**Three peroxomorphic $H_2O_2$ adducts of antibiotic furacin: the first cases of 2D hydrogen-bonded peroxide layers and concerted flip-flop hydrogen disorder of peroxide species.**

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**Table S1.** Geometric parameters of hydrogen bonds in the structure **1**.

| D–H…A | D–H, Å | H…A, Å | D…A, Å | ∠ D–H…A, ° |
|---|---|---|---|---|
| O1–H1…O4 | 0.849(19) | 2.449(19) | 3.2261(12) | 152.5(16) |
| O1–H1…O5 | 0.849(19) | 2.334(19) | 3.0429(13) | 141.3(16) |
| O2–H2…O3[1] | 0.881(19) | 1.791(19) | 2.6603(13) | 168.8(16) |
| N1–H11…O1 | 0.863(18) | 2.404(18) | 3.2246(14) | 159.1(15) |
| N1–H12…O6[2] | 0.856(17) | 2.477(17) | 3.2171(13) | 145.2(14) |
| N2–H21…O5[3] | 0.833(17) | 2.433(17) | 3.0798(13) | 135.1(14) |

[1] x, y-1, z; [2] x-½, -y+½, z+½; [3] x, y+1, z

**Table S2.** Geometric parameters of hydrogen bonds in the structure **2**.

| D–H…A | D–H, Å | H…A, Å | D…A, Å | ∠ D–H…A, ° |
|---|---|---|---|---|
| O1–H1…O3[1] | 0.876(18) | 1.878(18) | 2.7390(11) | 167.1(16) |
| O2–H2…O3 | 0.899(18) | 1.794(18) | 2.6893(11) | 173.2(17) |
| O7–H7…O5 | 0.837(19) | 2.23(2) | 2.9968(12) | 152.8(17) |
| O7–H7…O4 | 0.837(19) | 2.238(19) | 2.9043(11) | 136.6(17) |
| N1–H11…O7 | 0.839(16) | 2.324(16) | 3.1188(13) | 158.1(14) |
| N1–H12…O1 | 0.876(16) | 2.282(16) | 3.0927(13) | 153.9(14) |
| N2–H21…O2[2] | 0.879(16) | 2.028(16) | 2.8681(11) | 159.7(14) |

[1] -x+3/2, y+1/2, -z+1/2; [2] -x+3/2, y-1/2, -z+1/2

**Table S3.** Geometric parameters of hydrogen bonds in the structure **3**.

| D–H…A | D–H, Å | H…A, Å | D…A, Å | ∠ D–H…A, ° |
|---|---|---|---|---|
| O1–H1…O13 | 0.87(2) | 1.82(2) | 2.6958(15) | 180(2) |
| O2–H2A…O8 | 0.92(4) | 1.82(4) | 2.7379(17) | 173(4) |
| O2–H2B…O3[1] | 0.91(5) | 2.17(5) | 3.0409(19) | 159(4) |
| O3–H3…O23[1] | 0.89(2) | 1.81(2) | 2.6967(16) | 175(2) |
| O4–H4…O1 | 0.84(3) | 2.03(3) | 2.8582(17) | 166(2) |
| O5–H5…O22A | 0.95(2) | 1.87(2) | 2.8125(17) | 171(2) |
| O6–H6A…O6[1] | 0.92(7) | 1.86(6) | 2.728(3) | 155(7) |
| O6–H6B…O8[2] | 0.85 | 1.89 | 2.7371(19) | 179.9 |
| O7–H7…O4[2] | 0.847(10) | 2.121(13) | 2.906(2) | 154(2) |
| O8–H8B…O2 | 0.853(10) | 1.910(16) | 2.7379(17) | 163(4) |
| O8–H8A…O6[2] | 0.853(10) | 1.916(18) | 2.7371(19) | 161(4) |
| O9–H9…O12 | 0.877(10) | 1.935(10) | 2.8112(17) | 178(2) |
| O10–H10…O7 | 0.853(9) | 2.078(10) | 2.9272(19) | 173(2) |
| O11–H11…O14 | 0.85(2) | 2.29(2) | 3.0766(15) | 153.2(19) |
| O11–H11…O15 | 0.85(2) | 2.30(2) | 2.9728(16) | 136.7(18) |
| O12–H12…O23[3] | 0.86(2) | 1.85(2) | 2.6755(15) | 160(2) |
| O21A–H21…O24 | 0.906(16) | 2.262(18) | 3.0696(15) | 148.3(17) |
| O21A–H21…O25 | 0.906(16) | 2.33(2) | 2.9866(16) | 129.0(17) |
| O21B–H21…O24 | 0.926(16) | 2.262(18) | 3.079(14) | 147(2) |
| O21B–H21…O25 | 0.926(16) | 2.33(2) | 3.014(15) | 130(2) |
| O22A–H22…O13 | 0.914(16) | 1.90(2) | 2.7098(15) | 146.7(18) |
| O22B–H22…O13 | 0.933(16) | 1.90(2) | 2.605(15) | 130.7(17) |
| N11–H16…O11 | 0.82(2) | 2.33(2) | 3.1181(18) | 163.5(18) |
| N11–H17…O2 | 0.79(2) | 2.45(2) | 3.1696(19) | 153.7(18) |
| N12–H18…O25 | 0.85(2) | 2.12(2) | 2.9562(16) | 169.2(19) |
| C12–H13…O26 | 0.950(18) | 2.441(18) | 3.3795(18) | 169.7(15) |
| N21–H26…O21A | 0.833(19) | 2.408(19) | 3.2155(18) | 163.6(16) |
| N21–H26…O21B | 0.833(19) | 2.38(2) | 3.188(16) | 162.8(17) |
| N21–H27…O4 | 0.80(2) | 2.34(2) | 3.0779(18) | 154.3(18) |
| N22–H28…O15[4] | 0.82(2) | 2.19(2) | 2.9938(16) | 166.4(19) |
| C22–H23…O16[4] | 0.934(18) | 2.494(18) | 3.4270(18) | 176.8(15) |

