

Butane-1,2,3,4-tetracarboxylic acid–4,4'-bipyridine (1/2)

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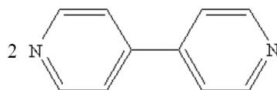
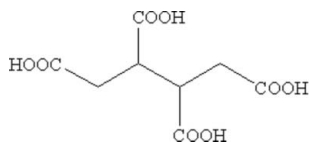
Received 17 July 2009; accepted 23 July 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.061; wR factor = 0.176; data-to-parameter ratio = 12.0.

The hydrothermal reaction of butane-1,2,3,4-tetracarboxylic acid (H_4butca), 4,4'-bipyridine (bipy) and $\text{Mn}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ afforded a new co-crystal, $\text{C}_8\text{H}_{10}\text{O}_8 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2$ or $\text{H}_4\text{butca} \cdot 2(\text{bipy})$, in which strong $\text{O}-\text{H} \cdots \text{N}$ hydrogen-bonding and weak $\pi-\pi$ stacking [centroid-centroid distance = 3.8459 (19) Å] interactions assemble the organic molecules into a three-dimensional supramolecular framework. $\text{C}-\text{H} \cdots \text{O}$ interactions are also present. The whole molecule has inversion symmetry.

Related literature

For the importance of hydrogen-bonding and $\pi-\pi$ stacking interactions in supramolecular chemistry, crystal engineering and biological recognition, see: Wang *et al.* (2007). Many organic co-crystals have been assembled from N -heterocycles and polycarboxylic acids, see: Li *et al.* (2007). For the 1:1 co-crystal $\text{H}_4\text{butca} \cdot \text{bipy}$, see: Najafpour *et al.* (2008).



Experimental

Crystal data

$\text{C}_8\text{H}_{10}\text{O}_8 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2$

$M_r = 546.53$

Triclinic, $P\bar{1}$
 $a = 7.4435$ (11) Å
 $b = 8.6990$ (13) Å
 $c = 11.438$ (2) Å
 $\alpha = 99.819$ (3)°
 $\beta = 105.662$ (3)°
 $\gamma = 111.361$ (2)°

$V = 633.57$ (17) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 296$ K
 $0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.969$, $T_{\max} = 0.969$

3287 measured reflections
 2196 independent reflections
 1721 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.176$
 $S = 1.07$
 2196 reflections

183 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.78$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{C14}-\text{H14} \cdots \text{O4}$ | 0.93 | 2.56 | 3.476 (3) | 168 |
| $\text{C9}-\text{H9} \cdots \text{O2}$ | 0.93 | 2.51 | 3.425 (4) | 167 |
| $\text{O3}-\text{H3A} \cdots \text{N1}^i$ | 0.82 | 1.78 | 2.595 (3) | 170 |
| $\text{O2}-\text{H2} \cdots \text{N2}^{ii}$ | 0.82 | 1.84 | 2.642 (3) | 167 |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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: AT2847).

References

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supplementary materials

Acta Cryst. (2009). E65, o2016 [doi:10.1107/S1600536809029237]

Butane-1,2,3,4-tetracarboxylic acid-4,4'-bipyridine (1/2)

N. Zhang, X.-M. Shi, M. Shao and M.-X. Li

Comment

Organic cocrystals involving hydrogen-bonding (Table 1, Fig. 2) and π - π stacking [between the (N1/C5–C9) pyridine rings of 4,4'-bipyridine group, centroid-to-centroid distance = 3.8459 (19) Å] interactions are important in the areas of supramolecular chemistry, crystal engineering, and biological recognition (Wang *et al.*, 2007). Many organic cocrystals have been assembled from N-heterocycle and polycarboxylic acids (Li *et al.*, 2007). 4,4'-Bipyridine (bipy) and butane-1,2,3,4-tetracarboxylic acid (H₄butca) are important organic ligands in preparing metal complexes.

In our course of preparing ternary complexes containing butane-1,2,3,4-tetracarboxylic acid and 4,4'-bipyridine, a new 1:2 cocrystal compound of H₄butca.2bipy was prepared unexpectedly. Previously, a 1:1 cocrystal of H₄butca.bipy has been synthesized by solution reaction (Najafpour, *et al.*, 2008). Herein we report the supramolecular framework of the title compound (I) (Fig. 1). The whole molecule has an inversion symmetry which lies on the midpoint of the C3—C3Aa bond of the butane-1,2,3,4-tetracarboxylic acid moiety.

