

2,6-Bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)-pyridine and its octahedral copper complex

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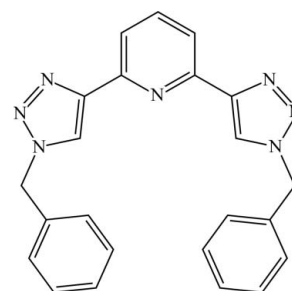
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In the tridentate ligand 2,6-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)-pyridine, C₂₃H₁₉N₇, both sets of triazole N atoms are *anti* with respect to the pyridine N atom, while in the copper complex aqua[2,6-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine](pyridine)-(tetrafluoroborato)copper(II) tetrafluoroborate, [Cu(BF₄)(C₅H₅N)(C₂₃H₁₉N₇)(H₂O)]BF₄, the triazole N atoms are in the *syn-syn* conformation. The coordination of the Cu^{II} atom is distorted octahedral. The ligand structure is stabilized through intermolecular C–H···N interactions, while the crystal structure of the Cu complex is stabilized through water- and BF₄-mediated hydrogen bonds. Photoluminescence studies of the ligand and complex show that the ligand is fluorescent due to triazole–pyridine conjugation, but that the fluorescence is quenched on complexation.

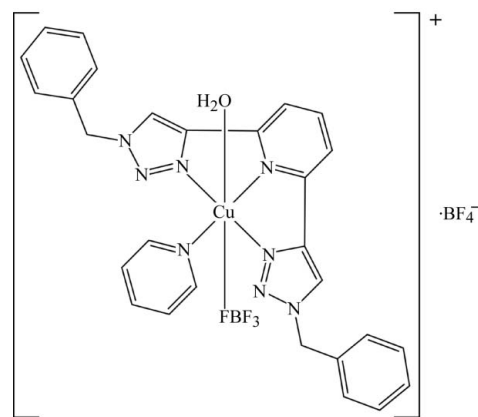
Comment

Huisgen's dipolar cycloaddition of organic azides with alkynes is the most direct route for the synthesis of 1,2,3-triazoles (Huisgen *et al.*, 1967). These are nitrogen heteroarenes which have found numerous applications in organic (Karthikeyan & Sankararaman, 2008), organometallic (Karthikeyan & Sankararaman, 2009) and medicinal chemistry (Shia *et al.*, 2002), as well as in materials chemistry (Crowley & Bandeen, 2010). 1,2,3-Triazole-based materials have advantageous properties for high-performance metal coatings and adhesives (Zhu *et al.*, 2006). However, there are major problems commonly associated with Huisgen's dipolar cycloaddition methodology, including the need for long reaction times and high temperatures, as well as the formation of regioisomeric mixtures of products when using unsymmetrical alkynes. It was found that cycloadditions of terminal alkynes with alkyl azides catalysed by Cu^I can be conducted at room temperature and are highly regioselective (Rostovtsev *et al.*, 2002). The cycloaddition of alkynes with azides under Cu^I-catalysed conditions leads exclusively to 1,4-disubstituted 1,2,3-triazoles in high yields. This type of copper catalysis, however, does not

promote the cycloaddition of internal alkynes. Mechanistic studies have demonstrated that these reactions involve terminal copper acetylides and proceed *via* a stepwise non-concerted process (Tornøe *et al.*, 2002). We prepared benzyl-triazole from benzyl azide and alkynes using a 'click reaction' (Horne *et al.*, 2004), which gave 1,4-disubstituted 1,2,3-triazoles. 1,2,3-Triazoles can be used for the preparation of bi- and tridentate ligands by appropriate choice of the alkynes that are used for the cycloaddition reaction. The tridentate triazole ligand 2,6-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine, (I), was prepared from 1,5-diethynylpyridine. The first published work on (I), abbreviated as BTP, was by Meudtner *et al.* (2007). The tridentate triazole coordination to a metal ion leads to conformational changes in the ligand. The conformational sensitivity of BTP can be suitably modulated to design nanoswitches (Piot *et al.*, 2009) sensitive to metal ions or pH changes.