[1] -x, -y+1, -z; [2] -x+1, -y+1, -z; [3] x+1, y-1, z; [4] x-1, y+1, z

**Compounds and Solvents.** Furacin was obtained by vacuum evaporation of 1:1500 pharmaceutical solution in 70% ethanol (Yaroslavl pharmaceutical factory, Russia).

60 wt% hydrogen peroxide was purchased from Fisher Scientific (Loughborough, UK). 96 wt% hydrogen peroxide was prepared by an evaporation method.[S1] Handling procedures for concentrated hydrogen peroxide are described in detail (danger of explosion!).[S2,S3]

When dissolving organic compounds in concentrated hydrogen peroxide, the following safety precautions must be observed:

1) The volume of hydrogen peroxide should not exceed 0.5 ml;

2) The temperature of solutions should not rise above 40° C, since with a further increase in temperature, self-accelerating oxidation processes may begin;

3) Only vials with PTFE septa and screw caps with holes should be used to prevent pressure build-up;

4) It is not recommended to tightly wrap the caps of the vials during long-term storage.

Yellow-orange crystals of **1**, **2**, and **3** were obtained by cooling to -21°C (for **1**) or -35°C (for **2** and **3**) saturated solutions (rt) of furacin in 96%, 50%, and 20% hydrogen peroxide, respectively. These samples were prepared by dissolving approximately 10-15 mg of furacin in 0.25 ml of hydrogen peroxide solutions in 2 ml vials.

According to our rough estimates, the solubility of furacin in 96% $H_2O_2$ is approximately an order of magnitude higher than in water or ethanol. Apparently, concentrated hydrogen peroxide is the best solvent for furacin among all known ones.

[S1] M. V. Vener, A. V. Churakov, A. P. Voronin, O. D. Parashchuk, S. V. Artobolevskii, O. A. Alatortsev, D. E. Makhrov, A. G. Medvedev, A. Filarowski, *Molecules* **2022**, *27*, 717(1-13).

[S2] W. C. Schumb, C. N.Satterfield, R. P. Wentworth, *Hydrogen peroxide,* Reinhold publishing corp., New York, **1955**.

[S3] O. Maass, W. H. Hatcher, *J. Am. Chem. Soc.* **1920**, *42*, 2548-2569.

