Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Three solvates of a bis-mesoionic fluorescent yellow pigment

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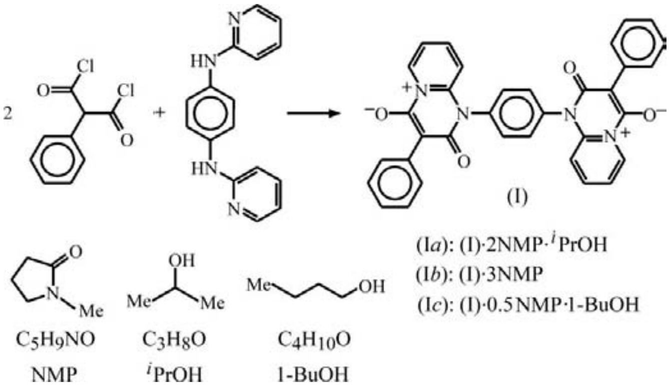
Received 20 March 2009
Accepted 19 May 2009
Online 27 June 2009

p-Phenylenebis(2-oxo-3-phenyl-1,2-dihydropyrido[1,2-*a*]pyrimidin-5-ium-4-olate), $C_{34}H_{22}N_4O_4$, is a bis-mesoionic yellow pigment that shows fluorescence in the solid state. During a polymorph screening, single crystals of three solvates were grown and their crystal structures determined. Solvent-free crystals were not obtained. A solvate with *N*-methylpyrrolidone (NMP) and propan-2-ol, $C_{34}H_{22}N_4O_4 \cdot 2C_5H_9NO \cdot C_3H_8O$, (I*a*), and an NMP trisolvate, $C_{34}H_{22}N_4O_4 \cdot 3C_5H_9NO$, (I*b*), crystallize with pigment molecules on inversion centres. The NMP/propan-2-ol mixed solvate (I*a*) forms O—H···O hydrogen bonds between the different solvent molecules. In both structures, at least one of the solvent molecules is disordered. A third solvate structure, $C_{34}H_{22}N_4O_4 \cdot 0.5C_5H_9NO \cdot C_4H_{10}O$, (I*c*), was obtained by crystallization from NMP and butan-1-ol. In this case, there are two symmetry-independent pigment molecules, both situated on inversion centres. The solvent molecules are heavily disordered and their contribution to the scattering was suppressed. This solvate displays a channel structure, whereas the other two solvates form layer structures.

Comment

Mesoionic compounds are 'dipolar five- (possibly six-) membered heterocyclic compounds in which both the negative and the positive charge are delocalized, for which a totally covalent structure cannot be written, and which cannot be represented satisfactorily by any one polar structure' (IUPAC, 1995). These substances represent a small class of compounds. Pyridopyrimidinium olates based on 2,4-dioxopyrimidine are mesoionic (Friedrichsen *et al.*, 1982; Schober & Kappe, 1988; Kappe, 1998; Fiksdahl *et al.*, 2000). Moreover, some of them exhibit yellow solid-state fluorescence. Fluorescence in the solid state is a rather unusual property since most compounds that fluoresce in solution lose this property when they are crystallized. Recently, the phenomenon of solid-state fluorescence in an organic pigment was explained by time-dependent density functional theory (TD–DFT) calculations (Dreuw *et al.*, 2005).

2-Oxo-3-phenyl-1,2-dihydropyrido[1,2-*a*]pyrimidin-5-ium-4-olate, (II), being a derivative of Chichibabin's malonyl α-aminopyridine (Tschitschibabin, 1924), is a mesoionic yellow compound [Plüg *et al.* (2000); Cambridge Structural Database (CSD; Allen, 2002) refcode XAKZEO]. It shows a high solubility in most organic solvents and it is therefore not feasible to be used as an industrially produced pigment. To enhance the insolubility, the title compound, (I), was synthesized. This compound actually shows a lower solubility and a strong yellow fluorescence (Metz & Plüg, 2005). Compound (I) is not industrially produced either.



