

Journal of Molecular Structure 644 (2003) 37-48



www.elsevier.com/locate/molstruc

Molecular structures of seven methylenedinitramines with plasticising abilities

Denis Spitzer^a, Bernd Wanders^a, Michael Richard Schäfer^a, Richard Welter^{b,*}

^aFrench-German Institut of Saint Louis (ISL), 5, rue du Général Cassagnou, 68301 Saint-Louis, France ^bLaboratoire DECMET UMR 7513, Université Louis Pasteur de Strasbourg I, 4, rue Blaise Pascal, 67000 Strasbourg Cedex, France

Received 5 June 2002; revised 8 August 2002; accepted 20 August 2002

Abstract

Crystal structures of seven methylenedinitramines with plasticising ability have been determined. These molecules, appropriate as energetic plasticisers of propellants, are used to give an environmental temperature independent combustion. The dinitramines are synthesized by condensation reactions of nitramines with formaldehyde in an acidic medium. This work gives their melting point and their melting enthalpy. Glass transition temperatures are also measured. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Methylenedinitramines; Molecular structure; Plasticisers; Propellant; nitrocellulose

1. Introduction

Propellants for barrelled weapons as solid propergols are used in several temperature conditions. Thus, a weapon can be fired after the propellant was submitted to extreme temperatures like -40 or +50 °C. The main result is a loss in the shoot precision due to the degradation of the material by its cracking under low temperatures. The incidence is a lack of the combustion surface control. The same inconvenience can take place in the rocket or booster launcher field by leading to a damage of the booster matrix by its cracking. These defects then produce a tremendous uncontrolled increasing of the burning surface. The final result is an uncontrolled combustion leading to anomalous combustion pressures.

The present study concerns particularly barrelled weapon propellants for small calibre (0.02 m), medium calibre (0.09 m) and large calibre (0.12 m). A typical propellant includes generally a polymeric binder which is the structural base. It is generally nitrocellulose [1]. Additionally to the stabilizer, which prevents the nitrocellulose chemical degradation, other high energetic charges are added to guarantee the energetic level of the propellant, also it is common to add a plasticiser which is of great importance. Plasticisers had in the past the only function to facilitate the propellant manufacturing. The best known or the most employed plasticisers are of course nitroglycerine (NGL or NG) and diethyleneglycoldinitrate (DEGDN or DEGN). Nitroglycerine is a high energetic nitrate ester [2,3] that is still the most used component for the gelatinisation of

^{*} Corresponding author. Tel.: +33-3-90-24-15-93; fax: +33-3-90-24-12-32.

E-mail address: welter@chimie.u-strasbg.fr (R. Welter).

 $\begin{array}{c} \mathsf{NO}_2 & \mathsf{NO}_2\\ \mathsf{CH}_3\mathsf{-}\mathsf{CH}_2\mathsf{-}\overset{\mathsf{N}}{\mathsf{N}}\mathsf{-}\mathsf{CH}_2\mathsf{-}\overset{\mathsf{N}}{\mathsf{N}}\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_3\\ \hline \textbf{DNDA7}\end{array}$





 $\begin{array}{c} NO_2 & NO_2 \\ CH_3 - N - CH_2 - N - CH_2 - CH_2 - CH_3 \\ \hline DNH \end{array}$

$$\begin{array}{c} \mathsf{NO}_2 & \mathsf{NO}_2\\ \mathsf{I} & \mathsf{I}\\\mathsf{CH}_3\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{CH}_3 \end{array}$$

$$DNU$$

Fig. 1. Chemical structure of dinitramines.

nitrocellulose. About 70% of the propellant world production is based on nitrocellulose/nitroglycerine propellants. Used to establish chemical bonding probably mostly done through solvatation process of the nitrocellulose, nitroglycerine gelatinises the nitrocellulose to build mechanically stable propellants. Since about 10 years, studies are conducted to develop plasticisers which can induce a temperature independent combustion of propellants. Thus, Langlotz et al. [4] included in nitrocellulose and RDX based propellants, a mixture of three dinitramines named DNDA57, and synthesised by Tartakovskii et al.



