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1,3,5-Tris(2*H*-tetrazol-5-ylmethoxy)-benzene

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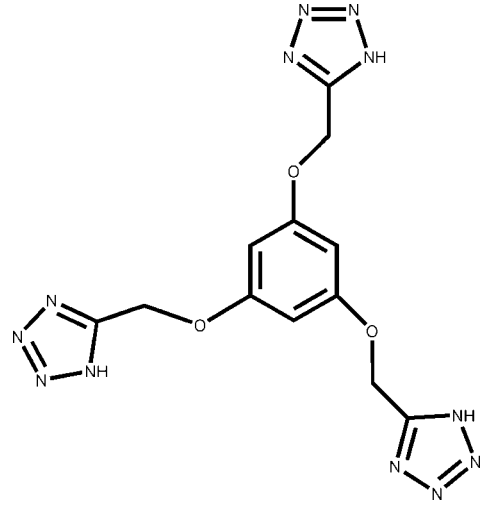
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.054; wR factor = 0.148; data-to-parameter ratio = 14.4.

The title compound, $C_{12}H_{12}N_{12}O_3$, was obtained by the hydrothermal reaction of 1,3,5-tricyanomethoxybenzene and $(CH_3)_3SiN_3$. The molecule is almost planar, with an r.m.s. deviation of 0.0976 Å from the plane through all atoms in the molecule. The three tetrazole rings make dihedral angles of 13.09 (19), 2.01 (19) and 11.56 (18)° with one another and corresponding angles of 8.66 (17), 5.44 (16) and 3.51 (17)° with the central benzene ring. In the crystal structure, intermolecular N—H···N hydrogen bonds form well separated one-dimensional planar sheets.

Related literature

For the use of tetrazole derivatives in coordination chemisty, see: Arp *et al.* (2000); Hu *et al.* (2007); Wang *et al.* (2005); Xiong *et al.* (2002).



Experimental

Crystal data

$C_{12}H_{12}N_{12}O_3$
M_r = 372.34
Triclinic, $P\overline{1}$
a = 4.9851 (4) Å
b = 11.8822 (7) Å
c = 14.1349 (13) Å
α = 99.60 (3)°
β = 92.87 (2)°
γ = 100.943 (15)°
V = 807.64 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 (2) K
0.25 × 0.2 × 0.12 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.891, T_{max} = 1
(expected range = 0.879–0.986)
8398 measured reflections
3686 independent reflections
2653 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.149
S = 1.05
3686 reflections
256 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N7^{i}	0.92 (3)	1.97 (3)	2.872 (3)	168 (3)
N5—H5A···N10^{ii}	0.89 (3)	2.01 (3)	2.892 (2)	171 (3)
N12—H12A···N3^{iii}	0.91 (3)	1.94 (3)	2.840 (3)	174 (2)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x-1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2442).

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supplementary materials

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1,3,5-Tris(2*H*-tetrazol-5-ylmethoxy)benzene

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Comment

In the past five years, we have focused on the chemistry of tetrazole derivatives 5 because of their multiple coordination modes as ligands to metal ions and for the construction of novel metal-organic frameworks (Wang, *et al.* 2005; Xiong, *et al.* 2002). We report here the crystal structure of the title compound, 1,3,5-tris((2*H*-tetrazol-5-yl)methoxy)benzene (I), (Fig.1).

In I, there are three chemically equivalent tetrazole moieties. The bond distances and bond angles of the three tetrazole rings are in the usual ranges (Wang, *et al.* 2005; Arp, *et al.* 2000; Hu, *et al.* 2007). The molecule is almost planar with an r.m.s. deviation of 0.0976 Å from the plane through all atoms in the molecule. Dihedral angles between the C8 and C10, C10 and C12 and C8 and C12 tetrazole rings are 13.56 (15), 2.01 (19) & 11.56 (18)°, respectively. Dihedral angles between the benzene ring and the C8, C10 and C12 tetrazole rings are 8.66 (17), 5.44 (16) & 3.51 (17)°, respectively. In each tetrazole ring, one N=N bond (N2=N3, N6=N7, and N10=N11), is distinctly shorter than the other two N—N distances (Table I). In the crystal structure, inversion related N1—H1A···N7^{i}, N5—H5A···N10^{ii}, and N12—H12A^{iii}···N3 hydrogen bonds link the molecules into infinite planar sheets. (Symmetry codes: (i) −*x* + 2, −*y* − 1, −*z* + 1; (ii) −*x*, −*y*, −*z* + 1; (iii) −*x* + 2, −*y*, −*z* + 2.) (Fig.2).

