

## Synthesis and characterization of 1-azido, 2,3-dihydroxy 2-azidomethylpropane (ADMP): A new energetic organic azide

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This paper reports the synthesis of title compound (ADMP) for its possible use as an energetic azido plasticizer. The synthesis was carried out by protecting readily available sugar D-mannitol (**1**) by treating it with acetone in presence of fused FeCl<sub>3</sub> at room temperature, leading to the formation of 1,2-5,6 di-O-isopropylidene-D-mannitol (**2**), which on further oxidation with sodium meta periodate in acetone gave 2,3- O-isopropylidene 1-propanal (**3**). The subsequent treatment with formaldehyde in presence of base (Aldol-Cannizarro condensation) yielded 2,3-O-isopropylidene 2-hydroxymethyl-1-propanol (**4**). Tosyl protection (**5**) of the resulting compound followed by introduction of azide substituents gave 2,3-O-isopropylidene-2- azidomethyl-1-propane (**6**) and finally deprotection of acetoimide functionality using 10% H<sub>2</sub>SO<sub>4</sub> gave title compound (ADMP, **7**). All the intermediates and the final product have been characterized by IR and NMR spectra. The differential scanning calorimetry (DSC) study on ADMP indicated that it undergoes exothermic decomposition in the temperature in the range of 191-260°C with heat release of the order of 1390 J/g. The theoretical performance parameters suggest its superior energetic in comparison to that of non-energetic plasticizers such as dioctyl phthalate, diamyl phthalate and dibutyl phthalate.

**Keywords:** ADMP, Aldol-Cannizarro condensation, Theoretical performance, Energetic azido plasticizer

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Incorporation of energetic groups like azido (-N<sub>3</sub>), nitro (NO<sub>2</sub>), nitrate (-O-NO<sub>2</sub>) as substitute of hydrogen in organic molecules results in the formation of energetic plasticizers<sup>1-5</sup> and polymers of binder value. The investigation of azido group containing energetic binders attracted the attention of high energy materials (HEMs) chemists in the last two decades. Azido group has a high positive heat of formation and it can produce more gases in the combustion products, thereby increasing the work capacity of propellant. Moreover, azido compounds offer exclusively smokeless combustion products with high amount of nitrogen, which are advantageous for specific application of system as gas generator. However, until now the mechanical properties of propellant based on azido polymers to the level of that of hydroxy terminated polybutadiene (HTPB) is subject of research and development work. In addition to the development of copolymers, search for suitable energetic plasticizers is viable approach to improve flexibility and low temperature characteristics of the polymers. The introduction of plasticizer between two segments of polymers separates polar groups apart,

thereby reducing the monotony of configuration and improving flexibility. The non-energetic plasticizers modify tensile strength and elongation, but do not contribute to the energy of the system whereas energetic plasticizers improve upon their attributes as well as contribute to the energy of the system thereby they are preferred choice as plasticizers in the rocket propellants. Low molecular weight azides, oligomers or monomer are generally reported for use as energetic plasticizers for azido polymers like glycidyl azide polymer (GAP) in view of their better compatibility.

In view of the above observations coupled with scanty reports on the energetic compounds, which can act both as plasticizer and monomer for further polymerization to high molecular weight polymeric molecules, the synthesis and characterization of a new energetic compound *viz.*, 1-azido-2,3-dihydroxy-2-azidomethyl propane (ADMP) is reported here. This new material could be potential candidate for plasticizer or energetic azido polymers based applications in propellants.

## Experimental Procedure

### Methods

All the yields reported refer to isolated material. The temperatures above and below ambient temperatures refer to bath temperatures unless otherwise stated. Solvents and anhydrous liquid reagents were dried according to established procedures using appropriate drying agent and distilled. Reagents were procured from Aldrich Chemical Co., SD fine chemicals, Spectrochem chemicals, India, and were used as such without purification. The progress of the reactions was monitored by thin layer chromatography (TLC) in hexane and ethyl acetate. Column chromatography was performed using silica gel (100-200 mesh, SD fine chemicals, India) by applying standard chromatographic techniques. All the nuclear magnetic resonance spectra were recorded on Varian-Mercury 75 MHz NMR spectrometer. IR spectra were taken on a Perkin-Elmer 1600 FTIR spectrometer. Differential scanning calorimetry (DSC) was obtained on Perkin Elmer-7 system at the heating rate of 10°C/min in nitrogen atmosphere. The performance parameters of the newly synthesized compounds were predicted using Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) code<sup>6-8</sup>. The heat of formation of ADMP was predicted using group additivity approach<sup>9</sup>.

