Syntheses, characterization and energetic properties of closo-(B12H12)2− salts of alkylmethylimidazolium derivatives

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Syntheses, characterization and energetic properties of *closo*-$(B_{12}H_{12})^{2-}$ salts of alkylmethylimidazolium derivatives

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***Abstract*— The diimidazolium derivative of acetylene and its salt 3,3'-(but-2-yne-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium)chloride (1) was synthesized by a solvent free sonochemical method and then the counter chloride ions were replaced by *closo*-dodecaborate $[(B_{12}H_{12})^{2-}]$ and perchlorate (ClO_4^-) anions respectively. Along with these two ionic salts, a series of salts with closo-dodecaborate and alkyl imidazolium cations were also synthesized. All the compounds were characterized by NMR and MASS spectral data, elemental analyses and thermogravimetric analyses. In addition to that enthalpy of combustion, enthalpy of formation and heat of explosion of all the compounds were experimentally determined. In addition to that impact and friction sensitivity of all the compounds were experimentally determined shown that these compounds were insensitive towards impact and friction. Hence these compounds have potential insensitive energetic materials in various fields in propellant research and technology such as solid rocket propellants and burn rate accelerators.**

Keywords- burn rate accelerators; dodecaborate salts; solid rocket propellant fuels

I. INTRODUCTION

Boron and aluminium release large amounts of energy per unit volume while burning (oxidation of B to B_2O_3 releases 58.8 kJ g^{-1}).[1] Hence, in order to enhance the energy output from a propellant or any other energetic compositions, boron or aluminium powder is added to them.[3] Apart from this these elements are known to influence the burning rate of the propellants.[2] However, the increase in the energy of the propellant added with these elements is much less compared to the theoretical potential.[4] This partial realization of the energy potential is mainly attributed to the incomplete combustion of these elements.

Compared to macroscopic materials, the nanoparticles in their oxidation reaction release greater amounts of energy per volume of the reactants. This can be attributed to their large surface to volume ratio.[5] With an aim of utilizing this property, numerous attempts were made to use B and Al as submicron sized particles in the energetic formulations instead of a simple elemental powder. However, the aggregation and oxidation on the surface of nanoparticles lead to incomplete burning of the nanoparticles resulting in a lower energy output from a propellant.[6] In order to circumvent these problems, we are interested in delivering boron into an energetic composition in a completely different form rather than simple nanoparticles.

Molecular inorganic clusters are steadily growing in importance because of their interesting structures and applications.[7] The core structure of a cluster molecule is an ensemble of atoms bound together themselves by covalent bonds or through bridging atom such as oxygen and nitrogen. The inorganic cluster molecules could be intermediate in size between an atom and a macroscopic material.[8] Since they are discrete molecules with a known structure, the size dependent properties of the materials made from these molecules could be altered for the required applications.[9] The size and discrete nature of clusters are expected to influence the burning property and overall energy release from propellants when these molecules are ingredients.[10]

Some of the boron clusters such as *closo*-dodecaborate, $(B_{12}H_{12})^{2-}$ are stable for atmospheric oxidation and hydrolysis by water under normal conditions and hence they could be useful molecules to deliver boron through the burning process in a propellant. Herein we report the synthesis and energetic properties of *closo*-$(B_{12}H_{12})^{2-}$, salts of imidazolium derivatives (Chart 1). The heats released by these molecules during combustion are determined experimentally and the results are compared with those of pure aluminium and boron.

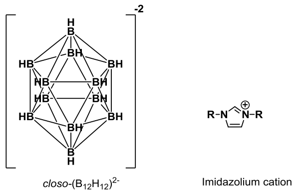


Chart 1. Structures of closo-dodecaborate anion and imidazolium cations.

II. RESULTS AND DISCUSSION

When an organic ionic salt is designed to contain a higher percentage of nitrogen, it is expected to release higher energy during their burning process. This is because, at burning temperature, the molecules will decompose releasing the constituent atoms.[1a] The nitrogen atoms obtained as a result of this process will combine to form a nitrogen molecule (N_2). In the process of triple bond formation huge amounts of energy will be released. Consequently, five member nitrogen containing rings such as imidazole, pyrazole, triazole, and tetrazole are interesting frameworks for energetic materials as they possess relatively high nitrogen contents. Hence, the syntheses of imidazolium, triazolium and tetrazolium salts to establish a library of compounds for screening as potential high energy materials have been pursued by many researchers.[11–13] Such an interest is reflected as a huge number of publications on synthesis of a variety of olium salts.[11]

The presence of a functional group in the molecular system may help to derivatize a molecule for structure–property relationship studies. If a molecule possess an acetylene group it may be useful for in situ generation of acetylene gas during decomposition. Acetylene gas on burning with pure oxygen can produce flame temperature of the range 3000–3300 °C. Hence, the design and synthesis of an ionic salt consisting of an acetylene moiety, an imidazolium cation and a dodecaborate anion within a molecule could be one more way forward in the chemistry of high energy materials.