Experimental

A mixture of benzene-1,3,5-triol (2.5 g, 0.02 mol), 10 g K_2CO_3, 30 ml and acetone 2-bromoacetonitrile (8.6 g, 0.023 mol) was refluxed overnight. After cooling, the resulting dark mixture was extracted with ether (30 ml), and then the extract was removed at reduced pressure to give a pale yellow solid crude product, which was recrystallized in ethanol to obtain white 1,3,5-tricyanomethoxy-benzene (2.4 g, 0.01 mol). A mixture of 1,3,5-tricyanomethoxy-benzene (24 mg, 0.1 mmol) and $(CH_3)_3SiN_3$ (67 mg, 0.6 mmol), ethanol (0.8 ml) and water (0.4 ml) was sealed in a Pyrex tube at 110 °C for one day. On cooling to room temperature, pale yellow block-like crystals suitable for X-ray analysis were obtained.

Refinement

Positional parameters of all H atoms bonded to C were calculated geometrically and allowed to ride on the C atoms to which they are bound, with d(C—H) = 0.93 Å for sp2 or d(C—H) = 0.97Å for sp3 and U_{iso}(H) = 1.2Ueq(C). The N—H hydrogen atoms of tetrazole rings were located in a difference Fourier map and refined freely with isotropic temperature factors.

Figures

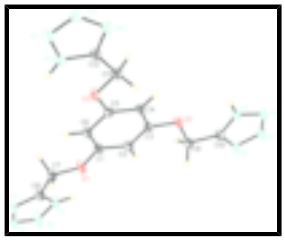

Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

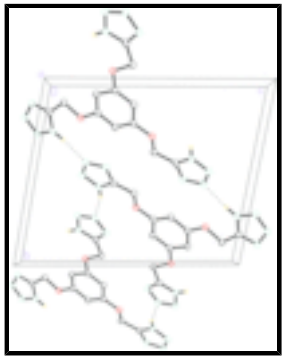

Fig. 2. Crystal packing of the title compound viewed along the *a* axis. All hydrogen atoms not involved in hydrogen bonding (dashed lines) were omitted for clarity.

1,3,5-Tris(2*H*-tetrazol-5-ylmethoxy)benzene

Crystal data

$C_{12}H_{12}N_{12}O_3$	$Z = 2$
$M_r = 372.34$	$F_{000} = 384$
Triclinic, $P\overline{1}$	$D_x = 1.531$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 4.9851$ (4) Å	Cell parameters from 1880 reflections
$b = 11.8822$ (7) Å	$\theta = 3.1$–27.5º
$c = 14.1349$ (13) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 99.60$ (3)º	$T = 293$ (2) K
$\beta = 92.87$ (2)º	Block, colorless
$\gamma = 100.943$ (15)º	0.25 × 0.2 × 0.12 mm
$V = 807.64$ (11) Å^3	

Data collection

Rigaku Mercury2 (2 × 2 bin mode) diffractometer	3686 independent reflections
Radiation source: fine-focus sealed tube	2653 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.036$
$T = 293(2)$ K	$\theta_{max} = 27.5$º
ω scans	$\theta_{min} = 3.1$º
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$h = -6 \rightarrow 6$

T_{min} = 0.891, T_{max} = 1	k = −15→15
8398 measured reflections	l = −18→18

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.054	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.149	$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.2604P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
3686 reflections	$\Delta\rho_{max}$ = 0.53 e Å^{-3}
256 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4944 (3)	0.29164 (13)	0.81580 (10)	0.0364 (4)
O2	0.0878 (3)	0.18419 (13)	0.49413 (10)	0.0343 (4)
O3	−0.1336 (3)	0.50558 (12)	0.70463 (9)	0.0309 (4)
N1	0.8441 (5)	0.23109 (18)	0.93683 (14)	0.0450 (6)
N2	1.0188 (5)	0.21973 (19)	1.00837 (15)	0.0543 (6)
N3	1.0297 (4)	0.30962 (18)	1.07529 (13)	0.0435 (5)
N4	0.8662 (4)	0.38061 (17)	1.04861 (13)	0.0419 (5)
N5	0.0149 (4)	0.07285 (16)	0.31051 (12)	0.0338 (4)
N6	0.0071 (4)	0.00274 (18)	0.22479 (13)	0.0433 (5)
N7	0.1856 (4)	−0.06057 (17)	0.23524 (13)	0.0426 (5)
N8	0.3127 (4)	−0.03434 (16)	0.32650 (12)	0.0369 (5)
N9	−0.6125 (4)	0.66664 (15)	0.62247 (12)	0.0329 (4)
N10	−0.6780 (4)	0.75385 (16)	0.68837 (13)	0.0363 (5)
N11	−0.5411 (4)	0.76527 (16)	0.77066 (13)	0.0381 (5)
N12	−0.3816 (4)	0.68545 (16)	0.75912 (13)	0.0318 (4)

