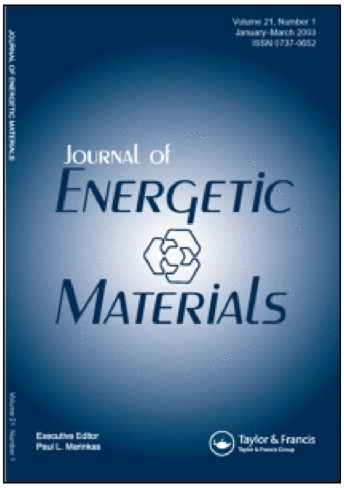

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ACID SALTS OF 8H-2,6,8,9,10-PENTAAZABICYCLO[5,2,1]-DECA-2,5,9,10-TETRAENE

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ABSTRACT

Some new acid salts of 8H-2,6,8,9,10-pentaazabicyclo[5,2,1]-deca-2,5,9,10-tetraene were prepared and characterised by spectral data (IR, ^{1}H-NMR and Mass) and elemental analysis. The purity of these compounds was confirmed by HPLC and was found to be > 95% pure. In addition, the compounds were subjected to impact and friction sensitivity tests and were found very safe.

INTRODUCTION

Over the decade a variety of different types of energetic materials has been synthesised using the triazole ring as a key building block[1-4]. Among them, some compounds find important applications as primary explosives [5,6], gas generators [7], insensitive [8-10] and thermally stable high explosives [11,12]. Keeping in view the above observations and, in continuation of our work on the synthesis of nitrated heterocyclic compounds having high density and high velocity of detonation, we have prepared several acid salts of 8H-2,6,8,9,10-pentaazabicyclo[5,2,1]-deca-2,5,9,10-tetraene as intermediates. The present communication describes the details of synthesis and characterisation of these new compounds.

EXPERIMENTAL

All reactions were conducted in oven dried flasks. Solvents were routinely distilled before use. The reagents used for reaction were of L.R. grade. All monoprotic acids were obtained commercially with specified strength. Tetra ethoxypropane and 3,5-diamino-1,2,4-triazole were purchased from E Merck (India) Ltd. Melting points are uncorrected and were determined in open capillaries by Mettler Apparatus. IR Spectra were recorded with a Perkin-Elmer Infrared Spectrophotometer on KBr pellets. ^{1}H-NMR Spectra were determined on Bruker 200 MHz with pulsed Fourier Transform System and chemical shifts are reported in δ units (parts per million, ppm) using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on JOEL DS-Spectrometer.

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Elemental analysis was performed on Elemental Analyser, EA-1101. The purity of the compounds was checked by thin layer chromatography (TLC, silica gel – "G") with chloroform-methanol (9:1) as the solvent system, and also by high performance liquid chromatography (HPLC), using C_8-micro-BP column, a mobile phase comprised of methanol-water (70:30) adjusted to pH 3.0, a flow rate of 1 ml/min, and UV detection at 232 nm. In all the cases the purity was found > 95% (Table-1).

Differential thermal analysis (DTA) was performed by heating 10 mg of the sample at a heating rate of 10°C/min in the presence of ambient air. The impact sensitivity of the compound was determined by Fall Hammer method by using a 2 kg drop weight. Friction sensitivity was measured on Julius-Peter Apparatus.

Synthesis :

1,1,3,3-tetraethoxypropane :

In a three necked round bottom flask equipped with pressure equalizer dropping funnel fitted with a calcium chloride tube at the top, a mixture of ethyl orthoformate(10 g , 0.068 mol) and BF_3 -etherate (0.09 ml) were taken to which vinylethylether (3 g, 0.042 mol) was added dropwise during 15 minutes at a temperature below 45°C. After the addition the mixture was stirred at 33°C for 1 hr. This was followed by addition of sodium carbonate, (0.3 g) and stirring was continued for additional 3 hrs at room temperature. The precipitate formed was filtered and the filtrate was fractionated in vacuum in the presence of a small quantity of sodium carbonate as an acid quencher to yield 1,1,3,3-tetraethoxypropane, 2.5 g (85%), b.p. 90°C/6 mm of Hg. The product was characterised by spectral and elemental analysis.