### Synthesis

#### Preparation of 1,2-5,6-Di-O-isopropylidene-D-mannitol(2)

Fused ZnCl<sub>2</sub> (91 g, 0.67 mol) was dissolved in dry acetone (400 cc) in 1 liter round bottom flask equipped with a mechanical stirrer. The reaction, which was slightly exothermic, was completed within 0.5 h, and then D-mannitol (**1**, 40 g, 0.25 mol) was added to the solution at room temperature. The mixture became slightly turbid and was stirred for 18 h at room temperature. A clear coloured solution was formed. At this moment 230 g of previously pulverized and sieved anhydrous K<sub>2</sub>CO<sub>3</sub> was added. After 1 h stirring, water (5 mL) was added for every 0.5 h (totaling to 30-60 mL) in order to realize the pH of 8-9. Stirring was continued for 1 h. The insoluble material was allowed to settle and supernatant solution was filtered through sintered glass funnel. Then acetone (200 mL) was added to the insoluble material in the reaction flask and was stirred for 0.5 h. The process was repeated twice. The combined filtrate was concentrated and solid mass obtained was dried under vacuum for 1 h at 50°C (m.p: 100-106°C).

The product was dissolved in hot toluene (100 mL). The insoluble material was filtered through cotton and hexane (100 mL) was added to the filtrate. The solution was left standing for 12-18 h at room temperature after which the resulting precipitate (**2**) was filtered and washed twice with hexane (50 mL). The average yield after crystallization was 60% (m.p: 119-121°C).

#### Preparation of 2,3-O-Isopropylidene-D-glyceraldehyde (**3**)<sup>10-12</sup>

##### a. Preparation of silica gel supported NaIO<sub>4</sub>

Sodium meta periodate (2.57 g, 12 mmol) was dissolved in hot water (5 mL). To the hot solution, silica gel (230-400 mesh, 10 g) was added with vigorous swirling and shaking. The resultant silica gel coated with NaIO<sub>4</sub> was in a powder form and was free flowing.

##### b. Procedure for glycol cleavage-oxidation

To a vigorously stirred suspension of silica gel supported NaIO<sub>4</sub> reagent (2 g) in dichloromethane (DCM: 5 mL) was added a solution of the vicinal diol (**2**, 1 mmol) in DCM. The reaction was monitored by TLC. The mixture was filtered (generally after 10 to 30 min) through sintered glass funnel and silica gel was thoroughly washed with CHCl<sub>3</sub>. Removal of solvent from filtrate afforded the aldehyde (**3**).

Yield 95%. Colourless oil  $R_f = 0.27$  in hexane/ethyl acetate (60:40).

#### Preparation of 2,3-O-Isopropylidene 2-hydroxymethyl 1-propanol (**4**)

To a stirred solution of **3** (1.6 g, 12.3 mmol) in THF (6 mL) was added NaOH (1.082 g, 27 mmol) dissolved in water (4 mL). To this reaction mixture, formaldehyde (1.04 mL, 14.76 mmol) was added and stirred for 12 h at room temperature (Aldol-Cannizarro's reaction<sup>13-17</sup>). THF was evaporated under reduced pressure and aqueous layer was extracted with chloroform (3 × 25 mL). Combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to give a crude mass, which was purified by column chromatography (hexane/ethyl acetate = 70:30) to give (**4**) as colourless oil.

Yield 60 %.  $R_f = 0.16$  in hexane/ethyl acetate (50:50).

