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Two Schiff Base Ligands Derived from 2,2-Dimethyl-1,3-propanediamine

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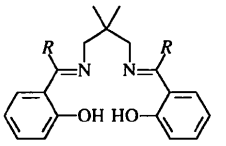
Abstract

The crystal structures of 2,2′-[2,2-dimethyl-1,3-propanediylbis(nitrilopropylidyne)]diphenol, $C_{23}H_{30}N_2O_2$, and 2,2′-{2,2-dimethyl-1,3-propanediylbis[nitrilo(phenyl)methylidyne]}diphenol, $C_{31}H_{30}N_2O_2$, have been determined. The N···O contact distances in both molecules are indicative of intramolecular hydrogen bonding. The molecular conformations are compared and shown to be very similar.

Comment

While Schiff base ligands are widely used in coordination chemistry (Calligaris & Randaccio, 1987) and in the enantioselective synthesis of organic molecules (Deng & Jacobsen, 1992), very few free ligand crystal structures have been reported (Corden, Errington, Moore & Wallbridge, 1996; Cannadine, Corden, Errington, Moore & Wallbridge, 1996). This paper reports the structures of two such ligands so that subsequent changes upon coordination can be investigated.

The molecular structures of compounds 2,2′-[2,2-dimethyl-1,3-propanediylbis(nitrilopropylidyne)]diphenol, (I), and 2,2′-[2,2-dimethyl-1,3-propanediylbis(nitrilophenylmethylidyne)]diphenol, (II), are shown in Figs. 1 and 2, respectively. The bond lengths and angles are unexceptional, but confirm that the enolimine tautomers are favoured. Furthermore, the shortest N···O distances [2.476 (2) and 2.502 (2) Å for (I); 2.518 (3) and 2.528 (2) Å for (II)] are indicative of intramolecular hydrogen bonding, as indicated by the dotted lines in the figures. There is a striking similarity in the angles between the planes of the two phenol rings in (I) and (II) of 45.37 (9) and 44.50 (9)°, respectively. These values are noticeably smaller than the corresponding angle of 68.66 (11)° in the ligand where the imine-C atom carries an H-atom substituent (Corden, Errington, Moore & Wallbridge, 1996). Moreover, in this ligand the torsion angle C9—C8—N1—C7 is 141.3 (3)° whereas in (I) and (II) the corresponding angles C11—C14—N2—C15 and C15—C18—N2—C19 are −153.9 (2) and −151.8 (2) respectively. Since the conformations of the ethyl [in (I)] and phenyl [in (II)] substituents show a close relationship (Fig. 3), it is probable that these two substituents have a similar influence on the respective torsion angles, and thus play a role in determining the orientation of the two phenyl rings.



(I) R = Et
(I) R = Ph

The conformation of the free ligand in the solid state is of interest with respect to that required in a metal complex. For such species to act in the usual manner as tetradentate ligands, significant rearrangements must occur as is emphasized by the large O1···O2 separations of 7.181 (5) and 7.166 (6) Å for (I) and (II), respectively. This distance is reduced to 3.006 (3) Å when the H-

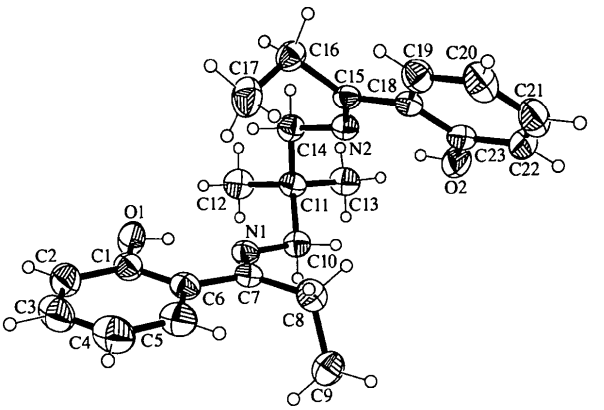


Fig. 1. View of molecule (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii.

