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Calculation of the Density and Detonation Properties of C, H, N, O and F Compounds: Use in the Design and Synthesis of New Energetic Materials

Rodney L. Willer

School of Polymers and High Performance Materials, University of Southern Mississippi, 118 College Drive #10076, Hattiesburg, MS 39406, e-mail: Rodney.Willer@usm.edu

Dedicated to the memory of Professor Ernest L. Eliel

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Abstract. The estimation of the density and detonation properties of *C*, *H*, *N*, *O*, *F* explosives is discussed. A simple computer program, "Energy", first developed at the Naval Weapons Center-China Lake in the early 1980's is presented in an updated form. This program allows the rapid calculation of the estimated properties of both known and hypothetical energetic materials. A review of the use of this program in the synthesis of new energetic materials is given.
Keywords: Density, Detonation Pressure, Detonation Velocity, Specific Impulse, Energetic Materials, Synthesis, Energetic Polymers, Cubanes, Nitramines, Furazans, Tetrazoles.

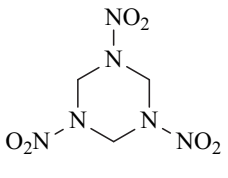
Resumen. Se describe la estimación de las propiedades de densidad y detonación de explosivos *C, H, N, O, F*. Se presenta en forma actualizada el programa sencillo de cómputo llamado *Energy*, desarrollado primeramente en el Centro de Armamento Naval de China Lake al comienzo de la década de los ochenta. Este programa permite el cálculo rápido de la estimación de las propiedades de materiales energéticos, tanto conocidos como hipotéticos. También se describe una revisión del uso de este programa para la síntesis de nuevos materiales energéticos.
Palabras clave: Densidad, presión de detonación, velocidad de detonación, impulso específico, materiales energéticos, síntesis, polímeros energéticos, cubanos, nitraminas, furazanos, tetrazoles.

Introduction

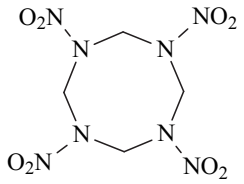
Recently in the *Journal of Pyrotechnics*, Will Meyerriecks gave an excellent summary of methods to estimate the enthalpy of formation of organic compounds [1]. The other important property of organic compounds considered for use as energetic materials is their density. This was recognized in the 1960's and a number of investigators published methods to estimate the density of organic compounds over the next 15 years. Included in these are papers by Exner [2], Nielsen [3], Tarver, Coon and Guimont [4], Tarver [5], Immirizi and Perini [6], Cady [7], Cichra, Holden and Dickinson [8], and Stine [9]. All of these methods are based on a regression analysis of the density and structures of organic compounds known at that time and usually have a standard deviation of ± 3%. With the heat of formation and density, a researcher can calculated the expected explosive performance of a hypothetical compound using the Kamlet Short Method [10] and the expected propellant performance by using the PEP program [11]. An alternative for calculating the explosive properties is to use the Rothstein-Peterson Method [12,13]. This method is based on a regression analysis of the performance of known explosives. In recent years, a number of theoretical chemists have even started using quantum mechanical calculations to calculate density, heat of formation and sensitivity of energetic materials. Excellent examples of this is the work by Rice at the Ballistic Research Laboratory [14,15,16]. It should also be noted that a recent Russian publication describes an improved regression analysis for the prediction of density but it uses hundreds of parameters in contrast to the fewer than 20 used in the Holden method [17].

Calculation of Density and Performance

In the early 1980's a major program sponsored by the Office of Naval Research and managed by Dr. Richard S. Miller was started at the Naval Weapons Center-China Lake and other U. S. Laboratories on the synthesis of new nitramine energetic materials. Caged Nitramines were selected as the target molecules because of the high density and performance of RDX and HMX. This was a very ambitious program since, except as noted later, only mono-cyclic nitramines were known compounds at the time. The author joined the staff at the Naval Weapons Center-China Lake Chemistry Division at about this time. My experience in working with the conformational analysis of 6-membered rings under Ernest L. Eliel prepared me well to work on this project. It was quickly realized that prediction of the density and detonation properties of proposed target molecules would be a valuable tool in directing the synthesis effort.



RDX



HMX

The hand calculation of the density and detonation properties using any of the density methods cited above and the

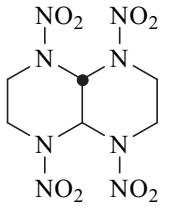
Rothstein-Petersen method was tedious. Thus, a simple computer program, "Energy" was written in the Basic computer language to automate the calculations [18]. The method chosen for the calculation of the density of the energetic materials was Holden's method because it used the smallest number of parameters and gave parameters for both liquid and solid materials [8]. This program was originally written for use on PDP-8 laboratory computers and Apple-2 personal computer since these were the most common machines available at the time. In addition to calculating the density of the compound by Holden's method, the program also calculated the expected detonation properties by the Rothstein-Peterson Method [12,13]. The program and a proper reference to it were widely distributed within the Energetic Materials Community in the USA shortly after it was written. Unfortunately, over the years, a number of authors have failed to give proper reference to the program even though it is obvious that they were using it [19].

Over the years it has been modified to run on a PC as a DOS program [20] and most recently the program has been re-written in the C^{++} language to run as a Windows program [21]. A copy of this program is available free by e-mailing a request to the author. The program is very simple. On the first panel the chemist inputs the name of the compound and it's molecular formula and then the program calculates the elemental composition of the compound. On the density panel, several questions about the structure of the compound are answered. These include the number of aromatic and non-aromatic rings, the number of nitro-groups, and the type of bonding present in the molecule. On the detonation velocity panel several additional structural questions are answered such as if the molecule is a solid or a liquid, the presence of nitrate esters or nitrate salts and carbonyl groups. The program then calculates the density, detonation velocity and detonation pressure. The results can be stored as a Notepad file and retrieved or transferred to a Word file.

