organic compounds

Influence of 1,4-dioxane solvent inclusion on the crystal structure of 5,5′-diphenyl-2,2′-(p-phenylene)-di-1,3-oxazole (POPOP)

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Crystallization of 5,5′-diphenyl-2,2′-(p-phenylene)di-1,3-oxazole (POPOP), $C_{24}H_{16}N_2O_2$, from chloroform or 1,4-dioxane yielded crystals in pure and solvated forms, respectively. The solvated crystals of POPOP were found to contain 1,4-dioxane in a strict 1:2 compound–solvent stoichiometry, $C_{24}H_{16}N_2O_2 \cdot C_4H_8O_2$, thus being a defined solvent-inclusion compound. The crystal system is monoclinic in both cases and the asymmetric unit of the cell contains only half of the molecule (plus one dioxane molecule in the case of the solvated structure), owing to the centrosymmetry of the di-1,3-oxazole molecule.

Comment

5,5′-Diphenyl-2,2′-(p-phenylene)di-1,3-oxazole (POPOP), (I), is a well known strong scintillator, capable of emitting a brief pulse of fluorescent light upon interaction with a high-energy particle or quantum (Bell & Hayes, 1958). It has also been used as an indicator in fluorescence-based liquid-phase thermometry (Bai & Melton, 1997), and more recently as a fluorescent dye in two-dimensional correlation capillary electrophoresis (Wang & Geng, 2000) or as a fluorescence lifetime standard for time and frequency domain fluorescence spectroscopy (Boens *et al.*, 2007). An early X-ray determination of the crystal structure of pure POPOP dates back to 1965 and was performed at T = 295 K (Ambats & Marsh, 1965). Crystal structures of different metal ion complexes containing POPOP have also been described (Chen, Lu, Xia & Zhai, 2005; Chen, Lu, Zhang *et al.*, 2005), but there is no further current report on the crystal structure of POPOP. Considering the topical interest in crystal engineering (Braga & Greponi, 2007; Tiekink & Vittal, 2005) in the realms of sensor development (Fei *et al.*, 2003; Imai *et al.*, 2007; Scott *et al.*, 2004) and fluorescent solid materials (Dreuw *et al.*, 2005; Mizobe *et al.*, 2009; Ooyama *et al.*, 2007), the X-ray crystal structure of POPOP has been redetermined at low temperature (153 K)

and, in addition to this, the crystal structure of a corresponding 1:2 solvent inclusion compound of POPOP with 1,4-dioxane, (II), commonly termed a clathrate (Weber, 1987), has been examined. We report the structural details here and present a comparative discussion of the two structures, drawing particular attention to the influence of the included solvent on both the molecular conformation and the crystalline packing of POPOP. In order to ensure a proper comparison between the two structures, we use the new data for POPOP, which were collected at 153 K as for the solvated compound.
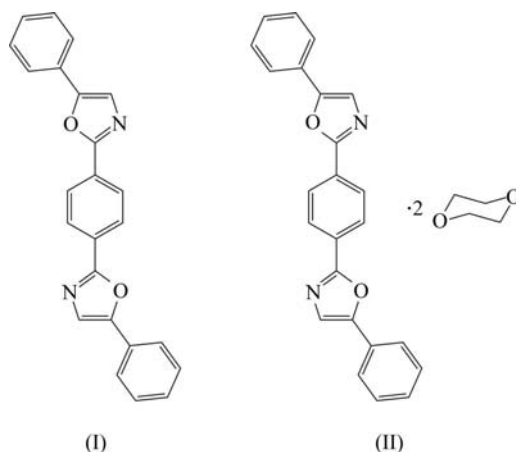
The structures of (I) and (II) are shown in Fig. 1. The crystal system of POPOP in either the solvent-free form, (I), or the inclusion compound, (II), is monoclinic. Owing to the centrosymmetry of the di-1,3-oxazole molecule, the asymmetric unit of the unit cell contains only half of the molecule
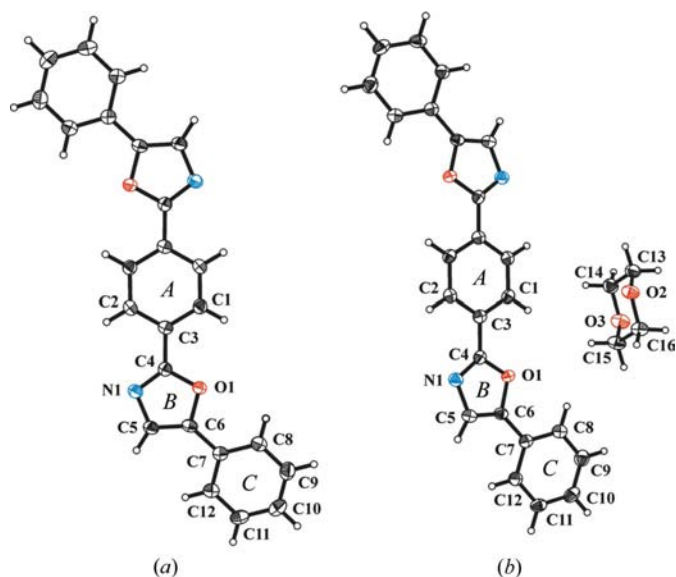

