

# Experimental and Theoretical Study on the Structure of Nitramide H<sub>2</sub>NNO<sub>2</sub>

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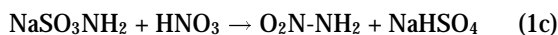
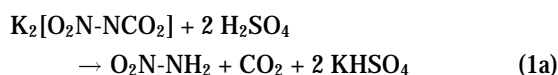
Computational Chemistry, Nitramide, Intermolecular Hydrogen Bond

Nitramide was investigated by multinuclear NMR spectroscopy, X-ray-diffraction and computational methods. The crystal structure analysis at various temperatures reveals a planar conformation of the molecule with a N-N bond length corresponding to a bond order between one and two. Hydrogen bonds connect the nitramide molecules side-on and end-on. This leads to the formation of layers in the crystal. Calculations were performed to explain the shorter N-N bond length in the crystal compared to the gas phase. The nitramide trimer is used as a model.

## Introduction

Nitro-compounds are of special interest because of their high energy content [1, 2]. The properties of such molecules were studied both theoretically and experimentally. Nitramides with aliphatic substituents are widely used high energetic materials, *e. g.* RDX [3], HMX [3] and CL-20 [4].

Nitramide H<sub>2</sub>N-NO<sub>2</sub> is a structural isomer of hyponitrous acid and the inorganic parent compound of the nitramides. Nitramide was first synthesised by Thiele and Lachman by hydrolysis of potassium nitrocarbamate [eq. (1a)] [5]. It was also formed by hydrolysis of nitrocarbamic acid [eq. (1b)] [6], from the reaction of NaSO<sub>3</sub>NH<sub>2</sub> with concentrated HNO<sub>3</sub> [eq. (1c)] [7] and from the reaction of N<sub>2</sub>O<sub>5</sub> with two equivalents of ammonia [eq. (1d)] [8].



Nitramide is a colorless solid with a melting range of 72 - 75 °C [9]. It has been characterized by vibrational spectroscopy in the solid state [10], in solution [10], in Ar-matrix [11] and in the gas phase [12] as well as by UV spectroscopy [13]. <sup>1</sup>H and <sup>14</sup>N NMR spectra were also recorded [14]. The gas phase structure was investigated by vibrational

spectroscopy [12] and electron diffraction [15]. X-ray structure determination was also reported with large standard deviations where the position of the hydrogen atoms could not be located precisely [16]. The bonding situation was studied with *ab initio* calculations and qualitative valence bond considerations by our group [1].

More precise data including the positions of the hydrogen atoms was obtained by our group from a low temperature X-ray structure determination [17]. To prove the apparent planarity of the molecule measurements were now performed at different temperatures. Theoretical calculations on a nitramide trimer were made to examine the influence of hydrogen bonding on the N-N bond length.

## Experimental Section

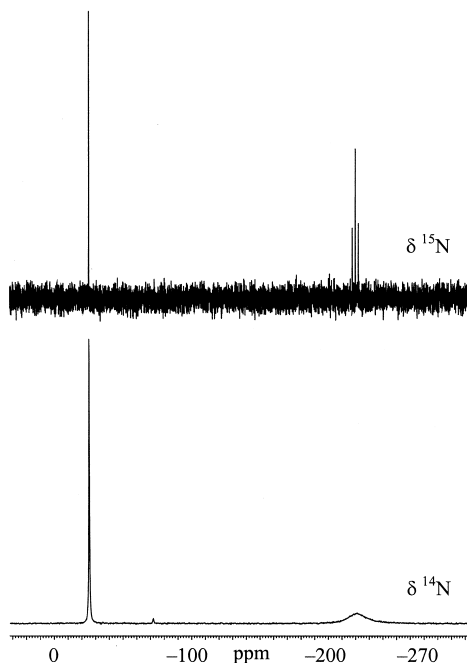
The NMR spectra were recorded in THF-D<sub>8</sub> solution using a JEOL Eclipse 400 NMR spectrometer with nitromethane as the external reference for <sup>14</sup>N / <sup>15</sup>N and TMS as the external reference for <sup>1</sup>H. The melting point was obtained on a Büchi B-540 apparatus and is uncorrected.