Eamples

Bicyclic Nitramines

One of the first molecules designed and synthesized to test the reliability of this computational method was *trans*-1,4,5,8-tetranitro-1,4,5,8-decalin (TNAD), **1** [22]. TNAD was synthesized by first nitrosating the known 1,4,5,8-tetraazadecalin to give the tetranitrosoamine. This is follow by two treatments with 100% nitric acid or one treatment with N_2O_5 in 100% nitric acid. Edwards and Webb had previously synthesized the isomeric compound TNSD, **2** [23]. Until this time, TNSD was the only bicyclic polynitramine known. Table 1 summarizes the predicted and measured properties of these two molecules. As would be expected, the program predicts the same density for the two isomers. The measured density for **1** is slightly higher than the normal ± 3% capability of the program. In contrast, the density of TNSD is slightly lower than that predicted by the program.



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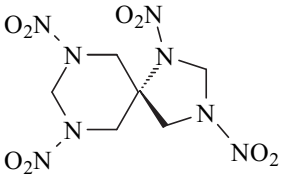

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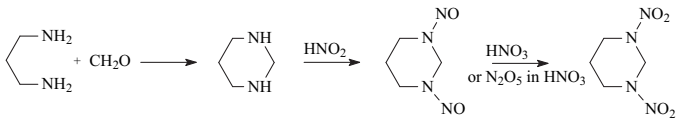
The differences can be attributed to the greater symmetry of TNAD as compared to TNSD. This illustrates one of the deficiencies of the program and the general approach of using regression analysis unless very specific regression parameters are used.

Table 1. Physical and Chemical Properties of TNAD and TNSD

Compound	Density, (g/cc)	Detonation Pressure, (kbar)	Detonation Velocity, (mm/msec)
TNAD, **1** (predicted)	1.74	310	8.20
TNAD, **1** (measured)*[24]	1.84	325	8.50
TNSD, **2** (predicted)	1.74	310	8.20
TNSD, **2** (measured)[24]	1.70		

*Calculated using the Kamlet Short Method [10] using the measured heat of formation and density

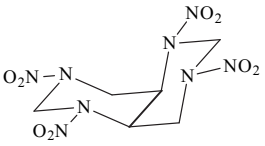
As part of the general program to develop new methods for the synthesis of cyclic nitramines, a method was developed that involved the trapping of an in-situ generated cyclic-1, 3-diamine with nitrous acid to generate a cyclic 1,3-dinitrosoamine. The cyclic 1, 3-dinitrosoamine is then converted to the cyclic 1,3-dinitramine by treatment with 100% nitric acid or a solution of N_2O_5 in 100% nitric acid [25]. This is illustrated in Scheme 1:



Scheme 1. Nitrosation-Nitrolysis Synthesis of Cyclic 1, 3-Dinitramines

Four additional isomers of TNAD and TNSD were synthesized using this method developed for synthesis of cyclic nitramines, these included *cis*-1,3 5,7-tetranitro-1,3,5,7-tetraazadecalin, **3**, *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin, **4**, (R^*, R^*)-1,1',3,3'-tetranitro-4, 4'-biimidazolidine, **5**, and (R^*, S^*)-1,1',3,3'-tetranitro-4,4'-biimidazolidine, **6** [26].

The interesting spiro-cyclic tetranitramine, **7,** was also synthesized by this method [25]. All four of the TNAD isomers have the same predicted density by the Energy Program. This is one of the limitations of the program. As might be expected, the decalin compounds are denser than the bi-imidazolidine compounds. The spiro-cyclic compound **7** turns out to have a density considerable higher than predicted. The measured density by X-ray Crystallography [27] is 1.74 g/cc while the predicted density is 1.67g/cc. This can again be attributed to the high symmetry of **7**. It is particularly interesting that **7** is even more dense than **2** even though it contains an additional methylene group.



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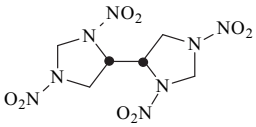

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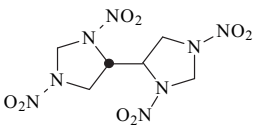

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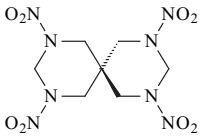

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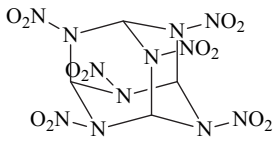
Caged Nitramines

That all of these newly synthesized bicyclic nitramines had densities close to that predicted by the Holden Method gave great credence to the calculations that caged nitramines would have the even higher densities predicted by the Holden Method. On this basis, considerable effort was directed toward the synthesis of caged nitramines. The original target molecules selected by A. T. Nielsen at NWC and other investigators were trinitroorthoamide derivatives of adamantane such as **8 [**28**].** These types of molecule calculate to be quite dense and energetic but there appeared to be no practical synthetic approach to them. After several years of futile work on this type of molecules [29,30], A. T. Nielsen turned his attention to the more approachable wurzitane type structures such as **9**. This was largely based on the previous success of the synthesis of TNAD from glyoxal and ethylenediamine. It is easily seen that a retro-synthetic analysis of **9** shows it to be derived from three glyoxal molecules and six ammonia molecules. This chemistry was proposed as early as 1982 by the author [31]. Eventually the corresponding iso-wurzitane structure, **10**, with benzyl groups was synthesized by A. T. Nielsen and D. J. Vanderah [32] and, after considerable work, this compound was eventually converted into hexanitrohexaazaisowurztane (HNIW, CL-20), **11** [33]. It might be noted that the author was a co-author on the early reports by A. T. Nielsen [29,30].



