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Synthesis and Characterization of New Azido Esters Derived from Malonic Acid

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Abstract: Three new α,α-diazidated azido esters derived from malonic acid were synthesized and characterized with a method of diazidation under mild reaction conditions. They are energy-rich, small, liquid molecules which contain up to six azido moieties. The three synthesized compounds were compared to already known azidated malonic acid esters regarding their density, thermal stability, calculated heat of formation and energetic properties. Further they were tested and classified for their sensitivities according to UN guidelines.

Keywords: azides · energy-rich liquids · azido esters · diazidation reaction · high nitrogen content compounds

1 Introduction

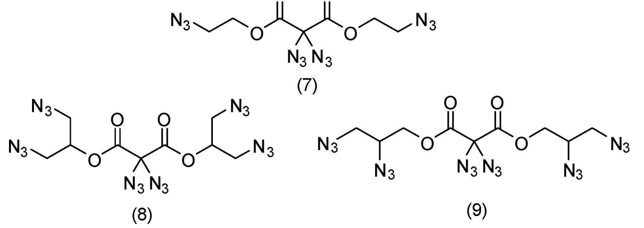
An important additive for solid rocket propellants and gun propellants are plasticizers [1]. Their task is the improvement of the mechanical behavior of polymer binders by increasing the flexibility of the polymer chains. To prevent the loss of energy in these formulations, so called "energetic" plasticizers were developed. By definition they are liquid materials with molecular weights in the range of 200–2000 g mol^{-1} and contain energetic moieties like nitro ($-NO_2$) or azido ($-N_3$) groups. Hence they improve the total energy and the performance of the propellant. Further they have also a positive effect on the oxygen balance and reduce the glass transition temperature.

Therefore organic azides play a crucial role in current research and have due to their versatility a broad range of application like in biology, medicine or material science [2]. Since molecules with one azido group are widely used, also compounds with two or more azido groups attached to the same carbon atom raised attention.

Several different approaches towards α,α-diazido-malonic acids were described in literature. The first synthesis of 2-azido malonate derivative was described in 1910 by Forster. He used a route by electrophilic halogenation and sodium azide substitution [3]. However recent methods use oxidative conditions. The diazidation reaction on the α-position was described by Kirsch et al. in 2012 and 2014 with a route involving IBX-SO_3K as a mild oxidant, sodium azide and catalytic amount of iodine [4]. On the other hand Kamble et al. investigated a synthesis with sodium periodate and sodium azide as reagent system for diazidation of aryl ketones [5]. In 2015 a direct diazidation with iodine and sodium azide at room temperature was published by Kirsch et al. [6]. Yanada suggest a way for synthesis of α,α-diazo-ketones using N-iodosuccinimide (NIS) and trimethylsilyl azide ($TMSN_3$) [7].

Although a great overview over synthesis and chemistry of organic diazides is given by Häring and Kirsch [8] and azido ester plasticizers have still great attention [9] the geminal diazidation of already azidized compounds wasn't described before.

Increasing the energy content of malonic acid esters by inserting more azido groups motivated for the synthesis of new high energy, geminal diazidated, liquid azido esters (**7**–**9**) described in Scheme 1.



Scheme 1. Desired geminal diazidated azido malonic acid ester compounds.

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2 Experimental Section

Caution: Organic azides are classified as toxic and highly explosive. Therefore, every reaction involving them was carried out under the appropriate security measures, including ear, hand and body protection. Although no difficulties in handling these energetic materials was experienced, small-scale use is always preferred.

The chemicals and solvents were purchased from Sigma Aldrich and used without further purification. NMR spectra were recorded with Bruker Avance III (400 MHz). d_6-CDCl3 (δ_H: 7.26, δ_C: 77.36) ($CDCl_3$) was used as solvent and the chemical shifts listed in ppm relative to ^1H and ^{13}C standard tetramethylsilane and ^{14}N standard $MeNO_2$. Elemental analyses were carried on an Elementar Vario el by pyrolysis of the sample and subsequent analysis of the formed gases.

