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# 4,9,12,15-Tetraoxa-3,5,8,10,14,16-hexaazatetracyclo[11.3.0.0$^{2,6}$.0$^{7,11}$]hexadeca-1(16),2,5,7,10,13-hexaen-3-ium-3-olate monohydrate

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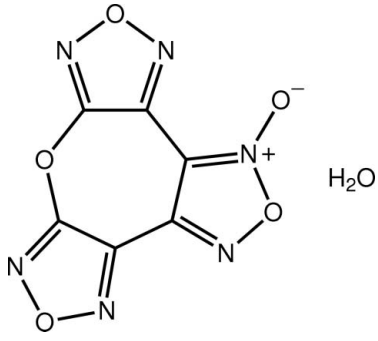
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.036; $wR$ factor = 0.097; data-to-parameter ratio = 12.5.

The organic molecule in the title monohydrate, $C_6N_6O_5\cdot H_2O$, presents an almost planar configuration, the greatest deviation from the least-squares plane through the atoms being 0.061 (1) Å for the O atom within the seven-membered ring. Each water H atom is bifurcated, one forming two O—H···N hydrogen bonds and the other forming O—H···N,O hydrogen bonds. The result of the hydrogen bonding is the formation of supramolecular layers with a zigzag topology that stack along [001].

## Related literature

For background to related energetic materials, see: Sheremetev *et al.* (2010); Zhou *et al.* (2011); Rozhkov *et al.* (2004); Ovchinnikov *et al.* (2009).




## Experimental

### Crystal data

$C_6N_6O_5\cdot H_2O$
$M_r$ = 254.14
Monoclinic, $P2_1/c$
$a$ = 9.324 (4) Å
$b$ = 9.727 (4) Å
$c$ = 10.391 (4) Å
$\beta$ = 106.305 (6)°
$V$ = 904.5 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.17 mm$^{-1}$
$T$ = 296 K
0.23 × 0.18 × 0.15 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.962, $T_{max}$ = 0.975
5058 measured reflections
2146 independent reflections
1808 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
$S$ = 1.04
2146 reflections
172 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.26 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O6—H1···N1$^{i}$ | 0.78 (3) | 2.52 (3) | 3.068 (2) | 128 (2) |
| O6—H1···N3$^{ii}$ | 0.78 (3) | 2.57 (3) | 3.234 (2) | 144 (3) |
| O6—H2···N5$^{iii}$ | 0.90 (3) | 2.40 (3) | 3.201 (2) | 149 (3) |
| O6—H2···O3$^{iii}$ | 0.90 (3) | 2.46 (3) | 3.092 (2) | 127 (3) |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5030).

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# supplementary materials

*Acta Cryst.* (2012). E**68**, o869 [doi:10.1107/S160053681200774X]

# 4,9,12,15-Tetraoxa-3,5,8,10,14,16-hexaazatetracyclo-[11.3.0.0$^{2,6}$.0$^{7,11}$]hexadeca-1(16),2,5,7,10,13-hexaen-3-ium-3-olate monohydrate

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## Comment

Furazan-ether compounds are typical energetic materials known for their high energy-density, large heat of formation and low melting point (Sheremetev *et al.*, 2010; Zhou *et al.*, 2011; Rozhkov *et al.*, 2004; Ovchinnikov *et al.*, 2009). We used 3,4-dinitrofurzanfuroxan as a raw material for the synthesis of a new furazan-ether compound, bifurazano[3,4 - b:3′,4′-f]furoxano[3″,4″-d]oxacyclohetpatriene, through a special etherifying reaction.

The organic molecule in the title monohydrate, $C_6N_6O_5.H_2O$, Fig. 1, presents an almost planar configuration with the greatest deviation from the least-squares plane through the atoms being 0.061 (1) Å for the O atom in the seven-membered ring.

## Experimental

At room temperature, 3,4-dinitrofurzanfuroxan (DNTF) (10.0 g, 0.0321 mol) and anhydrous sodium carbonate (4.6 g, 0.0434 mol) were taken into acetonitrile (25 mL). After reacting at 80 °C for 3.5 h, the resulting solution was transferred into water (80 mL), and then extracted with chloroform (60 mL) three times. The obtained organic phase was dried over anhydrous magnesium sulfate and then filtered. A white solid was obtained, yielding 3.8 g (50.1 %). *M*.pt. 265–267 K. $^{13}$C NMR (500 MHz, DMSO-$d_6$): 160.50, 159.98, 144.39, 137.78, 135.52, 105.03 ppm. IR (KBr, cm$^{-1}$): 1655, 1562, 1384, 1623, 1543, 1470, 997, 1151. Anal. Calcd for $C_6N_6O_5$: C 30.51, N 35.59%. Found C 30.87, N 35.99%. Crystals were obtained by slow evaporation of its acetonitrile-water solution.