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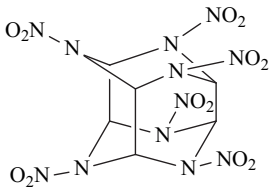

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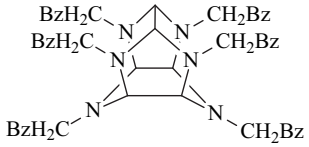

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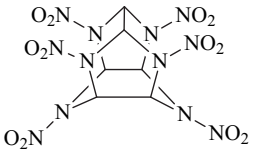

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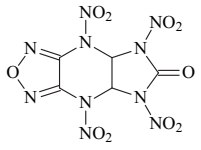
Saturated Heterocyclic Nitramines

One of the offshoots of this work on the bicyclic and caged nitramines was initiated by a letter from Dr. Everett Gilbert of Picatinney Arsenal to the author in 1981 [34]. Dr Gilbert forwarded an abstract of a Chinese paper that was to be presented at an ACS meeting in 1981. This paper described the synthesis of the 3,4-diaminofurazan [35] based compounds **12**, **13** and **14** [36]. The relationship between the synthesis of these compounds and the just completed synthesis of TNAD was clear. The "Energy" program allowed us to easily calculate the expected performance of these three compounds. This is summarized in the Table 2 below. We also calculated the properties of 2 related compounds, **15** and **16**, which proved to have even higher calculated densities and detonation properties.



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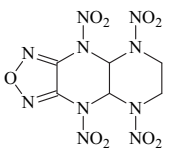

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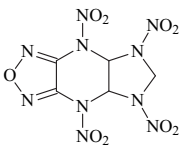

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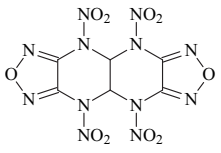

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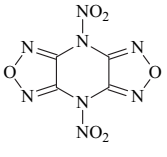

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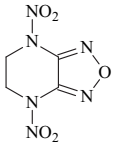

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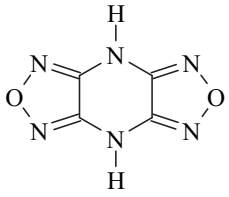
Compound **15** was quickly synthesized by the acid catalyzed condensation of 3,4-diaminofurazan with glyoxal followed by nitration using trifluoroacetic anhydride/100%

Table 2. Calculated Properties of 3, 4-Diaminofurazan Based Energetic Materials

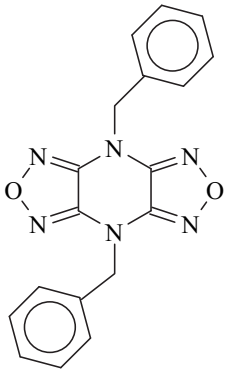
Compound	Calculated Density, (g/cc)	Calculated Detonation Velocity, (mm/msec)	Calculated Detonation Pressure, (kbar)
12	2.03	9.48	428
13	1.88	9.06	390
14	1.96	9.50	430
15	2.00	9.57	437
16	2.00	9.70	450
17	1.82	8.72	358

nitric acid [37]. Unfortunately, **15** proved to be rather thermally unstable and unusable as an energetic material. Not fully understanding the instability of **15**, a molecule, **17**, was designed which did not contain the peri-nitro interaction. Compound **17** was synthesized and proved to be stable [37]. Although originally synthesized as a model compound, the properties of **17** were actually good enough that it received significant attention as an energetic molecule.

Compound **16**, referred to by the author as DNDFP, proved to be a molecule of great intrigue. As noted earlier, this compound was first proposed in 1981. Some work was done on the synthesis of the parent compound, DFP (**18**), by the author while he was at NWC-China Lake. The project was continued by Dr. John Fischer who succeeded in synthesizing the dibenzyl analog, **19**, but failed to find a method to remove the protecting groups [38]. The parent compound was eventually synthesizes by two Russian Groups [39,40] and a Latvian Group [41] in the mid 1990's using a method close to that proposed by the author in 1985 [42].



DFP, 18



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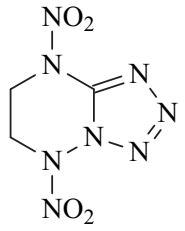
One other adventure in this area should be mentioned. After leaving NWC-China Lake the author started a project at Thiokol-Elkton on making tetrazole analogs of the furazan compounds made at NWC. One of the compounds synthesized was **20** [43]**.** This compound has six nitrogen atoms contiguously bonded, this is believed to be the most nitrogen atoms every seen bonded contiguously at the time. The compound did not exhibit great thermal stability. The calculated density (1.76 g/cc) is very close to the density determined by X-ray crystallography (1.78 g/cc [43]. The compound has a very high heat of formation (+124 kcal/mol) and calculates to be a powerful energetic material. Recently, Ermakov synthesized the isomeric compound **21** [44]. This compound exhibits much improved thermal stability and should make an interesting energetic material.



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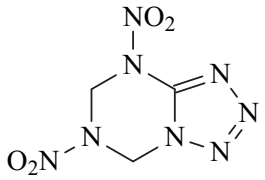

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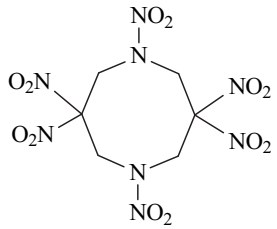
1, 3, 3-Trinitroazetidine, TNAZ

In 1983 Adolph and Cichra of the Naval Surface Weapons Center-White Oak reported the synthesis of 1,3,3,5,7,7-hexanitrodiazaocine, **22** [45]. This compound calculated to be slight-



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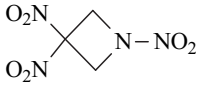

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Table 3. Predicted Performance of Gem-Dinitro-Nitramine Compounds

Compound	Calculated Density, (g/cc)	Calculated Detonation Velocity, (mm/msec)	Calculated Detonation Pressure, (kbar)
22	1.79	8.83	368
23	1.82	8.68	363

ly more energetic than HMX because of it's better oxygen balance. It is less dense than HMX and attracted little attention. Shortly after this, Baum et al reported the synthesis of the analogous 4-membered ring compound, 1,3,3-trinitroazetidine, **23** [46]. The predicted performance of these two compounds, **22** and **23** are summarized in Table 3.

