Propellants, Explosives, Pyrotechnics

Supporting Information

Synthesis and Characterization of Azido Esters as Green Energetic Plasticizers

Jovica Nešić,* Ilija N. Cvijetić, Jovica Bogdanov, and Aleksandar Marinković

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Synthesis and characterization of azido ester as green energetic plasticizers

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1 Synthesis

1.1 Oxybis(ethane-2,1-diyl)bis(2-chloroacetate) (DEG-Cl)

2,2'-oxybis(ethan-1-ol) (DEG; 3.94 g, 3.53 mL, 0.0372 mol) dissolved in dry tetrahydrofuran (THF; 10 mL) was added in the presence of triethylamine into a dried three-necked round bottom flask (100 mL) equipped with a magnetic stirrer, reflux condenser, calcium chloride tube, thermometer, dropping funnel, and ice-cold water bath. Then chloroacetyl chloride (ClAcCl; 8.417 g, 0.0745 mol) in dry THF (15 mL) was added dropwise for 2 hours at the temperature in the range from 0 to 5 ºC in the presence triethylamine (TEA; 10.39 ml, 7.53 g, 0.0745 mol). After that the temperature was allowed to rise to 20 ºC for the next 12 hours. Then the reaction mixture was heated to 50 ºC for another 2 hours. The product was purified using a two-step process. At first the solvent and the excess of ClAcCl were removed by distillation, and the remaining product was dissolved in chloroform, washed with aqueous sodium hydrogencarbonate (3 wt. %) and twice with deionized water. After drying with anhydrous sodium sulfate and solvent removal by distillation, the product DEG-Cl was obtained as a yellow oily product. Spectroscopic data and elemental analysis: ^{1}H NMR (400 MHz, DMSO-d_6, ppm) DEG-Cl: 3.68 (4H, *t*, C(4)H_2 and C(5)H_2), 4.08 (4H, s, C(1)H_2 and C(8)H_2), 4.34 (4H, t, C(3)H_2 and C(6)H_2). IR (ATR, cm-1): 3427 (OH), 2957, 2882, 1452, (CH_2), 1754 (ester), 1180 (C-O), 784 (C-Cl). $C_8H_{12}Cl_2O_5$ (259.08 g mol^{-1}): calc. C 37.09, H 4.67, found C 36.09, H 4.54 %.

1.2 Oxybis(ethane-2,1-diyl)bis(2-azidoacetate) (DEGBAA)

Reaction of oxybis(ethane-2,1-diyl)bis(2-chloroacetate) (DEG-Cl) with sodium azide (NaN_3, 5 % molar excess) was carried out in DMSO. The mixture was stirred for 10 hours at 60 ºC.
The obtained product was diluted with a large excess of deionized water and extracted with ethyl acetate three times. The combined organic solution was washed with deionized water, dried over sodium sulfate and the solvent was removed carefully under vacuum (p = 2000 Pa). A yellowish oily product was obtained (94 wt. % yield).

1.3 1-((1-(2-chloroacetoxy)propan-2-yl)oxy)propan-2-yl 2-chloroacetate (DPG-Cl)

