



## Heterocyclic Salt Synthesis and Rational Properties Tailoring<sup>\*)</sup>

Scott A. SHACKELFORD\* and John L. BELLETIRE†

*Air Force Research Laboratory, 10 East Saturn Blvd.,  
Edwards AFB, CA 93524-7680, USA*

*\*E-mail: scott.shackelford@edwards.af.mil*

**Abstract:** Chemical structure determines the inherent properties displayed by a given compound, and these properties, in turn, produce a specific performance behavior. Rationally designing chemical structure to predictably modify compound properties, such that performance behavior can be tailored in a controlled manner, defines the objective of a pertinent synthesis effort. Achieving this objective by introducing structural alterations in a neutral covalent compound offers only one approach for resultant properties modification. Heterocyclic salts significantly enhance the flexibility for achieving properties modification via three strategic approaches: (1) compositionally pairing various cation structural classes with a number of anion structural classes, (2) systematically altering the structure of the cation; and, (3) systematically altering the structure of the anion. To illustrate this premise, four general synthesis methods to synthesize heterocyclic salts, including several new binary heterocyclium icosahedral *closo*-borane and *closo*-carborane salts, first are outlined. Secondly, properties modification approaches of neutral covalent compounds are then compared with those approaches available for various heterocyclic salts. Lastly, a key example, using three unsaturated bridged heterocyclium di-cation salts, demonstrates how rational structure design, and its effect on resultant predictable properties modification, produces tailored performance behavior to reach the thermochemical initiation threshold needed for combustion. This is achieved with predictable properties modifications that increase salt energy content, or that accelerate the reaction kinetics of the thermochemical initiation process.

**Keywords:** binary heterocyclic salts, heterocyclic salt synthesis, ionic liquids, bridged heterocyclic di-cation salts, rational structure design, predictive properties modification, tailored performance behavior, thermochemical

<sup>\*)</sup> Presented at the 12th International Seminar “New Trends in Research of Energetic Materials”, University of Pardubice, Pardubice, Czech Republic, April 1-3, 2009.

<sup>†</sup> ERC, Inc. at AFRL/RZSP, Edwards AFB, CA (USA).

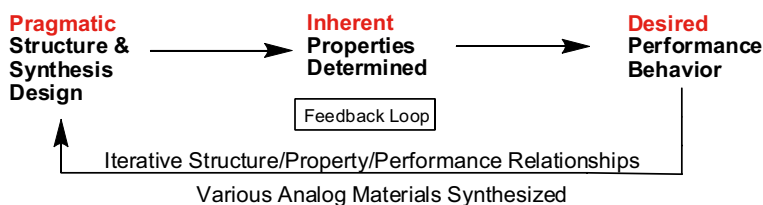
initiation, thermal initiation, self-sustained combustion

## Introduction

Heterocyclic salt synthesis can generate new chemical structures that provide the resultant energetic material properties needed to attain a desired performance behavior. In reality, however, a research chemist often must conduct chemical syntheses in a randomly empirical or pragmatic approach versus achieving the goal of conducting systematic chemical syntheses in a more rational and controlled predictive manner.

Normally, the research chemist is seeking a specific type of performance behavior before *empirically* or *pragmatically* designing a new chemical structure that incorporates the resultant *inherent* properties needed by a new material to deliver a *desired* performance behavior (Figure 1). Usually, however, the inherent properties exhibited by the new material do not provide the exact performance behavior sought. When this occurs, a feedback loop, for determining structure, property, and resultant performance behavior relationships, is initiated where the research chemist continues to *pragmatically* or *empirically* design and synthesize a number of other new materials with similar, but altered, chemical structures to vary each compound's *inherent properties* that hopefully lead to the *desired performance behavior*. The goal of the research chemist, however, is to *rationally* design a new chemical structure that affords a material with *predictable* properties that one knows will produce the *tailorable* performance behavior desired.

### Reality



### Goal



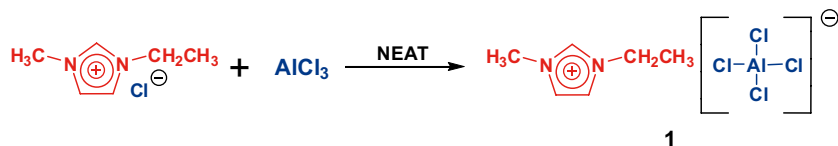
**Figure 1.** Comparison of synthesis to performance pathways: reality and goal.

This article explores the premise that compared to neutral covalent compounds, heterocyclic salts offer a greater flexibility to accomplish this synthesis goal. To support this point, first, the more common synthesis procedures used to prepare heterocyclic salts will be reviewed. Secondly, the approaches available for chemical structure design and resultant properties modification will be compared between neutral covalent compounds and heterocyclic salts. Finally, two examples are presented that demonstrate rational structure design giving resultant predictive properties modifications which achieve a tailorable performance behavior for thermochemically initiated combustion.

## Discussion

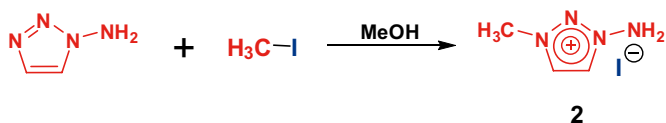
### General Methods for Heterocyclic Salt Synthesis

There are at least four general methods normally used to synthesize heterocyclic salts. The first method comes from a synthesis used 27 years ago to obtain the 1-ethyl-3-methyl-1,3-imidazolium (EMIM) tetrachloroaluminate salt (**1**), a liquid at room temperature, which immediately sparked a renewed interest in heterocyclic salt chemistry [1]. This ionic liquid forms by a Lewis acid/base reaction between the EMIM chloride salt and neutral aluminum trichloride which acts as the Lewis acid (Figure 2).



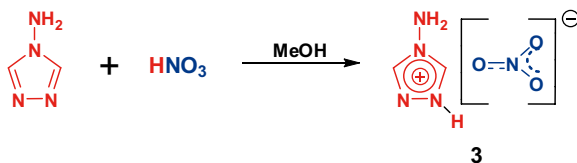
**Figure 2.** Synthesis of the EMIM tetrachloroaluminate salt (ionic liquid) by Lewis acid/base reaction.