Figure 1
The molecular structures of (*a*) (I) and (*b*) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
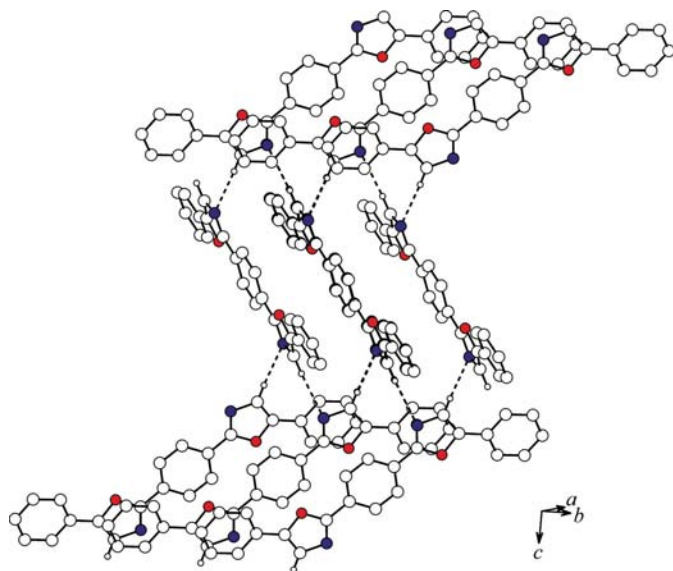
organic compounds

Figure 2
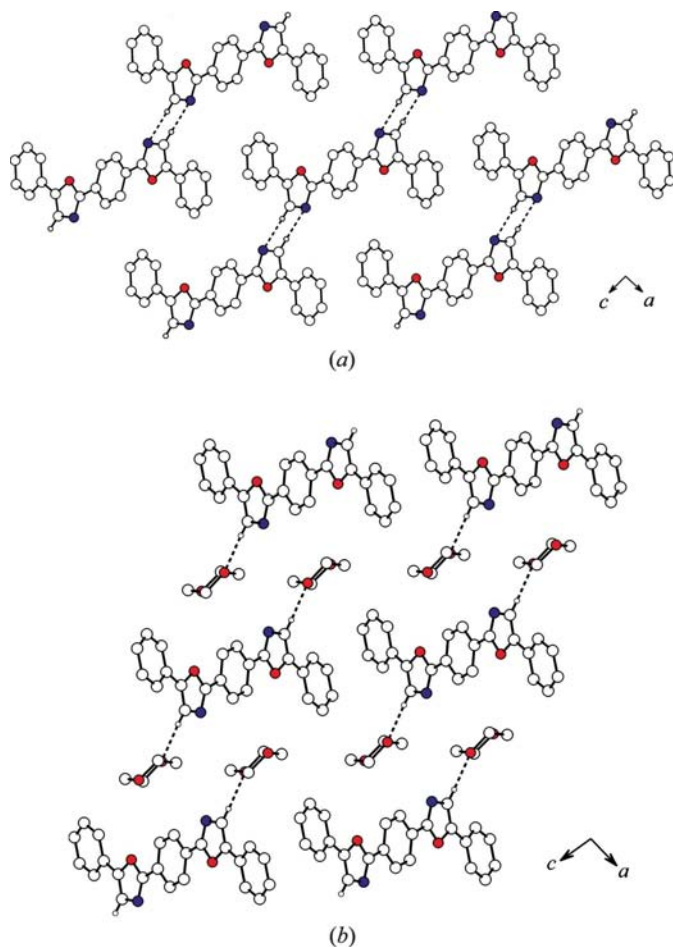Two types of stacks formed by di-1,3-oxazole molecules in the crystal structure of compound (I).

Figure 3
The packing structures of (a) (I) and (b) (II), viewed in each case along the b axis. Dashed lines indicate nonclassical hydrogen bonds.

(plus one dioxane molecule in the case of the solvated structure). The overall conformations of POPOP in the pure and

solvated forms are very similar. The *p*-phenylenedi-1,3-oxazole moieties do not deviate significantly from planarity [the interplanar angles between the least-squares planes of rings A and B are 3.89 (19) and 3.8 (2)°, respectively; the rings are defined in Fig. 1], making high conjugation of the π-system within this particular unit very likely. However, the peripheral benzene rings are twisted relative to the oxazole unit by 6.92 (10)° in (I) and 11.54 (9)° in (II) (Table 1).