Surprisingly, TNAZ also did not receive much immediate attention. This was partially due to the fact that a calculated performance for the compound failed to include the ring strain of the 4-membered ring in the estimation of the performance of TNAZ. The author had always recognized this as one of the limitation of the Rothstein-Petersen method since no strained ring compounds had been included in the regression analysis [12,13]. The author requested a sample of TNAZ from Fluorochem, Inc. and determined the heat of formation of TNAZ. It turned out that the "ring strain" was real and that TNAZ had a slightly higher calculated performance than HMX. The author interest at that time was in finding ways to improve the mechanical properties of TPE based propellants [47]. The author's group made several TNAZ containing TPE gun propellants and found significantly higher burn rates as compared to RDX based compositions.

Energetic Polymers

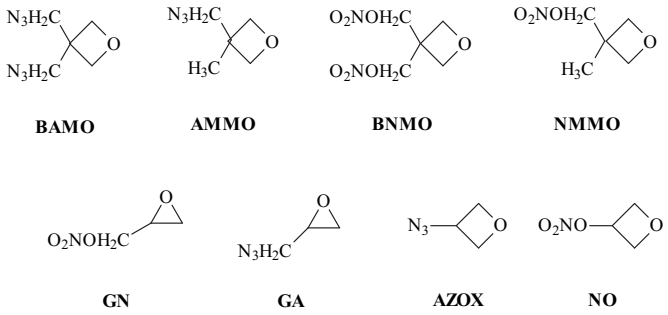
Considerable work has been reported on energetic polymers for composite energetic materials with the hopes of either 1.) improving the overall energy/performance of the composition or 2.) providing the same overall energy with lower (improved) response to hazards. . There are two reviews available [48,49]. In the mid 1980's, the Air Force Rocket Propulsion Laboratory at Edwards AFB issued a Request for Proposal for a Glycidyl Azide Polymer (GAP) Improvement Program. GAP had been developed by Rocketdyne in the late 1970's [50] and researchers were having problems getting adequate mechanical properties with the early material. The author had recently joined Thiokol-Elkton and was given the assignment of looking into whether or not Thiokol wanted to bid on the program. This was somewhat of a daunting assignment since the author had not really ever done any polymer chemistry. The Utah division of Thiokol was not interested because Gerald Manser, one of the principal sp proponents of the energetic poly (3,3-disubstituted oxetanes), had convinced management GAP was not worth looking at. A review of the published literature available on GAP at that time did not give much encouragement for developing a method for producing a better material. GAP is made by a S_n2 displacement of the chlorines of poly (epichlorohydrin) (PECH) with sodium azide. Both a solvent based process (DMSO) and a phase transfer catalyzed process had been used. During this literature review the author stumbled upon the fact that the nitrato- analog of GAP, poly (glycidyl nitrate) (PGN) was a reasonably well known material but that no work had been done on it in about 15 years. Unlike GAP, PGN is made by the direct polymerization of the monomer, glycidyl nitrate and it was thought that maybe the more modern polymerization techniques would allow a better material to be produced. The author spoke to several people who had worked on PGN earlier and came to the conclusion that it was worth reinvestigating. A comparison of the performance of the various energetic oxetane and oxirane monomers calculated by the "Energy" program is given below in Table 3. One can readily see that GN is one of the more energetic monomers and the literature already showed that the PGN was a liquid material.

All of the known energetic polymers at that time suffered from a variety of deficiencies. The symmetrically 3,3-disubstituted oxetanes (poly-BAMO, poly-BNMO) are too highly crystalline to be used as homopolymers and must be copolymerized with large amounts of the less energetic unsymmetrically 3,3-disubstituted oxetanes (AMMO, NMMO) in order to produce polymers with low T_m and T_g. This reduces their energy levels and makes the polymers harder to prepare consistently. The unsymmetrically 3,3-disubstituted oxetanes (AMMO, NMMO) are too low in energy and have too much of their molecular weight not included in the backbone.

The author's group started a small program to re-investigate PGN in 1987. A small amount of the monomer was synthesized and polymerized using boron trifluoride etherate-butanediol in methylene chloride, the method used in previous work. The material was very low in functionality and very difficult to cure into a rubber. The reason for this became clear upon examining the ^1H NMR spectrum of the material. A considerable amount of ethyl groups could be easily detected. When the polymerization was repeated using a catalyst-initiator complex that had been vacuum treated to remove the diethyl ether, a PGN was produced that was much higher in functionality and that could be easily cured into a rubber using a mixture of di- and tri-isocyanates. Several small additional improvements to the process were made over the next couple of years and very reproducible 10 mole scale (≈ 2.5 lb.) syntheses of PGN were accomplished and some initial propellant

Table 3. Predicted Performance of Oxetane and Oxirane Monomers

Monomer	Molecular Formula	Molecular Weight	Calculated Density, g/cc	Calculated Detonation Velocity, mm/isec
BAMO	$C_5H_8N_6O$	168.12	1.219	1.774
AMMO	$C_5H_9N_3O$	127.13	1.088	-2.273
BNMO	$C_5H_8N_2O_7$	208.12	1.398	5.508
NMMO	$C_5H_9NO_4$	147.12	1.203	2.971
GN	$C_3H_5NO_4$	119.07	1.373	4.717
GA	$C_3H_5N_3O$	99.07	1.220	1.094
AZOX	$C_3H_5N_3O$	99.07	1.220	1.094
NO	$C_3H_5NO_4$	119.07	1.373	4.717



evaluation work was started. This work was reported in 1989 [51]. It was quite interesting that a group of British researchers reported on their PGN work at the same meeting [52].

