Design and Evaluation of the Thermal Properties of Di-, Tri- and Tetra-Azido-Esters

Sandeep Kumar, Arvind Kumar, K. Durga Bhaskar Yamajala, Pinki Gaur, Deepak Kumar, Shaibal Banerjee*

Organic Synthesis Laboratory,
Defence Institute of Advanced Technology,
Department of Applied Chemistry
Girinagar, 411025 Pune (Maharashtra), India
**E-mail: shaibal.b2001@gmail.com*

Abstract: A group of polycyclic and aliphatic azido-esters (as energetic plasticizers) have been synthesized by simple synthetic routes and their molecular structures were confirmed by spectroscopic techniques. In addition, their thermal and rheological properties have been determined utilizing DSC, TGA, viscosity, and contact angle. Computational studies of these plasticizers have been performed by means of DFT (B3LYP/6-31G*) to estimate possible stable structures, energies, heat of formation, bond dissociation energies, IR and NMR spectra *etc*. Their compatibility with glycidyl azide polymer (GAP) binder was studied to explore their applicability in propellants. All of these molecules are novel and have been synthesized with the possibility of scale up.

Keywords: azido-esters, energetic plasticizers, DFT, contact angle

1 Introduction

Solid propellants are energetic composite materials in which a plasticizer is one of the components. Plasticizers used in this area may be inert or energetic. For a long time, inert plasticizers [1] have been used in propellants, normally being low to medium molecular weight organic compounds having ester functional groups. Their role is to improve the mechanical properties and processability [2] of a composite propellant. In order to increase the energy content of propellants [3], few research groups have ventured to replace inert plasticizers

with plasticizers containing energetic groups [2, 4-6], with positive heats of explosion [7]. These energetic plasticizers generally contain functional groups such as nitro-, di-fluoramino-, nitramino-, and azido-groups, which contain bonds such as N−N, N−O or N−F, wherein each atom is covalently bonded and has lone pairs of electrons in *p*-orbitals. These lone pair electrons contribute to the electrostatic repulsion, thereby weakening the bonds and ejecting gaseous products like N_2 and CO_2. By adding energetic groups, the energy of a composite propellant is enhanced in terms of specific impulse, burn rate, with little compromise on mechanical properties, and impact and friction sensitivity. Thus, energetic plasticizers play a significant role in improving the energetic properties of rocket and gun propellants [8]. Ethyleneglycol bis(azidoacetate) (EGBAA), diethyleneglycol bis(azidoacetate) (DEGBAA) and bis(azidoacetoxy) bis(azidomethyl)propane (BABAMP) are a few of the known azido-ester-based energetic plasticizers (shown in Figure 1). The ester group gives a better lubricative effect and azido-ester plasticizers raise the nitrogen content of the energetic plasticizer, thus improving the energy level of the solid rocket propellant in conjunction with good compatibility with the normal energetic binder components used in solid propellants.

ethyleneglycol bis(azidoacetate) (EGBAA)   diethyleneglycol bis(azidoacetate) (DEGBAA)

$$CH_2OCOCH_2N_3$$
$$N_3H_2C-\overset{|}{\underset{|}{C}}-CH_2N_3$$
$$CH_2OCOCH_2N_3$$
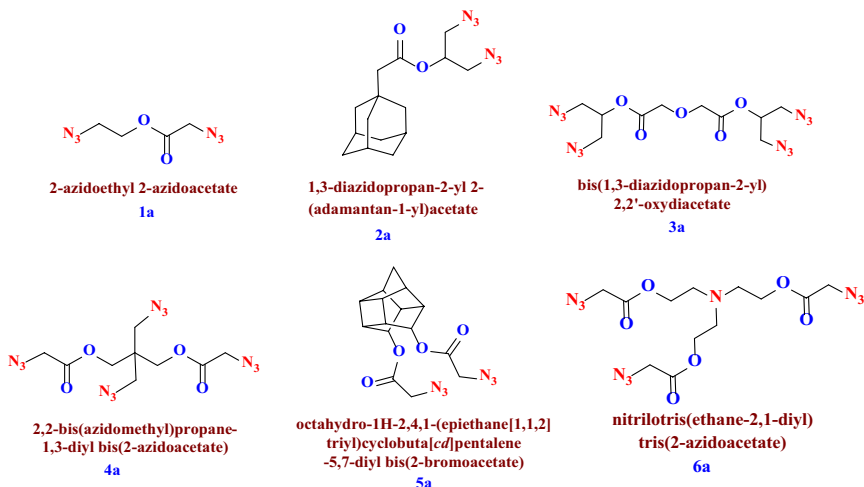
bis(azidoacetoxy) bis(azidomethyl)propane (BABAMP)
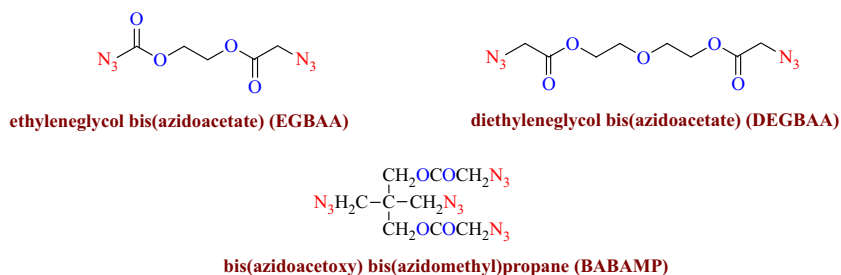
Figure 1.   Some reported energetic azido-esters

