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The 2:1 cocrystal of 2,6-ditriazol-4-ylpyridine and benzene-1,2,4,5-tetracarboxylic acid

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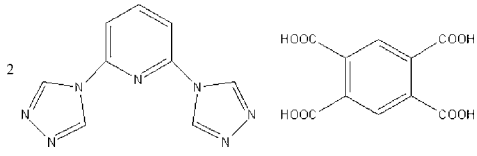
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.099; data-to-parameter ratio = 11.0.

The hydrothermal reaction of 2,6-ditriazol-4-ylpyridine, benzene-1,2,4,5-tetracarboxylic acid and $ZnSO_4{\cdot}7H_2O$ led to the formation of the cocrystal compound 2,6-ditriazol-4-ylpyridine–benzene-1,2,4,5-tetracarboxylic acid (2/1), $2C_9H_7N_7{\cdot}C_{10}H_6O_8$, in which hydrogen-bonding and π–π stacking interactions (3.404 Å) assemble the molecules into a three-dimensional supramolecular framework. The acid molecule lies on an inversion centre.

Related literature

For related literature, see: Wang, Xi *et al.* (2007); Wang, Ding *et al.* (2007); Xia *et al.* (2007).



Experimental

Crystal data

$2C_9H_7N_7{\cdot}C_{10}H_6O_8$
M_r = 680.58
Monoclinic, $P2_1/c$
a = 9.0972 (12) Å
b = 15.799 (2) Å
c = 10.0741 (13) Å
β = 100.523 (2)°
V = 1423.6 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 273 (2) K
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: none
7302 measured reflections
2520 independent reflections
1971 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.099
S = 1.04
2520 reflections
229 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···N3^{i}	0.82	1.82	2.639 (2)	172
O3—H3A···N7^{ii}	0.82	1.84	2.656 (2)	179

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

Data collection: *APEX* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); 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: AT2328).

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Xia, C. K., Lu, C. Z., Yuan, D. Q., Zhang, Q. Z., Wu, X. Y., Zhang, J. J. & Wu, D. M. (2007). *J. Mol. Struct.* **831**, 195–202.

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supplementary materials

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The 2:1 cocrystal of 2,6-ditriazol-4-ylpyridine and benzene-1,2,4,5-tetracarboxylic acid

W. Li, M. Shao, H.-J. Liu and M.-X. Li

Comment

Recently, there has been a growing interest in coordination polymers based on 1,2,4,5-benzenetetracarboxylate and 2,6-ditriazol-4-ylpyridine ligands (Wang, Xi, Su, Lan, Mao, You & Xie, 2007; Xia *et al.*, 2007). In the course of preparing mixed-ligand (ternary) complexes containing such organic ligands and metal ions, a new cocrystal compound of 2,6-ditriazol-4-ylpyridine (dtp) and benzene-1,2,4,5-tetracarboxylic acid (H_4Btec) was obtained which assembled by H-bonding and π-π stacking interaction. Hydrogen bonding and π-π interaction are important in the areas of supramolecular chemistry, crystal engineering, and biological recognition (Wang, Ding, Cheng, Liao & Yan, 2007). Herein we report the supramolecular framework of the title compound $(C_9H_7N_7)(C_{10}H_6O_8)_{1/2}$, (I).

As shown in Fig. 1, the asymmetric structural unit contains one dtp molecule and half of H_4Btec molecule. Bond lengths and angles are normal as expected. In dtp molecule, one triazole group is nearly planar with the pyridyl ring (dihedral angle of 3.1 (1)°), while the other triazole group has a dihedral angle of 33.5 (3)° with the pyridyl ring plane. Each carboxyl group of H_4Btec links a triazole N atom through H-bonding interaction. The distance between the aromatic rings of adjacent dtp and H_4Btec is *ca* 3.404 Å, which indicates the presence of some π-π stacking interaction. The intermolecular H-bonding and π-π stacking interaction assemble the molecules into a three-dimensional supramolecular framework (Fig. 2).