Fig. 2. Synthesis of symmetrical dinitramines by the self-condensation of nitramines.

[5] in 1993. This mixture induces a temperature independent combustion. Since this time, studies made by the French German Institute of Saint-Louis (ISL) have shown that this result can be obtained only with a few set of well defined quantities of each dinitramine in this ternary mixture. The DNDA57 mixture is composed of three different types of molecules. These molecules are the 2,4dinitro-2,4-diazapentane (or DNDA5), the 2,4-dinitro-2,4-diazahexane (or DNDA6) and the 3,5-dinitro-3,5diazaheptane (or DNDA7). In this work, we have also studied the crystal structures of analogous dinitramines: the 5-methyl-2,4-dinitro-2,4-diazahexane (or MDNH), the 2,6-dimethyl-3,5-dinitro-3,5-diazaheptane (or DMDNH), the 2,4-dinitro-2,4-diazaheptane (or DNH) and the 5,7-dinitro-5,7-diazaundecane (DNU). The chemical structures of these seven molecules are given in Fig. 1.

2. Experimental

2.1. Synthesis

All the described compounds have been synthesized at ISL [6,7]. The symmetrical compounds DNDA5, DNDA7, DMDNH and DNU were prepared by self-condensation reactions of methylnitramine, ethyl nitramine, isopropylnitramine and buthylnitramine, respectively with formaldehyde in an acidic medium according to the reaction schemes given in Fig. 2. The three unsymmetrical dinitramines DNDA6, MDNH and DNH were obtained by a chromatographic separation technique starting respectively from the ternary mixtures DNDA57, DN57 and DN59, respectively. The DNDA57 mixture is obtained by the condensation of methylnitramine with ethylnitramine. The DN57 mixture is obtained by the condensation of methylnitramine. The DN57 mixture is obtained by the condensation of methylnitramine with ethylnitramine with isopropylnitramine. The DN59 mixture is obtained by the condensation of methylnitramine with isopropylnitramine. The DN59 mixture is obtained by the condensation of methylnitramine with formaldehyde in an acidic medium. The synthetic pathways to these ternary mixtures are given in Fig. 3.

For the crystal structure analysis, each compound has been crystallised from ethanol in order to obtain a purity near to 100% (verified by HPLC).

2.2. Thermal properties

Table 1 resumes the principal thermal parameters measured of these seven dinitramine compounds [6]. The obtained values are characteristic for plasticiser compounds. We have in fact compounds with relative low melting points. In the case of the compounds DNDA6 and DNH, the melting points are very low and near the room temperature. In addition, their glass

39



DN59 mixture

Fig. 3. Synthesis of ternary mixtures of dinitramines.

transition temperatures of about -50 °C are also very low.

Studies made by ISL in order to explain the working mechanism of the DNDA57 plasticiser, were based on the determination of the binary and ternary phase diagrammes [8] and the measurement of the combustion in a closed vessel [9]. They revealed the existence of particular interactions between the molecules DNDA5 and DNDA6 and between

DNDA5 and MDNH. Thus, the occurrence of amorphous mixtures over very large composition ranges extending from 30 to 70 mol% of one component has been shown. The stability in dependence of time of such mixtures was also shown. 'Amorphous mixtures' means that in this case no melting or crystallization signal was detected, and this in a temperature range from -50 °C (corresponding to the glass transition temperature) to +100 °C.

	D. Spitzer et al.	/ Journal of	f Molecular	Structure	644	2003) 37-48
--	-------------------	--------------	-------------	-----------	-----	------	---------

Table 1 Thermal data of dinitramines

Compound	Melting point (°C)	Melting enthalpy (J/g)	Glass transition (°C)
DNDA5	54.4	102.3	-44.4
DNDA6	31.6	108.2	- 58.3
DNDA7	75	163.9	-10.1
MDNH	61.5	106.3	No
DMDNH	85.1	127	No
DNH	36	110	-57.6
DNU	72	125	No

The origin of these interactions is actually studied using the modulated DSC technique. Another way for a better understanding of the crystallisation process of these mixtures is to examine the intermolecular interactions. Work concerning these aspects is actually in progress, but remains confidential.