Herein, we report the synthesis of di-, tri- and tetra-azido containing aliphatic or cyclic esters and an evaluation of their properties. An azido-ester plasticizer has a low vapour pressure, high boiling point, low viscosity and good processability [2]. Low molecular weight glycidyl azide polymer (GAP) [9], a class of azido plasticizer [10, 11], is used for composite propellants, but the hydroxyl group of GAP reacts with isocyanate during the curing process so that the plasticizing effect is diminished. Strained molecules such as adamantanes, cubanes and tri-cyclic diones possess inherent energy due to bond angle deviations from the normal tetrahedral geometry. We have appended azido-ester functionalities onto these strained moieties, making them superior energetic plasticizers.
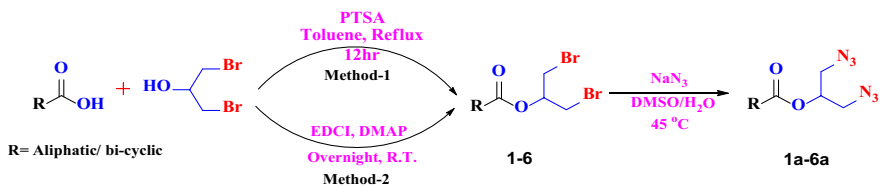
Scheme 1. Synthetic route to some azido-esters

Consequently, we explored the synthesis of a variety of azido-esters by using a simple and easy protocol such as esterification [12] and azidation (Scheme 1) with non-hazardous and low cost reagents. These molecules (**1a-6a**) have di-, tri- or tetra-azido groups along with the aliphatic or bicyclic esters (Figure 2).

2-azidoethyl 2-azidoacetate
1a

1,3-diazidopropan-2-yl 2-(adamantan-1-yl)acetate
2a

bis(1,3-diazidopropan-2-yl) 2,2'-oxydiacetate
3a

2,2-bis(azidomethyl)propane-1,3-diyl bis(2-azidoacetate)
4a

octahydro-1H-2,4,1-(epiethane[1,1,2] triyl)cyclobuta[cd]pentalene -5,7-diyl bis(2-bromoacetate)
5a

nitrilotris(ethane-2,1-diyl) tris(2-azidoacetate)
6a

Figure 2. Aliphatic and cyclic azido-esters

All of these molecules were well characterized by spectroscopic techniques such as FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry, followed by an investigation of their thermal properties, oxygen balance (OB), nitrogen content (NC), contact angle [13] and rheological properties. Finally, the physical properties of all of the synthesized molecules (**1a-6a**) were analyzed theoretically using density functional theory (DFT) from the Gaussian 09 [14] suite. We have computed the optimized stable [15] structures of these molecules, their energies, thermal properties (heat of formation) [16-19], bond dissociation energies and spectroscopic properties such as IR and NMR. These theoretical values were compared with the experimental results and were found to be in very

close agreement. In addition to the previously existing azido-ester plasticizers, these new polycyclic and aliphatic azido-esters are thermally stable, and quite compatible and easily mixed with binders.

2   Materials and Methods

All chemicals and organic solvents were obtained from commercial suppliers (Sigma Aldrich) and used without further purifications. All of the reactions were monitored by precoated silica gel 60 F_{254} (Merck) TLC plates. The instrument used for recording FT-IR spectra was a BRUKER ALPHA ECO ATR FT-IR spectrometer, as neat samples in the range of 500 cm^{-1} to 4000 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER (500 MHz and 125 MHz) instrument, internally referenced to tetramethylsilane (TMS) signals and dissolved in CDCl$_3$ or DMSO-d$_6$. ^{15}N NMR spectra were recorded on a BRUKER 500 MHz instrument using TMS as an internal reference with DMSO as the solvent. High resolution mass spectral measurements were carried out on Micromass Q-Tof Mass spectrometer. Differential Scanning Calorimetric (DSC) studies were carried out on a Perkin Elmer DSC-7 instrument operating at a heating rate of 10 °C/min in a nitrogen atmosphere with 1 mg to 2 mg of sample. Friction and impact sensitivities were calculated using OZM Research, BFH-10. Melting points and boiling points were recorded on a BUCHI M-560 apparatus. Gaussian 09 was used for computational or DFT calculations.

3   Experimental

3.1 Esterification Methods

(a) **Method A:** The alcohol and haloacetic acid were mixed with toluene (20 mL) and a catalytic amount of *p*-toluenesulphonic acid was added. The reaction mixture was then refluxed using a Dean and Stark apparatus. The reaction was terminated after 12 h, after monitoring the progress of the reaction by TLC, and the reaction mixture was then concentrated under vacuum. The concentrate was diluted with water and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic extract was washed sequentially with saturated NaHCO$_3$ solution (2 × 20 mL) and brine (2 × 15 mL), and then dried over anhydrous Na$_2$SO$_4$. The dried solution was filtered and evaporated under reduced pressure to obtain the crude product. This crude material was purified by silica-gel (100-230 mesh size) column chromatography using ethyl

acetate-hexane to obtain the pure product (**1a, 3a** and **4a**).