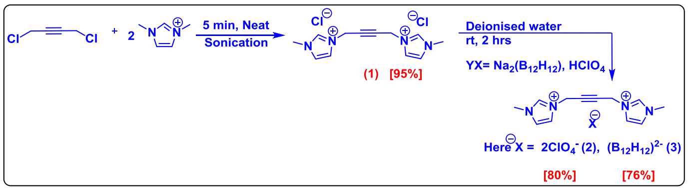
A. Synthesis

The disodium salt $Na_2(B_{12}H_{12})$ was prepared according to the literature procedure[14] and used for the syntheses of various salts of imidazolium derivatives (compounds **3**–**8**). In order to obtain the acetylene functionalized diimidazolium salts, the chloride salt of imidazolium held together by an acetylene moiety [1,4-diimidazolium-2-butyne (**1**)] was first prepared by a simple quarternization reaction of 1,4-dichloro-2-butyne with N-methylimidazole under ultrasonic radiation at room temperature (Scheme 1).

The compound **1** was reacted with perchloric acid at room temperature to obtain the compound **2** (Scheme 1). Similarly, when the chlorides in the compound 1 were exchanged with *closo*-$(B_{12}H_{12})^{2-}$ through a simple metathesis reaction with $Na_2(B_{12}H_{12})$ in deionised water the compound **3** was obtained (Scheme1). In the second reaction while both the starting materials were soluble in water, the insoluble product was just filtered, washed using deionised water and then dried by applying a high vacuum at room temperature to yield pure compound **3**. Both these metathesis reactions were carried out in a 0.5 g scale and later increased to a 2 g scale in water.

A few reports described (or proposed) the syntheses of the salts of *closo*-$(B_{12}H_{12})^{2-}$ with imidazolium and triazolium cations.[15] With an intention to study the energetic properties, we have prepared a series of salts containing *closo*-$(B_{12}H_{12})^{2-}$ (compounds **4–8**). The chemical structures of compounds are shown in Chart 2.

The compound **4** in Chart 2 was prepared by following the literature method.[14] In order to synthesize the compounds **5–8**, the corresponding N-alkylimidazolium chlorides were synthesized first using procedures modified from the solvent free sonochemical method reported earlier.[16] And then they were converted to the corresponding N-alkylimidazolium borates (compounds **5–8**). All these compounds (**3–8**) were obtained in good yields and their purity was confirmed from the elemental analyses. It is worth mentioning here that all these compounds were obtained from a reaction in water and did not require any further purification.



Scheme1. Syntheses of the salts of 1,4-diimidazolium-2-butyne.

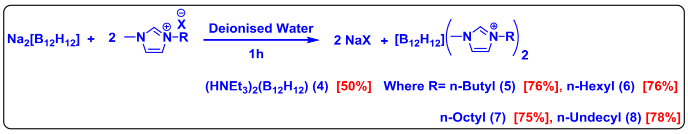


Chart 2. Structures of salts containing *closo*-dodecaborate anions and dialkylimidazolium or triethylammonium cations.

B. Characterization

All the compounds were characterized by ^{1}H, ^{13}C, $^{11}B\{^{1}H\}$NMR and HRMS spectral data as appropriate. The formation of the compound **1** was clearly evidenced from the ^{1}H NMR spectrum and its composition was confirmed from the LCMS spectrum and elemental analysis. It showed an M^+ peak at 287 in the mass spectrum matching with the molecular weight of 1,4-diimidazolium-2-butyne. Further it was confirmed from HRMS (M^+ = 287.0830).

In the $^{11}B\{^{1}H\}$ NMR spectra of the compounds **3–8**, the chemical shifts corresponding to the $[B_{12}H_{12}]^{2-}$ moiety were appearing around −15 ppm (singlet) (Fig. 1) whereas the same was appearing at −15.3 ppm for $Na_2(B_{12}H_{12})$. It showed that the cationic parts of these compounds did not have any effect on the boron chemical shifts. In the 1H NMR spectra the B–H chemical shifts of all these compounds were not well resolved and they were appearing as a very broad peak spanning 1.4–0.2 ppm. This was due to the quadrupolar interaction of the two nuclear isotopes (^{11}B, I = 3/2, 80.42% naturally abundant and ^{10}B, I = 3, 19.58% naturally abundant) of the adjacent boron. For the compounds **4–8**, the B–H peaks were overlapping with that of $–CH_2–$ or $–CH_3$ moieties making it difficult to get peak integration (Fig. 2a). However, in the case of the compound **3**, the peak was better identified (Fig. 2b). All these compounds have characteristic IR-stretching (Fig. 3) appearing around 2480 cm^{-1} corresponding to B–H.