1,1'-oxybis(propan-2-ol) and 3,3'-oxybis(propan-1-ol) (DPG; 5 g, 4.9 mL, 0.0372 mol) dissolved in dry THF (10 mL) was added in a dried three-necked round bottom flask (100 mL) equipped with a magnetic stirrer, reflux condenser, calcium chloride tube, thermometer, dropping funnel, and ice-cold water bath. Then ClAcCl (8.417 g, 0.0745 mol) in dry THF (15 mL) was added dropwise. In the first 2 hours, the reaction temperature was kept between 0 and 5 ºC in the presence of triethylamine (TEA; 10.39 ml, 7.53 g, 0.0745 mol). Afterward, the temperature was increased to 20 ºC, kept constant for 12 hours, followed by heating to 50 ºC and thermostating during the next 2 hours, which resulted in 1-((1-(2-chloroacetoxy) propan-2-yl)oxy)-propan-2-yl 2-chloroacetate. The product was purified using a two-step process. First, the solvent was distilled to remove unreacted or hydrolized ClAcCl, followed by product dissolution in chloroform, and washing with 3 wt. % sodium hydrogencarbonate and two times with deionized water. After drying with anhydrous sodium sulfate and solvent removal by distillation, the product DPG-Cl was obtained as a yellow oily product. Spectroscopic data and elemental analysis: *DPG-Cl mixture of structural isomers I and II. Structural isomer I*: ^{1}H NMR (400 MHz, DMSO-d_6, ppm), DPG-Cl: 1.23 (3H, *m*, -C(7)H_3), 1.28 (3H, *m*, -C(4)H_3), 3.71 (2H, m, C(5)H_2), 3.97 (2H, m, C(6)H_2), 4.05 (2H, *s,* C(10)H_2 2H), 4.09 (2H, s, C(1)H_2), 4.22 (2H, m, C(8)H_2), 4.96 (1H, m, C(3)H).

Structural isomer II: ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 1.28 (6H, *m*, -C(7)H_3 and C(4)H_3), 3.71 (2H, m, C(5)H_2), 3.97 (2H, m, C(6)H_2), 4.05 (2H, *s*, -C(10)H_2 and C(1)H_2), 4.96 (2H, m, C(3)H and C(8)H). IR (ATR, cm^{-1}): 3491 (OH), 2976, (CH_3), 1742 (ester), 1194 (C=O), 782 (C-Cl). $C_{10}H_{16}Cl_2O_5$ (287.13 g mol^{-1}): calc. C 41.83, H 5.62 %; found C 41.21, H 5.15 %.

1.4 1-((1-(2-azidoacetoxy)propan-2-yl)oxy)propan-2-yl 2-azidoacetate (DPGBAA)

The reaction of 1-((1-(2-chloroacetoxy) propan-2-yl)oxy)-propan-2-yl 2-chloroacetate with NaN_3 (2.05 mol, 5 % molar excess) was carried out in the presence dimethylformamide (DMF) at 60 ºC and stirred for 10 hours.

1.5 2.2.5. Hexane-1,2,6-triyl tris(2-chloroacetate) (HET-Cl)

Hexane-1,2,6-triol (HET; 5 g, 4.5 mL, 0.0372 mol) dissolved in dry THF (10 mL) was added in a dried three-necked round bottom flask (100 mL), equipped with a magnetic stirrer, reflux condenser, calcium chloride tube, thermometer, dropping funnel, and ice-cold water bath. Then chloroacetyl chloride (ClAcCl 8.90 ml, 12.64 g, 0,112 mol) in dry THF (15 mL) was added dropwise in the presence of triethylamine (TEA; 15.61 ml, 11.33 g, 0,112 mol). In the first 2 hours, the reaction temperature was between 0 and 5 ºC. After that, the temperature was risen to 20 ºC and kept for 12 hours. Then the temperature was risen to 50 ºC and kept constant for the next 2 hours. The product was purified in a two-step process, first one solvent removal by distillation followed by fractional distillation of the product. Spectroscopic data and elemental analysis: ^{1}H NMR (400 MHz, DMSO-d_6, ppm) HET-Cl: 1.22-1.54 (6H, m, C(4)H_2, C(5)H_2 and C(6)H_2), 4.08 (6H, t, C(1)H_2, C(10)H_2 and C(12)H_2), 4.13- 4.22 and 4.30-4.41 (4H, m, C(3)H_2 and C(8)H_2), 5.17 (1H, m, C(7)H). IR (ATR, cm^{-1}): 3427 (OH), 2957, 2882, 1452, (CH_2), 1754 (ester), 1180 (C=O), 784 (C-Cl). $C_{12}H_{17}Cl_3O_6$ (363.61 g mol^{-1}): calc. C 39.64, H 4.71 %, found C 38.74, H 4.64 %.