(b) Method B: The haloacetic acid and alcohol were mixed with CH_2Cl_2 (20 mL), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) was added. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI hydrochloride) was then added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After the completion of the reaction, the reaction mixture was washed sequentially with water (3×10 mL), saturated $NaHCO_3$ solution (3×10 mL) and brine (3×10 mL). The organic layer was dried over anhydrous Na_2SO_4 and then filtered. The dried organic solution was concentrated under vacuum, which gave the crude product. The crude material was purified by silica-gel column chromatography using ethyl acetate-hexane to obtain the pure product (**2a, 5a** and **6a**).

2-Bromoethyl 2-bromoacetate (**1**): as a pale yellow liquid (2.509 g, yield: 87%); FT-IR (neat, cm^{-1}) 2969 (C−H *str*) 1740 (C=O *str*) 1265 (C−O *str*) 731 (C−Br *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 4.46 (t, *J*=6.1 Hz, 2 H), 3.87 (s, 2 H), 3.46-3.58 (t, 2 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 166.85, 65.33, 28.17, 25.6; MS for $C_4H_6Br_2O_2$ [M+1, M+2, M+4] calculated 243.87, found 243.76, 245.69, 247.61.

1,3-Dichloropropan-2-yl 2-(adamantan-1-yl) acetate (**2**): as a colourless liquid (1.2821 g, yield: 81%); FT-IR (neat, cm^{-1}) 2902 (C−H *str*) 1736 (C=O *str*) 751 (C−Cl *str*). ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 5.20 (quin, *J*=5.1 Hz, 1 H), 3.72-3.84 (m, 4 H), 2.16 (s, 2 H), 2.00 (br. s., 3 H), 1.63-1.76 (m, 12 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 170.64, 71.47, 48.71, 42.51, 42.35, 36.66, 32.93, 28.60. MS for $C_{15}H_{22}Cl_2O_2$ [M+1, M+2, M+4] calculated 305.09, found 305.12, 307.09, 309.01.

*Bis(1,3-dichloropropan-2-yl) 2,2'-oxydiacet*ate (**3**): as a colourless liquid (4.9239 g, yield: 75%); FT-IR (neat, cm^{-1}) 2988 (C−H *str*) 1760 (C=O *str*) 1243 (C−O *str*) 763 (C−Cl *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 5.19-5.41 (m, 1 H), 4.35 (s, 2 H), 3.69-3.89 (m, 4 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 168.66, 72.46, 67.88, 42.25; MS for $C_{10}H_{14}Cl_4O_5$ [M+1, M+2, M+4] calculated 353.95, found 354.86, 356.72, 358.62.

2,2-Bis(bromomethyl)propane-1,3-diyl bis(2-bromoacetate) (**4**): as a viscous golden liquid (3.5328 g, yield: 92%); FT-IR (neat, cm^{-1}) 2984 (C-H *str*) 1750 (C=O *str*) 1264 (C-O *str*) 729 (C−Br *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm 4.31 (d, *J*=1.8 Hz, 2 H), 3.89 (s, 2 H), 3.56 (s, 2 H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ ppm 166.36, 64.62, 42.93, 32.87, 25.18; MS for $C_9H_{12}Br_4O_4$ [M+1,M+2, M+4] calculated 500.74, found 500.98, 502.89, 504.91.

Octahydro-1H-2,4,1-(epiethane[1,1,2]triyl)cyclobuta[cd]pentalene-5,7-diyl bis(2-bromoacetate) (**5**): as a white crystalline solid (1.0127 g, yield: 85%); FT-IR

(neat, cm^{-1}) 2981 (C−H *str*) 1729 (C=O *str*) 1264 (C−C *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 4.70-4.81 (m, 2 H), 4.06-4.18 (m, 3 H), 3.83-3.92 (m, 1 H), 2.90 (d, *J*=3.7 Hz, 2 H), 2.68-2.73 (m, 2 H), 2.55-2.63 (m, 2 H), 2.42-2.50 (m, 2 H), 1.73 (s, 1 H), 1.18 (dd, *J*=11.0, 1.5 Hz, 1 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 167.40, 73.89, 42.98, 42.1, 41.21, 39.23, 35.05, 34.05; MS for C$_{15}$H$_{16}$Br$_2$O$_4$ [M+1, M+2, M+4] calculated 418.94, found 418.76, 420.62, 422.71.

Nitrilotris(ethane-2,1-diyl)tris(2-chloroacetate) (**6**): (0.9 g, yield**:** 98%); FT-IR (neat, cm^{-1}) 2957 (C−H *str*) 1738 (C=O *str*) 1168 (C−O *str*) 779 (C−Cl *str*); ^{1}H NMR (500 MHz, DMSO-d$_6$) δ = 4.5-4.3 (m, 3 H), 4.2 (t, J = 5.6 Hz, 3 H), 2.8 (br. s., 3 H); ^{13}C NMR (125 MHz, DMSO-d$_6$) δ ppm 167.8, 64.3, 52.8, 41.6.