(I)



(II)

A view of ligand (I), with its 'horseshoe' conformation and the atom-numbering scheme, is shown in Fig. 1. The torsion angles N7–C14–C15–N4 [156.2 (3)°, antiperiplanar] and N7–C10–C9–N3 [–171.8 (3)°, antiperiplanar] show that the triazole moieties are positioned *anti-anti* with respect to the N atom of the pyridine ring. The *anti-anti* conformation is preferred by (I) due to electrostatic repulsion between the lone pairs of atoms N5 and N2 and N7. Protonation of these N atoms or coordination with metals can remove this electrostatic interaction and make the conformation between triazole and pyridine *syn-syn*. Density functional theory calculations (Meudtner *et al.*, 2007) on a model system predict the stabilization energy for the *syn-syn* phase to be 6.4 kcal mol^{–1} (1 kcal mol^{–1} = 4.184 kJ mol^{–1}) more than that for the *anti-*

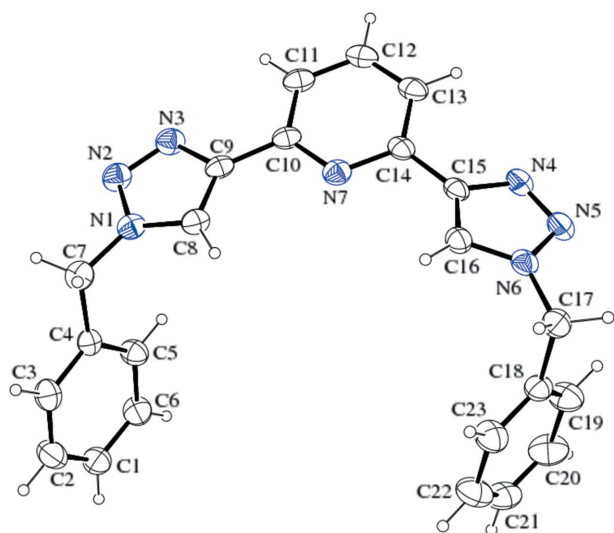


Figure 1
The molecular structure of ligand (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

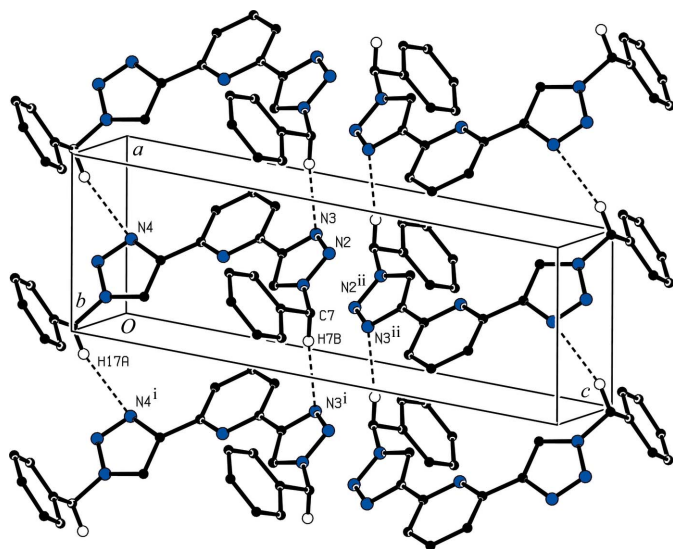


Figure 2
The packing of (I) in the unit cell. Intermolecular interactions are shown as dashed lines. [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 1 - y, 1 - z$.]

anti phase. The dihedral angles of the N1–N3/C9/C8 and N4–N6/C16/C15 triazole rings with the pyridine ring are 7.5 (3) and 22.5 (2)°, respectively. The C1–C6 and C18–C23 benzyl rings are inclined to each other at an angle of 14.3 (2)°. Analysis of the shortest intermolecular contacts shows that chains of molecules are developed along the *a* direction by C–H···N interactions (Table 1 and Fig. 2). The inversion-related N1–N3/C8/C9 five-membered rings at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ overlap significantly, with a centroid–centroid separation of 3.537 (2) Å, leading to an N2···N3– $(1 - x, 1 - y, 1 - z)$ separation of 3.576 (5) Å.