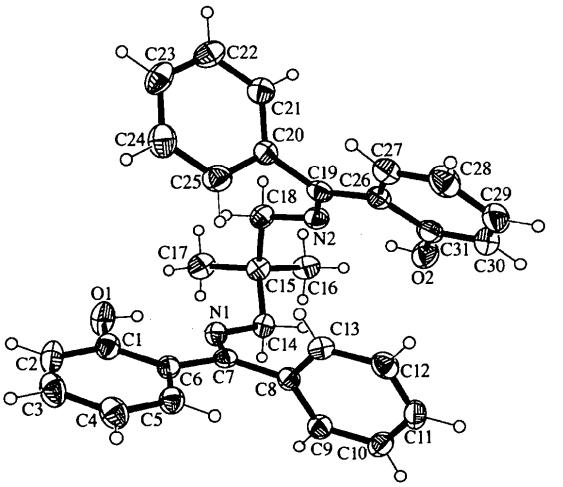


Fig. 2. View of molecule (II) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii.

substituted ligand is coordinated to a Ti^{IV} centre through the four N and O atoms (Corden, Errington, Moore & Wallbridge, 1995).

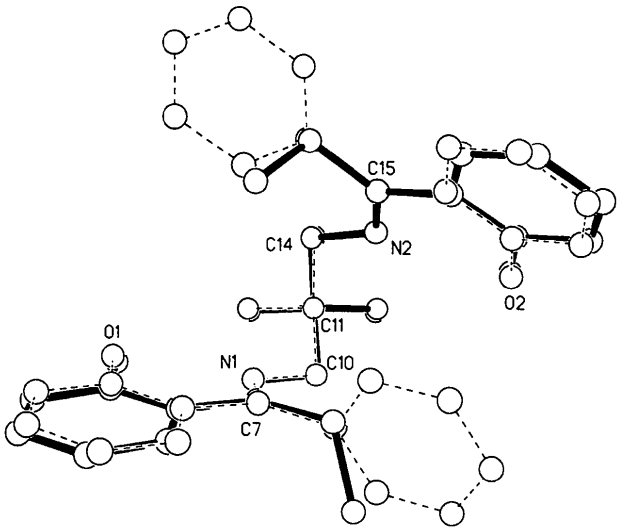


Fig. 3. Superposition of the two molecules. Atomic numbering refers to molecule (I) and H atoms are omitted for clarity.

Experimental

Ligand (I) was prepared in moderate yield (48%) by the condensation of 2-hydroxypropiophenone (68 mmol) with 2,2-dimethyl-1,3-propanediamine (34 mmol) in methanol (90 cm^3). The reaction mixture was stirred at 323 K for 2 h and then cooled to 273 K. The bright yellow solid which precipitated was washed and dried *in vacuo*. Crystals suitable for X-ray work were obtained by the slow evaporation of a saturated methanolic solution of the product.

Ligand (II) was prepared in good yield (68%) by the condensation of 2-hydroxybenzophenone (26 mmol) with 2,2-dimethyl-1,3-propanediamine (13 mmol) in methanol (50 cm^3). The reaction mixture was heated to 323 K for 1 h during which time a bright yellow solid precipitated. The solid was filtered, washed and dried *in vacuo*. Crystals suitable for X-ray work were obtained by the slow evaporation of a saturated methanolic solution of the product.

Compound (I)

Crystal data

$C_{23}H_{30}N_2O_2$
M_r = 366.49
Monoclinic
$P2_1/c$
a = 12.443 (10) Å
b = 13.286 (9) Å
c = 13.093 (8) Å
β = 108.37 (5)°
V = 2054 (3) $Å^3$
Z = 4
D_x = 1.185 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 2.24–25.10°
μ = 0.075 mm^{-1}
T = 120 (2) K
Block
0.32 × 0.26 × 0.22 mm
Yellow

Data collection

Delft Instruments FAST TV area detector (Dow, Drake, Hursthouse & Malik, 1993)
Area detector scans
Absorption correction: none
8860 measured reflections