Azidoethanol (1) Sodium azide (14.6 g, 224 mmol, 1.5 eq.) was added portion wise to a stirred mixture of 2-chloroethanol (12.0 g, 149 mmol, 1 eq.) in H_2O (80 mL) at 0 °C. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Additional sodium azide (9.71 g, 149 mmol, 1 eq.) was added and the solution was heated under reflux at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 × 50 mL) and the combined organic phases were washed with Brine (1 × 10 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colorless oil (10.57 g, 121.4 mmol, 81 %). **^1H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 3.77$ (q, 2H, CH_2–OH), 3.43 (t, 2H, CH_2–N_3), 2.16 (s, 1H, –OH). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 61.6$ (CH_2–OH), 53.7 (CH_2–N_3). **^{14}N NMR** ($CDCl_3$, ppm): $\delta = -134$ (N_β), -171 (N_γ), -319 (N_α). $C_2H_5N_3O$ (87.08 g mol^{-1}) calcd. N 48.25, C 27.59, H 5.79 %; found IS: > 40 J. FS: > 360 N.

1,3-diazidopropan-1-ol (2) 1,3-dichloropropan-2-ol (5 g, 38.8 mmol, 1 eq) was stirred in H_2O (25 mL) at 0 °C while sodium azide (7.58 g, 116 mmol, 3 eq) was added portion wise. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Afterwards additional Sodium azide (5.05 g, 77.5 mmol, 2 eq) was added and the reaction mixture was heated at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 × 50 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colorless oil (4.58 g, 32.23 mmol, 83 %). **^1H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 3.93$ (q, 1H, –CH), 3.46–3.73 (m, 2H, –CH_2), 3.00 (s, 1H, –OH). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 69.5$ (CH_2–OH), 53.8(CH–N_3). **^{14}N NMR** ($CDCl_3$, ppm): $\delta = -136$ (N_β), -171 (N_γ), -279 (N_α). $C_3H_6N_6$ (142.1 g mol^{-1}) calcd. N 59.13, C 25.35, H 4.26 %; found N 59.14, C 25.04, H 4.25 %. IS: 10 J. FS: 160 N.

2,3-diazidopropan-1-ol (3) 2,3-dibromopropan-1-ol (2.00 g, 9.18 mmol, 1 eq) was was stirred in H_2O (10 mL) at 0 °C while sodium azide (1.91 g, 29.4 mmol, 3 eq) was added portion wise. The reaction mixture was slowly warmed up to room temperature and stirred for another 4 h. Afterwards additional Sodium azide (1.19 g, 18.4 mmol, 2 eq) was added and the reaction mixture was heated at 80 °C overnight. After completion, the mixture was extracted with Et_2O (3 × 10 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colorless oil (0.82 g, 5.74 mmol, 61 %). **^1H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 3.75$ (m, 1H), 3.70–3.61 (m, 2H), 3.51–3.40 (m, 2H), 2.31 (s, 1H, –OH). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 62.8$ (CH_2–OH), 62.6 (CH–N_3), 51.7 (CH_2–N_3). **^{14}N NMR** ($CDCl_3$, ppm): $\delta = -134$ (N_β), -136 (N_β), -170 (N_γ), -277 (N_α). $C_3H_6N_6$ (142.1 g mol^{-1}) calcd. N 59.13, C 25.35, H 4.26 %; found N 58.77, C 25.05, H 4.09 % IS: 12.5 J. FS: 160 N.

Bis(2-azidoethyl) malonate (4) Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in MeCN (20 mL). 2-azidoethanol (1.67 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at room temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was washed with water (3 × 30 mL) and brine (3 × 30 mL). After removal of the solvent *in vacuo* the product was obtained as colorless oil (1.43 g, 5.89 mmol, 61 %). **^1H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 4.34$–4.32 (m, 4H), 3.53–3.50 (m, 4H), 3.49 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 166.0$ (COO–), 65.1 (–CH_2O), 49.7 (–CH_2N_3), 41.2 (–CH_2). **^{14}N NMR** ($CDCl_3$, ppm): $\delta = -134$ (N_β), -169 (N_γ), -319 (N_α). $C_7H_{10}N_6O_4$ (242.2 g mol^{-1}) calcd. N 34.70, C 34.71, H 4.16 %; found N 30.39, C 34.60, H 4.44 % IS: > 40 J. FS: > 360 N.

