

Occurrence Report

After 2003 Redesign

Firing Sites and HE Lab.

(Name of Facility)

Explosive

(Facility Function)

Los Alamos National Laboratory

Los Alamos National Laboratory

(Laboratory, Site, or Organization)

Name: Steve Westerhold

Title: DX Division Duty Officer

Telephone No.: (505) 606-0548

(Facility Manager/Designee)

Name: RICHARDSON, JOSEPH B

Title: OCCURRENCE INVESTIGATOR

Telephone No.: (505) 665-4844

(Originator/Transmitter)

Name: Matt Hardy

Date: 05/27/2005

(Authorized Classifier (AC))

1. Occurrence Report Number: ALO-LA-LANL-FIRNGHELAB-2005-0007

Two employees injured in unexpected violent chemical reaction in a laboratory.

2. Report Type and Date: NOTIFICATION

	Date	Time
Notification:	05/27/2005	20:09 (ETZ)
Initial Update:		(ETZ)
Latest Update:		(ETZ)
Final:		(ETZ)

3. Significance Category: 2

4. Division or Project: DX Division

5. Secretarial Office: NA - National Nuclear Security Administration

6. System, Bldg., or Equipment: Room 135 bench-top laboratory apparatus

7. UCNI?: No

8. Plant Area: TA-9-21-135

9. Date and Time Discovered: 05/27/2005 11:04 (MTZ)

10. Date and Time Categorized: 05/27/2005 13:00 (MTZ)

11. DOE HQ OC Notification:

Date	Time	Person Notified	Organization
NA	NA	NA	NA

12. Other Notifications:

Date	Time	Person Notified	Organization
05/27/2005	11:07 (MTZ)	Art Trujillo	NNSA

13. Subject or Title of Occurrence:

Two employees injured in unexpected violent chemical reaction in a laboratory.

14. Reporting Criteria:

10(2) - An event, condition, or series of events that does not meet any of the other reporting criteria, but is determined by the Facility Manager or line management to be of safety significance or of concern to other facilities or activities in the DOE complex. One of the four significance categories should be assigned to the occurrence, based on an evaluation of the potential risks and the corrective actions taken. (1 of 4 criteria - This is a SC 2 occurrence)

15. Description of Occurrence:

On May 27, 2005, at about 1045, two DX-2 employees were injured when the material they were weighing underwent a violent exothermic reaction. The employees, a post-doctoral researcher performing the work and an undergraduate student observing the work, were following an approved Integrated Work Document and were repeating a published procedure involving 1,5-diaminotetrazole when the accident happened. There was no fire or damage to the building. LANL Emergency Response resources were dispatched to the scene and were still in response mode at the time of this report submittal. Both employees were transported to the Los Alamos Medical Center Emergency Room where they received medical treatment. Both employees were wearing prescribed PPE including safety glasses at the time event, and there was no evidence of eye injuries. The student suffered multiple superficial pinpoint lacerations on the face and neck, and was released the afternoon of the accident with no work restrictions. The Post-Doc suffered multiple superficial facial and neck lacerations, with deeper lacerations and abrasion on the chest, abdomen and left hand. His left finger had more severe laceration requiring skin grafting, but there was no evidence of tendon or nerve damage. His right hand also had multiple minor lacerations with some embedded foreign bodies. Room 135 and the surrounding area remain under the control of LANL Emergency Management personnel. The scene of the accident has been stabilized and a re-entry is planned for Tuesday morning, 5/31/05.

16. Is Subcontractor Involved? No

17. Operating Conditions of Facility at Time of Occurrence:

Does not apply.

18. Activity Category:

03 - Normal Operations (other than Activities specifically listed in this Category)

19. Immediate Actions Taken and Results:

Both employees were transported to Los Alamos Medical Center for medical treatment.

Emergency Response personnel secured the work area, ensured that nearby operations were safed, and stabilized the work area to a safe condition.

DX-2 operations were suspended, and it is anticipated that operations not involving chemical synthesis will be resumed the morning of May 31, 2005.

