Co-crystallisation of Energetic Materials: HMX

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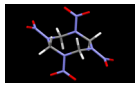
Energetic materials

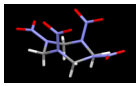
Energetic materials can be split into three groups: explosives, propellants and pyrotechnics, with explosives further divided into primary and secondary explosives. There is currently a drive towards decreasing the sensitivity of energetic materials with the aim of producing insensitive munitions, i.e. explosives that are safer to use.

The energetic material investigated in this study is HMX, a secondary explosive widely used in military applications.

HMX has three known polymorphs α, β and δ, and a hemihydrate known as the γ form.
The β form is the most stable at room temperature and the least sensitive to accidental initiation.
The molecules adopt a chair type conformation in the β polymorph while in the α, δ and γ forms it adopts a boat type conformation.



Molecular conformation found in β HMX[1]

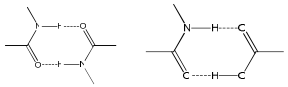


Molecular conformation found in α, δ and γ HMX[2]

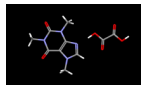
Co-crystallisation

A co-crystal is a crystal that contains two or more neutral components in a stoichiometric ratio.

The principles of supramolecular synthesis can be applied to the design of co-crystals, especially the use of supramolecular heterosynthons.This is termed crystal engineering.



Common example of supramolecular synthons.

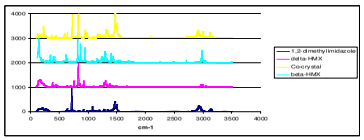


The asymetric unit of the caffeine:oxalic acid co-crystal

The co-crystallisation of caffeine is an example where co-crystallisation has successfully been used in the pharmaceutical industry. The co-crystallisation of caffeine with oxalic acid was found to reduce the absorption of water when compared to pure caffeine.[3]

Co-crystals of HMX

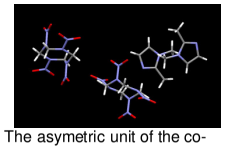
1:2 HMX:1,2-Dimethylimidazole co-crystal



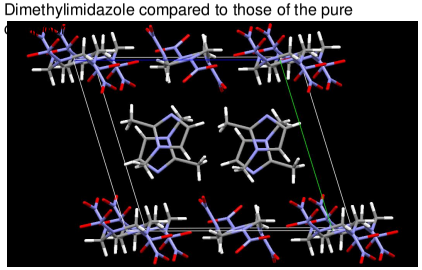
Raman spectrum of the co-crystal of HMX and 1,2-Dimethylimidazole compared to those of the pure compounds

Crystallographic Data	
Formula	$C_8H_{16}O_8N_8$:$C_{10}H_{16}N_4$
Space group	$P\bar{1}$
Unit cell parameters	*a* 8.0582(31) Å *b* 11.1815(4) Å *c* 12.7430(4) Å *α* 107.1160(10) *β* 90.3390(10) *γ* 93.7160(10)
Volume	1094.37 Å^3
Z	2

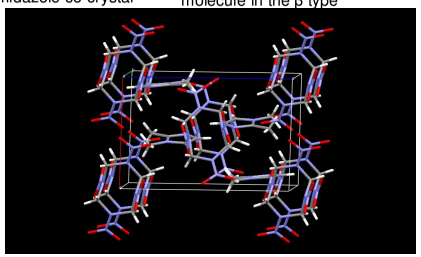
Crystallographic data for the 1:2 HMX:1,2-Dimethylimidazole co-crystal



The asymetric unit of the co-crystal showing the HMX molecule in the β type

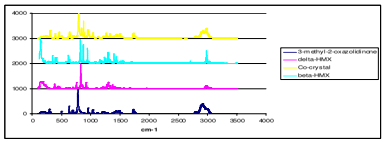


A projection of the packing of the co-crystal along the *a* crystallographic axis showing the layered structure



A projection of the packing of the co-crystal along the *b* crystallographic axis showing the layered structure

1:1 HMX:3-Methyl-2-oxazolidinone co-crystal

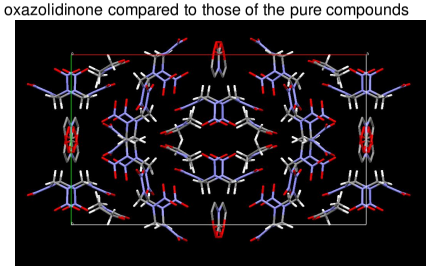


Raman spectrum of the co-crystal of HMX and 3-Methyl-2-oxazolidinone compared to those of the pure compounds

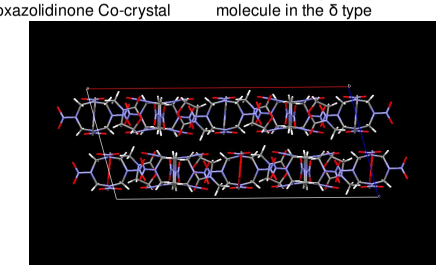
Crystallographic Data	
Formula	$C_{10}H_{19.2}N_{10.8}O_{10.8}$
Space group	$C2/c$
Unit cell parameters	*a* 26.8357(8) Å *b* 15.2883(4) Å *c* 11.9311(4) Å *α* 90 *β* 104.531(3) *γ* 90
Volume	4738.42 Å^3
Z	10

Crystallographic data for the 1:1 HMX:3-Methyl-2-oxazolidinone Co-Crystal

The asymetric unit of the co-crystal showing the HMX molecule in the δ type



A projection of the packing of the co-crystal along the *c* crystallographic axis showing the layered structure



A projection of the packing of the co-crystal along the *b* crystallographic axis showing the layered structure

Co-former Design

Known co-formers

3-Methyl-2-oxazolidinone

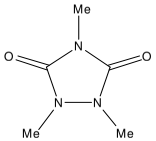
N-methylpyrrolidone

Dimethylformamide

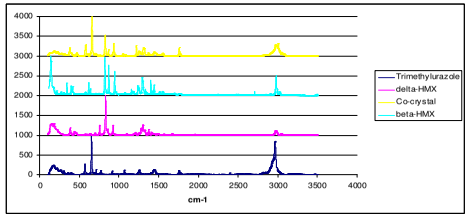
1,3-Dimethylimidazolidinone

Common Feature

Designed molecule



Trimethylurazole



Raman spectrum of the co-crystal of HMX and Trimethylurazole compared to those of the pure compounds

Future Work

Determining the sensitivity of the co-crystals to accidental initiation, e.g. drop weight tests
Design of energetic co-formers to give co-crystals with less penalty to the energetic performance.
Scale up of the production of the co-crystals to allow for larger scale performance and stability testing

References

1 C.S.Choi, H.P.Boutin, *Acta Crystallogr.,Sect.B:Struct.Crystallogr.Cryst.Chem.*, 1970, **26**, 1235

2 R.E.Cobbledick, R.W.H.Small, *Acta Crystallogr.,Sect.B:Struct.Crystallogr.Cryst.Chem.*, 1978, **30**, 1918

3 V. Trask, W. D. S. Motherwell, and W. Jones, *Cryst. Growth & Design*, 2005, **5**, 1013

Scottish Funding Council
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