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4-Nitramino-1,2,4-triazole

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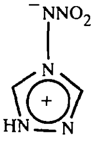
Abstract

4-Nitramino-1,2,4-triazole (4-NRTZ), $C_2H_3N_5O_2$, consists of two almost planar fragments, namely a triazole ring and nitroimide group, $N(NO_2)$; the angle between these two planes is 50.55 (6)°. The nitroimide group is connected to the triazole ring by the longest N—N bond. H atoms are localized near the C3, C5 and N2 atoms in the triazole ring. Analysis of the crystal structure suggests that the first stage of decomposition of 4-NRTZ is a breakage of the N4—N6 bond.

Comment

The nitramine derivatives of 1,2,4-triazoles are known as highly energetic compounds (Pevzner, 1997). This article focuses on 4-nitramino-1,2,4-triazole (4-NRTZ). There exist at least two different opinions about the 4-NRTZ structure. According to Katritzky & Mitchell (1973), 4-NRTZ exists in the *N*-nitroimide form. On the other hand, Gao *et al.* (1991) think that this compound is a primary nitramine. One needs to know the structure of 4-NRTZ in order to understand its ability to react, particularly with regard to the thermolysis mechanism.



4-NRTZ

The 4-NRTZ structure was investigated by the single-crystal X-ray technique. The molecule (Fig. 1) is not planar but consists of two practically planar fragments, namely a 1,2,4-triazole ring and a nitroimide group, $N(NO_2)$. The $N4N6(NO_2)$ group is also planar (r.m.s. deviation 0.0145 Å, maximum deviation 0.022 Å) and the N4—N6—N7—O2 torsion angle is −2.6 (2)°. The angle between the least-squares planes passing through the triazole ring and the nitroimide group is 50.55 (6)°.

The interatomic distances in the ring are not equal; they range from 1.300 to 1.362 Å. According to Ostrovskii *et al.* (1995), this is typical of 1,2,4-triazoles. The deviations of the C and N atoms from the least-squares plane is less than 0.10 Å. H atoms were located from the difference Fourier synthesis near the C3, C5 and N2 atoms of the triazole ring. The fact that the nitroimide group is connected to the triazole ring by the longest N—N bond (N4—N6) and that its plane deviates from the plane of the ring allows the supposition that the π systems of the nitroimide group and the ring do not interact. At the same time, there is a rather strong charge redistribution in the molecule, with the nitroimide group charged negatively and the triazole ring charged positively. A comparison of the 4-NRTZ structure with well known *N*-nitroimide structures, such as trimethylammonionitramidate (Cameron *et al.*, 1972) and pyridine 1-nitroimide (Arriau *et al.*, 1974), shows that nitroimide fragments have similar geometries. It should be noted, however, that in the 4-NRTZ molecule, the N6—N7 bond is somewhat shorter, while the N—O bonds are more unequal than the corresponding bonds in the above-mentioned compounds. The inequality is probably due to intermolecular hydrogen bonding between the N2 and O1 atoms; hydrogen-bond parameters are: O1—H2 1.84 (2), N2···O1 2.751 (2) Å and N2—H2···O1 158.5 (15)°. The bonding produces separate molecular chains along the *b* axis, as shown in Fig. 2. Analysis of the crystalline structure suggests that the first stage of decomposition of 4-NRTZ is a breakage of the N4—N6 bond which connects the triazole ring with the nitroimide group. The observed products of decomposition (Gao *et al.*, 1991) are probably the result of further interaction between a very strong oxidizer, dinitrogen dioxide (N_2O_2) in a C_{2v} conformation (Michels & Hinchen, 1992), and 1,2,4-triazole.

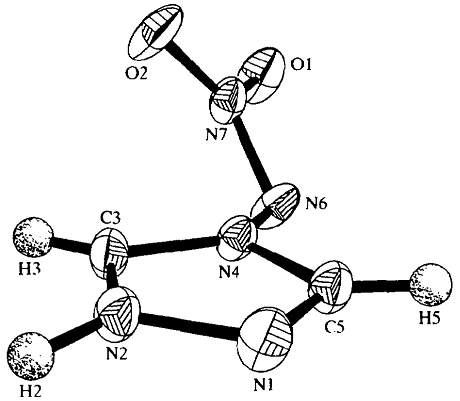


Fig. 1. The molecule of 4-NRTZ shown with 50% probability displacement ellipsoids for non-H atoms.

