

**Novel Insensitive High Explosive Compounds Based on Heterocyclic Nuclei:
Pyridines, Pyrimidines, Pyrazines and Their Benzo Analogues**

Ross W. Millar, Simon P. Philbin, Robert P. Claridge & Javid Hamid

Centre for Environmental Technology, Building A11,
QinetiQ Ltd., Fort Halstead, Sevenoaks, Kent TN14 7BP, United Kingdom
Tel. +44 1959 515630, Fax. +44 1959 516023, E-mail rwmillar@QinetiQ.com

Abstract

The rationale behind using heterocyclic compounds, particularly nitrogen heterocycles, as higher energy insensitive high explosives is discussed, including the potential advantages compared with carbocyclic compounds. The types of functional groups used to impart energy to heterocyclic nuclei, whilst maintaining insensitivity, and methodologies for their introduction, are covered. The latter include nitration (by conventional and clean synthetic methods), amination, and oxidation (on ring heteroatoms and of exocyclic amino groups). Strategies for maximising the energetic content of a given heterocyclic nucleus are also examined.

The syntheses of specific examples at QinetiQ are described, based on the following nuclei: pyridine, pyrimidine, pyrazine, quinoxaline, quinazoline, pteridine and purine. Strategies for obtaining the desired amino-nitro derivatives and their heterocyclic N-oxides are outlined. Optimisation of the synthetic routes for several candidates is discussed. The physical, explosive and thermal properties of the more successful candidates are described, with suggestions for their potential application in military stores.

Background

High performance has been for many years the driving force behind research in the field of explosive compounds for use in military warheads. Thus TNT, used up to and including World War I, was replaced by more powerful RDX-TNT mixtures between the two wars and in World War II. In turn, once HMX became available commercially (ca. 1960) it replaced RDX in the highest performance compositions, which contain

high proportions of this ingredient in either melt-cast (octols) or polymer bound (e.g. LX-14) compositions.

Although research to find explosive molecules with higher performance than HMX continues, many initially promising candidates have fallen by the wayside for various reasons [1], for instance tetranitroglycoluril, hexanitrobenzene and, recently, trinitroazetidine (TNAZ). Others, e.g. CL-20 and polynitrocubanes, are still under consideration, but seem unlikely in the short term to replace HMX as a high tonnage ingredient; the significance of this conclusion will be amplified below.

Since the 1970s the problem of warhead vulnerability has become increasingly more acute. To enhance resistance to aggressive stimuli (e.g. fire, bullet or fragment impact), in early work composite explosives were developed consisting of a three-dimensional polymer matrix encasing a conventional granular explosive (HMX etc.). However, increased intensity of attack on the warhead means that these conventional compositions fail to provide the required immunity to stimuli and alternative remedies must be sought. The approaches are twofold:-

- i) To incorporate a higher proportion of the polymer in the composition, thereby improving the isolation of the explosive particles and reducing their susceptibility to the stimuli, or
- ii) To use explosives which are intrinsically less sensitive; thus the proportion of polymeric binder can be maintained at a similar (low) level to traditional compositions.

Each approach is currently under investigation and their respective advantages and disadvantages are now briefly analysed.

The first approach has the major drawback that, other things being equal, the performance of the composition is reduced. To restore it to the previous level requires either: a) use of a higher energy explosive filler, or b) incorporation of energy in the binder molecules. As we have seen above, option a) is currently in abeyance owing to the non-availability of suitable higher performance explosives (at least on tonnage scale). Approach b) is currently being pursued with the use of energetic polymeric binders such as polyNIMMO, polyGlyN and BAMO copolymers; discussion of the results of these studies falls outside the scope of the present paper, but it

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should be borne in mind that, if compositions can be produced which satisfy the requirements for service use (particularly thermal stability and ageing tests), then a solution to the problem will have been found.

