 (m), 865 (m), 830 (w), 775 (s), 744 (m), 744 (m), 724 (m), 646 (vw); EA ($C_{24}H_{22}Ba_2N_{12}O_{23}$, 1121.16): calcd: C 25.71, H 1.98, N 14.99 %; found: C 25.74, H 1.77, N14.91 %; BAM drophammer: > 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.9 Guanidinium Iso-Picramate (7)

DTA (5 °C min^{-1}) onset: 250 °C (dec.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3411 (vs), 3350 (vs), 3173 (s), 3009 (m), 3001 (m), 1659 (vs), 1635 (m), 1620 (s), 1616 (s), 1563 (m), 1557 (s), 1549 (s), 1539 (s), 1521 (vs), 1489 (m), 1447 (m), 1421 (s), 1335 (s), 1310 (w), 1187 (vs), 1149 (vs), 1119 (vs), 992 (s), 992 (s), 906 (s), 870 (m), 828 (m), 794 (w), 776 (s), 741 (m), 735 (m), 693 (m), 678 (m); EA ($C_7H_{10}N_6O_5$, 258.19): calcd: C 32.56, H 3.90, N 32.55 %; found: C 32.56, H 3.98, N 32.25 %; BAM drophammer: 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.10 Sodium 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenolate · 4 H_2O (8)

DTA (5 °C min^{-1}) onset: 242 °C (dec.), 54/ 115 °C(endo.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3547 (w), 3477 (w), 3470 (w), 3404 (m), 3376 (m), 3310 (m), 3288 (m), 3277 (m), 3259 (m), 3214 (w), 3087 (w), 1663 (w), 1646 (w), 1529 (vs), 1494 (s), 1448 (w), 1427 (m), 1333 (s), 1249 (s), 1160 (m), 1103 (m), 993 (w), 907 (s), 888 (m), 826 (m), 803 (m), 775 (s), 745 (m), 729 (m), 657 (w); EA ($C_7H_{11}N_6NaO_9$, 364.19): calcd: C 24.29, H 3.20, N 24.28 %; found: C 23.95, H 3.16, N 24.60 %; BAM drophammer: > 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.11 Potassium 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenolate · H_2O (9)

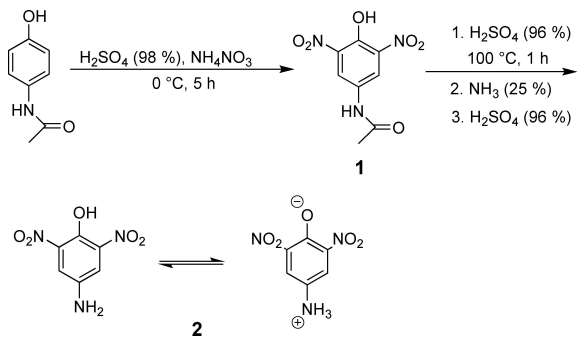
DTA (5 °C min^{-1}) onset: 260 °C (dec.), 88 °C(endo.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3624 (w), 3532 (w), 3483 (w), 3131 (m), 3092 (w), 3039 (w), 1836 (vw), 1637 (s), 1560 (s), 1541 (s), 1536 (s), 1491 (m), 1470 (s), 1438 (s), 1414 (m), 1335 (s), 1288 (s), 1247 (s), 1219 (s), 1190 (s), 1170 (s), 1111 (m), 1097 (s), 1097 (s), 1084 (s), 1021 (m), 972 (m), 906 (vs), 886 (s), 852 (m), 820 (m), 779 (s), 728 (s), 717 (m), 713 (m), 695 (m), 676 (w), 661 (m), ; EA ($C_7H_5KN_6O_6$, 308.25): calcd: C 27.28, H 1.64, N 27.26 %; found: C 27.17, H 1.84, N27.05 %; BAM drophammer: > 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.12 Copper(II) 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenolate · 6 H_2O (10)

