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Energetic Plasticisers at FOI in Sweden

Dr. Stefan Ek, PhD
FOI – the Swedish Defence Research Agency
stefan.ek@foi.se

Abstract: *This present paper describes the efforts at FOI to produce and investigate new energetic plasticisers.*

Keywords: *Energetic plasticisers; Synthesis; Characterisation.*

1. Background

FOI has put considerable effort into the development of new energetic plasticisers for more than two decades. As an energetic plasticiser has to fulfil many, and often contradictory, requirements, the work continues. Examples of the requirements are energy content, stability, compatibility, migratory ability. Furthermore, the plasticiser must be cheap to be included in weapon systems, which means that the number or synthesis steps from commercially available starting materials are limited. Environmental concerns are also becoming increasingly demanding in the defence business.

The reason to use energetic plasticisers is to maintain the energy content of a propellant or explosive charge without loss of performance and to allow the use of the formulation in a wide range of temperatures. This is especially important for propellants, as they have to be sufficiently elastic not to crack, which would change the burning behaviour.

2. Nitroaromatics

An early example at FOI was the investigation of K10, which is a mixture of di- and trinitroethylbenzene, see Figure 1. Despite its excellent thermal stability and compatibility, K10 has only limited application, due to its poor oxygen balance (< -110 %) and, what is most undesirable in propellant formulations, very high C/H ratio, resulting in increased average molecular weight of combustion products.

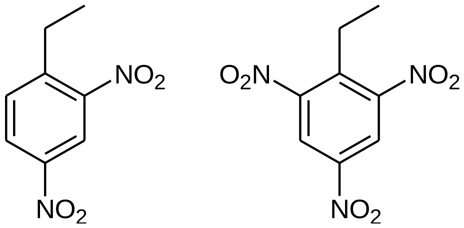

Figure 1. 2,4-Dinitro- and 2,4,6-trinitroethylbenzene - the two constituents of K10

It should be stated that the synthesis of this mixture is simple with only one synthesis step. However, it can be speculated that K10 will have similar toxicity to TNT.

3. *gem*-Dinitroaliphatics

The next group of plasticisers synthesised and investigated were different derivatives of 2,2-dinitro-1,3-propanediol.[1-4]

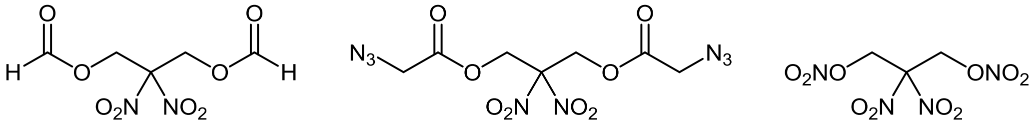

Figure 2. Three different esters of 2,2-dinitro-1,3-propanediol

This group of compounds all had high energy content and good low temperature properties. Unfortunately, all of them suffered from low long term thermal stability. One hypothesis was that this was a result of the high energy density. A new study of esters of 4,4-dinitroheptane-1,7-diol was started to investigate if this was the case.

Three different substances were prepared. The syntheses are shown in Figure 3 with the three target molecules on the right. The azidoacetic- and the nitrate- esters had melting points too high to be of value, but the diazide in the lower-right corner had an excellent glass transition temperature of -89.7 °C.[2, 5] Moreover, it had excellent thermal stability, when evaluated with heat flow calorimetry according to the conditions stated in STANAG 4582.[6] Although this standard is developed for the stability of nitrocellulose propellants, FOI uses it for an indication of the stability of new compounds and their compatibility to fillers and/or oxidisers. When the procedure was repeated with mixtures, the results indicated excellent compatibility to all compounds investigated including ammonium dinitramide (ADN), which is known to be one of the more demanding oxidisers in this respect.