Experimental

A mixture of H₄butca (0.0468 g, 0.2 mmol), 4,4'-bipyridine (0.0468 g, 0.30 mmol), Mn(SO₄)₂·H₂O (0.0510 g, 0.3 mmol) and H₂O (10 ml) was sealed in a 15 ml Teflon-lined stainless-steel reactor, which was heated at 413 K for 72 h. The reaction mixture was cooled to room temperature at a rate of 10 K h⁻¹. Light yellow block crystals suitable for X-ray diffraction were obtained in 56% yield (0.0273 g, based on H₄butca). Analysis calculated for C₂₈H₂₆N₄O₈ (%): C 61.53, H 4.795, N 10.25. Found: C 61.16, H 4.622, N 10.23. IR (KBr pellet, cm⁻¹): 3093w, 3040w, 2921w, 1711 s, 1601 s, 1539m, 1498m, 1414 s, 1396 s, 1365m, 1285 s, 1217 s, 1128 s, 1071 s, 1005 s, 882m, 816 s, 626 s, 534m.

Refinement

All H atoms were located geometrically, with C—H distances of 0.93 - 0.98 Å, O—H distances of 0.82 Å, and allowed to ride on their respective parent atoms with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Figures

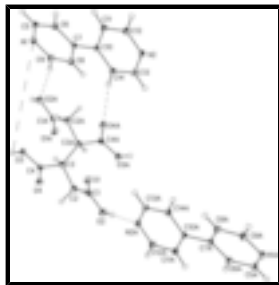


Fig. 1. View of (I), showing displacement ellipsoids drawn at the 30% probability level.

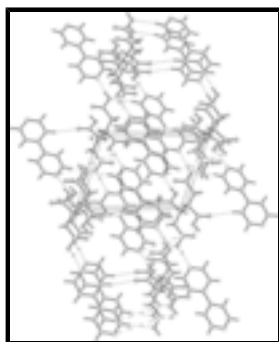


Fig. 2. Crystal packing diagram of compound (I)

Butane-1,2,3,4-tetracarboxylic acid–4,4'-bipyridine (1/2)

Crystal data

$C_8H_{10}O_8 \cdot 2C_{10}H_8N_2$

$M_r = 546.53$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.4435$ (11) Å

$b = 8.6990$ (13) Å

$c = 11.438$ (2) Å

$\alpha = 99.819$ (3)°

$\beta = 105.662$ (3)°

$\gamma = 111.361$ (2)°

$V = 633.57$ (17) Å³

$Z = 1$

$F_{000} = 286$

$D_x = 1.432$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1387 reflections

$\theta = 2.6$ – 26.6 °

$\mu = 0.11$ mm⁻¹

$T = 296$ K

Block, colourless

$0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

2196 independent reflections

1721 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$

$\theta_{max} = 25.0$ °

$\theta_{min} = 2.6$ °

$h = -8 \rightarrow 8$

$T_{\min} = 0.969$, $T_{\max} = 0.969$
3287 measured reflections

$k = -9 \rightarrow 10$
 $l = -13 \rightarrow 9$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | H-atom parameters constrained |
| $wR(F^2) = 0.176$ | $w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.4629P]$ |
| $S = 1.07$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2196 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 183 parameters | $\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$ |
| | 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|------------|-------------|----------------------------------|
| C1 | -0.1342 (5) | 0.6302 (4) | -0.0696 (3) | 0.0508 (7) |
| C2 | -0.0232 (5) | 0.7892 (4) | 0.0456 (3) | 0.0597 (9) |
| H2A | -0.1212 | 0.7939 | 0.0858 | 0.072* |
| H2B | 0.0844 | 0.7742 | 0.1058 | 0.072* |
| C3 | 0.0728 (5) | 0.9587 (3) | 0.0242 (3) | 0.0548 (8) |
| H3 | 0.1316 | 0.9400 | -0.0410 | 0.066* |
| C4 | 0.2542 (5) | 1.0895 (4) | 0.1447 (3) | 0.0498 (7) |
| C5 | -0.2914 (4) | 0.4885 (4) | 0.4266 (3) | 0.0479 (7) |
| H5 | -0.3917 | 0.4111 | 0.4485 | 0.057* |
| C6 | -0.1373 (4) | 0.6347 (4) | 0.5207 (3) | 0.0449 (7) |
| H6 | -0.1346 | 0.6548 | 0.6038 | 0.054* |
| C7 | 0.0146 (4) | 0.7522 (3) | 0.4900 (2) | 0.0368 (6) |
| C8 | -0.0007 (4) | 0.7138 (4) | 0.3640 (3) | 0.0490 (7) |
| H8 | 0.0963 | 0.7888 | 0.3387 | 0.059* |
| C9 | -0.1600 (5) | 0.5644 (4) | 0.2767 (3) | 0.0543 (8) |
| H9 | -0.1671 | 0.5408 | 0.1928 | 0.065* |