Research Approach

Turning to the approach ii) above, the use of intrinsically less sensitive explosives, historically this approach has been hampered by the lack of suitable candidate molecules possessing adequate performance. Few thermally-stable explosive molecules with low impact sensitivity were known before the 1960s [2,3]; the only compound reaching any appreciable production level in this era was TATB and although it has been incorporated in many compositions its performance is highly inferior to that of HMX and is often deemed inadequate. Its suitability is also compromised by problems in its synthesis, notably in getting rid of chloride contaminants and also achieving suitable particle size distributions for formulating, as well as shortcomings in its explosive performance: low power output (i.e. low detonation pressure), large critical diameter when unconfined plus the likelihood of incomplete detonation unless large booster charges are used. TATB, in the author's opinion, continues to be used only because no better alternative has been found.

Research during the space race in the 1960s and 70s turned up a number of thermally-stable explosives, many with improved performance over TATB, notably HNS and PYX (and other related heterocyclic compounds), but none exhibited sufficient all-round improvement in properties to replace TATB. Latterly, efforts have concentrated on "novel" heterocycles such as NTO (actually first synthesised in 1906, but virtually ignored for some 60 years thereafter), and although results for compositions containing this compound (either as sole energetic ingredient or, more often, in admixture with RDX) have been promising [4,5], there still remain problems arising from the compound's large critical diameter when unconfined, which may give rise to incomplete detonation, as well as some undesired effects arising from its acidic nature (pK_a 3.67 [5]). Therefore it remains a desirable aim to develop a compound or compounds which possess low sensitiveness whilst maintaining high

explosive performance. Novel approaches to achieve this aim are now considered in more detail.

IHE Compounds

The principal approach to new types of insensitive HEs described here is based on the incorporation of a higher proportion of nitrogen into the explosive molecules. This approach requires the following chemistries: a) use of nitrogen-rich heterocycles as a nitratable nucleus, with polyamino substitution to reduce sensitiveness, or b) the incorporation of heterocyclic N-oxide functions in conjunction with polyamino substitution; in certain target molecules both approaches are combined. These approaches are applied to three classes of compounds: i) monocyclic heterocycles, ii) bicyclic heterocycles with one heterocyclic ring, and iii) bicyclic heterocycles with two heterocyclic rings, and each class is considered separately.

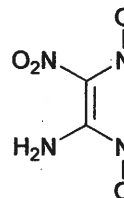
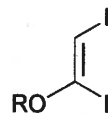
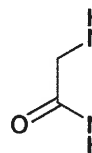
The aim is to obtain amino- or aminonitroheterocycles which can either be used as insensitive HEs in their own right (particularly aminonitroheterocycles), or used as precursors for N-oxidation, which will impart higher energy to the molecule. In certain cases appropriate aminoheterocycles, for instance the precursor for DADNPO (see below), or rarely aminonitroheterocycles, were commercially available. In general, though, this was not the case and the approach was to select commercially available halo- or halonitroheterocycles, either chloro or fluoro derivatives. (Fluoro derivatives are preferable since the rate of halide displacement is enhanced.) The appropriate halo- or halonitroheterocycle was then aminated and the resulting amino- or aminonitroheterocycle was N-oxidised, where possible.

MONOCYCLIC HETEROCYCLES

Attention was focussed mainly on pyrazine and pyrimidine derivatives, since other monocyclic heterocyclic nuclei (e.g. pyridazines, triazines) had proven less amenable to study. Some work on pyridine derivatives is described later.