A view of the copper complex with (I), namely aqua[2,6-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine](pyridine)(tetrafluoroborato)copper(II) tetrafluoroborate, (II), is shown in

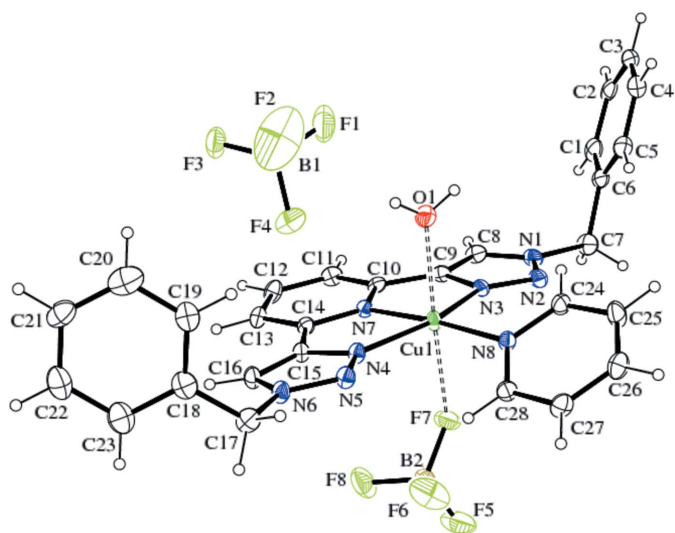


Figure 3
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one of the two disordered orientations for the C18–C23 ring is shown.

Fig. 3. The coordination geometry around the Cu^{II} ion is distorted octahedral. The two bite angles of the ligand with the metal atom are N4–Cu1–N7 = 78.94 (11)° and N7–Cu1–N3 = 78.54 (11)°. Atoms N3, N4, N7 and N8 form a near-regular plane, with the metal atom deviating slightly out of the mean plane in the direction of the water molecule [0.0755 (2) Å]. The water molecule is almost normal to the equatorial plane. The axial bond lengths [Cu1–O1 = 2.271 (3) Å and Cu1–F7 = 2.464 (4) Å] are considerably elongated compared with the four Cu–N coordination distances [Cu–N = 1.948 (3)–2.067 (3) Å]. This is common among octahedrally coordinated copper compounds (Silverstone *et al.*, 2007).

As would be expected, there is considerable conformational change between free ligand (I) and the coordinated ligand in complex (II). The pyridine and triazole moieties are nearly in the same plane, the dihedral angle between the two triazole moieties being 7.5 (2)° [the corresponding value in the ligand is 24.7 (2)°]. The triazole rings have almost rotated through 180° about the respective pyridine–triazole bonds, to bring both triazole N atoms into a *syn–syn* conformation with respect to the pyridine N atoms. The relevant torsion angles in the complex (with corresponding values in the ligand in square brackets) are N7–C10–C9–N3 = 0.1 (5)° [–171.8 (3)°] and N7–C14–C15–N4 = 2.2 (5)° [156.2 (3)°]. Similar conformational changes during complexation were noticed in 4-(2-pyridyl)-1,2,3-triazole (Meudtner *et al.*, 2007).

In the crystal structure of complex (II), the cations and anions are linked by O–H···F hydrogen bonds to generate chains which extend in the *a* direction; details are given in Table 2 and Fig. 4. In addition to the O–H···F hydrogen bonds, geometry calculations show other significant interactions, including C–H···F and C–H···O contacts and a C13–H13··· π interaction with the centroid of the C1–C6 phenyl ring at $(1 - x, -y, 2 - z)$; details are given in Table 2.