3248 independent reflections
2027 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0730
θ_{max} = 25.10°
$h = -8 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0453
$wR(F^2)$ = 0.1052
S = 0.852
3247 reflections
250 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0440P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.17 e $Å^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for (I)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	1.05373 (12)	1.12676 (11)	0.37839 (12)	0.0464 (4)
O2	0.53577 (13)	0.86066 (11)	0.12490 (11)	0.0482 (4)
N1	0.90074 (13)	1.00057 (12)	0.35076 (12)	0.0323 (4)
N2	0.65729 (13)	1.01349 (11)	0.13977 (12)	0.0315 (4)
C1	1.1142 (2)	1.0549 (2)	0.34964 (15)	0.0380 (5)
C2	1.2264 (2)	1.0768 (2)	0.3561 (2)	0.0495 (6)
C3	1.2923 (2)	1.0046 (2)	0.3297 (2)	0.0570 (7)
C4	1.2496 (2)	0.9104 (2)	0.2958 (2)	0.0569 (7)
C5	1.1393 (2)	0.8880 (2)	0.2884 (2)	0.0458 (6)
C6	1.0693 (2)	0.9582 (2)	0.31586 (14)	0.0343 (5)
C7	0.9531 (2)	0.93260 (15)	0.31467 (14)	0.0316 (5)
C8	0.9054 (2)	0.82977 (14)	0.2770 (2)	0.0395 (5)
C9	0.9341 (2)	0.7542 (2)	0.3697 (2)	0.0508 (6)
C10	0.7885 (2)	0.98763 (14)	0.36229 (15)	0.0337 (5)
C11	0.7143 (2)	1.08078 (14)	0.32463 (15)	0.0331 (5)
C12	0.7662 (2)	1.1730 (2)	0.3918 (2)	0.0449 (6)
C13	0.5991 (2)	1.0599 (2)	0.3389 (2)	0.0423 (6)
C14	0.7020 (2)	1.10215 (14)	0.20646 (15)	0.0345 (5)
C15	0.6762 (2)	0.99587 (14)	0.05059 (15)	0.0292 (5)
C16	0.7424 (2)	1.06466 (15)	0.0005 (2)	0.0371 (5)
C17	0.8661 (2)	1.0343 (2)	0.0268 (2)	0.0509 (6)
C18	0.6317 (2)	0.89966 (14)	−0.00363 (14)	0.0307 (5)
C19	0.6559 (2)	0.8679 (2)	−0.0956 (2)	0.0391 (5)
C20	0.6165 (2)	0.7780 (2)	−0.1465 (2)	0.0473 (6)
C21	0.5497 (2)	0.7178 (2)	−0.1055 (2)	0.0514 (6)
C22	0.5226 (2)	0.7457 (2)	−0.0154 (2)	0.0471 (6)
C23	0.5638 (2)	0.83622 (15)	0.0369 (2)	0.0368 (5)

Compound (II)

Crystal data

$C_{31}H_{30}N_2O_2$
M_r = 462.57
Triclinic
$P\bar{1}$
a = 10.261 (9) Å
b = 10.786 (6) Å
c = 12.425 (5) Å
α = 99.39 (6)°
β = 110.22 (5)°
γ = 99.35 (5)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 1.80–25.26°
μ = 0.078 mm^{-1}
T = 120 (2) K
Block
0.34 × 0.32 × 0.24 mm
Yellow

V = 1237.0 (14) Å^3
Z = 2
D_x = 1.242 Mg m^{-3}
D_m not measured

Data collection

Delft Instruments FAST TV area detector
Area detector scans
Absorption correction: none
5128 measured reflections
3510 independent reflections