The synthesis was later scaled-up to both the 100-mole scale and the 500-mole scale with excellent reproducibility. This work is summarized in 1990 in a JANNAF paper that, because of its restricted access, few people are aware of [53]. This paper included a great deal of propellant evaluation work that showed the great promise of the material. Much of this work was eventually published in a series of patents [54, 55, 56, 57, 58]. An interesting sidelight to this work on PGN was that we were able to make both optical isomers of the monomer (*R* and *S*) and polymerize them to the optically active polymers [59, 60]. As might be expected, the isotactic polymers had very different properties from the atactic polymer. Most notable was that they were crystalline polymers (m.p. 47.2 °C) where as the racemic polymer is an amorphous material.

Regrettable, by 1993, it had become quite clear that the standard PGN suffered from an aging problem in polyurethane propellants. The most reasonable explanation is that the urethane nitrogen displaces the terminal nitrato-group releasing nitric acid. This postulation is supported by the fact that PGN propellants cured with aromatic isocyanates display improved stability as compared to those cured with aliphatic isocyanates [61]. Several approaches to "fixing" the problem have been developed but none are really fully acceptable.

It should be noted that in two recent reviews [48,49], the authors failed to cite this work yet cited almost all of the British work on the subject. A conversation with one of the authors (J. P. Agrawal), revealed the fact that the British workers were not citing our competing work even though they were very well aware of it.

The author left the energetic material field in 1993 and did not return until 2002. Somewhat to his surprise, there was still considerable interest in PGN because of its high performance but no adequate solution to the aging problem had been found. One Saturday, sitting at his desk at home it struck him that the answer might be the isomeric molecule, poly (3-nitratooxetane) (PNO).

He was able to come up with a number of reasons PNO would be superior to PGN and one reason it would not. These are given below:

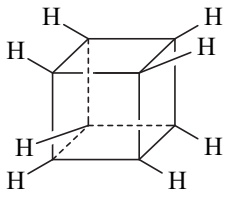
Table 4. Advantages/ Disadvantages of Poly (3-nitratooxetane) versus Poly (glycidyl nitrate)

1. 3-hydroxyoxetane is a stable molecule where as glycidol is not. 3-Hydroxyoxetane can most likely be nitrated using acetic anhydride/nitric acid.
2. The diol produced on polymerization is a primary diol instead of a secondary diol.
3. More of the polymer's molecular weight is in the backbone and it should give better mechanical properties.
4. The cure reversion seen in isocyanate cured unmodified PGN should not be seen in PNO.
5. The density of poly (3-nitratooxetane) should be equal or greater than PGN.
6. The one disadvantage of poly (3-nitratooxetane) is that the starting monomer requires a five step synthesis that will make the monomer expensive compared to glycidyl nitrate.

In a recent presentation, Dr. Anne Merritt of NAWC-China Lake confirmed that their work has shown that all the potential advantages of PNO versus PGN have been confirmed [62].

Energetic Cubanes and ADN

Cubane, **24**, was first synthesized by P. E.Eaton [63]. It has a strain energy of 160 kcal/mole. A significant research program to synthesize energetic cubanes was started in the 1980's by the U. S. Army [64]. The ultimate goal was to make octanitrocubane, **25.** This program was started by Drs. Everett Gilbert and Jack Alster. By the mid 1980's significant progress had been made on the program and both mono-nitro and 1,4-dinitrocubane had synthesized [65]. Several tetra-substituted cubanes were also synthesized as precursors to tetranitrocubane [66]. At this point, the Office of Naval Research decided to initiate its own program on energetic cubanes as part of the "Star Wars" effort. It was deemed important not to duplicate the Army effort. It seemed at the time that it might not be possible to make an octa-substituted cubane and that a tetra-substituted cubane was a more realistic goal. A significant number of calculations were made to determine if a tetra-substituted cubane could be energetic enough to provide the needed increase in specific impulse.



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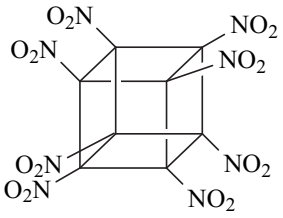

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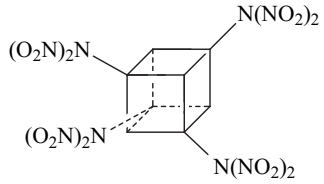
Careful calculation using the Energy program, estimations of heats of formation similar to those described by Meyerriecks [1] and the PEP program [11] on various tetra-substituted cubanes showed that only ones with unusual groups such as dinitramino would be energetic enough to provide a substantial increase in specific impulse. Because of this, a consortium was formed between Professor Eaton at the University of Chicago, the author at Thiokol-Elkton, R. Schmidt and J. Buttaro at SRI International and Fluorochem, Inc. to work on the synthesis of non-nitro group energetic tetra-substituted cubanes. The program, funded by Dr. Len Caveny of the Office of Innovative Science and Technology of the Strategic Defense Initiative Organization, was managed by Dr. Richard S. Miller of the Office of Naval Research. The calculation alluded to earlier clearly showed that only the dinitramino group (-$N(NO_2)_2$) was energetic enough to provide a tetra-substituted cubane that would provide the desired increase in propellant performance.

Target Molecules for SDIO Cubane Program



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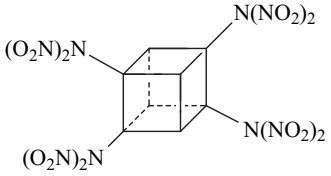

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Our approach to the synthesis of the desired molecule was rather straight forward. Previous work on dinitramines had shown that they could be made by nitrating a salt of a primary nitramine [67]. The first task then was to be able to synthesize cubane nitramines that were unknown compounds. We were able to synthesize both 1-nitraminocubane, **28**, and 1, 4-bis-nitraminocubane, **29**, from the corresponding methylurethanes [68,69].

