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Low-temperature study of a new nevirapine pseudopolymorph

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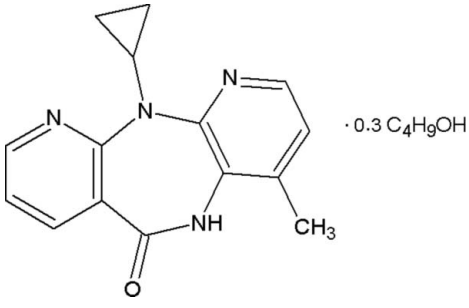
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.075; wR factor = 0.237; data-to-parameter ratio = 14.1.

The title compound (systematic name: 11-cyclopropyl-4-methyl-5,11-dihydro-6*H*-dipyrido[3,2-*b*:2′,3′-*e*][1,4]diazepin-6-one butanol 0.3-solvate), $C_{15}H_{14}N_4O\cdot0.3C_4H_9OH$, was crystallized in a new triclinic pseudopolymorphic form, a butanol solvate, and the crystal structure determined at 150 K. The molecular conformation of this new form differs from that reported previously, although the main intermolecular hydrogen-bond pattern remains the same. N—H···O hydrogen bonds [N···O = 2.957 (3) Å] form centrosymmetric dimers and the crystal packing of this new pseudopolymorph generates infinite channels along the *b* axis.

Related literature

For the crystal structure of an earlier polymorph, see: Mui *et al.* (1992). For spectroscopic studies of three further polymorphs, see: Reguri & Chakka (2005); World Health Organization (2005). For related literature, see: Ayala *et al.* (2007); Ren *et al.* (1995).



Experimental

Crystal data

$C_{15}H_{14}N_4O\cdot0.3C_4H_{10}O$
M_r = 288.54
Triclinic, $P\overline{1}$
a = 7.8116 (6) Å
b = 8.4302 (7) Å
c = 12.5451 (11) Å
α = 84.817 (5)°
β = 88.415 (5)°
γ = 68.252 (4)°
V = 764.18 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 150.0 (2) K
0.47 × 0.29 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
12941 measured reflections
3141 independent reflections
2295 reflections with $I > 2\sigma(I)$
R_{int} = 0.100

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.237
S = 1.08
3141 reflections
222 parameters
28 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2093).

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supplementary materials

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Low-temperature study of a new nevirapine pseudopolymorph

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Comment

Nevirapine (11-cyclopropyl-5,11-dihydro-4-methyl-6*H*-dipyrido[3,2 − b:2',3'-e][1,4]diazepin-6-one) (NVP) is an antiretroviral drug that belongs to the non-nucleoside inhibitors class of the HIV-1 virus reverse transcriptase (NNRTI). Only one crystal structure is known, reported by Mui *et al.*, in the centrosymmetric space group, $P2_1/c$ (Form I) [Mui *et al.*, 1992]. The literature also describes the existence of two polymorphs (Form II and III), useful as anti-psychotics, and one hemihydrate pseudopolymorph (Form IV). They were studied by X-ray powder diffraction, RAMAN and IR, but no crystal structure studies are available yet [World Health Organization, 2005; Reguri & Chakka, 2005]. We report here, the crystal structure of the pseudopolymorph butanol solvate of nervirapine, $C_{15}H_{14}N_4O$*0.3(CH_3OH), in the centrosymmetric space group $P\bar{1}$ (Figure 1), hereafter, Form V.

As most of the NNRTIs, nevirapine displays a "butterfly like" conformation, which is also preserved in complexes with the HIV-1 reverse transcriptase [Ren *et al.*, 1995]. Comparing the NVP conformations, it could be seen that the dihedral angle between the least square planes through the pyridine rings is 123.89 (9)°, somewhat larger than the one found by Mui *et al.*, 121°, but still smaller than the one determined from the enzyme-inhibitor complex structure and *ab initio* calculations (129.22°) [Ayala *et al.*, 2007].

An electron delocalization effect is presented by the amide moiety of the 7-membered ring, allowing this group to adopt a planar conformation with a C6—C5—N2—C4 torsion angle of −2.7 (4)° (slightly smaller than the one found for I, −4°) and to which the cyclopropyl substituent, evolving away from the molecular framework, subtends a dihedral angle of 68.5 (1)°.