## Refinement

The water-H atoms were located from a difference map and freely refined.

## Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

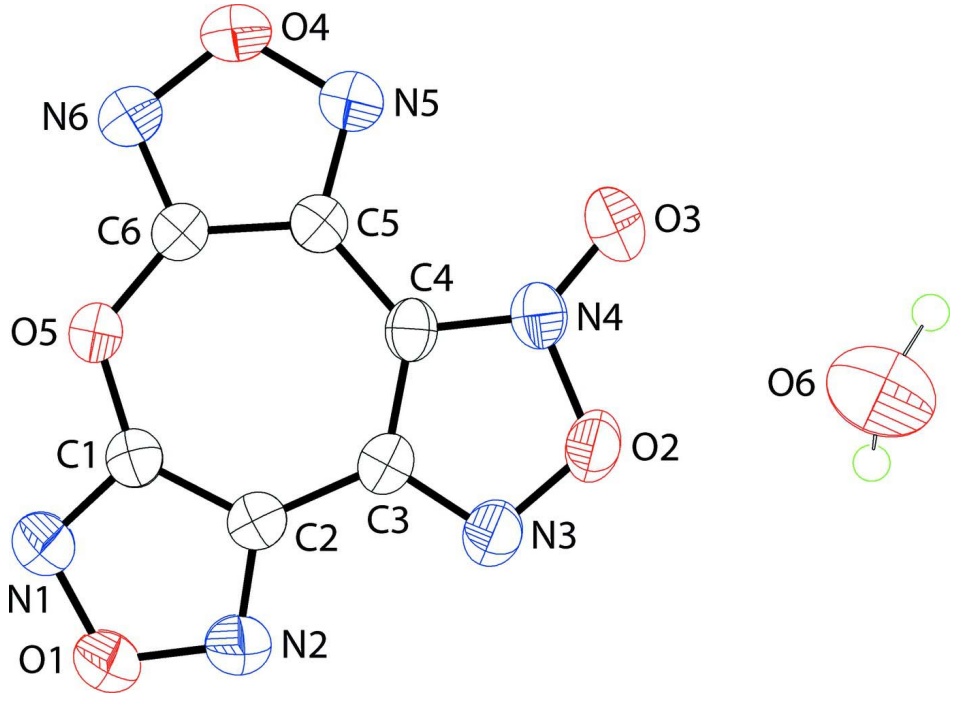


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radius.

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*Crystal data*

$C_6N_6O_5{\cdot}H_2O$
$M_r$ = 254.14
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 9.324 (4) Å
$b$ = 9.727 (4) Å
$c$ = 10.391 (4) Å
$\beta$ = 106.305 (6)°
$V$ = 904.5 (6) Å$^3$
$Z$ = 4
$F(000)$ = 512
$D_x$ = 1.866 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3631 reflections
$\theta$ = 2.9–28.1°
$\mu$ = 0.17 mm$^{-1}$
$T$ = 296 K
Block, yellow
0.23 × 0.18 × 0.15 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.962, $T_{max}$ = 0.975
5058 measured reflections
2146 independent reflections
1808 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025
$\theta_{max}$ = 28.2°, $\theta_{min}$ = 2.3°
$h$ = −12→5
$k$ = −12→12
$l$ = −13→13

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.04$
2146 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.3369P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.009 (2)