20. ISM:

21. Cause Code(s):

22. Description of Cause:

23. Evaluation (by Facility Manager/Designee):

24. Is Further Evaluation Required?: Yes

If YES - Before Further Operation? No

By whom? DX Division and PS-7

By when?

25. Corrective Actions

(* = Date added/revised since final report was approved.)

26. Lessons Learned:

27. Similar Occurrence Report Numbers:

28. User-defined Field #1:**29. User-defined Field #2:**

30. HQ Keyword(s):

08D--OSHA Reportable/Industrial Hygiene - Injury
11A--Other - Chemical Reaction/Pressurized Drum
11I--Other - Visiting Scientist/Researcher/Student
12H--EH Categories - Injuries Requiring Offsite Medical Treatment

31. HQ Summary:

Two Laboratory employees (a post-doctoral researcher performing an experiment involving 1,5-diaminotetrazole and an undergraduate student observer) were injured following an unexpected laboratory explosion at TA-9, Building 21. There was no fire or damage to the building, and both employees were transported to the Los Alamos Medical Center Emergency Room for treatment. The student suffered multiple pinpoint lacerations to the face/neck and was released the afternoon of the accident with no work restrictions. The researcher suffered moderate to severe injuries, including multiple facial/neck lacerations, and deeper lacerations on the chest, abdomen and left hand. The researcher's left finger had severe lacerations (which required skin grafting), and his right hand had multiple lacerations with embedded foreign bodies. All work was suspended, and Emergency Response personnel secured the work area, pending recovery operations.

32. DOE Facility Representative Input:

33. DOE Program Manager Input:

1,5-Diamino-1*H*-1,2,3,4-tetrazole

Alexander S. Lyakhov,* Pavel N. Gaponik and Sergei V. Voitekhovich

Research Institute of Physico-Chemical Problems, Belarusian State University,
Leningradskaya str. 14, Minsk 220080, Belarus

Correspondence e-mail: lyakhov@fhp.bsu.unibel.by

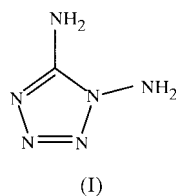
Received 30 June 2000

Accepted 6 November 2000

In the title compound, CH_4N_6 , the tetrazole ring is planar to within 0.001 (1) Å. The 5-amino group is conjugated with the π -system of the tetrazole ring. In contrast, the N atom of the 1-amino group is sp^3 hybridized and is not conjugated with the π system of the tetrazole ring. All H atoms are localized at the exocyclic N atoms. The molecules are connected by N—H...N hydrogen bonds, forming an infinite three-dimensional framework.

Comment

1,5-Diaminotetrazole, (I), being a simple bifunctional tetrazole derivative with high nitrogen content (84%), is attractive as a gas-generating agent (Gao *et al.*, 1991; Levchik *et al.*, 1993) and a valuable intermediate in the preparation of high-energy materials (Willer & Henry, 1988; Sinditskii & Fogelzang, 1997) and other useful tetrazole-containing compounds (Gaponik & Karavai, 1984; Desenko *et al.*, 1990; Krutikov *et al.*, 1991). However, the structure of (I) has not been investigated. Only a hypothesis about the preferable tautomeric form of (I) (amino-imino tautomerism), based on IR spectroscopy data, has been made (Gaponik & Karavai, 1984; Levchik *et al.*, 1993).



Our X-ray investigation shows that the tetrazole ring of (I) is planar to within 0.001 (1) Å. All the formal single endocyclic bonds are considerably shorter than those usually found for normal single bonds, but some formal double bonds are longer than the normal double bonds (*International Tables for Crystallography*, 1992, Vol. C). This indicates that the tetrazole ring of (I) reveals a conjugated system of bonds similar to that found in other tetrazole derivatives. On the other hand, significant differences in the endocyclic bond lengths show considerable localization of charge within the ring. In general,

the angles and bond distances in the hetero-ring of (I) are consistent with those observed previously for 1-mono- and 1,5-disubstituted tetrazoles.

