organic compounds

Cocrystallization of two tautomers: 4-(1-{[4-(dimethylamino)benzylidene]-hydrazono}ethyl)benzene-1,3-diol and 6-[(E)-1-{[4-(dimethylamino)benzyl-idene]hydrazino}ethylidene]-3-hy-droxycyclohexa-2,4-dien-1-one (1/1)

Zhen-Hua Wu, Jian-Ping Ma, Xiang-Wen Wu, Ru-Qi Huang and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, People's Republic of China
Correspondence e-mail: yubindong@sdnu.edu.cn

Two different tautomeric forms of a new Schiff base, $C_{17}H_{19}N_3O_2 \cdot C_{17}H_{19}N_3O_2$, are present in the crystal in a 1:1 ratio, namely the enol–imine form 4-(1-{[4-(dimethylamino)benzyl-idene]hydrazono}ethyl)benzene-1,3-diol and the keto–amine form 6-[(E)-1-{[4-(dimethylamino)benzylidene]hydrazino}-ethylidene]-3-hydroxycyclohexa-2,4-dien-1-one. The tauto-mers are formed by proton transfer between the hydroxy O atom and the imine N atom and are hydrogen bonded to each other to form a one-dimensional zigzag chain along the crystallographic *b* axis *via* intermolecular hydrogen bonds.

Comment

Schiff base ligands are of interest mainly because of the existence of typical hydrogen bonds and tautomerism between the phenol–imine and keto–amine forms (Costamagna *et al.*, 1992; Sridharan *et al.*, 2004; Fita *et al.*, 2005). Tautomerism in *o*-hydroxy Schiff bases both in solution and in the solid state has been investigated using IR (Ledbetter, 1977; Yildiz *et al.*, 1998), UV (Ottolenghi & McClure, 1967), ^{1}H NMR (Dudek & Holm, 1962; Dudek & Dudek, 1966), ^{13}C NMR (Salman *et al.*, 1991) and X-ray crystallographic techniques (Gavranic *et al.*, 1996; Kaitner & Pavlovic, 1996).

We have synthesized a new Schiff base compound, (I) (Fig. 1). This compound undergoes tautomerism by proton transfer between the hydroxy O atom and the imine N atom, forming two tautomers, (I*a*) and (I*b*), and the two different tautomeric forms of the same molecule cocrystallized in a 1:1 ratio. Form (I*a*) is the phenol–imine tautomer, while (I*b*) is the keto–amine tautomeric form.

The compound crystallizes in the monoclinic form in the space group $P2_1/c$. The tautomerism of the compound causes a series of differences between (I*a*) and (I*b*). When the phenol–imine tautomer is transformed into the keto–amine tautomer,
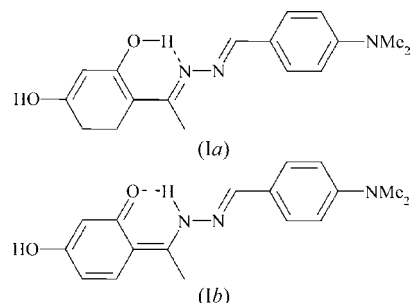
an appreciable increase in the C—N distance is observed [C7—N2 = 1.290 (3) Å *versus* C24—N4 = 1.304 (3) Å]. A concomitant decrease in the C—O distance is also noted [C5—O1 = 1.344 (3) Å *versus* C22—O3 = 1.316 (2) Å]. The C7—N2 and C5—O1 distances are similar to the corres-ponding distances in 2,2′-(azinodimethylene)diphenol [1.285 (7) and 1.364 (8) Å; Xu *et al.*, 1994] and 2,2′-[(1,2-ethanediyl)bis(nitrilopropylidyne)]bisphenol [1.295 (3) and 1.351 (3) Å; Corden *et al.*, 1997], which both exist in the phenol–imine tautomeric form. Likewise, the C24—N4 and C22—O3 bond lengths are similar to the corresponding distances in 2-{[tris(hydroxymethyl)methyl]aminomethylene}-cyclohexa-3,5-dien-1(2H)-one [1.2952 (18) and 1.3025 (18) Å, respectively; Odabaşoğlu *et al.*, 2003] and 3-[(2-oxo-1-naphthylidene)methylamino]benzoic acid [1.319 (3) and 1.290 (2) Å; Pavlović & Sosa, 2000], which both show the keto–amine tautomeric form. Hence, the C—O and C—N bond lengths verify the phenol–imine form of (I*a*) and the keto–amine form of (I*b*). In addition, the degrees of planarity for the two molecules in the asymmetric unit are different. The maximum dihedral angle in (I*a*) is 7.06 (9)°, for the dihedral angle between the C3-containing benzene ring and the C10-containing benzene ring, while the corresponding dihedral angle in (I*b*) is 11.62 (7)°.
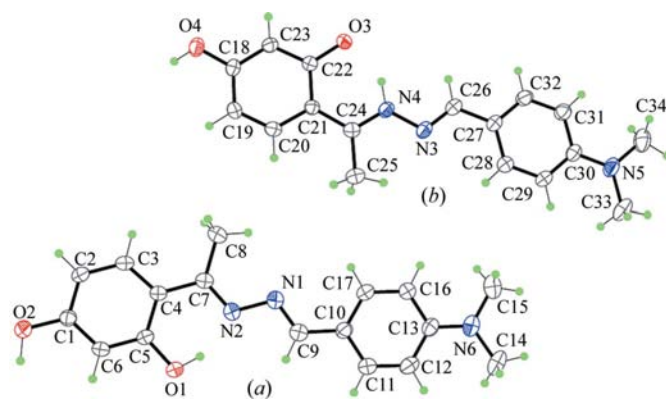