**Table S4.** Crystal data and details of X-ray analysis.

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_6H_8N_4O_6$ | $C_6H_9N_4O_7$ | $C_{12}H_{26}N_8O_{22}$ |
| *F*w | 232.16 | 249.17 | 634.41 |
| colour, habit | yellow, prism | orange, prism | orange, plate |
| cryst size (mm) | 0.22×0.08×0.04 | 0.25×0.20×0.20 | 0.45×0.20×0.03 |
| temperature (K) | 100 | 100 | 100 |
| crystal system | monoclinic | monoclinic | triclinic |
| space group | $P2_1/n$ | $C2/c$ | $P$-1 |
| $a$ (Å) | 7.3836(3) | 12.6420(4) | 8.8432(3) |
| $b$ (Å) | 8.3568(3) | 8.4671(3) | 12.7456(5) |
| $c$ (Å) | 15.1792(5) | 18.6298(6) | 13.2427(5) |
| $\alpha$ (deg) | 90 | 90 | 105.6813(13) |
| $\beta$ (deg) | 98.580(1) | 101.447(1) | 108.5010(13) |
| $\gamma$ (deg) | 90 | 90 | 103.7032(14) |
| $V$ (Å$^3$) | 926.12(6) | 1954.49(11) | 1274.85(8) |
| $Z$ | 4 | 8 | 2 |
| $D_c$ (g·cm$^{-3}$) | 1.665 | 1.694 | 1.653 |
| $\mu$ (mm$^{-1}$) | 0.150 | 0.156 | 0.161 |
| $F$(000) | 480 | 1032 | 660 |
| $\theta$ range (deg) | 2.71 to 28.00 | 2.23 to 30.00 | 1.77 to 29.00 |
| refl collcd | 12635 | 15596 | 19704 |
| indep reflns / $R_{int}$ | 2228 / 0.025 | 2855 / 0.026 | 6764 / 0.028 |
| reflns $I>2\sigma(I)$ | 1987 | 2473 | 5311 |
| No of param | 178 | 190 | 495 |
| GooF on $F^2$ | 1.029 | 1.048 | 1.027 |
| $R_1$ ($I>2\sigma(I)$) | 0.0315 | 0.0315 | 0.0426 |
| $wR_2$(all data) | 0.0799 | 0.0844 | 0.1107 |
| largest diff peak / hole (e·Å$^{-3}$) | 0.35 / -0.21 | 0.37 / -0.26 | 0.45 / -0.39 |
| CCDC number | 2279089 | 2279090 | 2279091 |

**X-ray crystallography**

The samples were withdrawn from the crystallization vials using corrosion-resistant steel spatula and immediately placed inside a drop of perfluorinated Fomblin YR-1800 oil on the microscope slides. The appropriate single crystals were mounted on the top of Mitegen MicroLoops and transferred instantly to a cold nitrogen stream on the diffractometer.

Experimental data sets were collected on a Bruker D8 Venture diffractometer using graphite monochromatized Mo-*K*α radiation (λ = 0.71073 Å). Absorption corrections based on measurements of equivalent reflections were applied.[S4] The structures were solved by direct methods and refined by full matrix least-squares on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms.[S5] In all cases, partial substitutional disorder of hydrogen peroxide by water molecules[S6-S9] was not observed since no residual peaks with an intensity more than 0.3 e·A$^{-3}$ were seen in the hydrogen peroxide molecule regions. All hydrogen atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters (except for peroxide molecules in **3**). In the structure **3**, atoms H2, H6 and H8 were found to be equally disordered over two positions; all peroxide H atoms were refined with restrained O-H distances. Details of X-ray studies are listed in Table S4. The single-crystal X-ray

diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS. Crystallographic data deposited with Cambridge Structural Database (see Table S4).

[S4] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.
[S5] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
[S6] A. V. Churakov, P. V. Prikhodchenko, J. A. K. Howard, *CrystEngComm* **2005**, *7*, 664-669.
[S7] B. F. Pedersen, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 746-754.
[S8] B. F. Pedersen, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 1014-1016.
[S9] G. Laus, V. Kahlenberg, K. Wurst, T. Lörting, H. Schottenberger, *CrystEngComm* **2008**, *10*, 1638-1644.

**Optical microscopy.** Photos of crystalline 1 were taken on Olympus SZ-61TR stereomicroscope equipped with CAM-LC30 camera at 50x magnification. Thermographic movie was recorded on Olympus BX43 microscope equipped with QIClick 1394 video camera and Linkam DSC600 heating stage in temperature range 30-120° C at heating rate 10 deg/sec.