Experimental

A mixture of dtp (0.10 mmol), H_4betc (0.10 mmol), $ZnSO_47H_2O$ (0.20 mmol), and water (8 ml) was sealed in a Teflon-lined stainless steel vessel, which was heated at 393 K for 4 days and cooled to room temperature at a rate of 10 K/h. Light yellow crystals suitable for X-ray diffraction were obtained.

Refinement

The H atoms were located geometrically, with C—H = 0.93 and O—H = 0.82 Å, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O).

Figures

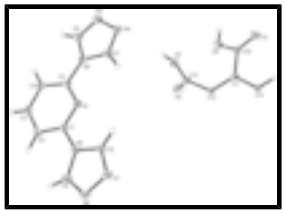

Fig. 1. View of (I), showing displacement ellipsoids drawn at the 30% probability level.

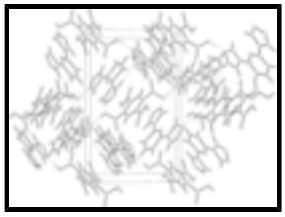

Fig. 2. A crystal packing diagram of compound (I).

2,6-ditriazol-4-ylpyridine–benzene-1,2,4,5-tetracarboxylic acid (2/1)

Crystal data

$2C_9H_7N_7{\cdot}C_{10}H_6O_8$	F_{000} = 700
M_r = 680.58	D_x = 1.588 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 2052 reflections
a = 9.0972 (12) Å	θ = 2.4–24.7º
b = 15.799 (2) Å	μ = 0.12 mm^{-1}
c = 10.0741 (13) Å	T = 273 (2) K
β = 100.523 (2)º	Block, light-yellow
V = 1423.6 (3) Å^3	0.20 × 0.20 × 0.10 mm
Z = 2	

Data collection

Bruker SMART CCD diffractometer	1971 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.026
Monochromator: graphite	θ_{max} = 25.1º
T = 273(2) K	θ_{min} = 2.3º
ω scans	h = −10→10
Absorption correction: none	k = −15→18
7302 measured reflections	l = −10→11
2520 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.4345P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.099	$(\Delta/\sigma)_{max} < 0.001$
S = 1.04	$\Delta\rho_{max}$ = 0.23 e Å^{-3}
2520 reflections	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
229 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Extinction coefficient: 0.0056 (11)

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}
N1	0.36742 (16)	0.16599 (9)	0.69912 (15)	0.0334 (4)
N2	0.61300 (16)	0.12340 (10)	0.75896 (15)	0.0364 (4)
N5	0.11742 (16)	0.19751 (10)	0.62929 (15)	0.0356 (4)
C5	0.49874 (19)	0.18189 (11)	0.77677 (18)	0.0332 (4)
C8	0.0829 (2)	0.12795 (12)	0.55123 (19)	0.0418 (5)
H8	0.1489	0.0842	0.5430	0.050*
N3	0.82721 (18)	0.05862 (12)	0.77901 (18)	0.0501 (5)
C11	0.64839 (19)	−0.02667 (12)	0.03665 (17)	0.0335 (4)
N4	0.72429 (18)	0.01326 (11)	0.68780 (17)	0.0476 (5)
C12	0.59825 (19)	0.04348 (12)	0.09964 (17)	0.0333 (4)
N7	−0.05551 (18)	0.13098 (11)	0.48951 (17)	0.0470 (5)
C1	0.25722 (19)	0.21877 (11)	0.71126 (18)	0.0326 (4)
C14	0.54929 (19)	−0.06941 (12)	−0.06162 (17)	0.0349 (4)
H14	0.5824	−0.1165	−0.1030	0.042*
C7	0.5986 (2)	0.05369 (12)	0.67899 (19)	0.0405 (5)
H7	0.5095	0.0369	0.6245	0.049*
N6	−0.11620 (19)	0.20543 (12)	0.52764 (19)	0.0579 (5)
C10	0.8071 (2)	−0.05768 (14)	0.06808 (19)	0.0401 (5)
C13	0.6961 (2)	0.09339 (13)	0.20797 (19)	0.0371 (5)
C4	0.5271 (2)	0.24769 (13)	0.86786 (19)	0.0400 (5)
H4	0.6202	0.2550	0.9225	0.048*
C6	0.7595 (2)	0.12313 (14)	0.8190 (2)	0.0490 (6)
H6	0.8046	0.1636	0.8802	0.059*
C2	0.2718 (2)	0.28829 (12)	0.79400 (19)	0.0410 (5)
H2	0.1920	0.3247	0.7965	0.049*
C3	0.4101 (2)	0.30172 (13)	0.87337 (19)	0.0439 (5)
H3	0.4245	0.3480	0.9314	0.053*
C9	−0.0114 (2)	0.24308 (15)	0.6100 (2)	0.0529 (6)
H9	−0.0225	0.2948	0.6510	0.064*
O3	0.72577 (16)	0.05287 (9)	0.32395 (13)	0.0483 (4)