In order to search for different crystallographic phases, hydrates or solvates of (I), a polymorph screening was performed. Different crystallization methods were used, including recrystallization from various solvents and solvent mixtures by heating and subsequent slow cooling, overlaying a solution of the compound with an anti-solvent (Fock, 1888), and diffusion of an anti-solvent into a solution of the compound *via* the gas phase. The solvents used included

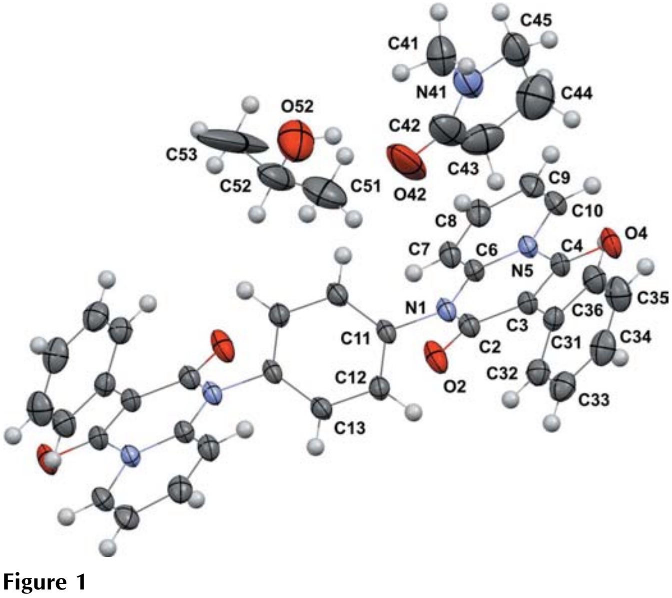


Figure 1
The molecular structure of (I*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

doi:10.1107/S0108270109018952

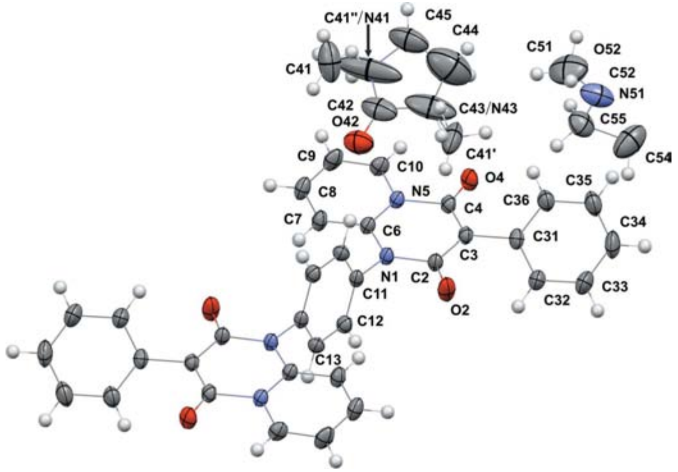


Figure 2
The molecular structure of (I*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. See the *Experimental* section for a description of the disorder present in this structure.

the most common organic solvents, *e.g.* dimethyl sulfoxide, *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylformamide, different ethers and esters, propan-2-ol (^{i}PrOH), butan-1-ol (1-BuOH) and other alcohols, and water.

In several experiments, single crystals could be grown, and the crystal structures could be determined for three solvates, namely (I)·2NMP·^{i}PrOH, denoted (I*a*), (I)·3NMP, (I*b*), and (I)·0.5NMP·1-BuOH, (I*c*).