**Figure S1.** Hydrogen bonded 2D layers parallel to the (101) plane of the lattice in the structure **1**.

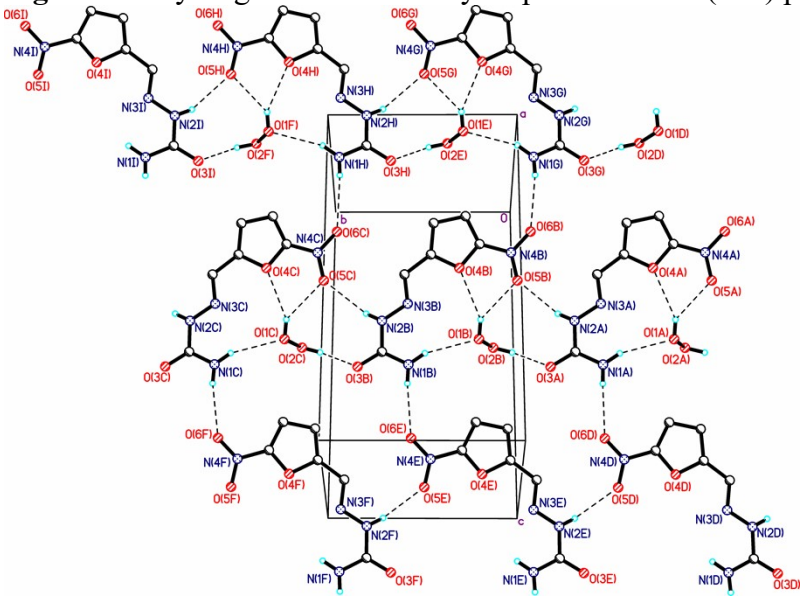

**Figure S2.** The [2,2] hydrogen bonding mode for H7-O7-O7A-H7A molecule in the structure **2**.

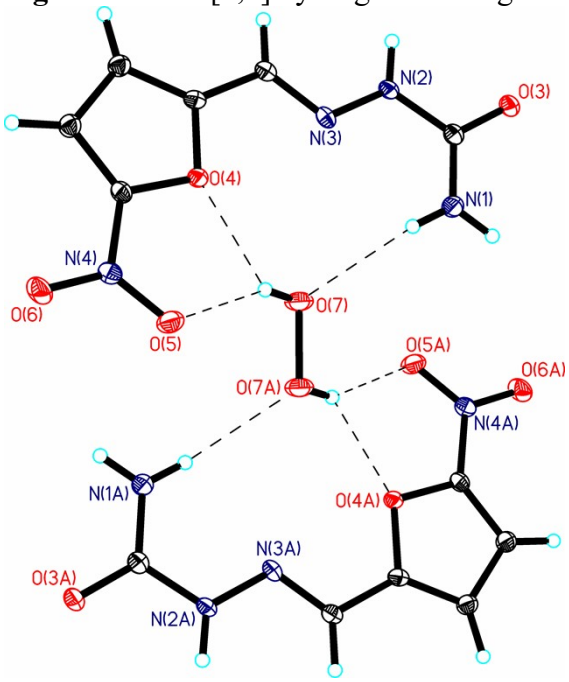


**Figure S3.** The [2,2] hydrogen bonding mode H1-O1-O2-H2 molecule in the structure **2**.

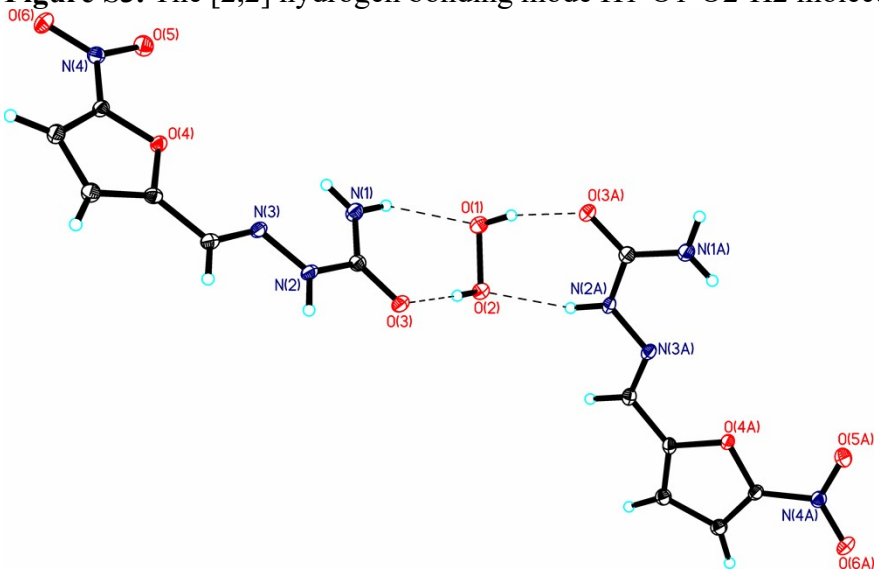