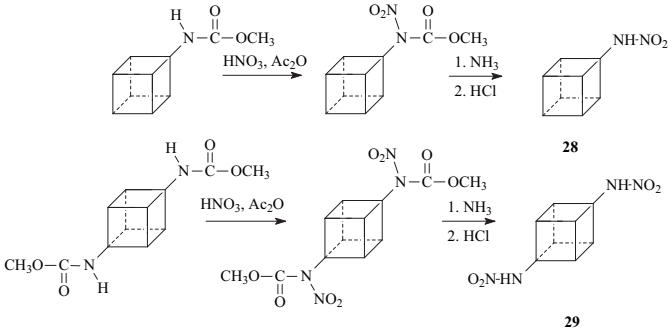


Fig. 1. Synthesis of Nitraminocubanes.

^{1}H NMR experiments showed that we could form the corresponding dinitramines in solution but they were very unstable. However, the 1,4-bis-(dinitramino)cubane, **31**, appeared to be much more stable than the mono compound, **30**. It appeared that the compounds were decomposing by formation of a cubyl cation and a dinitramine anion.

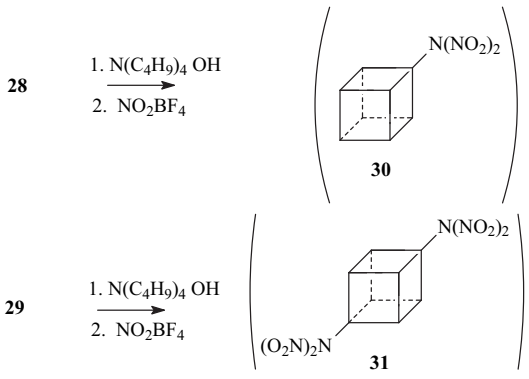
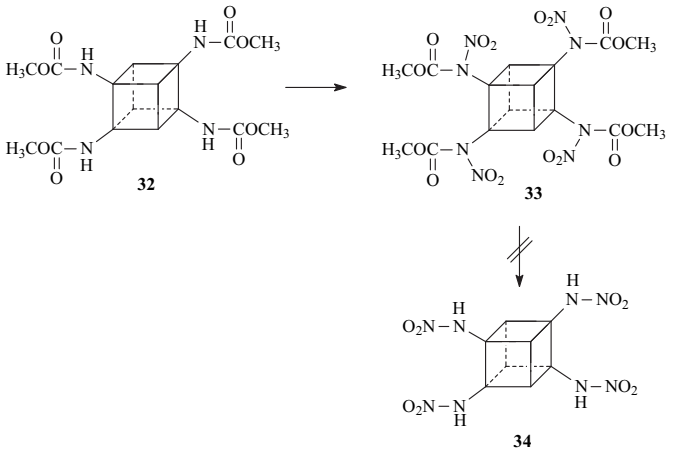


Fig. 2. Synthesis of Dinitraminocubanes.

The greater stability of **31** as compared to **30** gave hope that a tetrasubstituted dinitraminocubane would be stable enough to isolate. With great difficulty the 1,2,4,7-tetra(meth oxycarbinolamino)cubane, **32**, was synthesized and nitrated using dinitrogen pentoxide in methylene chloride to give the corresponding tetranitrotetraurethane, **33**. However, all attempts to hydrolyze **33** to the 1,2,4,7-tetranitraminocubane, **34**, failed. Unfortunately, this work was never published in a Journal that is abstracted by Chemical Abstracts. The crystal structures of **29** and **33** were published by R. Gilardi and his group at the Naval Research Laboratory [70]. A recent book by Agrawal and Hodson makes the erroneous statement that cubanes with a nitramino group directly attached to the cubane nucleus are unknown compounds [71].

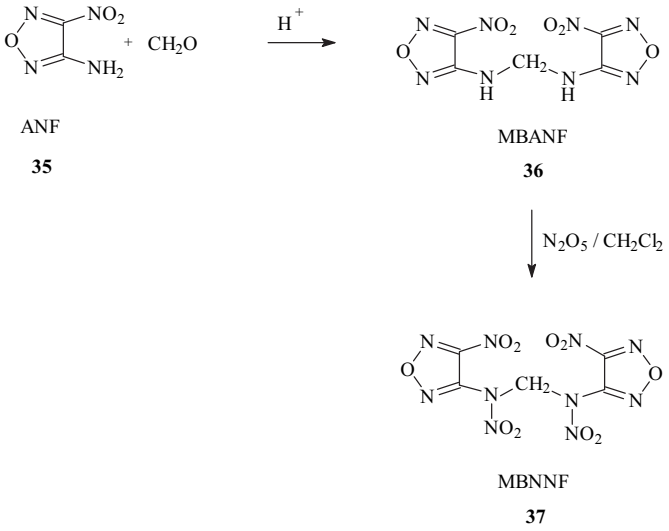


32 **33** **34**

This program was, however, not without an enormous success. R. Schmidt and J. Bottaro at SRI International became intrigued with the question of was the dinitramide anion actually the leaving group and were led to the US synthesis of this very energetic anion [72]. It should also be noted that Professor Eaton was recently able to synthesize octanitrocubane after a 20 year effort [73]. It is extremely interesting that the measured density of octanitrocubane (1.96 g/cc) [73] is significant below the density of 2.16g/cc predicted for it by the Holden method.[18]

Methylene Bridged Nitramines and Organic Analogs of ADN

3-Amino-4-Nitrofurazan (ANF), **35**, was first synthesized by Coburn in 1968 [35]. It is a very energetic molecule but suffers from having a high vapor pressure and an amino group that interferes with the isocyanate cure used in most composite propellants and explosives. One approach to overcoming these problems was to couple two ANF molecules together using a methylene bridge and then nitrating the resulting methylenediamine (MBANF), **36**, to the methylene dinitramine, **37**. The resulting compound, MBNNF, calculated to have better detonation properties than CL-20 and impressive performance as a propellant ingredient. The synthesis of the compound is summarized below along with its calculated properties [74]. The original melting point reported for the compound was incorrect and Russian investigators published the correct melting point [75]. Both **36** and **37** have been evaluated as propellant ingredients with very encouraging results.