Alkylation of a ring nitrogen atom in a neutral heterocycle, using an alkyl halide reactant, represents a second method (Figure 3). This synthesis approach affords an alkylated heterocyclium halide salt, in this case, 1-amino-3-methyl-1,2,3-triazolium iodide (**2**) which, in turn, can be converted into other alkylated heterocyclic salts that contain different anions. In fact, the EMIM chloride reactant, used in the Lewis acid/base reaction to form the EMIM tetrachloroaluminate ionic liquid (**1**), is obtained by this type of alkyl halide alkylation [1].



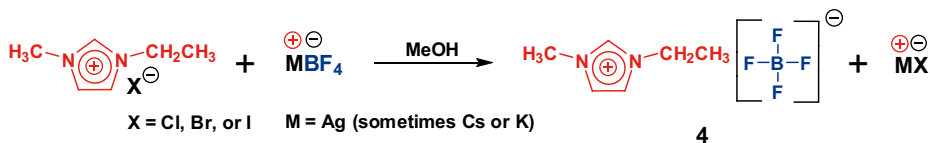
**Figure 3.** Synthesis of a heterocyclic halide salt by alkylation with an alkyl halide.

A third method for heterocyclic salt formation is to protonate the ring nitrogen of a neutral heterocyclic compound using a strong Brønsted acid which contains the anionic species intended for incorporation into the resultant heterocyclic salt (Figure 4). The first triazolium nitrate salts, such as 4-amino-1,2,4-triazolium nitrate (**3**), were synthesized in this fashion [2].



**Figure 4.** Synthesis of a heterocyclic salt by protonation with a strong acid.

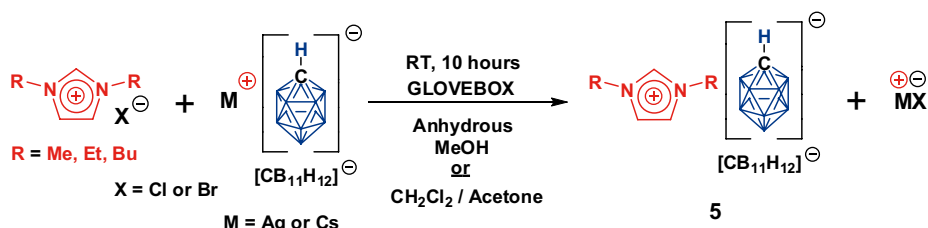
The one-step metathesis reaction represents a fourth method and is perhaps the most common procedure used in heterocyclic salt syntheses (Figure 5). Normally, either a protonated, or an alkylated heterocyclium halide is reacted with a silver salt that possesses the anion of interest for pairing with the selected heterocyclic cation [3]. In this example, the EMIM tetrafluoroborate salt (**4**) is obtained. While silver salts often are used in this type of metathesis reaction, potassium and cesium salts also have been employed [4, 5, 6].



**Figure 5.** Synthesis of a heterocyclic salt by double displacement metathesis reaction.

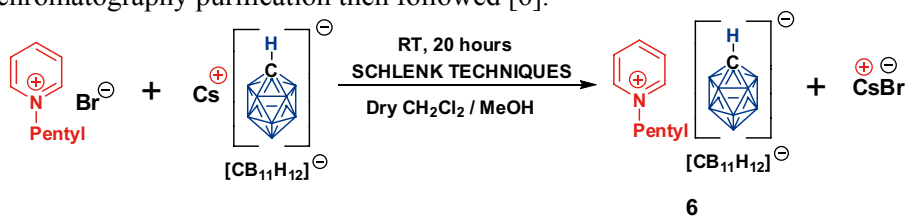
Some of the heterocyclic triazolium and imidazolium salts appearing in this paper contain icosahedral *closo*-borane [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> and *closo*-carborane [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anionic species. These recently reported heterocyclium borane and carborane salts all are synthesized by the one-step metathesis reaction [4] as are earlier reported di-alkylated imidazolium [5], and one N-pentylpyridinium [6], carborane [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> salts.

The highly alkylated imidazolium carborane salts [5] and the one N-pentylpyridinium carborane salt [6] were formed using more stringent metathesis reaction procedures than what, in some cases, might be needed. The dialkyl-substituted imidazolium carborane salts (**5**) were synthesized by stirring the cesium or silver carborane salt with the appropriate imidazolium halide salt in an anhydrous organic solvent or solvent mixture inside an inert-atmosphere glove box for 10 hours (Figure 6). The solid phase cesium halide or silver halide byproduct was removed from the supernatant by filtration through Celite. Subsequent removal of solvent then provided the white crystalline salt product [5].



**Figure 6.** Previous reaction conditions for binary dialkyl-substituted imidazolium carborane salt synthesis [5].

The N-pentylpyridinium carborane (**6**) was synthesized in a similar manner over 20 hours using air-free Schlenk techniques (Figure 7). Column chromatography purification then followed [6].

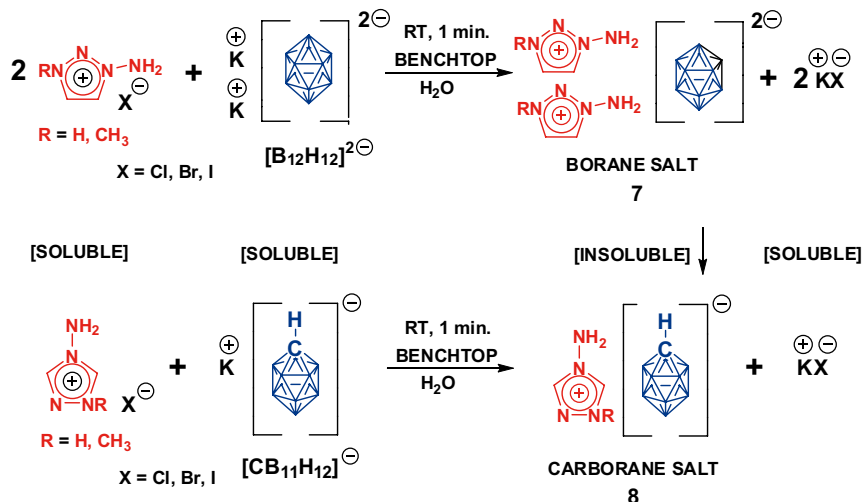


**Figure 7.** Previous reaction conditions for binary N-pentylpyridinium carborane salt synthesis [6].

Recently, several new binary triazolium and one additional imidazolium carborane  $[\text{CB}_{11}\text{H}_{12}]^-$  salts are reported [4] which supplement those already appearing in the literature [5, 6]. Additionally, novel binary heterocyclium borane  $[\text{B}_{12}\text{H}_{12}]^{2-}$  salts, which previously had no literature precedence, highlight this same article [4].