Figure 3 only shows the final step in the three-step synthesis of 4,4-dinitroheptane-1,7-diol from potassium dinitromethane, which is not commercially available. The step shown is a reduction, which is difficult to scale up as a consequence of the reagents used. 1,7-Diazido-4,4-dinitroheptane is an excellent plasticiser, until a much simpler synthesis is developed, it is unlikely to be used on the large scale due to high cost.

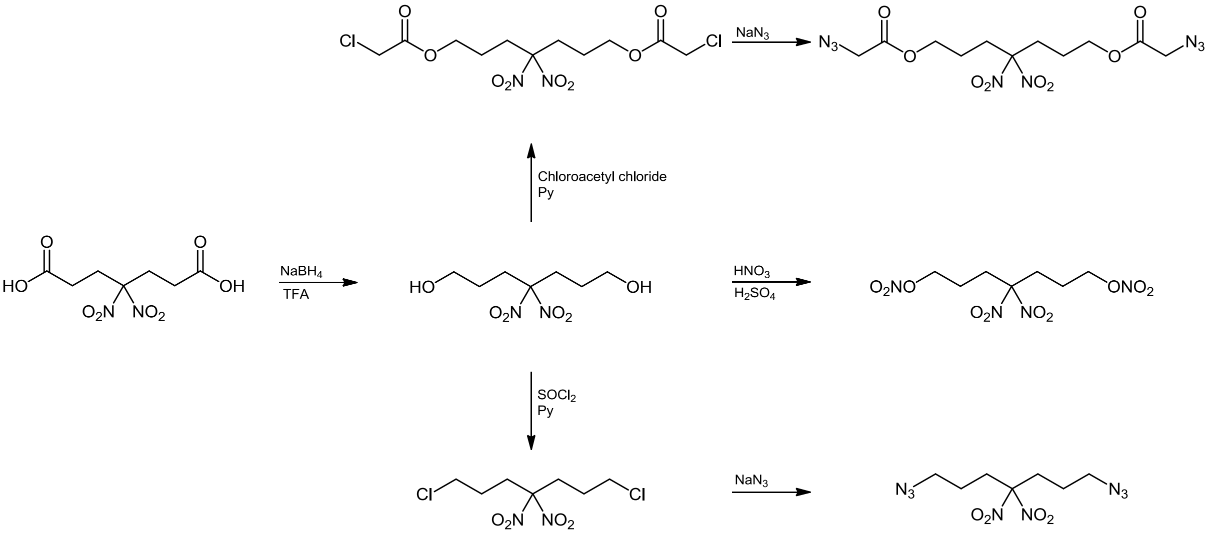

Figure 3. Syntheses of plasticisers from 4,4-dinitro-1,7-heptanediol with the intended plasticisers on the right

4. Derivatives of 3(5),4-dinitropyrazole

A new strategy was therefore investigated – the derivatisation of 3(5),4-dinitropyrazole. Although different substances were prepared, the only one with a sufficiently low glass transition temperature was 1-allyl-3(5),4-dinitropyrazole;[7-9] its synthesis of this is shown in Figure 4.

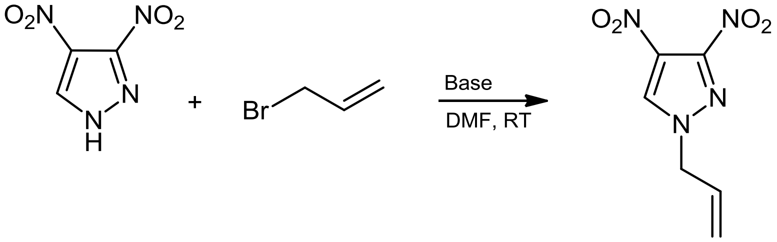

Figure 4. Allylation of 3(5),4-dinitropyrazole into 1-allyl-3(5),4-dinitropyrazole

1-allyl-3(5),4-dinitropyrazole had a decomposition temperature (onset) over 200 °C and a glass transition temperature of -72 °C. Despite being stable during the HFC measurements, the compound discoloured in contact with air during storage.