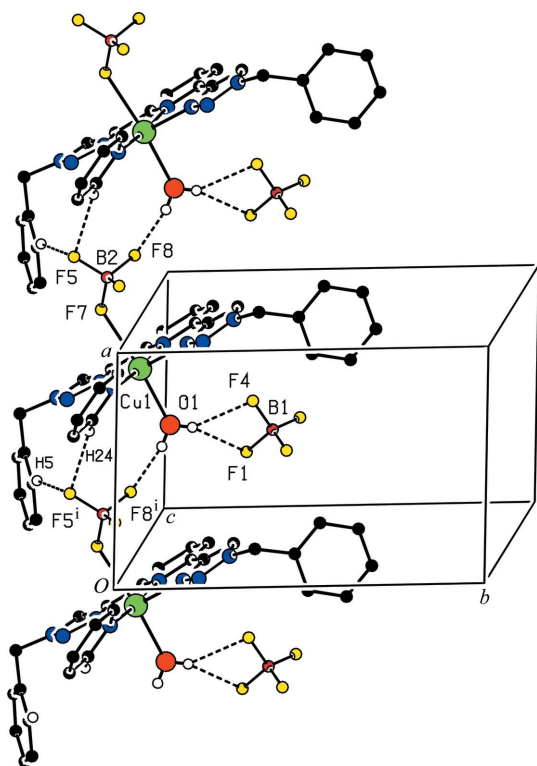


Figure 4
A view of the hydrogen-bonded chain extending along the *a* direction in (II). For symmetry codes, see Table 2.

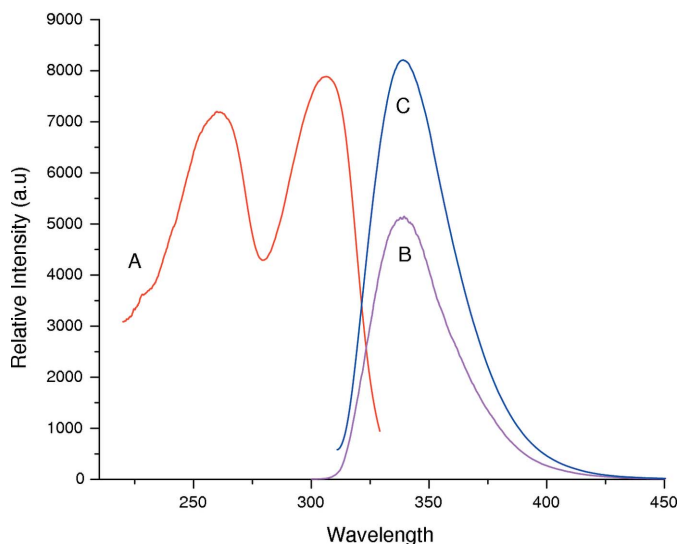


Figure 5
The fluorescence spectra of (I) in acetonitrile ($5 \times 10^{-5} M$). Key: (A) excitation spectrum of (I) ($\lambda_{\text{emission}} = 339 \text{ nm}$), (B) emission spectrum of (I) ($\lambda_{\text{excitation}} = 237 \text{ nm}$), and (C) emission spectrum of (I) ($\lambda_{\text{excitation}} = 301 \text{ nm}$).

There are also π - π interactions, with an almost complete overlap of the coordinated pyridine rings at (x, y, z) and $(1 - x, -y, 2 - z)$, and a centroid-centroid separation of $3.815(2) \text{ \AA}$ and a slippage of only 0.60 \AA (slippage is the distance between the centroid of one ring and the perpendicular projection of the centroid of the second ring on the plane of the first ring).