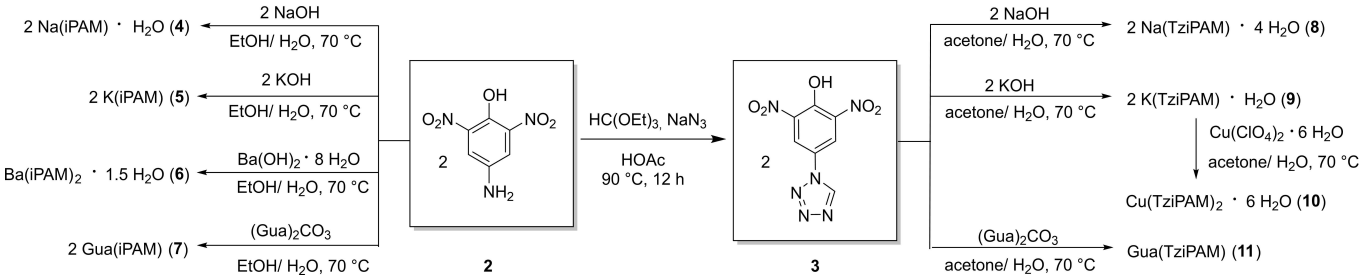
DTA (5 °C min^{-1}) onset: 249 °C (dec.), 114 °C(endo.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3541 (m), 3380 (s), 3129 (s), 3056 (m), 1836 (vw), 1775 (vw), 1756 (vw), 1636 (m), 1621 (m), 1539 (vs), 1509 (s), 1474 (m), 1454 (s), 1404 (m), 1351 (s), 1332 (s), 1309 (s), 1259 (s), 1226 (s), 1195 (s), 1178 (s), 1118 (m), 1097 (s), 1097 (s), 1086 (s), 1031 (m), 1014 (s), 915 (m), 897 (s), 881 (m), 826 (w), 781 (s), 732 (m), 712 (s), 698 (s), 660 (m); EA ($C_{14}H_{18}CuN_{12}O_{16}$, 673.91): calcd: C 24.95, H 2.69, N 24.94 %; found: C 24.84, H 2.53, N39.81 %; BAM drophammer: > 40 J; friction tester: > 360 N (at grain size < 100 μm).

2.13 Guanidinium 2,6-Dinitro-4-(5*H*-Tetrazol-1-yl)Phenolate (11)

DTA (5 °C min^{-1}) onset: 258 °C (dec.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3441 (m), 3414 (m), 3349 (s), 3340 (s), 3302 (m), 3295 (m), 3276 (m), 3182 (s), 3145 (s), 3114 (s), 3093 (s), 2945 (m), 2791 (m), 2438 (m), 2206 (m), 2166 (m), 1820 (vw), 1656 (vs), 1632 (s), 1542 (vs), 1536 (vs), 1503 (s), 1490 (s), 1459 (s), 1438 (s), 1408 (m), 1356 (m), 1330 (vs), 1285 (s), 1232 (vs), 1214 (vs), 1185 (s), 1124 (s), 1106 (s), 1081 (s), 1035 (m), 1006 (m), 987 (m), 941 (w), 904 (s), 890 (m), 858 (s), 821 (w), 781 (s), 770 (s), 712 (s), 659 (w); EA ($C_8H_9N_9O_5$, 311.21): calcd: C 30.87, H 2.91, N 40.51 %; found: C 40.48, H 30.77, N 2.90 %; BAM drophammer: 40 J; friction tester: > 360 N (at grain size < 100 μm).



Scheme 1. Synthesis route of iso-picramic acid (**2**) and equilibrium thereof.



Scheme 2. Synthesis of ionic compounds **4**–**11** of iso-picramic acid (**2**) and 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**).

3 Results and Discussion

3.1 Synthesis

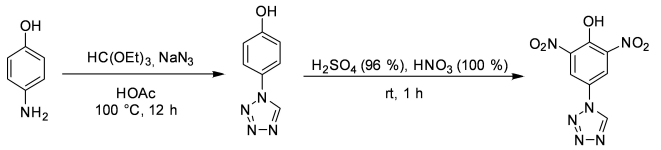
The synthesis of iso-picramic acid was first described by Dabney in 1884 [19]. In this procedure, 5-benzamido-2-hydroxybenzoic acid was used as starting material and was nitrated with a mixture of nitric acid and acetic acid. By splitting off the carboxyl group at the position 2 directly next to the hydroxy group, 4-benzamido-2,6-dinitrophenol was obtained. The benzoyl group was removed and the free amine was obtained by heating in concentrated hydrochloric acid.

In this work, iso-picramic acid (**2**) was prepared according to a different synthetic route (Scheme 1) [20].

Paracetamol is used as starting material, which in contrast to the starting molecule of Dabney does not have a carboxyl group on the benzene ring and in which the amino group is acetyl-protected. Nitration of the two positions next to the hyrdoxyl group with a mixture of concentrated sulfuric acid and ammonium nitrate yields 4-acetamino-2,6-dinitrophenol (**1**). Deprotection to the free amine is achieved by heating in concentrated sulfuric acid. Ammonium iso-picramate precipitates by the addition of ammonia. Treatment with sulfuric acid again yields the neutral compound. Scheme 1 shows the investigated reaction route for iso-picramic acid, an demonstrates that iso-picramic acid (**2**) exists in equilibrium as a zwitterionic compound.

The obtained iso-picramic acid (**2**) was reacted with triethyl orthoformate and sodium azide in acetic acid yielding of 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**). The reaction pathway is shown in Scheme 2.

In addition, an alternative synthesis of 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**) was developed which does not proceed via iso-picramic acid (**2**). Therefore, para-aminophenol was used as starting material. In this route, the tetrazole ring closure with triethyl orthoformate and sodium azide in acetic acid was performed first, whereby 4-(5*H*-tetrazol-1-yl)phenol (**3a**) was obtained. Since the amino group has already reacted to form the tetrazole and is thus blocked, no further protective group chemistry is required and the nitration process can be continued directly. **3a** was then reacted in a nitration reaction with mixed acid to obtain 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**), shown in Scheme 3.