5. Organic azides

The desirable properties of 1,7-diazido-4,4-dinitroheptane prompted us to look at simpler organic azides. Two products were prepared, see Figure 5, by treatment of the corresponding chlorides with sodium azide.

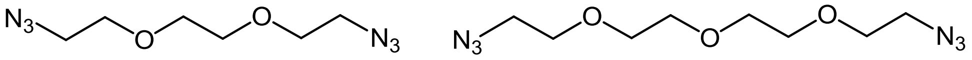

Figure 5. Tri- and tetraethyleneglycoldiazide

Both had glass transition temperatures below -100 °C and no reactions were observed at maximum load in the fall hammer test (50 J). Triethyleneglycoldiazide (TEGDA)[10-12] had some compatibility issues initially, but this was the result of contamination, which was later resolved. Plasticisation of GAP was excellent with TEGDA, which is shown in Figure 6, along with the commercially available plasticisers Bu-NENA and TEGDN for reference. All results from the evaluation of TEGDA were very promising, until the volatility was measured with isothermal thermogravimetric analysis (TGA). As TEGDA was an otherwise promising compound, an analogue with one more ethyleneglycol unit was produced, in an attempt to remedy the high volatility.

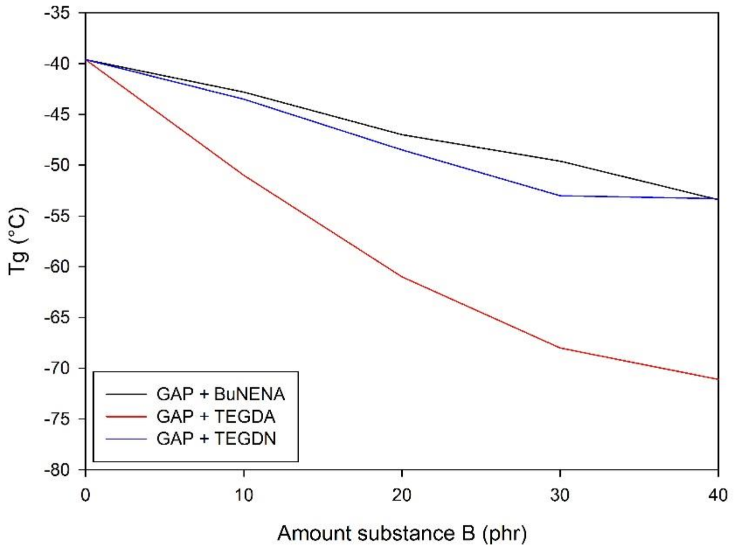

Figure 6. Glass transition temperatures for cured GAP and plasticiser added in parts per hundred rubber

This new compound was tetraethyleneglycoldiazide (4EGDA).[13] As mentioned above, it also had a very low glass transition temperature. Furthermore, it showed very little weight loss in the TGA measurements. To our surprise, it dissolved ADN very well (>25 %). No investigations in the mechanism of this fact have been made, but one hypothesis is that it is due to a crown ether-like effect.

As 4EGDA could be a plasticiser for other propellants not containing ADN, our investigations continues. The compatibility measurements with the first batch of 4EGDA were initially very promising. However, later batches produced conflicting and inconsistent results, which could have been a consequence of the stabilisers present in the ether used in the work-up. To this end, MTBE was used instead, as it contains no stabiliser. However, this produced the least stable 4EGDA investigated. It seems as if the stabiliser from the ether used in the first batch had stabilised the product. In later, larger batches the ratio of solvent to product was smaller, which caused the inconsistent results.

6. Conclusions

On a bad day, the research on new energetic plasticisers feels like the never ending work of Sisyphus, or as Tom Jobim sang '*Tristeza não tem fim, felicidade sim*'. However, the researchers involved persevere, rolling the stone up the hill, with the hope that one day the Holy Grail of energetic plasticisers might finally be obtained.

7. References

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