Table 1. Reported NMR data for nitramide.

Method	H <sub>2</sub> N-NO <sub>2</sub>	H <sub>2</sub> N-NO <sub>2</sub>
<sup>1</sup> H NMR (DMSO-D <sub>6</sub> ) [14 a]	δ = 11.5	
<sup>1</sup> H NMR (CH <sub>3</sub> CN) [14 b]	δ = 9.2	
<sup>1</sup> H NMR (Et <sub>2</sub> O) [14 b]	δ = 9.5	
<sup>1</sup> H NMR (CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> ) [14 b]	δ = 9.5	
<sup>14</sup> N NMR { <sup>1</sup> H} [14 b]	-	δ = 222

Method	$\text{H}_2\text{N}-\text{NO}_2$	$\text{H}_2\text{N}-\text{NO}_2$	$\text{H}_2\text{N}-\text{NO}_2$	$\Delta\nu_{1/2}(\text{NH}_2)$	$^1J_{\text{NH}}$
$^{14}\text{N}$ NMR (THF- $\text{D}_8$ )		-221	-26	400 Hz	
$^{15}\text{N}$ NMR (THF- $\text{D}_8$ )		-220.3	-25.5		89.7 Hz
$^1\text{H}$ NMR (THF- $\text{D}_8$ )	10.1				

Table 2. NMR data for nitramide.

Fig. 1.  $^{14}\text{N}$  and  $^{15}\text{N}$  NMR spectra of nitramide in THF- $\text{D}_8$ .

Nitramide was prepared by the reaction of  $\text{NaSO}_3\text{NH}_2$  with concentrated  $\text{HNO}_3$  [7]. The product was purified by sublimation under reduced pressure. The colorless crystals have a melting range of 81 - 84 °C.  $^{15}\text{N}$ -NMR: (THF- $\text{D}_8$ )  $\delta = -25.5$  (s,  $\text{H}_2\text{NNO}_2$ ),  $-220.3$  (t,  $\text{H}_2\text{NNO}_2$ ,  $^1J_{\text{NH}} = 90$  Hz).  $^{14}\text{N}$ -NMR: (THF- $\text{D}_8$ )  $\delta = -26$  ( $\text{H}_2\text{NNO}_2$ ),  $-221$  ( $\text{H}_2\text{NNO}_2$ ,  $\Delta\nu_{1/2} = 400$  Hz).  $^1\text{H}$  NMR: (THF- $\text{D}_8$ )  $\delta = 10.1$  ( $\text{H}_2\text{NNO}_2$ ).

Crystals suitable for an X-ray crystallographic study were grown by vacuum sublimation at room temperature. The data sets were collected on a NONIUS KAPPA CCD diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation at various temperatures (*a*: 100 K, *b*: 140 K, *c*: 170 K, *d*: 230 K, *e*: 260 K). The structure was solved by direct methods with the SHELXS-97 program [18] and refined with SHELXL-97 [19]. All hydrogen atoms were refined without constraints.

The semiempirical PM3 computation was carried out employing a VSTO-3G basis set [20]. The ab initio HF [21] and DFT hybrid B3PW91 [22] and MPW1PW91 [23] computations were carried out employing a polar-

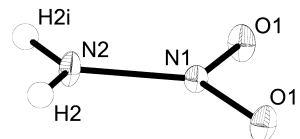


Fig. 2. ORTEP-Plot of nitramide (*b*) (thermal ellipsoids represented by 25% probability); selected bond lengths [Å] and angles [°]: N(1)-N(2) 1.321(2), N(1)-O(1) 1.237(1), N(2)-H(2) 0.86(2); O(1)-N(1)-O(1i) 123.0(1), O(1)-N(1)-N(2) 118.51(6), N(1)-N(2)-H(2) 117(1); Symmetry code for equivalent atoms: *i*:  $-x, y, -z + 1/2$ .

