

Acta Cryst. (1996). **C52**, 2057–2058

A New Energetic Material: an Azidoethylamine Salt of Triazole

SHUAN DONG,^a GUOZHEN ZHANG,^a BOREN CHEN,^b
YUXIANG OU^b AND HUIPING JAI^b

^aDepartment of Chemistry, Shandong Teacher's University, Jinan 250014, People's Republic of China, and ^bDepartment of Chemical Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

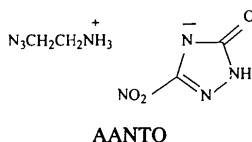
(Received 21 June 1995; accepted 16 April 1996)

Abstract

The title compound, 2-azidoethylammonium 3-nitro-1,2,4-triazol-5-onate, $\text{N}_3\text{CH}_2\text{CH}_2\text{NH}_3^+\cdot\text{C}_2\text{HN}_4\text{O}_3^-$, is a new salt of 3-nitro-1,2,4-triazol-5-one. The triazole ring is planar within 0.0067 (5) Å, the nitro group is rotated 14.0 (4)° out of the ring plane. The H atom on the anion is in position 1.

Comment

3-Nitro-1,2,4-triazol-5-one, (NTO) is an insensitive, high-energy explosive (Lee & Coburn, 1985) and many salts of NTO, especially its amine salts, have been studied (Lee & Stinecipher, 1989). We have synthesized a new salt using the high-energy azido amine $\text{N}_3\text{CH}_2\text{CH}_2\text{NH}_2$. The product, 2-azidoethylammonium 3-nitro-1,2,4-triazol-5-onate (AANTO) has a potential application as a high-energy propellant (Dong, Chen & Ou, 1995).



The bond lengths and angles in the triazole anion are very similar to those of the ethylenediammonium and 1,3-diaminoguanidinium salts of NTO, but the rotation angle of the nitro group out of the anion plane is very different. In the ethylenediammonium salt of NTO, the rotation angle is less than 1°, in the 1,3-diaminoguanidinium salt it is 2.9 (2)°; both of these values are much less than that found in AANTO (Cromer, Hall, Lee & Ryan, 1988*a,b*). O(1) and the triazole ring are planar within 0.0197 (4) Å, and N(4) and the triazole ring are planar within 0.0525 (3) Å. There are a number of hydrogen bonds between the cations and anions through N(5), N(2), O(1) and N(1), as given in Table 3. The bond lengths of the azido group of AANTO are almost the same as those in the azido-methane (Livingston & Rao, 1960).

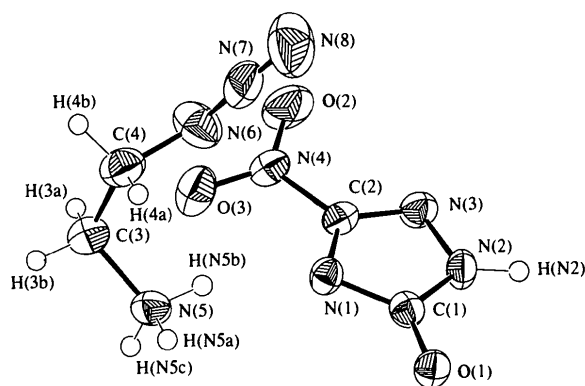


Fig. 1. The molecular structure and atom-labelling scheme of AANTO. Displacement ellipsoids are at the 50% probability level.

Experimental

Synthesis of AANTO was carried out by mixing β -azidoethylamine with NTO (molar ratio 1.2:1) in water at room temperature. The title compound was recrystallized from alcohol.