**Figure S4.** Hydrogen bonded 3D packing motif in the structure **2**.

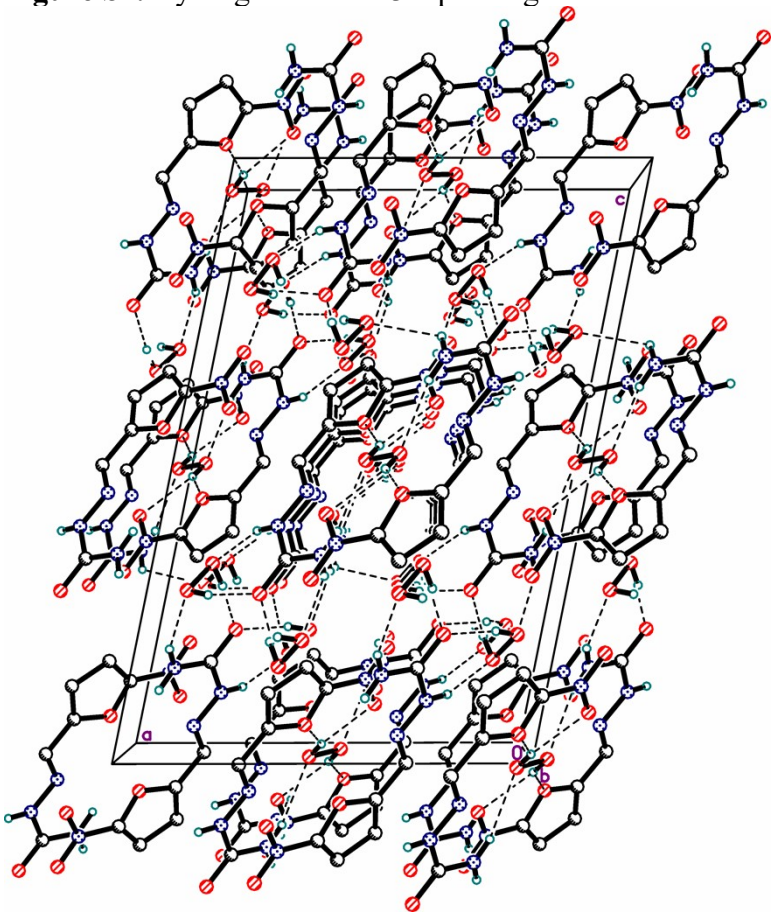

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**Figure S5.** Hydrogen bonds (dashed lines) formed by H1-O1-O2-H2 molecule in **3**.

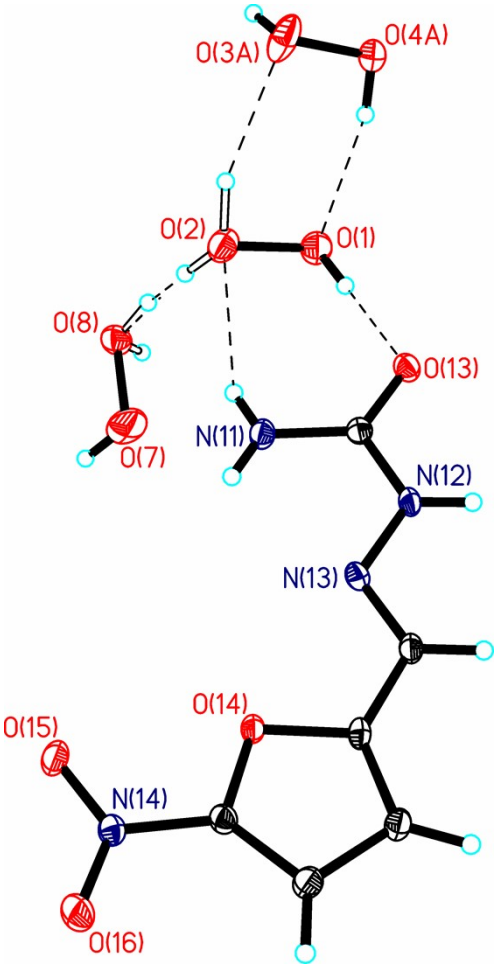


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**Figure S6.** Hydrogen bonds (dashed lines) formed by H3-O3-O4-H4 molecule in **3**.