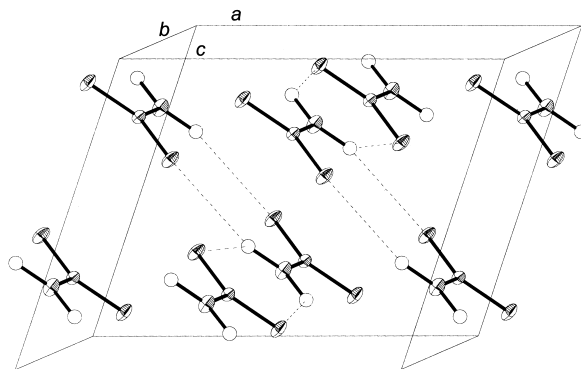


Fig. 3. Intermolecular hydrogen bonds in nitramide (*b*) (thermal ellipsoids represented by 25% probability); hydrogen bonds: distances [Å] ( $\text{NH}\cdots\text{O}$  angle [°]): N(2)-H(2) $\cdots$ O(1) 0.86(2), 2.25(2), 3.071(1), 161(1); 0.86(2), 2.47(2), 3.032(1), 124(1).

ized 6-31G basis set [24] with an augmented diffuse function.

## Results and Discussion

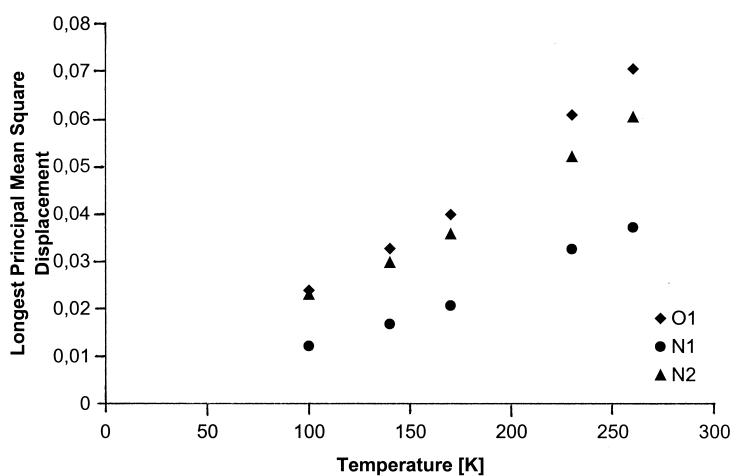
### NMR

The NMR shifts of nitramide given in the literature in reference to several standards (Table 1) [14 a, b] are not mutually consistent.

To obtain consistent NMR shifts of nitramide the  $^1\text{H}$ ,  $^{14}\text{N}$  and  $^{15}\text{N}$  spectra of the compound were recorded in THF- $\text{D}_8$  (Table 2). The  $^{14}\text{N}$  NMR spectrum (Fig. 1) shows a sharp signal at  $\delta = -26$  which

Table 3. Crystallographic data, details of data collection and structural refinement for nitramide.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Compound	– Nitramide –				
Empirical formula	– H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> –				
Formula weight [gmol <sup>-1</sup> ]	– 62.03 –				
Crystal System	– monoclinic –				
Space Group	– C2/c –				
<i>Z</i>	– 4 –				
<i>F</i> (000) [e]	– 128 –				
<i>hkl</i> Range	– 10 ≤ <i>h</i> ≤ 10, –6 ≤ <i>k</i> ≤ 5, –8 ≤ <i>l</i> ≤ 8 –				
Temperature [K]	100(2)	140(2)	170(2)	230(2)	260(2)
Unit cell dimensions: <i>a</i> [Å]	7.7392(5)	7.7648(4)	7.7888(5)	7.8393(5)	7.8651(5)
<i>b</i> [Å]	4.7383(3)	4.7419(3)	4.7447(3)	4.7523(3)	4.7577(3)
<i>c</i> [Å]	6.4468(4)	6.4823(4)	6.5122(4)	6.5816(4)	6.6196(4)
<i>β</i> [Å]	111.192(3)	111.389(3)	111.540(3)	111.904(3)	112.086(3)
Volume <i>V</i> [Å <sup>3</sup> ]	220.42(2)	222.24(2)	223.85(2)	227.50(2)	229.53(2)
Density (calcd) [gcm <sup>-3</sup> ]	1.8692(2)	1.8539(2)	1.8406(2)	1.8110(2)	1.7950(2)
Absorp. coeff. [mm <sup>-1</sup> ]	0.191	0.190	0.188	0.185	0.184
2 $\theta$ Range [°]	54.76	54.92	54.84	55.02	54.96
Reflections collected	1821	1832	1857	1900	1913
Independent reflections	246	250	254	258	261
Observed reflections	241	241	244	242	242
Max. and min. transmission	0.9842 and 0.9495	0.9844 and 0.9499	0.9845 and 0.9502	0.9846 and 0.9500	0.9847 and 0.9509
Data/restraints/parameters	246/0/24	250/0/24	254/0/24	258/0/24	261/0/24
Goodness-of-fit <i>F</i> <sup>2</sup>	1.116	1.123	1.118	1.139	1.139
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0276, 0.0707	0.0287, 0.0696	0.0285, 0.0723	0.0341, 0.0846	0.0330, 0.0801
Largest diff. peak and hole [e/Å <sup>3</sup> ]	0.151/–0.302	0.149/–0.303	0.132/–0.268	0.161/–0.272	0.110/–0.202