The molecular superposition of I and V, calculated by minimizing the root square distance between the atoms of the 7-membered rings, shows that the main conformational differences are mainly concentrated in the cyclopropyl group, which presents C14—C13—N4—C10 and C15—C13—N4—C11 torsion angles of 81.9 (3)°, −69.9 (3)° in V, and 74.6°, −78.1° in I, respectively. In addiction, the superposition shows a small difference in conformation of the methyl substituted pyridine ring. The asymmetric unit in V is completed by the presence of a disordered butanol molecule with an occupation factor of 0.3.

The analysis of the intermolecular interaction shows that, like in I, NEV molecules are linked essentially by two N—H···O hydrogen bonds, forming centrosymmetric dimers.

It is interesting to note that the main difference between both polymorphs is related to the crystal packing: while in I the intermolecular interaction generates a close packing with flat layers of nevirapine molecules separated by less than 4.4 Å, in V the three-dimensional arrangement generates infinite channels along de *b* axis with a diameter of more than 10.5 Å (Figure 2). These infinite channels are filled with highly disordered molecules of butanol, and this new Nevirapine form is stable even when a solvent occupation factor as low as 30%.

These findings indicate that a wide spectrum of new nevirapine pseudopolymorphs could be generated by just changing the solvent used in the crystallization process, as long as the volume of the solvent matches the available channel volume.

Experimental

NVP raw materials from different commercial sources were analyzed. USP standards of anhydrous and hemihydrate NEV were used as references.

Refinement

All the hydrogen atoms were observed in the difference Fourier map, but positioned stereochemically (C—H: 0.95, C—H_2: 0.97, C—H_3:0.96, N—H: 0.88, O—H: 0.82 Å) and allowed to ride with isotropic displacement factors tied to those of their hosts by a factor of 1.2 (C—H, C—H_2, N—H) and 1.5 (C—H_3, O—H).

Figures

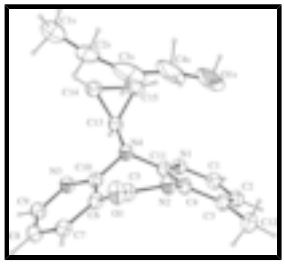

Fig. 1. The molecular structure of the butanol solvate of Nervirapine, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radius.

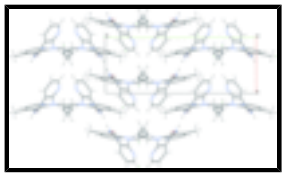

Fig. 2. Crystal packing of nevirapine, a) flat chain disposition of the molecules in Form I, and b) Channel formation with the solvent molecules inside.

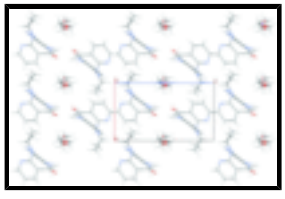

Fig. 3. Supplementary figure.

11-cyclopropyl-4-methyl-5,11-dihydro-6*H*-dipyrido[3,2 – b:2',3'-e][1,4] diazepin-6-one butanol 0.3-solvate

Crystal data

$C_{15}H_{14}N_4O·0.3C_4H_{10}O$	$Z = 2$
$M_r = 288.54$	$F_{000} = 305.2$
Triclinic, $P\bar{1}$	$D_x = 1.254$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.8116$ (6) Å	Cell parameters from 37940 reflections
$b = 8.4302$ (7) Å	$\theta = 2.9$–26.4º
$c = 12.5451$ (11) Å	$\mu = 0.08$ mm^{-1}
$\alpha = 84.817$ (5)º	$T = 150.0$ (2) K

β = 88.415 (5)°	Prism, colourless
γ = 68.252 (4)°	0.47 × 0.29 × 0.07 mm
V = 764.18 (11) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	3141 independent reflections
Radiation source: fine-focus sealed tube	2295 reflections with $I > 2\sigma(I)$
Monochromator: horizonally mounted graphite crystal	R_{int} = 0.100
Detector resolution: 9 pixels mm^{-1}	θ_{max} = 26.8°
T = 150.0(2) K	θ_{min} = 3.4°
φ scans and ω scans winth κ offsets	h = −9→9
Absorption correction: none	k = −10→10
12941 measured reflections	l = −15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.075	H-atom parameters constrained
$wR(F^2)$ = 0.237	$w = 1/[\sigma^2(F_o^2) + (0.1266P)^2 + 0.361P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max} < 0.001$
3141 reflections	$\Delta\rho_{max}$ = 0.51 e Å^{-3}
222 parameters	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
28 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.37 (8)