In contrast to the two previously reported imidazolium [5] and pyridinium [6] carborane salts, these novel first-reported [4] binary heterocyclium borane  $[\text{B}_{12}\text{H}_{12}]^{2-}$  salts (**7**), and the newly reported [4] binary heterocyclium carborane

salts (**8**), are synthesized in a simple open-air procedure because of their limited water solubility and their air stability at room temperature (Figure 8). These metathesis reactions, conducted in a benchtop fume hood with standard open atmosphere chemical glassware vessels in deionized water solvent, require reaction times of only several minutes [4]. The desired heterocyclium borane and carborane salt products either formed immediately by precipitation or were crystallized from the aqueous solution while cooling in a refrigerator. The reactions are conducted by mixing aqueous solutions of the desired heterocyclium halide salt with a stoichiometric amount of the potassium borane or potassium carborane salt. The water insoluble heterocyclium borane or carborane salts then are readily separated by filtration leaving the water-soluble potassium halide in the supernatant.



**Figure 8.** Convenient, open-air benchtop reaction conditions for novel binary heterocyclium borane and new heterocyclium carborane salt syntheses [4].

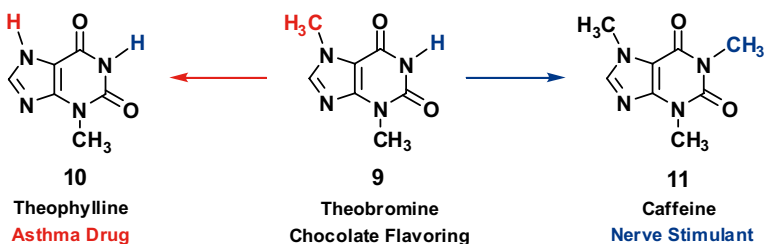
The novel heterocyclium borane and carborane salts uniquely contain cationic and anionic species that possess two different types of aromaticity. The heterocyclic borane salts pair an aromatic polyhedral  $[\text{B}_{12}\text{H}_{12}]^{2-}$  borane di-anion with an aromatic planar heterocyclium cation. The  $[\text{B}_{12}\text{H}_{12}]^{2-}$  borane di-anion is a super-aromatic polyhedral-shaped counterpart of the planar benzene molecule with 26 delocalized valence electrons in its  $\sigma$ -bonded framework [7] and possesses an overall negative two charge. The heterocyclium cations each are planar and possess six delocalized valence electrons in a  $\pi$ -bonded cyclic structure and carry

a positive one charge. The difference between the  $[\text{CB}_{11}\text{H}_{12}]^-$  carborane anion in salt (8) and the borane  $[\text{B}_{12}\text{H}_{12}]^{2-}$  di-anion in preceding salt (7) comes from structure and charge. The carborane anion  $[\text{CB}_{11}\text{H}_{12}]^-$  possesses a carbon atom in the apex position of the icosahedral structure that is bonded to a hydrogen atom, and contains an overall negative one charge. The heterocyclium carborane salts pair the aromatic  $\sigma$ -electron delocalized icosahedral *closo*-carborane anion  $[\text{CB}_{11}\text{H}_{12}]^-$  with one aromatic  $\pi$ -electron delocalized planar heterocyclic cation. A boron atom is bonded to a hydrogen atom in the borane di-anion  $[\text{B}_{12}\text{H}_{12}]^{2-}$  at this same apex position, contains an overall negative two charge, and is paired with two singly-charged heterocyclium cations.

### Neutral Covalent Compound and Heterocyclic Salt Properties Modification

Significant properties modification is accomplished by altering the chemical structure of a neutral covalent compound either by substitution of a different pendant group/atom on the skeletal/core structure, or by altering the skeletal/core structure of the compound itself. Compared to neutral covalent compounds, where only chemical structure may be altered, heterocyclic salts significantly improve the flexibility for material properties modification by providing the opportunity to vary both chemical composition and structure by one of three ways. First, a compositional change can be made by exchanging either the cation or the anion using a plethora of available or easily synthesized cationic or anionic species. Secondly, either pendant substituents or skeletal/core structural alterations can be made in the cation; or thirdly, anion pendant substituents or skeletal/core structural alterations also can be accomplished.

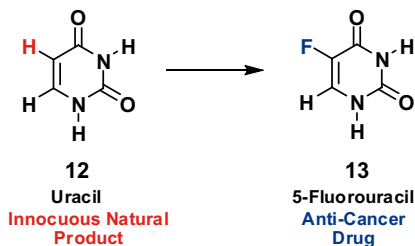
Examples of pendant substituent alteration and resultant properties modification with a neutral covalent compound that provides a different performance behavior are illustrated starting with the compound, theobromine (9). Theobromine is the alkaloid that gives chocolate its distinctive flavor (Figure 9).



**Figure 9.** Resultant properties modification and performance behavior changes by pendant group/atom structural alteration in a neutral covalent alkaloid compound.

If the pendant methyl group (red) on the fused five-membered ring of theobromine (**9**) is altered to a hydrogen atom (red), the asthma drug theophylline (**10**) is obtained. On the other side of the theobromine (chocolate) structure (**9**), if the pendant hydrogen atom (blue) in the fused six-membered ring is altered to a methyl group (blue), the nerve stimulant caffeine (**11**) results. Both the structurally altered asthma drug, theophylline (**10**), and the nerve stimulant, caffeine (**11**), possess very different modified properties from the theobromine (**9**) chocolate flavoring compound, which, in turn, provide each a significantly different type of performance behavior. Compound (**9**) is a food flavoring, compound (**10**) a drug for asthma, and compound (**11**) is a nerve stimulant that can disrupt sleep. In this example, properties modification and performance behavior change are achieved by interchanging pendant groups and atoms in the compound structure.

