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"Approaches to the Synthesis of Energetic Heterocyclic Compounds Suitable for Use in Insensitive Explosive and Propellant Compositions"

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Abstract

The rationale behind developing insensitive energetic compounds (IECs) for incorporation into insensitive munition (IM) formulations (rather than the alternative approach of desensitising higher energy but sensitive compounds) is discussed. With the aim of selecting a maximum of 2-3 IECs suitable for use in insensitive explosive and propellant compositions, a survey of the literature on IECs published in the last 20 years was carried out. From around 50 candidates, a selection was made of eight prime candidates, all heterocyclic compounds (principally monocyclic or fused-ring bicyclic compounds of the di- or triazine, triazole or oxadiazole classes), which displayed explosive performance significantly better than that of the ubiquitous IEC, TATB. The criteria for inclusion of compounds in these listings are described.

Screening of the eight candidate compounds against further performance criteria reduced the list to five compounds which were evaluated in detail – these were: CL-14 (5,7-diamino-4,6-dinitrobenzofuroxan), ANPZ-i (2,5-diamino-3,6-dinitropyrazine), NNHT (2-nitrimino-5-nitro-hexahydro-1,3,5-triazine), NTAPDO (5-nitro-2,4,6-triaminopyrimidine-1,3-dioxide) and PANT (4-(picrylamino)-5-nitro-1,2,3-triazole). A detailed analysis of scale-up issues associated with each compound was then made, including cost and availability of precursors, hazards (chemical and explosive), effluent streams and other scale-up issues (e.g. materials of plant construction). A further downselection using these criteria gave the present short-list comprising three compounds (the first three listed above) and further evaluation is in progress.

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Introduction

In the latter part of the 20th century various approaches were adopted to derive explosive compounds which are intrinsically insensitive (as opposed to the alternative approach which was to desensitise existing high performance compounds such as HMX); such compounds were required for specialised applications such as space exploration as well as nuclear applications, where ultimate stability was required [1-3].

Many compounds were prepared and tested for the former application, mostly based on the strategy of incorporating picryl (2,4,6-trinitrophenyl) moieties into molecules, often based on heteroaromatic nuclei (e.g. PYX, 2,6-di-(picrylamino)-3,5-dinitropyridine), but their properties for the most part resembled those of trinitroaromatics rather than heterocyclic explosives and, although low sensitivities were achieved, performance was low. In nuclear weapons technology, on the other hand, attention was focussed on just one class of compound, which had alternating nitro and amino groups arranged around a benzene ring, of which there are only two members of practical importance – TATB and DATB (1,3,5-triamino- and 1,3-diamino-2,4,6-trinitrobenzene respectively). These compounds had, incidentally, been known since the 1880s but were ignored owing to their extreme insensitivity to initiation (and large critical diameter), which made efficient detonation almost impossible. With developments in PBXs including desensitisation with appropriate plasticizers and binders, it became possible to modify the performance of TATB/DATB based compositions by the addition of more energetic molecules, particularly HMX, so that the composition could be detonated [3,4].

This approach however could only go so far towards generating highly insensitive compositions (for IM compliance), owing to the presence of nitramine molecules as a component – a component necessary to achieve efficient detonation. Therefore a re-appraisal of how to achieve efficient detonation yet retain high insensitivity became necessary during the 1990s.

Re-appraisal of Insensitive High Explosives

We need to re-examine compounds studied earlier as a result of changing priorities – particularly the current emphasis on IM, which will require newer types of compounds. Also, compounds previously considered uneconomic may become viable, because cheaper sources of the chemicals required to make them have been found, or smaller quantities are required (e.g. use in boosters/trains rather than main charge).