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}	Occ. (<1)

C1	0.1486 (4)	1.0251 (4)	0.1362 (2)	0.0486 (7)	
H1	0.0843	1.1222	0.0887	0.058*	
C2	0.2621 (4)	1.0419 (4)	0.2131 (2)	0.0484 (7)	
H2	0.2773	1.1481	0.2162	0.058*	
C3	0.3543 (4)	0.9043 (3)	0.2859 (2)	0.0446 (7)	
C4	0.3290 (4)	0.7507 (3)	0.27637 (19)	0.0413 (6)	
C5	0.4871 (4)	0.4427 (3)	0.3419 (2)	0.0429 (7)	
C6	0.4937 (4)	0.3825 (3)	0.23304 (19)	0.0412 (6)	
C7	0.6468 (4)	0.2423 (3)	0.2073 (2)	0.0445 (7)	
H7	0.7470	0.1928	0.2563	0.053*	
C8	0.6523 (4)	0.1755 (4)	0.1104 (2)	0.0483 (7)	
H8	0.7572	0.0819	0.0902	0.058*	
C9	0.5019 (4)	0.2482 (4)	0.0438 (2)	0.0473 (7)	
H9	0.5058	0.2010	−0.0226	0.057*	
C10	0.3470 (4)	0.4485 (3)	0.15882 (19)	0.0398 (6)	
C11	0.2150 (4)	0.7433 (3)	0.19405 (19)	0.0408 (6)	
C12	0.4723 (5)	0.9217 (4)	0.3731 (2)	0.0544 (8)	
H12A	0.4862	1.0328	0.3613	0.082*	
H12B	0.5939	0.8294	0.3725	0.082*	
H12C	0.4138	0.9142	0.4425	0.082*	
C13	0.0187 (4)	0.6077 (3)	0.1266 (2)	0.0427 (6)	
H13	0.0156	0.6333	0.0471	0.051*	
C14	−0.0852 (4)	0.4999 (4)	0.1721 (2)	0.0513 (7)	
H14A	−0.0327	0.4195	0.2358	0.062*	
H14B	−0.1522	0.4595	0.1216	0.062*	
C15	−0.1544 (4)	0.6888 (4)	0.1854 (2)	0.0550 (8)	
H15A	−0.2643	0.7643	0.1433	0.066*	
H15B	−0.1448	0.7244	0.2573	0.066*	
N1	0.1247 (3)	0.8771 (3)	0.12553 (17)	0.0447 (6)	
N2	0.4074 (3)	0.6114 (3)	0.35485 (16)	0.0438 (6)	
H2A	0.4033	0.6390	0.4211	0.053*	
N3	0.3494 (3)	0.3815 (3)	0.06598 (17)	0.0438 (6)	
N4	0.1863 (3)	0.5888 (3)	0.18231 (16)	0.0406 (6)	
O1	0.5584 (3)	0.3371 (2)	0.41782 (15)	0.0558 (6)	
O1S	−0.0302 (14)	0.767 (2)	0.4857 (14)	0.151 (2)	0.30
H1S	−0.1389	0.8162	0.5006	0.227*	0.30
C1S	−0.0352 (18)	0.1631 (17)	0.4483 (10)	0.080 (3)	0.30
H11S	−0.1619	0.2166	0.4262	0.120*	0.30
H12S	−0.0245	0.0799	0.5077	0.120*	0.30
H13S	0.0377	0.1074	0.3899	0.120*	0.30
C2S	0.036 (2)	0.2730 (18)	0.4746 (9)	0.066 (3)	0.30
H21S	0.1625	0.1944	0.4872	0.079*	0.30
H22S	−0.0175	0.2782	0.5454	0.079*	0.30
C3S	0.0709 (18)	0.419 (2)	0.4881 (14)	0.109 (6)	0.30
H31S	0.1876	0.3703	0.5263	0.131*	0.30
H32S	0.1055	0.4342	0.4141	0.131*	0.30
C4S	0.019 (2)	0.578 (2)	0.5080 (18)	0.151 (2)	0.30
H41S	0.1126	0.5594	0.5620	0.182*	0.30
H42S	−0.0885	0.5808	0.5494	0.182*	0.30