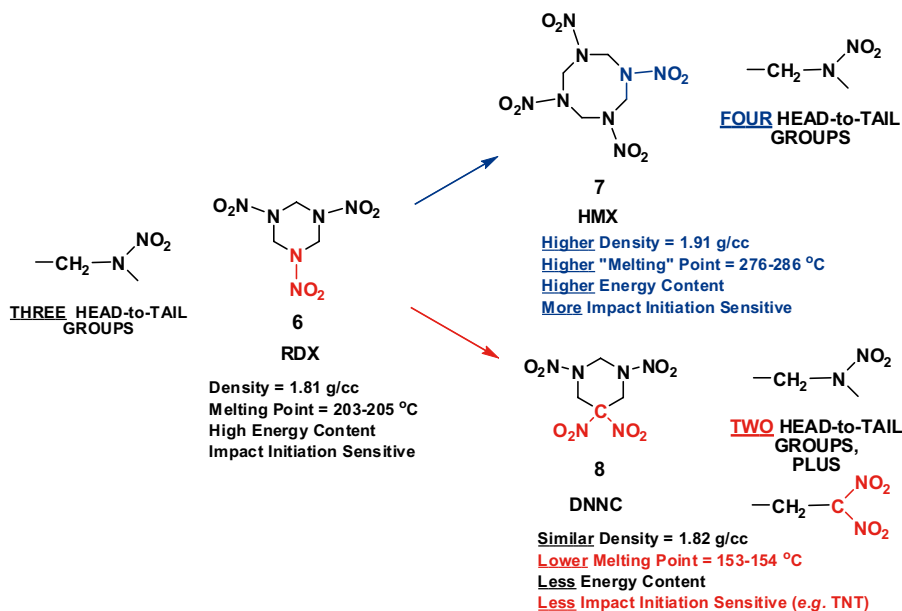
Changing one pendant atom in a chemical structure to a different atom also can drastically modify the properties and resultant performance behavior of a neutral heterocyclic compound. This is illustrated with the uracil (**12**) alkaloid (Figure 10). Altering the hydrogen atom (red) at the 5-ring position on uracil (**12**) to a fluorine atom (blue), affords 5-fluorouracil (**13**). In terms of performance behavior, this structure alteration modifies properties such that uracil (**12**) is converted, from being an innocuous natural product, into a well-known anti-cancer drug (**13**).



**Figure 10.** Resultant properties modification and performance behavior change by pendant atom structure alteration in a neutral covalent alkaloid heterocycle.

Properties modification of a neutral heterocyclic compound by structural alteration in the skeletal/core structure, and resultant changes in performance behavior, are illustrated with the high explosive nitramine, RDX (**14**). The RDX ring structure is comprised of three methylene nitramine groups ( $\text{CH}_2\text{N-NO}_2$ ) that are joined in a head to tail fashion to form a six-membered cyclic ring structure. This cyclic six-membered structural ring assembly affords certain inherent density, melting point, energy content properties for RDX (**14**) along with a defined impact initiation performance behavior (Figure 11).



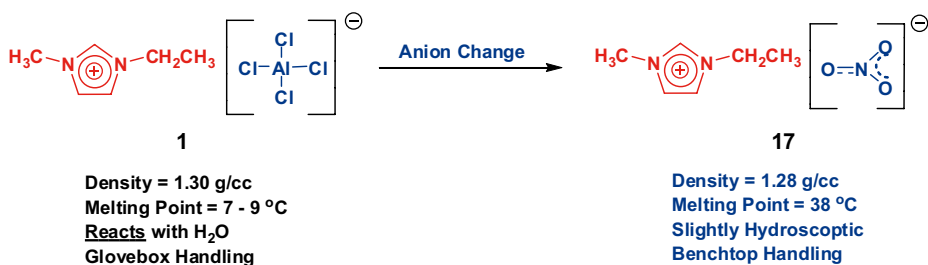


**Figure 11.** Resultant properties modification and performance behavior change by skeletal/core structure alteration in neutral covalent energetic materials.

If a fourth methylene nitramine structural fragment is placed into the RDX six-membered ring, expanding it to an analogous eight-membered ring, the higher energy HMX (**15**) explosive results as do distinctive properties modifications. HMX (**15**) possesses a higher density, a higher melting point, a higher energy content, and in terms of performance behavior, is a more powerful explosive with a lower impact initiation threshold (more sensitive) than that displayed by RDX (**14**). If the RDX (**14**) six-membered cyclic ring structure is altered in a different manner, where one of the nitrated ring nitrogen atoms (red) is replaced with a *gem*-dinitro bearing carbon atom (red), the energetic six-membered cyclic compound DNNC (**16**) results. Except for having a similar density like RDX (**14**), DNNC (**16**) displays, a lower melting point and a lower energy content; but in terms of performance behavior, DNNC possesses a higher impact initiation threshold (less sensitive) than does RDX (**14**). The nitramine DNNC (**16**) has an energy content and an impact sensitivity similar to the nitroaromatic TNT explosive.

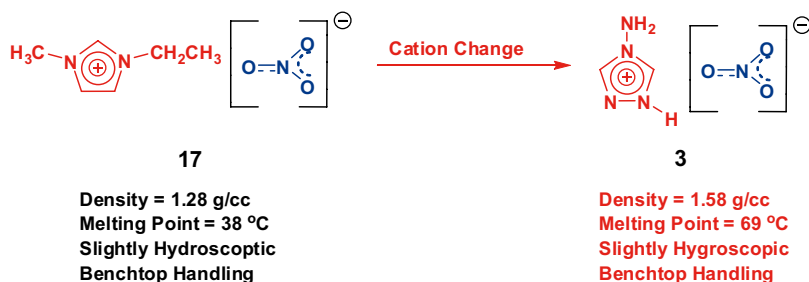
A greater flexibility for properties modification with heterocyclic salts is derived from either changing the salt composition (cation or anion exchange) or from altering the chemical structure (pendant substituents and skeletal/core assembly) of the cation or of the anion.