*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 $F^2 > \sigma(F^2)$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.26986 (16) | 1.03267 (15) | 0.18452 (14) | 0.0369 (3) |
| C2 | 0.36461 (15) | 0.95599 (14) | 0.29024 (14) | 0.0360 (3) |
| C3 | 0.32627 (16) | 0.87768 (14) | 0.39420 (14) | 0.0357 (3) |
| C4 | 0.18293 (16) | 0.86773 (13) | 0.41014 (13) | 0.0349 (3) |
| C5 | 0.04614 (16) | 0.92642 (14) | 0.32715 (14) | 0.0346 (3) |
| C6 | 0.02700 (15) | 1.00935 (14) | 0.21087 (14) | 0.0347 (3) |
| N1 | 0.34793 (16) | 1.08919 (16) | 0.11423 (15) | 0.0529 (4) |
| N2 | 0.49995 (15) | 0.96680 (16) | 0.28215 (14) | 0.0503 (3) |
| N3 | 0.42478 (15) | 0.81056 (14) | 0.48677 (13) | 0.0466 (3) |
| N4 | 0.19345 (15) | 0.79332 (13) | 0.51789 (12) | 0.0404 (3) |
| N5 | −0.08269 (15) | 0.91226 (14) | 0.34987 (14) | 0.0456 (3) |
| N6 | −0.11096 (15) | 1.04463 (14) | 0.16482 (14) | 0.0456 (3) |
| O1 | 0.49242 (14) | 1.04823 (15) | 0.17392 (13) | 0.0611 (4) |
| O2 | 0.34869 (13) | 0.75438 (12) | 0.56793 (11) | 0.0504 (3) |
| O3 | 0.10766 (14) | 0.75282 (12) | 0.57909 (12) | 0.0529 (3) |
| O4 | −0.18181 (12) | 0.98452 (13) | 0.25032 (12) | 0.0519 (3) |
| O5 | 0.12137 (11) | 1.05420 (11) | 0.14306 (10) | 0.0425 (3) |
| O6 | 0.21407 (18) | 0.18370 (15) | 0.41116 (15) | 0.0614 (4) |
| H1 | 0.290 (3) | 0.221 (3) | 0.442 (3) | 0.096 (10)* |
| H2 | 0.159 (4) | 0.189 (4) | 0.470 (3) | 0.132 (12)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0383 (7) | 0.0365 (7) | 0.0359 (7) | −0.0011 (5) | 0.0104 (6) | 0.0001 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0363 (7) | 0.0351 (7) | 0.0357 (7) | −0.0001 (5) | 0.0086 (5) | −0.0038 (5) |
| C3 | 0.0391 (7) | 0.0320 (7) | 0.0334 (6) | 0.0018 (5) | 0.0059 (5) | −0.0015 (5) |
| C4 | 0.0431 (7) | 0.0287 (6) | 0.0315 (6) | −0.0004 (5) | 0.0084 (5) | 0.0004 (5) |
| C5 | 0.0370 (7) | 0.0305 (6) | 0.0363 (7) | −0.0017 (5) | 0.0102 (5) | −0.0027 (5) |
| C6 | 0.0352 (7) | 0.0328 (6) | 0.0347 (6) | 0.0009 (5) | 0.0077 (5) | −0.0015 (5) |
| N1 | 0.0451 (8) | 0.0623 (9) | 0.0529 (8) | −0.0031 (6) | 0.0162 (6) | 0.0134 (7) |
| N2 | 0.0390 (7) | 0.0614 (9) | 0.0504 (8) | −0.0012 (6) | 0.0123 (6) | 0.0053 (6) |
| N3 | 0.0463 (7) | 0.0464 (7) | 0.0445 (7) | 0.0033 (6) | 0.0084 (6) | 0.0070 (6) |
| N4 | 0.0485 (7) | 0.0346 (6) | 0.0381 (6) | −0.0018 (5) | 0.0121 (5) | 0.0014 (5) |
| N5 | 0.0402 (7) | 0.0492 (7) | 0.0486 (7) | −0.0001 (5) | 0.0143 (6) | 0.0035 (6) |
| N6 | 0.0388 (7) | 0.0493 (7) | 0.0474 (7) | 0.0047 (5) | 0.0100 (5) | 0.0044 (6) |
| O1 | 0.0431 (6) | 0.0820 (9) | 0.0614 (8) | −0.0038 (6) | 0.0197 (6) | 0.0184 (7) |
| O2 | 0.0537 (7) | 0.0486 (6) | 0.0446 (6) | 0.0047 (5) | 0.0067 (5) | 0.0137 (5) |
| O3 | 0.0644 (8) | 0.0499 (7) | 0.0495 (6) | −0.0045 (5) | 0.0245 (6) | 0.0093 (5) |
| O4 | 0.0357 (6) | 0.0612 (7) | 0.0592 (7) | 0.0037 (5) | 0.0141 (5) | 0.0052 (6) |
| O5 | 0.0389 (5) | 0.0492 (6) | 0.0387 (5) | 0.0043 (4) | 0.0101 (4) | 0.0117 (4) |
| O6 | 0.0607 (8) | 0.0617 (8) | 0.0641 (8) | −0.0195 (7) | 0.0214 (7) | −0.0226 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N1 | 1.290 (2) | C6—N6 | 1.2867 (19) |
| C1—O5 | 1.3458 (18) | C6—O5 | 1.3449 (17) |
| C1—C2 | 1.414 (2) | N1—O1 | 1.3744 (19) |
| C2—N2 | 1.292 (2) | N2—O1 | 1.3611 (19) |
| C2—C3 | 1.446 (2) | N3—O2 | 1.3598 (18) |
| C3—N3 | 1.3034 (19) | N4—O3 | 1.2186 (17) |
| C3—C4 | 1.395 (2) | N4—O2 | 1.4444 (18) |
| C4—N4 | 1.3135 (18) | N5—O4 | 1.3716 (18) |
| C4—C5 | 1.442 (2) | N6—O4 | 1.3773 (18) |
| C5—N5 | 1.295 (2) | O6—H1 | 0.78 (3) |
| C5—C6 | 1.422 (2) | O6—H2 | 0.90 (3) |
| | | | |
| N1—C1—O5 | 116.47 (13) | N6—C6—C5 | 109.95 (13) |
| N1—C1—C2 | 109.63 (14) | O5—C6—C5 | 133.21 (13) |
| O5—C1—C2 | 133.88 (13) | C1—N1—O1 | 104.97 (13) |
| N2—C2—C1 | 108.37 (13) | C2—N2—O1 | 106.04 (13) |
| N2—C2—C3 | 122.83 (13) | C3—N3—O2 | 106.07 (13) |
| C1—C2—C3 | 128.80 (13) | O3—N4—C4 | 136.06 (14) |
| N3—C3—C4 | 112.18 (13) | O3—N4—O2 | 117.75 (12) |
| N3—C3—C2 | 122.97 (14) | C4—N4—O2 | 106.19 (12) |
| C4—C3—C2 | 124.82 (12) | C5—N5—O4 | 105.73 (12) |
| N4—C4—C3 | 107.14 (12) | C6—N6—O4 | 104.91 (12) |
| N4—C4—C5 | 124.74 (13) | N2—O1—N1 | 110.99 (12) |
| C3—C4—C5 | 128.12 (13) | N3—O2—N4 | 108.41 (10) |
| N5—C5—C6 | 108.29 (13) | N5—O4—N6 | 111.13 (11) |
| N5—C5—C4 | 123.98 (13) | C6—O5—C1 | 123.18 (11) |
| C6—C5—C4 | 127.73 (13) | H1—O6—H2 | 108 (3) |
| N6—C6—O5 | 116.83 (13) | | |
| | | | |
| N1—C1—C2—N2 | −0.24 (18) | C3—C2—N2—O1 | −179.44 (13) |