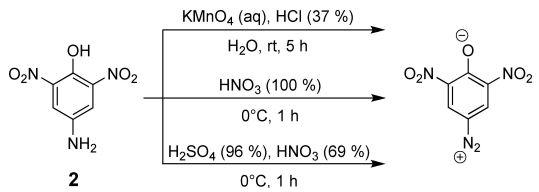


Scheme 3. Alternative synthesis of 2,6-dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**).

The two synthesis routes differ in the order of functionalization. In route 1 (Scheme 2), nitration is carried out first and then the tetrazole ring is closed, in route 2 (Scheme 3) it is the other way round. In route 1, the amine must be protected before nitration can take place and it must be deprotected after nitration. Therefore, route 2 is faster and easier because the tetrazole ring is able to resist the nitration conditions and thus two reaction steps can be saved.

Furthermore, oxidation and azo-coupling of iso-picramic acid was tried. For this purpose, **2** was reacted e. g. with potassium permanganate in hydrochloric acid. Nevertheless, the azo-coupled compound was not obtained, but rather 4-diazo-2,6-dinitrophenol (iso-DDNP) as can be seen in Scheme 4. Also, when trying to nitrate iso-picramic acid (**2**) with different mixed acids or pure nitric acid, again iso-DDNP was obtained.

In addition, various ionic compounds of compound **2** and **3** were synthesized as shown in Scheme 2.



Scheme 4. Synthesis of iso-DDNP starting from iso-picramic acid (**2**).

3.2 Characterization

The synthesized neutral compounds **1**–**3** and **3a** were characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Additionally compound **3** was characterized by proton coupled ^{15}N and two dimensional ^{1}H, ^{15}N HMBC NMR spectroscopy. The measured two dimensional ^{1}H, ^{15}N HMBC spectrum of compound **3** is depicted in Figure 3.

More detailed information about the NMR spectra can be found in the SI.

In addition to NMR spectroscopy compounds **1**–**3** were analysed by IR spectroscopy. The spectra of all compounds can be found in the SI in Figure S1–S3. Comparison of the spectra of picramic acid and iso-picramic acid (**2**) are shown in Figure 4.

Iso-PAM exists as a zwitterionic compound. Thus, a hydroxy group is not present and therefore cannot be found in the IR spectrum. The signals of the stretching vibration of the amino group is slightly shifted compared to PAM but can be assigned to the peaks at 3185 cm^{-1} and 3098 cm^{-1}.

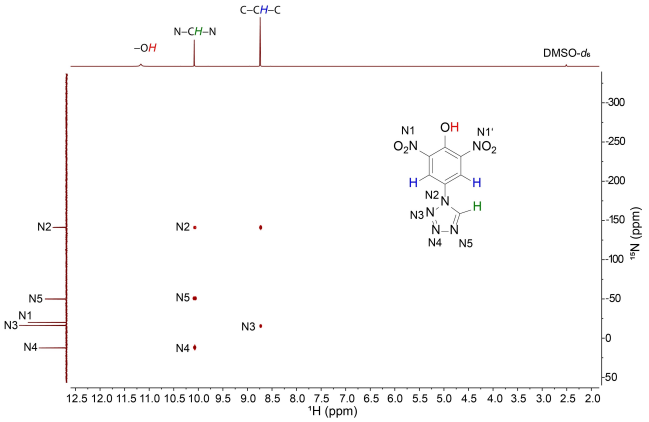


Figure 3. Two dimensional ^{1}H, ^{15}N HMBC NMR spectrum of compound **3**.

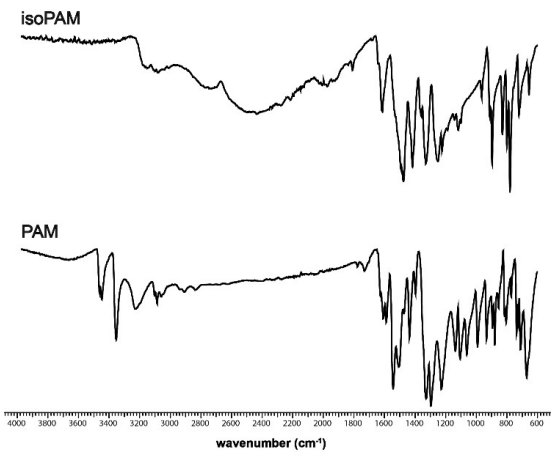


Figure 4. IR spectra of iso-picramic acid (**2**) (top) and picramic acid (bottom) [12].

3.3 Crystal Structures

Single crystal X-ray diffraction experiments of compounds **1**–**3** and **8**–**11** were performed. The crystal structures have been uploaded to the CSD database and are available under the CCDC number 2094681 (**1**), 2094679 (**2**), 2094677 (**3a**), 2094674 (**3**), 2094680 (**8**), 209467 (**9**), 2094676 (**10**) and 2094678 (**11**). Details of the measurement and refinement of the crystal structures can be found in the SI in Table S1–S4.