supplementary materials

| | | | | |
|-----|-------------|------------|--------------|------------|
| C10 | 0.1856 (4) | 0.9112 (3) | 0.5876 (2) | 0.0373 (6) |
| C11 | 0.2302 (4) | 0.9316 (4) | 0.7163 (3) | 0.0467 (7) |
| H11 | 0.1531 | 0.8442 | 0.7436 | 0.056* |
| C12 | 0.3888 (4) | 1.0814 (4) | 0.8037 (3) | 0.0515 (7) |
| H12 | 0.4160 | 1.0920 | 0.8897 | 0.062* |
| C13 | 0.4643 (4) | 1.1920 (4) | 0.6489 (3) | 0.0500 (7) |
| H13 | 0.5455 | 1.2815 | 0.6249 | 0.060* |
| C14 | 0.3093 (4) | 1.0477 (4) | 0.5543 (3) | 0.0452 (7) |
| H14 | 0.2869 | 1.0409 | 0.4692 | 0.054* |
| N1 | -0.3041 (4) | 0.4522 (3) | 0.3059 (2) | 0.0486 (6) |
| N2 | 0.5053 (3) | 1.2116 (3) | 0.7720 (2) | 0.0480 (6) |
| O1 | -0.1175 (4) | 0.6219 (3) | -0.1724 (2) | 0.0646 (6) |
| O2 | -0.2488 (4) | 0.5023 (3) | -0.0413 (2) | 0.0675 (7) |
| H2 | -0.3115 | 0.4168 | -0.1043 | 0.101* |
| O3 | 0.4001 (3) | 1.1949 (3) | 0.11635 (17) | 0.0535 (6) |
| H3A | 0.4895 | 1.2695 | 0.1816 | 0.080* |
| O4 | 0.2601 (3) | 1.0897 (3) | 0.25184 (19) | 0.0617 (6) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|--------------|-------------|
| C1 | 0.0491 (16) | 0.0413 (16) | 0.0448 (17) | 0.0165 (13) | 0.0013 (13) | 0.0039 (13) |
| C2 | 0.0589 (19) | 0.0442 (17) | 0.0560 (19) | 0.0128 (15) | 0.0062 (15) | 0.0121 (14) |
| C3 | 0.0543 (17) | 0.0355 (15) | 0.0479 (17) | 0.0079 (13) | -0.0013 (14) | 0.0065 (12) |
| C4 | 0.0508 (17) | 0.0385 (15) | 0.0391 (16) | 0.0143 (13) | -0.0039 (13) | 0.0051 (12) |
| C5 | 0.0422 (15) | 0.0415 (15) | 0.0449 (16) | 0.0070 (13) | 0.0106 (12) | 0.0105 (12) |
| C6 | 0.0477 (15) | 0.0451 (15) | 0.0353 (14) | 0.0143 (13) | 0.0142 (12) | 0.0103 (12) |
| C7 | 0.0358 (13) | 0.0365 (13) | 0.0354 (13) | 0.0156 (11) | 0.0095 (11) | 0.0098 (11) |
| C8 | 0.0465 (16) | 0.0501 (16) | 0.0375 (15) | 0.0092 (13) | 0.0148 (12) | 0.0096 (12) |
| C9 | 0.0551 (17) | 0.0537 (17) | 0.0353 (15) | 0.0106 (14) | 0.0126 (13) | 0.0038 (13) |
| C10 | 0.0348 (13) | 0.0363 (13) | 0.0370 (14) | 0.0146 (11) | 0.0102 (11) | 0.0079 (11) |
| C11 | 0.0471 (15) | 0.0432 (15) | 0.0377 (14) | 0.0086 (13) | 0.0138 (12) | 0.0100 (12) |
| C12 | 0.0498 (16) | 0.0526 (17) | 0.0360 (15) | 0.0120 (14) | 0.0100 (13) | 0.0068 (13) |
| C13 | 0.0447 (16) | 0.0410 (15) | 0.0536 (17) | 0.0087 (13) | 0.0148 (13) | 0.0159 (13) |
| C14 | 0.0453 (15) | 0.0460 (15) | 0.0395 (15) | 0.0142 (13) | 0.0145 (12) | 0.0150 (12) |
| N1 | 0.0450 (13) | 0.0419 (13) | 0.0417 (14) | 0.0105 (11) | 0.0060 (10) | 0.0056 (10) |
| N2 | 0.0398 (12) | 0.0424 (13) | 0.0469 (14) | 0.0088 (10) | 0.0098 (10) | 0.0079 (10) |
| O1 | 0.0678 (15) | 0.0481 (13) | 0.0711 (16) | 0.0150 (11) | 0.0286 (12) | 0.0185 (11) |
| O2 | 0.0788 (16) | 0.0500 (13) | 0.0436 (12) | 0.0084 (12) | 0.0114 (11) | 0.0034 (10) |
| O3 | 0.0456 (11) | 0.0456 (12) | 0.0373 (11) | 0.0028 (9) | -0.0005 (9) | -0.0005 (9) |
| O4 | 0.0599 (13) | 0.0513 (13) | 0.0424 (12) | 0.0047 (10) | 0.0019 (10) | 0.0097 (9) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|--------|-----------|
| C1—O1 | 1.209 (4) | C7—C10 | 1.484 (4) |
| C1—O2 | 1.285 (4) | C8—C9 | 1.374 (4) |
| C1—C2 | 1.513 (4) | C8—H8 | 0.9300 |
| C2—C3 | 1.482 (4) | C9—N1 | 1.325 (4) |
| C2—H2A | 0.9700 | C9—H9 | 0.9300 |

