

Scientific paper

Two Ketimine Polymorphs of 2-{1-[(2-Aminophenyl)imino]ethyl}phenol

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Abstract

Two polymorphic structures of the Schiff base 2-{1-[(2-aminophenyl)imino]ethyl}phenol, compound (**1**), C₁₄H₁₄N₂O are reported. Depending on the solvent used for recrystallization it crystallizes as either a monoclinic or an orthorhombic polymorph. The monoclinic form, polymorph [**1**] contains three, while the orthorhombic polymorph [**2**] contains only one molecule in the asymmetric unit. In both polymorphs, a strong intramolecular O–H...N hydrogen bond is present from the stereochemical reason due to the rigidity of the chelate ring. Weak intermolecular N–H...O interactions appearing in both structures combine the molecules in the form of infinite columns by the graph-set motif C₂²(7).

Keywords: Schiff base polymorphs, enol-imine tautomers, intra- and intermolecular hydrogen bond, supramolecular connection, crystal and molecular structure

1. Introduction

Schiff base ligands have a significant role in the development and synthesis of new transition-metal complexes for a number of applications.¹ The *ortho*-hydroxy Schiff bases have the ability to create strong intramolecular hydrogen bonds.² Proton in OHN hydrogen bridge could be clearly localized or delocalized between oxygen and nitrogen atoms. This fact depends on steric interactions of the alkyl or aryl substituents on C and N atoms.³ Potential applications of this kind of compounds as photo- and thermochromic materials and as electronically functional materials is the consequence of proton transfer.^{4,5}

The number of investigations on ketimine polydentate Schiff bases made from aromatic ketones and aromatic diamines is relatively small probably due to some preparation difficulties. The syntheses of unsymmetrical monoimine tridentate NNO Schiff base are possible only when ketones fail to react with primary amines under catalytic acidic conditions with concomitant azeotropic removal of water.

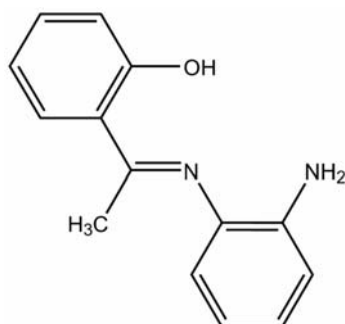
We recently reported the synthesis and structure determination of two solvent induced polymorphs of 2-{[(2-aminophenyl)imino]phenylmethyl}phenol derived from

o-phenylenediamine and 2-hydroxybenzophenone.⁶ Here we report the synthesis and the structural analysis of the similar type of ketimines as potential tridentate ligands for the future synthesis of the Schiff base transition metal complexes.

2. Experimental

2.1. Synthesis and Crystallization

The 2-{1-[(2-aminophenyl)imino]ethyl}phenol, compound (**1**) (Scheme 1) was prepared from *ortho*-phenylenediamine (540 mg, 5 mmol) and 2-hydroxyacetophenone (1.25 mL, 10 mmol) in the molar ratio 1:2 in 30 mL methanol. This mixture was refluxed for 3 h. The water formed during the reaction was removed by a Dean-Stark trap. At the end of reaction the formation of yellow, oleaginous translucent solution was observed. The mother liquor was left in the refrigerator for crystallization. The compound precipitates as a brown solid substance after solvent evaporation. Recrystallization from methyl formate by the vapour diffusion method, using *n*-hexane as the precipitant, resulted in the crystallization of pale yellow plates of polymorph [**1**]. Yellow prismatic crystals of



Scheme 1. Two-dimensional diagram of 2-[1-[(2-aminophenyl)imino]ethyl]phenol.

polymorph [2] were grown by slow evaporation from dichloromethane solution of compound (1).