Azidation Method: A mixture of the halo-ester (**1-6**) and sodium azide (NaN$_3$) were mixed with DMSO/H$_2$O (8:2), the mixture was slowly warmed to 45 °C in an oil bath, and stirred for 24 h. After TLC monitoring, the reaction mixture was poured into cold water and extracted with ethyl acetate (3 × 20 mL). The combined organic extract was washed with brine (3 × 20 mL) and then dried over Na$_2$SO$_4$. The dried solution was evaporated under vacuum, and the crude product was purified by silica-gel column chromatography using ethyl acetate-hexane to give the pure product (**1a-6a**).

2-Azidoethyl 2-azidoacetate (**1a**): as a pale yellow liquid (1.046 g, yield: 84%); B.P. 167.5-168.5 °C; FT-IR (neat, cm^{-1}) 2978 (C−H *str*) 2103 (N$_3$ *str*) 1748 (C=O *str*) 1264 (C−O *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm 4.33-4.38 (t, 2 H), 3.93 (s, 2 H), 3.49-3.56 (t, 2 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 168.11, 64.09, 50.11, 49.50; MS for C$_4$H$_6$N$_6$O$_2$ [M+1] calculated 171.05, found 171.30. Theoretical ^{1}H NMR at 5-H (δ 4.5), 6-H (δ 4.3), 12-H (δ 4.3), 2-H (δ 3.8), 3-H (δ 3.8), 11-H (δ 3.5). ^{13}C NMR at 8-C (δ 181.4), 4-C (δ 73.0), 10-C (δ 58.4), 1-C (δ 56.9).

1,3-Diazidopropan-2-yl 2-(adamantan-1-yl)acetate (**2a**): as a viscous light yellow liquid (0.5089 g, yield: 75%); B.P. 198.1-200 °C; FT-IR (neat, cm^{-1}) 2905 (C−H *str*) 2102 (N$_3$ *str*) 1735 (C=O *str*) 1264 (C−O *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm 5.05 (quin, *J*=5.2 Hz, 1 H), 3.45-3.58 (m, 4 H), 2.16 (s, 2 H), 2.00 (br. s., 3 H), 1.61-1.77 (m, 12 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 170.72, 70.21, 51.03, 48.61, 42.33, 36.66, 32.92, 28.57; MS for C$_4$H$_6$N$_6$O$_2$ [M+1] calculated 319.18, found 319.63. Theoretical ^{1}H NMR peaks are noted at 33-H (δ 5.1), 38-H (δ 3.7), 36-H (δ 3.4), 35-H (δ 3.3), 39-H (δ 3.2), 14, 8, 9-H (δ 1.7), 13, 12, 10, 15, 7, 17-H (δ 1.6), 18, 20, 24-H (δ 1.4),21-H (δ 1.1). ^{13}C NMR: 2-C (δ 153.7), 4-C (δ 153.7), 6-C (δ 153.5), 1-C (δ 148.5), 5,3-C (δ 148.4), 25-C (δ 145.9), 22-C (δ 144.6), 19-C (δ 144.4), 16-C (δ 139.5), 26-C (δ 136.5), 37-C (δ 135.0), 34-C (δ 132.1), 32-C (δ 109.3).

Bis(1,3-diazidopropan-2-yl) 2,2'-oxydiacetate (**3a**): as a viscous light

yellow liquid (1.7609 g, yield: 91%); B.P. 175.2-177 °C; FT-IR (neat, cm^{-1}) 2990 (C−H *str*) 2091 (N$_3$ *str*) 1764 (C=O *str*) 1244 (C−O *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 5.18 (quin, *J*=5.3 Hz, 1 H), 4.34 (s, 2 H), 3.42-3.61 (m, 4 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 168.76, 71.77, 67.94, 50.84; MS for C$_{10}$H$_{14}$N$_{12}$O$_5$ [M+1] calculated 383.12, found 383.10. Theoretical ^{1}H NMR peaks are 23-H (δ 5.4), 14-H (δ 4.9), 28-H (δ 4.3), 8-H (δ 4.2), 18-H (δ 4.1), 18,25-H (δ 4.1), 2,13-H (δ 4.0), 2,13-H (δ 4.0),17-H (δ 4.0), 29-H (δ 2.8), 7-H (δ 3.4), 26-H (δ 2.8). ^{13}C NMR for the M2 9-C (δ 180.0), 10-C (δ 171.8), 1-C (δ 82.3), 22-C (δ 82.3), 16-C (δ 76.6), 12-C (δ 76.7), 27-C (δ 63.2), 6-C (δ 61.8), 24-C (δ 60.9), 3-C (δ 58.6).

2,2-Bis(azidomethyl)propane-1,3-diyl bis(2-azidoacetate) (**4a**): as a pale yellow liquid (1.181 g, yield: 94%); B.P. 115.3-116.3 °C; FT-IR (neat, cm^{-1}) 2987 (C−H *str*) 2096 (N$_3$ *str*) 1764 (C=O *str*) 1245 (C−C *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 4.33 (s, 2 H), 3.96 (s, 2 H), 3.45-3.61 (m, 2 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 167.61, 64.25, 50.30, 42.60, 32.77; MS for C$_9$H$_{12}$N$_{12}$O$_4$ [M+1] calculated 353.11, found 353.90. Theoretical ^{1}H NMR peaks are observed at 11-H (δ 5.2), 12-H (δ 4.7), 16-H (δ 4.6), 2-H (δ 4.5), 3-H (δ 4.4), 3,33-H (δ 4.3), 18-H (δ 4.2), 15-H (δ 3.9), 21-H (δ 3.5), 34-H (δ 3.3), 19-H (δ 3.2), 22-H (δ 3.1). ^{13}C NMR 7-C (δ 177.4), 30-C (δ 176.3), 14-C (δ 82.2), 10-C (δ 74.0), 20-C (δ 63.9), 1-C (δ 59.9), 17-C (δ 59.3), 32-C (δ 56.5), 13-C (δ 55.4).