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0560 (16)	0.0426 (15)	0.0444 (15)	−0.0156 (13)	0.0005 (12)	−0.0005 (11)
C2	0.0591 (17)	0.0413 (14)	0.0469 (15)	−0.0208 (13)	0.0056 (13)	−0.0067 (11)
C3	0.0519 (15)	0.0423 (14)	0.0412 (14)	−0.0189 (12)	0.0041 (11)	−0.0067 (11)
C4	0.0494 (15)	0.0394 (14)	0.0346 (12)	−0.0155 (11)	0.0021 (11)	−0.0050 (10)
C5	0.0534 (15)	0.0420 (14)	0.0343 (13)	−0.0187 (12)	−0.0031 (11)	−0.0031 (10)
C6	0.0527 (15)	0.0400 (14)	0.0340 (13)	−0.0209 (12)	−0.0010 (11)	−0.0029 (10)
C7	0.0497 (15)	0.0437 (15)	0.0412 (14)	−0.0182 (12)	−0.0021 (11)	−0.0033 (11)
C8	0.0508 (16)	0.0484 (16)	0.0445 (15)	−0.0160 (13)	0.0013 (12)	−0.0082 (12)
C9	0.0535 (16)	0.0506 (16)	0.0380 (13)	−0.0184 (13)	0.0008 (11)	−0.0095 (11)
C10	0.0468 (14)	0.0399 (13)	0.0353 (12)	−0.0193 (11)	0.0013 (10)	−0.0029 (10)
C11	0.0493 (14)	0.0393 (14)	0.0338 (12)	−0.0163 (11)	0.0015 (11)	−0.0034 (10)
C12	0.0700 (19)	0.0494 (17)	0.0504 (16)	−0.0285 (15)	−0.0023 (14)	−0.0087 (13)
C13	0.0461 (14)	0.0468 (15)	0.0364 (13)	−0.0177 (12)	−0.0007 (11)	−0.0069 (11)
C14	0.0552 (17)	0.0576 (18)	0.0460 (15)	−0.0259 (14)	0.0021 (12)	−0.0076 (13)
C15	0.0492 (16)	0.0623 (19)	0.0524 (16)	−0.0167 (14)	0.0000 (13)	−0.0163 (14)
N1	0.0514 (13)	0.0425 (12)	0.0396 (12)	−0.0172 (10)	0.0010 (10)	−0.0023 (9)
N2	0.0568 (14)	0.0426 (12)	0.0313 (11)	−0.0172 (10)	−0.0010 (9)	−0.0048 (9)
N3	0.0512 (13)	0.0453 (13)	0.0353 (11)	−0.0179 (10)	0.0004 (9)	−0.0063 (9)
N4	0.0489 (13)	0.0398 (12)	0.0340 (11)	−0.0168 (10)	−0.0026 (9)	−0.0049 (8)
O1	0.0797 (15)	0.0442 (11)	0.0369 (10)	−0.0150 (10)	−0.0094 (9)	−0.0014 (8)
O1S	0.024 (3)	0.217 (5)	0.210 (5)	−0.017 (4)	0.017 (4)	−0.131 (4)
C1S	0.067 (6)	0.095 (7)	0.060 (5)	−0.011 (5)	0.008 (5)	−0.007 (5)
C2S	0.065 (6)	0.080 (7)	0.048 (5)	−0.026 (5)	0.016 (4)	0.009 (5)
C3S	0.022 (5)	0.171 (15)	0.100 (10)	0.006 (8)	−0.011 (6)	−0.017 (10)
C4S	0.024 (3)	0.217 (5)	0.210 (5)	−0.017 (4)	0.017 (4)	−0.131 (4)

Geometric parameters (Å, °)