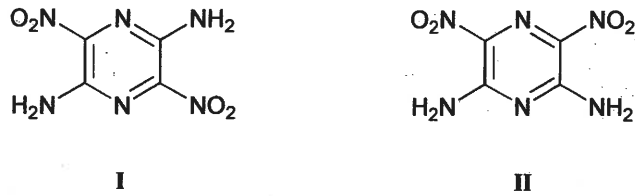
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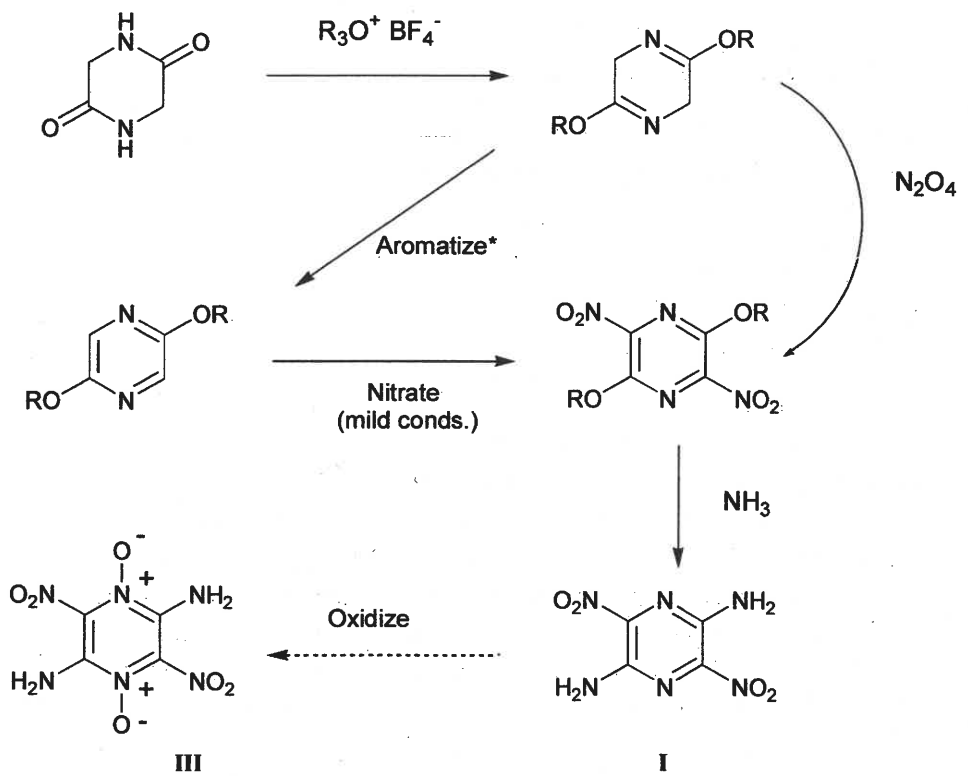


*Reagents: I

Thus a pyrazine derivative, ANPZ-i (I), was studied, which is an isomer of ANPZ (II) [6,7]. The synthesis was fully described elsewhere [8,9], but brief details are given in



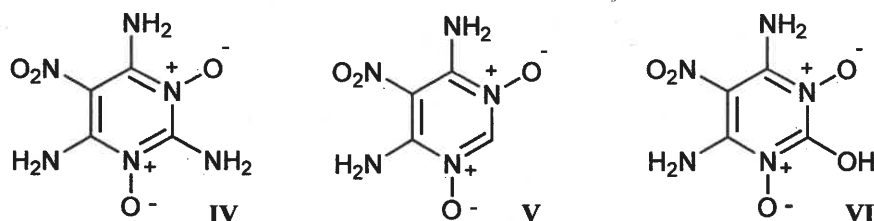
Scheme 1. It should be noted that conditions to effect the full oxidation of ANPZ-i, which would give the novel explosive PZDO (III), however could not be found. The detonation pressure (P_{CJ}) of PZDO was calculated to be 337 kbar [18].



*Reagents: N-chlorosuccinimide + azobis(isobutyrylnitrile)

Scheme 1

The further developments in the pyrimidine work are now presented. Nitration and N-oxidation of two aminopyrimidines were intensively studied, with a view to synthesising target novel insensitive HE molecules: these were 5-nitro-2,4,6-triaminopyrimidine-1,3-dioxide (IV) and 5-nitro-4,6-diaminopyrimidine-1,3-dioxide (V). Unfortunately compound V could not be synthesised without contamination by its mono-N-oxide [10]; attention was therefore focussed on compound IV and its synthesis is now discussed.