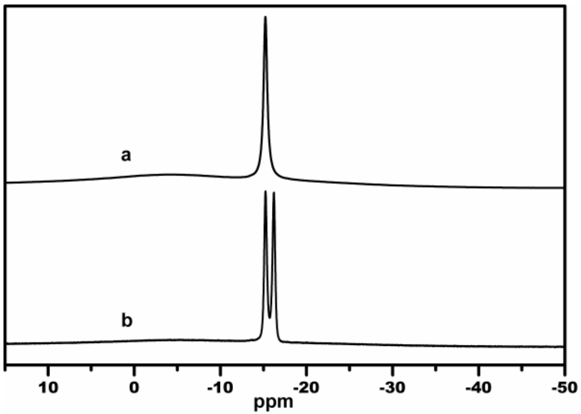


Fig 1. (a) $^{11}B\{^1H\}$NMR (b) ^{11}B NMR spectra of compound **5**

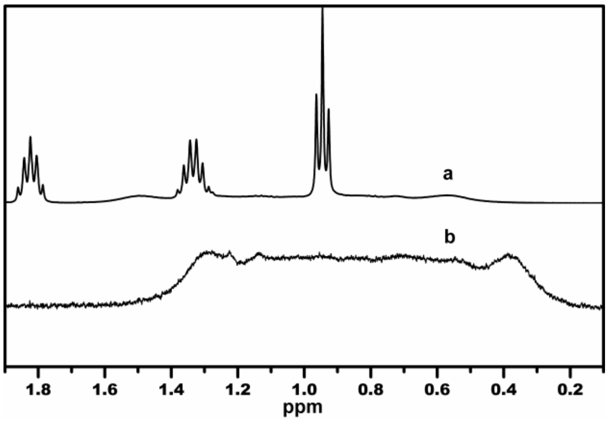


Fig 2. ^1H NMR spectra of the observed peak corresponding to B–H protons of $(B_{12}H_{12})^{2-}$ in; (a) compound **5** in CD_3Cl, (b) compound **3** in DMSO-D6.

Fig

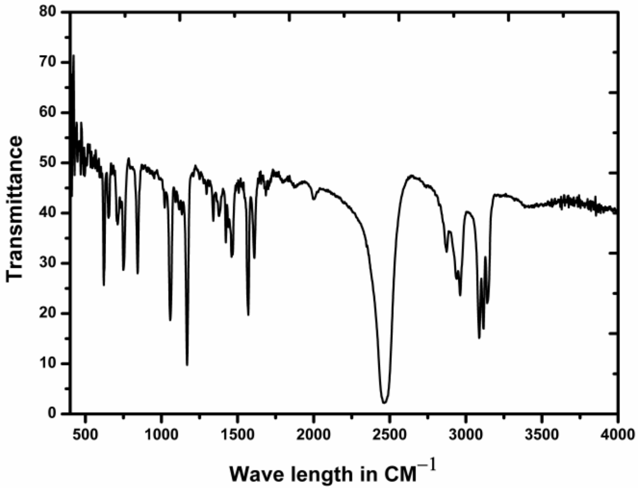


Fig 3. FT-IR spectrum of compound **5**; B–H 2480cm^{-1}

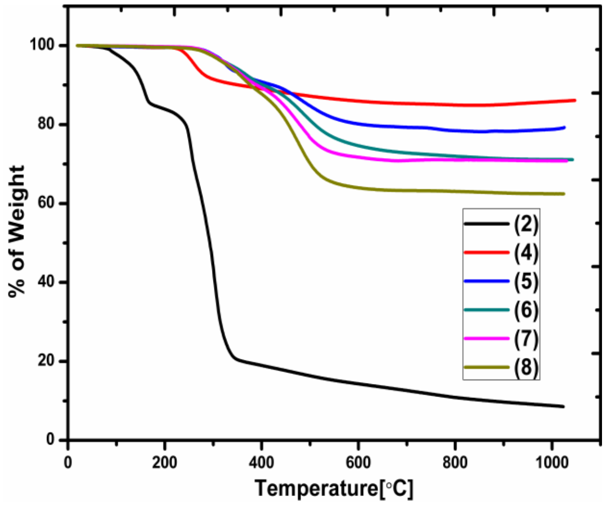


Fig 4. TG-DTA graphs of the compound **2** and **4-8**.

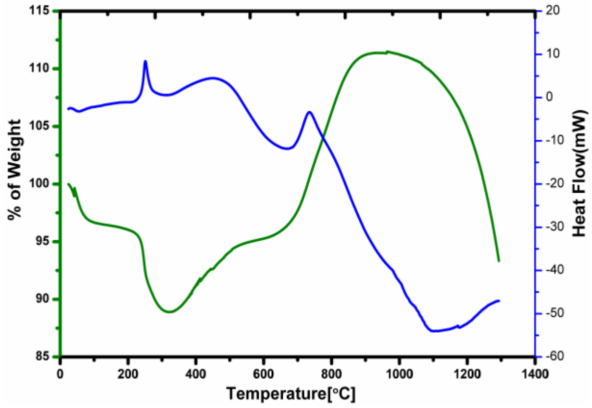


Fig 5.TG-DTA graphs of the compound **3.**

The HRMS spectra of the compounds **2** and **3** showed (M +23)$^+$ peaks respectively at 437.0288 and 381.3434, which ere matching with their chemical structures. Similarly, the respective molecular weights of the compounds **5–8** determined from the LCMS and HRMS spectra showed the presence of two units of the imidazolium cations in these compounds. Unfortunately, none of these compounds yielded any good quality crystal for molecular structure determination through X-ray crystallography. However, the elemental analysis results were consistent with the exact composition of all the compounds.