2573 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0806
θ_{max} = 25.26°
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 9$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0514
$wR(F^2)$ = 0.1402
S = 0.950
3507 reflections
320 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0750P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	−0.4860 (2)	0.1703 (2)	0.73844 (15)	0.0411 (5)
O2	0.0741 (2)	0.3330 (2)	0.52971 (15)	0.0389 (4)
N1	−0.3256 (2)	0.1374 (2)	0.6273 (2)	0.0257 (4)
N2	−0.1306 (2)	0.3939 (2)	0.5778 (2)	0.0288 (5)
C1	−0.3885 (2)	0.1426 (2)	0.8300 (2)	0.0294 (5)
C2	−0.4169 (3)	0.1374 (2)	0.9306 (2)	0.0382 (6)
C3	−0.3212 (3)	0.1086 (2)	1.0265 (2)	0.0395 (6)
C4	−0.1939 (3)	0.0841 (2)	1.0241 (2)	0.0353 (6)
C5	−0.1640 (2)	0.0886 (2)	0.9249 (2)	0.0285 (5)
C6	−0.2589 (2)	0.1177 (2)	0.8257 (2)	0.0244 (5)
C7	−0.2289 (2)	0.1174 (2)	0.7171 (2)	0.0231 (5)
C8	−0.0892 (2)	0.0946 (2)	0.7176 (2)	0.0229 (5)
C9	−0.0829 (2)	−0.0147 (2)	0.6441 (2)	0.0274 (5)
C10	0.0464 (2)	−0.0317 (2)	0.6418 (2)	0.0309 (6)
C11	0.1710 (2)	0.0598 (2)	0.7108 (2)	0.0326 (6)
C12	0.1660 (2)	0.1682 (2)	0.7845 (2)	0.0308 (6)
C13	0.0377 (2)	0.1850 (2)	0.7882 (2)	0.0274 (5)
C14	−0.3086 (2)	0.1363 (2)	0.5155 (2)	0.0260 (5)
C15	−0.3649 (2)	0.2431 (2)	0.4588 (2)	0.0283 (5)
C16	−0.3441 (3)	0.2308 (2)	0.3419 (2)	0.0348 (6)
C17	−0.5240 (2)	0.2277 (2)	0.4352 (2)	0.0357 (6)
C18	−0.2851 (2)	0.3764 (2)	0.5409 (2)	0.0304 (6)
C19	−0.0432 (2)	0.4698 (2)	0.6779 (2)	0.0268 (5)
C20	−0.0953 (2)	0.5497 (2)	0.7574 (2)	0.0257 (5)
C21	−0.1174 (2)	0.6694 (2)	0.7390 (2)	0.0326 (6)
C22	−0.1718 (3)	0.7421 (2)	0.8077 (2)	0.0356 (6)
C23	−0.2056 (2)	0.6964 (2)	0.8938 (2)	0.0374 (6)
C24	−0.1843 (3)	0.5780 (2)	0.9132 (2)	0.0391 (6)
C25	−0.1282 (3)	0.5050 (2)	0.8453 (2)	0.0347 (6)
C26	0.1102 (2)	0.4762 (2)	0.7127 (2)	0.0262 (5)
C27	0.2098 (2)	0.5486 (2)	0.8239 (2)	0.0309 (6)
C28	0.3521 (3)	0.5470 (2)	0.8609 (2)	0.0394 (6)
C29	0.3999 (3)	0.4745 (2)	0.7861 (2)	0.0405 (6)
C30	0.3066 (3)	0.4053 (2)	0.6762 (2)	0.0379 (6)
C31	0.1623 (3)	0.4045 (2)	0.6374 (2)	0.0312 (6)

Table 3. *Selected geometric parameters (Å, °) for compounds (I) and (II)*

	(I)		(II)
O1—C1	1.341 (2)	O1—C1	1.343 (3)
O2—C23	1.345 (2)	O2—C31	1.344 (3)
N1—C7	1.288 (2)	N1—C7	1.289 (3)
N1—C10	1.461 (3)	N1—C14	1.457 (3)
N2—C14	1.467 (2)	N2—C18	1.460 (3)
N2—C15	1.283 (2)	N2—C19	1.296 (3)
C7—N1—C10	124.5 (2)	C7—N1—C14	122.4 (2)
C15—N2—C14	122.9 (2)	C19—N2—C18	121.4 (2)
O1—C1—C2	118.2 (2)	O1—C1—C2	118.8 (2)
C1—C6—C7	120.0 (2)	C1—C6—C7	120.4 (2)
N1—C7—C6	116.1 (2)	N1—C7—C6	117.8 (2)
N1—C7—C8	124.2 (2)	N1—C7—C8	123.5 (2)
N1—C10—C11	111.8 (2)	N1—C14—C15	112.4 (2)
N2—C15—C18	116.4 (2)	N2—C19—C26	118.4 (2)
N2—C15—C16	124.5 (2)	N2—C19—C20	121.6 (2)
O2—C23—C22	118.2 (2)	O2—C31—C30	119.0 (2)
O1—C1—C6—C5	−179.4 (2)	O1—C1—C6—C5	−179.5 (2)
O1—C1—C6—C7	−1.9 (3)	O1—C1—C6—C7	−2.0 (3)
C10—N1—C7—C6	−176.2 (2)	C14—N1—C7—C6	−178.6 (2)
C1—C6—C7—N1	−3.4 (2)	C1—C6—C7—N1	−1.6 (3)
C7—N1—C10—C11	−137.4 (2)	C7—N1—C14—C15	−139.8 (2)
N1—C10—C11—C14	58.7 (2)	N1—C14—C15—C18	59.8 (2)
C10—C11—C14—N2	55.7 (2)	C14—C15—C18—N2	53.1 (2)
C14—N2—C15—C18	175.9 (2)	C18—N2—C19—C26	176.1 (2)
N2—C15—C18—C23	5.5 (3)	N2—C19—C26—C31	1.9 (3)

H atoms were added at calculated positions and refined using a riding model with U_{iso}(H) = xU_{eq}(parent atom), where x = 1.5 for methyl and hydroxyl H atoms and 1.2 for others. Anisotropic displacement parameters were refined for all non-H atoms. Hydroxyl H atoms were then subject to a planarity restraint involving the relevant C, O, H and N atoms.

