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3-Nitro-1-nitromethyl-1*H*-1,2,4-triazole

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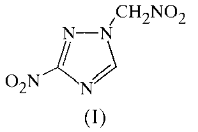
The title compound, $C_3H_3N_5O_4$, consists of three planar fragments twisted in relation to each other, namely a triazole ring, a nitromethylene group and a nitro group. Molecular conformation analysis shows that the first stage of thermal decomposition is a breakage of the $H_2C—NO_2$ bond. There are essential conformational differences in the molecule in comparison with semi-empirical calculations.

Comment

Nitro derivatives of 1,2,4-triazole are of interest as highly energetic compounds (Pevzner, 1997). X-ray structure investigation of the compounds is important not only for providing unambiguous confirmation of their molecular structure: since one of the basic characteristics of explosives is their density, it is necessary to know their structure parameters to reveal factors that have an influence on crystal density (Stein, 1981), with the ultimate aim of enabling a computer search of hypothetical high-density highly energetic compounds and their subsequent synthesis (Coburn *et al.*, 1986). No less important is that knowledge of the structure parameters of a highly energetic molecule allows the prediction of its reaction ability, in particular its thermal stability (Manelis *et al.*, 1996). Accordingly, the structure of the title compound, (I), was investigated using single-crystal X-ray techniques.



(I)

The molecule of (I) (Fig. 1) consists of three bonded planar fragments, namely a 1,2,4-triazole ring, a nitromethylene group and a nitro group (H atoms are omitted from the consideration). The triazole cycle is practically planar [r.m.s. deviation 0.0014 (8), maximum deviation 0.002 (8) Å]. The interatomic distances within the cycle are not equal, ranging from 1.304 (2) to 1.355 (2) Å. The nitro group bonded to the triazole ring is located at 17.8 (2)° with respect to the ring plane. The nitromethylene group is strictly planar and is located nearly orthogonal [83.25 (6)°] to the triazole ring, while the torsion angle O3—N8—C7—N1 is 2.8 (2)°. The C—NO_2 bond lengths are not equal [1.450 (2) and 1.509 (2) Å]: the greater value relates to the bond in the nitroalkyl fragment of the molecule. On the whole, bond lengths and angles in (I) are close to the corresponding values in other nitro derivatives of 1,2,4-triazole (Closset *et al.*, 1975; Starova *et al.*, 1977; Nikitina *et al.*, 1982).

The structure of (I) has been investigated theoretically by semi-empirical Modified Neglecting of Diatomic Overlap (MNDO), Augusting Model 1 (*AM*1) and Parametrization Model 3 (*PM*3) methods (Stepanov *et al.*, 2000). In contrast with the experimental data, these calculations show that the location of the nitro group orthogonal to the triazole ring is more preferable. This disagreement might be due to the incorrect evaluation of the resonance effect between the triazole cycle and the nitro group. In accordance with the semi-empirical calculations, the torsion angle O3—N8—C7—N1 is in the range 44–60°, depending on the calculation method. Calculated C—NO_2 bond lengths are somewhat overestimated, with values of 1.482–1.512 and 1.553–1.571 Å for nitro groups bonded to the triazole cycle and the methylene fragment, respectively. However, the X-ray results confirm earlier inference concerning the preference of nitro-group breakage in the nitromethylene part of (I) during thermal decomposition (Stepanov *et al.*, 2000).

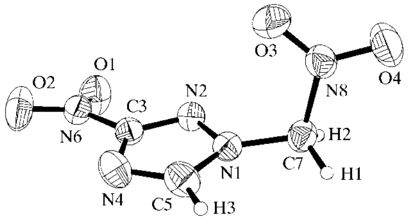


Figure 1
The molecule of (I) showing the atom-numbering scheme and displacement ellipsoids at 50% probability. H atoms are drawn as small spheres of arbitrary radii.

In conclusion, we note that the density of (I) (1.76 Mg m^{-3}) exceeds the density of the formula isomer 1-methyl-3,5-dinitro-1,2,4-triazole (1.63 Mg m^{-3}; Starova *et al.*, 1977). This fact leads to the expectation of an increase in the value of the detonation velocity by 400–500 m s^{-1} for (I) in comparison with the latter compound. It would be expected that the high density of a crystal composed of organic molecules is associated with short intermolecular distances, but all intermolecular atom–atom distances in the crystal of (I) exceed the corresponding sums of ordinary van der Waals radii.

Experimental

Compound (I) (Stepanov *et al.*, 2000) was obtained by double recrystallization from water (m.p. 453 K, with decomposition). Single crystals were obtained by evaporation of a saturated ethanol solution.

Crystal data

$C_3H_3N_5O_4$
$M_r = 173.10$
Monoclinic, $P2_1/c$
$a = 6.6305$ (4) Å
$b = 9.2888$ (3) Å
$c = 10.9828$ (6) Å
$\beta = 104.837$ (5)°
$V = 653.87$ (6) Å^3
$Z = 4$
$D_x = 1.758$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 22$–30°
$\mu = 1.439$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.35 × 0.30 × 0.25 mm

Data collection

Kuma KM-4 four-circle diffractometer
Profile data from $\omega/2\theta$ scans
2493 measured reflections
1195 independent reflections
1015 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 69.98$°
$h = -8 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 13$
2 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.087$
$S = 1.029$
1195 reflections
122 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.1343P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0170 (15)

Table 1
Selected geometric parameters (Å, °).

N1—C7	1.4261 (17)	N8—C7	1.5088 (18)
C5—N1—C7—N8	−91.94 (16)	N2—N1—C7—N8	78.49 (14)

The C—H range is 0.94 (2)–0.98 (2) Å.

Data collection: *KM*-4 *Software* (Kuma, 1991); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1037). Services for accessing these data are described at the back of the journal.

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