2.3. X-ray structure analysis

The selected crystals have been mounted on a Nonius Kappa-CCD area detector diffractometer (Mo K α , $\lambda = 0.71073$ Å). The conditions of data collection (Denzo software [10,11]) and structure refinements are gathered in Tables 2 and 3. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SIR97 [12]) and refined against F^2 using the SHELXL97 software [13]. No absorption correction was carried out. All non-hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97.

The ORTEP plots [14] of the molecular structure are drawn on Figs. 4 and 5. Selected geometric parameters for the seven molecules are reported in Table 4.

For all the studied compounds, no classical hydrogen bonds have been detected. However, it is worth to notice that only the compound DNDA5 has two unique molecules in the asymmetric unit.

Crystallographic data (excluding structure factors) for these seven structures have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC 186129 (DNDA7), 186130 (DNDA6), 186131 (DNDA5), 186132 (DNU), 186133 (DNH), 186134 (MDNH) & 186326 (DMDNH). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Discussion

The discussion is focused on to the thermal parameters (melting temperature, melting enthalpy) of the different methylenedinitramines, the bonding length and the angles for each structure.

3.1. Evolution of the thermal parameters

The melting is discussed here because it is an indication of the crystal cohesion. In Table 1, we mentioned the melting point of the methylenedinitramines. This evolution is shown once again in Fig. 6. It is known that the melting temperature increases with increasing molecule weight. We noticed that there are some exceptions to this rule. These exceptions are the unsymmetrical linear dinitramines labelled DND6, DNH, and probably MDNH. This characteristic is particularly visible in the case of the dinitramines DNDA6 and DNH which have low melting temperatures. It can be explained by the fact that in the case of these structures (DNDA6, DNH, MDNH), there are very few hydrogen bonds leading to a very low crystal cohesion. So, for DNDA6 we did not detect any H-bond in the elementary cell, whereas in the case of DNH and MDNH the H-type bonds are rather weak.

Zeman et al. [15] studied the thermal parameters of several other methylenenitramines including the DNDA5 molecule. He proposed two relations predicting respectively the melting temperature (Mp_{NA}) and the melting enthalpy (ΔH_{NA}) of the methylenenitramines derived both respectively from the melting temperature (Mp_{HMP}) and the melting enthalpy (ΔH_{HMP}) of the corresponding aliphatic structural analogues (i.e. homomorphs). He measured the parameters using DSC by applying a heating rate of 20 °C/min. He found the following relations for linear methylenenitramines:

41

Table 2	
Crystal data and details of the structure determination for DMDNH, MDNH, DNH and DNU (all cryst	tals are colourless)