Crystal data

$\text{C}_2\text{H}_7\text{N}_4^+\cdot\text{C}_2\text{HN}_4\text{O}_3^-$

$M_r = 216.2$

Monoclinic

$P2_1/c$

$a = 11.364 (2) \text{ \AA}$

$b = 8.485 (2) \text{ \AA}$

$c = 9.868 (2) \text{ \AA}$

$\beta = 109.24 (3)^\circ$

$V = 898.4 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.598 \text{ Mg m}^{-3}$

$D_m = 1.603 \text{ Mg m}^{-3}$

D_m measured by flotation in EtI and CCl_4

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8-13^\circ$

$\mu = 0.127 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.45 \times 0.40 \times 0.12 \text{ mm}$

Pale yellow

Data collection

Rigaku AFC-6S diffractometer

$\theta/2\theta$ scans

Absorption correction: none

1797 measured reflections

1580 independent reflections

790 observed reflections

$[F > 5\sigma(F)]$

$R_{\text{int}} = 0.0215$

$\theta_{\text{max}} = 25.0^\circ$

$h = -13 \rightarrow 12$

$k = -10 \rightarrow 0$

$l = 0 \rightarrow 11$

3 standard reflections

monitored every 150 reflections

intensity decay: none

Refinement

Refinement on F

$R = 0.0501$

$wR = 0.0551$

$S = 1.65$

790 reflections

146 parameters

$w = 1/[\sigma^2(F) + 0.0002F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.208$

$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Extinction correction:

$F^* = F[1 + 0.002\chi \times F^2/\sin(2\theta)]^{-1/4}$

Extinction coefficient:

$\chi = 0.0017 (5)$

Atomic scattering factors from SHELXTL-Plus (Sheldrick, 1990)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
N(1)	0.8698 (4)	0.0668 (5)	0.5393 (4)	0.029 (1)
N(2)	0.9187 (4)	-0.1698 (5)	0.6313 (4)	0.034 (2)
N(3)	0.8548 (4)	-0.1971 (5)	0.4900 (4)	0.035 (2)
N(4)	0.7632 (4)	-0.0224 (6)	0.2950 (5)	0.037 (2)
N(5)	0.8306 (4)	0.0998 (6)	-0.0506 (5)	0.037 (2)
N(6)	0.5843 (5)	0.2438 (6)	-0.0988 (6)	0.056 (2)
N(7)	0.5191 (5)	0.2833 (6)	-0.0280 (6)	0.053 (2)
N(8)	0.4617 (6)	0.3363 (8)	0.0346 (7)	0.084 (3)
O(1)	0.9870 (3)	0.0408 (4)	0.7854 (3)	0.033 (1)
O(2)	0.7121 (4)	-0.1335 (5)	0.2191 (4)	0.061 (2)
O(3)	0.7654 (4)	0.1121 (5)	0.2512 (4)	0.051 (2)
C(1)	0.9291 (5)	-0.0132 (6)	0.6607 (5)	0.031 (2)
C(2)	0.8294 (4)	-0.0520 (6)	0.4462 (5)	0.030 (2)
C(3)	0.7122 (5)	0.0431 (7)	-0.1560 (6)	0.043 (2)
C(4)	0.6017 (5)	0.0749 (7)	-0.1088 (6)	0.048 (2)

Table 2. Selected geometric parameters (Å, °)

N(1)—C(1)	1.349 (6)	N(1)—C(2)	1.339 (6)
N(2)—N(3)	1.363 (5)	N(2)—C(1)	1.357 (6)
N(2)—H(N2)	0.908 (4)	N(3)—C(2)	1.305 (6)
N(4)—O(2)	1.225 (6)	N(4)—O(3)	1.224 (6)
N(4)—C(2)	1.455 (6)	N(5)—C(3)	1.484 (6)
N(6)—N(7)	1.221 (9)	N(6)—C(4)	1.455 (8)
N(7)—N(8)	1.13 (1)	O(1)—C(1)	1.275 (5)
C(3)—C(4)	1.500 (9)		
C(1)—N(1)—C(2)	100.9 (4)	N(3)—N(2)—C(1)	111.4 (4)
N(3)—N(2)—H(N2)	112.5 (4)	C(1)—N(2)—H(N2)	136.0 (4)
N(2)—N(3)—C(2)	99.4 (4)	O(2)—N(4)—O(3)	124.2 (4)
O(2)—N(4)—C(2)	118.4 (4)	O(3)—N(4)—C(2)	117.4 (4)
N(7)—N(6)—C(4)	115.5 (5)	N(6)—N(7)—N(8)	172.5 (7)
N(1)—C(1)—N(2)	108.7 (4)	N(1)—C(1)—O(1)	128.7 (4)
N(2)—C(1)—O(1)	122.7 (4)	N(1)—C(2)—N(3)	119.7 (4)
N(1)—C(2)—N(4)	121.2 (4)	N(3)—C(2)—N(4)	119.1 (4)
N(5)—C(3)—C(4)	112.5 (5)	N(6)—C(4)—C(3)	110.2 (5)
C(4)—N(6)—N(7)—N(8)	176.9 (6)	N(5)—C(3)—C(4)—N(6)	63.6 (6)
N(7)—N(6)—C(4)—C(3)	-162.1 (5)		