The crystal structure of 4-acetamino-2,6-dinitrophenol (**1**) can be seen in Figure 5 (left). It crystallizes as a yellow-orange block in the monoclinic space group $P2_1/c$ with a recalculated density of 1.65 g cm^{-3} at 298 K and four molecules per unit cell.

Figure 5 (right) shows the crystal structure of iso-picramic acid (**2**). Here, the compound is presented as a zwitterionic compound with a deprotonated hydroxyl group and a protonated amino group. Iso-PAM (**2**) crystallizes as orange rods in the monoclinic space group $P2_1/c$ with four molecules per unit cell and a density recalculated to room temperature of 1.78 g cm^{-3}. The crystals of iso-picramic acid (**2**) have a golden color and shine viewing without magnification, which can be seen in the microscope images in Figure S8.

Comparing the bond lengths of C4–N3 in **1** (1.408(2) Å) and C4–N2 in **2** (1.453(3) Å), it can be seen that the carbon -nitrogen bond is 0.05 Å longer. The main effect therefore is the acetyl deprotection of the amino group. The bond lengths between the four carbons of the benzene ring and the nitrogen atoms of the nitro groups are in both compounds almost the same between 1.455 Å and 1.465 Å (**1**: 1.459(2) Å, 1.465(2) Å; **2**: 1.458(3) Å, 1.457(3) Å). The bond length C1–O1 is 0.05 Å shorter for the deprotonated oxy-

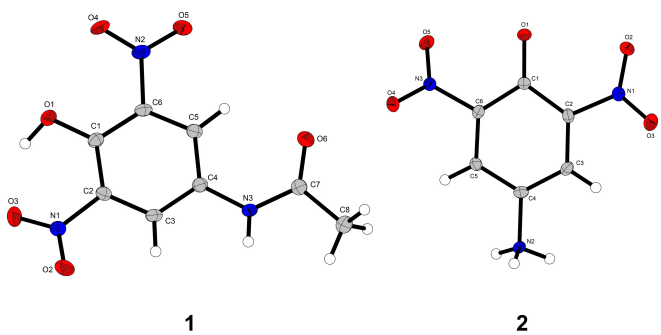


Figure 5. Molecular structure of **1** (left) and **2** (right). Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected bond lengths for **1** (Å): C1–O1 1.3287(18), C4–N3. Selected bond lengths for **2** (Å): C1–O1 1.283(3), C4–N2 1.453(3).

gen of iso-picramic acid (**2**: 1.283(3) Å) than for compound **1** (1.3287(18) Å). The bond angles of compounds **1** and **2** show that the angle between C–C–O of the deprotonated hydroxyl group in iso-picramic acid (123.0(2)°) becomes slightly smaller compared to the protonated hydroxyl group of compound **1** (125.40(14)°). The angle C–C–N to the protonated amino group in **2** (119.3(2)°), on the other hand, becomes slightly larger compared to the protected amino group in **1** (117.46(13)°). Because of the sp^2-hybridization, in compound **2**, the benzene ring, the aromatic protons, the hydroxyl oxygen and all nitrogens are in one plane, only the amino group protons and the oxygens of the nitro groups extend out of the plane.

The crystal structure of 4-(5*H*-tetrazol-1-yl)phenol (**3a**) is shown in Figure 6 (left). It crystallizes as colorless needles in the orthorhombic space group $P2_12_12_1$ with a density of 1.48 g cm^{-3} at 298 K and four molecules per unit cell.

In compound **3a**, the benzene ring and the oxygen of the hydroxy group are in one plane, the tetrazole ring in contrast, turns out of this plane by 38.6(5)° (C3–C4–N1–N2).

Figure 6 (right) shows the crystal structure of compound **3**. 2,6-Dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**) crystallizes as colorless needles in the orthorhombic space group $P2_12_12_1$ with a density of 1.78 g cm^{-3} recalculated to 298 K and four molecules per unit cell.

In compound **3** again, the tetrazole ring and nitro groups turns out of the benzene plane (C5–C4–N2–N3 16.2(4)°, C5–C6–N6–O4 33.8(4)°, C3–C2–N1–O 34.7(4)°). Comparing the structures of **3a** and **3**, the bond length C–O of the hydroxyl group do not differ enormously (**3a**: 1.369(4) Å; **3**: 1.337(4) Å). The bond angle of C2–C1–O1 for the same position, however, becomes slightly larger due to the introduction of the nitro groups in compound **3** (**3a**: 117.8(3)°, **3**: 124.8(3)°). The bond lengths of the tetrazole ring of the two compounds are also comparable (**3a**: 1.359(4) Å, 1.285(4) Å, 1.362(4) Å, 1.320(4) Å, 1.328(5) Å; **3**: 1.361(3) Å, 1.295(4) Å, 1.374(4) Å, 1.314(4) Å, 1.342(4) Å).