Crystal data Di	PMDNH	MDNH	DNH	DNU	
Formula C_7 Formula weight (g mol ⁻¹) 22	² ₇ H ₁₆ N ₄ O ₄ 20 24	C ₅ H ₁₂ N ₄ O ₄ 192 19	C ₅ H ₁₂ N ₄ O ₄ 192 19	C ₉ H ₂₀ N ₄ O ₄ 248 29	
Crystal system M	Ionoclinic	Orthorhombic	Monoclinic	Monoclinic	
Space group P2	2 ₁ (No. 4)	$Pna2_1$ (No. 33)	$P_{2_1/c}$ (No. 14)	C_2/c (No. 15)	L
$a(\text{\AA})$ 7.5	.898(5)	13.244(5)	5.985(5)	26.817(5)	2.5
$b(\mathbf{A})$ 6.	.167(5)	9.470(5)	15.126(5)	9.413(5)	pit
c (Å) 10	0.933(5)	7.144(5)	10.521(5)	11.155(5)	zer
α (°) 90	0	90	90	90	et
β (°) 97	7.18(1)	90	108.845(5)	108.155(5)	al.
γ (°) 90	0	90	90	90	7
$V(\text{\AA}^3)$ 52	28.3(6)	896.0(9)	901.4(9)	2675.7(19)	nnc
Z 2		4	4	8	nal
Density (obs) $(g \text{ cm}^{-3})$ 1.	.323	1.396	_	_	of
Density (calc) $(g \text{ cm}^{-3})$ 1.	.384	1.425	1.416	1.233	Mo
μ (Mo K α) (mm ⁻¹) 0.	.113	0.122	0.121	0.097	lec
F(000) 23	36	408	408	1072	ula
Crystal size (mm) 0.4	$.08 \times 0.10 \times 0.13$	$0.09 \times 0.09 \times 0.11$	$0.10 \times 0.08 \times 0.12$	$0.15 \times 0.06 \times 0.09$	r Sti
Data collection					ruch
Temperature (K) 18	83	183	183	183	лre
Radiation (Å) M	10 Kα – 0.71069	Μο Κα – 0.71069	Μο Κα – 0.71069	Μο Κα – 0.71069	64
θ Min–Max (°) 2.0	.6, 25.0	2.6, 25.0	2.5, 27.4	2.3, 27.5	4
Dataset $(h; k; l)$ –	-7/9; -6/7; -12/11	-13/17; -12/10; -8/9	-7/5; -18/19; -10/13	- 34/33; 0/12; 0/14	200
Tot., Uniq. Data, $R(int)$ 40	060, 1777, 0.027	6161, 1952, 0.036	6517, 2045, 0.040	2947, 2946, 0.034	3)
Observed data $[I > 2\sigma(I)]$ 16	632	1568	1353	1875	37-4
Refinement					18
N reflections, N parameters 17	777, 136	1952, 118	2045, 118	2946, 154	
R, wR_2, Goof 0.0	.0357, 0.0933, 1.10	0.0395, 0.0924, 1.03	0.0555, 0.1671, 1.04	0.0539, 0.1628, 0.94	
$P = (Fo^2 + 2Fc^2)/3 \qquad w$	$\sigma = 1/[\sigma^2(\text{Fo}^2) + (0.0464P)^2 + 0.0392P]$	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0503P)^2]$	$w = 1/[\sigma^{2}(\text{Fo}^{2}) + (0.0917P)^{2} + 0.1179P]$	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0846P)^2]$	
Max. and Av. shift/error 0.0	.01, 0.00	0.01, 0.00	0.00, 0.00	0.00, 0.00	
Flack x –	-0.20(14)	0.90(12)	_	_	
Min., Max. Resd. Dens. $(e/Å^3)$ –	-0.29, 0.22	-0.31, 0.19	-0.29, 0.34	-0.23, 0.23	

 Table 3

 Crystal data and details of the structure determination for DNDA5, DNDA6 and DNDA7 (all crystals are colourless)