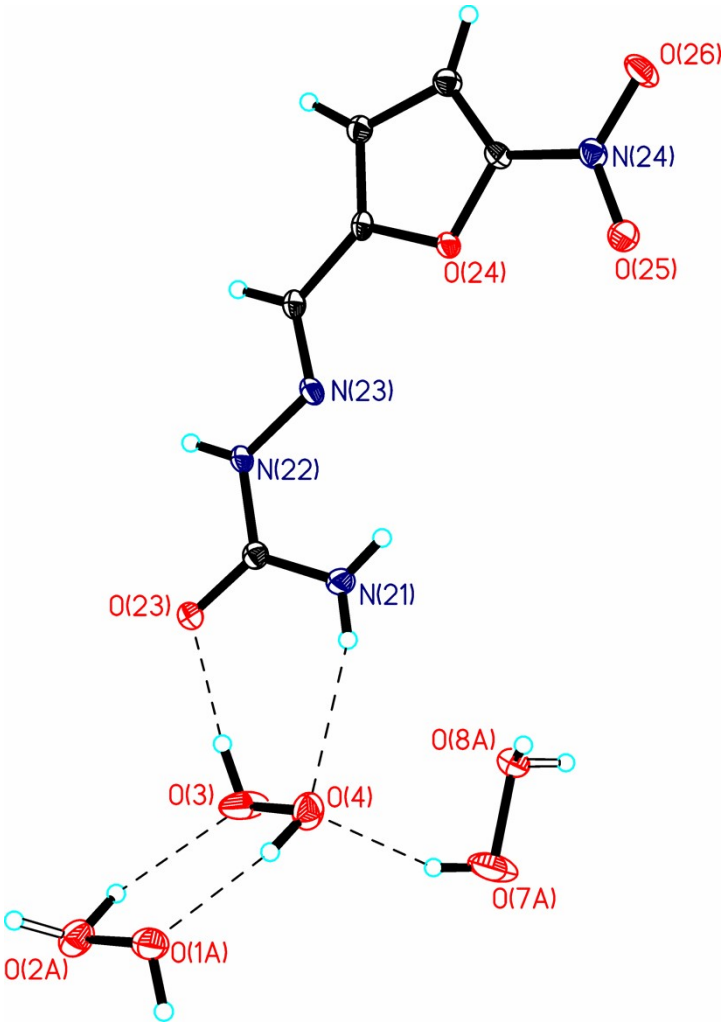


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**Figure S7.** Hydrogen bonds (dashed lines) formed by H5-O5-O6-H6 molecule in **3**.

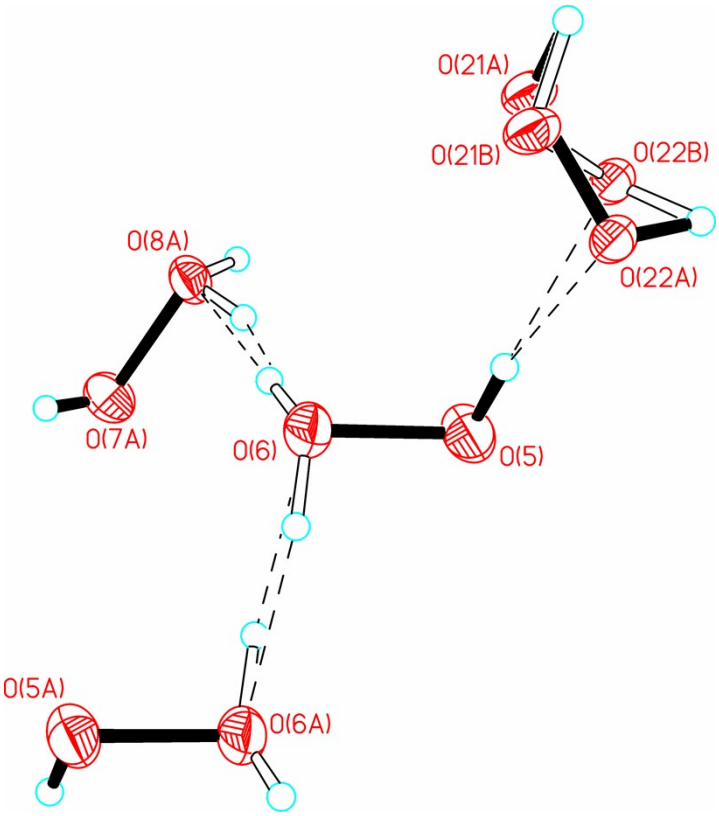


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**Figure S8.** Hydrogen bonds (dashed lines) formed by H7-O7-O8-H8 molecule in **3**.