Bis(2-azidoethyl) 2,2-diazidomalonate (7) Di-2-azidoethylmalonate (0.50 g, 2.06 mmol, 1 eq) was dissolved in a DMSO/H2O mixture (2 : 1, 20 mL). Sodium azide (0.54 g, 8.26 mmol, 4 eq), Sodium hydrogen carbonate (0.69 g, 8.26 mmol, 4 eq) and iodine (1.15 g, 4,54 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at room temperature and after completion a saturated solution of $Na_2S_2O_3$ was added to quench the remaining iodine. H_2O (15 mL) was added and the mixture was transferred to a separation funnel. The mixture was extracted with EtOAc (3 × 50 mL), the combined organic phases were washed with cold water (3 × 50 mL) and brine (30 × 50 mL). The solution was dried over $MgSO_4$ and the solvent was removed *in vacuo*, to yield the product (0.41 g, 1.28 mmol, 62 %) as yellowish oil. **^1H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 4.46$–4.45 (m, 2H), 3.58–3.57 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 163.2$ (COO–), 80.0 (–C(N_3)$_2$), 66.2 (–CH_2O), 49.4 (–CH_2N_3). **^{14}N NMR** ($CDCl_3$, ppm): $\delta = -134$ (N_β), -142 (N_β), -170 (N_γ), -320 (N_α). $C_7H_8N_{12}O_4$ (342.2 g mol^{-1}) calcd. N 51.84, C 25.93, H 2.49 %; found N 51.72, C 26.28, H 2.60 % IS: 1 J. FS: 36 N.

Bis(1,3-diazidopropan-1-yl) malonate (5) Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in MeCN (10 mL). 1,3-diazido-propan- 2-ol (2.73 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at room temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was then washed with water (3 × 30 mL) and brine (3 × 30 mL). After removal of the solvent *in* *vacuo* the product (2.30 g, 6.55 mmol, 68 %) was obtained as colorless oil. ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 5.05$ (dd, 2H), 3.53–3.43 (m, 8H), 3.34–3.32 (m, 2H). ^{13}**C NMR** ($CDCl_3$, ppm): $\delta = 165.1$ (*C*OO–), 72.0 (–*C*H), 50.6 (–*C*H_2N_3), 40.9 (–CH_2). ^{14}**N NMR** ($CDCl_3$, ppm): $\delta = -135$ (N_β), -170 (N_γ), -324 (N_α). $C_9H_{12}N_{12}O_4$ (352,28 g mol^{-1}) calcd. N 47.71, C 30.69, H 3.43 %; found N 45.59, C 30.73, H 3.61 % IS: 35 J. FS: 160 N.

Bis(1,3-diazidopropyl) 2,2-diazidomalonate (8) Bis(1,3-diazidopropan-1-yl) malonate (0.50 g, 1.42 mmol, 1 eq) was dissolved in a DMSO/H_2O mixture (2 : 1, 14 mL). Sodium azide (0.36 g, 5.68 mmol, 4 eq), Sodium hydrogen carbonate (0.48 g, 5.68 mmol, 4 eq) and iodine (0.90 g, 3.53 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at room temperature and after completion a saturated solution of $Na_2S_2O_3$ was added to quench the remaining iodine. H_2O (15 mL) was added and the mixture was extracted with EtOAc (3×50 mL). The combined organic phases were washed with cold water (3×50 mL) and brine (3×50 mL). The solution as then dried over $MgSO_4$ and the solvent was removed *in vacuo*, to yield the product (0.27 g, 0.69 mmol, 49 %) as yellowish oil. ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): $\delta =$ 5.19–5.12 (m, 2H), 3.67–3.52 (m, 8H). ^{13}**C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 162.5$ (*C*OO–), 79.8 (–*C*$(N_3)_2$), 74.5 (–*C*H), 53.8 (–*C*H_2N_3). ^{14}**N NMR** ($CDCl_3$, ppm): $\delta = -135$ (N_β), -143 (N_β), -171 (N_γ), -320 (N_α). $C_9H_{10}N_{18}O_4$ (434.30 g mol^{-1}) calcd. N 58.05, C 24.89, H 2.32 %; found C 25.55, H 2.52 %IS: < 1 J. FS: 36 N.