5-nitro-2,4,6-triamino-pyrimidine-1,3-dioxide (III)

IV was prepared in 51% yield by the reaction of 5-nitroso-2,4,6-triaminopyrimidine with 30% hydrogen peroxide in trifluoroacetic acid, using a procedure much modified from that reported in the literature [11]. The major problems encountered in this synthesis were: i) preventing the isolation of incompletely oxidised product (i.e. 5-nitro-2,4,6-triaminopyrimidine-1-oxide), and ii) avoiding decomposition of the product by hydrolysis (to give VI). The former problem was overcome by judicious choice of solvents and conditions to inhibit the premature precipitation of the monoxide, whilst the purification described in the literature had to be amended to prevent inadvertent conversion of IV to VI. Batches of IV of some 16-17 g could then be prepared routinely and were submitted for hazard testing.

IV has a density (from pycnometric studies) of 1.81 gcm^{-3} , giving a calculated detonation pressure of 288 kbar [12]. The hazard properties of this compound have now been assessed (see Fig. 1). The figure of insensitiveness (F of I) of 91 (RDX = 80), although less than certain IHEs - e.g. for NTO, F of I = 100 [13] - nevertheless qualifies IV as an insensitive material and its behaviour in the friction tests places it

in this category. The major problems were with ignition (T of I) and RDX, T of I. It is indicated that there should be no problem to hand, it is a performance scale hazard munitions.

Work on this has been carried out. N-oxide experiments on ANPZ (studied).

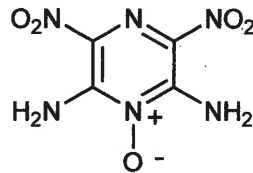
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in this category also. The electrostatic and train tests suggest likewise that no problems will be encountered in the handling of IV. Finally, the temperature of ignition (T of I) figure of 256°C is again somewhat intermediate in behaviour - e.g. for RDX, T of I = 219°C [14], but for NTO, T of I = 259°C [13]. Therefore these data indicate that hazards in handling IV are well within accepted limits and there should be no problems in scaling up its production. Once larger amounts of the material are to hand, it will be possible to initiate a programme of functional testing to evaluate the performance of IV as a component of an explosive train, and together with large-scale hazard test results, assess its suitability as a component of insensitive munitions.

Work on the thermal stability of IV (5-nitro-2,4,6-triaminopyrimidine-1,3-dioxide) has been carried out. For comparison, data were also obtained for another heterocyclic N-oxide explosive, PZO, as well as a non-N-oxide containing heterocyclic explosive, ANPZ (structures VII and II respectively).

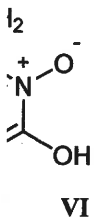
When heat flow calorimetry (HFC) measurements were made on the explosives mentioned above, together with TATB as a reference compound, very low heat flows were obtained from all four compounds, with ANPZ and TATB apparently giving the lowest values. The data were insufficiently consistent to permit calculations to be made of the activation energies of the respective compounds towards decomposition. This variation was thought, in the case of IV at least, to result from changes in the reaction mechanism of the decomposition at different temperatures.



VII

Nevertheless, it appears from these results that both the N-oxide explosives, PZO and IV, and probably more so PZO, possess sufficient thermal stability to permit their further study as components of formulations, and subject to satisfactory chemical

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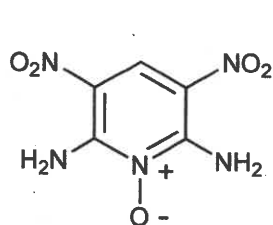
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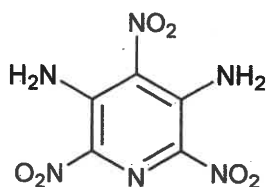
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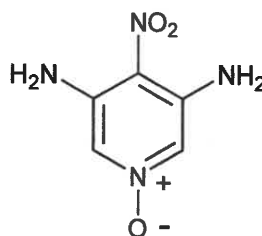
Aminonitropyridines



VIII



IX



X

The compound DADNPO (VIII), originally reported in 1993 [15] and investigated subsequently in the US [16], was also synthesised at QinetiQ in the late 1990s [17] and found to have high insensitiveness, although somewhat low explosive power – $P_{CJ}(\text{calc.})$ 277 kbar [18].