H3A	0.7924	0.0777	0.3751	0.073*
O2	0.89983 (15)	−0.00163 (10)	0.13212 (17)	0.0637 (5)
H2A	0.9826	−0.0232	0.1549	0.096*
O4	0.73355 (17)	0.16479 (10)	0.19046 (15)	0.0566 (4)
O1	0.84301 (16)	−0.12654 (10)	0.03551 (17)	0.0615 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0241 (8)	0.0378 (9)	0.0356 (8)	−0.0001 (7)	−0.0019 (6)	−0.0005 (7)
N2	0.0213 (8)	0.0418 (9)	0.0426 (9)	0.0003 (7)	−0.0032 (6)	0.0017 (7)
N5	0.0229 (8)	0.0405 (9)	0.0395 (9)	0.0033 (7)	−0.0043 (6)	−0.0019 (7)
C5	0.0249 (9)	0.0364 (10)	0.0359 (10)	−0.0018 (8)	−0.0008 (7)	0.0059 (8)
C8	0.0310 (11)	0.0417 (12)	0.0477 (12)	0.0029 (9)	−0.0058 (9)	−0.0059 (10)
N3	0.0244 (9)	0.0629 (12)	0.0597 (11)	0.0039 (8)	−0.0012 (8)	−0.0004 (10)
C11	0.0228 (9)	0.0433 (11)	0.0336 (10)	0.0020 (8)	0.0025 (8)	0.0056 (8)
N4	0.0318 (9)	0.0533 (11)	0.0558 (11)	0.0051 (8)	0.0029 (8)	0.0003 (9)
C12	0.0241 (9)	0.0435 (11)	0.0314 (10)	−0.0018 (8)	0.0025 (7)	0.0037 (8)
N7	0.0323 (9)	0.0533 (11)	0.0498 (10)	0.0010 (8)	−0.0074 (8)	−0.0056 (9)
C1	0.0247 (9)	0.0374 (10)	0.0333 (10)	0.0001 (8)	−0.0007 (7)	0.0027 (8)
C14	0.0280 (10)	0.0415 (11)	0.0352 (10)	0.0025 (8)	0.0054 (8)	0.0004 (8)
C7	0.0281 (11)	0.0450 (12)	0.0453 (12)	0.0000 (9)	−0.0010 (8)	−0.0025 (10)
N6	0.0323 (10)	0.0647 (13)	0.0680 (12)	0.0101 (9)	−0.0137 (9)	−0.0146 (10)
C10	0.0261 (10)	0.0540 (13)	0.0390 (11)	0.0035 (9)	0.0028 (8)	0.0021 (10)
C13	0.0236 (10)	0.0454 (12)	0.0411 (11)	−0.0012 (9)	0.0028 (8)	0.0015 (9)
C4	0.0288 (10)	0.0459 (12)	0.0404 (11)	−0.0052 (9)	−0.0064 (8)	−0.0010 (9)
C6	0.0257 (11)	0.0601 (14)	0.0563 (13)	−0.0001 (10)	−0.0050 (9)	−0.0063 (11)
C2	0.0368 (11)	0.0416 (12)	0.0425 (11)	0.0051 (9)	0.0017 (9)	−0.0053 (9)
C3	0.0449 (12)	0.0440 (12)	0.0395 (11)	−0.0044 (10)	−0.0006 (9)	−0.0076 (9)
C9	0.0305 (11)	0.0556 (14)	0.0660 (14)	0.0114 (10)	−0.0090 (10)	−0.0137 (11)
O3	0.0453 (9)	0.0526 (9)	0.0406 (8)	−0.0104 (7)	−0.0091 (6)	0.0017 (7)
O2	0.0222 (7)	0.0780 (11)	0.0839 (11)	0.0094 (7)	−0.0086 (8)	−0.0231 (9)
O4	0.0513 (9)	0.0497 (10)	0.0638 (10)	−0.0160 (8)	−0.0024 (7)	0.0079 (8)
O1	0.0362 (9)	0.0576 (10)	0.0872 (12)	0.0137 (7)	0.0018 (8)	−0.0096 (9)