Bis(2,3-diazidopropan-1-yl) malonate (6) Malonic acid (1.00 g, 9.61 mmol, 1 eq) was dissolved in MeCN (20 mL). 2,3-diazidopropanol (2.73 g, 19.2 mmol, 2 eq) and DCC (3.97 g, 19.2 mmol, 2 eq) were added. The mixture was stirred for 30 min at room temperature. After completion the mixture was filtered through silica to remove the newly formed urea. The filtrate was washed with water (3×30 mL) and brine (3×30 mL). After removal of the solvent *in vacuo* the product was obtained as colorless oil (2.06 g, 5.86 mmol, 61 %). ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): $\delta = 4.36$–4.30 (dd, 2H), 4.28–4.22 (dd, 2H), 3.81 (m, 2H), 3.51 (s, 2H), 3.47-3.40 (m, 4H). ^{13}**C NMR** ($CDCl_3$, ppm): $\delta = 165.5$ (*C*OO–), 63.7 (–*C*H_2O), 59.6 (–*C*HN_3), 51.6 (–*C*H_2N_3), 41.0 (–CH_2). ^{14}**N NMR** ($CDCl_3$, ppm): $\delta = -135$ (N_β), -137 (N_β), -169 (N_γ), -323 (N_α). $C_9H_{12}N_{12}O_4$ (342.28 g mol^{-1}) calcd. N 47.71, C 30.69, H 3.43 %; found N 46.53, C 30.95, H 3.47 % IS: 35 J. FS: 160 N.

Bis(2,3-diazidopropyl) 2,2-diazidomalonate (9) Bis(2,3-diazidopropan-1-yl) malonate (0.50 g, 1.42 mmol, 1 eq) was dissolved in a DMSO/H_2O mixture (2 : 1, 14 mL). Sodium azide (0.36 g, 5.68 mmol, 4 eq), Sodium hydrogen carbonate (0.48 g, 5.68 mmol, 4 eq) and iodine (0.90 g, 3.53 mmol, 2.5 eq) were added. The mixture was stirred for 4 h at room temperature and after completion a saturated solution of $Na_2S_2O_3$ was added to quench the remaining iodine. H_2O (15 mL) was added and the mixture was extracted with EtOAc (3×50 mL). The combined organic phases were washed with cold water (3×50 mL) and brine (3×50 mL). The solution as then dried over $MgSO_4$ and the solvent was removed *in vacuo*, to yield the product (0.31 g, 0.72 mmol, 51 %) as yellowish oil. ^{1}**H NMR** (400 MHz, $CDCl_3$, ppm): $\delta =$ 4.48–4.35 (m, 4H), 3.88–3.83 (m, 2H), 3.52–3.44 (m, 4H). ^{13}**C NMR** (101 MHz, $CDCl_3$, ppm): $\delta = 163.0$ (*C*OO–), 80.1 (–*C*$(N_3)_2$), 66.7 (–*C*H_2O), 59.3 (–*C*HN_3), 51.4 (–*C*H_2N_3). ^{14}**N NMR** ($CDCl_3$, ppm): $\delta = -135$ (N_β), -136 (N_β), -142 (N_β), -168 (N_γ), -327 (N_α). $C_9H_{10}N_{18}O_4$ (434.30 g mol^{-1}) calcd. C 24.89, H 2.32 %; found C 25.40, H 2.43 % IS: < 1 J. FS: 36 N.

3 Results and Discussion

3.1 Synthesis

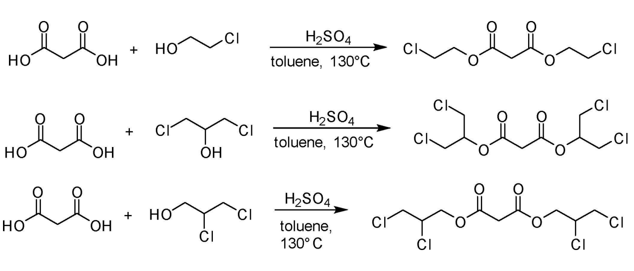
Before conducting the reaction of geminal diazidation the syntheses of the three malonic acid esters as precursors were carried out in two different ways.