C1—N1	1.346 (3)	C12—H12C	0.9800
C1—C2	1.379 (4)	C13—N4	1.450 (3)
C1—H1	0.9500	C13—C15	1.480 (4)
C2—C3	1.387 (4)	C13—C14	1.496 (4)
C2—H2	0.9500	C13—H13	1.0000
C3—C4	1.396 (4)	C14—C15	1.504 (4)
C3—C12	1.501 (4)	C14—H14A	0.9900
C4—C11	1.403 (4)	C14—H14B	0.9900
C4—N2	1.419 (3)	C15—H15A	0.9900
C5—O1	1.232 (3)	C15—H15B	0.9900
C5—N2	1.347 (3)	N2—H2A	0.8800
C5—C6	1.493 (3)	O1S—C4S	1.497 (17)
C6—C7	1.390 (4)	O1S—H1S	0.8200
C6—C10	1.408 (4)	C1S—C2S	1.315 (15)
C7—C8	1.379 (4)	C1S—H11S	0.9600
C7—H7	0.9500	C1S—H12S	0.9600
C8—C9	1.372 (4)	C1S—H13S	0.9600

C8—H8	0.9500	C2S—C3S	1.380 (16)
C9—N3	1.343 (4)	C2S—H21S	0.9700
C9—H9	0.9500	C2S—H22S	0.9700
C10—N3	1.336 (3)	C3S—C4S	1.293 (15)
C10—N4	1.416 (3)	C3S—H31S	0.9700
C11—N1	1.333 (3)	C3S—H32S	0.9700
C11—N4	1.422 (3)	C4S—H41S	0.9700
C12—H12A	0.9800	C4S—H42S	0.9700
C12—H12B	0.9800		
N1—C1—C2	122.9 (3)	C13—C14—C15	59.12 (19)
N1—C1—H1	118.5	C13—C14—H14A	117.9
C2—C1—H1	118.5	C15—C14—H14A	117.9
C1—C2—C3	120.3 (3)	C13—C14—H14B	117.9
C1—C2—H2	119.9	C15—C14—H14B	117.9
C3—C2—H2	119.9	H14A—C14—H14B	115.0
C2—C3—C4	117.3 (2)	C13—C15—C14	60.19 (19)
C2—C3—C12	121.2 (2)	C13—C15—H15A	117.8
C4—C3—C12	121.4 (2)	C14—C15—H15A	117.8
C3—C4—C11	118.7 (2)	C13—C15—H15B	117.8
C3—C4—N2	119.2 (2)	C14—C15—H15B	117.8
C11—C4—N2	122.0 (2)	H15A—C15—H15B	114.9
O1—C5—N2	121.4 (2)	C11—N1—C1	117.2 (2)
O1—C5—C6	119.2 (2)	C5—N2—C4	129.0 (2)
N2—C5—C6	119.5 (2)	C5—N2—H2A	115.5
C7—C6—C10	117.9 (2)	C4—N2—H2A	115.5
C7—C6—C5	117.8 (2)	C10—N3—C9	117.1 (2)
C10—C6—C5	123.9 (2)	C10—N4—C11	114.7 (2)
C8—C7—C6	119.6 (3)	C10—N4—C13	116.68 (19)
C8—C7—H7	120.2	C11—N4—C13	115.8 (2)
C6—C7—H7	120.2	C4S—O1S—H1S	108.6
C9—C8—C7	118.0 (3)	C2S—C1S—H11S	113.2
C9—C8—H8	121.0	C2S—C1S—H12S	109.4
C7—C8—H8	121.0	H11S—C1S—H12S	109.5
N3—C9—C8	124.6 (2)	C2S—C1S—H13S	105.8
N3—C9—H9	117.7	H11S—C1S—H13S	109.5
C8—C9—H9	117.7	H12S—C1S—H13S	109.5
N3—C10—C6	122.8 (2)	C1S—C2S—C3S	164.8 (16)
N3—C10—N4	117.1 (2)	C1S—C2S—H21S	98.8
C6—C10—N4	120.1 (2)	C3S—C2S—H21S	95.5
N1—C11—C4	123.5 (2)	C1S—C2S—H22S	92.2
N1—C11—N4	116.4 (2)	C3S—C2S—H22S	89.7
C4—C11—N4	120.1 (2)	H21S—C2S—H22S	103.2
C3—C12—H12A	109.5	C4S—C3S—C2S	152.3 (18)
C3—C12—H12B	109.5	C4S—C3S—H31S	100.9
H12A—C12—H12B	109.5	C2S—C3S—H31S	100.7
C3—C12—H12C	109.5	C4S—C3S—H32S	97.0
H12A—C12—H12C	109.5	C2S—C3S—H32S	94.3
H12B—C12—H12C	109.5	H31S—C3S—H32S	104.1
N4—C13—C15	115.3 (2)	C3S—C4S—O1S	158.0 (19)