2. 2. X-Ray Crystallographic Studies

The details of general and crystallographic data and structure refinement of the reported polymorphs are listed in Table 1. Diffraction data for both were collected with MoK α

radiation using the Oxford Diffraction X-Calibur 3 Kappa CCD diffractometer. Data analysis was carried out with CRYSLIS program.⁷ The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from consecutive δ -Fourier maps and the hydrogens were refined using a riding model.⁸ Programs ORTEP-3 and Mercury were used for preparing the figures.^{9,10}

2. 3. Thermal and Spectroscopic Analysis

Thermogravimetric analysis was carried out using a Mettler TG 50 thermobalance and the differential scanning calorimetric measurement was performed on a DSC 30 calorimeter using inert nitrogen atmosphere with a flow rate of 200 cm³/min. The heating rate was 10 cm³/min. The data collection and analysis was performed using the program package STAR^e Software 9.01.¹²

The Fourier Transform Infrared (FTIR) spectrum of the title compound has been recorded in the range of 4000–400 cm⁻¹ using KBr pellet with an EQUINOX 55 FT-IR spectrophotometer at room temperature. The data collection and analysis was performed using the program

Table 1. General, crystallographic data and the summary of experimental details for polymorphs [1] and [2].¹

	Polymorph [1]	Polymorph [2]
Molecular formula	C ₁₄ H ₁₄ N ₂ O	C ₁₄ H ₁₄ N ₂ O
M_r	226.27	226.27
Crystal system	Monoclinic	Orthorhombic
Space group	<i>Cc</i>	<i>P na2₁</i>
$a / \text{Å}$	21.919(4)	7.325 (3)
$b / \text{Å}$	21.756(4)	22.605 (10)
$c / \text{Å}$	7.2424(14)	7.165 (3)
$\beta / ^\circ$	90.28(3)	
$V / \text{Å}^3$	3453.6(11)	1186.4(9)
Z	12	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.306	1.267
$\lambda(\text{MoK}\alpha) / \text{Å}$, graphite monochromator	0.7107	0.7107
T / K	183	298(2)
Crystal dimension / mm ³	0.3 × 0.3 × 0.1	0.6 × 0.22 × 0.20
μ / mm^{-1}	0.08	0.08
$F(000)$	1440	480
θ range / °	2.6–26	4–26
hkl range	–26, 26; –25, 26; –8, 8	–9, 8; –25, 27; –8, 8
Number of measured reflections	12379	4114
Number of independent reflections	3369	2126
Number of reflections with $I > 4\sigma(I)$	2193	1172
Number of parameters	485	166
$\Delta r_{\text{max}}, \Delta r_{\text{min}} / \text{e Å}^{-3}$	0.22, –0.18	0.19, –0.14
Flack parameter, x^2	–	0(3)
$R[F^2 > 4\sigma(F^2)]$	0.047	0.048
$wR(F^2)$	0.125	0.168
Goodness-of-fit, S	0.98	1.02

¹ Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 822971 and 822972 for polymorph [1] and polymorph [2], respectively. Copies of these data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

² For the note on Flack parameters see the footnote in Results and Discussion.

OPUS 4.0.¹¹ NMR spectra were measured on Varian Gemini XL 300 spectrometer.

3. Results and Discussion

3.1. Crystal and Molecular Structure

Diffraction experiment showed that the polymorph [1] crystallizes in the monoclinic system with space group *Cc*. The asymmetric unit contains three crystallographic independent molecules labelled as molecule (1), molecule (2) and molecule (3), respectively. The crystals of polymorph [2] belong to the orthorhombic system, space group *P na2₁*. During the structure determination a distinct stereochemical resemblance of polymorph [2] molecule with molecule (2) of polymorph [1] was observed. The analogy pertains to the molecular geometry, i.e. conformation as well as to the molecular packing and interconnection.*

Molecular structure of three crystallographic independent molecules of polymorph [1] and that one of polymorph [2] are depicted in Figures 1 and 2, respectively. Selected bond distances and bond angles are listed in Table 2, while the hydrogen bond geometry is shown in Table 3.

No difference was observed by comparing the molecular geometry parameters of polymorph [1] and [2], respectively using the 3 *s.u.* as equalizing criterion for bond lengths and bond angles. Slight disproportion in *Nn2–Cn10*

and *Cn10–Cn11* exists (*n* refers to the molecule (1), (2) and (3), respectively of polymorph [1] or does not appear at all in the atom numbering scheme of the polymorph [2] molecule). The later is due to the involvement of the primary *Nn2* amino group substituent in intermolecular H-bond.