Compounds (I*a*) and (I*b*) crystallize in space group $P\overline{1}$ with $Z = 1$ (Figs. 1 and 2), whereas (I*c*) crystallizes in space group $P\overline{1}$ with $Z = 2$. In (I*a*) and (I*b*), the pigment molecules (I) are situated on crystallographic inversion centres. In (I*c*), there are two symmetry-independent pigment molecules, both on inversion centres (Fig. 3). For (I*c*), the refinement of the pigment molecules could be performed without any difficulties, but the solvent molecules are heavily disordered. In the difference Fourier synthesis, there are six peaks with electron densities of 1.0 to 2.3 e Å^{-3}. No reasonable model could be found for a successful refinement with either NMP or butan-1-ol as solvent. A comparison with the crystal structures of (I*a*) and (I*b*) showed that the solvent molecules should occupy a volume of 374 Å^3 per unit cell. According to Hofmann's volume increments (Hofmann, 2002), an NMP molecule has a volume of 147 Å^3 and butan-1-ol a volume of 117 Å^3. Hence, the unit cell may contain, for example, two molecules of butan-1-ol and one molecule of NMP (sum 381 Å^3), or two molecules of NMP and a partial molecule of butan-1-ol. In the former case, the crystal would have a composition of 2(I)·NMP·2(1-BuOH). Lattice energy minimizations were performed with the aim of obtaining possible positions for the solvent molecules but the results were inconclusive. Thus, in (I*c*), the contribution of the solvent molecules to the scattering was suppressed using the SQUEEZE procedure in *PLATON* (van der Sluis & Spek, 1990; Spek, 2009; see *Experimental*). By this means the void is calculated to contain about 48 electrons, which is much less than assumed by the formula 2(I)·NMP·2(1-BuOH) (138 electrons). This indicates that the solvent positions might be only partially occupied.

The structures of (I*a*) and (I*b*) are pseudo-isomorphic. The lattice parameters are similar and the pigment molecules and two NMP molecules have similar arrangements in both structures, but the disordered propan-2-ol molecule in (I*a*) is replaced by a disordered NMP molecule in (I*b*). Correspondingly, the unit-cell volume of (I*a*) is 52 Å^3 smaller than that of (I*b*). In all three structures, the pigment molecules are essentially planar, except for the linking phenylene moieties,

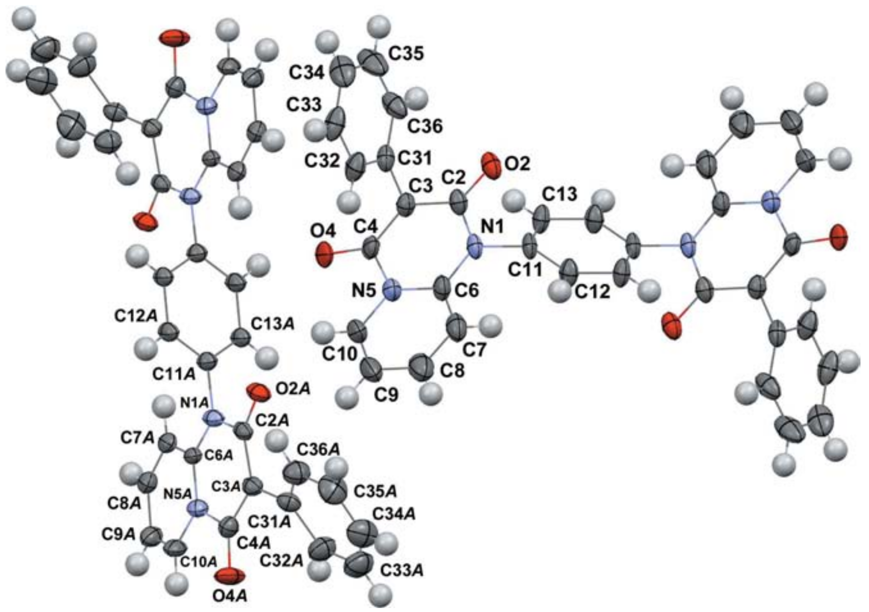


Figure 3
The molecular structure of (I*c*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

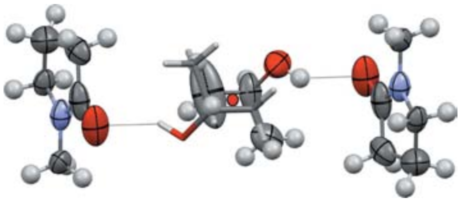


Figure 4
The disorder of one propan-2-ol molecule between two NMP molecules in (I*a*). The crystallographic inversion centre is shown as a small circle. Hydrogen bonds are drawn as dotted lines.