Changes in the classes of compounds suitable for the application of insensitive high explosives (IHEs) have resulted from this change of emphasis. Thus, to achieve greater explosive output with maintained or improved insensitiveness, the following considerations are relevant:
- change in types of functional groups
- previous approach (60s/70s) to incorporate large polynitroaromatic substituents – achieved lowering of sensitiveness at expense of performance
- new approach to raise nitrogen content by:
  - o using heterocyclic nuclei instead of carbocyclic – improves oxygen balance (because ring N forms N_2 as product of explosion)
  - o incorporating more amino groups and fewer nitro groups (amino group H-bonding increases stability)
  - o using alternative energy-rich groups such as heterocyclic N-oxides instead of nitro groups (reduces sensitiveness)
- also to raise density (often accompanies change to heterocyclic molecules, particularly asymmetric ones).

It is notable that many new candidate compounds display one or more of these features (see Figure 1):

- e.g. PZO, DADNPO, NTAPDO: amino-substituted nitroheterocyclic N-oxides
- ANPZ, ANPZ-i : amino-substituted nitroheterocycles
- CL-14, ADNBF: amino-nitro-substituted benzoheterocyclic N-oxides
- NNHT: nitroheterocycle with free N-H groups (H-bonding)
- FOX-7: unsaturated aliphatic amino-nitro compound
- TEX: nitrogen heterocycle, nitramine functionalised, with anomalously high density.

On the other hand main charge/booster explosives in current service – largely derived from WW2 or earlier technology are either:

- carbocyclic, e.g. TNT, tetryl, HNS, TATB (though latter has H-bonding amino groups giving it v. low sensitiveness but also low performance), or
- simple heterocycles without amino substitution: RDX & HMX, or
- contain other functional groups, esp. nitrate ester, which degrade sensitiveness & stability – e.g. PETN, NG and other nitrate ester plasticizers (N.B. nitrate ester on polymeric backbones displays better stability than small-molecule counterparts).

We can therefore conclude that new classes of explosive molecules need to be studied based on heterocyclic nuclei with nitro, amino and, optionally, N-oxide substitution, in order to achieve the aims of improved insensitiveness with maintained or improved explosive performance.

Selection of Candidate Compounds

The object of the current programme of work [5] was to examine a number of new energetic materials, which have been developed on a laboratory scale, to determine the feasibility of scaling up production from a few grams to kilogram quantities. The programme therefore addresses factors such as the availability of raw materials, cost of raw materials as well as the synthetic routes themselves and the practicality and safety of scaling up the synthesis. Disposal of waste streams has also been addressed.

In order to generate a list of candidate compounds, available up-to-date literature [6-9] was consulted to identify crystalline explosive compounds within the constraint that the compounds should be heterocycles but excluding specific types being studied by other groups within the collaboration [5], (particularly isowurtzitanes, melamine derivatives etc.).

The sources mentioned above were searched according to the general criterion of finding compounds which possess performance equal to or superior to TATB/DATB; thus P_{CJ} >= 25 GPa at normal pressing densities. The selected compounds should
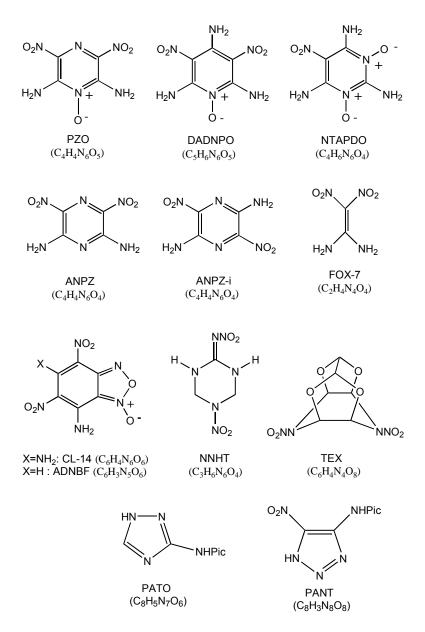
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Figure 1: Structures of Insensitive High Explosives

also not be excessively sensitive to impact, as measured by drop weight testing – mainly from US data (BRL machine) or, occasionally, UK F of I data (Rotter machine). Owing to the strong correlation between density of explosives and their power output [10], and the fact that crystal densities are frequently quoted as a characteristic of an explosive, this characteristic was also used as a primary selection criterion, and compounds with densities >= 1.75 gcm^{-3} are considered.