C. Thermal stabilities

Generally, the melting and boiling points of the lower boranes are low and they are pyrophoric too. These undesirable properties make them highly objectionable for the propellant

Table 1. Energetic properties of the dodecaborate salts with alkylimidazolium derivatives

C	***Mp (°C)***	***Td (°C)***	***$\Delta_c H^{\circ}_m$ (kJmol^{-1})***	***$\Delta_f H^{\circ}_m$ (kJmol^{-1})***	***Q (kJmol^{-1})***	***IS (J)***	***FS (N)***
2	--	145	-5910	-986	-14262	>50	>360
3	228	232	-15493	-811	-43264	>50	>360
4	268	270-275	-15338	-3253	-44303	>50	>360
5	217	270-275	-19134	-745	-45529	>50	>360
6	163	270-275	-21031	-1566	-44149	>50	>360
7	190	270-275	-23843	-1465	-44779	>50	>360
8	198	270-275	-27903	-1487	-45251	>50	>360
B	--	--	--	-635	-58800	>50	>360
Al	--	--	--	-834	-30900	>50	>360

C: Compound; Mp: melting Point;T_d: Temperature of decomposition; Δc H°m: standard molar heat of combustion; Δf H°m: standard molar heat of formation; Q: Heat of explosion; IS: Impact Sensitivity; FS: Friction Sensitivity; B: Boron; Al: Aluminium

processing. Interestingly, the compounds **3-8**, containing higher borane i.e. *closo*-dodecaborate anion, possess high melting points. They were not sensitive to air and moisture and also not pyrophoric. Thermal stabilities and decomposition behaviour of all these compounds were explored through simultaneous thermogravimetric and differential thermal analyses (TG-DTA). In the instrument, the compounds were heated with the heating rate of 20°C min^{-1} up to 1100°C in an inert atmosphere. The study revealed (Fig. 4) that the compounds **3–8** were thermally stable up to 270 °C. For example, the compound **3** started decomposing at 232 °C, while the compound **2** at 145 °C. The melting points and decomposition temperatures of these compounds are provided in Table 1. In the TGA graph, it was observed that the major part of the compound **2** was decomposed below 400 °C. But the behavior of other compounds was not similar. Even at 1100 °C, the weight loss of 30% (compound **8**) was the maximum for the compounds **3–8**. This may be because the major parts of the borates were remaining without decomposing.

At this juncture it is worth stating the following. Generally the propellants would be burning through a deflagration process.[1] presumably, the organic part of the molecule would burn first to release energy. And this energy may then be used to break the covalent bonds between boron atoms of the cluster molecules to release boron for the burning. This can be explained from the observation in the bomb calorimeter experiments (vide-infra). It was witnessed that the pure $Na_2(B_{12}H_{12})$ was not ignitable inside the bomb by a simple electrical shock. However, all these salts **3–8**, which contain organic moieties as cations, were easily ignitable.

During the TGA-DTA studies, all molecules except compound **3** were observed lose weight gradually or in discrete steps. Every considerable weight loss was accompanied with an endothermic peak in the DTA curve. This indicated that, on supply of heat the molecules were fragmenting by means of losing the slice of it. However, in the case of compound **3**, it was observed from the TGA curve that it lost around 12% of its weight in the first step. And the temperature at which the weight loss occurred was matching with an exothermic peak in the DTA curve (Fig. 5). This might be because this compound decomposed violently releasing the heat instantaneously.

D. Combustion studies

As discussed above the molecules **3–8** are expected to release boron for oxidation reactions. Since the oxidation of boron is an exothermic reaction, it is expected to increase the overall energy release from a propellant added with these kinds of compounds. To understand the possibility to use as high energy materials, a study on the energetic properties of the compounds **3–8** is required. The standard enthalpy of formation, enthalpy of combustion and heat of explosion are the essential characteristics of a high energetic material. Hence we have determined these parameters for the compounds **3–8**.

In the bomb calorimetric experiments in an oxygen atmosphere, the enthalpies of combustion of the compounds **2–8** at constant volume have been determined. From these values, the heats of explosion (i.e. the energy released on burning of one kg of a compound) of these compounds were also calculated. The enthalpies of formation were calculated from enthalpies of combustion using Hess thermochemical equations. All these values are displayed in Table 1 in comparison with that of pure aluminium and boron which are normally used as fuels in the propellant formulations.[1] The method adopted for the calculation of enthalpies of formation from the bomb calorimeter experiments is explained below taking compound **3** as an example. For the dodecaborane based salts, the assumption was made that the compounds **3–8** form boron trioxides as side products apart from the carbondioxide, nitrogen and water. However, the formation of B_2O_3 was confirmed from the powder XRD patterns[17] of the residual solids collected from the bomb after each experiment.