| | | | |
|------------------------|-----------|-------------|-----------|
| C2—H2B | 0.9700 | C10—C11 | 1.383 (4) |
| C3—C4 | 1.536 (4) | C10—C14 | 1.395 (4) |
| C3—C3 ⁱ | 1.542 (6) | C11—C12 | 1.374 (4) |
| C3—H3 | 0.9800 | C11—H11 | 0.9300 |
| C4—O4 | 1.214 (3) | C12—N2 | 1.327 (4) |
| C4—O3 | 1.301 (4) | C12—H12 | 0.9300 |
| C5—N1 | 1.332 (4) | C13—N2 | 1.324 (4) |
| C5—C6 | 1.377 (4) | C13—C14 | 1.373 (4) |
| C5—H5 | 0.9300 | C13—H13 | 0.9300 |
| C6—C7 | 1.393 (4) | C14—H14 | 0.9300 |
| C6—H6 | 0.9300 | O2—H2 | 0.8200 |
| C7—C8 | 1.386 (4) | O3—H3A | 0.8200 |
| O1—C1—O2 | 124.5 (3) | C6—C7—C10 | 121.7 (2) |
| O1—C1—C2 | 126.0 (3) | C9—C8—C7 | 119.6 (3) |
| O2—C1—C2 | 109.5 (3) | C9—C8—H8 | 120.2 |
| C3—C2—C1 | 117.3 (3) | C7—C8—H8 | 120.2 |
| C3—C2—H2A | 108.0 | N1—C9—C8 | 123.5 (3) |
| C1—C2—H2A | 108.0 | N1—C9—H9 | 118.3 |
| C3—C2—H2B | 108.0 | C8—C9—H9 | 118.3 |
| C1—C2—H2B | 108.0 | C11—C10—C14 | 116.6 (2) |
| H2A—C2—H2B | 107.2 | C11—C10—C7 | 121.5 (2) |
| C2—C3—C4 | 110.8 (2) | C14—C10—C7 | 121.8 (2) |
| C2—C3—C3 ⁱ | 116.5 (3) | C12—C11—C10 | 119.8 (3) |
| C4—C3—C3 ⁱ | 108.9 (3) | C12—C11—H11 | 120.1 |
| C2—C3—H3 | 106.7 | C10—C11—H11 | 120.1 |
| C4—C3—H3 | 106.7 | N2—C12—C11 | 123.5 (3) |
| C3 ⁱ —C3—H3 | 106.7 | N2—C12—H12 | 118.2 |
| O4—C4—O3 | 125.2 (2) | C11—C12—H12 | 118.2 |
| O4—C4—C3 | 123.6 (3) | N2—C13—C14 | 124.0 (3) |
| O3—C4—C3 | 111.2 (3) | N2—C13—H13 | 118.0 |
| N1—C5—C6 | 123.4 (3) | C14—C13—H13 | 118.0 |
| N1—C5—H5 | 118.3 | C13—C14—C10 | 119.2 (3) |
| C6—C5—H5 | 118.3 | C13—C14—H14 | 120.4 |
| C5—C6—C7 | 119.2 (2) | C10—C14—H14 | 120.4 |
| C5—C6—H6 | 120.4 | C9—N1—C5 | 117.3 (2) |
| C7—C6—H6 | 120.4 | C13—N2—C12 | 116.9 (2) |
| C8—C7—C6 | 117.0 (2) | C1—O2—H2 | 109.5 |
| C8—C7—C10 | 121.3 (2) | C4—O3—H3A | 109.5 |