Analysis Calculated for $C_{11}O_4H_{24}$: C, 60.00; H, 10.90

Found : C, 59.64; H, 10.46

IR (neat) cm^{-1} : 3000, 2950, 1444, 1380, 1116, 1068, 994

^{1}H-NMR (CD_3COCD_3) δ ppm : 1.0 (t, 12H), 1.75 (t, 2H), 3.2 – 3.55 (m, 8H), 4.35 – 4.5 (t, 2H)

Acid salts of 8H-2,6,8,9,10-pentaazabicyclo (5,2,1,)-deca-2,5,9,10-tetraene (1a–1d)

General procedure :

To a 100 ml three necked round bottom flask a mixture of monoprotic acid (6 ml) and water (15 ml) were taken. To this 3,5-diamino-1,2,4-triazole (3 g, 30 m mole) was added portionwise with stirring and subsequently heated to 50°C. 1,1,3,3-tetraethoxy propane (6.6 g, 30 mmole) was added dropwise at this temperature. The resulting mixture was stirred for 2-3 hrs maintaining a constant temperature of 50°C, affording a light yellow precipitate. The mixture was cooled, filtered under vacuum, recrystallised from water and finally washed with acetone to remove water. The product was dried and the yield was 90-95%, homogeneous on TLC plate (silica gel-G; chloroform-methanol, 9:1).

All other monobasic acid salts of diaminotriazole (1a–1d) in this series were synthesised following the above mentioned procedure. The physical contstants and spectral data (IR, ^{1}H-NMR, Mass) along with their elemental compositions are given in Tables-1&2.

8H-2,6,8,9,10-pentaazabicyclo(5,2,1)-deca-2,5,9,10-tetraene (2)

Monoprotic acid salt (2 g, 0.15 mole) was dissolve in minimum quantity of water in a 100 ml round bottom flask. The solution was neutralised and made slightly basic using 10% NaOH solution. It was then extracted with ethyl acetate. The organic layer was separated, dried and finally evaporated to afford acid free diaminotriazole condensed product, yield 50%, m.p. 195°C. The purity of the compound was checked on thin layer chromatographic silica gel plate and was further confirmed by High Performance Liquid Chromatography (HPLC). The spectral data are consistent with structure.

IR (KBr) cm^{-1} : 3398 (br, d), 1628, 1488, 1416, 1348, 1060

^{1}H-NMR (DMSO-d$_6$/TMS) δ ppm : 8.93 – 8.44 (dd, J=10.0, 9.0 Hz, NH), 7.78-6.89 (m, 2H, = CH, J = 10.5 Hz), 2.05 (2H, CH$_2$)

EI, 70 ev, m/z : 136 (m$^+$ + 1 1%), 135 (m+, 100%), 106, 95

Analysis calculated for $C_5H_5N_5$ (M. Wt.135) : C, 44.44; H, 3.70; N, 51.87

Found : C, 44.94; H, 3.68; N,51..87

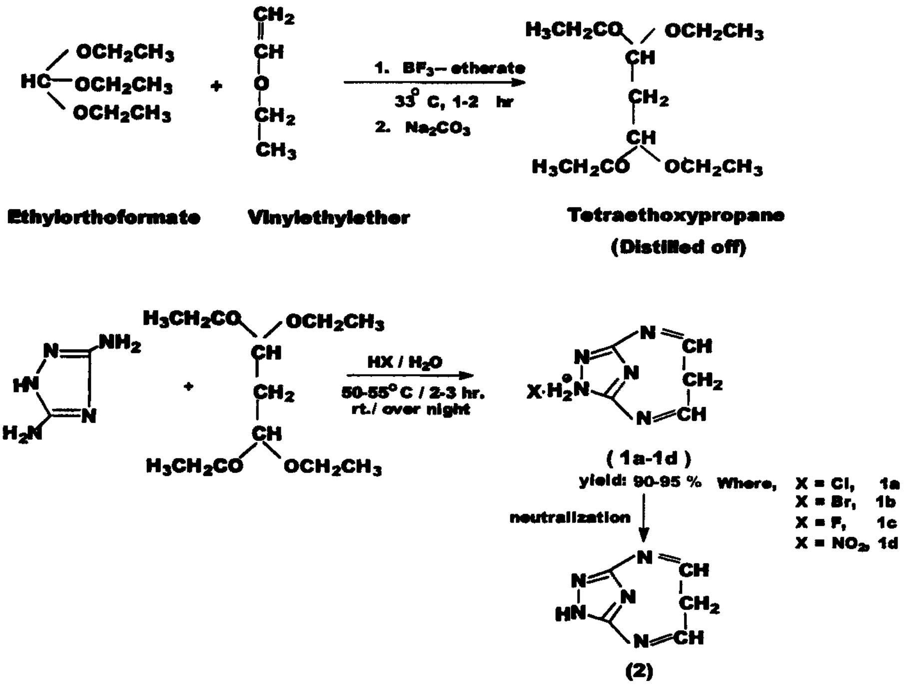
DTA (endotherm) temp °C : 196 (melting)