Compositional change, and the resultant properties modification, are illustrated beginning with the heterocyclic ionic liquid, EMIM tetrachloroaluminate (**1**) seen in Figure 2. If the tetrachloroaluminate anion (blue) is changed to a nitrate anion (blue) to give EMIM nitrate (**17**), a similar density to EMIM tetrachloroaluminate (**1**) is maintained by the EMIM nitrate salt (**17**), but the melting point noticeably increases, and the requirements for handling drastically change (Figure 12). EMIM tetrachloroaluminate (**1**) is extremely air and water sensitive and must always be handled in a glove box where it is continually exposed to an inert atmosphere. The EMIM nitrate (**17**) is only slightly hygroscopic, meaning that it can be handled in the open atmosphere, but can pick up water if stored in a loosely sealed or unsealed vessel.



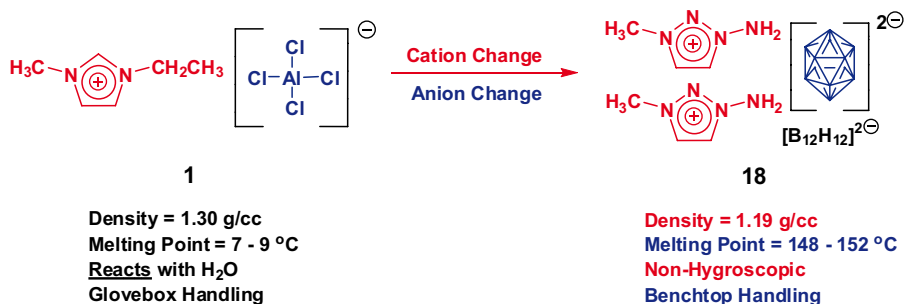
**Figure 12.** Properties modification by changing salt anion with the same cation.

If the EMIM cation (red) in the nitrate salt (**17**) is replaced with the 4-amino-1,2,4-triazolium (4AT) cation (red), the 4AT nitrate salt (**3**) forms (Figure 13). Compared to the EMIM nitrate (**17**), the 4AT nitrate (**3**) possesses a significantly higher density and melting point, and also, is only slightly hygroscopic which also allows benchtop handling techniques to be employed.



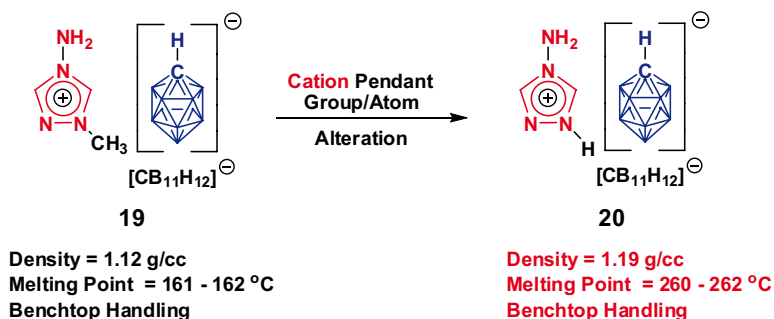
**Figure 13.** Properties modification by changing salt cation with the same anion.

The binary 1-amino-3-methyl-1,2,3-triazolium (1ATMe) borane salt (**18**), not surprisingly, exhibits properties drastically different from any of the three other salts (**1**), (**3**), and (**17**), because both the cation and anion are different (Figure 14). Note that this 1ATMe borane salt (**18**) has the lowest density, highest melting point, and is non-hygroscopic so that it is easily handled with simple benchtop procedures [1] and can be stored in the open environment without taking any special precautions.



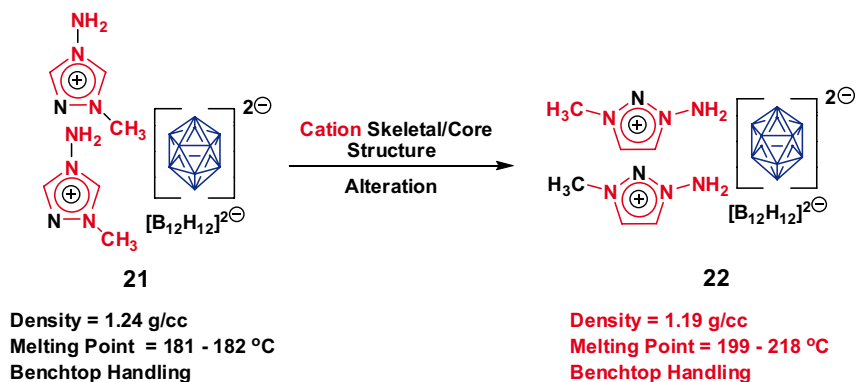
**Figure 14.** Properties modification by cation and anion change (entirely new salt).

In addition to effecting properties modification in heterocyclium salts by cation or anion compositional exchange, alteration in both the pendant substituent and the skeletal/core structure of the cation illustrate a second method that introduces properties modification. Conversion of the methyl group at the 1-position in the 4-amino-1-**methyl**-1,2,4-triazolium cation in carborane salt (**19**) to a hydrogen atom to form the 4-amino-1-**H**-1,2,4-triazolium (4AT) carborane salt (**20**) slightly raises density and significantly raises the melting point (Figure 15).



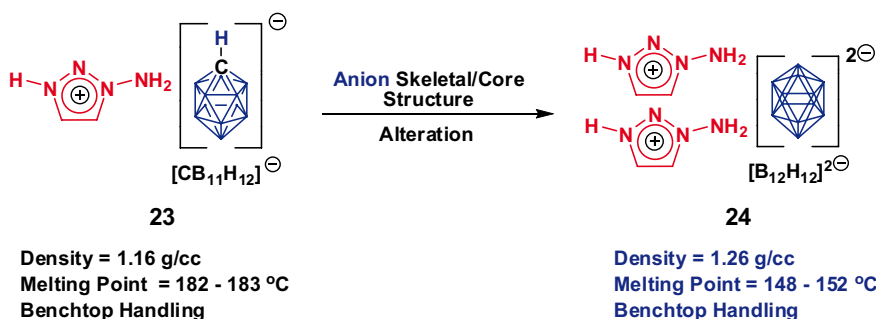
**Figure 15.** Properties modification by cation pendant group/atom alteration with the same anion.