Symmetry codes: (i) $-x, -y+2, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C14—H14 \cdots O4 | 0.93 | 2.56 | 3.476 (3) | 168 |
| C9—H9 \cdots O2 | 0.93 | 2.51 | 3.425 (4) | 167 |
| O3—H3A \cdots N1 ⁱⁱ | 0.82 | 1.78 | 2.595 (3) | 170 |
| O2—H2 \cdots N2 ⁱⁱⁱ | 0.82 | 1.84 | 2.642 (3) | 167 |

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

Fig. 1

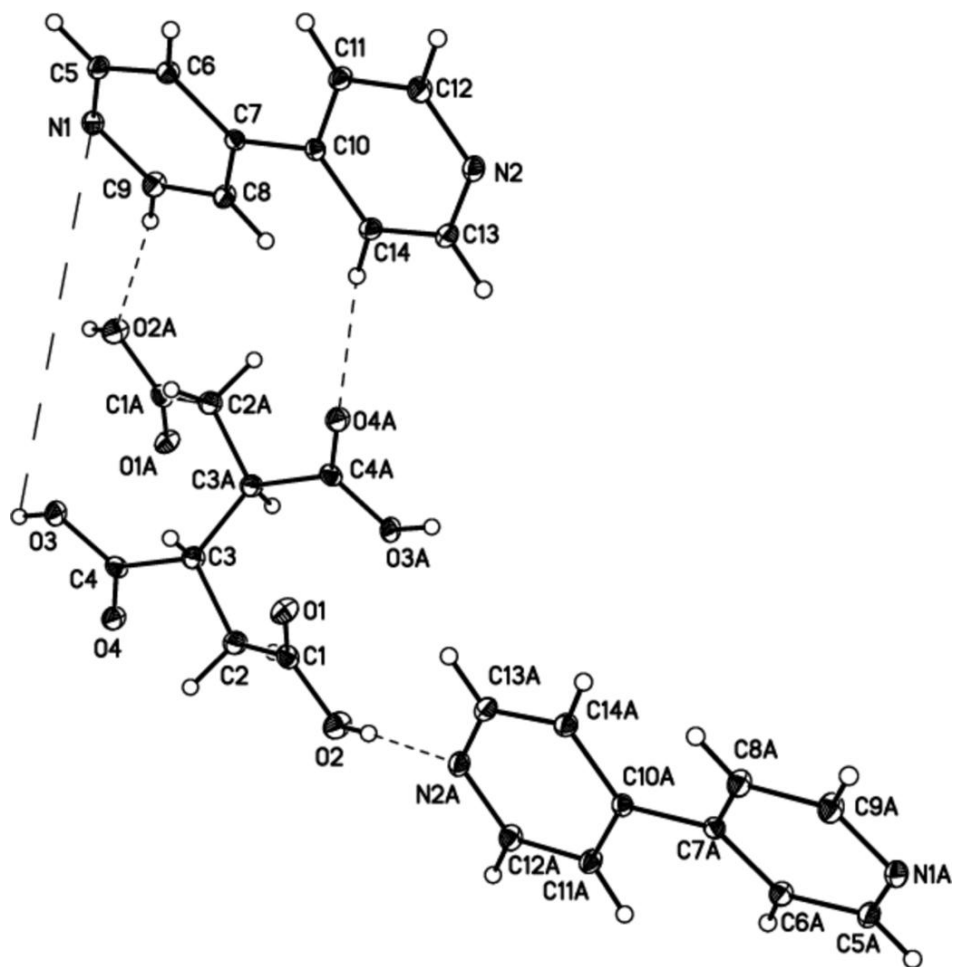


Fig. 2