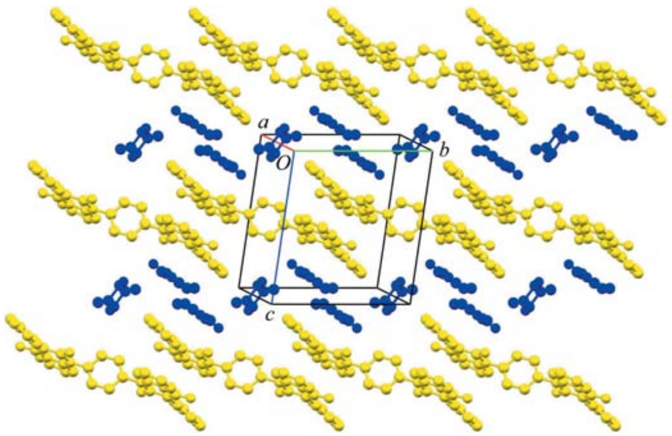


Figure 5
The packing of (I*a*); molecules of (I) are shaded light and solvent molecules are dark (yellow and blue, respectively, in the electronic version of the paper).

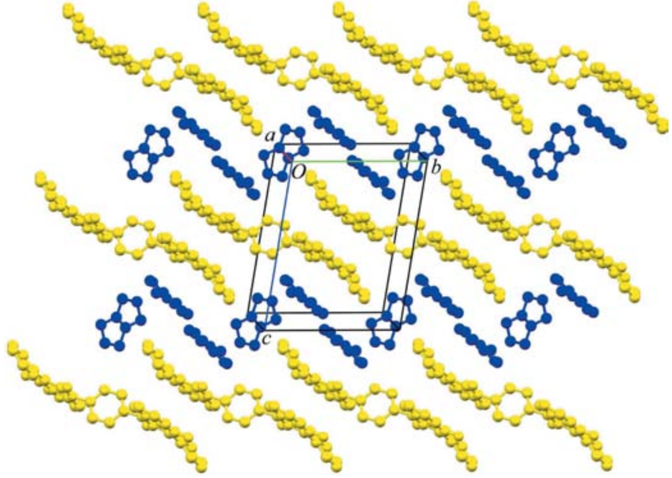


Figure 6
The packing of (I*b*); molecules of (I) are shaded light and solvent molecules are dark (yellow and blue, respectively, in the electronic version of the paper).

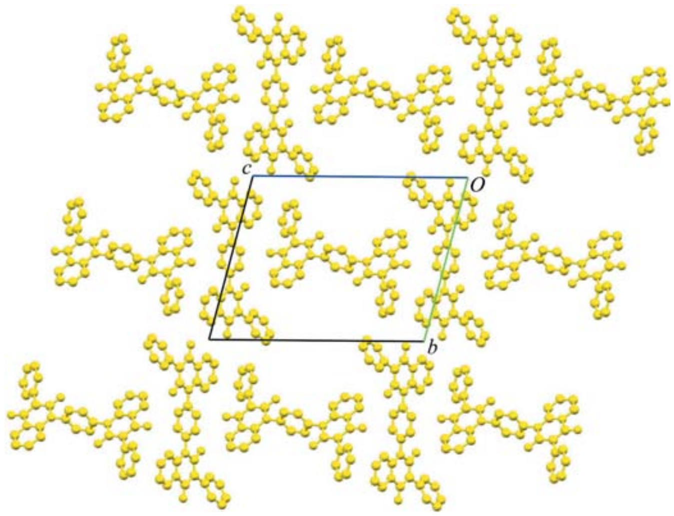


Figure 7
The packing of (I*c*), viewed along [100]. The channels are filled by disordered solvent molecules, which were omitted from the model.