Few other constraints were placed on the selection process, save that the impact figure should not be lower than 70 cm (US h$_{50\%}$) and that the compound should be reasonably

thermally stable - melting point (or DSC exotherm) preferably >200°C. Those compounds for which reliable literature data were not available, and/or were inadequately performing, were rejected.

This process generated an answer set of 15 compounds, which fell into the following structural classes:
- 1,2,5-Oxadiazoles (furoxans)
- 1,2,4-Triazoles (including derivatives of ANTA [3-amino-5-nitro-1,2,4-(2*H*)-triazole])
- 1,2,3-Triazoles
- Pyrazoles
- Other monocyclic heterocycles (especially pyrazines and triazines)
- Non-heterocycles

Some of the more important compounds are shown in Figure 1.

A decision not to investigate derivatives of ANTA (see above), owing to the difficulty in scaling up the synthesis of such molecules, limited the answer set to the twelve compounds shown in Figure 1, and a further criterion that the candidates should not be commercialized removed three more compounds – TEX, FOX-7 and DADNPO. With the removal of ADNBF on the grounds of its inferior performance compared to CL-14, the short-list was reduced to eight compounds.
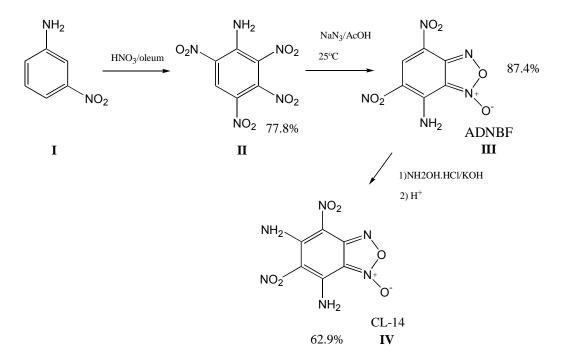
Two further compounds were eliminated on grounds of inconsistencies in their performance against quoted values: PATO has been quoted to possess a high crystal density [11] but figures for material prepared in our laboratories, albeit measured by helium pycnometry, have indicated lower values [12]; in similar vein, the impact sensitivity of PZO, as prepared at QinetiQ, has been found to be quite high with values similar to RDX [4]. For these reasons, PATO and PZO (and also ANPZ, the precursor of PZO) were rejected.

This process reduced the list to five compounds which were evaluated in detail – these were: CL-14 (5,7-diamino-4,6-dinitrobenzofuroxan), NNHT (2-nitrimino-5-nitro-hexahydro-1,3,5-triazine), ANPZ-i (2,5-diamino-3,6-dinitropyrazine), NTAPDO (5-nitro-2,4,6-triaminopyrimidine-1,3-dioxide) and PANT (4-(picrylamino)-5-nitro-1,2,3-triazole). A detailed analysis of scale-up issues associated with each compound was then made, including cost and availability of precursors, hazards (chemical and explosive), effluent streams and other scale-up issues (e.g. materials of plant construction). A further downselection using these criteria gave the present short-list comprising three compounds (the first three listed above), which are now described in detail.

Discussion of Syntheses and Uses

CL-14

The synthesis of this compound was first reported by American researchers at NAWC China Lake [13-15], where the route used in **Scheme 1** was employed.

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Scheme 1: Synthesis of CL-14 (Preferred Route)

In the three stages starting from *meta*-nitroaniline (**I**), the intermediate tetranitroaniline (**II**), which possesses a labile nitro group in the 3-position, is first prepared and this is then reacted with azide ion which upon heating is cyclized to the furoxan (**III**) without isolation of the intermediate azido compound. **III** is also known as ADNBF (7-amino-4,6-dinitrobenzofuroxan) and is an insensitive HE in its own right but less thermally stable and slightly less powerful than CL-14. Finally, a vicarious amination using hydroxylamine hydrochloride is carried out to give CL-14 (**IV**).
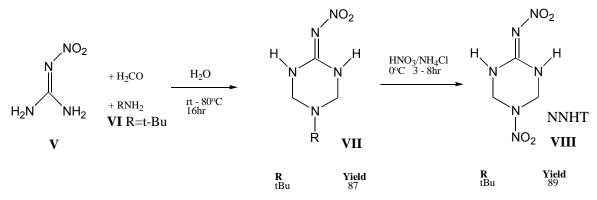
Alternative published routes were either not repeatable in our hands [16], required the isolation of potentially hazardous azido intermediates [17-19], or have not yet been evaluated [20]. It should be noted that although tetranitroaniline (**II**) is not excessively hazardous when isolated as a pure compound (F of I: >100), its synthesis can nevertheless prove problematic if adequate precautions are not taken, especially if intermediates are allowed to dry out [21], resulting in uncontrolled exothermic reactions.