Geometric parameters (Å, °)

N1—C1	1.327 (2)	N7—N6	1.383 (2)
N1—C5	1.327 (2)	C1—C2	1.371 (3)
N2—C7	1.357 (2)	C14—C12^{i}	1.389 (2)
N2—C6	1.359 (2)	C14—H14	0.9300
N2—C5	1.426 (2)	C7—H7	0.9300
N5—C8	1.355 (2)	N6—C9	1.290 (3)
N5—C9	1.359 (2)	C10—O1	1.199 (2)
N5—C1	1.424 (2)	C10—O2	1.309 (2)
C5—C4	1.380 (3)	C13—O4	1.201 (2)
C8—N7	1.299 (2)	C13—O3	1.316 (2)
C8—H8	0.9300	C4—C3	1.373 (3)

N3—C6	1.293 (3)	C4—H4	0.9300
N3—N4	1.386 (2)	C6—H6	0.9300
C11—C14	1.387 (2)	C2—C3	1.379 (3)
C11—C12	1.394 (3)	C2—H2	0.9300
C11—C10	1.503 (2)	C3—H3	0.9300
N4—C7	1.299 (2)	C9—H9	0.9300
C12—C14^{i}	1.389 (2)	O3—H3A	0.8200
C12—C13	1.500 (2)	O2—H2A	0.8200
C1—N1—C5	116.15 (16)	N4—C7—N2	111.73 (17)
C7—N2—C6	104.03 (16)	N4—C7—H7	124.1
C7—N2—C5	127.36 (15)	N2—C7—H7	124.1
C6—N2—C5	128.60 (17)	C9—N6—N7	106.57 (16)
C8—N5—C9	104.15 (16)	O1—C10—O2	124.45 (18)
C8—N5—C1	128.01 (16)	O1—C10—C11	122.52 (18)
C9—N5—C1	127.83 (17)	O2—C10—C11	113.02 (17)
N1—C5—C4	124.99 (17)	O4—C13—O3	124.71 (18)
N1—C5—N2	113.67 (16)	O4—C13—C12	122.26 (17)
C4—C5—N2	121.33 (16)	O3—C13—C12	112.86 (16)
N7—C8—N5	110.47 (17)	C3—C4—C5	116.33 (17)
N7—C8—H8	124.8	C3—C4—H4	121.8
N5—C8—H8	124.8	C5—C4—H4	121.8
C6—N3—N4	108.15 (16)	N3—C6—N2	110.38 (19)
C14—C11—C12	119.20 (16)	N3—C6—H6	124.8
C14—C11—C10	117.78 (17)	N2—C6—H6	124.8
C12—C11—C10	123.01 (16)	C1—C2—C3	116.90 (18)
C7—N4—N3	105.71 (17)	C1—C2—H2	121.5
C14^{i}—C12—C11	119.27 (16)	C3—C2—H2	121.5
C14^{i}—C12—C13	117.42 (17)	C4—C3—C2	120.86 (19)
C11—C12—C13	123.31 (16)	C4—C3—H3	119.6
C8—N7—N6	107.43 (16)	C2—C3—H3	119.6
N1—C1—C2	124.69 (17)	N6—C9—N5	111.38 (19)
N1—C1—N5	114.08 (16)	N6—C9—H9	124.3
C2—C1—N5	121.23 (17)	N5—C9—H9	124.3
C11—C14—C12^{i}	121.52 (18)	C13—O3—H3A	109.5
C11—C14—H14	119.2	C10—O2—H2A	109.5
C12^{i}—C14—H14	119.2		

