

Structures of Two Polymorphs of 1,1'-Dinitro-3,3'-azo-1,2,4-triazole*

BY DON T. CROMER,† KIEN-YIN LEE AND ROBERT R. RYAN

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545, USA

(Received 1 March 1988; accepted 25 April 1988)

Abstract. $C_4H_2N_{10}O_4$, $M_r = 254.12$, $\lambda(\text{Mo } K\alpha_1) = 0.70926 \text{ \AA}$, $F(000) = 256$. Yellow polymorph, $P2_1/c$, $a = 7.208 (1)$, $b = 5.724 (1)$, $c = 12.254 (2) \text{ \AA}$, $\beta = 101.00 (2)^\circ$, $V = 496.26 \text{ \AA}^3$, $Z = 2$, $D_x = 1.701 \text{ Mg m}^{-3}$, $\mu = 1.41 \text{ cm}^{-1}$, room temperature, final $R = 0.028$ for 378 observed reflections with $I > 3\sigma(I)$ out of 873 independent reflections. Orange polymorph, $P2_1/a$, $a = 5.423 (3)$, $b = 17.067 (5)$, $c = 5.449 (1) \text{ \AA}$, $\beta = 113.89 (3)^\circ$, $V = 460.94 \text{ \AA}^3$, $Z = 2$, $D_x = 1.831 \text{ Mg m}^{-3}$, $\mu = 1.52 \text{ cm}^{-1}$, room temperature, final $R = 0.051$ for 292 observed reflections with $I > 3\sigma(I)$ out of 601 independent reflections. The molecules in both forms are virtually planar with normal bond lengths. A possible weak C–H...O hydrogen bond [C...O = $3.51 (1) \text{ \AA}$] contributes to the more-efficient packing of the orange form.

Experimental. The title compound is a possible candidate for high-energy propellant applications. The synthesis is given by Lee (1985). Pale-yellow crystals (N-DNATYE) were crystallized from ethanol while pale-orange crystals (N-DNATOR) were obtained from acetone. Pertinent experimental parameters are given in Table 1. Standard reflections showed no significant

variation. Structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971), H atoms from difference Fourier synthesis. Least squares minimized $\sum w(\Delta F)^2$ with $w = [\sigma_c^2(F) + 0.015F^2]^{-1}$, $\sigma_c^2(F)$ based on counting statistics. Scale factor, positional parameters, anisotropic thermal parameters for C, N, O atoms and isotropic thermal parameters for H atoms were refined. For N-DNATYE, a type-II extinction parameter (Larson, 1969) was added: $1.3 (2) \times 10^{-5} \text{ mm}$. The ratio of observations to parameters is not as large as usual because the crystals, particularly the orange form, were quite small. Because of the smaller amount of data collected, the errors for N-DNATOR are much larger than for N-DNATYE. Scattering factors f (RHF for C, N, O and SDS for H), f' , f'' from *International Tables for X-ray Crystallography* (1974). Calculations on CDC-7600 and CRAY-1 using the *Los Alamos Crystal Structure System* developed primarily by A. C. Larson.‡

Fig. 1 is an *ORTEP* (Johnson, 1965) drawing of molecule N-DNATYE and shows the atom-numbering scheme. Final non-H-atom parameters are given in Table 2. Bond lengths and angles involving C, N and O atoms are given in Table 3. The configuration of the molecules is virtually the same in both forms. Both molecules are virtually planar. In N-DNATYE the nitro group is rotated $2.4 (1)^\circ$ and in N-DNATOR $6.7 (6)^\circ$.

* This work was performed under the auspices of the US Department of Energy.

† Author to whom correspondence should be addressed.