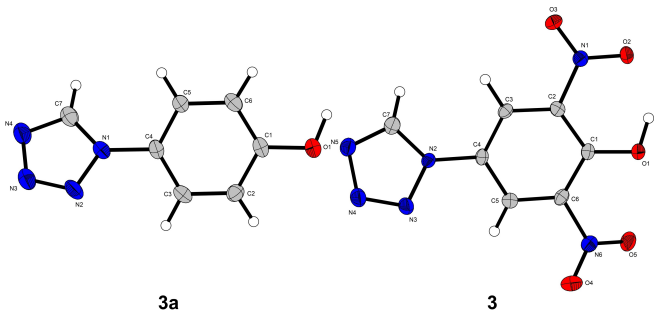


Figure 6. Molecular structure of **3a** (left) and **3** (right). Selected bond lengths for **3a** (Å): C1–O1 1.369(4), C4–N1 1.436(4), N1–N2 1.359(4), N2–N3 1.285(4), N3–N4 1.362(4), N4–C7 1.320(4), C7–N1 1.328(5). Selected bond lengths for **3** (Å): C1–O1 1.337(4), C2–N1 1.467(4), N1–O2 1.246(3), N1–O3 1.217(3), C4–N2 1.426(4), N2–N3 1.361(3), N3–N4 1.295(4), N4–N5 1.374(4), N5–C7 1.314(4), C7–N2 1.342(4).

Comparing the angles C–C–N to the nitro groups of compound **2** and **3**, they are in a similar range (**2**: 120.2(2)°, 118.2(2)°, 115.8(2)°, 116.5(2)°; **3**: 120.3(3)°, 119.6(3)°, 116.6(3)°, 116.9(3)°).

Figure 7 (left) shows the molecular structure of the potassium salt **9** from compound **3**. Compound **9** crystallizes as a monohydrate in the orthorhombic space group *Pnma* with a density of 1.878 g cm^{-3} at 102 K. The guanidinium salt **11** of compound **3** is shown in Figure 7 (right). It crystallizes anhydrously in the triclinic space group *P*-1 with a density of 1.735 g cm^{-3} at 106 K.

3.4 Thermal Analysis

For thermal characterization, differential thermal analysis (DTA) was performed for all compounds using a heating rate of 5°/min. In addition, thermogravimetric analysis (TGA) was performed for **1**, **2** and **3**.

The endothermic and exothermic onset points of all compounds and picramic acid in comparison are shown in Table 1. In addition, the DTA plots of the compounds **1**–**11** are shown in the SI in Figure S4–S6.

For the neutral compounds **1** and **2** both, endothermic and exothermic, signals are detected in the DTA measurement. To determine whether the endothermic signals are due to solvent evaporation or a melting point, additional TGA measurements were carried out and can be found in Figure 8 and Figure S3.

Both compounds **1** and **2** show no loss of weight in the TGA at the temperatures (**1**: 171 °C, **2**: 158 °C) of the respective endothermic signals. Therefore, the endothermic signals can be identified as the melting points of the respective compounds. The exothermic signals from the DTA measurement and the visible mass loss in the TGA agree in temperature (**1**: 223 °C, **2**: 183 °C), so this considers as the decomposition temperature of the compounds. A broadened second exothermic signal at 273 °C can be seen in the DTA plot of iso-picramic acid (**2**). This is probably the decomposition of a previously formed decomposition product. For compounds **3** and **3a**, no endothermic signals are detected in the DTA measurement. The exothermic signals

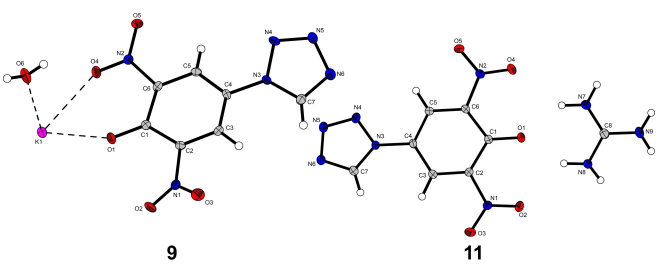


Figure 7. Molecular structure of **9** (left) and **11** (right). Selected bond lengths for **9** (Å): K1–O1 2.8459(12), K1–O4 2.7340(12), K1–O6 2.850(2).

Table 1. Thermal stability as well as sensitivities towards impact, friction and ESD of compounds **1**–**11** and picramic acid for comparison.