Crystal data	DNDA5	DNDA6	DNDA7	
Formula	$C_3H_8N_4O_4$	$C_4H_{10}N_4O_4$	$C_5H_{12}N_4O_4$	
Formula weight $(g \text{ mol}^{-1})$	164.13	178.16	192.19	
Crystal system	Orthorhombic	Monoclinic	Monoclinic	
Space group	<i>Fdd</i> 2 (No. 43)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	D.
a (Å)	20.815(5)	8.076(5)	8.531(5)	Spi
b (Å)	43.427(5)	10.827(5)	5.774(5)	tze
<i>c</i> (Å)	6.236(5)	9.528(5)	18.500(5)	r ei
$\alpha(^{\circ})$	90	90	90	al
β (°)	90	101.27(1)	100.821(5)	~
γ (°)	90	90	90	lou
$V(\text{\AA}^3)$	5637(5)	817.0(8)	895.1(10)	rna
Z	32	4	4	ıl o
Density (obs) $(g \text{ cm}^{-3})$	1.498	1.419	1.384	fМ
Density (calc) $(g \text{ cm}^{-3})$	1.547	1.448	1.426	lole
μ (Mo K α) (mm ⁻¹)	0.141	0.128	0.122	cui
<i>F</i> (000)	2752	376	408	ar
Crystal size [mm]	$0.11 \times 0.11 \times 0.12$	$0.09 \times 0.09 \times 0.11$	$0.10 \times 0.08 \times 0.12$	Stru
Data collection				ctur
Temperature (K)	183	183	183	<i>e</i> 6
Radiation (Å)	Μο Κα – 0.71069	Μο Κα – 0.71069	Μο Κα – 0.71069	4
θ Min–Max (°)	1.9, 27.5	2.9, 27.5	2.2, 40.3	(20
Dataset $[h; k; l]$	-26/20; -56/52; -8/7	- 10:10; 0:13; 0:12	-15/14; -8/10; -22/33	03
Tot., Uniq. Data, R(int)	9714, 3123, 0.038	1846, 1845, 0.020	10250, 5559, 0.045	3
Observed data $[I > 2\sigma(I)]$	2207	1416	2592	-48
Refinement				
Nreflections, Nparameters	3123, 199	1845, 110	5559, 118	
R, wR_2, Goof	0.0553, 0.1560, 1.03	0.0499, 0.1481, 1.02	0.0564, 0.1664, 1.00	
$P = (Fo^2 + 2Fc^2)/3$	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0957P)^2]$	$w = 1/[\sigma^{2}(\text{Fo}^{2}) + (0.0809P)^{2} + 0.1530P]$	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0620P)^2 + 0.0302P2]$	
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00	0.00, 0.00	
Flack x	0.10(19)	-	-	
Min, Max. Resd. Dens. (e/Å ³)	-0.31, 0.30	-0.30, 0.44	-0.46, 0.31	

D. Spitzer et al. / Journal of Molecular Structure 644 (2003) 37-48



Fig. 4. Molecular structure of DMDNH (a), MDNH (b), DNH (c) and DNU (d); ORTEP plot with atom numbering. Thermal ellipsoids are drawn at 50% probability level.







Fig. 5. Molecular structure of DNDA5 (a), DNDA6 (b) and DNDA7 (c); ORTEP plot with atom numbering. Thermal ellipsoids are drawn at 50% probability level.

45

Selected geo	metric para	meters $(X-Y)$	Å) and $Y-X$	√-Z (°)). Stand	lard deviati	on is given in	parentheses						
DMDNH		HNUM		DNH		DNU		DNDA5		DNDA6		DNDA7	
C1 – C6	1.518(3)	C1-N3	1.453(2)	C1-N2	1.449(3)	C6-C7	1.513(3)	N1-04	1.233(3)	C4-C1	1.506(3)	C3-C2	1.520(2)
C1-C7	1.513(3)	C1-N1	1.456(2)	N2-N1	1.351(2)	C6-C2	1.508(3)	N1-N5	1.341(4)	C1-N1	1.464(2)	C2-N1	1.465(2)
C1-N4	1.493(2)	N1-C3	1.456(2)	N2-C2	1.458(3)	C2-C3	1.519(3)	N5-C5	1.460(4)	N1-C2	1.453(2)	N1-C1	1.457(2)
N4-C2	1.462(2)	N1-N4	1.347(2)	C2-N3	1.443(3)	C3-N1	1.455(2)	N5-C2	1.452(4)	C2-N3	1.447(2)	N1-N3	1.351(2)
N4-N1	1.355(2)	N4-02	1.234(2)	N1-01	1.228(2)	N1-C1	1.443(2)	C2-N8	1.436(4)	N1-N2	1.340(2)	N3-01	1.233(1)
N1-03	1.225(2)			N3-N4	1.352(3)	N1-N4	1.354(2)			N2-01	1.235(2)	C3-C2-N1	113.5(1)
		N3-C1-N1	113.1(1)	N3-C3	1.470(3)	N4-02	1.228(2)	N1-N5-C5	117.3(2)			C2-N1-N3	118.3(1)
C3-N2-C2	125.8(2)	C1-N1-C3	123.2(1)	C3-C4	1.497(3)			C2-N5-C5	123.4(2)	C4-C1-N1	113.2(2)	C2-N1-C1	120.5(1)
N2-C2-N4	113.4(1)	C1 - N1 - N4	116.2(2)	C4-C5	1.514(3)	C1-N1-C3	121.1(2)	N8-C2-N5	114.0(2)	C1-N1-N2	119.2(2)	N1-C1-N2	113.5(1)
		N4-N1-C3)	117.6(1)			N1-C3-C2	113.9(2)			C2-N1-N2	116.8(1)		
				C1-N2-C2	121.6(2)	C3-C2-C6	111.7(2)			N1-C2-N3	114.1(1)		
				N3-C2-N2	113.6(2)	C2-C6-C7	112.9(2)			C3-N3-N4	117.7(2)		
				C3-N3-C2	122.2(2)								
				C4-C3-N3	114.4(2)								
				C5-C4-C3	111.0(2)								