HPLC, Retention time (Purity) : 2.98 min (95%) (conditions as described above)

RESULTS AND DISCUSSION :

Our interest has been focused on 3,5- diamino-1,2,4-triazole ring and its condensation products because of two prime considerations. First, the triazole moiety serves as an important synthon for construction of high energy materials[13,14] and secondly, the triazole ring and the cojugated imino groupa are able to withstand high temperature properties and low pressures. During the course of our studies on a high density and high velocity of detonation (VOD) compound based on the 1,2,4-triazole ring, we have synthesized a series of monoprotic acid salts of 8H-2,6,8,9,10-pentaazabicyclo (5,2,1,)-deca-2,5,9,10-tetraene as intermediate products (Scheme-1). The compounds were synthesised in 90-95% yield by the condensation of 1,1,3,3-tetraethoxypropane with 3,5-diamino 1,2,4-triazole in presence of the monoprotic acid. All compounds were subsequently neutralised with 10% NaOH solution to obtain the free base. A commercial source of 1,1,3,3-tetraethoxypropane (TEP) was used initially, but it was later synthesised and characterised in our laboratory to enhance cost effectiveness..

Scheme - 1



The physico-chemical properties and spectral data of the salts as given in Table 1 & 2 were in good agreement with the structures. The IR spectra all showed the presence of N-H stretching around 3400-3300 cm^{-1} and that of C-H stretching in the range 3100-3000 cm^{-1}. The absorption bands at 1674 – 1628 cm^{-1} and 1488-1470 cm^{-1} were attributed to. C=N stretching and N-H bending vibrations. The C-H bending vibrations were observed in the range 1400–1348 cm^{-1}. The ^1H-NMR spectra were taken in DMSO-d_6 solvent. The chemical shifts of NH protons in general were found in the range δ 8.9 – 8.44 and undergo slow exchange. The =CH protons appeared in the range δ 7.73 – 6.89 and the methylene protons were resonated at δ 2.10 – 2.0.

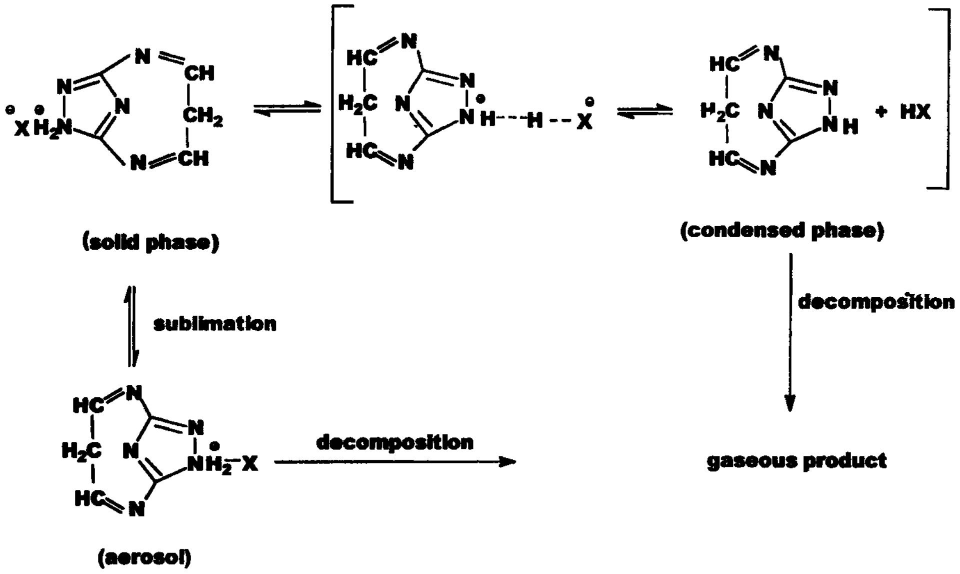
Being acid salts and having high melting point, they are practically nonvolatile which limits conventional chemical ionization or electron impact as possible modes of mass spectrometry for characterization. However, attempts were made to record the Electron Impact mass spectra of the compounds at 70 eV and the spectra of all these monoprotic acid salts (1a–1d) were conspicuous by the presence of a very strong peak at m/z 135 which arose by the loss of HX (X=Cl, Br, F & NO_3) from the molecular ion peaks. The ion at m/z 95 constituted one of the significant ions in the spectra of all the salts, and arises from cleavage of the –CH-CH_2-CH group from peak at m/z 135. The compounds showed other diagnostic peaks at m/z 136 and for HX fragments.