Therefore efforts in the area of pyridine derivatives were focussed on the target trinitro compound (IX), which was a more challenging synthetic target. In this instance the problem of effecting pentasubstitution of the pyridine ring meant that a preferred approach was to use fluorinated precursors, which are known to be more readily displaced by nitrogen nucleophiles such as ammonia [19]. In fact, the synthesis route was based on a specially synthesized fluoropyridine, 3,5-difluoropyridine [20], but studies failed to yield the desired product, and instead the intermediate (X) was isolated [10].

Finally, methods were investigated in order to convert exocyclic amino groups on heterocyclic nuclei into nitro groups, i.e.



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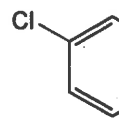
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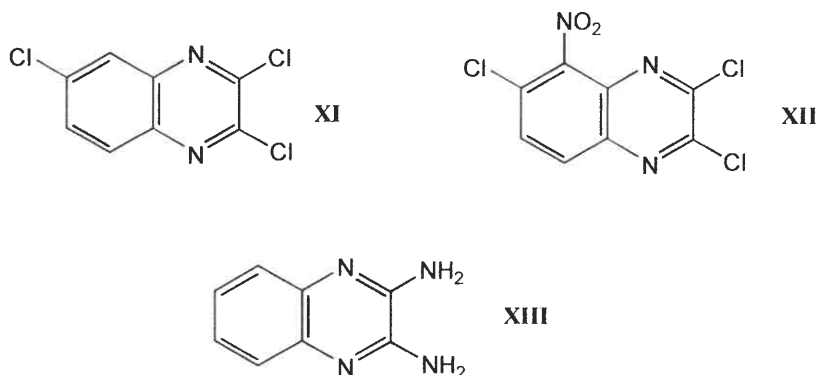
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However, with the two oxidising systems tried, peroxytrifluoroacetic acid in dichloromethane or dimethyldioxirane (DMD) in acetone, yields of less than 5% of the desired nitro compounds were obtained, together with small amounts of products resulting from further oxidation (N-oxides, e.g. 2-nitropyridine-N-oxide). These routes were therefore not pursued further for the synthesis of nitroheterocycles.

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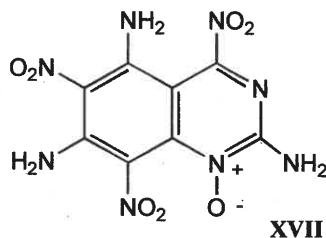
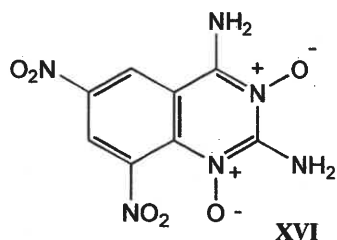
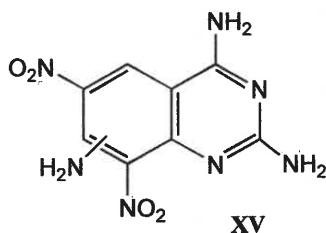
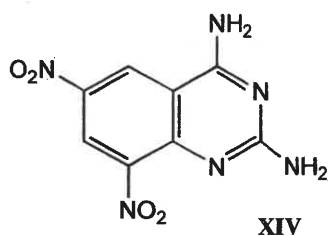
Benzodiazines – Quinoxalines and Quinazolines

The chemistry of these systems was covered in detail at a previous conference [8]. In summary, only one chloroquinoxaline was successfully nitrated - 2,3,6-trichloroquinoxaline (XI), which gave the 5-nitro derivative (XII), a new compound, in 64% yield [21]. With different degrees of chloro substitution, e.g. 2,3-dichloro- or 2,3,6,7-tetrachloroquinoxalines, the reaction failed, and, surprisingly, little success was achieved in nitrating aminoquinoxalines (e.g. 2,3-diaminoquinoxaline XIII) either. Therefore the strategy was changed and hydroxy- or alkoxyquinoxalines were used instead as substrates, and some nitrated products were obtained [21]. Recently, some of these products have been successfully aminated.