We regard CL-14 to be a "mature" explosive, and conclude that early consideration should be given to scale up work. Here we consider that N_2O_5 in sulfuric acid should be examined as a replacement for HNO_3 / oleum in the first stage nitration since this should give smoother nitration at moderate temperatures and obviate the problems in the present process involving tetranitroaniline (see above). There would appear to be few other problems in implementing the scale-up of this material, although disposal of waste streams containing nitroheterocyclic by-products will require attention.

Although not currently used in munitions, CL-14 has been considered for application in pressable explosive compositions based on EVA binder [3], and as melt-castable explosive compositions in conjunction with carnauba/ozokerite waxes [22].

NNHT

This compound was first synthesized at Aerojet Corp., Calif. [23,24], and the method was subsequently modified and improved by the original workers [25] and also both Russian [26,27] and Australian [28,29] researchers. The present method is shown at **Scheme 2**, where the starting materials – nitroguanidine (**V**) and an aliphatic amine,

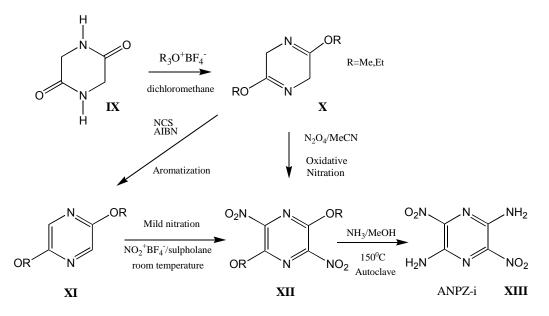

Scheme 2: Synthesis of NNHT

preferably *t*-butylamine (**VI**), are condensed with formaldehyde to give the partially nitrated intermediate (**VII**), which is then nitrolysed to give NNHT (**VIII**).

NNHT, like CL-14, is in effect a "mature product", at least in terms of published research interest, and we are giving serious consideration to commencing a programme of work geared towards product yield scale up. As the Australian reaction method involves a 16 hr reaction time in the first stage and up to 8 hrs in the second stage, any scale up work programme should address as a matter of prime interest the reduction in these reaction time scales. Work is underway to address these issues.

NNHT has been proposed as an energetic filler/oxidiser for gun propellant compositions, either alone or in admixture with RDX [30]. Reasons for the comparative insensitivity of NNHT have been investigated [31].

ANPZ-i

The synthesis of this compound was first reported in a Russian communication [32], and was subsequently elaborated at QinetiQ [33]. The synthesis as shown in **Scheme 3** requires four steps starting from glycine anhydride (**IX**) and proceeds via the dialkoxy intermediate (**X**) which is aromatised to **XI**, nitrated to **XII** and finally aminated to give ANPZ-i (**XIII**) in an overall yield of 25%. It is claimed [32] that the transformation of **X** to **XII** can be effected with N_2O_4 (or sodium nitrate in trifluoroacetic anhydride) but neither of these variations has been attempted in our laboratories to date. Also, the ring nitrogen atoms on ANPZ-i have been found to be resistant to N-oxidation [34,35] which contrasts with the behaviour of ANPZ, which oxidized under mild conditions to PZO [6,36].