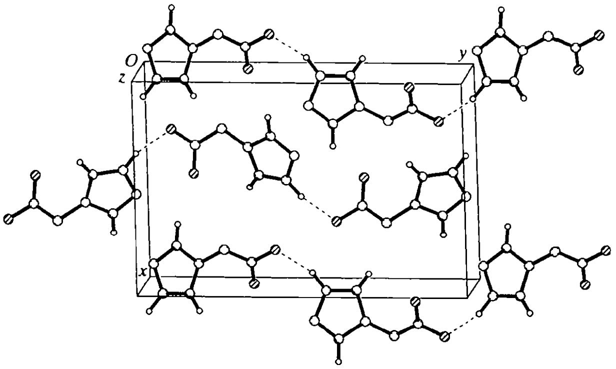


Fig. 2. The unit-cell structure of 4-NRTZ; dashed lines indicate hydrogen bonds.

Experimental

4-NRTZ was synthesized using a modified procedure (Katritzky & Mitchell, 1973); absolute alcohol was omitted and some extra sodium was used. Moreover, ethyl nitrate was substituted by commercially available nitro esters (diethyleneglycol dinitrate or pentaerythritol tetranitrate). Ethanolic sodium ethoxide (from 17.2 g of sodium and 200 ml of 95% ethanol), 4-amino-1,2,4-triazole (13.3 g) and diethyleneglycol dinitrate (12 ml; or 12.5 g pentaerythritol tetranitrate) were heated under reflux for 1.5 h. After cooling the mixture, the precipitated sodium salt of 4-NRTZ was collected by filtration. It was then used without further purification. Concentrated hydrochloric acid (13 ml) was added dropwise to a 4-NRTZ sodium-salt suspension in water (40 ml). The mixture was stirred well during this process and the temperature was kept at 273–278 K. The solid product was then isolated and recrystallized from ethanol to yield 12.2 g (60%) of 4-NRTZ [m.p. 445 K (with explosion)].

Crystal data

$C_2H_3N_5O_2$
$M_r = 129.09$
Orthorhombic
$P2_12_12_1$
$a = 9.2989\ (7)$ Å
$b = 14.057\ (1)$ Å
$c = 3.6066\ (3)$ Å
$V = 471.44\ (6)$ Å^3
$Z = 4$
$D_x = 1.819$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 21.5$–$46.0°$
$\mu = 1.404$ mm^{-1}
$T = 293\ (2)$ K
Transparent lump
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Kuma KM-4 four-circle diffractometer
Profile-measured $\omega/2\theta$ scans
Absorption correction: none
936 measured reflections
535 independent reflections (plus 241 Friedel-related reflections)
757 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 66.98°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 4$
2 standard reflections every 50 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.073$
$S = 1.096$
776 reflections
95 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.0552P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.206$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.182$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.077 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Geometric parameters (Å, °)*

N1—C5	1.300 (2)	N4—C5	1.358 (2)
N1—N2	1.362 (2)	N4—N6	1.407 (2)
N2—C3	1.308 (2)	C5—H5	0.96 (2)
N2—H2	0.98 (2)	N6—N7	1.319 (2)
C3—N4	1.341 (2)	N7—O2	1.235 (2)
C3—H3	0.90 (2)	N7—O1	1.259 (2)
C5—N1—N2	104.1 (1)	C5—N4—N6	121.9 (1)
C3—N2—N1	112.0 (1)	N1—C5—N4	110.9 (1)
C3—N2—H2	126.5 (15)	N1—C5—H5	125.5 (11)
N1—N2—H2	121.1 (14)	N4—C5—H5	123.6 (11)
N2—C3—N4	106.1 (1)	N7—N6—N4	110.7 (1)
N2—C3—H3	126.4 (11)	O2—N7—O1	122.3 (1)
N4—C3—H3	127.3 (11)	O2—N7—N6	124.1 (1)
C3—N4—C5	107.0 (1)	O1—N7—N6	113.7 (1)
C3—N4—N6	130.5 (1)		
N4—N6—N7—O2	−2.6 (2)		

Data collection: *KM*-4 *Software* (Kuma, 1997). Cell refinement: *KM*-4 *Software*. Data reduction: *DATARED* in *KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (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: AV1027). Services for accessing these data are described at the back of the journal.

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