Fused phenyl *Cn1–Cn6* and pseudo-aromatic chelate ring *On1Hn1Nn1Cn1Cn2Cn7* considering both polymers do not show significant departure from co-planarity

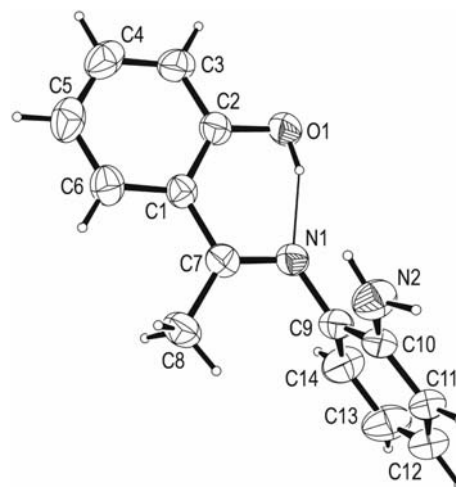


Figure 2. The molecular structure of polymorph [2]. Thermal ellipsoids are drawn with 30% probability. Dotted line represents the hydrogen bond.

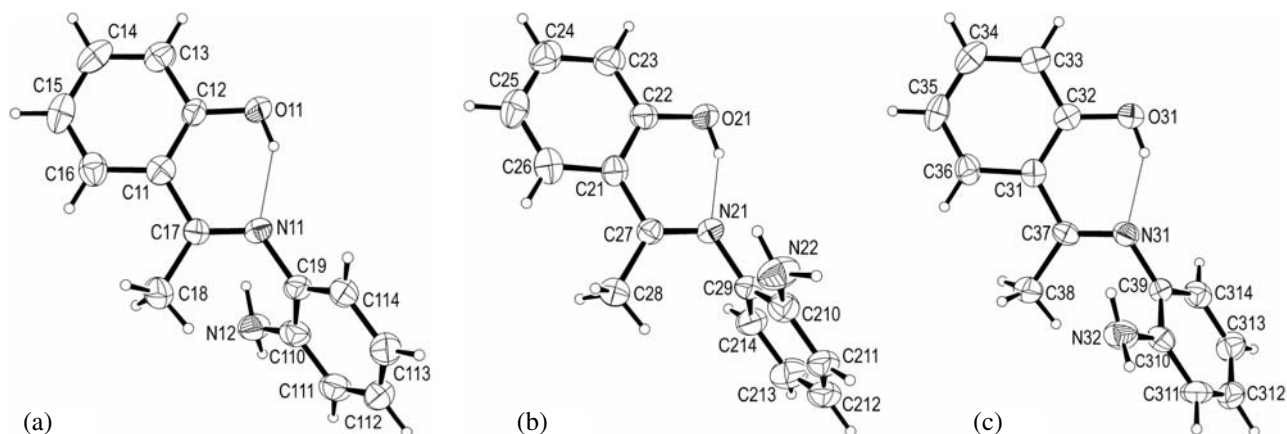


Figure 1. ORTEP-3 drawings (a) to (c) are showing the molecular structure and atom labelling scheme of three independent molecules of polymorph [1]. The displacement ellipsoids are shown at the 50% probability level. The intramolecular hydrogen bonds are shown as dotted lines.

* Both compounds crystallizing in non-centrosymmetric space group consist of light C, H, N and O atoms showing only a small anomalous dispersion effect. This is why the determination of absolute configuration and the direction of the polar axes in case of polymorph [2] became disputable. Flack parameters for polymorph [1] calculated for the model and the inverted structure were incoherent and the refinement finished with Friedel pairs merged. On the contrary, Flack parameter for polymorph [2] showed to be 0(3) for one of inverted models. The later, in spite of large *s.u.*, was accepted as a likely correct one for plausible determination of the direction of two-fold axes.

being 1.88, 1.05 and 2.86° consecutively for molecules (1), (2) and (3), respectively in polymorph [1] and 3.12° in polymorph [2].

Intrinsic stereochemical feature of all four molecules is interplanar angle between the best planes calculated through the fused rings, one of them is the pseudo-chelate ring, and the aminophenyl residue attached to the *Nn1* imino nitrogen atom. For polymorph [1] they amount:

Table 2. Selected bond lengths and torsion angles

	Polymorph [1]			Polymorph [2]
	Molecule (1)	Molecule (2)	Molecule (3)	
Bond length (Å)				
On1–Cn2	1.339(5)	1.347(5)	1.353(5)	1.353(4)
Nn1–Cn7	1.290(5)	1.291(5)	1.296(5)	1.302(4)
Nn1–Cn9	1.428(5)	1.427(5)	1.427(5)	1.425(4)
Nn2–Cn10	1.366(6)	1.370(6)	1.394(5)	1.396(5)
Cn1–Cn2	1.407(6)	1.412(6)	1.408(5)	1.411(4)
Cn1–Cn7	1.476(6)	1.465(6)	1.473(5)	1.463(4)
Cn7–Cn8	1.498(6)	1.499(6)	1.493(5)	1.492(5)
Torsion angles (°)				
Nn1–Cn7–Cn9–Cn10	–5.6(6)	6.4(6)	4.2(5)	5.6(4)
Cn8–Cn7–Nn1–Cn9	0.7(6)	0.8(6)	–1.1(6)	–1.4(4)
Cn7–Nn1–Cn9–Cn10	71.1(5)	–91.4(5)	–71.1(5)	–93.8(4)

64.05, 82.84 and 63.74°, respectively and for polymorph [2] 86.11°. Another, even more significant characteristic that can be used in describing the molecular stereochemistry is the value of torsion angle that involves imino group atoms, i.e. Cn7–Nn1–Cn9–Cn10; they amount consecutively: –71.06, –91.41 and +71.08° in polymorph [1] and –93.80° in polymorph [2]. The stereochemical diversity of three independent molecules (1), (2) and (3), respectively of polymorph [1] is illustrated in Figure 3, (a) to (c) by overlapping the molecules and in Figure 4 presenting the overlapping of three polymorph [1] molecules with single molecule of polymorph [2]. In polymorph [1] the largest divergence between independent conformers can be noticed by overlapping molecule (1) with molecule (2) in Fig. 3(a) and molecule (1) with molecule (3) in Fig. 3(c).

It is due to the sign of the torsion angles that beam the aminophenyl residue NH₂ group of molecule (1) towards viewer and those of molecules (2) and (3) against the viewer. On the other hand, the least conformational

discrepancy shows the molecular overlapping of polymorph [2] molecule with polymorph [1] molecule (2) as clearly visible in Fig. 4(b).

In the condensed state both polymorphs are present in enol-imine tautomeric form which is indicated by the position of hydrogen atom in the strong intramolecular O–H...N hydrogen bond being approx. 2.537, 2.530, 2.530 Å in polymorph [1] and 2.536 Å in polymorph [2]. Despite the position of the hydrogen atom being unequivocally revealed from the δF map the position of H-atom inside of the O–H...N hydrogen bond is determined as well by the Cn2–On1 bond length 1.339, 1.347, 1.353 Å in polymorph [1] and 1.353 Å in polymorph [2] that is single in nature corresponding to the generally accepted value for the C–O single bond of 1.362 Å in phenols.¹³ At the same time this statement implies that the Cn7–Nn1 bond has to be a double bond and this is true according to its length ranging from 1.290 to 1.302 Å in polymorphs [1] and [2], respectively (generally accepted C=N double