C1	0.3201 (4)	0.31401 (17)	0.74592 (14)	0.0260 (4)
C2	0.3001 (4)	0.23846 (17)	0.65792 (14)	0.0276 (5)
H2A	0.3999	0.1794	0.6492	0.033*
C3	0.1271 (4)	0.25444 (17)	0.58426 (13)	0.0248 (4)
C4	−0.0233 (4)	0.34265 (17)	0.59459 (13)	0.0251 (4)
H4A	−0.1373	0.3525	0.5438	0.030*
C5	0.0037 (4)	0.41535 (16)	0.68380 (13)	0.0235 (4)
C6	0.1764 (4)	0.40318 (17)	0.76073 (13)	0.0262 (4)
H6A	0.1941	0.4533	0.8197	0.031*
C7	0.5606 (5)	0.37403 (19)	0.90189 (14)	0.0337 (5)
H7B	0.3966	0.3825	0.9342	0.040*
H7C	0.6471	0.4494	0.8885	0.040*
C8	0.7525 (4)	0.32884 (18)	0.96283 (14)	0.0304 (5)
C9	0.2734 (4)	0.10828 (18)	0.47337 (14)	0.0288 (5)
H9B	0.2553	0.0514	0.5158	0.035*
H9C	0.4608	0.1520	0.4819	0.035*
C10	0.2012 (4)	0.04925 (17)	0.37119 (14)	0.0271 (4)
C11	−0.2956 (4)	0.52921 (18)	0.62784 (14)	0.0278 (5)
H11A	−0.4333	0.4607	0.6002	0.033*
H11B	−0.1816	0.5516	0.5777	0.033*
C12	−0.4281 (4)	0.62620 (17)	0.66905 (14)	0.0256 (4)
H12A	−0.268 (5)	0.681 (2)	0.8099 (19)	0.048 (7)*
H5A	−0.090 (7)	0.126 (3)	0.318 (2)	0.077 (10)*
H1A	0.808 (6)	0.176 (3)	0.882 (2)	0.064 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0490 (9)	0.0375 (8)	0.0236 (7)	0.0275 (7)	−0.0165 (7)	−0.0079 (6)
O2	0.0413 (9)	0.0390 (8)	0.0234 (7)	0.0269 (7)	−0.0091 (6)	−0.0103 (6)
O3	0.0391 (8)	0.0347 (8)	0.0221 (7)	0.0253 (7)	−0.0067 (6)	−0.0033 (6)
N1	0.0618 (14)	0.0433 (11)	0.0291 (10)	0.0286 (10)	−0.0201 (9)	−0.0090 (9)
N2	0.0733 (16)	0.0548 (13)	0.0368 (11)	0.0376 (12)	−0.0231 (11)	−0.0061 (10)
N3	0.0542 (13)	0.0512 (12)	0.0267 (10)	0.0262 (10)	−0.0139 (9)	−0.0014 (9)
N4	0.0558 (13)	0.0448 (11)	0.0241 (9)	0.0238 (10)	−0.0154 (9)	−0.0069 (8)
N5	0.0411 (11)	0.0361 (10)	0.0257 (9)	0.0227 (9)	−0.0054 (8)	−0.0046 (8)
N6	0.0566 (13)	0.0449 (11)	0.0283 (10)	0.0256 (10)	−0.0070 (9)	−0.0086 (8)
N7	0.0576 (13)	0.0404 (11)	0.0303 (10)	0.0252 (10)	−0.0025 (9)	−0.0078 (8)
N8	0.0483 (12)	0.0362 (10)	0.0279 (9)	0.0245 (9)	−0.0041 (8)	−0.0051 (8)
N9	0.0360 (10)	0.0357 (10)	0.0305 (9)	0.0208 (8)	−0.0076 (8)	0.0030 (8)
N10	0.0386 (11)	0.0351 (10)	0.0391 (10)	0.0221 (8)	−0.0043 (8)	0.0034 (8)
N11	0.0452 (11)	0.0385 (10)	0.0338 (10)	0.0251 (9)	−0.0039 (8)	−0.0009 (8)
N12	0.0381 (10)	0.0347 (10)	0.0258 (9)	0.0218 (8)	−0.0064 (8)	0.0002 (7)
C1	0.0287 (10)	0.0285 (10)	0.0215 (9)	0.0131 (8)	−0.0066 (8)	0.0010 (8)
C2	0.0317 (11)	0.0266 (10)	0.0254 (10)	0.0161 (8)	−0.0037 (8)	−0.0026 (8)
C3	0.0275 (10)	0.0260 (10)	0.0194 (9)	0.0097 (8)	−0.0031 (8)	−0.0032 (8)
C4	0.0262 (10)	0.0293 (10)	0.0205 (9)	0.0127 (8)	−0.0050 (8)	0.0011 (8)
C5	0.0241 (10)	0.0246 (10)	0.0238 (9)	0.0131 (8)	0.0004 (8)	0.0013 (8)