According to literature the syntheses of the chloro-derivatives via acid esterification reaction of malonic acid and the chloro-alcohols in toluene was performed, shown in Scheme 2 [10]. Followed then by the chlorine azide exchange reaction, the yield of the obtained azido ester precursors (**4**–**6**) within this way was significantly lower than expected (lower than 40 %);

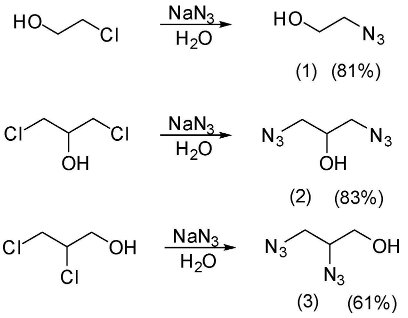
Therefore a second way via direct coupling of the respective azidoalcohols with malonic acid in milder reaction conditions was tried.

For these reactions the required starting materials, 2-azidoethanol (**1**) and the two diazidopropanols (1,3-diazidopropanol (**2**) and 2,3-diazidopropanol (**3**)), were synthesized from their corresponding chloro-derivatives via halogen azide exchange reaction in water [11]. Syntheses are shown in Scheme 3. The azido alcohols (**1**)–(**3**) could be obtained in over 80 % yields.

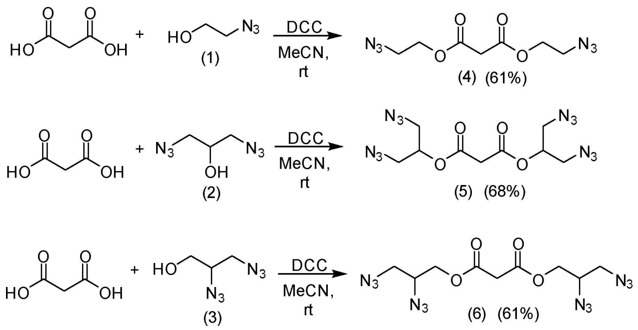
The esterification reactions were now carried out at room temperature via coupling reagent DCC and the respective synthesized azidoalcohols (**1**)–(**3**) to increase the yield [12]. The products bis(2-azidoethyl) malonate (bAEM, **4**), bis(1,3-diazidopropan-1-yl) malonate (b-1,3-DAPM, **5**) and bis(2,3-diazidopropan-1-yl) malonate (b-2,3-DAPM, **6**) could be obtained in good yields (over 60 %) without further purification steps [12]. The coupling reactions are shown in Scheme 4.



Scheme 2. Syntheses of chloro malonic acid esters.



Scheme 3. Synthesis of 2 azidoethanol (**1**), 1,3-diazidopropanol (**2**) and 2,3-diazidopropanol (**3**).



Scheme 4. Synthesis of azido ester malonates.

Based on the synthesized precursor azido ester compounds (**4**)–(**6**), the α,α-diazidation reaction was performed and different conditions from literature were tried.

Neither with IBX-SO_3K nor via the sodium periodate route the desired geminal diazidated azido malonates could be yielded. Although compound **7** could be observed by NMR spectroscopy, purification within these routes was not possible. The reaction conditions of 50 °C lead to degradation of the formerly synthesized azido esters.

Therefore an alternative route with milder reaction conditions was tried for the azido esters [6]. Sodium bicarbonate and iodine was used together with sodium azide in DMSO/H_2O at room temperature. Within this method bis(2-azidoethyl) 2,2-diazidomalonate (DA-bAEM, **7**) was yielded according to Scheme 5 and characterized for the first time.