Octahydro-1H-2,4,1-epiethane[1,1,2]triyl)cyclobuta[cd]pentalene-5,7-diyl bis(2-azidoacetate) (**5a**): as a white solid (0.6931 g, yield: 87%); M.P. 71 °C; FT-IR (neat, cm^{-1}) 2971 (C−H *str*) 2107 (N$_3$ *str*) 1737 (C=O *str*) 1202 (C−O *str*); ^{1}H NMR (CDCl$_3$, 500 MHz): δ ppm = 4.75 (dq, *J*=2.7, 1.6 Hz, 2 H), 3.88 (s, 4 H), 2.89 (d, *J*=3.7 Hz, 2 H), 2.65-2.73 (m, 2 H), 2.58 (s, 2 H), 2.46 (td, *J*=3.5, 1.8 Hz, 2 H), 1.75 (s, 1 H), 1.18 (dt, *J*=10.9, 1.6 Hz, H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ ppm 168.35, 73.57, 50.44, 42.96, 42.19, 39.22, 35.12, 34.04. MS for C$_9$H$_9$N$_6$O$_4$ [M+1] calculated 345.12, found 345.32. Theoretical ^{1}H NMR peaks are found at 5, 23, 21, 6-H (δ 4.0), 19, 17-H (δ 6.1), 36, 28-H (δ 4.4), 37, 27-H (δ 4.0), 11, 13-H (δ 3.1), 14, 15-H (δ 2.9), 9-H (δ 2.0), 8-H (δ 1.7). ^{13}C NMR 34-C (δ 170.0), 25-C (δ 169.3), 22-C (δ 142.6), 20-C (δ 142.2), 1-C (δ 140.5), 4-C (δ 140.1), 18-C (δ 128.5), 16-C (δ 127.8), 7-C (δ 59.6), 26-C (δ 58.5), 35-C (δ 58.4), 2,3-C (δ 55.3), 12-C (δ 51.6), 10-C (δ 51.1).

Nitrilotris(ethane-2,1-diyl)tris(2-azidoacetate) (**6a**): (0.16 g; yield: 53%); B.P. 119.6-121.2 °C; FT-IR (neat, cm^{-1}) 2925 (C−H *str*) 2105 (N$_3$ *str*) 1741 (C=O *str*) 1189 (C-O *str*); ^{1}H NMR (500 MHz, DMSO-d6) δ = 4.2-4.1 (m, 3 H), 4.2-4.1 (m, 4 H), 2.9-2.8 (m, 3 H); ^{13}C NMR (125 MHz, DMSO-d6) δ = 169.1, 63.8, 52.9, 50.0; HRMS for C$_{12}$H$_{18}$N$_{10}$O$_6$ [M+1, M+2] calculated 398.1411, found 398.1396. Theoretical ^{1}H NMR 24-H (δ 5.8), 34, 18-H (δ 5.5), 16-H (δ .3),

12-H (δ 5.0), 43-H (δ 4.9), 42, 33-H (δ 4.7), 15, 13-H (δ 4.9), 19-H (δ 4.0), 10,7,3-H (δ 3.8), 9, 6, 4, 25-H (δ 3.6). ^{13}C NMR 21-C (δ 191), 39-C (δ 186.9), 30-C (δ 182.9), 14-C (δ 91.6), 11-C (δ 87.1), 17-C (δ 86.9), 2-C (δ 80.9), 8-C (δ 80.2), 5-C (δ 80.0), 41-C (δ 72.0), 32-C (δ 70.0), 23-C (δ 68.4).

4   Results and Discussion

At the outset, all of the molecules (**1-6**) were synthesized by esterification (PTSA, toluene and reflux or EDCI and DMAP) (method A) followed by the azidation protocol (**1a-6a**) (NaN$_3$ in DMSO/H$_2$O) as shown in Scheme 1. Molecules (**5a**, **2a** and **6a**) were synthesized by method B, as these molecules are acidic and heat sensitive, resulting in decomposition above 100 °C in acidic medium. Each step of the process was monitored by TLC and the presence of the functional groups was confirmed by FT-IR. The existence of ester peaks in the range 1730 cm^{-1} to 1740 cm^{-1} confirmed the esterification process in the first step, and a peak observed at approximately 2100 cm^{-1} validated the formation of an azide in the second step. Furthermore, the structure of these molecules was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra, δ values of the azido compounds (2nd step) are slightly different when compared with the esterification products (1st step). When a bromo group is replaced with an azide group, the δ value of the azide vicinal protons is increased, whereas a decrease was observed in the vicinal protons when a chloro group was replaced by azide (shown in Supporting Information (S.I.)), leaving all other protons unaltered in the products. Substitution of an azide group was confirmed by ^{15}N NMR (**4a**) (Figure 3) and mass analysis.
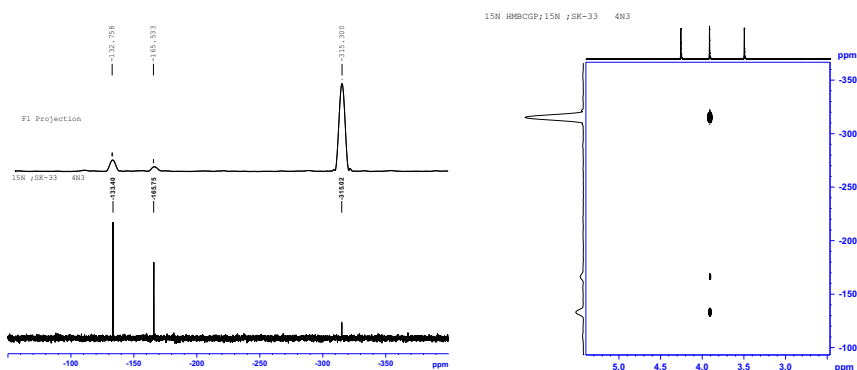
Figure 3. ^{15}N NMR and HMBCGP ^{15}N of molecule **4a**