Table 1. Pertinent experimental data for 1,1'-dinitro-3,3'-azo-1,2,4-triazole

	N-DNATYE	N-DNATOR
Color	Pale yellow	Pale orange
Crystal size (mm)	0.27 × 0.16 × 0.05	0.25 × 0.10 × 0.02
CAD-4 diffractometer	θ -2 θ scan	θ -2 θ scan
Scan range ($^\circ$)	$1 + 0.34 \tan \theta$	$1 + 0.34 \tan \theta$
Scan speed ($^\circ \text{ min}^{-1}$)	1.0 to 5.5	1.6 to 5.5
Background	1st and last 1/6 of scan	1st and last 1/6 of scan
Cell, 25 reflections	$6 < 12^\circ \theta$	$6 < 14^\circ \theta$
Absorption corr.	None	None
($\sin \theta$)/ λ max. (\AA^{-1})	0.60	0.54
Index range, h	0.8	0.5
Index range, k	0.6	0.18
Index range, l	-14, 14	-5, 5
Standard reflections	32I and 32I'	150 and 210
No. of reflections measured	945	674
R_f merge	0.017	0.012
Final ΔF Fourier synthesis ($e \text{ \AA}^{-3}$)	$0.11 > \rho > -0.13$	$0.22 > \rho > -0.24$
No. of obs./No. of parameters	4.4	3.4
Max. Δ/σ last cycle	0.03	0.01
Goodness of fit	1.4	2.5
R	0.028	0.051
wR	0.027	0.057

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44986 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

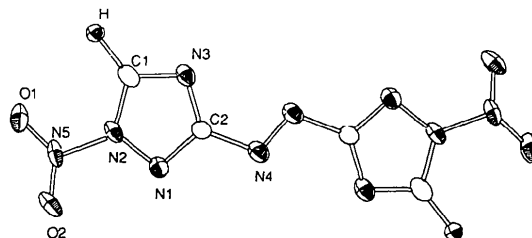


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the asymmetric unit to show atom-numbering scheme. Thermal ellipsoids are 30% probability. H atoms are arbitrarily sized.

Table 2. Final least-squares parameters for the C, N and O atoms in 1,1'-dinitro-3,3'-azo-1,2,4-triazole (positional parameters $\times 10^4$, equivalent isotropic $U \text{ \AA}^2 \times 10^2$)
$$U_{eq} = 1/3 \sum U_{ii}$$

	N-DNATYE				N-DNATOR			
	x	y	z	U_{eq}	x	y	z	U_{eq}
C(1)	8046 (5)	1995 (6)	7145 (3)	5.6 (4)	-64 (22)	3861 (6)	-442 (23)	4 (1)
C(2)	8830 (4)	2912 (6)	5659 (3)	4.9 (4)	2292 (19)	4386 (6)	3317 (19)	4 (1)
N(1)	7921 (3)	947 (5)	5376 (2)	5.7 (3)	432 (19)	4013 (4)	3897 (18)	4 (1)
N(2)	7418 (3)	402 (5)	6349 (2)	5.5 (3)	-1016 (16)	3697 (5)	1491 (18)	3 (1)
N(3)	8949 (3)	3647 (4)	6733 (2)	5.3 (3)	2091 (16)	4302 (5)	783 (18)	4 (1)
N(4)	9567 (4)	4080 (4)	4826 (2)	5.5 (3)	4285 (17)	4804 (4)	5443 (18)	4 (1)
N(5)	6377 (4)	-1714 (6)	6462 (3)	7.4 (5)	-3296 (16)	3201 (5)	1129 (22)	4 (1)
O(1)	6109 (4)	-2031 (5)	7398 (2)	10.2 (3)	-4538 (15)	2986 (4)	-1163 (17)	6 (1)
O(2)	5939 (4)	-2854 (4)	5635 (2)	9.3 (4)	-3605 (13)	3049 (4)	3161 (15)	6 (1)

Table 3. Bond distances (\AA) and angles ($^\circ$) for C, N and O atoms in the two forms of 1,1'-dinitro-3,3'-azo-1,2,4-triazole