I.R (neat) 3436 cm<sup>-1</sup> (broad OH group), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.462 (s, 3 H, -CH<sub>3</sub>), 1.465 (s, 3 H, -CH<sub>3</sub>), 2.3 (bs, 2H, 2 X OH exchangeable with D<sub>2</sub>O), 3.7 (s, 2 H, -OCH<sub>2</sub>), 3.706 (s, 2 H, -OCH<sub>2</sub>), 3.955 (s, 2 H, -OCH<sub>2</sub>). <sup>13</sup>CNMR (CDCl<sub>3</sub>)

$\delta$  26.998 (2 X  $-\text{CH}_3$ ), 64.031 (2 X  $-\text{CH}_2$ ), 68.049 ( $-\text{CH}_2$ ), 83.098 [ $\text{C}(\text{CH}_3)_2$ ], 110.068 [ $\text{C}(\text{CH}_3)_2$ ].

Anal. Calcd for  $\text{C}_7\text{H}_{14}\text{O}_4$ : C, 51.84; H, 8.64; Found: C, 50.92; H, 8.22.

**Preparation of 2,3-O-Isopropylidene 2-tosyloxymethyl 1-O-tosylpropane(5)**

The product **4** (1 g, 6.1 mmol) was dissolved in pyridine (5 mL) and cooled to  $0^\circ\text{C}$  and tosyl chloride (2.8 g, 14.8 mol) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. Water was added and resulting reaction mixture was extracted with ethyl acetate. The organic layer on drying and evaporation afforded tosyl derivative **5** (2.1 g, 72%) as thick liquid.  $R_f = 0.4$  in hexane/ethyl acetate (80:20).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (s, 6 H, 2 X  $-\text{CH}_3$ ), 2.46 (s, 6 H, 2 X Ar- $\text{CH}_3$ ), 3.85 (s, 2 H,  $-\text{OCH}_2$ ), 3.93 (s, 4 H,  $-\text{CH}_2-\text{OTs}$ ), 7.344 and 7.37 each (d,  $J = 8.4$  Hz, 2H ArH), 7.74 & 7.77 each (d,  $J = 8.4$  Hz, 2H ArH).  $^{13}\text{CNMR}$  ( $\text{CDCl}_3$ )  $\delta$  21.65 (2 X  $-\text{CH}_3$ ), 26.28 (2 X Ar- $\text{CH}_3$ ), 67.69 ( $\text{CH}_2-\text{OTs}$ ), 68.56 ( $\text{CH}_2-\text{OTs}$ ), 76.58 ( $\text{OCH}_2$ ), 79.0 ( $\text{C}_2$ ), 111.48 [ $\text{C}(\text{CH}_3)_2$ ], 127.97, 129.68, 129.87, 129.97, 132.0, 145.30 (ArC).

Anal. Calcd for  $\text{C}_{21}\text{H}_{26}\text{O}_8$ : C, 62.06; H, 6.4; Found: C, 61.40; H, 6.120.

**Preparation of 2,3-O-Isopropylidene 2-Azidomethane 1-Azidopropane (6)**

A mixture of **5** (1.2 g, 2.5 mmol) and  $\text{NaN}_3$  (1.47 g, 22.3 mmol) in anhydrous DMF was stirred at  $100^\circ\text{C}$

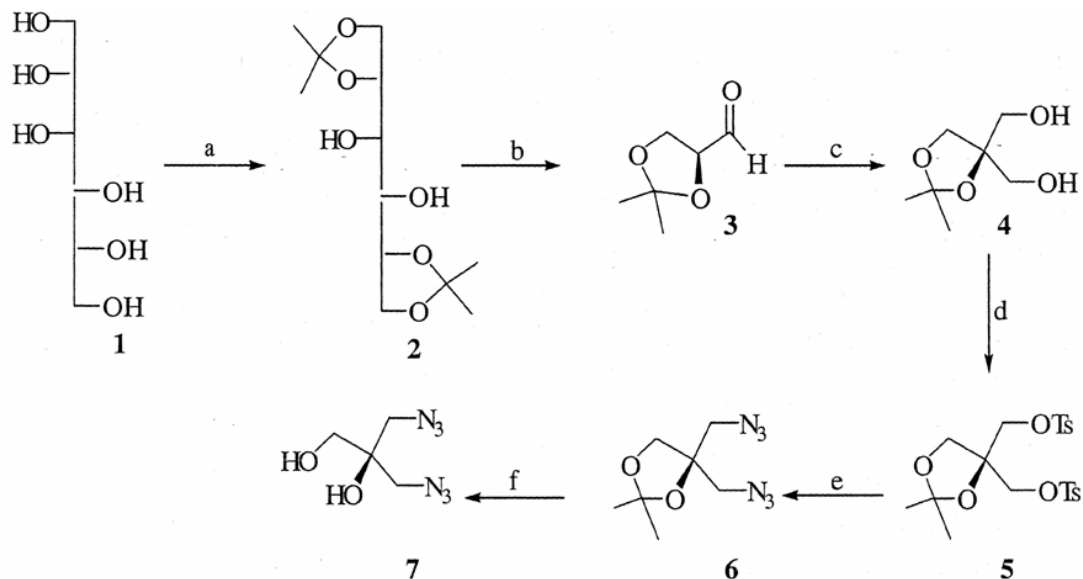
for 24 h. The reaction mixture was cooled to room temperature. The water was added and the reaction mixture was extracted with ethyl acetate. The organic layer was dried and concentrated to furnish azido compound **6**, which was purified by column chromatography (hexane/ethyl acetate = 90:10) to give **6** (0.41 g, 75%) as colorless oil.  $R_f = 0.8$  in hexane/ethyl acetate (80:20). I.R. (neat)  $2104\text{ cm}^{-1}$  ( $\text{N}_3$ ).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (s, 6H, 2 X  $-\text{CH}_3$ ), 3.39 (s, 2H, 2 X  $\text{CH}_2$ ), 3.88 (s, 2H,  $-\text{CH}_2$ ).