As shown in the ^{15}N NMR spectrum (Figure 3), an azide group has three well resolved, covalently bonded peaks, observed at δ ppm −132.0 ($N_β$), −165.1 ($N_γ$), −314.5 ($N_α$).

4.1 Computational studies

The heats of formation of the newly synthesized azido-esters (**1a-6a**) were calculated using density functional theory (DFT) methods. All calculations were executed by the Gaussian 09 program. Several chemically intuitive possible structures, obtained mainly by rotating different groups attached to the side chains ($-CO-O-CH(CH_2N_3)_2$), were considered for the structural optimization of the azido-esters at the B3LYP/6-31G* level of theory. We have chosen to describe only the low energy conformers in this paper. All of the structures were recognized as minima using harmonic force constant analysis at the same level of theory. The heat of formation ($ΔH_f$) is a critical parameter when evaluating theoretical studies of energetic materials.

Isodesmic reactions (shown in S.I.) were considered to calculate the reaction enthalpy ($ΔH_{Reac}$) at 298 K. The heats of formation ($ΔH^o_f$) of the azido-esters listed in Table 1 were determined from the computed $ΔH_{Reac}$ values and the known $ΔH^o_f$ data of the other reactants and products (see S.I. for details). In order to compare the heat of formation, we have grouped the azido-esters into two types, as bicyclic and as acyclic azido-ester compounds (Figure 2). The values of the heats of formation of the azido-esters (**1a-6a** as shown in Table 1) were observed in the following order **4a > 3a > 5a > 1a > 2a > 6a**. This trend is fairly similar to other energetic materials containing the azide group in which substitution of the azide group increases the energy content of a molecule by 290-330 kJ/mol. An increase in energy was observed when moving from compounds with two azido groups to compounds with four azido groups. In addition to this, bicyclic compounds with two azido groups had more energy than the acyclic compounds with the same number of azido groups. In order to verify the thermal stability of the azido-esters, bond dissociation energies (BDE) of selected bonds of the azido-esters were evaluated (Table 1). The calculated BDEs of bonds in the side-chains of the azido-esters are higher. These azido-esters are thermally stable molecules and rather high temperatures may be required to break the bonds of the side-chains of the azido-esters.

4.2 Oxygen balance (OB)

Oxygen balance is the index of the concentration of oxygen in a compound. For greater stability and performance, the oxygen balance in an energetic plasticizer is preferably negative. The oxidizers present in propellants supply the required

oxygen to the propellant for complete combustion because the fuel, binders and plasticizers have negative OBs. The oxygen balance of all six molecules (**1a-6a**) was calculated theoretically by using the formula from Ref. [11]. The OBs ranged from −195.6 to −84.6%. Of these, molecules **2a** and **5a** had the lowest OBs and **1a** the highest OB. The results are listed in Table 1.

4.3 Nitrogen content

Azido plasticizers can influence the average molecular weight of the combustion products, increase the nitrogen content and hence reduce the characteristic signal, and improve the energy and specific impulse of the propellants. Azido-ester molecules having a nitrogen content of more than 40% are preferred. The nitrogen contents of all six synthesized molecules (**1a-6a**) were in the range of 24.41% to 49.40%. Of these, the three azido-ester molecules having a nitrogen content greater than 40% are preferred, due to the high nitrogen containing energetic plasticizers reported in the literature [11]. Azido-esters **2a** and **5a** have a nitrogen content of 26.40% and 24.41% respectively, but these two plasticizers are stable up to 220 °C due to their strained structure.

Table 1. Theoretical calculation results

Molecule	Oxygen balance (OB) [%]	Nitrogen content (NC) [%]	Bond disociation energy (BDE) [kcal/mol]	Heat of formation ($\Delta_f H$) [kcal/mol]	Energy of molecule (E) [a.u.]
1a	−84.64	49.40	336.94	78.66	−635.0761
2a	−195.63	26.40	323.9	53.12	−1063.9726
3a	−92.07	43.97	643.2	144.41	−1422.7068
4a	−90.84	47.71	601.4	181.33	−1308.1500
5a	−157.99	24.41	388.5	131.37	−1210.6953
6a	−108.45	35.16	134.6	28.43	−1467.12

4.4 Electron charge density of molecules 1a-6a

All of the azido-esters **1a-6a** were optimized and found to be stable molecular structures. After optimization of the spatial arrangement of the atoms and functional groups in the structures, the physical properties of the molecules were calculated. It was observed that molecules **1a-6a**, have electron rich and electron deficient groups, as depicted by red and blue colours respectively. It may be concluded that electron density is higher at the oxygen and nitrogen atoms due to their high electronegativity. The red coloured areas placed at the ester and azido groups indicate maximum electron density and nucleophilic character (see S.I.).