Empirical formula of the compound **3**: $C_{12}H_{28}N_4B_{12}$, molecular weight: 358.11. The average value (from at least three measurements) obtained from the isoperibol bomb calorimeter,

$\Delta_c U^{\circ}_m = 10.3 \text{ kcal g}^{-1} \Rightarrow 43.2 \text{ kJ g}^{-1} \Rightarrow 15\,458 \text{ kJ mol}^{-1}$.

Equation of combustion for the compound 3 is given below.

$$C_{12}H_{28}N_4B_{12} \longrightarrow 28\,O_2 + 12\,CO_2 + 14\,H_2O + 2\,N_2 + 6\,B_2O_3 \quad (1)$$

The standard molar enthalpy of combustion (ΔcH°m) of any compound can be derived from the constant volume of combustion energy ($\Delta_c U^{\circ}_m$) by using the following equation:

$$\Delta_c H^{\circ}_m = \Delta_c U^{\circ}_m + \Delta nRT \quad (2)$$

$$\Delta n = \sum ni(\text{products, g}) - \sum ni(\text{reactants, g})$$

where Σni is the total amount (in mol) of gases present in eqn (1) as products or as reactants. Applying eqn (2) for the compound **3**,

$$\Delta cH^{\circ}_m (C_{12}H_{28}N_4B_{12}, s) = -15\,458 + (-14)\,(8.314/1000)\,(303)$$
$$= -15\,493 \text{ kJ mol}^{-1}$$

Hess thermochemical equation for the compound (1) is

$$\Delta_f H^{\circ}_m (C_{12}H_{28}N_4B_{12}, s) = \{[12\ \Delta_f H^{\circ}_m (CO_2, g)] + [14\ \Delta_f H^{\circ}_m (H_2O, l)] + [6\ \Delta f H^{\circ}_m (B_2O_3, s)]\} - \Delta_c H^{\circ}_m (C_{12}H_{28}N_4B_{12}, s) \quad (3)$$

Where $\Delta_f H^{\circ}_m$ = standard molar enthalpy of formation. Substituting the standard molar enthalpy of formation of CO_2 (g), H_2O (l) and B_2O_3 (s) as −393.5 kJ mol^{-1}, −285.8 kJ mol^{-1} and −1263.6 kJ mol^{-1} respectively, in eqn (3), the $\Delta_f H^{\circ}_m$ ($C_{12}H_{28}N_4B_{12}$, s) = −811.9 kJ mol^{-1}. Further, heat of explosion, Q, is −43 264 kJ Kg−1 [defined as heat release from a kg of a compound in an adiabatic condition, i.e. ($\Delta_c H^{\circ}_m$ × 1000)/M Wt]. Adopting a similar method, the heats of formation and heats of explosion of other compounds were calculated.

Heat of a reaction is conventionally defined as the difference between enthalpies of formation of the products and those of the reactants. Using this practice, a large heat release from a combustion reaction is a large negative heat of reaction. It can be understood from Table 1 that all the compounds reported here possess very high heats of explosion. The molecules **3–8** possess the heats of explosion ranging from 43 264 to 45 529 kJ kg^{-1} (mean = 44 546 kJ kg^{-1}; average deviation = 314 kJ kg−1; standard deviation = 822 kJ kg^{-1}). These values are better than that of the pure aluminium, but approximately 40% less compared to that of the pure boron powder. Generally, inefficient pyrolyzability of the pure boron powder hinders its use in a solid rocket propellant. In order to address this problem, a few additives, energetic binders and hydrocarbon fuels are added to energetic composites.[18] However, the presence of hydrocarbon chains in these ionic salts **3–8** made them easily ignitable even in the absence of any additives. Since these alkyl chains can burn easily, the amount of energy released could be useful to initiate the oxidation of a borane fragment. Though not much variation in heat of explosion of these compounds was observed, increase in the length of the alkyl chain is expected to release more thrust gas in the propulsion system.

E. Sensitivity

The performance and safety characteristics of molecules need to be evaluated for safe handling of energetic materials. Impact and friction sensitivity are more important characteristics in the manufacturing context. Therefore, the impact and friction sensitivities of all the compounds from compound **2-8** of *closo*-dodecaborate salts were measured using the standard BAM fall hammer, and BAM friction techniques. About 20mg of compound **3** and all the dodecaborate salts were subjected to a fall-hammer test using a 5 or 10 kg dropping weight. The impact sensitivity of all the dodecaborate salts of dialkylimidazolium cations were above 50J while the friction sensitivity of the salts was greater than 360N was depicted in Table 1.

F. Conclusion

We have synthesized seven different salts of *closo*- $(B_{12}H_{12})^{2-}$ with various imidazolium derivatives. All these compounds were unambiguously characterized from multinuclear NMR and MASS spectral data. We have also studied their decomposition behaviour and energetic properties. The synthesized molecules possess promising enthalpies of combustion to be used as fuels in solid rocket propellants. The molecules were found to decompose releasing boron for the oxidation reaction. Since these boron atoms were bound by covalent bonds in a cluster molecule there cannot be any chance for agglomeration and prior oxidation. Hence these molecules may find potential application as insensitive high energy materials.