Figure 1
A view of the molecules of (*a*) (I*a*) and (*b*) (I*b*), with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii.
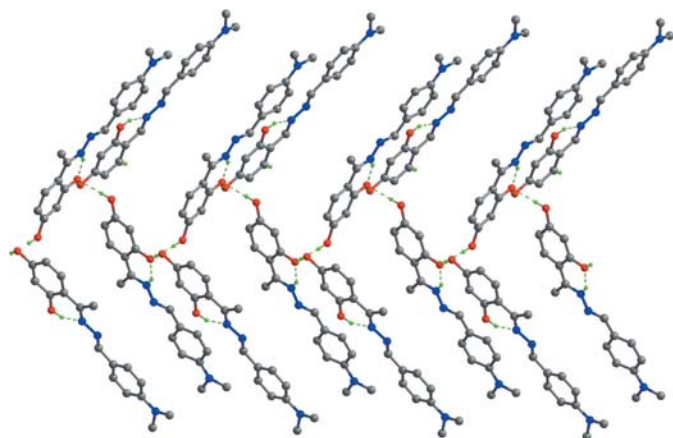
Figure 2
The intra- and intermolecular hydrogen bonding in (I).

Both intra- and intermolecular hydrogen bonds are found in the crystal structures of the tautomers (Fig. 2). The intra-molecular hydrogen bonds (O—H···N and N—H···O) of the two tautomeric forms are rather short, as expected (Table 1). In (I*a*), the hydrogen-bonded ring is nearly coplanar with the adjacent ring, with a dihedral angle of 1.37 (7)°, while (I*b*) is not quite as planar, with a dihedral angle of 5.46 (7)° between the two corresponding rings. The two tautomers are connected *via* intermolecular O—H···O hydrogen bonds (Table 1) into a one-dimensional zigzag chain extended along the crystallographic *b* axis.

In conclusion, a new Schiff base has been synthesized and characterized by X-ray diffraction analysis. Two different tautomeric forms are found in the solid state, and these are hydrogen bonded to one another to form an infinite chain.

Experimental

Compound (I) was prepared according to a literature method (Diehl *et al.*, 1950). 2,4-Dihydroxyacetophenone (2.00 g, 13.2 mmol) and hydrazine hydrate (4.00 g, 40 mmol) were dissolved in ethanol (40 ml) and four drops of methanoic acid were added. The mixture was stirred at room temperature for 5 h. A yellow powder, namely 4-(1-hydrazonoethyl)benzene-1,3-diol, was filtered off, washed with ethanol and dried in a vacuum. 4-(1-Hydrazonoethyl)benzene-1,3-diol (0.20 g, 1.3 mmol) and *p*-(dimethylamino)benzaldehyde (0.19 g, 1.3 mmol) were dissolved in ethanol (20 ml), and then four drops of methanoic acid were added and the mixture was stirred at room temperature for 5 h. The resulting yellow powder was filtered off, washed several times with ethanol and then dried in a vacuum (yield 89%, m.p. 482.7–483.9 K). Well shaped crystals were obtained by slow evaporation of an ethanol solution.

Crystal data

$C_{17}H_{19}N_3O_2 \cdot C_{17}H_{19}N_3O_2$
$M_r = 594.70$
Monoclinic, $P2_1/c$
$a = 11.872$ (3) Å
$b = 9.630$ (2) Å
$c = 28.442$ (6) Å
$\beta = 108.067$ (8)°

$V = 3091.4$ (12) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
$0.49 \times 0.40 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
15831 measured reflections

5758 independent reflections
3521 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.140$
$S = 1.02$
5758 reflections
418 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N2	0.864 (10)	1.709 (17)	2.507 (3)	153 (3)
O2—H2A···O3^i	0.97 (3)	1.71 (3)	2.668 (2)	169 (2)
O4—H4···O3^{ii}	0.85 (3)	1.86 (3)	2.674 (2)	161 (3)
N4—H4A···O3	0.922 (10)	1.739 (15)	2.558 (2)	146 (2)

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

H atoms attached to C atoms were idealized and included as riding atoms [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH hydrogens, and C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH$_3$ hydrogens]. H atoms attached to N and O atoms were located in a difference map and refined isotropically with O—H and N—H distance restraints of 0.83 (3) and 0.96 (2) Å, respectively; the refined distances are given in Table 1. In total, two geometric restraints (DFIX) were used.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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