D. Spitzer et al. / Journal of Molecular Structure 644 (2003) 37-48

Melting enthalpy (in kJ mol⁻¹):

 $\Delta H_{\rm NA} = 2.5071 \Delta H_{\rm HMP} - 3.3197,$

correlation: 0.9980

Melting temperature (onset) (in °C):

 $lnMp_{NA} = 0.7248 lnMp_{HMP} + 2.2408,$

correlation: 0.9490

These equations were used to verify the accuracy of the so calculated thermal parameters with the experimental values of the melting enthalpy and the melting temperature of the DNDA5, DNDA6, DNDA7, MDNH, DMDNH, DNH, and DNU methylenedinitramines.

Table 5 shows the result of this comparison where in the case of the symmetrical methylenedinitramines (DNDA5, DNDA7) the accuracy of the melting enthalpy is good once the information is obtained. However, the relation established by Zeman is not valid for unsymmetrical methylenedinitramines (DNDA6, DNH).

Concerning the melting temperature, the relationship given by Zeman cannot be used for the compounds studied in the present work, excepted for DNDA5.

3.2. Evolution of the bonding length

Analysing the two middle CN length, it is first interesting to note that the symmetrical DNDA5 molecule has two central C-N covalent bonds with two different length (1.436 and 1.452 Å). In the case of the two unsymmetrical molecules (DNDA6, DNH), these two length are different as expected (DNDA6: 1.447 and 1.453 Å; DNH: 1.458 and 1.443 Å). For the unsymmetrical MDNH molecule, this difference is not revealed, as the difference between the two lengths is the measuring accuracy of the experiment.

The NC bond outside the NCN dinitraza bridge has about the same value (range: 1.449–1.465 Å), except for the DMDNH molecule for which it is rather long (1.493 Å).

The NO bond length, and the NN bond length are about the same for all the molecules $(1.225-1.235 \text{ \AA})$ and (1.340–1.355 Å), respectively.

Table 4





Fig. 6. The methylenedinitramine melting temperatures.

3.3. Evolution of the bonding angles

This parameter was studied on different locations in each molecule and result in following remarks:

The dinitraza bridge angle (central bridge of the molecule) NCN exhibits the highest value for the molecules DNDA5 and DNDA6 (respectively 114 and 114.1°) whereas in the case of the other molecules

this angle is a little smaller (MDNH: 113.1°; DMDNH: 113.4°; DNDA7: 113.5°; DNH: 113.6°). This information is important because it shows that in the case of DNDA5 and DNDA6, the dinitraza bridge is more open so it might induce a higher hindrance effect.