1.6 2.2.6 Hexane-1,2,6-triyl tris(2-azidoacetate) (HETTAA)

Hexane-1,2,6-triyl tris(2-azidoacetate) reaction with NaN_3 (5 % molar excess) was done in the presence of DMF. The mixture was stirred at 60 ºC for 10 h.

2 ^{1}H NMR Spectroscopy

2.1 Oxybis(ethane-2,1-diyl)bis(2-azidoacetate) (DEGBAA)

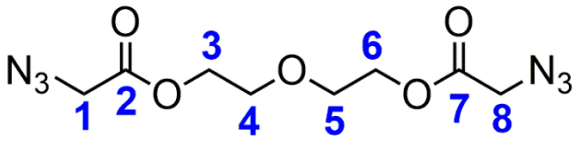

Figure S1 Structure of DEGBAA with the atom numeration

2.2 1-((1-(2-azidoacetoxy)propan-2-yl)oxy)propan-2-yl 2-azidoacetate (mix isomer) (DPGBAA)

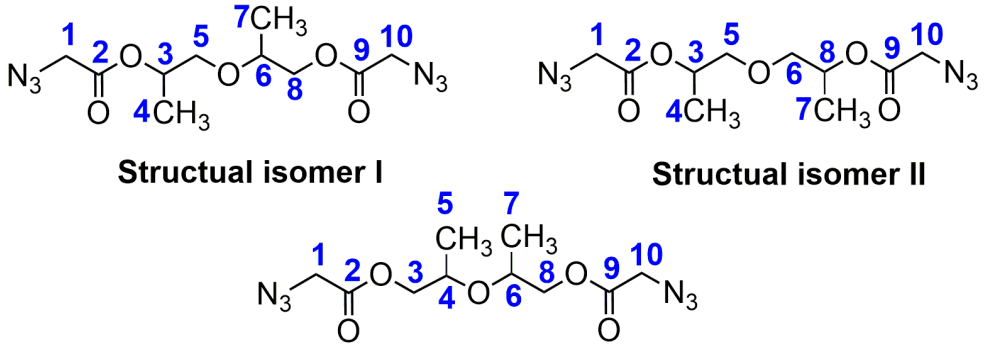

Figure S2 Structural isomerism of DPGBAA with the atom numeration

2.3 Hexane-1,2,6-triyl tris(2-azidoacetate) (HETTAA)

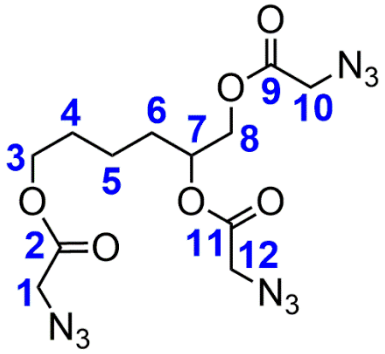

Figure S3 Structure of HETTAA with the atom numeration

3 IR Spectroscopy

3.1 Oxybis(ethane-2,1-diyl)bis(2-azidoacetate) (DEGBAA)

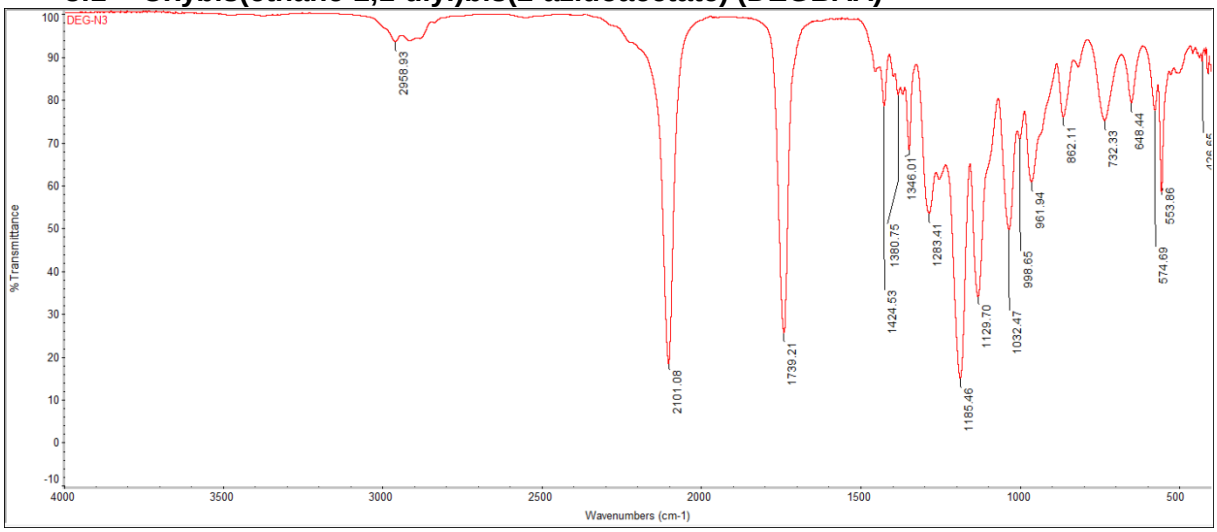

Figure S4 FTIR spectrum of DEGBAA

3.2 1-((1-(2-azidoacetoxy)propan-2-yl)oxy)propan-2-yl 2-azidoacetate (mix isomer) (DPGBAA)

