

Non-linear optical crystals of 2,2,3-trimethyl-3-(1*H*-1,2,3,4-tetrazol-5-yl)-butanenitrile

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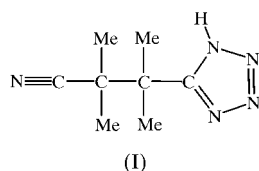
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The title compound, $C_8H_{13}N_5$, is a novel functionally substituted 5-alkyltetrazole. The substituent on the tetrazole C atom is symmetrical, with intrinsic symmetry close to *m*. There is intermolecular $N-H \cdots N$ hydrogen bonding between adjacent tetrazole rings, which is responsible for the formation of one-dimensional polymeric chains running along the *c* axis. The polycrystalline compound exhibits frequency doubling for incident light ($\lambda = 1064$ nm) from a YAG:Nd pulsed laser.

Comment

Interest in 5-monosubstituted tetrazoles has arisen for several reasons. The *N*-unsubstituted tetrazolyl group is a non-classic isostere for the carboxylic acid group and hence may be a suitable substitute for it in drug design (Herr, 2002). Moreover, 5-monosubstituted tetrazoles, since they are coordinated by diverse modes, are interesting ligands in transition metal complexes, and these complexes possess some unique properties (Yelamos *et al.*, 2001). To date, only one 5-alkyltetrazole and two functionally substituted 5-alkyltetrazoles have been structurally characterized [Cambridge Structural Database (CSD); Version 5.24 of November 2002; Allen, 2002], namely 5-methyltetrazole (Ohno *et al.*, 1999), 5-(trichloromethyl)-tetrazole (Geisenberg *et al.*, 1987) and zwitterionic 5-(1-piperidiniomethyl)-1*H*-tetrazolide (Lyakhov *et al.*, 2003). In this paper, we report the synthesis and the molecular and



crystal structures of a novel representative of functionally substituted 5-alkyltetrazoles, *viz.* the title compound, 2,2,3-trimethyl-3-(1*H*-1,2,3,4-tetrazol-5-yl)butanenitrile, (I) (Fig. 1).

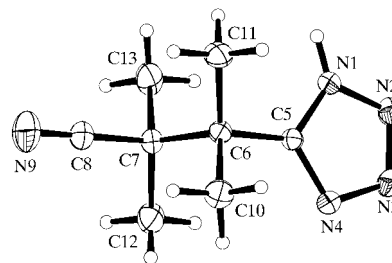


Figure 1
ORTEP-3 (Farrugia, 1997) plot of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

The tetrazole ring geometry in (I) is typical of the 5-substituted tetrazoles listed in the CSD. The $N2=N3$ [1.285 (2) Å] and $N4=C5$ [1.323 (2) Å] formal double bonds are the shortest bonds in the ring, and the ring is planar within 0.001 (1) Å.

The bond distances and angles in the substituent on the C atom of the tetrazole ring (Table 1) are consistent with those observed previously for similar fragments (CSD; Allen, 2002). The substituent is almost symmetrical, with intrinsic symmetry close to *m* (the pseudo-mirror plane is perpendicular to the tetrazole ring plane). If the tetrazole ring was also symmetrical, the space group would be the centrosymmetric *Pcam* group. However, the tetrazole H atom is unambiguously located on only one N atom, and the tetrazole ring is non-symmetrical, so the obtained data correspond to the non-centrosymmetric *Pca2*₁ space group. These results are supported by an investigation of the optical properties of (I). The polycrystalline compound exhibits visually detected frequency doubling for incident pumping light ($\lambda = 1064$ nm, 10 ns pulses, 100 mJ pulse⁻¹) from a YAG:Nd pulsed laser.

Classical intermolecular $N1-H1 \cdots N4(\frac{3}{2}-x, y, \frac{1}{2}+z)$ hydrogen bonds connect adjacent tetrazole rings in the

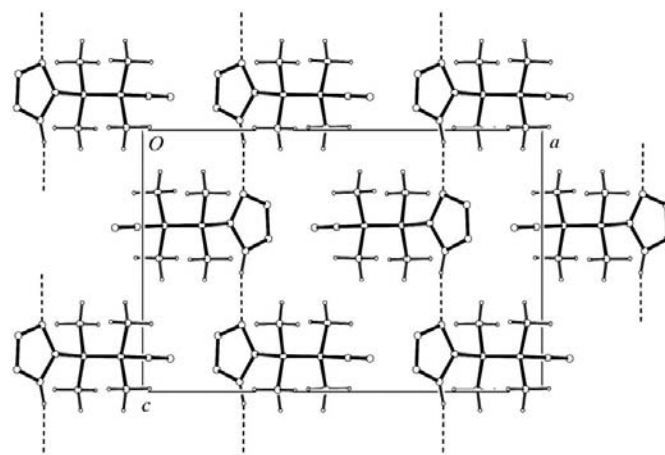


Figure 2
The crystal structure of (I), viewed along the *b* axis. Dashed lines indicate $N-H \cdots N$ hydrogen bonding.

structure of (I) (Table 2). These bonds are responsible for the formation of one-dimensional polymeric chains that extend along the *c* axis (Fig. 2).