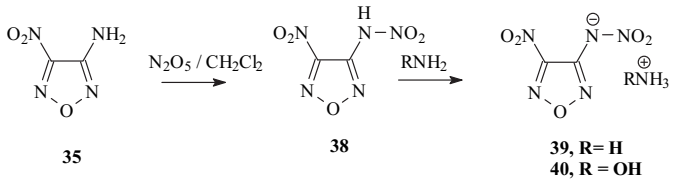
ANF **35** MBANF **36** MBNNF **37**

The high performance of MBNNF led to the design of other molecules that exploited ANF's potential. The synthesis of ADN by Schmidt and Buttaro suggested that salts of the nitrated ANF might be stable and calculations by the "Energy" program predicted they would be very energetic. We were able to make these compounds by first nitrating ANF using dinitrogen pentoxide in methylene chloride to give 3-nitramino-4-nitrofurazan (NNF), **38**. This compound was isolated by vacuum removal of the methylene chloride and excess dinitrogen pentoxide. NNF is a very sensitive compound as might be expected. The salts were made by dissolving the NNF in an appropriate solvent, adding the appropriate amine or metal hydroxide and evaporating the solvent [76]. The salts are much less sensitive and appear to be viable energetic materials based on their thermal stability [77]. The best of the salts were the ammonium salt, ANNF, **39** and the hydroxylammonium salt, HANNF, **40**. The crystal structures of these compounds were determined by R. Gilardi and C. George at the Naval Research Laboratory [78]. The structures of ANNF and HANNF were quite interesting. The two compounds had essentially the same crystal structure with the hydroxyl group in HANNF occupying what is empty space in the ANNF structure. The observed density of HANNF (1.875 g/cc) is greater than that of ANNF by more than would be expected because of this.

The greatest impediment to the development of these ANF derived energetic materials just discussed was, in fact, the synthesis of ANF. As mentioned previously, 3-amino-4-nitrofurazan was first synthesized by Coburn in 1968 by the per-

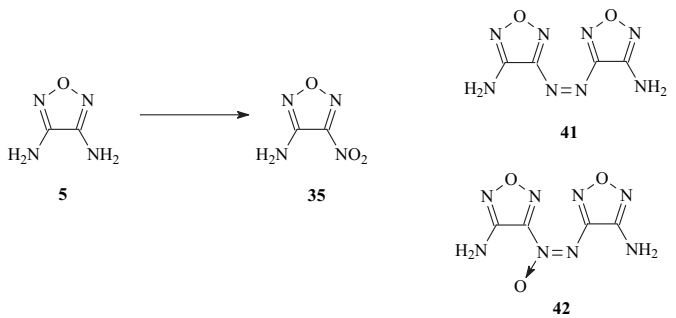
Table 4. Calculated Properties of MBANF, MBNNF, NNF, ANNF and HANNF

Compound	Calculated Density (g/cc)	Calculated Detonation Velocity (mm/msec)	Calculated Detonation Pressure (kbar)
ANF	1.84	9.31	412
MBANF	1.80	8.88	372
MBNNF	1.92	9.69	447
NNF	1.95	9.86	464
ANNF	1.82	9.88	465
HANNF	1.89	10.01	478



35 **38** **39, R= H** **40, R = OH**

oxytrifluoroacetic acid oxidation of 3, 4- Diaminofurazan [35]. It was next synthesized by Solodyuk et al. [79] in 1981 using various mixtures of H_2O_2, H_2SO_4 and ammonium persulfate ($(NH_4)_2S_2O_8$). They were able to obtain ANF, along with azofurazan, **41,** and azoxyfurazan, **42**, in varying proportions. Their best yield reported ANF was 49.5%. A communication by Novikova *et al*. [80] reported the successful oxidation of various aminofurazans to the corresponding nitrofurazans using mixtures of aq. H_2O_2, conc.H_2SO_4, $(NH4)_2S_2O_8$ and sodium tungstate (Na_2WO_4). The communication reports a 78% yield for the synthesis of ANF. However, the details of the precise conditions for each oxidation described are somewhat vague. The reaction conditions are selected by comparing a calculated ionization potential of the starting aminofurazan with the calculated "active oxygen content" of the oxidizing mixture. R. D. Schmidt of Lawrence Livermore National Laboratory developed a modified procedure that did not use the ammonium persulfate but gave a slightly lower yield [81].



5 **35** **41** **42**

We developed an innovative modified procedure based on the Schmidt procedure that increased the yield to above 90% and allowed multi-pound quantities of ANF to be synthesized in a day in a 50-liter reactor. The main changes were to raise the reaction temperature, increase the hydrogen peroxide concentration from 30% to 50-70% and not isolating the ANF after each addition [82]. The ready availably of ANF suggests that molecules such as HANNF and ANNF should be re-examined as energetic materials.

Energetic Structural Polymers

In recent years, the author has become interested in another class of energetic polymers; ones that can be used in a structural sense, for example, bomb or warhead casings or combustible cases for gun and artillery ammunition. The one example of which we are aware is the use of nitrocellulose for combustible cases. This material is not very strong and has the problems of stability that all nitrate ester materials do. We have been looking at an entirely new class of "energetic polymers" based on 1,2,4-oxadiazoles and/or 1,2,5-oxadiazoles. These materials would be expected to be strong like Kevlar® yet about as energetic as TNT.

Target Polymers

There are two systems that were felt to offer good possibilities to produce polymers with the desired properties. These are shown in Figure 6 below and their predicted properties are given in Table 5.