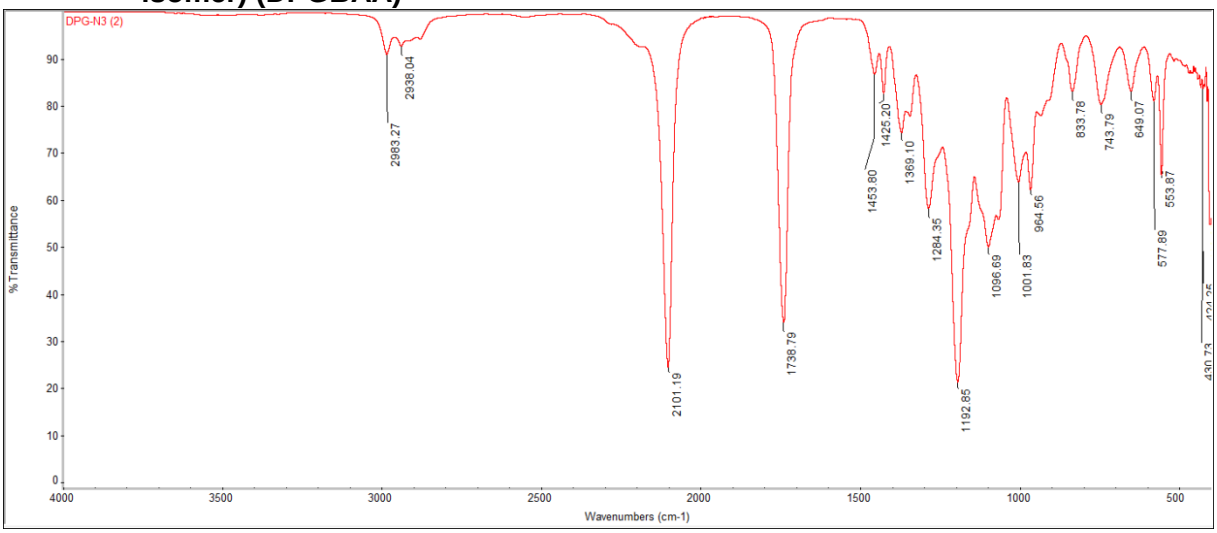

Figure S5 FTIR spectrum of DPGBAA

3.3 Hexane-1,2,6-triyl tris(2-azidoacetate) (HETTAA)

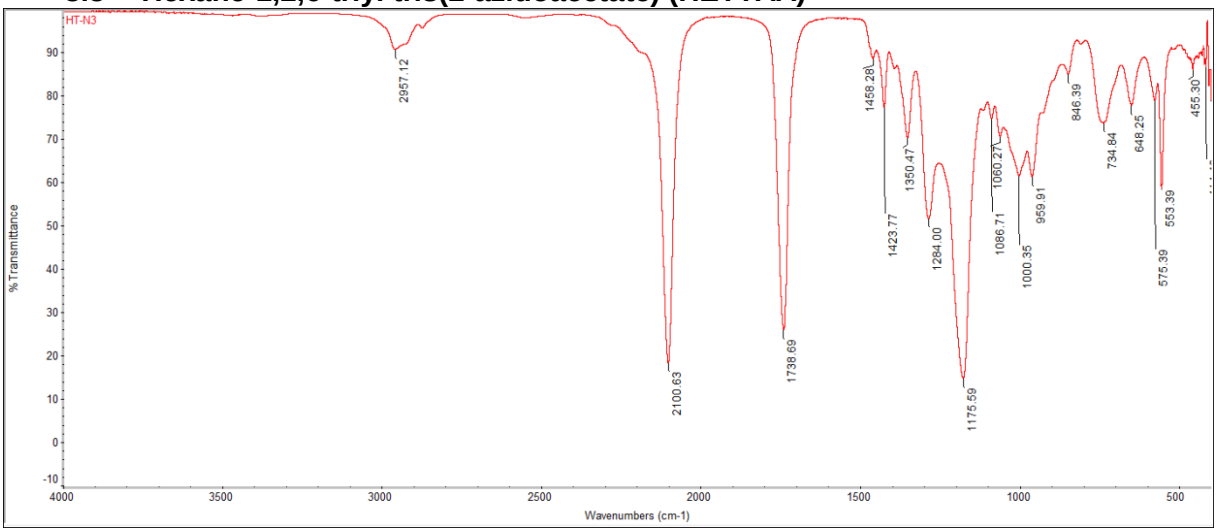

Figure S6 FTIR spectrum of HETTAA

4 Calculation

The electronic enthalpies of C, H, N and O atoms and their corresponding experimental heats of formation ($\Delta_f H^0_{atoms,298}$) are listed in Table 1.

Table 1. CBS-4M enthalpies of C, H, N, and O atoms and experimental heats of formations from [1]

CBS-4M	H298, a.u.	$\Delta_f H^0_{atoms,298}$ kJ/mol (NIST),
C	-37.786156	717.2
H	-0.500991	218.2
N	-54.522462	473.1
O	-74.991202	249.5

The condensed phase HOF is a necessary parameter for estimating physical properties of novel EMs. It can be determined from the Hess's law, using the gas-phase HOF and enthalpy of vaporization (for liquid samples, or sublimation for solids):

$$\Delta_{\mathrm{f}}H^{0}_{liquid} = \Delta_{\mathrm{f}}H^{0}_{gas} - \Delta H_{\mathrm{vaporization}}$$

The enthalpy of vaporization might be predicted from the quantities derived from MEP, using the Politzer's approach [2,3], which can be expressed as:

$$\Delta H_{\mathrm{vaporization}} = \mathrm{a}\sqrt{\mathrm{SA}} + \mathrm{b}\sqrt{\sigma^{2}_{tot}v} + \mathrm{c}$$

SA is the surface area of an isolated molecule represented by 0.001 electron/bohr^3 isosurface of the electronic density of a molecule, and v and σ_{tot}^2 denotes the same quantities as in Equation (2); parameters a, b and c are the empirical constants (a = 2.0132. b = 0.9301, c = –17.8440).

References

[1] E. P.J. Linstrom and W.G. Mallard, NIST Standard Reference Database Number 69 https://webbook.nist.gov/chemistry/. National Institute of Standards and Technology, Gaithersburg MD, 20899, https://webbook.nist.gov/chemistry/, **2021**.

[2] P. Politzer and J. S. Murray, *Quantitative Treatments of Solute/Solvent Interactions*. Amsterdam: Elsevier Scientific, **1994**.

[3] P. Politzer and J. S. Murray, Relationships between Lattice Energies and Surface Electrostatic Potentials and Areas of Anions, *The Journal of Physical Chemistry A*, vol. 102, no. 6, pp. 1018–1020, Feb. **1998**.