The exocyclic C5—N6 bond of 1.334 (1) Å is shorter than that of 1.47 Å in ethylenediamine (Ohno *et al.*, 1998), longer than that of 1.29 Å in 1,3-dimethyl-5-iminotetrazoline hydrochloride (Bryden, 1955) and close to the value in *p*-nitroaniline (1.355 Å; Colapietro *et al.*, 1982). The difference between the C5—N1 and C5—N4 bond lengths is rather small. It should be noted that the 5-amino group lies in the tetrazole ring plane; the deviation of the N6 atom from the least-squares tetrazole ring is 0.045 (2) Å. The angles around the N6 atom are close to 120° and have values of 118 (1)° for two C5—N6—H angles and of 119 (1)° for the H—N6—H angle. These data indicate a conjugation between the π systems of the tetrazole ring and the 5-amino group. The results obtained confirm an assumption about the preference of the 5-aminotetrazole form (I) rather than the iminotetrazoline form in the solid (Gaponik & Karavai, 1984).

Similar to the N6 atom, the N5 atom also lies in the tetrazole ring plane. The N1—N5 bond length of 1.383 (1) Å is shorter than that of 1.42 Å in tetramethylhydrazine (Ohno *et al.*, 1998) and similar to that in 2-aminobenzotriazole (1.386 Å; Foces-Foces *et al.*, 1990). The lone electron pair of the N5 atom is not conjugated with the π system of the hetero-ring. This conclusion follows from the H-atom positions of this amino group. The three bond angles around the N5 atom are equal to 107 (1)°; this value being close to a tetrahedral angle indicates that the N5 atom has sp^3 hybridization. It should be noted that the H atoms of the 1-amino group are located on different sides of the tetrazole plane (Fig. 1) and consequently the N5

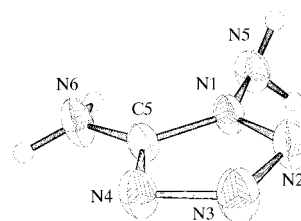


Figure 1

The molecular structure of (I) with the atom-numbering scheme (non-H atom displacement ellipsoids are drawn at the 50% probability level).

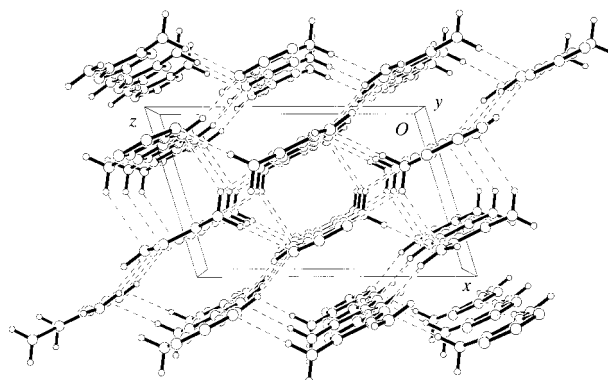


Figure 2

A packing diagram of (I).

lone pair must lie in this plane. These data confirm the conclusions of a theoretical study concerned with the hybridization and conformation of the amino group in *N*-aminoazoles (Foces-Foces *et al.*, 1990), where sp^3 hybridization of amino groups was found to be favoured over sp^2 , and the amino lone pair eclipses the ring in monocyclic *N*-aminoazoles, including 1-aminotetrazole.

Inspection of the molecular packing (Fig. 2) reveals that the individual molecules are linked by N—H...N hydrogen bonds, forming an infinite three-dimensional framework.

Experimental

The title compound was prepared according to a previously described method (Gaponik & Karavai, 1984). Trimethylsilyl azide was used as the azidation agent instead of a mixture of sodium azide and ammonium chloride. This increases the yield of (I) from 60 to 80%. Single crystals were grown by slow crystallization from aqueous solution.

