Synthesis and characterization of some new styphnyl-bis-ß-alanine derivatives

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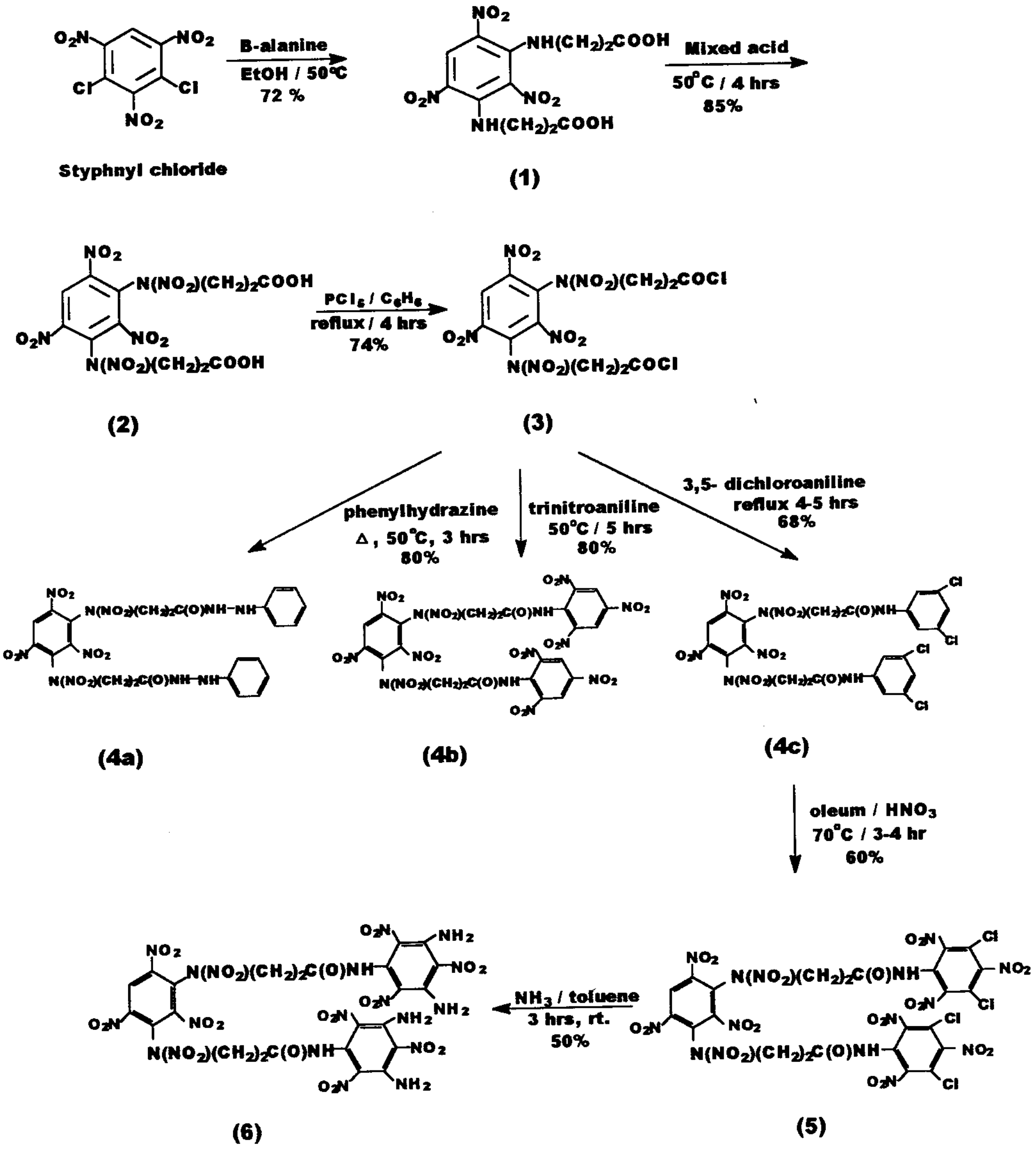
A new series of N,N′ –dinitro-styphnyl-bis-ß-alanine derivatives have been prepared, characterised and evaluated for its preliminary explosives properties in order to find its suitability to explosives and propellants formulations.