C6	0.0314 (11)	0.0290 (10)	0.0183 (9)	0.0136 (8)	−0.0053 (8)	−0.0022 (8)
C7	0.0420 (12)	0.0352 (12)	0.0234 (10)	0.0191 (10)	−0.0117 (9)	−0.0048 (9)
C8	0.0375 (12)	0.0319 (11)	0.0219 (10)	0.0158 (9)	−0.0064 (9)	−0.0028 (8)
C9	0.0341 (11)	0.0279 (10)	0.0254 (10)	0.0156 (9)	−0.0024 (8)	−0.0020 (8)
C10	0.0317 (11)	0.0247 (10)	0.0261 (10)	0.0122 (8)	−0.0013 (8)	0.0015 (8)
C11	0.0313 (11)	0.0333 (11)	0.0216 (10)	0.0176 (9)	−0.0044 (8)	0.0017 (8)
C12	0.0272 (10)	0.0269 (10)	0.0235 (9)	0.0099 (8)	−0.0036 (8)	0.0032 (8)

Geometric parameters (Å, °)

O1—C1	1.375 (2)	N11—N12	1.344 (2)
O1—C7	1.410 (2)	N12—C12	1.334 (3)
O2—C3	1.384 (2)	N12—H12A	0.91 (3)
O2—C9	1.418 (2)	C1—C6	1.382 (3)
O3—C5	1.378 (2)	C1—C2	1.394 (3)
O3—C11	1.417 (2)	C2—C3	1.379 (3)
N1—C8	1.330 (3)	C2—H2A	0.9300
N1—N2	1.342 (3)	C3—C4	1.393 (3)
N1—H1A	0.92 (3)	C4—C5	1.389 (3)
N2—N3	1.294 (3)	C4—H4A	0.9300
N3—N4	1.362 (3)	C5—C6	1.397 (3)
N4—C8	1.312 (3)	C6—H6A	0.9300
N5—C10	1.333 (3)	C7—C8	1.488 (3)
N5—N6	1.345 (2)	C7—H7B	0.9700
N5—H5A	0.89 (3)	C7—H7C	0.9700
N6—N7	1.288 (3)	C9—C10	1.490 (3)
N7—N8	1.368 (2)	C9—H9B	0.9700
N8—C10	1.315 (3)	C9—H9C	0.9700
N9—C12	1.312 (2)	C11—C12	1.486 (3)
N9—N10	1.373 (2)	C11—H11A	0.9700
N10—N11	1.292 (3)	C11—H11B	0.9700
C1—O1—C7	117.89 (15)	O3—C5—C4	123.76 (16)
C3—O2—C9	116.70 (15)	O3—C5—C6	113.94 (16)
C5—O3—C11	117.10 (15)	C4—C5—C6	122.29 (17)
C8—N1—N2	108.52 (18)	C1—C6—C5	117.55 (17)
C8—N1—H1A	131.7 (18)	C1—C6—H6A	121.2
N2—N1—H1A	119.7 (18)	C5—C6—H6A	121.2
N3—N2—N1	106.11 (18)	O1—C7—C8	106.33 (16)
N2—N3—N4	110.95 (17)	O1—C7—H7B	110.5
C8—N4—N3	105.18 (17)	C8—C7—H7B	110.5
C10—N5—N6	108.75 (17)	O1—C7—H7C	110.5
C10—N5—H5A	131 (2)	C8—C7—H7C	110.5
N6—N5—H5A	120 (2)	H7B—C7—H7C	108.7
N7—N6—N5	105.78 (17)	N4—C8—N1	109.23 (18)
N6—N7—N8	111.65 (17)	N4—C8—C7	125.76 (18)
C10—N8—N7	104.66 (17)	N1—C8—C7	124.96 (17)
C12—N9—N10	105.02 (16)	O2—C9—C10	106.34 (16)
N11—N10—N9	111.16 (16)	O2—C9—H9B	110.5
N10—N11—N12	105.82 (17)	C10—C9—H9B	110.5