| | | | |
|---|---|---|---|
| O5—C1—C2—N2 | 177.82 (16) | C4—C3—N3—O2 | −0.36 (16) |
| N1—C1—C2—C3 | 179.10 (14) | C2—C3—N3—O2 | 177.97 (12) |
| O5—C1—C2—C3 | −2.8 (3) | C3—C4—N4—O3 | 179.40 (16) |
| N2—C2—C3—N3 | −0.9 (2) | C5—C4—N4—O3 | −0.4 (3) |
| C1—C2—C3—N3 | 179.87 (14) | C3—C4—N4—O2 | −1.09 (14) |
| N2—C2—C3—C4 | 177.24 (14) | C5—C4—N4—O2 | 179.08 (12) |
| C1—C2—C3—C4 | −2.0 (2) | C6—C5—N5—O4 | 0.01 (16) |
| N3—C3—C4—N4 | 0.97 (16) | C4—C5—N5—O4 | 179.09 (13) |
| C2—C3—C4—N4 | −177.33 (13) | O5—C6—N6—O4 | 179.16 (12) |
| N3—C3—C4—C5 | −179.21 (14) | C5—C6—N6—O4 | −0.25 (16) |
| C2—C3—C4—C5 | 2.5 (2) | C2—N2—O1—N1 | 0.32 (19) |
| N4—C4—C5—N5 | 0.1 (2) | C1—N1—O1—N2 | −0.46 (19) |
| C3—C4—C5—N5 | −179.73 (14) | C3—N3—O2—N4 | −0.33 (15) |
| N4—C4—C5—C6 | 178.95 (13) | O3—N4—O2—N3 | −179.47 (12) |
| C3—C4—C5—C6 | −0.8 (2) | C4—N4—O2—N3 | 0.92 (15) |
| N5—C5—C6—N6 | 0.16 (17) | C5—N5—O4—N6 | −0.17 (16) |
| C4—C5—C6—N6 | −178.88 (13) | C6—N6—O4—N5 | 0.26 (17) |
| N5—C5—C6—O5 | −179.12 (15) | N6—C6—O5—C1 | 175.58 (13) |
| C4—C5—C6—O5 | 1.8 (3) | C5—C6—O5—C1 | −5.2 (2) |
| O5—C1—N1—O1 | −178.03 (13) | N1—C1—O5—C6 | −175.61 (14) |
| C2—C1—N1—O1 | 0.41 (18) | C2—C1—O5—C6 | 6.4 (2) |
| C1—C2—N2—O1 | −0.06 (17) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O6—H1···N1$^{i}$ | 0.78 (3) | 2.52 (3) | 3.068 (2) | 128 (2) |
| O6—H1···N3$^{ii}$ | 0.78 (3) | 2.57 (3) | 3.234 (2) | 144 (3) |
| O6—H2···N5$^{iii}$ | 0.90 (3) | 2.40 (3) | 3.201 (2) | 149 (3) |
| O6—H2···O3$^{iii}$ | 0.90 (3) | 2.46 (3) | 3.092 (2) | 127 (3) |

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, −*y*+1, −*z*+1.