An example of the change that a cation skeletal/core structure introduces to properties modification is shown in Figure 16. By altering the 4-amino-1-methyl-1,2,4-triazolium cation in borane salt (**21**) to the 1-amino-3-methyl-1,2,3-triazolium cation in borane salt (**22**), while retaining the same borane di-anion, altered salt (**22**) possesses a decreased density and higher melting point than does salt (**21**). In this case, the ring nitrogen atom at the 2-position (black in color) in 1,2,4-triazolium cation of salt (**21**), by IUPAC convention, appears at a different 2-position (black in color) in the 1,2,3-triazolium cation of salt (**22**) which possesses three consecutively bonded nitrogen atoms in the skeletal/core heterocyclium ring structure.



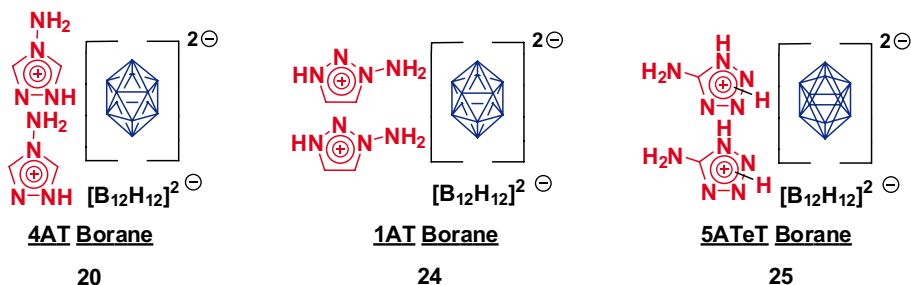
**Figure 16.** Properties modification by cation skeletal/core structure alteration with the same anion.

The third possibility for properties modification of a heterocyclium salt comes from altering the skeletal/core structure of the anionic species (Figure 17). Here the carborane anion in the 1-amino-1,2,3-triazolium salt (**23**) is altered to a borane di-anion in the 1-amino-1,2,3-triazolium (1AT) salt (**24**). The structural difference results from the **C-atom**, in the apex position of the icosahedral carborane structure of salt (**23**), possessing instead, a **B-atom** at the same apex position in borane di-anion of salt (**24**). This change of a carborane salt (**23**) to a borane salt (**24**), each with the same 1AT cation, results in a noticeably higher density and significantly lower melting point for the 1AT borane salt (**24**).



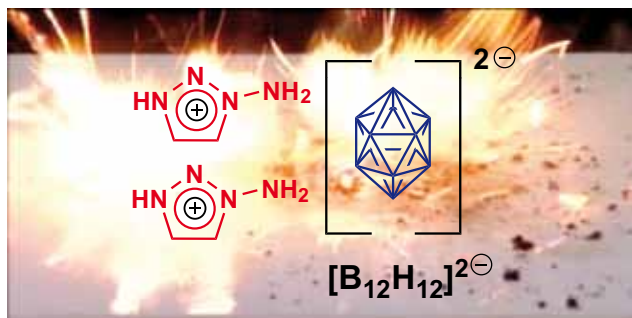
**Figure 17.** Properties modification by anion skeletal/core structure alteration with the same cation.

The three binary fuel-like heterocyclium salts, 4AT borane (**20**), 1AT borane (**24**), and 5-amino-H-tetrazolium (5ATeT) borane (**25**), each possesses the property of a reasonably high energy content (Figure 18). This property translates into an impressive thermally initiated combustion performance behavior.



**Figure 18.** Three new binary heterocyclium borane salts initiated thermally to a rapid self-sustained combustion in air.

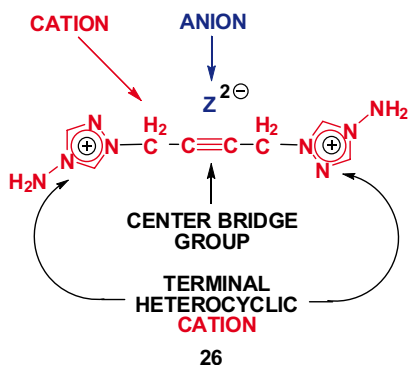
This performance behavior is demonstrated when a small sample of each salt (**20**), (**24**), and (**25**) is placed on the surface of a hot plate that maintains an oil bath at 165 °C [8]. As exemplified in Figure 19 by the 1AT borane (**24**), each salt initiates to a rapid self-sustained combustion in the weak air oxidizer. The combustion characteristics of each salt differ somewhat when observed in real time. This difference especially shows when the two triazolium borane salts are compared to the tetrazolium borane (**25**) combustion response.



**Figure 19.** Single frame picture from a film showing the self-sustained combustion of 1AT borane salt (**24**) in air on hot plate surface.

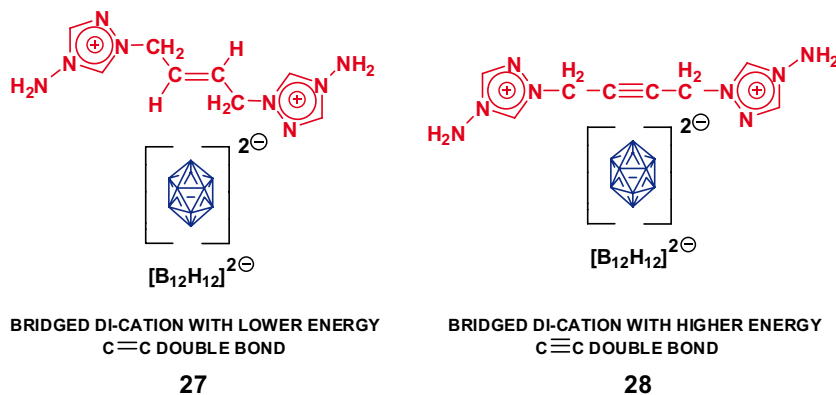
### Rational Structure Design, Predictable Properties Modification, and Tailored Performance Behavior

Beyond the flexibility that binary heterocyclium salts offer for accomplishing rational structure design to obtain predictable material properties, resulting in tailorable performance behavior, bridged heterocyclium di-cation salts offer even more opportunity. The bridged heterocyclium di-cations being addressed have an unsaturated functional structural feature at the center of an alkyl bridge structure to which a heterocyclium cation is tethered at each terminal end (Figure 20). In the case of the illustrated propargyl bridged heterocyclium di-cation (**26**), three structural sites can be altered. The di-cation itself at either end of the unsaturated alkyl bridge can be transformed (two positions), and the unsaturated structural site in the central alkyl bridge itself can be changed.



