

5-Nitro-2-nitromethyl-2H-1,2,3,4-tetrazole

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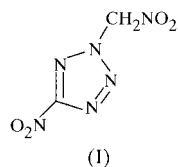
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The molecule of the title compound, C₂H₂N₆O₄, consists of three planar fragments, namely a tetrazole ring, a nitromethyl group and a nitro group. The nitro group and the tetrazole cycle are arranged in the same plane, but the planar nitromethyl group is located nearly orthogonal to this plane. The molecules are packed in the crystal *via* van der Waals interactions.

Comment

Derivatives of tetrazole attract the attention of chemists in the field of explosives thanks to their large endothermicity and high nitrogen content and, at the same time, the relative stability of the tetrazole heterocycle. In principle, by the use of a combination of the tetrazole cycle with the usual explosophoric groups (–NO₂, –N₃, =NNO₂, *etc.*), the creation of new high explosives is possible (Ostrovskii & Koldobskii, 1997). The structure of the title compound, (I), of this new high-explosive tetrazole class, has been investigated using single-crystal X-ray techniques.



Earlier, we investigated the structure of 3-nitro-1-nitromethyl-1H-triazole, (II) (Vasiliev *et al.*, 2000). Compound (I) differs from (II) in the replacement of the =CH– fragment in the 1,2,4-triazole ring by an =N– fragment; the result is another heterocycle ring, *i.e.* tetrazole. One can expect that, after this replacement, the energetic and detonation parameters will increase at the expense of density, oxygen balance and an increase in the heat of explosive formation. At the same time, it is not absolutely clear how the transition from the triazole cycle to tetrazole will affect the thermal stability of

the compound. Therefore, the first aim of the present work is to clarify how the replacement of the =CH– molecular fragment by =N– will affect the geometric parameters of the molecule, especially the lengths of the C–NO₂ bonds, the strength of which determine the thermal stability of nitro compounds (Manelis *et al.*, 1996).

The geometric conformation of molecule (I) is close to that of (II). Similar to (II), the molecule of (I) (Fig. 1) consists of three planar fragments, namely a tetrazole ring, a nitromethyl group and a nitro group (H atoms are omitted from the present consideration). The tetrazole cycle is practically planar [r.m.s. deviation of 0.0018 (9) Å and a maximum deviation of 0.0025 (9) Å]. The interatomic distances in the cycle are not equal, ranging from 1.302 (2) to 1.338 (2) Å. The nitro group bonded to the tetrazole cycle is rotated by 0.9 (3)° with respect to the ring plane. The nitromethyl group is strictly planar and is located nearly orthogonal [86.02 (7)°] to the tetrazole ring, while the O3–N8–C7–N2 torsion angle is –6.9 (2)°.

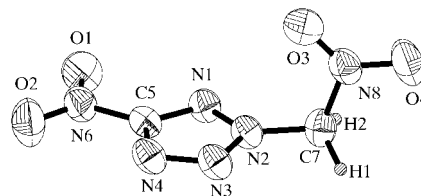


Figure 1

The molecule of (I) showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

The C–NO₂ bond lengths are not equal [1.441 (2) and 1.503 (2) Å]; the greater value corresponds to the bond in the nitroalkyl fragment of the molecule. Thus, the C–NO₂ bonds in (I) are slightly stronger than those in (II) [1.450 (2) and 1.509 (2) Å, respectively; Vasiliev *et al.*, 2000]. However, there is no evidence to suggest a similar or greater thermal stability of (I) in comparison with (II). The thermal decomposition of (II) begins with the breaking of the weaker C–NO₂ bond, whereas for (I), an alternate path of thermal decomposition, typical for 2,5-substituted tetrazole derivatives (Manelis *et al.*, 1996; Ostrovskii & Koldobskii, 1997), is possible, namely, the breaking of the N2–N3 bond. At the same time, it is known that a series of nitroalkyl 2,5-substituted tetrazoles decompose with an initial breaking of the C–NO₂ bond (Stepanov *et al.*, 2000). The X-ray data for the bond lengths in (I) do not indicate a preference for one of these probable thermolysis paths. We are now carrying out an experimental study of the kinetics and mechanism of the thermal decomposition of (I), which will give an answer to the problems discussed above.

As expected, the density of (I) is greater than that of (II) (1.80 versus 1.76 Mg m^{–3}). The density of (I) allows the consideration of its detonation parameters as being close to those of such a well known explosive as RDX, the former slightly exceeding the latter in the heat of explosion, at the expense of a greater heat of formation and better oxygen balance.

Experimental

Single crystals of (I) were obtained by crystallization from ethanol [m.p. 408 K (decomposition)].

Crystal data

$C_2H_2N_6O_4$	$D_x = 1.800 \text{ Mg m}^{-3}$
$M_r = 174.10$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 9.213 (3) \text{ \AA}$	$\theta = 20\text{--}28^\circ$
$b = 7.7610 (10) \text{ \AA}$	$\mu = 1.52 \text{ mm}^{-1}$
$c = 10.180 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 118.04 (2)^\circ$	Lump, colourless
$V = 642.5 (3) \text{ \AA}^3$	$0.27 \times 0.25 \times 0.24 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 four-circle diffractometer	$\theta_{\max} = 69.9^\circ$
Profile measured $\theta/2\theta$ scans	$h = 0 \rightarrow 10$
1254 measured reflections	$k = -5 \rightarrow 9$
1177 independent reflections	$l = -12 \rightarrow 10$
978 reflections with $I > 2\sigma(I)$	2 standard reflections every 50 reflections
$R_{\text{int}} = 0.023$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.0898P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.09$	$\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
1177 reflections	$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
118 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
All H-atom parameters refined	Extinction coefficient: 0.0097 (16)

The refined C—H distances are 0.95 (2) and 0.97 (2) Å.

Data collection: *KM-4 Software* (Kuma, 1991); cell refinement: *KM-4 Software*; data reduction: *DATARED* in *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1078). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Kuma (1991). *KM-4 Software User's Guide*. Version 5.2. Kuma Diffraction, Wrocław, Poland.
- Manelis, G. B., Nazin, G. M., Rubtsov, Yu. I. & Strunin, V. A. (1996). *Thermal Decomposition and Combustion of Explosives and Powders*, edited by F. I. Dubovitsky, pp. 223–234. Moscow: Nauka.
- Ostrovskii, V. A. & Koldobskii, G. I. (1997). *Russ. Khim. Zh.* **41**, 84–98. (In Russian.)
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1995). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stepanov, R. S., Astachov, A. M., Kruglyakova, L. A. & Golubtsova, O. A. (2000). *Russ. J. Gen. Chem.* **70**, 999–1001. (In Russian.)
- Vasiliev, A. D., Astachov, A. M., Golubtsova, O. A., Kruglyakova, L. A. & Stepanov, R. S. (2000). *Acta Cryst.* **C56**, 999–1000.