Anal. Calcd for  $\text{C}_7\text{H}_{12}\text{N}_6\text{O}_2$ : C, 39.64; H, 5.66; N, 39.62; Found: C, 38.6; H, 5.32; N, 39.12.

**Preparation of 1-Azido 2,3 dihydroxy 2-Methylazido propane diol (ADMP, 7)**

Compound **6** (0.2 g) was dissolved in 5:1 methanol:water mix. The mixture was kept under stirring and 10%  $\text{H}_2\text{SO}_4$  (0.6 mL) was added. Stirring at room temperature was continued for 4 h. The excess of  $\text{H}_2\text{SO}_4$  was neutralized with saturated  $\text{K}_2\text{CO}_3$ . Methanol solvent was evaporated under reduced pressure and the aqueous layer was extracted with chloroform ( $3 \times 5$  mL), dried on  $\text{Na}_2\text{SO}_4$  and solvent was evaporated to obtain a thick liquid, which was purified by column chromatography (hexane/ethyl acetate = 60:40) to give **7** (0.41 g, 75%) as colourless oil (0.140 g, 82%).

I.R. (neat)  $3440\text{ cm}^{-1}$  (broad OH group),  $2107\text{ cm}^{-1}$  ( $\text{N}_3$ ).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.42 (s, 2H, 2 X  $-\text{CH}_2-\text{N}_3$ ), 3.88 (s, 2H,  $-\text{CH}_2-\text{OH}$ ), 3.0 (bs, 2H, 2 X OH)



Reagents and conditions: a)  $\text{FeCl}_3$ , acetone  $25^\circ\text{C}$ , 18h, 60% b)  $\text{NaIO}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{SiO}_2$ ,  $25^\circ\text{C}$ , 30 min, 95% c)  $\text{HCHO}$ ,  $\text{NaOH}$ ,  $\text{THF}/\text{H}_2\text{O}(3:2)$ ,  $25^\circ\text{C}$ , 12h, 60% d)  $\text{TsCl}$ , Pyridine, 12 h,  $0-25^\circ\text{C}$ , 72% e)  $\text{NaN}_3$ , DMF,  $100^\circ\text{C}$ , 24h, 75% f) 10%  $\text{H}_2\text{SO}_4$ , MeOH,  $\text{H}_2\text{O}$ ,  $25^\circ\text{C}$ , 4h, 82%

Scheme 1

Table 1—Theoretical performance prediction of ADMP and comparison with conventional plasticizer

