The *m*-phenylene-bridged bis-oxazole 4,4′,5,5′-tetraphenyl-2,2′-*m*-phenylenedi-1,3-oxazole and its bulkily substituted analogue 4,4′,5,5′-tetrakis(4-*tert*-butylphenyl)-2,2′-*m*-phenylenedi-1,3-oxazole

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The title *m*-phenylene-bridged bis-oxazoles, $C_{36}H_{24}N_2O_2$, (I), and $C_{52}H_{56}N_2O_2$, (II), feature different aryl substituents in the 4- and 5-positions of the oxazole units. In the solid state, aside from the different twist of the peripheral aryl rings, the molecules show distinctly different conformations, with *anti* and *syn* orientations of the O and N atoms for (I) and (II), respectively. Connected with this property, in the crystal structure of (I), extensive π-stacking is found between the molecules, while the crystal structure of (II) only involves dimer formation as the prominent packing motif.

Comment

Owing to the highly fluorescent behaviour emanating from their structure, aryl-substituted oxazoles are an interesting class of compounds (Wiley, 1945). Derived from this property, some 2,5-diaryloxazoles have found commercial application as solutes in liquid scintillators (Bell & Hayes, 1958). A well known representative of this compound type is 1,4-bis(5-phenyloxazol-2-yl)benzene, usually termed POPOP (Hayes *et al.*, 1955). Other arylene- and heteroarylene-bridged bis-oxazoles or bis-benzoxazoles behave as brightening agents (Schinzel *et al.*, 1987) or as efficient ligands for metal-ion complexation (Singh *et al.*, 2008; Drew *et al.*, 2004; Rüttimann *et al.*, 1992). In view of these potential applications, the new title compounds, (I) and (II), featuring *m*-phenylene-bridged bis-oxazole derivatives with different aryl substituents in the 4- and 5-positions of the oxazole units, have been synthesized and their crystal structures are reported here.

Perspective views of the molecular structures of (I) and (II) are shown in Fig. 1. The conformations of the molecules of (I) and (II) may be described by the relevant interplanar angles between the ring fragments (Table 1; ring definitions in Fig. 1).

(I) *R* = H
(II) *R* = Me₃C−
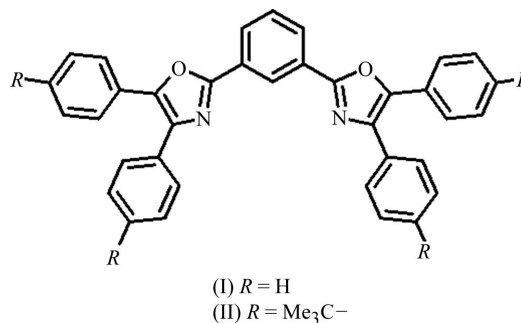
The crystal structure of bis-oxazole (I) shows bond distances within the oxazole rings which permit exact distinction between N and O [C1−N1 = 1.303 (2) Å and C1−O1 = 1.337 (2) Å for ring *A*; C22−N2 = 1.297 (2) Å and C22−O2 = 1.350 (2) Å for ring *A*′], so that the molecule adopts a conformation with an *anti* arrangement of identical heteroatoms (Fig. 1*a*). The central tricyclic part of the molecule is not perfectly planar; the planes of the oxazole rings are inclined slightly to that of the phenylene unit (Table 1). Except for phenyl ring *C*, the other peripheral phenyl rings are considerably twisted with reference to the oxazole unit to which they are bound (Table 1).

The crystal structure of (I) is characterized by a columnar packing of molecules in the direction of the *a* axis. As shown in Fig. 2, extensive π–π interactions (Dance, 2004; Janiak, 2000) between phenyl ring *C* and oxazole ring *A*′ occur along the stacking axis of molecules. The closest distances between the centroids of interacting rings vary from 3.558 (3) Å at ($x + \frac{1}{2}$, y, $-z + \frac{1}{2}$) to 3.597 (3) Å at ($x - \frac{1}{2}$, y, $-z + \frac{1}{2}$). The molecular stacking following from that seems to be stabilized as well by additional π–π interactions between *A* and *D* at ($x - \frac{1}{2}$, y, $-z + \frac{1}{2}$), with a centroid–centroid distance of 3.615 (3) Å. Only one of the N atoms participates in hydrogen bonding (H5···N1 = 2.56 Å and C5−H5···N1 = 168°). Further details of the C−H···N, C−H···O and C−H···π interactions are given in Table 2.