DA-bAEM **7** shows two different signals in the ^1H NMR spectrum at 4.45 ppm and 3.58 ppm for the two methylene groups. The resonances in the ^{13}C spectrum appear at 163 ppm for the carboxylic acid ester carbon, at 80 ppm for the geminal diazidated carbon atom and at 66 ppm and 50 ppm for the CH_2-groups. The α,α-diazidated carbon is now shifted from 65 ppm for the non-azidated carbon to 80 ppm.

To introduce more azido groups, the geminal diazidation was also carried out from the formerly synthesized azidopropanol esters (**5**) and (**6**).

Both desired products, bis(1,3-diazidopropyl) 2,2-diazidomalonate (**8**) and bis(2,3-diazidopropyl) 2,2-diazidomalonate (**9**) could be yielded within this method and characterized for the first time.

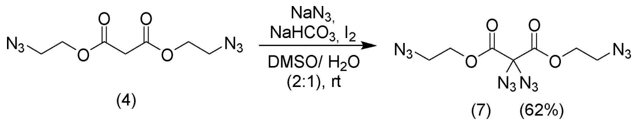
Syntheses of both propyl azido esters (**8** and **9**) are represented in Scheme 6 and Scheme 7.

For compound **8** the two hydrogen signals appear at 5.15 ppm and 3.60 ppm. The carbon signals in the ^{13}C NMR spectrum can be assigned at 163 ppm for the carboxylic acid ester carbon, at 80 ppm for the geminal diazidated carbon and at 75 ppm and 54 ppm for the carbons of the azido propyl residue.

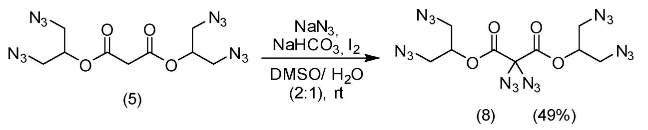
In the ^1H NMR the three signals for the hydrogens from the propyl residue of compound **9** appear at 4.40 ppm, 3.85 ppm and 3.50 ppm with integrals of 4:2:4. The carbon signals in the ^{13}C NMR spectrum can be allocated at 163 ppm for the carboxylic acid ester carbon, at 80 ppm for the geminal diazidated carbon and at 67 ppm, 60 ppm and 51 ppm for the propyl residue carbons.

3.2 Physicochemical and Energetic Properties

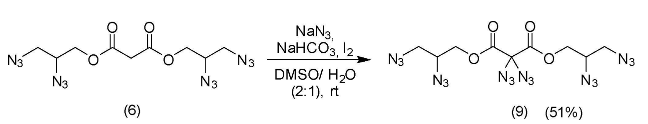
The physicochemical and energetic properties of the three new geminal diazidated azido malonic acid esters are shown in Table 1. They were compared to the synthesized precursor azido esters (**4–6**). The energetic parameters like heat of combustion, detonation pressure, detonation velocity and volume of gaseous products were calculated using version 6.03 of Explo5 [13]. Decomposition temperatures were measured via differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 °C min^{-1} and in a range of room temperature to 400 °C. Concerning the decomposition temperatures of the azido



Scheme 5. Synthesis of DA-bAEM (**7**).



Scheme 6. Synthesis of DA-b-1,3-DAPM (**8**).



Scheme 7. Synthesis of DA-b-2,3-DAPM (**9**).

Table 1. Physicochemical and energetic properties according to Explo 5V6.03.

Formula	bAEM (**4**) $C_7H_{10}N_6O_4$	DA-bAEM (**7**) $C_7H_8N_{12}O_4$	b-1,3-DAPM (**5**) $C_9H_{12}N_{12}O_4$	DA-b-1,3-DAP (**8**) $C_9H_{10}N_{18}O_4$	b-2,3-DAPM (**6**) $C_9H_{12}N_{12}O_4$	DA-b-2,3-DAPM (**9**) $C_9H_{10}N_{18}O_4$
M [$g\,mol^{-1}$]	242	324	352	434	352	434
Ω^a [%]	−99	−69	−90	−70	−91	−70
$T_{dec}{}^b$ [°C]	191	158	162	136	162	136
ρ^c [$g\,cm^{-3}$]	1.38	1.49	1.38	1.51	1.30	1.50
$\Delta H_f{}^{od}$ [$kJ\,mol^{-1}$]	−176	542	466	1186	440	1160
Explo 5V6.03						
$-\Delta_{Ex}U^{oe}$[$kJ\,kg^{-1}$]	−2828	−4001	−3647	−4359	−3578	−4300
$T_{det}{}^f$ [K]	2150	3016	2769	3227	2636	3207
$P_{CJ}{}^g$ [k bar]	118	170	160	181	119	178
$V_{det}{}^h$ [$m\,s^{-1}$]	6192	6974	6576	7147	6252	7087
Vo^i [$L\,kg^{-1}$]	562	514	530	507	588	509