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N(5)—H(N5a)...O(1 ⁱ)	2.24 (7)	2.998 (5)	146 (4)
N(5)—H(N5b)...N(1 ⁱⁱ)	2.06 (8)	2.954 (6)	162 (6)
N(5)—H(N5c)...O(1 ⁱⁱⁱ)	2.03 (7)	2.815 (6)	159 (4)
N(5)—H(N2)...O(1 ^{iv})	1.85 (5)	2.697 (5)	154.3 (5)

Symmetry codes: (i) 2 - x, -y, 1 - z; (ii) x, ½ - y, z - ½; (iii) x, y, z - 1; (iv) 2 - x, y - ½, ¾ - z.

H atoms on N(2) and N(5) were located by difference Fourier synthesis, while others were placed in calculated positions using a riding model. All H atoms were given fixed isotropic *U* values.

Structure solution and refinement were performed by direct methods using *SHELXTL-Plus* (Sheldrick, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cromer, D. T., Hall, J. H., Lee, K. Y. & Ryan, R. (1988a). *Acta Cryst.* **C44**, 1144–1147.

Cromer, D. T., Hall, J. H., Lee, K. Y. & Ryan, R. (1988b). *Acta Cryst.* **C44**, 2206–2208.

Dong, S., Chen, B. & Ou, Y. (1995). *The Third Beijing International Symposium on Pyrotechnics and Explosives*, Beijing, China, pp. 117–120.

Lee, K. Y. & Coburn, M. D. (1985). Report LA-10302-MS. Los Alamos National Laboratory, New Mexico, USA.

Lee, K. Y. & Stinecipher, M. M. (1989). *Propellants Explos. Pyrotech.* pp. 241–244.

Livingston, R. L. & Rao, C. N. (1960). *J. Phys. Chem.* **64**, 756–759.

Sheldrick, G. M. (1990). *SHELXTL-Plus. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). **C52**, 2058–2060

Antihypertensive 2-(1,3-Dioxolan-2-yl)-2-methyl-6-nitro-4-(2-oxo-1-pyrrolidinyl)-2H-1-benzopyran

WHANCHUL SHIN,^{a*} CHONG HAK CHAE^a AND SUNG EUN YOO^b

^aDepartment of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea, and ^bKorea Research Institute of Chemical Technology, PO Box 9, Daedeog-Danji, Daejeon 305-606, Korea. E-mail: nswcshin@plaza.snu.ac.kr

(Received 8 March 1995; accepted 19 February 1996)

Abstract

The title compound, 1-[2-(1,3-dioxolan-2-yl)-2-methyl-6-nitro-2H-1-benzopyran-4-yl]-2-pyrrolidinone, C₁₇H₁₈N₂O₆, is a highly potent potassium-channel activator. The dioxolane moiety is in the pseudo-axial position. The overall conformation, in terms of the relative orientation of the oxopyrrolidine ring with respect to the benzopyran ring, is similar to that of cromakalim.

Comment

Potassium-channel activators are promising in cardiovascular therapy as antihypertensives and coronary vasodilators and consist of several structural groups including benzopyran compounds (Robertson & Steinberg, 1990). The title compound, (I), is a highly potent potassium-channel activator and shows higher (*ca* nine times) activity than cromakalim, (II), the first of this class of compounds to enter clinical trials as an antihypertensive agent (Ashwood *et al.*, 1986).

In the crystal structure of cromakalim (Cassidy *et al.*, 1989), the oxopyrrolidine ring was found to be orthogonal to the benzopyran ring. From an NMR study, it was suggested that rotation about the C—