	N-DNATYE	N-DNATOR		N-DNATYE	N-DNATOR
C(1)-N(2)	1.349 (4)	1.376 (10)	N(2)-C(1)-N(3)	109.5 (3)	105.0 (9)
C(1)-N(3)	1.304 (4)	1.321 (12)	N(1)-C(2)-N(3)	117.0 (3)	115.9 (10)
C(2)-N(1)	1.314 (3)	1.334 (11)	N(1)-C(2)-N(4)	117.0 (3)	116.5 (9)
C(2)-N(3)	1.368 (3)	1.348 (10)	N(3)-C(2)-N(4)	126.0 (3)	127.6 (10)
C(2)-N(4)	1.407 (4)	1.416 (11)	C(2)-N(1)-N(2)	99.8 (3)	99.2 (8)
N(1)-N(2)	1.347 (3)	1.339 (11)	C(1)-N(2)-N(1)	111.9 (3)	114.5 (8)
N(2)-N(5)	1.445 (4)	1.445 (10)	C(1)-N(2)-N(5)	127.3 (3)	125.5 (9)
N(4)-N(4)	1.256 (1)	1.259 (1)	N(1)-N(2)-N(5)	120.7 (3)	120.0 (8)
N(5)-O(1)	1.213 (3)	1.210 (9)	C(1)-N(3)-C(2)	101.9 (3)	105.4 (8)
N(5)-O(2)	1.196 (3)	1.213 (10)	C(2)-N(4)-N(4)	112.6 (2)	109.8 (5)
			N(2)-N(5)-O(1)	113.3 (3)	114.0 (9)
			N(2)-N(5)-O(2)	115.7 (3)	115.3 (9)
			O(1)-N(5)-O(2)	131.0 (4)	130.7 (9)

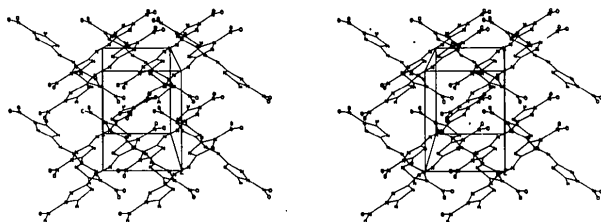


Fig. 2. Stereo drawing of the N-DNATYE structure. The origin is at the upper left rear with view along z.

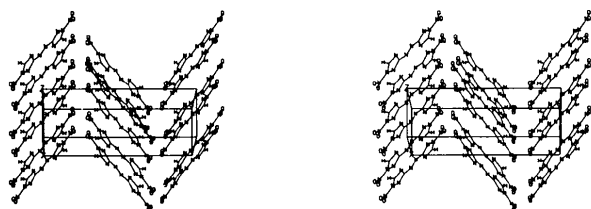


Fig. 3. Stereo drawing of the N-DNATOR structure. The origin is at the upper left rear with view along z. The suggested hydrogen bond is, for example, from the H atom at the lower left to the O atom of the nitro group just above.

In N-DNATYE (Fig. 2) the molecules are seen to alternate in orientation. In N-DNATOR (Fig. 3) the molecules form ribbons with the ribbons forming a herringbone pattern. This latter arrangement is a more efficient packing. Within the ribbons the molecules are disposed so that weak C(1)-H...O(2) hydrogen bonds perhaps form. The angle about H is 163 (5) $^\circ$. The

C(1)...O(2) distance is 3.51 (1) \AA . The ring parameters are similar to other triazoles (see reference below). Likewise, the N=N azo bond is the same as others have found, e.g. in 2,2',4,4',6,6'-hexanitroazobenzene (Graebner & Morosin, 1974).

Related literature. Cromer, Hall, Lee & Ryan (1988) give references on structures of triazoles and small energetic molecules. Gabe, Wang & Le Page (1981) and references therein describe other azo compounds. Sutor (1962) and Cromer, Coburn, Ryan & Wasserman note other possible C-H...O hydrogen bonds.

References

- CROMER, D. T., COBURN, M. D., RYAN, R. R. & WASSERMAN, H. J. (1986). *Acta Cryst.* C42, 1428-1430.
- CROMER, D. T., HALL, J. H., LEE, K.-Y. & RYAN, R. R. (1988). *Acta Cryst.* C44, 1144-1147.
- GABE, E. J., WANG, Y. & LE PAGE, Y. (1981). *Acta Cryst.* B37, 980-981.
- GERMAIN, G., MAIN, P. & WOLFSON, M. M. (1971). *Acta Cryst.* A27, 368-376.
- GRAEBER, E. J. & MOROSIN, B. (1974). *Acta Cryst.* B30, 310-317.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291-296. Munksgaard: Copenhagen.
- LEE, K.-Y. (1985). *Synthesis of 1,1'-Dinitro-3,3'-azo-1,2,4-triazole*. Report LA-10346-MS. Los Alamos National Laboratory, New Mexico, USA.
- SUTOR, D. J. (1962). *Nature (London)*, 195, 68-69.