N4—C13—C14	116.6 (2)	C3S—C4S—H41S	95.7
C15—C13—C14	60.7 (2)	O1S—C4S—H41S	97.1
N4—C13—H13	117.3	C3S—C4S—H42S	96.0
C15—C13—H13	117.3	O1S—C4S—H42S	98.3
C14—C13—H13	117.3	H41S—C4S—H42S	103.6
N1—C1—C2—C3	−1.8 (4)	C4—C11—N1—C1	1.1 (4)
C1—C2—C3—C4	1.0 (4)	N4—C11—N1—C1	179.3 (2)
C1—C2—C3—C12	−177.4 (3)	C2—C1—N1—C11	0.7 (4)
C2—C3—C4—C11	0.7 (4)	O1—C5—N2—C4	175.9 (3)
C12—C3—C4—C11	179.1 (2)	C6—C5—N2—C4	−2.5 (4)
C2—C3—C4—N2	−174.4 (2)	C3—C4—N2—C5	−141.5 (3)
C12—C3—C4—N2	4.0 (4)	C11—C4—N2—C5	43.5 (4)
O1—C5—C6—C7	−32.6 (4)	C6—C10—N3—C9	−1.6 (4)
N2—C5—C6—C7	145.8 (3)	N4—C10—N3—C9	−179.9 (2)
O1—C5—C6—C10	141.0 (3)	C8—C9—N3—C10	1.1 (4)
N2—C5—C6—C10	−40.5 (4)	N3—C10—N4—C11	−118.4 (2)
C10—C6—C7—C8	1.5 (4)	C6—C10—N4—C11	63.2 (3)
C5—C6—C7—C8	175.6 (2)	N3—C10—N4—C13	21.7 (3)
C6—C7—C8—C9	−1.9 (4)	C6—C10—N4—C13	−156.7 (2)
C7—C8—C9—N3	0.6 (4)	N1—C11—N4—C10	119.0 (2)
C7—C6—C10—N3	0.3 (4)	C4—C11—N4—C10	−62.8 (3)
C5—C6—C10—N3	−173.4 (2)	N1—C11—N4—C13	−21.5 (3)
C7—C6—C10—N4	178.6 (2)	C4—C11—N4—C13	156.7 (2)
C5—C6—C10—N4	4.9 (4)	C15—C13—N4—C10	150.4 (2)
C3—C4—C11—N1	−1.9 (4)	C14—C13—N4—C10	82.0 (3)
N2—C4—C11—N1	173.1 (2)	C15—C13—N4—C11	−70.0 (3)
C3—C4—C11—N4	−179.9 (2)	C14—C13—N4—C11	−138.3 (2)
N2—C4—C11—N4	−4.9 (4)	C1S—C2S—C3S—C4S	41 (7)
N4—C13—C14—C15	105.5 (3)	C2S—C3S—C4S—O1S	−105 (6)
N4—C13—C15—C14	−107.6 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1^{i}	0.88	Missing	2.957 (3)	Missing

Symmetry codes: (i) −*x*, −*y*, −*z*.