III. EXPERIMENTAL SECTION

Caution: All the compounds described here were not sensitive to friction and moisture. They were stable until they were ignited inside the bomb of the calorimeter. However, generally the molecules possessing high energy are extremely hazardous because they are sensitive to shock, friction, heat and moisture which may lead to explosion. Hence, appropriate safety precautions, such as kevlar gloves, face shields, leather jackets, ear plugs, teflon spatulas safety goggles and earthened equipment, must be employed otherwise serious injury may occur. The substances should be handled by experienced personnel.

Materials

All chemicals were purchased from commercial sources as follows. $NaBH_4$ (95%, SRL, India); N-methylimidazole (99%, Merck); 1,4-diimidazolium-2-butyne (99%, Sigma-Aldrich). The solvents were purified by standard procedures while deionised water was utilized for synthesis. The compounds $Na_2(B_{12}H_{12})$ and $(HNEt_3)_2(B_{12}H_{12})$ (3) were synthesized according to the literature procedure.[14] Butylmethylimidazolium iodide, hexylmethylimidazolium bromide, octylmethylimidazolium bromide, undecylmethylimidazolium bromide were synthesized by the solvent free sonochemical method.[16] The remaining compounds were synthesized by following the methods as mentioned below.

Instruments

Infrared spectra were recorded using KBr pellets for solids on a JASCO FT/IR 5300, Japan. Elemental analyses (C, H, and N) were performed on an EA 1112 series Thermo Finnigon, France. LCMS was recorded using an LCMS 2010A himadzu, Japan. The ^{1}H, ^{13}C, ^{11}B NMR spectra were recorded using a Bruker Avance 400 MHz instrument and the spectra were referenced to either tetramethylsilylchloride or BF_3-ether as appropriate. TG-DTA analyses were performed using a TA instrument SDT Q 600 and Perkin Elmer. The heats of combustion of the compounds were determined using an isoperibol bomb calorimeter (Parr 6200). The compounds were burned in an oxygen pressure of 2.9 MPa (29 atm). The calorimeter was standardized using benzoic acid (SRM 39i, NIST) as a standard reference sample. Since a Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) cal cm^{-1} of wire burned has been applied in all standardization and calorific value determinations. After each run, the residual solids were collected and analysed by IR and ^{11}B, ^{1}H NMR spectral data. If any evidence of the unburned compound was seen, the run was discarded. Further, the formation of boron trioxide as a side product from the burning reactions of borane derivatives was confirmed from its powder XRD patterns (B_2O_3 cubic, JCPDS No: 060297). Typically combustion values are taken as an average of at least three experiments of the same sample.

The impact and friction sensitivity were performed on a standard BAM fall Hammer and BAM friction Techniques. About 20mg of compounds were subjected to a fall-hammer test using a 5 or 10kg dropping weight. The range in impact sensitivities according to the UN Recommendations are as follows (insensitive >40J; less sensitive ⩾35J; sensitive ⩾4J; very sensitive ⩽ 3J). Friction, Insensitive >360N, less sensitive=360N; sensitive >360N <80N; very sensitive ⩽80N; extremely sensitive ⩽ 10N; according to the United Nations recommendations on the transport of dangerous goods.

Synthesis of 3,3′-(but-2-yne-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium) chloride (1)

Compound **1** was synthesized according to the reported procedure as follows; 5 mmol of 1,4-dichloro-2-butyne was mixed with 11 mmol of N-methyl imidazole in a closed vessel and then sonicated for 4 to 5 minutes. The reaction flask was kept aside for 30 minutes, then the product was obtained as a brown colored solid in quantitative yield. Caution: do not apply sonication continuously, apply one minute sonication and cooling to room temp and then apply again up to 5 minutes because this reaction is an exothermic reaction. IR: 3352 w, 2965 m, 1651 s, 1574 s, 1433 s, 1342 s, 1261 s, 1176 s, 1028 s, 860 s, 765 s, 615 s. ^{1}H NMR (DMSO): δ 9.60 (s, 2H, NCH_2N of imidazolium), 7.89 (s, 2H, imidazolium), 7.77 (s, 2H, imidazolium), 5.37 (s, 4H, NCH_2Cu), 3.90 (s, 6H, NMe). ^{13}C NMR (DMSO): δ 137.34, 124.42, 122.72, 80.43, 39.76, 36.42. LCMS: M^+ 287. HRMS: M^+ = 287.0830. Elem. Anal. Calcd (found) for $C_{12}H_{16}Cl_2N_4$: C, 50.19 (50.25); H, 5.62 (5.71); N, 19.51 (19.47); Cl, 24.68 (24.57).