Compound	M.W.	% Composition (wt.)				OB (%)	VOD (km/s)	CJ Pr (GPa)	SI (db)	$\rho$ (g/cm <sup>3</sup> )	$\Delta H_f$ (kJ/kg)	$H_e$ (kJ/kg)	RS	$V_e$ (l/kg)	PR (%)
		C	H	N	O										
ADMP	156	22.78	3.82	53.15	20.23	-70.82	5.69	12.27	220	1.40	440.4	3256	155	1344	162
DAP	306	70.55	8.55	-	20.88	-234.9	3.59	3.80	78.2	1.03	-720.9	1556	-132	2390	-137
DBP	278	69.04	7.96	-	22.99	-224.1	3.68	4.04	85.6	1.05	-723.4	1420	-115	2292	-120
DOP	390	73.8	9.8	-	16.38	-258.0	3.47	3.41	64.8	0.98	-723.5	1625	-150	2601	-156

exchangeable with D<sub>2</sub>O), <sup>13</sup>CNMR (CDCl<sub>3</sub>)  $\delta$  53.8, 53.9 (2X CH<sub>2</sub>-N<sub>3</sub>), 74.58 (CH<sub>2</sub>-OH), 111.2 (C<sub>2</sub>).

Anal. Calcd for C<sub>4</sub>H<sub>8</sub>N<sub>6</sub>O<sub>4</sub>: C, 27.90; H, 4.65; N; 48.81; Found: C, 27.12; H, 4.38; N; 47.86.

## Results and Discussion

According to generalized sequence outlined in scheme 1, the strategy adopted here to synthesize a new compound namely, 1-azido-2,3-dihydroxy-2-azidomethylpropane (ADMP) is centered on protecting hydroxyl groups by acetoide functionality in polyhydroxy compounds prior to azidation. The deprotection of acetoide functionality after azidation gives title compound having both azido as well as hydroxyl functionality.

An attractive feature of this route is that the synthesis starts with protecting easily available sugar D-Mannitol with acetone. The formation of 2,3-*O*-isopropylidene-2-hydroxymethyl-1-propanol (**4**) through Aldol-Cannizarro's reaction is crucial to this method.

Transformation of D-mannitol to 1,2-5,6-Di-*O*-isopropylidene-D-mannitol (**2**) was effected in 60% yield, and the latter on treatment with sodium metaperiodate on silica afforded 2,3-*O*-isopropylidene-D-glyceraldehyde (**3**) in quantitative yield. Compound (**3**) underwent Aldol Cannizarro's reaction with formaldehyde in presence of base leading to 2,3-*O*-isopropylidene-2-hydroxymethyl-1-propanol (**4**) in 60% yield. In the next step (**4**) was tosylated. The synthesized tosyl derivative (**5**) is an inherently stable compound and could be easily prepared in high yields (72%). Transformation of tosyl derivative (**5**) to azido compound (**6**) was effected without much difficulty by refluxing (**5**) with NaN<sub>3</sub> in DMF. The desired compound ADMP is obtained in quantitative yields by deprotection of (**6**) by using 10% sulphuric acid. A review of the literature indicates that these compounds are relatively inaccessible. Moreover, the compound that has been described appears to exhibit the good stability and does not undergo deprotection even under drastic azidation step. The spectral and

analytical data obtained for the newly synthesized compounds matches with the structure assigned.

## Thermal and explosive properties

The DSC of ADMP showed its exothermic decomposition in the temperature region of 191-260°C with heat release of the order of 1390 J/g. These results suggest the energetic nature of the compound. The theoretically predicted parameters of ADMP showed its superior detonation factor, velocity of detonation (*VOD*), CJ pressure (CJ Pr), heat of explosion (*H<sub>e</sub>*), volume of explosion products (*V<sub>e</sub>*), relative strength (RS), sound intensity (SI) and power index (PR) in comparison to conventional plasticizers such as dioctyl phthalate, diamyl phthalate and dibutyl phthalate (Table 1).

## Conclusion

During this work, a new approach of synthesis of ADMP has been developed which uses D-mannitol and acetone as starting materials. In this synthetic route, key step involves the formation of 2,3-*O*-isopropylidene-2-hydroxymethyl-1-propanol (**4**) from 2,3-*O*-isopropylidene-D-glyceraldehyde by Aldol-Cannizarro's reaction, which provides two hydroxyl groups, which are latter converted to azide groups. Significantly, energetic azido groups are introduced in the final step of sequence, which is desirable from safety considerations. ADMP appear to be a potential candidate as energetic plasticizers as well as energetic monomer for the preparation of azido polymers for propellant applications.

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