A literature survey revealed that some of the styphnyl based compounds had a combination of desirable properties as explosives and propellants, [4,5]. This led us to find an efficient route for the synthesis of a new class of polynitroaromatics containing a nitrated bis-ß-alanine moiety attached to a styphnyl molecule. Our study was also extended to include the explosive behaviour of the compounds reported herein.

The strategy to synthesize the new target dinitrostyphnyl-bis-ß-alanine derivatives **4a, 4b** and **4c** from the condensation reactions of **3** with phenyl hydrazine, trinitroaniline and 3,5-dichloroaniline under reflux in polar aprotic solvent for 3 hours, is outlined in Scheme 1. However, **3** was prepared in three steps with 70% yield starting from styphnlychloride via condensation, nitration and chlorocarbonylation reactions. Compound **6** was made via the amination reaction of **5** in toluene for a optimum of 3 hours passing ammonia gas into the solution at room temperature. Our intention behind the preparation of **6** was to improve upon the density, insensitivity and



Scheme 1

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Table 1 Physico-chemical and explosives properties of compounds

Sample no.	Properties	**4a**	**4b**	**5**	**6**
1	Melting point, °C	136–138	156–158	210–213	315–318
2	Density, g/cm^3 (experimental)	2.05	1.85	1.33	1.92
3	DTA °C, (exo.)	136	165 (endo) 175 (exo)	180	318
4	Impact sensitivity cm (50% ht of explosion)	137	86	38	62.3
5	Friction sensitivity up to kg	36	36	28.8	36
6	Deflagration temperature (°C)	NI	NI	NI	NI
7*	Oxygen balance (OB), %	-115.67	-56.18	–45.60	-56.00
8**	Velocity of detonation (VOD), m/s	5735	7436	6396	7684
9**	Detonation pressure (Pc-J), kbar	169.2	255.2	143.0	283.8

NI = Not ignited. The deflagration temperature is the temperature at which a small quantity of sample of explosive in a test tube when heated externally burns into flame, decomposes rapidly or detonated violently.

*OB represents the compound's lack or excess of oxygen needed to produce the most stable products, OB is calculated according to the eqn in ref. 7

**VOD and detonation pressure were calculated as per formulae given in ref. 8.

energetic properties. The structure assignment of compounds was established unequivocally by means of spectroscopic data and elemental analysis. The slight variation for nitrogen analysis may be attributed to the high nitrogen content and explosive nature of the molecules. The electron impact mass spectra (EIMS) of compounds offered a satisfactory means of characterization.

The compounds were subjected to differential thermal studies with 10 mg of sample at a heating rate of 10ºC/min over the temperature range 25-600 ºC. The DTA curves exhibit only one sharp exotherm in all the cases except in **4b** which shows an endotherm at 165ºC, followed by an immediate exhibition of an exotherm at 175ºC (Table 1). The compound **6** shows the highest decomposition temperature at 318ºC representing a good heat resistant thermally stable explosive which can be used at high temperature.

In addition, the compounds were evaluated for several introductory explosive properties. All compounds display high density and are substantially insensitive to impact and friction tests[11] (Table 1). A combination of good thermal stability and insensitivity is a unique feature as observed in **6**. However despite high density and favourable insensitiveness to heat, friction and impact, the calculated energetic properties (velocity of detonation, D; detonation pressure, Pc-j; oxygen balance, OB) (Table 1) of **6** are inferior to those as found for nitramine based explosives like RDX and HMX[9]. These compounds are safe, reliable and possess a high density with good thermal stability. They can be identified as attractive ingredients for development of high energetic insensitive explosive and propellants formulations.

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Techniques used : IR, ^{1}H-NMR and mass spectrometry

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Scheme 1

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