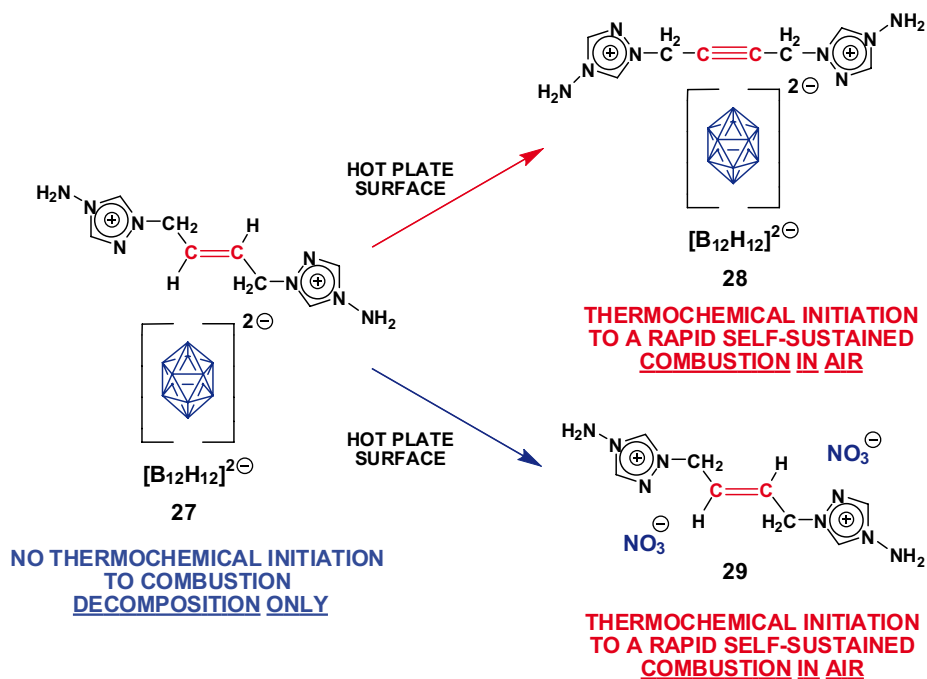
**Figure 20.** Structural architecture and site features of the heterocyclic 1,4-di-(4-amino-1,2,4-triazolium)-2-butynyl di-cation (red).

First, the terminal heterocyclium cation structures can be altered by either pendant substituent or skeletal/core changes. Second, the terminal heterocyclic cations can be exchanged for others (*e.g.* exchanging a triazolium cation for an imidazolium cation). Finally, the central unsaturated structural feature in the alkyl-based bridge can be designed in rational manner to give predictable properties and a resultant tailored performance behavior (Figure 20). Changing an allyl-based bridged di-cation, that possess a carbon-carbon double bond in its central unsaturated bridge and two terminal 4AT heterocyclium cations (**27**), to an analogous bridged heterocyclium di-cation that possesses a higher energy carbon-carbon triple bond in its alkyl-based bridge, and the same two 4AT terminal heterocyclium cations (**28**), predictably produces a bridged heterocyclium di-cation, and its associated salt, with a higher overall energy content (Figure 21).



**Figure 21.** Analogous bridged heterocyclium di-cations with center bridge site altered.

A demonstrated example of how rational structure design can provide predictable properties modification to produce a desirable tailored performance behavior appears in Figure 22. Shown are where two of the three aspects of flexible heterocyclic salt compositional exchange or structural alteration are implemented. In this case, the tailored performance behavior illustrated is the thermochemical initiation process to achieve a self-sustained combustion much like what is seen with the binary 1AT borane salt (**24**) in Figure 19. At the left of Figure 22 is the allyl-based bridged heterocyclium di-cation borane salt (**27**) with a central alkenyl carbon-carbon double bond and two terminal 4AT heterocyclium cations.



**Figure 22.** Demonstrated rational structure design, resultant predicted properties modification, and tailored performance behavior for hot plate thermochemical initiation to combustion.

When a small sample of borane salt (**27**) is placed on the surface of the same hot plate at the same temperature that initiated the three binary heterocyclium borane salts (**20**), (**24**) and (**25**) to a rapid self-sustained combustion in air (Figure 18), no combustion results. Instead, thermochemical decomposition ensues giving a dark decomposed solid. If the structure of the bridged heterocyclium di-cation of salt (**27**) is designed differently to alter the central alkenyl carbon-carbon double bond to a higher energy alkynyl carbon-carbon triple bond, the analogous propargyl-based bridged heterocyclium di-cation borane salt (**28**) results. Predictably, the propargyl-based bridged heterocyclium di-cation, as well as the borane salt (**28**) itself, would contain a higher overall energy content. With a higher energy content, it reasonably is predicted that this enhanced higher energy modified property would result in salt (**28**) needing a lower energy of activation to reach the thermochemical initiation process threshold. A lower energy of activation for bridged borane salt (**28**) then could permit its thermochemical initiation to a rapid self-sustained combustion more readily than



with the analogous bridged borane salt (**27**). Thus, bridged borane salt (**28**), when placed on the same hot plate, initiates into a rapid self-sustained combustion in a heterogeneous solid salt interaction with the weak gaseous air oxidizer. The thermochemical initiation performance behavior of bridged borane salt (**27**) is tailored by altering the central alkene bond (red) in the unsaturated alkyl bridge to the higher energy alkyne bond (red) found in the bridged heterocyclic di-cation of borane salt (**28**). This predictable properties modification lowers the activation energy needed to reach the thermochemical initiation threshold while maintaining the same borane di-anion in both salts.