47

The CNC angles are rather constant and the evolution does not reveal any significant aspect

Table	5
-------	---

Comparison between calculated and measured melting temperatures and enthalpies of the methylene dinitramines

Component	Measured melting enthalpy (J/g)	Calculated melting	Measured melting point	Calculated melting	Homomorph		
		chulaipy (J/g)	(onset) (°C)	point (C)	Name	Melting enthalpy (J/g)	Melting point (°C)
DNDA5	102.3	108.2	54.4	69.9	<i>n</i> -pentane	72.15	- 130.15
DNDA6	108.2	164.4	31.6	128.9	<i>n</i> -hexane	86.18	- 95.5
DNDA7	163.9	166.7	75	137.1	<i>n</i> -heptane	100.2	-90.15
MDNH	106.3		61.5	90.3	2-methyl- <i>n</i> -hexane	100.2	-118.3
DMDNH	127		85.1	116.1	2,6-dimethyl-n-heptane	128.26	-102.9
DNH	110	166.7	36	137.1	<i>n</i> -heptane	86.18	-90.15
DNU	125		72	237.5	<i>n</i> -undecane	156.31	-25.6

going from 121.1° for DNU to 125.8° for DMDNH. The CNN angles are rather constant to $(116.2-119.2^{\circ})$.

4. Concluding remarks

The most interesting result from this present study is the determination of rather unexpected crystal structures in the case of the unsymmetrical methylenedinitramines (DNDA5, DNDA6 and DNH). This is especially the case of the DNDA5 molecule which has two unique molecules in the asymmetric unit. For all the studied compounds, no classical hydrogen bonds have been detected, in some case no hydrogen bonds have been detected, which probably could be the explanation of the existence of amorphous mixtures over very large composition ranges for DNDA5/DNDA6 and DNDA5/MDNH, in a temperature range from -50 °C (corresponding to the glass transition temperature) to +100 °C, due to the presence of particular intermolecular interactions and very low crystallisation kinetics. The nature of these interactions will be examined. Considering the thermal results and the determined crystal structures, molecular simulation to evaluate the interaction between the plasticiser and the nitrocellulose in the solid state is started. These calculations are performed on the base of a collaboration between ISL and the GMO group from IPCMS laboratory (ULP, Strasbourg I).

References

- J. Quinchon, J. Tranchant, Les nitrocelluloses et autres matières premières de base des poudres et propergols, Lavoisier, Tec et Doc, 1984.
- [2] T. Urbanski, Nitrate esters, Chemistry and Technology of Explosives 4 (1984) 295.
- [3] T. Urbanski, Production of nitroglycerine, Chemistry and Technology of Explosives 2 (1984) 62.
- [4] W. Langlotz, D. Diehl, I.C.T. Mueller, Propellant power for barrelled weapons, PCT, WO 98/34891, 1998.
- [5] V.A. Tartakovskii, A.S. Ermakov, V.A. Koroban, Preparation of *N*,*N*[']-dialkyl methylenebisnitramines, Russian Chemical Bulletin 42 (1993) 11.
- [6] D. Spitzer, H. Ritter, S. Braun, Etude du comportement thermique de dinitramines linéaires à propriétés plastifiantes, Rapport ISL, S-R111/2001.
- [7] D. Spitzer, B. Wanders, Synthèse, caractérisation thermique et étude des mélanges de nouvelles méthylène-dinitramines linéaires à propriétés plastifiantes, Rapport ISL, S-R124/2001.
- [8] D. Spitzer, M.R. Schäfer, F. Ciszek, A. Carriere, Diagrammes binaires et ternaire du mélange plastifiant DNDA57, Rapport ISL, 2002.
- [9] D. Spitzer, B. Baschung, M.R. Schäfer, M. Scharf, F. Ciszek, Etude du mélange plastifiant DNDA57 utilisé dans les poudres propulsives TU, SPU 604/2002.
- [10] KappaCCD Operation Manual, Nonius B.V., Delft, The Nederlands, 1997.
- [11] Z. Otwinowski, W. Minor, Methods in Enzymology 276 (1997) 307.
- [12] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, SIR J. Appl. Cryst. 22 (1989) 389.
- [13] G.M. Sheldrick, SHELXL97. Program for the refinement of crystal structures, University of Gottingen, Germany, 1997.
- [14] A.L. Spek, PLATON98, Utrecht University, The Netherland, 1998.
- [15] S. Zeman, Thermochimica Acta, 302, 1997,11-16.