In bis-oxazole (II), the molecular structure of which is illustrated in Fig. 1(*b*), the presence of the bulky *tert*-butyl residues markedly changes the molecular conformation and the packing behaviour of the molecules in the crystal structure compared with (I). The *m*-phenylene bis-oxazole fragment of (II) is approximately planar, with the largest deviation of any atom of the fragment from the mean plane being 0.055 (2) Å for atom C23. Without exception, and thus differing most markedly from (I), all the peripheral aryl rings show a distinct twist with reference to the oxazole unit to which they are bound (Table 1). Moreover, unlike in (I), corresponding heteroatoms of the heterocyclic rings adopt a *syn* arrangement, so that in the solid state the molecule has pseudo-mirror symmetry (point group C_s), with atoms C18 and C21 lying in the pseudo-symmetry plane.

The steric requirement of the *tert*-butyl substituents drastically reduces the extent of intermolecular interaction, which
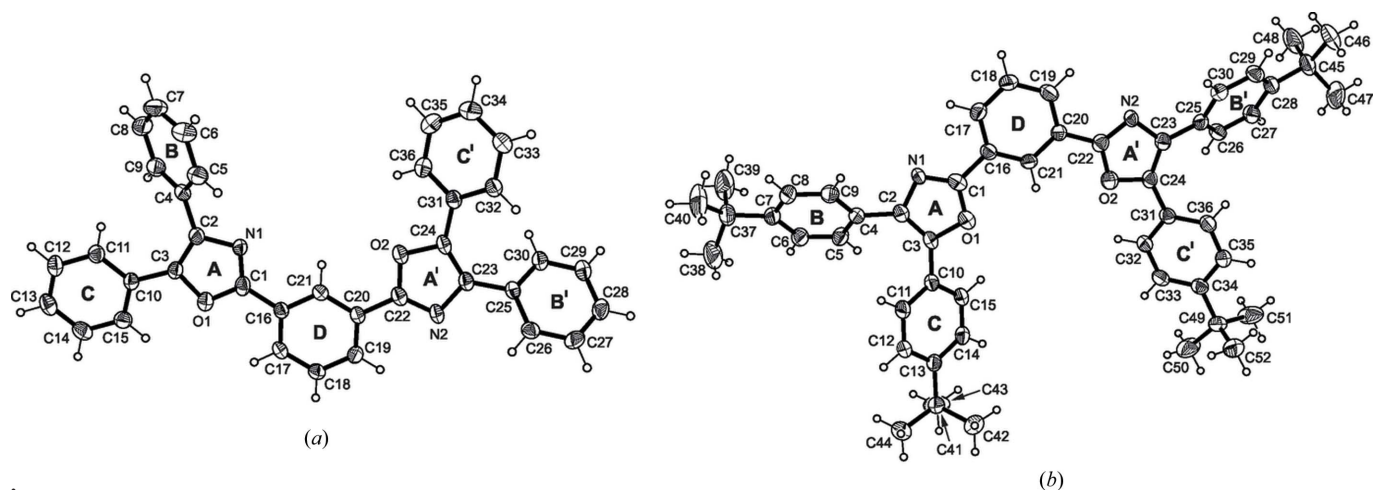
Figure 1
Perspective views of the molecular structures of (*a*) compound (I) and (*b*) compound (II), showing the atom-numbering schemes and the ring specifications. Displacement ellipsoids are drawn at the 50% probability level.
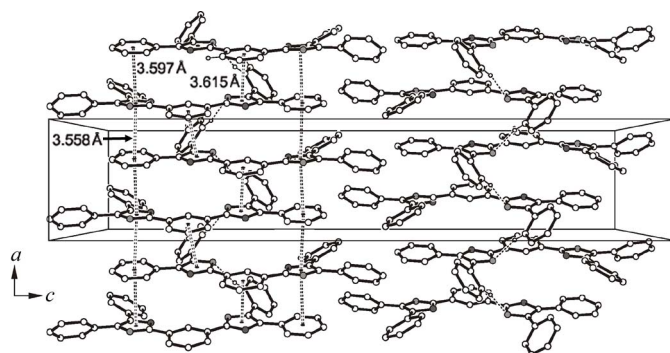

Figure 2
The crystal packing of (I), viewed down the crystallographic *b* axis. O atoms are displayed as dark-grey and N atoms as light-grey spheres. Dashed lines represent hydrogen bonds and double-dashed lines represent arene stacking interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

Figure 3
The crystal packing of (II). O atoms are displayed as dark-grey and N atoms as light-grey spherees. H atoms have been omitted for clarity.

is restricted to the few C—H···π contacts (Nishio, 2004) listed in Table 3. Hence, the crystal structure is stabilized by van der Waals forces rather than directed noncovalent bonding. As shown in the crystal packing diagram (Fig. 3), the crystal structure of (II) is composed of weakly bound dimers centred about an inversion centre.