Returning to the allyl-based bridged heterocyclium di-cation borane salt (**27**) in Figure 22, a new bridged heterocyclium di-cation di-nitrate salt (**29**) contains the same bridged heterocyclium di-cation, with the central alkenyl carbon-carbon double bond, as does borane salt (**27**), but salt (**29**) represents a new salt composition design where two oxidizer-like nitrate anions are exchanged for the fuel-like borane di-anion of salt (**27**). The bridged heterocyclium di-cation di-nitrate salt (**29**) contains these two oxidizer-like nitrate anions in an intimate crystalline level contact with the fuel-like allyl-based bridged heterocyclium di-cation. This intimate, homogeneous fuel/oxidizer crystalline level contact would, relative to the heterogeneous air contact with solid borane salt (**27**), result in a predictable properties modification that permits an acceleration of the initial chemical kinetics for the oxidation reactions that drive the thermochemical initiation process. This reaction kinetics acceleration generates enough energy, during a specified time period, to reach the thermochemical initiation threshold needed to achieve a self-sustained combustion [9]. Placement of the bridged heterocyclium di-cation di-nitrate salt (**29**) on the same hot plate surface, under the same conditions as salt (**27**), initiates a rapid self-sustained combustion. Once again, the thermochemical initiation behavior of bridged borane salt (**27**) is tailored to achieve a thermochemical initiation to a self-sustained combustion performance behavior. In this instance, thermochemical initiation tailoring is accomplished by changing the composition of the bridged borane di-anion (blue) salt (**27**) to the bridged di-nitrate anion (blue) salt (**29**), while retaining the lower energy alkenyl carbon-carbon double bond in the central structural site of both bridged heterocyclium di-cation salts.

## Summary and Conclusions

Heterocyclic salts offer additional flexibility for rational chemical structure design to attain the predictable properties modification needed for tailoring the resultant performance behavior desired for a given energetic material. Neutral covalent compound properties modification can only be attained by altering the chemical structure, either by changing pendant groups and atoms or the skeletal/core structure itself, but, properties modification with heterocyclic salts is achievable in three ways. First, chemical composition can be altered by exchanging the cation or the anion. Secondly, structural alteration can be accomplished by changing the pendant groups/atoms or by altering the skeletal/core structure of the cation; and thirdly, the same type of structural alterations can be applied to the anion.

Use of three unsaturated allyl or propargyl bridged heterocyclium di-cation salts demonstrates this flexibility. Structure design that alters an alkenyl-based bridged heterocyclium di-cation, which displayed no thermochemical initiation to combustion as a borane salt, from possessing a carbon-carbon double bond to a higher energy carbon-carbon triple bond, provides an alkynyl-based bridged heterocyclium di-cation borane salt analogue that rapidly initiates to a self-sustained combustion in air. The predictable modified property, a higher overall energy content in the alkynyl-based bridged heterocyclium di-cation borane salt, lowers the energy of activation needed to reach the thermochemical initiation threshold. In doing so, the threshold needed to initiate a combustion performance behavior is attained.

Alternatively, a structural design that changes the original lower energy alkenyl-based bridged heterocyclium di-cation borane salt to the analogous di-nitrate salt, via a compositional anion exchange, produces an alkenyl-based bridged heterocyclium di-cation di-nitrate salt that readily undergoes thermochemical initiation to a self-sustained combustion in the weak gaseous air oxidizing environment. This results from placing the oxidizer-like nitrate anions in an intimate contact with the fuel-like alkenyl-based heterocyclium di-cation at the crystalline level giving a predictable properties modification that permits the chemical reaction kinetics to be accelerated during the initial thermochemical initiation process. This reaction kinetics acceleration then proceeds rapidly enough to reach the threshold needed to achieve a thermochemically initiated, self-sustained combustion performance behavior.

These last two examples demonstrate two of the three stated options that heterocyclic salts provide for achieving the rational chemical structure design and predictable properties modifications necessary for producing desired

tailorable performance behavior: (1) structural alteration of a cation and (2) the compositional exchange of an anion.

### Acknowledgement

The Propulsion Directorate Chief Scientist, Dr. Alan Garscadden, Wright-Patterson AFB, OH, and the Space and Missile Systems Division, Edwards AFB, CA, provided funding and technical support.

## References and Notes

- [1] Wilkes J.S., Levisky J.A., Wilson R.A., Hussey C.L., Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis, *Inorg. Chem.*, **1982**, *21*, 1263-1264.
- [2] Drake G., Hawkins T., Brand A., Hall L., McKay M., Vij A., Ismail I., Energetic Low-Melting Salts of Simple Heterocycles, *Propellants, Explos., Protech.*, **2003**, *28*, 174-180.
- [3] Wilkes J.S., Zaworotko M.J., Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids, *J. Chem. Soc. Chem. Commun.*, **1992**, 965-967.
- [4] Shackelford S.A., Belletire J.L., Boatz J.A., Schneider S., Wheaton A.K., Wight B.A., Hudgens L.M., Ammon H.L., Strauss S.H., Pairing Heterocyclic Cations with *closo*-Icosahedral Borane and Carborane Anions. I. Benchtop Aqueous Synthesis of Binary Triazolium and Imidazolium Salts with Limited Water Solubility, *Org. Lett.*, **2009**, *11*, 2623-2626.
- [5] Larsen A.S., Holbrey J.D., Tham F.S., Reed C.A., Designing Ionic Liquids: Imidazolium Melts with Inert Carborane Anions, *J. Am. Chem. Soc.*, **2000**, *122*, 7264-7272.
- [6] Zhu Y., Ching C., Carpenter K., Xu R., Selvaratnam S., Hosmane N.S., Maguire J.A., Synthesis of the Novel Ionic Liquid [N-pentylpyridinium]<sup>+</sup> [*closo*-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> and Its Usage as a Reaction Medium in Catalytic Dehalogenation of Aromatic Halides, *Appl. Organometal. Chem.*, **2003**, *17*, 346-350.
- [7] (a) Grimes R.N., Supercarboranes, *Angew. Chem., Int. Ed.*, **2003**, *42*, 1198-1200; (b) Muetterties E.L., Knoth W.H., *Polyhedral Boranes*, M. Dekker, New York **1969**.
- [8] The hot plate surface temperature could be as high as 281 °C. This was the temperature setting required by a computerized hot plate/stirrer to maintain the same oil bath at 165 °C in the same fumehood location.
- [9] Shackelford S.A., Role of Thermochemical Decomposition in Energetic Material Initiation Sensitivity and Explosive Performance, *Centr. Europ. J. Energ. Mater.*, **2008**, *5*, 75-101.