This is due to the strong electron withdrawing effect, along with the electronic repulsions within the azido group due to several π bonds within a confined location. Similarly, lower electron charge density was observed at carbon atoms.

4.4 Viscosity

Viscosity plays a very important role in the mixing of a plasticizer with a binder and the flow of the composite propellant. If the viscosity of the plasticizer is low, it can easily mix with the binder and diffuse within the entire propellant grain. We have calculated the viscosity (η) and shear rate (γ̇) of the six molecules **1a-6a**. For this purpose, we have prepared compositions containing 90% GAP + 10% azido-ester molecules, which were allowed to stand for three weeks. No phase separations were observed. Of these, **1a** and **2a** displayed the lowest (0.71 mps) and highest (1.77 mps) viscosity respectively, at 28 °C. All of these molecules exhibit Newtonian behaviour and molecule **1a** is the easiest to process. The viscosity of the molecules **1a-5a** is shown in the following charts:
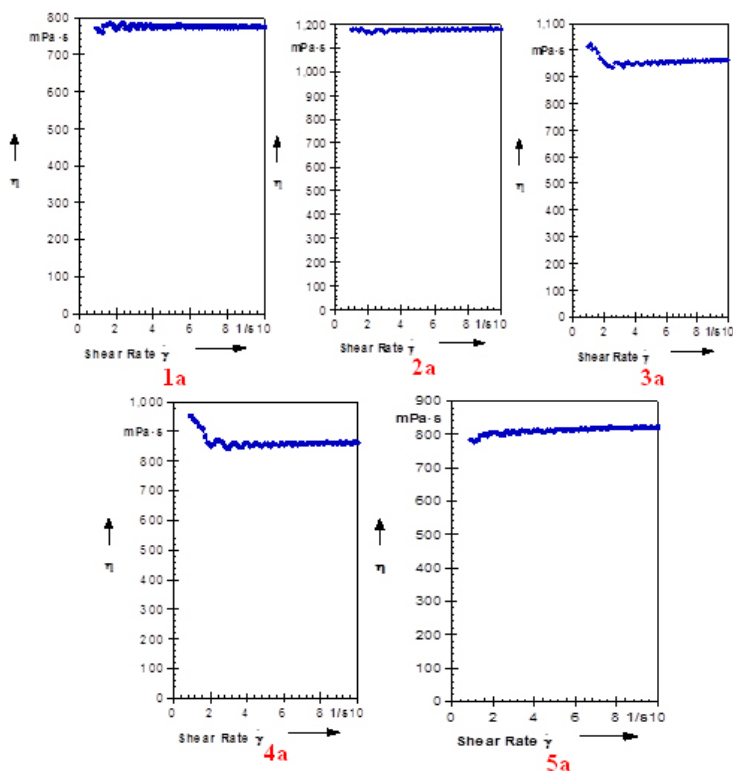

Figure 4.   Viscosity of **1a-5a** azido-esters

4.5 Contact angle

Contact angle is one of the measurements to determine the hydrophilic or hydrophobic character of a material or molecule. For example, if a liquid drop is placed on a surface and the contact angle with the surface is >90°, it shows hydrophobic character; however if the contact angle is <90°, then it shows hydrophilic character. Molecules **1a-6a** have contact angles >90° and of these, **2a** showed the highest contact angle (105.7°) on a surface (Figure 4). For this reason, all of these molecules are hydrophobic in nature, since their contact angles are in the range of 104.4° to 105.7°. Molecule **2a** was found to have the highest hydrophobicity due to its strained geometric configuration with multiple aliphatic chains. The hydrophobic nature of these molecules enables them to be mixed properly with the binder in propellants. It also prevents moisture absorption in the propellant grain, thereby increasing the shelflife.
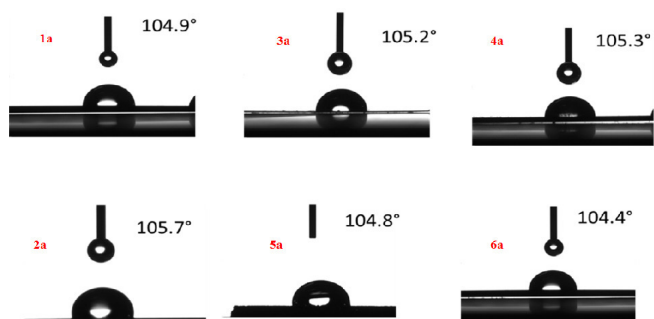
Figure 5.   Contact angle measurements of **1a-6a**