Scheme 3: Synthesis of ANPZ-i

In view of the complexity of the synthetic method given in Scheme 3, some alternative routes might be considered in order to improve the process, both in terms of ease of synthesis and overall yields obtained. Such routes would be based on alternative precursors such as 2-amino-5-chloro- [37-40], 2-amino-5-bromo- [41] or 2,5-dichloro-[42,43] pyrazines. Research efforts in this direction are continuing.

It should be noted that, on account of its currently poor availability, there are no published uses of ANPZ-i.

Explosive Performance

Calculated values for the three candidate compounds are shown below:

Compound	Formula	Exptl. Density /gcm^{-3}	Calc. Density /gcm^{-3}	ΔH_f /kcalmol^{-1}	P_{cj} from exptl. Density /GPa	P_{cj} from calc. Density /GPa
CL-14	$C_6H_4N_6O_6$	1.91	1.94	21	32.4	33.3
ANPZ-i	$C_4H_4N_6O_4$	n/k	1.88	23.2	n/k	34.9
NNHT	$C_3H_6N_6O_4$	1.75	1.764	16.3	29.9	29.3

(Enthalpies of formation (ΔH_f) were calculated using the software MOPAC Version 6.00 with the PM3 semi-empirical method, density calculations were carried out using the MOLPAK 2.0 software – the results obtained are the highest theoretical densities calculated by this program – and Cheetah 2.0 was used for detonation pressure (P_{cj}) calculations.)

The most powerful candidates (CL-14 and ANPZ-i) thus show explosive output, as indicated by P_{cj}, comparable to that of RDX.

Conclusions

A survey of the literature has indicated that there are explosive compounds which possess high performance yet exhibit low sensitivity to initiation by undesired stimuli, and are also capable of being synthesised in quantity. Such compounds could enable high performance explosive compositions which are intrinsically insensitive to be devised (i.e. those which do not contain sensitive ingredients, particularly cyclic or cage polynitramines). Three such candidate compounds have been described here, and although work remains to be done, the outlook for achieving high insensitiveness and high explosive performance in a single molecule appears promising.

Acknowledgements

References

1. T. Urbanski, *Chemistry & Technology of Explosives*, Vols. 1-3 (1964) and 4 (1984), Pergamon Press, Oxford.
2. T. Urbanski & S. K. Vasudeva, *J. Sci. Ind. Res.* **1978** 37 250.
3. R.M. Doherty & R. L. Simpson, "A Comparative Evaluation of Several Insensitive High Explosives", *Proc. Int. Ann. Conf. ICT (1997), 28th,* 32/1-32/23.
4. R. W. Millar, S. P. Philbin, R. P. Claridge & J. Hamid, *Prop. Explos, Pyrotech.*, **2004** 29(2) 81-92 and references contained therein.
5. Research & Technology Programme (RTP) No. 10 of Common European Priority Area (CEPA) 14: "Synthesis of Nitrocompounds for Use in Energetic Materials", United Kingdom effort (funded by U.K. Ministry of Defence) contracted to Industrial Entities QinetiQ Ltd. and Nobel Energetics.
6. P. F. Pagoria, G. S. Lee, A. R. Mitchell & R. D. Schmidt, *Thermochimica Acta*, **2002** 384(1-2) 187-204.
7. J. P. Agrawal, *Prop., Explos., Pyrotech.*, **2005** 30(5) 316-328.
8. R. W. Millar, Unpublished MOD Report, Nov. 1999.
9. R. W. Millar & J. Hamid, "Molecular Modelling and Synthesis Studies of High Energy Ingredients for Explosive and Propellant Applications" Unpublished QinetiQ Report, May 2002.
10. M. J. Kamlet & S. Jacobs, *J Chem. Phys.* **1968** 48 23.
11. M. D. Coburn & T. E. Jackson, *J. Heterocyc. Chem.* **1968** 5,199-203.
12. J. Hamid, T. Griffiths, R. Claridge & T. Jordan, "New Trends in Research of Energetic materials", Proc. 7th Seminar, Pardubice, Czech Republic, April 20-24, 2004, Vol. 2, 717-720.