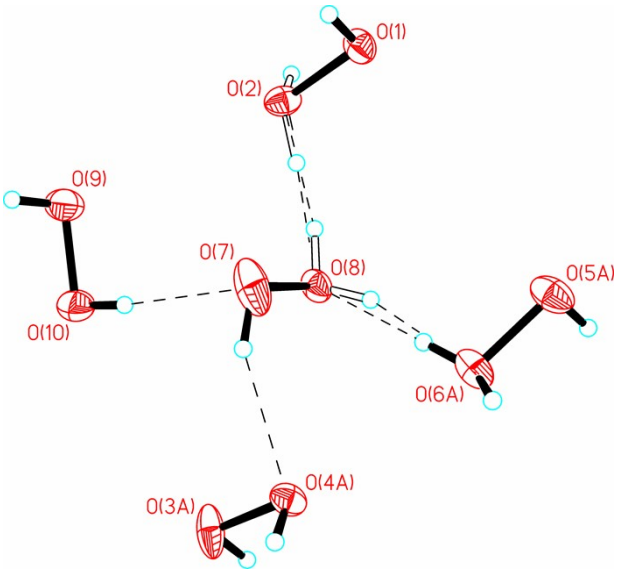


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**Figure S9.** Hydrogen bonds (dashed lines) formed by H9-O9-O10-H10 molecule **3**.

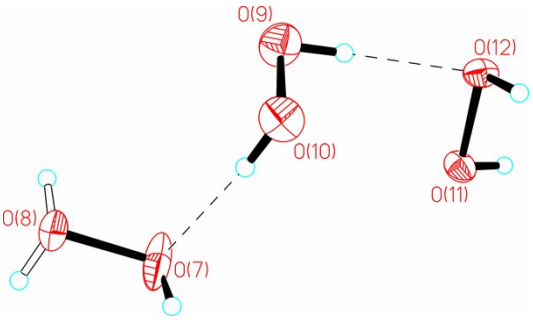


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**Figure S10.** Hydrogen bonds (dashed lines) formed by H11-O11-O12-H12 molecule in **3**.

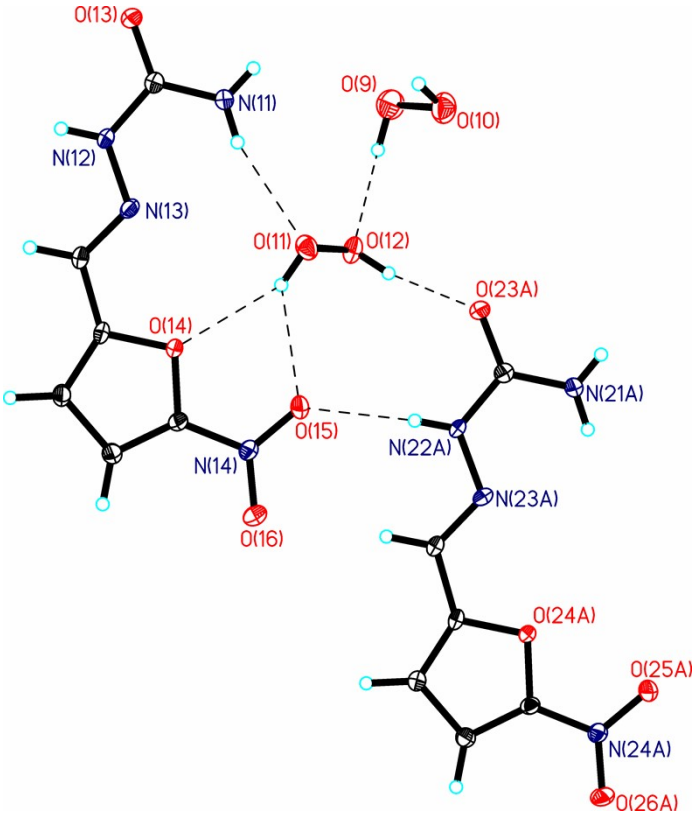


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**Figure S11.** Hydrogen bonds (dashed lines) formed by H21-O21-O22-H22 molecule in **3**.