In both structures, the di-1,3-oxazole moieties are arranged in stacks forming an *ABAB* pattern, where two adjacent stacks are aligned almost orthogonally to each other (Fig. 2). As a result of the extensive π-electron system of the molecules, the heterocyclic rings (*B*) within the stacks form offset face-to-face contacts (Sony & Ponnuswamy, 2006) with the neighboring benzene rings (*A* and *C*); the centroid–centroid distances are summarized in Table 1. Adjacent stacks of di-1,3-oxazole units form edge-to-face C—H···π contacts (Nishio, 2004) due to the orthogonal alignment of the stacks. The packing indices of compound (I) and (II) are 68 and 72%, respectively (*PLATON*; Spek, 2009).

In the case of the solvent-free structure, (I), the di-1,3-oxazole layers are connected by C—H···N interactions (Mazik *et al.*, 2001) involving only the atoms of the heterocyclic oxazole moieties (Fig. 3a), where one oxazole ring connects with two oxazole moieties of the neighboring stack. This specific pattern of intermolecular contacts is prevented in the crystal structure of the inclusion compound, (II), by the insertion of additional layers of 1,4-dioxane molecules which are in an alternating arrangement with the di-1,3-oxazole stacks. The host and guest molecules are connected by C—H···O contacts involving dioxane as the acceptor and oxazole moieties of POPOP as the hydrogen-bond donor sites (Fig. 3b). Although the contacts described above are only rather weak nonclassical hydrogen-bond interactions (Desiraju & Steiner, 1999), they sum up to form a stable crystal structure.

Experimental

Compound (I) was synthesized according to the literature procedure of Hayes *et al.* (1955). Colourless single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent from solutions of (I) in chloroform and 1,4-dioxane for (I) and (II), respectively. The unsolvated form, (I), has a melting point of 517–519 K. In the case of the inclusion compound, (II), solvent desorption can be observed at temperatures above 381 K, followed by a melting process at 517–519 K.

Compound (I)

Crystal data

$C_{24}H_{16}N_2O_2$	$V = 920.3$ (3) $Å^3$
$M_r = 364.39$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.1393$ (14) Å	$\mu = 0.09$ mm^{-1}
$b = 5.2461$ (8) Å	$T = 153$ K
$c = 19.204$ (3) Å	$0.27 \times 0.14 \times 0.11$ mm
$\beta = 91.807$ (11)°	

Table 1
Interplanar angles and intermolecular centroid–centroid distances (°, Å) of POPOP in (I) and in its 1,4-dioxane inclusion analogue, (II).

Rings	(I)		(II)	
	Angle	Distance	Angle	Distance
A/B	3.89 (19)	3.7160 (9)	3.8 (2)	3.6917 (7)
B/C	6.92 (10)	3.7380 (9)	11.54 (9)	4.0761 (8)

Table 2
Geometry of shortest intermolecular contacts (Å, °) for (I).

$Cg1$ is the centroid of the C7–C12 ring.

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
C5—H5···N1[i]	0.95	2.44	3.3932 (16)	176
C11—H11···$Cg1$[ii]	0.95	2.90	3.6966 (14)	142

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

Table 3
Geometry of shortest intermolecular contacts (Å, °) for (II).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
C14—H14A···N1[i]	0.99	2.72	3.4728 (18)	133
C5—H5···O3	0.95	2.43	3.3821 (16)	178
C15—H15B···O2[ii]	0.99	2.69	3.5146 (18)	141
C14—H14B···N1[iii]	0.99	2.66	3.5697 (18)	153
C13—H13A···O3[i]	0.99	2.70	3.5138 (18)	140

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

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min} = 0.978$, $T_{\max} = 0.991$

16533 measured reflections
2107 independent reflections
1644 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 1.03$
2107 reflections

127 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Compound (II)

Crystal data

$C_{24}H_{16}N_2O_2 \cdot 2C_4H_8O_2$
$M_r = 540.60$
Monoclinic, $P2_1/n$
$a = 12.2424$ (6) Å
$b = 5.9115$ (3) Å
$c = 18.5046$ (9) Å
$\beta = 97.977$ (3)°

$V = 1326.24$ (11) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 153$ K
$0.44 \times 0.11 \times 0.09$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\min} = 0.960$, $T_{\max} = 0.992$

22800 measured reflections
2324 independent reflections
1857 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.075$
$S = 1.01$
2324 reflections

181 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

H atoms were positioned geometrically and treated as riding, with C—H = 0.95 Å, or 0.99 Å in the dioxane solvent, and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

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

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