Fig. 4. Relationship between longest principal mean square atomic displacement  $U_{\perp}$  and measurement temperature.

corresponds to the nitro group [25] and a broad signal at  $\delta = -221$  ( $\Delta\nu_{1/2} = 400$  Hz) which is assigned to the amide group [14 a]. The <sup>15</sup>N NMR spectrum (Fig. 1) shows signals for the nitro and amide group with chemical shifts of  $\delta = -25.5$  and  $\delta = -220.3$ , respectively. The signal of the nitro group is a singlet and the signal of the amide group is a triplet with

a coupling constant of  $^1J_{\text{NH}} = 89.7$  Hz in a typical range for amides [25]. The nitramide protons have a signal at  $\delta = 10.1$  in the <sup>1</sup>H NMR spectrum [14 a, b].

#### Crystal structure

Single crystals suitable for X-ray diffraction were obtained by vacuum sublimation at room tempera-

Table 4. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for nitramide.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor and  $U_{\perp}$  as the longest principal mean square atomic displacement.

<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{\perp}$
<i>Atom O1:</i>				
<i>a</i> 1398(1)	<i>a</i> 5353(2)	<i>a</i> 3740(1)	<i>a</i> 14.7(3)	<i>a</i> 0.0239
<i>b</i> 1395(1)	<i>b</i> 5349(2)	<i>b</i> 3735(1)	<i>b</i> 19.6(3)	<i>b</i> 0.0327
<i>c</i> 1393(1)	<i>c</i> 5344(2)	<i>c</i> 3730(1)	<i>c</i> 23.7(3)	<i>c</i> 0.0399
<i>d</i> 1387(1)	<i>d</i> 5335(2)	<i>d</i> 3717(2)	<i>d</i> 34.7(4)	<i>d</i> 0.0609
<i>e</i> 1384(1)	<i>e</i> 5330(2)	<i>e</i> 3709(2)	<i>e</i> 40.4(4)	<i>e</i> 0.0706
<i>Atom N1:</i>				
<i>a</i> 0000	<i>a</i> 4105(3)	<i>a</i> 2500	<i>a</i> 10.5(3)	<i>a</i> 0.0122
<i>b</i> 0000	<i>b</i> 4103(3)	<i>b</i> 2500	<i>b</i> 13.5(3)	<i>b</i> 0.0168
<i>c</i> 0000	<i>c</i> 4103(2)	<i>c</i> 2500	<i>c</i> 16.1(3)	<i>c</i> 0.0207
<i>d</i> 0000	<i>d</i> 4098(3)	<i>d</i> 2500	<i>d</i> 23.2(4)	<i>d</i> 0.0326
<i>e</i> 0000	<i>e</i> 4096(3)	<i>e</i> 2500	<i>e</i> 26.8(4)	<i>e</i> 0.0372
<i>Atom N2:</i>				
<i>a</i> 0000	<i>a</i> 1316(3)	<i>a</i> 2500	<i>a</i> 14.0(3)	<i>a</i> 0.0231
<i>b</i> 0000	<i>b</i> 1317(3)	<i>b</i> 2500	<i>b</i> 18.2(3)	<i>b</i> 0.0298
<i>c</i> 0000	<i>c</i> 1319(3)	<i>c</i> 2500	<i>c</i> 22.0(4)	<i>c</i> 0.0358
<i>d</i> 0000	<i>d</i> 1325(3)	<i>d</i> 2500	<i>d</i> 31.4(4)	<i>d</i> 0.0521
<i>e</i> 0000	<i>e</i> 1325(3)	<i>e</i> 2500	<i>e</i> 36.4(4)	<i>e</i> 0.0605