	T_{endo} [a] [°C]	T_{exo} [b] [°C]	IS [J][c]	FS [N][d]
Acetaminodinitrophenol (**1**)	171	223	>40	>360
Iso-picramic acid (**2**)	158	183	>40	>360
4-Tetrazolylphenol (**3a**)	–	209	>40	>360
2,6-Dinitro-4-(5*H*-tetrazol-1-yl)phenol (**3**)	–	175	30	>360
Na(iPAM)·H_2O (**4**)	139	270	>40	>360
K(iPAM) (**5**)	–	270	>40	>360
Ba(iPAM)$_2$·1.5 H_2O (**6**)	175	277	>40	>360
Gua(iPAM) (**7**)	–	250	>40	>360
Na(TziPAM)·4 H_2O (**8**)	54/115	242	>40	>360
K(TziPAM)·H_2O (**9**)	88	260	>40	>360
Cu(TziPAM)$_2$·6 H_2O (**10**)	114	249	>40	>360
Gua(TziPAM) (**11**)	–	258	>40	>360
PAM [12]	178	217	>40	>360

[a] Onset point of the endothermic event; [b] Onset point of the exothermic event; [c] impact sensitivity according to the BAM drop-hammer (method 1 of 6); [d] friction sensitivity according to the BAM friction tester (method 1 of 6).

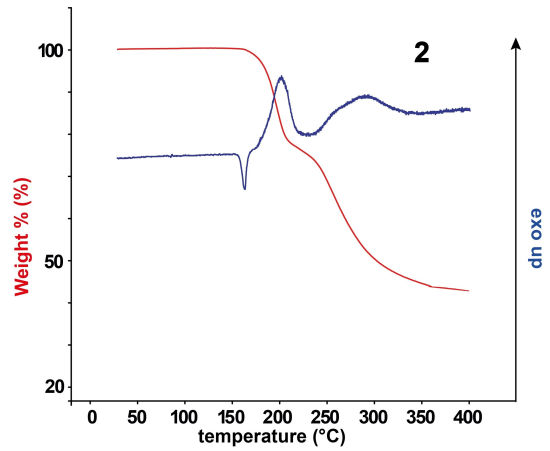


Figure 8. TGA measurement of compound **2**.

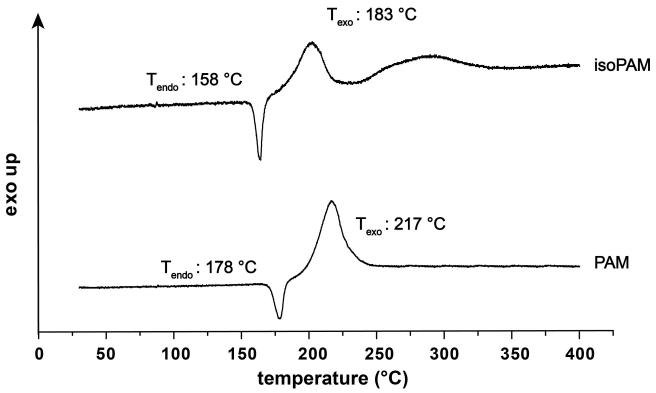


Figure 9. DTA measurement of iso-picramic (**2**, top) acid and picramic acid (bottom) [12].

therefore represent the decomposition temperature of the compounds.

To compare the thermal stability of picramic acid and iso-picramic acid (**2**), their DTA plots are shown in Figure 9.

Here, a melting point for both compounds can be observed. However, the melting point of iso-picramic acid (**2**) is 20 °C lower than that of PAM. The decomposition temperature of iso-picramic acid (**2**) is 34 °C lower than the one of picramic acid. Thus, the symmetric isomer is thermally less stable.

For the ionic compounds, all hydrates (**4**, **6**, **8**, **9**, **10**) show an endothermic signal indicating water loss. All anhydrous ionic compounds (**5**, **7**, **11**) have only an exothermic signal.

3.5 Sensitivities and Energetic Properties

To determine the sensitivities of all compounds **1**–**11**, the sensitivities toward impact (IS) and friction (FS) were tested. The determined values of **1**–**11** and picramic acid for comparison are shown in Table 2.

Considering the impact sensitivities, all compounds, except **3**, with values of >40 J are classified as insensitive according to the UN Recommendations on the Transport of Dangerous Goods [21]. Compound **3** with an impact sensitivity of 30 J is classified as sensitive. All values for friction sensitivity are >360 N and are therefore classified as friction insensitive.

The energetic properties were calculated using the EXPLO5 code version 6.05.04[22] and can be found in Table 2. EXPLO5 calculations are based on the density of the compounds as well as their enthalpy of formation.

The calculated detonation velocity for compound **3** is 7300 m s^{-1}, which is between HNS (7132 m s^{-1}) and picric acid (7426 m s^{-1}) and is higher than the values for TNT (6797 m s^{-1}) and DDNP (6864 m s^{-1}).

Comparing compounds **2** and **3**, it can be seen that both compounds have the same density of 1.78 g cm^{-3} at

Table 2. Energetic properties of compounds **2**, **3** and picramic acid.