C12—N12—N11	109.01 (16)	O2—C9—H9C	110.5
C12—N12—H12A	132.7 (17)	C10—C9—H9C	110.5
N11—N12—H12A	118.2 (17)	H9B—C9—H9C	108.7
O1—C1—C6	123.45 (17)	N8—C10—N5	109.17 (17)
O1—C1—C2	114.07 (16)	N8—C10—C9	125.23 (18)
C6—C1—C2	122.48 (17)	N5—C10—C9	125.60 (17)
C3—C2—C1	117.63 (17)	O3—C11—C12	106.70 (15)
C3—C2—H2A	121.2	O3—C11—H11A	110.4
C1—C2—H2A	121.2	C12—C11—H11A	110.4
C2—C3—O2	122.91 (17)	O3—C11—H11B	110.4
C2—C3—C4	122.66 (17)	C12—C11—H11B	110.4
O2—C3—C4	114.43 (16)	H11A—C11—H11B	108.6
C5—C4—C3	117.38 (17)	N9—C12—N12	108.99 (17)
C5—C4—H4A	121.3	N9—C12—C11	125.19 (17)
C3—C4—H4A	121.3	N12—C12—C11	125.81 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···N7^{i}	0.92 (3)	1.97 (3)	2.872 (3)	168 (3)
N5—H5A···N10^{ii}	0.89 (3)	2.01 (3)	2.892 (2)	171 (3)
N12—H12A···N3^{iii}	0.91 (3)	1.94 (3)	2.840 (3)	174 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*−1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

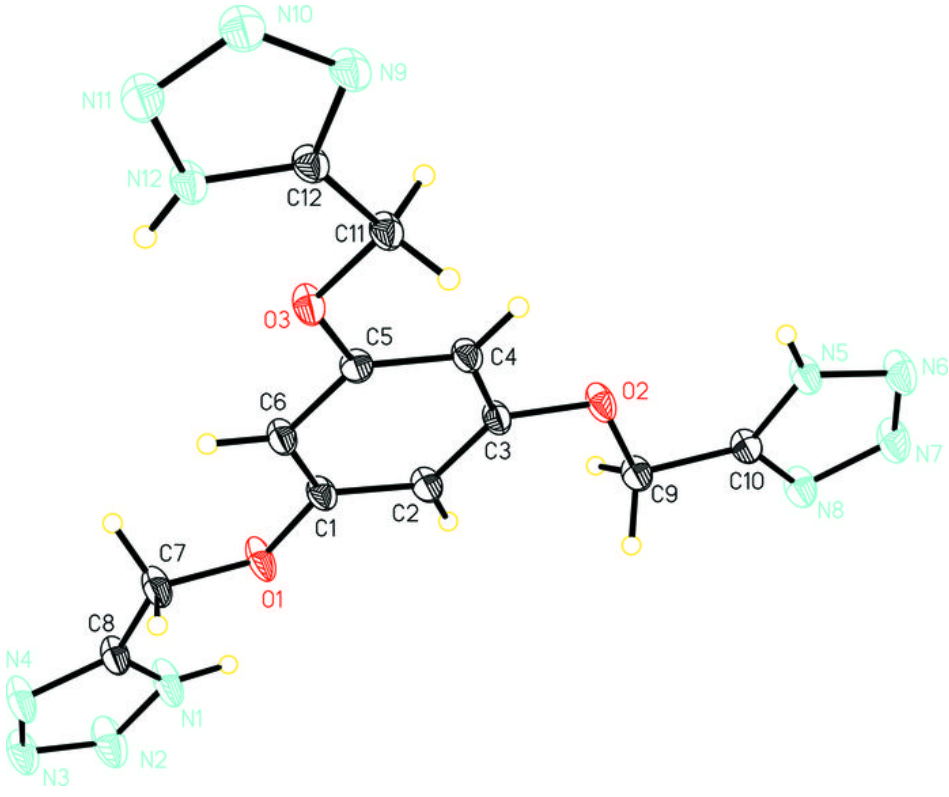
N10
N9
N11
N12
C12
C11
O3
C5
C4
C6
O2
C3
N5
N6
N7
C10
C9
N8
C2
C1
C7
O1
C8
N4
N1
N2
N3

Fig. 2