Experimental

The title compound was obtained unexpectedly during the cycloaddition of the azide ion to tetramethylsuccinonitrile according to the method described by Finnegan *et al.* (1958). Although there was a twofold excess of azide ions, only one nitrile group was involved in the reaction. A mixture of tetramethylsuccinonitrile (11.0 g, 81 mmol), sodium azide (10.5 g, 162 mmol) and ammonium chloride (8.7 g, 162 mmol) in dimethylformamide (130 ml) was stirred at 388–403 K for 40 h. The solvent was removed at reduced pressure on a steam bath, and the residue was dissolved in water (100 ml) and acidified with concentrated hydrochloric acid (15 ml). The precipitate was filtered off, washed with several portions of water and dried. Crystallization from ethyl acetate gave the title compound [9.4 g, yield 65%; m.p. 462–463 K (decomposition, uncorrected)]. ¹H NMR (100 MHz, DMSO-*d*₆, p.p.m.): δ 1.29 (*s*, 6H, 2CH₃), 1.58 (*s*, 6H, 2CH₃); ¹³C NMR (25 MHz, DMSO-*d*₆, p.p.m.): δ 26.5 (2CH₃), 26.9 (2CH₃), 42.8 and 43.9 (2 × quaternary C), 127.7 (CN), 164.0 (tetrazole C). Single crystals were grown by recrystallization from ethyl acetate at 288–293 K.

Crystal data

C ₈ H ₁₃ N ₅	Mo <i>K</i> α radiation
<i>M_r</i> = 179.23	Cell parameters from 25 reflections
Orthorhombic, <i>Pca</i> 2 ₁	<i>a</i> = 15.070 (3) Å
<i>a</i> = 15.070 (3) Å	<i>b</i> = 6.4292 (12) Å
<i>b</i> = 6.4292 (12) Å	<i>c</i> = 9.8694 (18) Å
<i>c</i> = 9.8694 (18) Å	<i>V</i> = 956.2 (3) Å ³
<i>V</i> = 956.2 (3) Å ³	<i>Z</i> = 4
<i>Z</i> = 4	<i>D_x</i> = 1.245 Mg m ⁻³
<i>D_x</i> = 1.245 Mg m ⁻³	

Data collection

Nicolet <i>R3m</i> four-circle diffractometer	<i>θ</i> _{max} = 30.1°
<i>ω/2θ</i> scans	<i>h</i> = -1 → 21
1571 measured reflections	<i>k</i> = 0 → 9
1475 independent reflections	<i>l</i> = 0 → 13
1309 reflections with <i>I</i> > 2σ(<i>I</i>)	3 standard reflections
<i>R</i> _{int} = 0.028	every 100 reflections
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.0423P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
1475 reflections	$\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
122 parameters	
H-atom parameters constrained	

Methyl H atoms were included at calculated positions (C–H = 0.96 Å) and refined using a riding model, with *U*_{iso}(H) values equal to 1.5*U*_{eq} of the corresponding C atom. The tetrazole H atom was positioned from a Δ*F* map and refined using a riding model, with an N–H distance of 0.86 Å and a *U*_{iso}(H) value equal to 1.2*U*_{eq} of the N atom. Because the compound contains only C, N and H atoms, the absolute structure was not determined.

Table 1

Selected geometric parameters (Å, °).

N1–C5	1.334 (2)	C6–C11	1.536 (3)
N1–N2	1.347 (2)	C6–C7	1.5817 (17)
N2–N3	1.285 (2)	C7–C8	1.4784 (19)
N3–N4	1.365 (2)	C7–C13	1.531 (3)
N4–C5	1.323 (2)	C7–C12	1.532 (3)
C5–C6	1.5113 (16)	C8–N9	1.139 (2)
C6–C10	1.535 (3)		
C5–N1–N2	109.23 (15)	C5–N4–N3	106.59 (15)
N3–N2–N1	106.69 (17)	N4–C5–N1	107.37 (11)
N2–N3–N4	110.12 (17)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···N4 ⁱ	0.86	1.97	2.8004 (18)	162

Symmetry code: (i) $\frac{3}{2} - x, y, \frac{1}{2} + z$.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); 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: AV1140). Services for accessing these data are described at the back of the journal.

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