Fig. 1

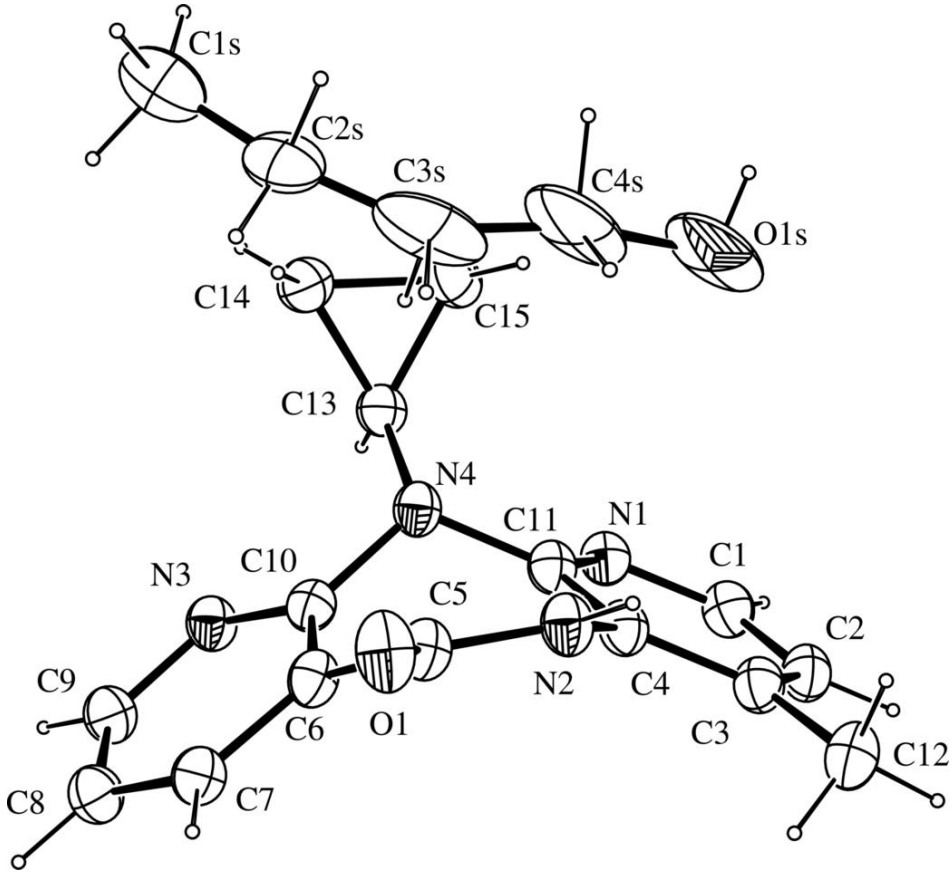
C1s
C2s
C3s
C4s
O1s
C14
C15
C13
N4
C11
N1
C1
N3
C10
C5
C2
C9
N2
C4
C6
O1
C3
C12
C8
C7

Fig. 2

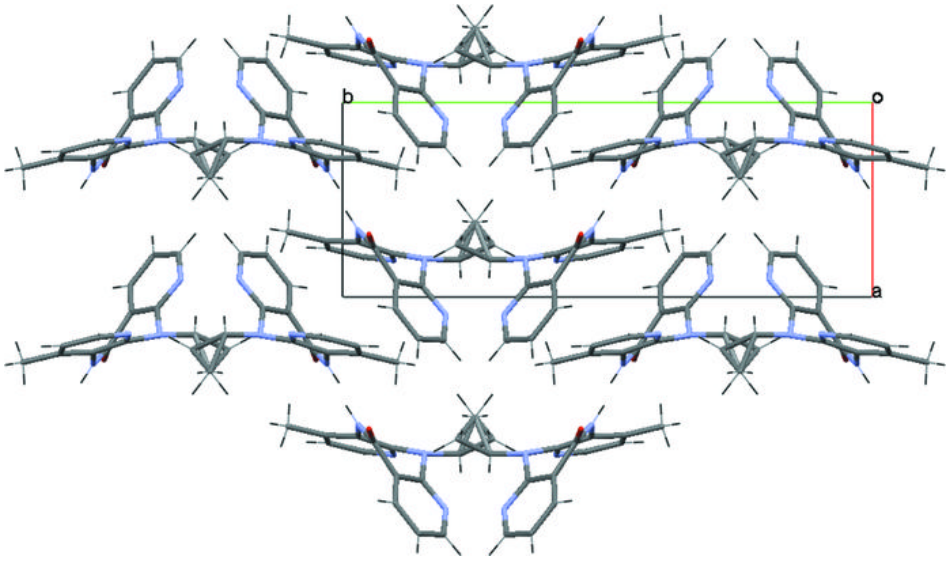

Fig. 3