	2	**3**	PAM [12]
Formula	$C_6H_5N_3O_5$	$C_7H_4N_6O_5$	$C_6H_5N_3O_5$
FW [g mol^{-1}]	199.12	252.15	199.12
N [%][a]	21.10	33.33	21.10
$\rho_{calc.}$ (298 K) [g cm^{-3}] [b]	1.78	1.78	1.69
$T_{dec.}$ [°C][c]	183	175	217
$\Delta_f H°$ [kJ mol^{-1}][d]	−0.5	159.4	−262.4
Ω_{CO} [%][e]	−28.1	−25.4	−28.1
EXPLO5 version	V6.05.04	V6.05.04	V6.05.04
$P_{C\text{-}J}$ [GPa][f]	22.5	21.0	16.2
V_{det} [m s^{-1}][g]	7458	7300	6553
$-\Delta_{ex}U°$ [kJ kg^{-1}][h]	4568	4072	3347
T_{det} [K][i]	3139	3047	2543
V_0 [L kg^{-1}][j]	638	635	643

[a] Nitrogen content; [b] X-ray density converted to RT; [c] temperature of decomposition indicated by exothermic event according to DTA (onset temperatures at a heating rate of 5 °C min^{-1}); [d] calculated (CBS-4M) heat of formation; [e] Oxygen balance; [f] detonation pressure; [g] detonation velocity; [h] Energy of explosion; [i] Explosion temperature; [j] Assuming only gaseous products.

Table 3. Values for the calculation of the energetic parameters in comparison.

	iPAM zwitterionic exp.	iPAM neutral calc.	PAM neutral exp.	PAM neutral calc.	PAM zwitterionic cal.
$\Delta_f H°$ [kJ mol^{-1}][a]	−0.5	−214.3	−262.4 [12]	−262.4 [12]	−139.2
$\rho_{X\text{-}Ray}$ [g cm^{-3}] [b]	1.78	–	1.69 [12]	–	–
ρ_{Holden} [g cm^{-3}] [c]	–	1.68	–	1.68	1.67
EXPLO5 version	V6.05.04	V6.05.04	V6.05.04	V6.05.04	V6.05.04
$P_{C\text{-}J}$ [GPa][d]	22.5	16.6	16.3	16.0	17.5
V_{det} [m s^{-1}][e]	7458	6607	6546	6513	6716

[a] calculated (CBS-4M) heat of formation; [b] X-ray density converted to 298 K; [c] calculated density according to Holden; [d] detonation pressure; [e] detonation velocity.

298 K, but compound **2** has a better calculated detonation velocity of 7458 m s^{-1}.

Comparing the isomers iso-picramic acid (**2**) and picramic acid, it can be seen that the zwitterionic compound **2** has a significantly higher enthalpy of formation (−0.5 kJ mol^{-1} vs −262.4 kJ mol^{-1}) as well as a higher density (1.78 g cm^{-3} vs 1.69 g cm^{-3}) than PAM. This results in a calculated detonation velocity of 7458 m s^{-1} and in a detonation pressure of 22.5 GPa, these values are very similar to the values of picric acid (V_{det}: 7426 m s^{-1}, $P_{C\text{-}J}$: 23.2 GPa).

In order to draw a conclusion from the calculated parameters with regard to the initial theory that higher symmetry leads to better energetic properties, calculations were also carried out for the neutral iso-picramic acid (see Scheme 1) and hypothetical zwitterionic picramic acid. For this purpose, the enthalpy of formation and the densities according to Holden [23] of the hypothetical isomers were calculated, which can be seen in Table 3. The obtained calculated density for neutral iso-PAM is 1.68 g cm^{-3}, which is the same for PAM (calculated) due to the same binding increments. However, since the CBS-4M heat of formation with −214.3 kJ mol^{-1} for the neutral iso-PAM is higher than that of PAM (−262.4 kJ mol^{-1}), we also obtain better energetic parameters for the neutral iso-PAM (6607 m s−1 and 16.6 GPa) than for PAM (6513 m s^{-1} and 16.0 GPa with Holden density 1.68 g cm^{-3}). A hypothetical zwitterionic PAM shows the same trend in having a higher heat of formation.

4 Conclusion

In this work, iso-picramic acid (**2**), an isomer of picramic acid, was synthesized and characterized. Moreover, the trend that symmetric isomers have better energetic properties could be proofed.

For the symmetric zwitterionic isomer of picramic acid, **2**, a density of 1.78 g cm^{-3} (298 K) was obtained and in addition higher performance parameters than that of PAM can also be determined.

Because iso-picramic acid shows a zwitterionic structure, most of the reactions to transform the -NH_3 group failed and oftentimes iso-DDNP was obtained as the product. The amine could successfully converted to a 5*H*-tetrazole substituent which shows very similar energetic parameters.

Moreover some selected ionic compounds of **2** and **3** were synthesized, investigated and compared but mostly showing poor energetic characteristics.

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. Moreover, the authors would like to thank Dr. Peter Mayer for helping with X-ray crystal structure analysis and Dr. Burkhard Krumm for NMR measurements. Open Access funding enabled and organized by Projekt DEAL.

Data Availability Statement

No data are available.