Crystal data

CH ₄ N ₆	$D_x = 1.571 \text{ Mg m}^{-3}$
$M_r = 100.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 6.780 (1) \text{ \AA}$	$\theta = 21.0\text{--}23.7^\circ$
$b = 6.112 (1) \text{ \AA}$	$\mu = 0.124 \text{ mm}^{-1}$
$c = 10.694 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 107.25 (1)^\circ$	Prism, colourless
$V = 423.2 (1) \text{ \AA}^3$	$0.56 \times 0.48 \times 0.26 \text{ mm}$
$Z = 4$	

Data collection

Nicolet R3m four-circle diffractometer	$\theta_{\max} = 30.05^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
1378 measured reflections	$k = 0 \rightarrow 8$
1239 independent reflections	$l = -15 \rightarrow 14$
1069 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.020$	every 100 reflections
	intensity decay: 3.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.0322P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.077$	$\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
1239 reflections	$\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$
80 parameters	
All H-atom parameters refined	

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C5	1.345 (1)	N3—N4	1.367 (1)
N1—N2	1.363 (1)	N4—C5	1.327 (1)
N1—N5	1.383 (1)	C5—N6	1.334 (1)
N2—N3	1.279 (1)		
C5—N1—N2	108.84 (8)	C5—N4—N3	105.56 (8)
C5—N1—N5	126.02 (9)	N4—C5—N6	128.17 (8)
N2—N1—N5	125.13 (8)	N4—C5—N1	107.90 (8)
N3—N2—N1	105.79 (8)	N6—C5—N1	123.87 (9)
N2—N3—N4	111.92 (9)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N5—H5A...N2 ⁱ	0.90 (2)	2.48 (2)	3.063 (1)	123 (1)
N5—H5A...N6 ⁱⁱ	0.90 (2)	2.54 (1)	3.277 (2)	139 (1)
N5—H5B...N4 ⁱⁱⁱ	0.91 (2)	2.26 (2)	3.172 (2)	175 (1)
N6—H6A...N4 ^{iv}	0.94 (2)	2.16 (2)	3.074 (1)	162 (1)
N6—H6B...N3 ^v	0.88 (2)	2.15 (2)	2.982 (2)	157 (2)

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, -y, 1-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $x, y-1, z$.

H-atom positions were found from the ΔF map and all associated parameters were refined freely.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors would like to thank Dr L. S. Ivashkevich for discussions concerning the obtained results.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1058). Services for accessing these data are described at the back of the journal.

References

- Bryden, J. H. (1955). *Acta Cryst.* **8**, 211–217.
- Colapietro, M., Domenicano, A., Marcianite, C. & Portalone, G. (1982). *Z. Naturforsch. Teil B*, **37**, 1309–1311.
- Desenko, S. M., Orlov, V. D., Gaponik, P. N. & Karavai, V. P. (1990). *Khim. Geterotsikl. Soedin.* pp. 1533–1535. (In Russian.)
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Foces-Foces, C., Cano, F. H., Claramunt, R. M., Sanz, D., Catalan, J., Fabero, F., Fruchier, A. & Elguero, J. (1990). *J. Chem. Soc. Perkin Trans. 2*, pp. 237–244.
- Gao, A., Oyumi, Y. & Brill, T. B. (1991). *Combust. Flame*, **83**, 345–352.
- Gaponik, P. N. & Karavai, V. P. (1984). *Khim. Geterotsikl. Soedin.* pp. 1683–1686. (In Russian.)
- Krutikov, V. I., Kovalenko, A. L. & Sukhanovskaya, E. B. (1991). *Zh. Obshch. Khim.* **61**, 257–258. (In Russian.)
- Levchik, S. V., Balabanovich, A. I., Ivashkevich, O. A., Lesnikovich, A. I., Gaponik, P. N. & Costa, L. (1993). *Thermochim. Acta*, **225**, 53–65.
- Nicolet (1980). *R3m Software*. Nicolet XRD Corporation, Cupertino, California, USA.
- Ohno, Y., Akutsu, Y., Arai, M., Tamura, M., Matsunaga, T. & Iida, M. (1998). *Acta Cryst.* **C54**, 1160–1162.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Sinditskii, V. P. & Fogelzang, A. E. (1997). *Russ. Khim. Zh.* **4**, 74–80. (In Russian.)
- Willer, R. L. & Henry, R. A. (1988). *J. Org. Chem.* **53**, 5371–5374.