13. A. P. Chafin & R. L. Atkins, US Pat. 4754040 (28/06/88).

14. W. P. Norris, US Pat. 5039812 (13/8/91).

15. W. P. Norris, D. J. Vanderah & M. P. Kramer, US Stat. Invent. Regist. 1078 H1 (7/7/92).

16. B. Chen & Z. Liao, *Proc. Int. Ann. Conf. ICT (1990), 21st (Technol. Polym. Compd. Energ. Mater.), 58/1-58/4.*

17. A. K. Mehilal,. Sikder; Sikder, Nirmala, *Indian Journal of Heterocyclic Chemistry* **2001** 11(2), 149-154; *Chem. Abs.* 137:337831.

18. M.N. Sikder, S. Chougule, A. Sikder and B. Gandhe, *J. Energetic Mats.*, **2004**, 22, 117-126.

19. O. R. Klyuchnikov, V. I. Starovoitov, F. G. Khairutdinov & V. V. Golovin, *Chem. Heterocyc. Comp.*, **2003** 39(1) 135-6.

20. V.L. Zbarsky, D.M. Stepahkov & N.V. Yuidin, "New Trends in Research of Energetic materials", Proc. 7th Seminar, Pardubice, Czech Republic, April 20-24, 2004, Vol. 1, 133-141.(Chem. Abs. 141, 298157w).

21. D. J. Vanderah, *J. Energetic Materials* **1990** 8(5) 378-91.

22. US Pat. 6641683 B1 (04/11/2003).

23. US Pat. 4937340 A (26/06/1990).

24. D.-S. Huang & R. R. Rindone, "NNHT: A new low cost, insensitive nitramine" *Proc ADPA Internat. Symp. on Energetic Materials Technol., New Orleans, 5-7 Oct. 1992*, 326-333.

25. US Pat. 5391736 A (21/02/1995).

26. A. S. Ermakov, S. A. Serkov, V. A. Tartakovsky, T. S. Novikova, & L. I. Khmelnitsky, *Khimiya Geterotsiklicheskikh Soedinenii* **1994** (8), 1129-32.

27. A. S. Ermakov, S. A. Serkov, V. A. Tartakovskii, T. S. Novikova & L. I. Khmel'nitskii, *Izvestiya Akademii Nauk, Seriya Khimicheskaya* **1995**, (4), 719-21.

28. M.D. Cliff, I.J. Dagley, & R.P. Parker; *Prop. Explos. Pyrotech.*; **1998**, 23, 179.

29. M.D. Cliff, *Heterocycles*, **1998**, 4, 657.

30. US Pat. 5325782 A (05/07/1994).

31. A.J. Bracuti, CPIA publication 1999, 691 (JANNAF Combustion Sub Committee Meeting 199, Vol 2, 239-247).

32. I. L. Yudin, A. B. Sheremetev, O. P. Shotov, V. A. & Tartakovskii, *Mendeleev Commun.* **1995** 196.

33. S.P. Philbin, R.W. Millar & R. G. Coombes, *Prop. Explos. Pyrotech*, **2000**, 25,302.

34. S. P. Philbin, PhD Thesis, Brunel University, 2001.

35. A. Sheremetev, personal communication, 2002.

36. J. Kerth, & W. Kuglstatter, *32nd Int. Ann. Conf. of the ICT, Karlsruhe*, 2001, Paper 166.

37. US Pat. 4160834, to Eli Lilly, Dec 17, 1977.

38. Dallacker *et al.*, *Annalen*, **1962**, 660, 98-103.

39. Palamidessi & Bernardi , *J. Org. Chem.* **1964**, 29, 2491.

40. B. Klein, N. Hetman and M. E. O'Donnell, *J. Org. Chem* ., **1963**, 28, 1682-6.

41. R. C. Ellington & R. L. Henry, *J. Am. Chem. Soc.* **1949**, 71, 2798-800.

42. L. Cere, A. Marchese & P. F. Rossi, *Rass. Chem.* **1975**,276, 294-6.

43. P. Tuntwachwuttikul, T. J. Bardas & M. Bobek, *J. Heterocyc. Chem.* **1991**, 28, 1131-7.