Synthesis of 3,3′-(but-2-yne-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium)perchlorate (2)

Dissolved 3 mmol (0.861 g) of compound **1** in 15 ml of deionised water in a 100 ml round bottom flask and 6 mmol (0.6028 g) of $HClO_4$ were added slowly to this solution. The reaction mixture was continuously stirred for 2 hours. The solvent was then evaporated to obtain a light brown coloured solid compound. It was dried completely by applying a high vacuum at room temperature. The isolated yield was (1.0000 g, 2.4086 mmol, 80.29%). MP: 250 °C. IR: 3146 s, 3067 s, 2945 s, 2017 s, 1714 s, 1568 s, 1454 s, 1342 s, 1084 m, 852 s, 746 s, 626 s. ^{1}H NMR (DMSO): δ 9.15 (2H, s), 7.78 (2H, s), 7.73 (2H, s), 5.28 (4H, s), 3.86 (6H, s). ^{13}C NMR (DMSO): δ 137.10, 124.52, 122.65, 80.18, 39.03, 36.47. LCMS: M^+ 416. HRMS: $(M + 23)^+$ = 437.0288. Elem. Anal. Calcd (found) for $C_{12}H_{16}Cl_2N_4O_8$: C, 34.71 (34.85); N, 13.49 (13.28); H, 3.88 (3.81).

Synthesis of 3,3′-(but-2-yne-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium)dodecaborate (3)

Dissolved 3 mmol (0.570 g) of Na2(B12H12) in 15 ml of deionised water in a 100 ml round bottom flask and 3 mmol (0.861 g) of Compound 1 in 10 ml of deionised water in another flask. The second solution was added to a solution of $Na_2(B_{12}H_{12})$ lowly. Immediately a large voluminous precipitate was formed and the stirring continued for a further 45 minutes. Then the reaction mixture was filtered and the residue was washed with 5 ml of deionised water. Then the compound was air dried followed by drying by applying a high vacuum at room temperature. It was a colourless solid compound. The isolated yield was (0.8200 g, 2.2898 mmol, 76.35%). MP: 228 °C. IR (cm−1): 3626 s, 3148 s, 3113 s, 2474 s, 1626 s, 1574 s, 1467 s, 1421 s, 1354 s, 1323 s, 1284 s, 1176 s, 1060 s, 952 s, 817 s, 756 s, 734 s, 673 s, 621 s, 609 s. NMR: ^{1}H (DMSO) δ 9.17 (s, 2H, NCH2N of imiodazolium), 7.80 (s, 2H, imidazolium), 7.75 (s, 2H, imidazolium), 5.30 (s, 4H, acetylene), 3.87 (s, 6H, N-Me), 1.3–0.4 (broad, 12H, B–H). ^{13}C{^{1}H} (DMSO) δ 137.09, 124.54, 122.68, 80.22, 39.05, 36.51. ^{11}B{^{1}H} (128.3 MHz, DMSO) δ −15.60 [s, $(B_{12}H_{12})^{2-}$]. LCMS: M^+ 358. HRMS: $(M + 23)^+$ = 381.3434. Elem. Anal.: Calcd (found) for $C_{12}H_{28}B_{12}N_4$: C, 40.25 (40.48); H, 7.88 (7.56); N, 15.65 (15.56); B, 36.23 (36.40).

Bis(butylmethylimidazolium)dodecahydroborate (5)

The Compound 5 was synthesized using 3 mmol (0.570 g) of Na2(B12H12) and 6 mmol (1.5968 g) of butylmethylimidazolium iodide by following the same procedure mentioned for the compound **1**. The isolated yield was (0.8200 g, 1.9512 mmol, 76.35%). MP: 217 °C; IR (cm^{-1}): 3142 s, 3115 s, 3088 s, 2961s, 2937 s, 2872 s, 2469 s, 1608 s, 1570 s, 1462 s, 1168 s, 842 s, 752 s, 652 s, 621 s. NMR: ^{1}H (CD_3CN) δ 8.60 (s, 2H, NCH_2N of imidazolium), 7.39 (s, 2H, imidazolium), 7.36 (s, 2H, imidazolium), 4.16 (t, J = 7.2 Hz, 4H, NCH_2–), 3.85 (s, 6H, NMe), 1.82 (m, 4H, –CH_2–), 1.33 (m, –CH_2–, overlapping with B–H), 0.95 (t, J = 7.4 Hz, –CH_3, overlapping with B–H), 1.4–0.2 (broad, B–H, overlapping with –CH_2– and CH_3). ^{11}B{^{1}H} (128.3 MHz, CD3CN) δ −15.26 [s, $(B_{12}H_{12})^{2-}$]. ^{13}C{^{1}H} (CD_3CN) δ 136.16, 123.61, 122.21, 49.31, 35.91, 31.63, 19.00, 12.69. LCMS: M^+ 421. HRMS: $(M + 23)^+$ = 443.4485. Elem. Anal.: Calcd (found) for $C_{16}H_{42}B_{12}N_4$: C, 45.73 (45.68); H, 10.07 (09.96); B, 30.87 (30.91); N, 13.33 (13.45).