For both compounds, data collection: *MADNES* (Pflugrath & Messerschmidt, 1992); cell refinement: *MADNES*; data reduction: *SHELXTL-Plus* (Sheldrick, 1991); program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*93.

We wish to thank Professor M. B. Hursthouse and the EPSRC X-ray Crystallographic Service (University of Wales, Cardiff) for collecting the diffraction data, and BP Chemicals Sunbury for a grant in support of this work. We also wish to acknowledge the use of the EPSRC's Chemical Database Service at the Daresbury Laboratory, Warrington, Cheshire (Allen *et al.*, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Methoxy-1,4-benzoquinone 4-Oxime

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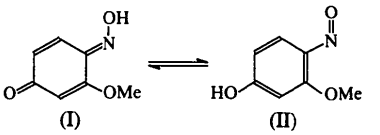
Abstract

The crystal structure of the title compound, $C_7H_7NO_3$, shows a strong quinoid character. The oximic function is *anti* with respect to the methoxy group so that no intramolecular hydrogen bonds involving the acidic H atom are formed, instead a strong intermolecular interaction is favoured. Two molecules are present in the asymmetric unit and they show no significant differences in their bond lengths and angles, but they do have different packing interactions.

Comment

The asymmetric unit of the title compound, (I), contains two molecules which do not differ significantly from one another in terms of bond lengths and angles, but their packing contacts are quite different (see Figs. 1 and 2). It is well known that 1,4-quinone 4-oximes can present a tautomeric equilibrium between the quinone monooximic (I) and the nitrosophenolic (II) forms (see Scheme). In the structure presented here, both the experimental location of the H atoms and the alternation



of short and long bonds within the hexaatomic ring clearly indicate that the quinoid structure (I) prevails. In addition, the bond lengths of the carbonyl and oxime groups compare well with expected values for a quinone monooxime structure (Carugo, Charalambous, Raghvani & Sardone, 1996). No charge delocalization involving the methoxy group is observed since the O2—C2 (O2′—C2′) bond length is within the expected range for single O—C_{sp^2} bonds (Allen *et al.*, 1987).

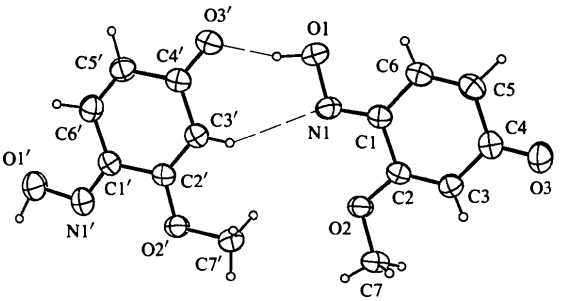


Fig. 1. Perspective view of the asymmetric unit of the title compound shown with 50% probability ellipsoids.

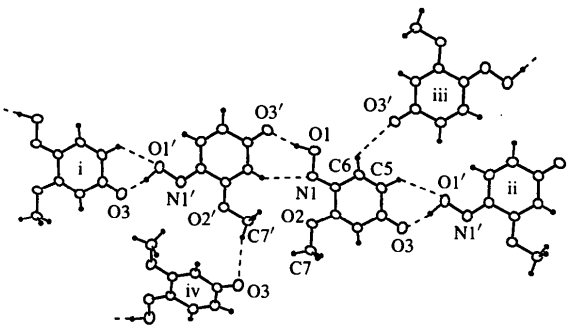


Fig. 2. The hydrogen-bonding interactions in the title compound. Symmetry codes: (i) $1+x, y, z-1$; (ii) $x-1, y, 1+z$; (iii) $-x, -y, 2-z$; (iv) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$.

Both six-membered rings deviate slightly from planarity leading to a pseudo-boat conformation in which the quinoid C1 and C4 atoms (C1′ and C4′) lie up (and down) with respect to the mean plane. The least-squares planes of the two rings in the asymmetric unit form a dihedral angle of 3.1 (7)°.

The oximic group is *anti* with respect to the methoxy moiety and therefore no intramolecular hydrogen bond involving the acidic H atom is formed, thus favouring a strong intermolecular interaction. The two molecules, which are not equivalent symmetrically, are connected through two hydrogen bonds, *i.e.* a strong O—H···O interaction [HO1···O3′ 1.73 (3),

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