Table 5. Bond lengths [ $\text{\AA}$ ] and angles [ $^{\circ}$ ] for nitramide.

Atoms	Bond length	Atoms	Angle
O(1)-N(1)	<i>a</i> 1.239(1)	O(1)-N(1)-O(1i)	<i>a</i> 123.0(1)
	<i>b</i> 1.237(1)		<i>b</i> 123.0(1)
	<i>c</i> 1.236(1)		<i>c</i> 123.1(1)
	<i>d</i> 1.233(1)		<i>d</i> 123.1(1)
	<i>e</i> 1.231(1)		<i>e</i> 123.0(1)
N(1)-N(2)	<i>a</i> 1.322(2)	O(1)-N(1)-N(2)	<i>a</i> 118.52(6)
	<i>b</i> 1.321(2)		<i>b</i> 118.51(6)
	<i>c</i> 1.321(2)		<i>c</i> 118.46(6)
	<i>d</i> 1.318(2)		<i>d</i> 118.48(6)
	<i>e</i> 1.318(2)		<i>e</i> 118.50(6)
N(2)-H(2)	<i>a</i> 0.86(2)	N(1)-N(2)-H(2)	<i>a</i> 116(1)
	<i>b</i> 0.86(2)		<i>b</i> 117(1)
	<i>c</i> 0.86(2)		<i>c</i> 116(1)
	<i>d</i> 0.85(2)		<i>d</i> 116(1)
	<i>e</i> 0.85(2)		<i>e</i> 116(1)

Symmetry code: i:  $-x, y, 0.5 - z$ .

ture. The melting range was found to be between 81 - 84  $^{\circ}\text{C}$  in contrast to the reported melting range of 72 - 75  $^{\circ}\text{C}$  [9].

The structure of nitramide was determined at different temperatures between 260 and 100 K. The bond lengths and angles are given in Table 5. They do not vary noticeably with temperature. The N-N

Table 6. Hydrogen bonding parameters ( $\text{\AA}$ , deg).

N(2)-H(2)	H(2)···O(1i)	N(2)···O(1i)	N(2)-H(2)···O(1i)
<i>side-on:</i>			
<i>a</i> 0.86(2)	<i>a</i> 2.24(2)	<i>a</i> 3.064(1)	<i>a</i> 162(1)
<i>b</i> 0.86(2)	<i>b</i> 2.25(2)	<i>b</i> 3.071(1)	<i>b</i> 161(1)
<i>c</i> 0.86(2)	<i>c</i> 2.25(2)	<i>c</i> 3.079(1)	<i>c</i> 162(1)
<i>d</i> 0.85(2)	<i>d</i> 2.28(2)	<i>d</i> 3.095(1)	<i>d</i> 162(2)
<i>e</i> 0.85(2)	<i>e</i> 2.29(2)	<i>e</i> 3.105(1)	<i>e</i> 161(2)
<i>end-on:</i>			
<i>a</i> 0.86(2)	<i>a</i> 2.47(2)	<i>a</i> 3.028(1)	<i>a</i> 124(1)
<i>b</i> 0.86(2)	<i>b</i> 2.47(2)	<i>b</i> 3.032(1)	<i>b</i> 124(1)
<i>c</i> 0.86(2)	<i>c</i> 2.48(2)	<i>c</i> 3.036(1)	<i>c</i> 124(1)
<i>d</i> 0.85(2)	<i>d</i> 2.50(2)	<i>d</i> 3.046(2)	<i>d</i> 123(2)
<i>e</i> 0.85(2)	<i>e</i> 2.50(2)	<i>e</i> 3.050(2)	<i>e</i> 124(1)

Symmetry code: i:  $x - 0.5, 0.5 - y, z - 0.5$ ; ii:  $-x, y - 1, 0.5 - z$ .