4.5 Differential scanning calorimetry (DSC)

In DSC, physical parameters like mass, heat flow, heat capacity and enthalpy [20] are measured with respect to time and temperature. This technique is useful for thermal studies of nitrogen rich energetic molecules. A DSC curve indicates the difference between the heat flow supplied to the sample as compared to that supplied to the reference, and it is given per unit mass of sample. From the literature, it is recognized that the glass transition temperature (T_g) of azido compounds is lower than that of ester compounds, and that an azido group is more thermally stable than a nitrate ester [11]. The low T_g value of these compounds makes them ideal contenders as plasticizers in composite propellants. All of the synthesized compounds except **1a** showed good thermal stability and **2a** and **6a** had the highest decomposition temperature, 242.5 °C; **5a** had the lowest thermal decomposition, 224.8 °C, as listed in Table 2. The heat released by all of the molecules **1a-6a** was high, in the range 1640-2347 J/g. Molecule **5a** had the

highest heat release (2397 J/g) compared with the other molecules. Hence, it may be summarized by stating that plasticizers **1a-6a** are quite energetic in nature.

4.6 Thermogravimetric analysis (TGA)

For molecules **2a** and **3a** the wt.% loss occurred in two steps and for **4a** and **5a** in three steps. All of the molecules except **1a** have thermal stability above >160 °C. The thermal decomposition of **1a** was observed to occur in a single step at 118 °C to 182 °C. Molecule **3a** had the greater stability as compared with the other molecules because its decomposition temperature (1st step) was 200 °C; for the others it was 164 °C, 188 °C, 189 °C and 180 °C (for **2a**, **4a**, **5a** and **6a**, respectively) – see Table 2.

Table 2.   DSC and TGA studies of azido-esters **1a-6a**

Molecule	DSC [°C]	Heat release Hr [J/g]	Viscocity [Pa·s]	Contact angle [°]	TGA	
					[wt.%]	[°C]
1a	-	-	0.78	104.9	92.15	118-182
2a	242.5	−1640	1.77	105.7	54.35	164-290
					24.44	291-402
3a	240.6	−2395	0.96	105.2	59.35	200-259
					17.72	260-458
4a	225.4	−1756	0.86	105.3	27.04	188-264
					38.97	265-352
					10.19	353-456
5a	224.87	−2397	0.81	104.8	31.14	189-266
					21.03	267-343
					14.32	344-454
6a	242.5	−1876	-	104.4	66.23	180-280

The glass transition temperature is also one of the significant factors for compatibility with propellant binders such as HTBP, BAMO and GAP *etc*. For the azido-ester molecules (Table 4; **1a-6a**) glass transition temperatures below −40 °C were observed, except for **5a** which is in the solid form and has a very low melting point (Table 3). The sensitivities of these energetic materials to impact, friction and decomposition temperature have been evaluated, which is mandatory for assessing the hazards in manufacture, handling, storage and transportation. The susceptibility to these stimuli, results in either combustion or detonation.

4.7 Impact sensitivity

Impact sensitivity is an important parameter concerned with safe handling of

energetic materials. Therefore, any new formulation must necessarily to be examined for its impact sensitivity. Hence, the sensitivities of these azido-esters to impact stimuli were determined by the fall hammer method using a 2 kg drop weight as per the Bruceton staircase approach. The experiment was performed by dropping a 2 kg drop weight from different heights onto a powdered sample (liquid or solid sample adsorbed on silica), which was held between the two coaxial steel cylinders with a guiding steel ring. Ten consecutive tests were performed and the percentage of ignition was noted for each drop height. The presentation of the test results is in terms of the relation between the percentage of ignition/explosion and the height of the drop weight. The impact sensitivity is reported in terms of the 50% probability of explosion ($h_{50}\%$) of the sample within the uncertainty limits of ± 5 cm.

4.8 Friction sensitivity

Energetic compounds are often subjected to friction during processing, handling and transportation, and are thus likely to cause an accidental initiation/ explosion. A BAM friction apparatus was used for the determination of the friction sensitivities of the azido-esters. The apparatus consists of a porcelain plate of standard roughness over which a test sample (10 mg) is uniformly distributed, and a cylindrically shaped porcelain pestle load rests on the top of the sample. Variations in the load from 0.5-36 kg can be applied to the pestle. The porcelain plate moves to and fro in arcs of 10 mm with the help of an electric motor having a velocity of 10 cm/s. The friction sensitivity was measured by applying a constant load on the pestle while the porcelain plate executes a to- and fro-motion under the pestle. The friction sensitivity is reported in terms of the maximum load on the pestle under which no ignition/explosion/deflagration was observed in five consecutive tests and expressed in Newton.

Table 3. Thermal and sensitivity properties of molecules **1a-6a**

Molecule	Impact [cm]	Friction [N]	Decomposition temp. [°C]	Tg [°C]
1a	198	55	-	−59.6
2a	191	52	242.5	15
3a	161	39	240.6	−56.6
4a	160	39	225.4	−42.2
5a	192	52	224.8	-
6a	165	40	242.5	−57.9

5   Conclusions

Scalable, cost effective novel azido-esters **1a-6a** were synthesized using a simple protocol and their thermal and physical properties (viscosity and contact angle) were studied. Properties such as geometrical optimization, ESP, BDE and heat of formation were calculated by DFT theory. In addition, oxygen balance, heat release and nitrogen content were calculated. Most of these molecules demonstrated good thermal stabilities and physical properties. Furthermore, the azido-esters were observed to have good compatibility with binders and may have applications in propellants or other energetic formulations.

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