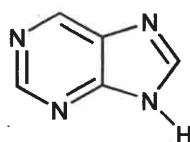
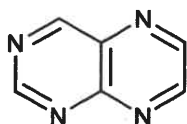
Quinazolines are likewise in general resistant to nitration, with ring breakdown generally supervening. However, ring synthesis with the nitro groups already in

place is possible and a key intermediate, XIV, could be further functionalised to XV. Notably, an N-oxidised quinazoline (XVI) has recently been synthesised for the first time, although the synthesis of the target compound XVII has not been realised [21].

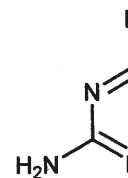


Heterocycles with Both Rings Heterocyclic – Pteridines & Purines

Work in this area is directed towards target molecules in which both rings are heterocyclic (cf. benzoheterocycles, above). Although the synthetic routes are somewhat more complex, the potential pay-off is greater since a higher proportion of nitrogen can be incorporated in the heterocyclic nuclei. The family of compounds selected for initial studies is the pteridines (XVIII), in which a pyrimidine nucleus is fused to a pyrazine ring, giving a nitrogen-rich system (N:C ratio 4:6); further studies (see below) included the purine system (XIX) in which an even higher ratio is achieved (4:5).



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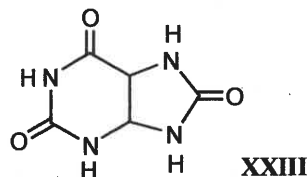
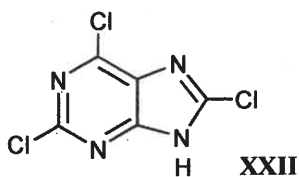
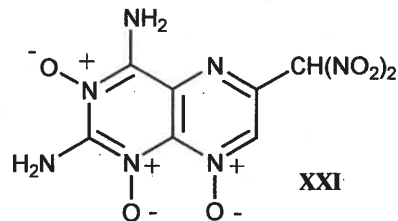
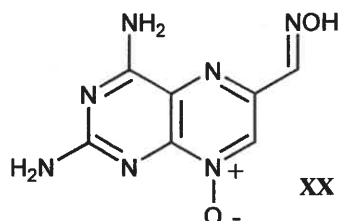
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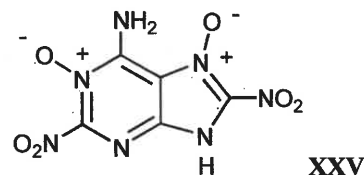
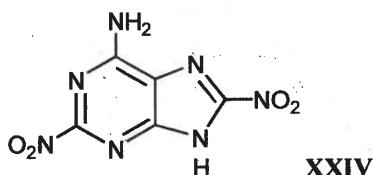
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realised [21].

Using a synthetic strategy involving ring synthesis, which has been detailed elsewhere [10], the pteridine (XX) was synthesised in good yield. However, the further oxidised and nitrated compound (XXI) was not realizable.



Attention was switched to the purine system, a 6-5 fused ring system containing 4 nitrogen atoms (XIX).

Again using strategies detailed elsewhere [10] the primary target molecule, the 2,6,8-trichloro derivative (XXII), was prepared (by chlorination of uric acid (XXIII)), and XXII was mono-aminated under controlled conditions [21]. Sequential replacement of the chlorine substituents by nitro groups using 'Umpolung' nitration methodology [22], would yield an aminodinitro derivative (XXIV) which could then be further elaborated to an N-oxide derivative such as XXV (not prepared).