The halides salts show only endotherms related to melting (Table-1); in case of HF salts two endotherms (200°C and 293°C) were observed. The first endotherm may be due to rearrangement/phase transition and the second one may involve sublimation and dissociative vapourisation process. It appears that sublimation dominates at lower temperature and sample was continued to heat until about 450°C. The combination of significant sublimation and endothermic/exothermic degradation results in the formation of gaseous products. It seems the overall process commence in two ways :

1. In the first, transfer of protons through an activated complex, forms iminium ion and halide/nitrate ion in the condensed phase. Further decomposition may involve deimination and ring rupture to form gaseous products.
2. It may sublime to form aerosol prior to decomposition into the gaseous products (Scheme-2). However, more experiments are necessary to reach a trustworthy

values to prove sublimation, dissociative vaporization and complete decomposition.

Scheme- 2



The nitrate salt, **1d** showed only an exotherm at 190°C, corresponding to chemical decomposition. Based on the data obtained from different heating rates i.e. 5, 10, 15 and 50°C, the calculated activation energy at decomposition temperatures for compound, **1d** according to the method of Ozawa[15] was found 152.23 kcal / mole.

Further, the compounds were subjected to a preliminary explosives tests, impact and friction sensitivity, as determined by drop hammer method using 2 kg drop weight and on Julius-Peter apparatus. The results showed 20% explosion at a height of 170 cm for compounds of bromide and nitrate salts whereas no explosion was observed for fluoride and chlorides salts. All compounds are insensitive to friction upto 36 kg. Some of the useful energetic parameters of **2**, have been predicted theoretically and found that the properties (density, 1.72 g/cm^3; velocity of detonation, 6708 m/s; detonation pressure, 193.3 k bar) are not within the appreciable limit.

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Table-1 : Selected physico-chemical and thermal properties of the monoprotic acid salts of 8H-2,6,8,9,10-pentaazabicyclo[5,2,1]-deca-2,5,9,10-tetraene

Compd No.	HX	% yield	Melting point °C	Molecular formula (mol.wt)	Elemental analysis Found, %	Elemental analysis Calctd. (%)	Tm °C
1a	HCl	95.5	270 (decomp)	$C_5H_6N_5Cl$ (171.5)	C 34.89 H 3.70 N 40.25 Cl 21.28	34.98 3.49 40.71 20.70	271 (endo)
1b	HBr	93	295-300	$C_5H_6N_5Br$ (215.5)	C 28.99 H 2.48 N 33.01	28.84 2.78 32.48	295 (endo)
1c	HF	90	195-198	$C_5H_6N_5F$ (155)	C 38.25 H 3.61 N 44.85	38.90 3.87 45.16	200 (endo)
1d	HNO_3	92	189-191	$C_5H_6N_6O_3$ (198)	C 30.97 H 2.88 N 43.00	30.50 3.03 42.62	190 (exo)

Table-2 : Spectral and HPLC data of monoprotic acid salts of 8H-2,6,8,9,10-pentaazabicyclo[5,2,1]-deca-2,5,9,10-tetraene

Compd No.	IR (KBr) cm^{-1}	^1H-NMR DMSO- d_6/TMS) δ ppm J (Hz)	EIMS (70 eV) m/z	HPLC	
				Ret. Time (min)	Purity %
1a	3408,3146, 3076 1674,1566,1406, 1270,1190, 1086 814,752,702	8.7-8.5 (dd,J=10, 9.0 Hz NH) 7.36-7.27 (m, 2H, =CH, J=10.8 Hz) 2.10 (m, 2H, CH_2)	1.35 (m^+-HCl), 136,134, 95, 79	2.96	95.3
1b	3302, 3184 (w) 1672,1400,1270, 1184, 922	8.85-8.83 (dd, J=10, 9.5 Hz, NH) 7.44-7.36 (m, 2H,=CH, J=10.5 Hz), 2.0 (m, 2H, CH_2)	1.35 (m^+-HBr) 136, 95, 81, 80	2.95	99
1c	3410, 3192(w) 3073(w), 1674 1564, 1402,1080, 722	8.9-8.6 (dd,J=10, 9.0 Hz NH),7.35-7.20.(m, 2H ,=CH, J=11),2.1 (m, 2H, CH_2)	135(m–HF) base peak 136, 85, 85 (m/z 135,-CH CH_2 CH)	2.98	95
1d	3412,3186,1674 1556,1384,1182, 1020814,744,700	8.9-8.65 (dd, J=10, 8.5 Hz,NH), 7.41-7.35 (m,2H,=CH, J=11.5 Hz) 2.15 (m, 2H, CH_2)	135 (m^+-HNO_3) 136(m^++1) 95,63	2.92	97