References

[1] T. M. Klapötke, Chemistry of High-Energy Materials, 5th ed., DE GRUYTER, Berlin/Boston **2019**.
[2] P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt, A review of energetic materials synthesis, *Thermochim. Acta* **2002**, *384*, 187–204.
[3] L. E. Fried, M. R. Manaa, P. F. Pagoria, R. L. Simpson, Design and Synthesis of Energetic Materials, *Annu. Rev. Mater. Sci.* **2001**, *31*, 291–321.
[4] D. M. Budgujar, M. B. Talawar, S. N. Asthana, P. P. Mahulikar, Advances in science and technology of modern energetic materials: An overview, *J. Hazard. Mater.* **2008**, *151*, 289–305.
[5] A. K. Skider, N. Skider, A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications, *J. Hazard. Mater.* **2004**, *112*, 1–15.
[6] J. P. Agrawal, R. D. Hodgson, Organic Chemistry of Explosives, 1st ed., Wiley-VCH, Weinheim **2006**.
[7] J. Köhler, R. Meyer, A. Homburg, Explosivstoffe, 10th ed., Wiley-VCH, Weinheim **2008**.
[8] S. S. Talmage, D. M. Opresko, C. J. Maxwell, C. J. E. Welsh, F. M. Cretella, P. H. Reno, F. B. Daniel, Nitroaromatic munition compounds: environmental effects and screening values, *Rev. Environ. Contam. Toxicol.* **1999**, *161*, 1–156.
[9] T. B. Brill, K. J. James, Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives, *Chem. Rev.* **1993**, *93*, 2667–2692.
[10] E. de Vries, Advances in the Explosive Industry, *Chem.-Ztg.* **1908**, *32*, 765–781.
[11] H. Sprengel, The Discovery of Picric Acid, 2nd ed., Eyre & Spottiswoode, London **1903**.
[12] M. H. H. Wurzenberger, J. T. Lechner, M. Lommel, T. M. Klapötke, J. Stierstorfer, Salts of Picramic Acid-Nearly Forgotten Temperature-Resistant Energetic Materials, *Propellants Explos. Pyrotech.* **2020**, *45*, 898–907.
[13] K. M. Aitken, R. A. Aitken, Nitroarenes, *Sci. Synth.* **2007**, *31*, 1183–1320.
[14] V. Merz, G. Zetter, Ueber einige Derivate des Resorcins und Orcins, *Ber. Dt. Chem. Ges.* **1879**, *12*, 2035–2049.
[15] R. Matyáš, J. Pachman, Primary Explosives, 1st ed., Springer, Berlin, Heidelberg **2013**.
[16] Z. Yang, Y. Liu, D. Liu, L. Yan, J. Chen, Synthesis and characterization of spherical 2-diazo-4,6-dinitrophenol (DDNP), *J. Hazard. Mat.* **2010**, *177*, 938–943.
[17] a) T. M. Klapötke, A. Preimesser, J. Stierstorfer, Synthesis and Energetic Properties of 4-Diazo-2,6-dinitrophenol and 6-Diazo-3-hydroxy-2,4-dinitrophenol, *Eur. J. Org. Chem.* **2015**, *2015*, 4311–4315; b) J.-l. Wang, C. Cao, J.-Y. Cao, Y.-M. Yan, L.-Z. Chen, D.-L. Cao, Synthesis, Characterization and Decomposition of 4-Diazo-2,6-dinitrophenol, *Propellants Explos. Pyrotech.* **2021**, *46*, 1–10.
[18] a) S. P. Agrawal, J. P. Agrawal, Chemistry of metal picramates. I. Picramates of iron, *Indian J. Chem.* **1969**, *7*, 1264–1267; b) S. P. Agrawal, J. P. Agrawal, Chemistry of Metal Picramates, *Def. Sci. J.* **1970**, *20*, 237–248; c) S. P. Agrawal, B. D. Agrawal, Chemistry of zinc, cadmium, and mercury picramates, *Indian J. Chem.* **1972**, *10*, 1106–1107; d) R. S. Srivastava, S. P. Agrawal, H. N. Bhargava, Chemistry of Titanium, Zirconium and Thorium Picramates , *Propellants Explos. Pyrotech.* **1976**, *1*, 101–103.
[19] C. W. Dabney, An Isopicramic Acid, *Am. Chem. J.* **1884**, *5*, 20–38.
[20] www.sciencemadness.org/whisper/viewthread.php?action=printable&tid=439&page=5, accessed 12.2020.
[21] Impact: insensitive >40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive >360 N, less sensitive $=360$ N, sensitive <360 N and >80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.
[22] M. Sućeska, Explo5V6.05.04, Zagreb (Croatia), **2020**.
[23] a) D. A. Cichra, J. R Holden. C. Dickinson, NSWC TR-79-273, **1979**; b) R. L. Willer, Calculation of the Density and Detonation Properties of C, H, N, O and F Compounds: Use in the Design and Synthesis of New Energetic Materialss, *J. Mex. Chem. Soc.* **2009**, *53*, 108–119; c) S. Wahler, Rose Boom 2.0, Munich (Germany), **2021**.

Manuscript received: July 14, 2021
Revised manuscript received: December 10, 2021
Version of record online: January 27, 2022