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Conclusions

Several heterocyclic compounds bearing nitro, amino and N-oxide substituents have been studied as potential higher energy replacements for existing insensitive explosives such as TATB and NTO. Two front-runners are shown in Fig. 1 – the pyrimidine derivative NTAPDO (IV), developed at QinetiQ, and PZO (VII), developed at LLNL Calif. [6] – and these are currently the most promising candidates.

A new compound PZDO (III) [8,9], anticipated to have superior power output to either of the above compounds, would, if synthesizable, prove to be the candidate of choice.

An evaluation of the monocyclic system most suitable for scale-up will need to be made, based on its suitability for end-use (i.e. performance, stability, compatibility etc.) and also the economics of production, taking into account cost of starting materials and complexity of the synthetic transformations required. Of the three front-runners, PZO looks attractive on account of its high predicted P_{C-J} (330 kbar) but requires a relatively expensive starting material (2,6-dichloropyrazine). PZDO, on the other hand, originates from a cheap precursor (glycine anhydride) but requires currently expensive reagents to effect the synthetic transformations. NTAPDO (IV), although offering lower performance (P_{C-J} = 288 kbar), originates from cheap starting materials and requires fewer synthetic steps, and this advantage may prove decisive and lead to its selection. Although a detailed analysis of costs should be deferred until this selection is made, it is clear that all of these compounds will be much more expensive to produce than current materials such as TATB and NTO.

The syntheses of several benzoheterocycles (quinoxalines and quinazolines) have been investigated but, with a few exceptions, their chemistry is not conducive to the introduction of the types of functional groups mentioned above. In particular, nitrations are difficult to achieve, with decomposition often supervening, and aminations require more carefully chosen conditions than the monocyclic systems (i.e. pyrimidines and pyrazines). A diaminodinitroquinazoline (XIV) was found to be the most promising intermediate. Therefore there appears to be little benefit, at least for the time being, in investigating the benzodiazines further.

Bicyclic heterocyclic compounds are some of the most promising once the functional group problems. Nevertheless, there appear to be nitrogen atom

Acknowledgements

This work would like to thank Eamon Colclough for his collaboration gratefully acknowledged.

References

1. SANDELL, J. *Material*, Belgium
2. URBAN, C. *Material*, Belgium
3. URBAN, C. *Material*, Belgium
4. COBURG, G. *Material*, Belgium
5. BECUW, J. *Material*, Belgium
6. PAGOFF, J. *Experim Munitio*
7. KERTH, J. *Material*, 2001, p. 1
8. PHILBIL, J. *Substit*, Nov./Dec.
9. PHILBIL, J. *Pyrotec*
10. MILLAF, J. *Insensit Relatec Energie*

Bicyclic heterocycles with four nitrogen atoms (pteridines and purines) suffered from some of the problems mentioned above but also were generally much less soluble once the functional groups had been introduced, leading to severe handling problems. None of the target molecules could therefore be synthesised. Therefore there appears to be little benefit in investigating further the heterocycles with four nitrogen atoms.

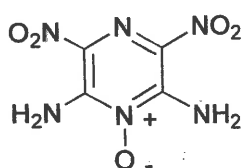
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References