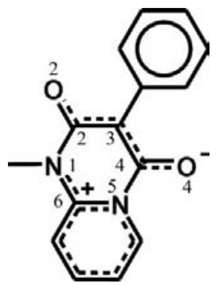


Figure 8
Charge delocalization and the atom numbering in the mesoionic heterocycle of (I).

which are rotated out of the pyrido[1,2-*a*]pyrimidin-1-ium plane by 82.17 (6)° in (I*a*), 79.51 (8)° in (I*b*), and 88.16 (12) and 79.07 (10)° for the two independent molecules in (I*c*). Thus, the phenylene groups are oriented nearly orthogonal to the rest of the molecule, to avoid steric hindrance between the phenylene H atoms and the atoms of the heterocyclic system. The terminal phenyl ring is also rotated out of the pyrido[1,2-*a*]pyrimidin-1-ium plane. The dihedral angles are 23.24 (7)° in (I*a*), 28.76 (10)° in (I*b*), and 44.79 (15) and 35.68 (15)° in (I*c*). Apparently this dihedral angle can be easily influenced by the molecular packing. In (I*a*), only the propan-2-ol is disordered (see Fig. 4), whereas in (I*b*) all NMP molecules are disordered (Fig. 2). In one NMP molecule, the N—CH$_3$ group (atoms N41 and C41) is disordered with a CH$_2$ group (atom C43), whereas the C$=$O group maintains its position. The other NMP molecule is located on a crystallographic inversion centre between the N atom and the carbonyl C atom, which leads to a disorder of all atoms. In (I*a*), the propan-2-ol molecule forms a hydrogen bond to an NMP molecule (Fig. 4, Table 1). Compounds (I*a*) and (I*b*) display layer structures in which the pigment and solvent molecules are arranged in alternating layers (Figs. 5 and 6). In compound (I*c*), the molecules form columns in the [100] direction; the solvent molecules are embedded in channels situated between the columns (Fig. 7).

In all three structures, the out-of-plane rotation of the central phenylene ring results in a cross-shaped molecular conformation which hinders efficient molecular packing (as for several spiro compounds). This may be the reason that the solvent molecules are incorporated into the crystals.

The bond lengths in the mesoionic ring system (see Table 2 and Fig. 8) are in agreement with the values found for (II). The bond lengths show that the positive charge is delocalized over the N1—C6—N5 fragment and the adjacent pyridine ring, whereas the negative charge is distributed over the O2—C2–C3—C4—O4 fragment. Between these two fragments the conjugation is weak, as can be seen from the long N1—C2 and C4—N5 bonds.

Solvent-free single crystals of (I) could not be obtained. All crystals of (I) collapse when they are dried at room temperature, resulting in powders of such low crystallinity that crystal structure solution from the powder data, which nowadays can be done routinely (David *et al.*, 1998; Nowell *et al.*, 2002; van de Streek *et al.*, 2009), failed. None of the powder patterns could be indexed in a reasonable way [*DIVCOL06* (Boultif & Louër, 2004) and *MCMAILLE* (Version 4.0; Bergmann *et al.*, 2004)]. The powder patterns of (I) were unrelated to the simulated powder patterns of (I*a*), (I*b*) or (I*c*). Therefore, the crystal structure of solvent-free compound (I) could not be determined.