Bis(hexylmethylimidazolium)dodecahydroborate (6)

The Compound 6 was synthesized using 3 mmol (0.570 g) of $Na_2(B_{12}H_{12})$ and 6 mmol (1.482 g) of hexylmethylimidazolium bromide by following the same procedure mentioned for the compound 1. Yield (1.0907 g, 2.2896 mmol, 76.32%). MP: 163 °C; IR (cm−1): 3146 s, 3111 s, 957 s, 2930 s, 2860 s, 2467 s, 1610 w, 1570 s, 1466 s, 1425 s, 1379 s, 1340 s, 1165 s, 1059 s, 831 s, 754 s, 717 s, 655 s, 619 s. NMR: 1H (CD_3CN) δ 8.57 (s, 2H, NCH_2N of imidazolium), 7.40 (s, 2H, imidazolium), 7.37 (s, 2H, imidazolium), 4.16 (t, J = 8.0 Hz, 4H, NCH_2–,), 3.86 (s, 6H, NMe), 1.97 (m, 4H, –CH_2–), 1.33 (s, 12H), 0.92 (t, 6H, CH_3, J = 8.0 Hz), 1.4–0.3 (broad, B–H, overlapping with –CH_2– and CH_3). $^{11}B\{^1H\}$ (128.3 MHz, CD_3CN) δ −15.28 [s, $(B_{12}H_{12})^{2-}$]. $^{13}C\{^1H\}$ (CD_3CN): δ 136.11, 123.60, 122.21, 49.57, 35.90, 30.77, 29.59, 25.38, 22.11, 13.21. LCMS: M+ 478. HRMS: $(M + 23 + H)^+$ = 501.4822. Elem. Anal. Calcd (found) for $C_{20}H_{50}B_{12}N_4$: C, 50.43 (50.35); H, 10.58 (10.49); B, 27.23 (27.51); N, 11.76 (11.65).

Bis(octylmethylimidazolium)dodecahydroborate (7)

The Compound **7** was synthesized using 3 mmol (0.570 g) of $Na_2(B_{12}H_{12})$ and 6 mmol (1.6513 g) of octylmethylimidazolium bromide by following the same procedure mentioned for the compound **1**. Yield (1.2049 g, 2.2628 mmol, 75.43%). MP: 190 °C. IR (cm^{-1}): 3153 s, 3115 s, 2926 s, 2856 s, 2474 s, 1568 s, 1467 s, 1381 s, 1340 s, 1168 s, 1101 s, 1060 s, 827 s, 738 s, 657 s, 617 s. NMR: ^1H CD_3CN) δ 8.58 (s, 2H, NCH_2N of imidazolium), 7.40 (s, 2H, imidazolium), 7.37 (s, 2H, imidazolium),4.16 (t, J = 8.0 Hz, 4H, NCH_2–), 3.87 (s, 6H, NMe), 1.85 (m, 4H), 1.31 (m, 20H), 0.91 (t, 6H, J = 6.0 Hz). 1.7–0.4 (broad, B–H, overlapping with –CH_2– and CH_3). ^{11}B NMR (128.3 MHz, CD_3CN): δ −15.28 [s, $(B_{12}H_{12})^{2-}$]. ^{13}C NMR (CD_3CN): δ136.16, 123.59, 122.10, 49.57, 35.90, 31.45, 29.64, 28.76, 28.57, 25.71, 22.32, 13.35. LCMS: M^+ 532. HRMS: $(M + 23)^+$ = 555.5270. Elem. Anal.: Calcd (found) for $C_{24}H_{58}B_{12}N_4$: C, 54.14 (54.25); H, 10.98 (10.86); B, 24.36 (24.23); N, 10.52 (10.66).

Bis(undecylmethylimidazolium)dodecahydroborate (8)

The Compound **8** was synthesized using 3 mmol (0.570 g) of $Na_2(B_{12}H_{12})$ and 6 mmol (1.902 g) of undecylmethylimidazolium bromide by following the same procedure mentioned for the compound **3**. Yield (1.4489 g, 2.3497 mmol, 78.31%). MP: 198 °C. IR (cm^{-1}): 3158 s, 3115 s, 2924 s, 2854 s, 2476 m, 1626 w, 1570 s, 1466 s, 1381 s, 1340 s, 1168 s, 1103 s, 1060 s,1020 m, 827 s, 740 s, 659 s, 617 s. ^1H NMR (CD_3CN): δ 8.63 (s, 2H), 7.38 (2H, s), 7.36 (2H, s), 4.16 (t, 4H, J = 7.2 Hz), 3.85 (s, 6H), 1.83 (m, 4H,), 1.28 (32 H, s), 0.88 (6 H, t, J = 6.4 Hz) 1.7–0.4 (broad, B–H, overlapping with –CH_2– and CH_3). ^{11}B NMR (128.3 MHz, CD_3CN): δ −15.26 [s, $(B_{12}H_{12})^{2-}$]. ^{13}C NMR (CD_3CN): δ 136.25, 123.57, 122.18, 49.56, 35.92, 31.64, 29.68, 29.31, 29.26, 29.12, 29.07, 28.65, 25.74, 22.40, 13.40. LCMS: M+ 617. HRMS: $(M + 23)^+$ = 639.8402. Elem. Anal.: Calcd (found) for $C_{30}H_{70}B_{12}N_4$: C, 58.43 (58.21); H, 11.44 (11.44); B, 21.04 (21.13); N, 9.09 (9.22).

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