After several unsuccessful approaches to the synthesis of **43**, we examined the reaction of *n*-propyl 4-aminofurazan-3-carboxylate with potassium hydride (KH). The first reaction was run using one equivalent of KH. The *n*-propyl 4-aminofurazan-3-carboxylate was added over a ten minute period to the KH/THF slurry at room temperature. The evolution of hydrogen was slow at first but increased to a noticeable rate accompanied by a slight but noticeable increase in the tem-

Table 5. Calculated Properties of Energetic Structural Polymers

Compound	Calculated Density (g/cc)	Calculated Detonation Velocity (mm/msec)	Calculated Detonation Pressure (kbar)
43	1.77	7.44	238
44	1.80	7.37	231

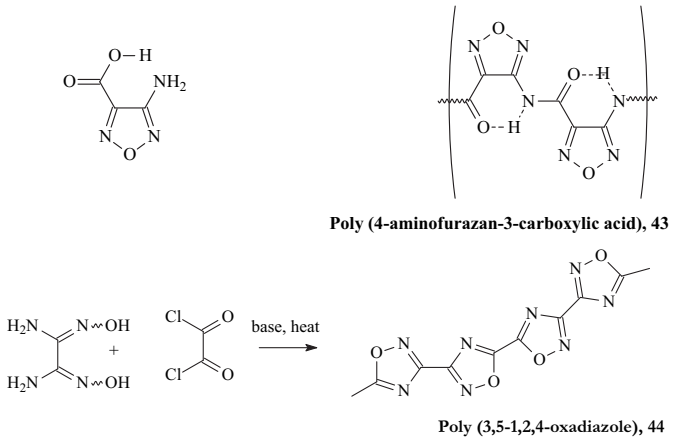


Fig. 6. Target Polymers

perature. After the hydrogen evolution slowed, the temperature was raised to 50 °C for three hours. A very insoluble product was obtained that appeared by C-13 CP/MAS spectrum to be a "dimer" because it contained both furazan resonances and propyl resonances. The reaction was repeated using two equivalents of KH. An even more insoluble product was obtained that is clearly polymer. Figure 14 and 15 show the C-13 and N-15 CP/MAS spectra of the product. An additional piece of evidence is that the yield is essentially 100% of theory and that the polymer is hydrolyzed back to 4-aminofurazan-3-carboxylic acid with acid.

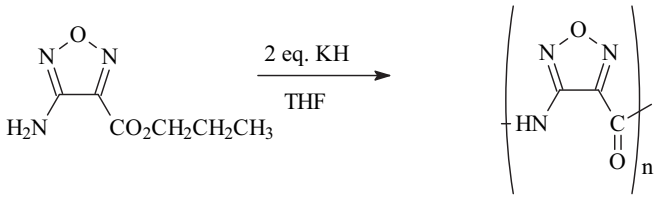


Fig. 7. Reaction of n-Propyl 4-aminofurazan-3-carboxylate with KH

We are currently in the process of characterizing this exciting polymer.

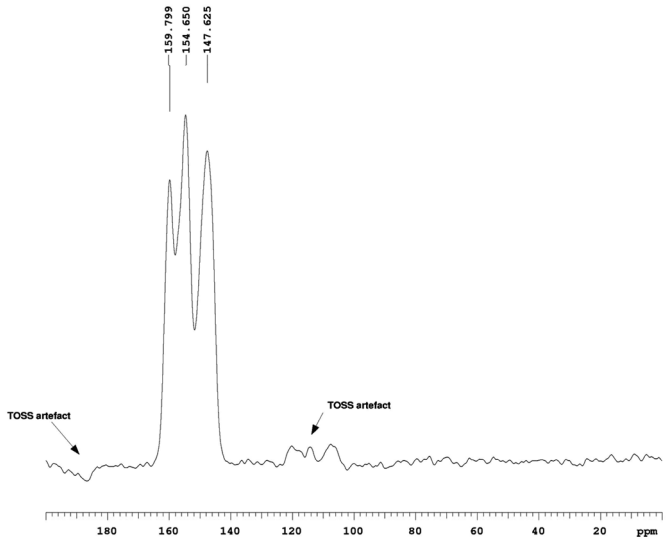


Fig. 8. C-13 CPMAS Spectrum of Poly (4-aminofurazan-3-carboxylic acid)

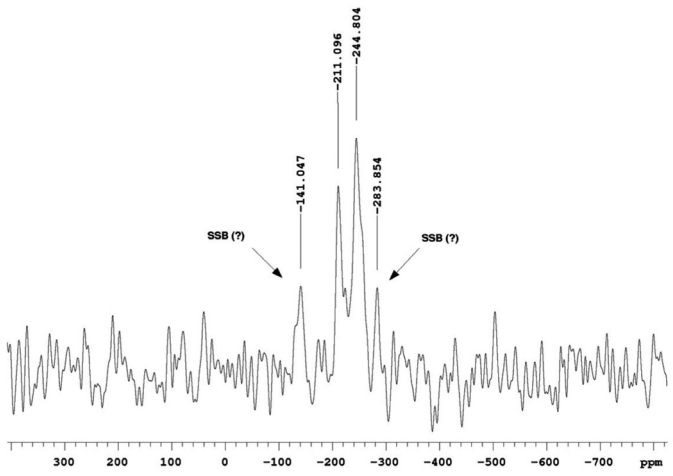
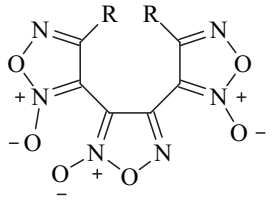


Fig. 9. N-15 CPMAS Spectrum of Poly (4-aminofurazan-3-carboxylic acid)

Conclusions

The simple program "Energy" has proven very useful in the design of new energetic materials. It can also be used to indicate if a compound that a chemist is working with is potentially an energetic material and that due caution should be exercised. For example, a recent paper on the synthesis of the

trimeric furoxan system, **45**, for application as vasodilators, described the synthesis of several compounds that are clearly energetic materials based on their calculated detonation velocity and detonation pressure, yet no warning appeared in the paper [83]. Also a recent publication on an improved synthesis of 3-aminofurazan-4-carboxlyic acid, **46**, fails to mention that the compound calculates to be a moderate explosive [84].



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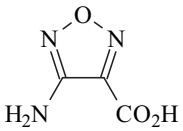

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Acknowledgements

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