1. SANDERSON, A. (and NIMIC staff), "What Makes a Useable New Energetic Material?", Proc. 1994 NIMIC Workshop, NATO Headquarters, Brussels, Belgium, 1994.
2. URBANSKI T., VASUDEVA S. K., J Sci. Ind. Res., No. 37, 1978, 250-5.
3. URBANSKI T., "Chemistry & Technology of Explosives", No. 4, Ch. 7, Pergamon Press, Oxford, 1984.
4. COBURN M. et al, J Energetic Materials, 1987, No. 5, 27-33.
5. BECUWE A., DELCLOS A., Prop., Explos. & Pyrotech., 1993, No. 18, 1-10.
6. PAGORIA P. F., MITCHELL A. R., SCHMIDT R. D., "Synthesis, Scale-up and Experimental Testing of LLM-105", Proc. NDIA(ADPA) Conference on Insensitive Munitions & Energetic Materials Technology, San Diego CA, 1998.
7. KERTH J., KUGLSTATTER W., Proc. 32nd Internat. Ann. Conf. of ICT, Karlsruhe, 2001, p. 166/1-166/11.
8. PHILBIN S. P., MILLAR R. W., COOMBES R. G., "Studies of Novel Nitro-Substituted Nitrogen Heterocycles", Proc. NDIA(ADPA) Conference, Tampa FL, Nov./Dec. 1999.
9. PHILBIN S. P., MILLAR R. W., COOMBES R. G., Propellants, Explosives & Pyrotechnics No. 25, 2000, p. 302-6.
10. MILLAR R. W., PHILBIN S. P., CLARIDGE R. P., HAMID J., "Novel Heterocyclic Insensitive High Explosive Compounds: Pyridines, Pyrimidines, Pyrazoles and Related Compounds", Proc. NDIA(ADPA) Conference on Insensitive Munitions & Energetic Materials Technology, Bordeaux, France, 8-12 October 2001.

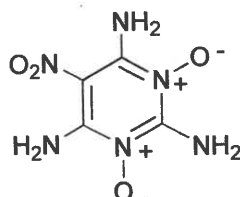
11. DELIA T. J., PORTLOCK D. E., VENTON D. L., *J Heterocyclic Chem.*, **1968**, No. 5, 449-451. An adaptation of this work was reported more recently: WILSON, W. S. *et al.*, *J Heterocyclic Chem.*, **1996**, No. 33, 895-904.
12. COOK M. D., DERA Fort Halstead, personal communication **1995**.
13. Royal Ordnance Provisional Hazard Data Sheet No. 82A, March **1989**.
14. MOD SCC Manual, General Appendix E, March **1981**.
15. LICHT H.-H., RITTER H, *Proc. 24th Internat. Ann. Conf. of ICT, Karlsruhe, 1993*, p. 6/1-6/8.
16. See ref. 11, 2nd citation (Wilson *et al.*).
17. CLARIDGE R. P. *et al.*, unpublished MOD report **2001**.
18. FELLOWS J., DERA Fort Halstead, personal communication **1999**.
19. SITZMANN M. E., LAWRENCE G. W., ADOLPH H. G., CHAYKOVSKY M., US Pat. Appl. 6341401 (filed 21 Jan. **1982**).
20. CHAMBERS R. D., HALL C., HUTCHINSON J., MILLAR R. W., *J Chem. Soc. Perkin Trans. 1*, **1998** p.1705-13.
21. MILLAR R. W., CLARIDGE R. P., HAMID J., SHAW D., PHILBIN S. P., unpublished MOD report **1998**.
22. MILLAR R. W., CLARIDGE R. P., "Reversed Dipole ('Umpolung') Nitrations: Novel Syntheses of Polynitroaromatic Compounds" *Proc. 29th Internat. Annual Conf. ICT, Karlsruhe, Germany, June 30 - July 3 1998*.



PZO (VII)

$C_4H_4N_6O_5$; P_{C-J} 330 kbar

F of I = 54 (RDX = 80)
 F of F = 5.2 (insens.)
 Mallet: Steel/steel 50%
 T of I = 328°C
 Train: Supports
 Electrostat.: 4.5 J (not 0.45 J)



NTAPDO (IV)

$C_4H_6N_5O_4$; P_{C-J} 288 kbar

F of I = 91 (RDX = 80)
 F of F = 5.5 (insens.)
 Mallet: nil (all surfaces)
 T of I = 256°C
 Train: Supports
 Electrostat.: 4.5 J (not 0.45 J)

**Fig. 1: Properties of Novel Insensitive Explosives
 (Pyrazines/Pyrimidines)**

Abstract

This paper from comm chlorinated to 250g rea produced is always pre trichlorobe to eliminat picrate. Th crystal size

We are sca order for tl and assess reliably an

Keywords

Synthesis,