Table 7. Structural data for nitramide and dimethylnitramide.

	X-ray dif- fraction ( <i>b</i> )	X-ray dif- fraction [16]	Electron dif- fraction [15]
$d(\text{N-N})/\text{\AA}$	1.321(2)	1.40 <sup>#</sup>	1.381 <sup>#</sup>
$d(\text{N-O})/\text{\AA}$	1.237(1)	1.18 <sup>#</sup>	1.232 <sup>#</sup>
$d(\text{N-H})/\text{\AA}$	0.86(2)		
$d(\text{N-C})/\text{\AA}$			
$\angle(\text{HNH})/^{\circ}$			120.9 <sup>#</sup>
$\angle(\text{CNC})/^{\circ}$			
$\angle(\text{ONO})/^{\circ}$	123.0(1)	129 <sup>#</sup>	132.7 <sup>#</sup>
$\angle(\text{ONN})/^{\circ}$	118.51(6)		
$\angle(\text{HNN})/^{\circ}$	117(1)		109.7 <sup>#</sup>
$\angle(\text{CNN})/^{\circ}$			
$\angle(\Sigma \text{N}_{(\text{amide})})/^{\circ}$	360	360	340.3

<sup>#</sup> No standard deviation given.

bond lengths [1.318(2)  $\text{\AA}$  (*f*) to 1.322(2)  $\text{\AA}$  (*a*)] are significantly shorter than in the gas phase (1.381  $\text{\AA}$ ) [15] and also shorter than the reported crystal phase N-N bond length of 1.40  $\text{\AA}$  [16]. The authors of the previously reported crystal structure analysis assumed that nitramide is planar [16]. A previous low temperature measurement (200 K) gave no direct evidence for planarity [17]. The thermal ellipsoid of the NH<sub>2</sub> nitrogen atom has a long major axis perpendicular to the molecular plane, and it was assumed that the molecule is planar [17], but the long axis might have been caused by thermal movement or by a statistical disorder of a non-planar molecule about the symmetry plane (Fig. 2).

Table 8. Calculated bond lengths and angles for [H<sub>2</sub>N-NO<sub>2</sub>]<sub>3</sub>.

	PM3/VSTO-3G		HF/6-31+G(d,p)		B3PW91/6-31+G(d,p)		MPW1PW91/6-31+G(d,p)		Gas phase, electron dif- fraction [15]	Solid phase, X-ray dif- fraction (b)
	H <sub>2</sub> N-NO <sub>2</sub>	[H <sub>2</sub> N-NO <sub>2</sub> ] <sub>3</sub> , central unit	H <sub>2</sub> N-NO <sub>2</sub>	[H <sub>2</sub> N-NO <sub>2</sub> ] <sub>3</sub> , central unit	H <sub>2</sub> N-NO <sub>2</sub>	[H <sub>2</sub> N-NO <sub>2</sub> ] <sub>3</sub> , central unit	H <sub>2</sub> N-NO <sub>2</sub>	[H <sub>2</sub> N-NO <sub>2</sub> ] <sub>3</sub> , central unit	H <sub>2</sub> N-NO <sub>2</sub>	[H <sub>2</sub> N-NO <sub>2</sub> ] <sub>n</sub>
-E/a.u.	-0.008776	-0.009041	259.657127	778.999898	260.956540	782.899526	260.986117	782.991907		
<i>zpe</i>	23.7	74.5	27.1	85.0	24.9	76.8	25.1	77.5		
kcal mol <sup>-1</sup>										
NIMAG	0	0	0	0	0	0	0	0		
d(N-N)/Å	1.430	1.379	1.352	1.315	1.379	1.329	1.373	1.324	1.381 <sup>#</sup>	1.321(2)
d(N-H)/Å	1.000	1.016	0.997	1.000	1.012	1.024	1.010	1.022		0.86(2)
d(N-O)/Å	1.211	1.223	1.192	1.204	1.222	1.236	1.218	1.232	1.232 <sup>#</sup>	1.237(1)
∠(HNH)/°	113.0	114.9	118.1	123.4	117.4	123.9	117.6	124.1	120.9 <sup>#</sup>	
∠(ONO)/°	127.1	123.7	126.7	124.1	127.1	123.3	127.1	123.3	132.7 <sup>#</sup>	123.0(1)
∠(HNN)/°	114.7	115.7	111.3	114.6	111.1	114.8	111.2	114.9	109.7 <sup>#</sup>	117(1)
∠(ONN)/°	116.4	118.1	116.6	117.9	116.4	118.3	116.4	118.4		118.51(6)
∠(SN <sub>(HNH)</sub> )/°	342.4	346.2	340.8	352.6	339.5	353.5	339.9	353.9	340.3	360
∠(SN <sub>(ONO)</sub> )/°	359.9	359.9	360.0	360.0	359.9	360.0	359.9	360.0	360	360