Symmetry codes: (i) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2A···N3^{ii}	0.82	1.82	2.639 (2)	172
O3—H3A···N7^{iii}	0.82	1.84	2.656 (2)	179

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

Fig. 1

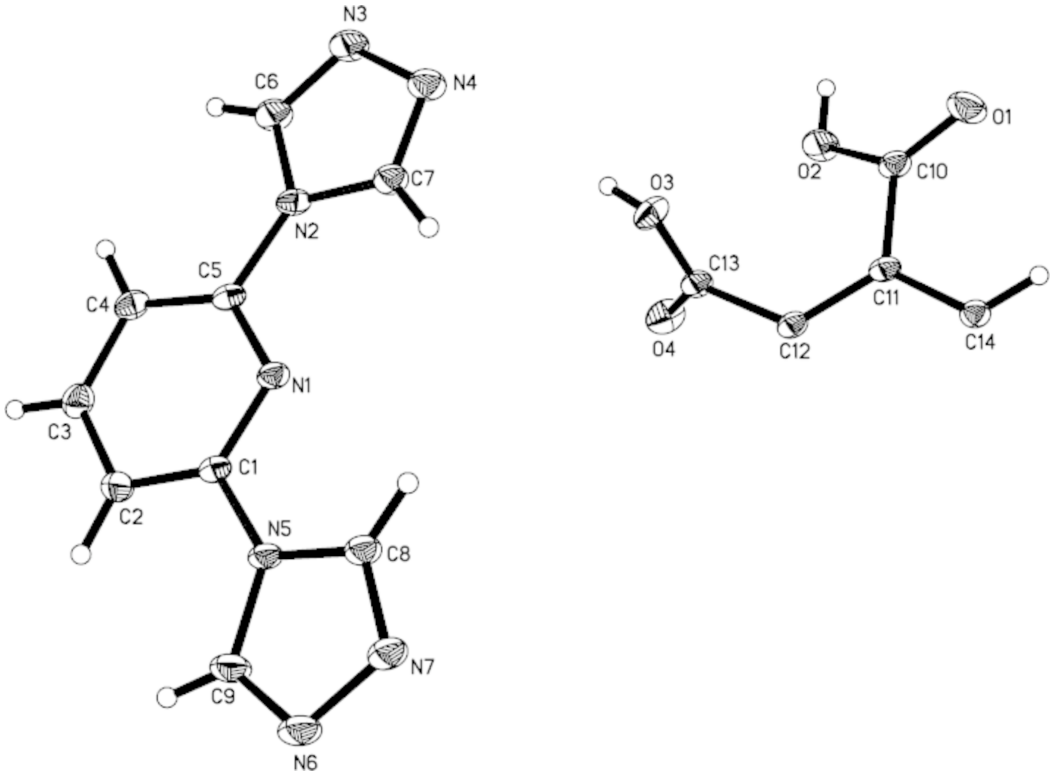
N3
C6
N4
C7
N2
C5
C4
N1
C3
C1
C2
N5
C8
N7
C9
N6
O1
O2
C10
O3
C13
C11
O4
C12
C14

Fig. 2