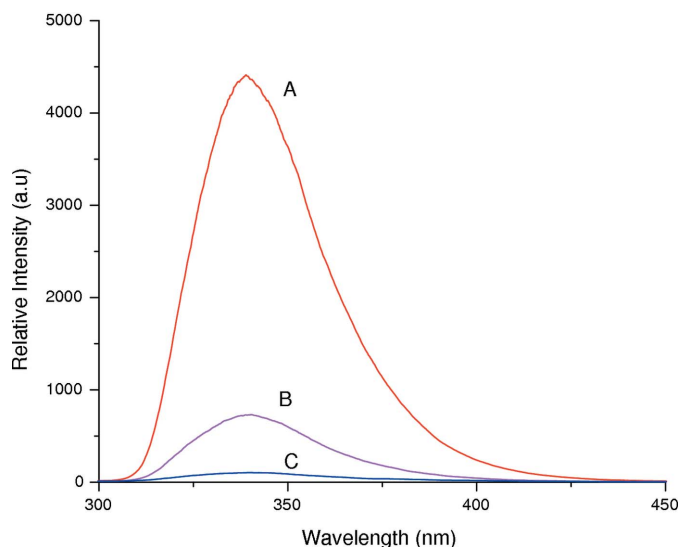


Figure 6
The fluorescence emission spectra of (I) in acetonitrile ($5 \times 10^{-5} M$) with (A) $1 \times 10^{-5} M$ copper tetrafluoroborate, (B) $2 \times 10^{-5} M$ copper tetrafluoroborate and (C) $3 \times 10^{-5} M$ copper tetrafluoroborate.

The C1–C6 phenyl ring and its equivalent at $(-x, -1 - y, 2 - z)$ have a centroid-centroid separation of $3.837(2) \text{ \AA}$ but with a slippage of 1.95 \AA ; the distance between the centroid of one ring and the plane of the inversion-related ring is $3.302(2) \text{ \AA}$.

Ligand (I) is photoluminescent and Fig. 5 shows the excitation and emission spectra. There are two excitation bands centred at 237 and 301 nm, and an emission band at 339 nm. The luminescence is quenched on complexation or protonation of the ligand; Fig. 6 shows the luminescence being quenched when copper tetrafluoroborate is added to the ligand solution. The conformational change of the pyridine-triazole moiety, from *anti-anti* in the ligand to *syn-syn* in the complex, is the cause of the quenching (Choi *et al.*, 2006). The ligand could thus be potentially useful as a pH or metal ion sensor.

Experimental

The Sonogashira coupling reaction (Sonogashira *et al.*, 1975) of 2,6-dibromopyridine with 2-methylbut-3-yn-2-ol gave 4,4'-(pyridine-2,6-diyl)bis(2-methylbut-3-yn-2-ol) in good yield. 2,6-Diethynylpyridine was prepared from 4,4'-(pyridine-2,6-diyl)bis(2-methylbut-3-yn-2-ol) by treating it with KOH in toluene at 353 K in 70% yield (Shinohara *et al.*, 2001). 2,6-Diethynylpyridine (0.25 g, 2 mmol) was dissolved in $t\text{-BuOH-H}_2\text{O}$ (1:1 *v/v*, 4.0 ml), and benzyl azide (0.53 g, 4 mmol), CuSO_4 (20 mg) and sodium ascorbate (40 mg) were added. The resulting mixture was stirred at room temperature overnight, diluted with saturated aqueous NaCl (50 ml) and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The crude products were purified by flash chromatography on silica gel eluting with CH_2Cl_2 -EtOAc, to yield the corresponding ligand, (I). The compound (m.p. 475 K) was crystallized from chloroform by slow evaporation of the solvent at room temperature in an open tube.

For the preparation of complex (II), (I) (0.1 g, 0.03 mmol) and copper(II) tetrafluoroborate (0.08 g, 0.03 mmol) were dissolved in acetonitrile. A drop of pyridine was added and the mixture warmed

to give a clear solution. The clear solution was allowed to stand in an open tube for crystallization of (II) by slow evaporation.