In summary, the most remarkable distinguishing feature between the crystal structures of (I) and (II) is the different molecular conformations with respect to the orientation of the O and N atoms of the oxazole units: *anti* in (I) and *syn* in (II). This might be a result of the long-range π-stacking interaction between the molecules in the structure of (I), whereas the bulky *tert*-butyl groups of (II) prevent extensive π-stacking but cause the molecules to associate into weakly bound dimers centred about inversion centres, with the hetero atoms in a *syn* conformation. Moreover, compared with the almost flat structure of crystalline POPOP (Schindler *et al.*, 2010), which makes efficient conjugation of the π-systems very likely, the molecular conformations of (I) and (II) are much more twisted, in particular with respect to the peripheral aryl–oxazole bonds. This could be one of the reasons contributing
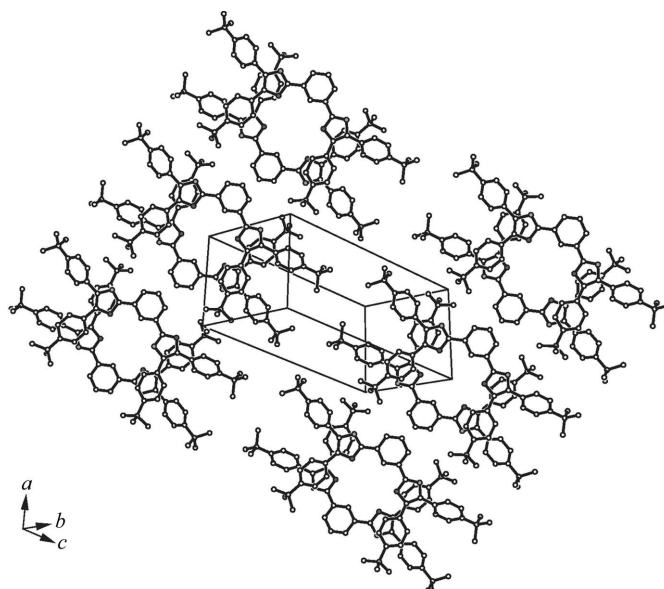
to the lack of fluorescence of bis-oxazoles (I) and (II) in the solid state, while POPOP is highly fluorescent.

Experimental

The starting benzoins (IV*a*) (Breuer & Zincke, 1879) and (IV*b*) (Hahn *et al.*, 1981) were synthesized *via* benzoin condensation from the corresponding benzaldehydes following the described procedures.

For the preparation of the bis(keto esters) (III*a*) and (III*b*), triethylamine (15 ml, 0.11 mol, dried over potassium hydroxide) was added slowly over a period of 3 h to a refluxing solution of the corresponding benzoin (IV*a*) or (IV*b*) (20 mmol) and isophthaloyl dichloride (V) (2.03 g, 10 mmol) in dry toluene (20 ml, dried over sodium and freshly distilled before use). After evaporation of the solvent, ethanol (10 ml) was added to the oily residue and the mixture stirred for 2 h. The solid which formed was collected and crystallized.

For (III*a*), benzoin (IV*a*) (4.24 g, 20 mmol) was reacted; crystallization from 1,4-dioxane yielded a colourless powder (yield 40%; m.p. 440 K). For (III*b*), benzoin (IV*b*) (6.44 g, 20 mmol) was reacted; crystallization from 1,4-dioxane yielded a colourless powder (yield 96%; m.p. 421 K).
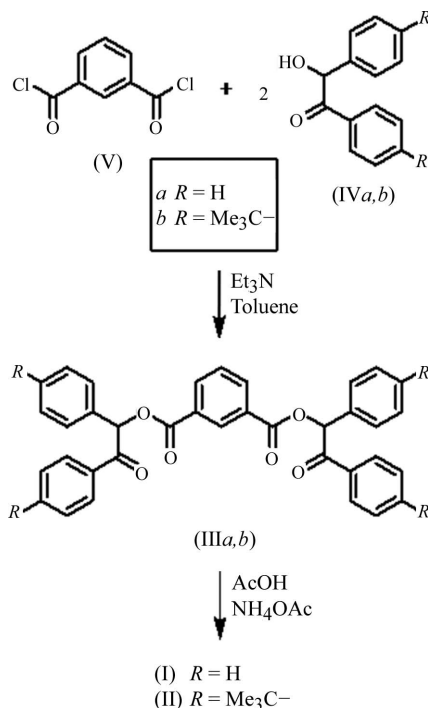
For the preparation of the title bis-oxazoles (I) and (II), the corresponding bis(keto ester) (III*a*) or (III*b*) (7.5 mmol) and ammonium acetate (3.46 g, 45 mmol) were dissolved in concentrated acetic acid (55.0 ml) and refluxed for 3.5 h. After cooling of the reaction mixture to room temperature, the precipitate which formed was collected, neutralized with aqueous sodium hydrogen carbonate, washed several times with water, dried and crystallized. For (I), compound (III*a*) (4.16 g) was used for the reaction; crystallization from 1,4-dioxane–acetonitrile (1:1, *v*/*v*) yielded colourless crystals (yield 88%; m.p. 476 K). For (II), compound (III*b*) (5.84 g) was used for the reaction; crystallization from 1,4-dioxane yielded a colourless powder (yield 93%; m.p. 585 K) and X-ray quality crystals were obtained by recrystallization from chloroform.