Experimental

Compound (I) was synthesized according to the method of Metz & Plüg (2005) (see scheme in the *Comment*). The obtained powder was stirred in dimethylformamide for 30–60 min, filtered, and dried at 353–373 K, giving 10 g of (I). For the preparation of (I*a*), a suspension of compound (I) (10 mg) in *N*-methylpyrrolidone (2 ml) was heated in a beaker to 477 K, then cooled to room temperature. The beaker was placed in a larger beaker and propan-2-ol (4 ml) was added to the smaller beaker. The larger beaker was sealed and set aside for 3 d. Yellow fluorescent crystals of (I*a*) were obtained, with sizes up to 0.8 × 0.4 × 0.4 mm. For (I*b*), the crystallization was carried out as for (I*a*), but butan-1-ol (2 ml) was used instead of propan-2-ol. After 2 d, yellow fluorescent crystals of (I*b*) were obtained, with sizes up to 1.2 × 1.2 × 0.4 mm. For (I*c*), the crystallization was carried out as for (I*a*), but butan-1-ol (4 ml) was used instead of propan-2-ol. Yellow fluorescent crystals of (I*c*) were obtained, with sizes up to 1.8 × 0.9 × 0.9 mm.

For the phase analysis, the powder samples were measured on a Stoe Stadi-P powder diffractometer [curved Ge(111) primary monochromator, Cu $K\alpha_1$ radiation, $\lambda = 1.5406$ Å] in transmission geometry from 2 to 74° in 2θ. All samples were prepared between two polyacetate films. An image-plate position-sensitive detector (IPPSD) was used. For data acquisition, the Stoe software *WinXPOW* (Stoe & Cie, 2004) was used.

Compound (I*a*)

Crystal data

$C_{34}H_{22}N_4O_4\cdot 2C_5H_9NO\cdot C_3H_8O$
$M_r = 808.91$
Triclinic, $P\overline{1}$
$a = 8.7737$ (10) Å
$b = 10.4982$ (11) Å
$c = 11.7877$ (12) Å
$\alpha = 98.463$ (8)°
$\beta = 101.314$ (8)°
$\gamma = 104.750$ (8)°
$V = 1007.07$ (19) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 173$ K
0.53 × 0.32 × 0.26 mm

Data collection

Stoe IPDS-II two-circle diffractometer
19547 measured reflections
4103 independent reflections
3305 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.181$
$S = 1.06$
4103 reflections
290 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.72$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Compound (I*b*)

Crystal data

$C_{34}H_{22}N_4O_4\cdot 3C_5H_9NO$
$M_r = 847.95$
Triclinic, $P\overline{1}$
$a = 8.8137$ (8) Å
$b = 10.1565$ (9) Å
$c = 12.7300$ (11) Å
$\alpha = 99.212$ (7)°
$\beta = 99.567$ (7)°
$\gamma = 105.102$ (7)°
$V = 1059.84$ (16) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 173$ K
0.24 × 0.23 × 0.13 mm

Data collection

Stoe IPDS-II two-circle diffractometer
15396 measured reflections
4290 independent reflections
3513 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.223$
$S = 1.20$
4290 reflections
298 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.90$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.05$ e Å^{-3}

Compound (I*c*)

Crystal data

$C_{34}H_{22}N_4O_4\cdot 0.5C_5H_9NO\cdot C_4H_{10}O$
$M_r = 674.24$
Triclinic, $P\overline{1}$
$a = 5.7853$ (6) Å
$b = 15.2219$ (17) Å
$c = 19.198$ (2) Å
$\alpha = 75.321$ (9)°
$\beta = 87.393$ (8)°
$\gamma = 84.740$ (9)°
$V = 1628.1$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 173$ K
0.21 × 0.09 × 0.09 mm

Data collection

Stoe IPDS-II two-circle diffractometer
23578 measured reflections
6641 independent reflections
3364 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.088$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.218$
$S = 0.95$
6641 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

In (I*a*), the propan-2-ol molecule is disordered across a centre of inversion over two equally occupied sites. The C—C bonds and C—C—O angles in this molecule were restrained to be equal with effective s.u. values of 0.02 Å and 0.04°, respectively. The highest peak in the final difference density map (0.72 e Å^{-3}) is located 0.93 Å from atom H41*B*.