(a) Oxygen balance assuming the formation of CO_2 (b) Onset decomposition point T_{dec} from DSC measurement (c) RT densities (d) Enthalpy and of formation calculated by the CBS-4M method using Gaussian 09.23 (e) Predicted heat of combustion, (f) detonation temperature (g) detonation pressure, (h) detonation velocity, and (i) volume of gaseous products.

esters **4–6**, the compounds show an appropriate thermal stability of 191 °C for **4** and around 160 °C for **5** and **6**. The temperatures of geminal diazidated compounds **7–9** decrease around 20 °C in comparison to the precursor's cause of higher energy content at α-carbon atom. The density of the compounds was determined by mass and volume using a 1 mL syringe and Excellence Analytical Balance XA204 from Mettler Toledo. The value was calculated as the average from five measurements at 22 °C. The density of the synthesized geminal diazidated compounds increases from around 1.35 $g\,cm^{-3}$ for azido esters to 1.50 $g\,cm^{-3}$ for geminal diazidated compounds. The calculations of the heat of formation (H_f) were carried out using Gaussian 09 [14] and the modified method of Complete Basis Set (CBS-4 M) developed by Petersson and co-workers to obtain accurate values [15].

3.3 Sensitivities

Further the sensitivities of all synthesized azido compounds against impact and friction were determined according to BAM [16] (Bundesanstalt für Materialforschung und -prüfung) standards using a BAM drop hammer and a BAM friction apparatus [17]. The compounds were classified in compliance with UN guidelines [18] (see Table 2). Azidoethanol (**1**) turned out to be insensitive towards friction and impact. Both diazidopropanols (**2** and **3**) could be classified as sensitive towards friction and impact according to UN guidelines. The azido ester with ethyl residue (**4**) is classified as insensitive, while the azido esters with propyl residue (**5** and **6**) are sensitive.

The geminal diazidated compounds (**7–9**) increase as expected their sensitivity and can be classified as very sensitive.

Table 2. Impact and friction sensitivities and classification according to UN Guideline.

Compound	Impact sensitivity	Friction sensitivity	UN Guideline
AzEtOH (**1**)	>360 N	>40 J	insensitive
1,3-DAP (**2**)	160 N	12.5 J	sensitive
2,3-DAP (**3**)	160 N	10 J	sensitive
bAEM (**4**)	>360 N	>40 J	insensitive
b-1,3-DAPM (**5**)	160 N	35 J	sensitive
b-2,3-DAPM (**6**)	160 N	35 J	sensitive
DA-bAEM (**7**)	36 N	1 J	very sensitive
DA-b-2,3-DAPM (**8**)	36 N	<1 J	very sensitive
DA-b-1,3-DAPM (**9**)	36 N	<1 J	very sensitive

4 Conclusions

Three new liquid azido esters of high energy content derived from malonic acid were synthesized with a method of α,α-diazidation reaction. Therefore, the azido ester precursors were prepared via coupling reaction of malonic acid and the respective previously synthesized azidoalcohols. Further mild reaction conditions were used together with sodium bicarbonate, sodium azide and iodine to achieve the geminal diazidation of the formerly synthesized azido esters. Their characterization included measurements of sensitivities towards heat, impact and friction. Their energetic properties were calculated using Explo5 V6.03. The synthesized α,α-diazido azido esters have high nitrogen content, positive heat of formation and high detonation velocity.

These properties could fit the requirements for suitable additives in propellant formulations.

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