Spectroscopic and other synthetic details for compounds (I) and (II) are available in the archived CIF.

Compound (I)

Crystal data

$C_{36}H_{24}N_2O_2$	$V = 5277.5$ (2) Å^3
$M_r = 516.57$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 7.1523$ (2) Å	$\mu = 0.08$ mm^{-1}
$b = 20.0145$ (5) Å	$T = 153$ K
$c = 36.8669$ (8) Å	$0.48 \times 0.34 \times 0.17$ mm

Data collection

Nonius Kappa APEXII CCD area-detector diffractometer	80848 measured reflections
	10121 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5826 reflections with $I > 2\sigma(I)$
$T_{min} = 0.962$, $T_{max} = 0.986$	$R_{int} = 0.062$

Table 1
Interplanar angles (°) in (I) and (II).

Ring definitions are given in Fig. 1.

Planes	(I)	(II)
A/*B*	46.1 (1)	39.6 (1)
A′/*B*′	40.5 (1)	42.6 (1)
A/*C*	5.5 (1)	31.3 (1)
A′/*C*′	25.1 (1)	27.1 (1)
A/*D*	2.3 (1)	2.3 (2)
A′/*D*′	8.2 (1)	3.5 (2)
B/*C*	50.3 (1)	54.4 (1)
B′/*C*′	51.3 (1)	54.2 (1)

Table 2
C—H···*X* and C—H···π interactions for (I) (Å, °).

Ring definitions are given in Fig. 1 and *Cg* denotes a ring centroid.

	Symmetry code	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···N1	$(-\frac{1}{2} + x, y, \frac{1}{2} - z)$	2.56	3.489 (1)	168
C29—H29···*CgC*′	$(1 - x, -y, -z)$	2.76	3.486 (1)	134
C33—H33···*CgB*′	$(-x, -y, -z)$	2.81	3.550 (1)	136

Table 3
C—H···π interactions for (II) (Å, °).

Ring definitions are given in Fig. 1 and *Cg* denotes a ring centroid.

	Symmetry code	H···*A*	*D*···*A*	*D*—H···*A*
C51—H51*A*···*CgB*	$(2 - x, 2 - y, 2 - z)$	2.88	3.691 (2)	141
C26—H26···*CgC*	$(2 - x, 2 - y, 2 - z)$	2.87	3.470 (2)	122
C43—H43*A*···*CgB*	$(2 - x, 2 - y, 2 - z)$	2.89	3.810 (2)	157

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	361 parameters
$wR(F^2) = 0.156$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
10121 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Compound (II)

Crystal data

$C_{52}H_{56}N_2O_2$	$\gamma = 108.463$ (2)°
$M_r = 740.99$	$V = 2140.25$ (11) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.3121$ (3) Å	Mo $K\alpha$ radiation
$b = 11.1215$ (3) Å	$\mu = 0.07$ mm^{-1}
$c = 19.8676$ (6) Å	$T = 153$ K
$\alpha = 91.593$ (2)°	$0.32 \times 0.18 \times 0.17$ mm
$\beta = 96.918$ (2)°	

Data collection

Nonius Kappa APEXII CCD area-detector diffractometer	33601 measured reflections
	9309 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5281 reflections with $I > 2\sigma(I)$
$T_{min} = 0.978$, $T_{max} = 0.988$	$R_{int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	517 parameters
$wR(F^2) = 0.180$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
9309 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}

organic compounds

H atoms were positioned geometrically and treated as riding, with C—H = 0.95 (aromatic) or 0.98 Å (aliphatic) and U_{iso}(H) = kU_{eq}(C), where k = 1.2 for aromatic H or k = 1.5 for aliphatic H atoms.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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