Compound (I)

Crystal data

$C_{23}H_{19}N_7$	$\gamma = 104.61 (3)^\circ$
$M_r = 393.45$	$V = 994.6 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.8800 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.460 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 16.140 (3) \text{ \AA}$	$T = 298 \text{ K}$
$\alpha = 103.53 (3)^\circ$	$0.25 \times 0.22 \times 0.20 \text{ mm}$
$\beta = 99.31 (3)^\circ$	

Data collection

Bruker Kappa-APEXII CCD area-detector diffractometer	10767 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	3417 independent reflections
$T_{\min} = 0.934$, $T_{\max} = 0.973$	1811 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	1 restraint
$wR(F^2) = 0.185$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
3417 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
272 parameters	

Compound (II)

Crystal data

$[\text{Cu}(\text{BF}_4)(\text{C}_5\text{H}_5\text{N})(\text{C}_{23}\text{H}_{19}\text{N}_7)(\text{H}_2\text{O})]\text{BF}_4$	$\beta = 84.76 (3)^\circ$
$M_r = 727.73$	$\gamma = 87.36 (3)^\circ$
Triclinic, $P\bar{1}$	$V = 1552.7 (5) \text{ \AA}^3$
$a = 8.2990 (17) \text{ \AA}$	$Z = 2$
$b = 12.956 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 14.520 (3) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$\alpha = 88.56 (3)^\circ$	$T = 173 \text{ K}$
	$0.41 \times 0.22 \times 0.20 \text{ mm}$

Data collection

Bruker Kappa-APEXII CCD area-detector diffractometer	20211 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	7222 independent reflections
$T_{\min} = 0.761$, $T_{\max} = 0.903$	4381 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.149$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$
7222 reflections	
459 parameters	
72 restraints	

One of the benzyl groups (C18–C23) in (II) is disordered. The occupancies assigned to the disordered components were refined as least-squares variables with their sum kept at 1. When the refinement converged, the occupancies were almost 0.5 each. In the final refinement, the occupancies of the components were set at 0.5. The disordered rings were constrained as idealized hexagons, with C–C = 1.39 Å. The methylene H atoms associated with atom C17 were fixed geometrically with respect to both disordered components of the benzyl moiety. Each of these four H atoms was given an occupancy of 0.5. Their positions were fixed only after the refinement convergence

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C7-H7B\cdots N3^i$	0.97	2.45	3.411 (5)	171

Symmetry code: (i) $x - 1, y, z$.

Table 2

Hydrogen-bond geometry (Å, °) for (II).

C_g is the centroid of the C1–C6 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H2A\cdots F4$	0.79 (5)	2.34 (5)	3.040 (5)	150 (4)
$O1-H2A\cdots F1$	0.79 (5)	2.19 (5)	2.901 (5)	150 (4)
$O1-H1A\cdots F8^i$	0.81 (5)	1.94 (5)	2.718 (5)	162 (4)
$C5-H5\cdots F5^i$	0.95	2.50	3.379 (6)	154
$C24-H24\cdots F5^i$	0.95	2.35	3.051 (5)	130
$C22-H22\cdots F5^{ii}$	0.95	2.37	3.213 (4)	147
$C11-H11\cdots O1^{iii}$	0.95	2.55	3.366 (4)	144
$C13-H13\cdots C_g^{iii}$	0.95	2.55	3.331 (4)	140

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

and hence not refined in the last set of cycles. The $U_{\text{iso}}(\text{H})$ values of these H atoms were fixed at $1.2U_{\text{eq}}(\text{C17})$. Water H atoms were located in a difference map and refined isotropically without restraints. In both compounds, the remaining H atoms bound to C atoms were constrained as riding, with C–H = 0.95 Å for aromatic CH and 0.97 Å for secondary CH₂ groups, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Thermal motion analysis of BTP (refined without restraints) showed the difference between the mean-square displacements of atoms N7 and C10 in the direction of the N7–C10 bond as 0.0205 \AA^2 and the standard uncertainty as 0.0027 \AA^2 . To avoid this apparent inconsistency, a rigid-bond restraint was set between N7 and C10. In CUBTP, pseudo-isotropic restraints were applied to the C atoms of the disordered phenyl ring to remove minor inconsistencies among displacement parameters caused by disorder.

For both compounds, data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3196). Services for accessing these data are described at the back of the journal.

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