All *N*-methylpyrrolidone molecules of (I*b*) are disordered over two equally occupied sites. One is located on a centre of inversion and the other is on a general position. In both of them, the atoms sharing the same site were refined with coordinates and displacement parameters constrained to the same values. The bonds between the

Table 1
Hydrogen-bond geometry (Å, °) for (I*a*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O52—H52···O42	0.84	2.02	2.691 (5)	137

Table 2
Selected bond lengths in solvates (I*a*)–(I*c*) and CSD refcode XAKZEO, (II).

See Fig. 8 for atom numbering.

Bond	(I*a*)	(I*b*)	(I*c*)†	(I*c*)†	XAKZEO, (II)
N1—C2	1.432 (2)	1.433 (2)	1.424 (5)	1.446 (5)	1.3961 (13)
C2—O2	1.230 (2)	1.229 (3)	1.232 (4)	1.232 (4)	1.2464 (12)
C2—C3	1.436 (2)	1.440 (3)	1.432 (5)	1.426 (5)	1.4273 (14)
C3—C4	1.403 (2)	1.405 (3)	1.399 (5)	1.409 (5)	1.4115 (14)
C4—O4	1.230 (2)	1.234 (2)	1.232 (4)	1.238 (4)	1.2225 (13)
C4—N5	1.494 (2)	1.500 (2)	1.491 (5)	1.499 (5)	1.4903 (13)
N5—C6	1.358 (2)	1.363 (2)	1.372 (5)	1.370 (4)	1.3575 (13)
C6—N1	1.357 (2)	1.366 (2)	1.365 (5)	1.373 (5)	1.3376 (13)

† Two independent molecules.

methylene C atoms were restrained to 1.500 (1) Å. The highest peak in the final difference density map (0.90 e Å^{-3}) is located 0.43 Å from atom C54.

From the enlarged atomic displacement parameters for some atoms of the solvent molecules in (I*a*) and (I*b*), it was evident that the solvent molecules were highly disordered and that the best refined models only approximate the true average arrangement. The geometric parameters of the solvent molecules should therefore be considered to be only approximate.

The H atoms for (I*a*), (I*b*) and (I*c*) were located in difference maps, but were positioned geometrically and refined using a riding model with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,O) or 1.5$U_{\rm eq}$(methyl C)] and with O—H = 0.84 Å, aromatic C—H = 0.95 Å, methylene C—H = 0.99 Å or methyl C—H = 0.98 Å. The methyl groups were allowed to rotate but not to tip. The torsion angle about the C—O bond of each hydroxyl group was refined.

The solvent molecules in (I*c*) were severely disordered and could not be modelled. The contribution of the disordered solvent to the calculated structure factors was taken into account following the BYPASS algorithm (van der Sluis & Spek, 1990), implemented as the SQUEEZE option in *PLATON* (Spek, 2009). The final $F_{\rm o}^2/F_{\rm c}^2$ data were calculated with the FCF routine of *PLATON* and include the disordered solvent contribution. *PLATON* found one void (volume = 386 Å^3) in the unit cell (located at $x = -0.053$, $y = 0.000$, $z = \frac{1}{2}$) and estimated that there are approximately 48 electrons in this void. For calculating M_r, μ, ρ, *etc.*, we assumed a composition of (I)·0.5NMP·1-BuOH. Although we suppressed the contribution of the solvent to the scattering power for (I*c*), the figures of merit remain rather high. This is most probably due to the low quality of the crystal (expressed in $R_{\rm int}$ = 0.0875 and R_σ = 0.1178). However, this crystal was the best obtainable.

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Version 2.0; Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

The authors thank Dr Carsten Plüg and Dr Thomas Metz (both Clariant, Frankfurt) for the synthesis and supply of the raw material. Clariant GmbH is acknowledged for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3130). Services for accessing these data are described at the back of the journal.

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