<sup>#</sup> No standard deviation given.

Therefore, the changes of anisotropy and the volume of the N2 thermal ellipsoid with temperature were investigated. In fact the anisotropy remains constant when the temperature decreases from 260 to 100 K, whereas the volume of the ellipsoid decreases. The curves of the longest mean square atomic displacements of O1, N1 and N2 run towards zero with decreasing temperature (Fig. 4). These facts lead to the conclusion that the large displacement has a true thermal character.

The crystal structure shows two types of hydrogen bonding (Fig. 3) between oxygen and hydrogen atoms with N-O distances between 3.028(1) and 3.105(1) Å and O-H distances between 2.24(2) and 2.50(2) Å (Table 6). These values agree with intermolecular hydrogen bonds in 1,3,5-triamino-2,4,6-trinitrobenzene with values between 2.93 and 3.00 Å for the N-O distances and values between 2.24 and 2.40 Å for the O-H distances. The hydrogen bonded nitramide molecules form layers. The molecules are connected end-on and side-on (Fig. 3). Between the layers there are no hydrogen bonds and this explains the easy sublimation.

#### Computational details

The influence of the hydrogen bonds on the planar structure was investigated with quantum chemical calculations. A trimer of side-on connected nitramide molecules was used as a model compound (Fig. 5, Table 8).

The N-N bonds of the central units are shorter than the NN bonds of the external molecules. The calculations on the MPW1PW91 level of theory



Fig. 5. Nitramide trimer calculated at MPW1PW91 level of theory.

give the best agreement with the experimental data. The N-N bond length from electron diffraction in the gas phase is 1.381 Å [15]. The calculated bond length of the external molecules is 1.373 Å, and the N-N bond length of the central unit is shortened to 1.324 Å, in good agreement with the value [1.319(2) Å] determined here by X-ray diffraction. The hydrogen bonds clearly lead to a shorter N-N bond length. The N-O bond length of the central molecule is 1.232 Å, shorter than the length of the external ones and in good agreement with the X-ray diffraction value of 1.233(1) Å. The gas phase structure of nitramide shows that the sum of angles at the NH<sub>2</sub> nitrogen atom is 340.3° [15]. The theoretically calculated sum of angles of 339.9° is in good agreement with the experimental value. For the central unit the sum of angles is larger (353.9°) and thus closer to the value of 360° found by X-ray diffraction. The trimer is favoured by 21 kcal/mol (19 kcal/mol after *zpe* correction). This is an aver-

age amount of 5.3 kcal/mol (4.7 kcal/mol after *zpe* correction) per hydrogen bond, which lowers the energy of the trimer.

### Conclusion

Structural investigations of nitramines in general show a relation between the N-N bond length and the torsion angle [26]. The torsion angles in nitramines with short N-N bond lengths are small.

Nitramide is found to be planar in the crystal phase with an N-N bond length shorter than a NN single bond (1.45 Å in hydrazine [27]). These results are in agreement with the proposed relation. The

calculations show the influence of the hydrogen bonds on the bond lengths, especially the N-N bond length, and the angles, especially the sum of angles at the NH<sub>2</sub> nitrogen atom. The trimer of nitramide molecules is energetically favoured by the hydrogen bonds, and the central unit a conformation closer to planarity.

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