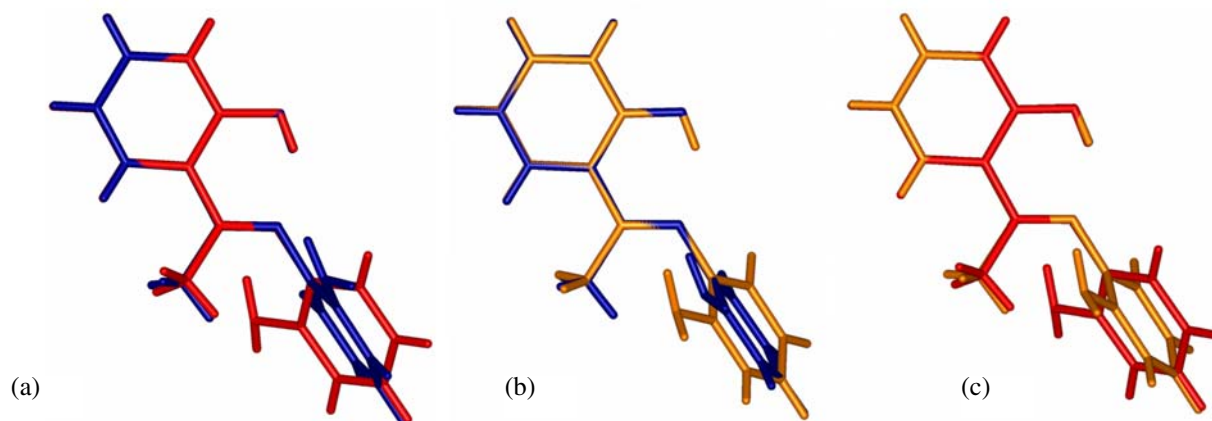


Figure 3. Overlapping view of three discrete molecules of polymorph [1]. Three different colours for polymorph [1] conformers were used – red for molecule (1), blue for molecule (2) and orange for molecule (3), respectively for molecules to be distinguished in graphical presentation of the overlapping. The purpose of the drawings (a), (b) and (c), respectively is the conformational distinction of molecules (1), (2) and (3), respectively to be pointed out. Picture (a) shows overlapping of molecules (1) with molecule (2), picture (b) overlapping molecule (2) with molecule (3) and picture (c) overlapping molecule (1) with molecule (3). Confer the Results and Discussion paragraph for the numerical values of torsion angles Cn7–Nn1–Cn9–Cn10 that differentiate the conformation of molecules (1), (2) and (3), respectively one relatively to each other.

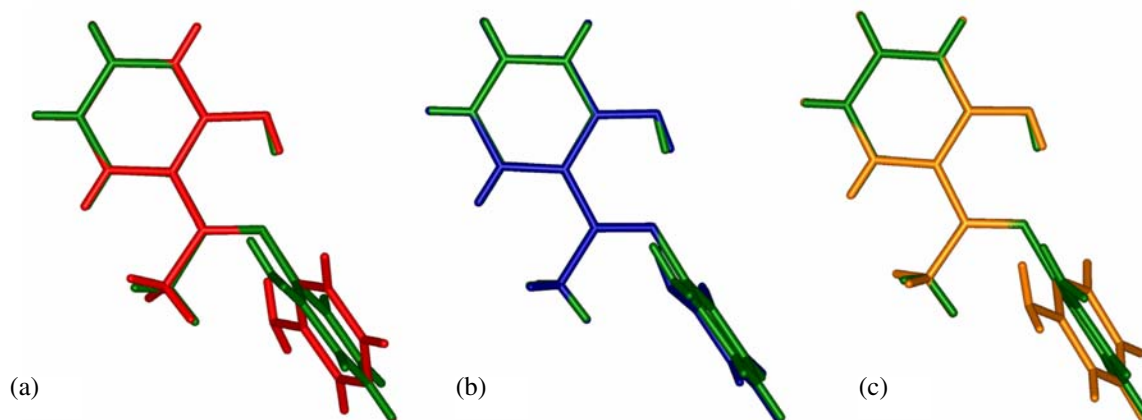


Figure 4. Overlapping diagrams depicting the stereochemical difference between polymorph [2] molecule (coloured in green) and the polymorph [1] conformers (1), (2) and (3), respectively. The least conformational difference exists between polymorph [2] molecule and the conformer (2) of polymorph [1].

bond length in imino group is 1.279 Å).¹³ Obtained results are consistent with the literature values for similar ketimines.^{14–16} Other geometrical parameters are as expected, with carbon-carbon bond distances of the aromatic system in the range of 1.360(6) to 1.416(6) Å.

The arrangement of the independent molecules (1), (2) and (3) of polymorph [1] is in the form of infinite column protracting along the [001] direction. Each column is build up of identical molecules (1), (2) or (3), respectively. The columns pile up parallel one to each other in the manner pictured in Fig. 5.

The columns made up of conformers (1) and (3), respectively are connected one to each other *via* intermolecular hydrogen bond $Nn2-H\cdots On1^i$ [3.109 Å and 3.070 Å, respectively; (i): $x, -y+1, z-\frac{1}{2}$] and appreciably longer, meaning weaker $Cn14-H\cdots On1^{iii}$ [3.508 for $n = 1,$

symmetry code (i); 3.469 Å for $n = 3,$ symmetry code (ii): $x, -y+1, z+\frac{1}{2}$] hydrogen bond, adjacent to the standard van der Waals attraction forces.

This arrangement corresponds to the graph set $C_2^2(7)$ creating the rings with graph-set motif $R_4^4(13)$ inside of the column (Figures 6(a) and 6(c)).¹⁷ The conformers (2) of polymorph [1] and the molecules of polymorph [2] stack in columns (Fig. 6(b)) that are essentially the same as columns of conformers (1) and (3), respectively of polymorph [1]. The only difference between them is in the molecular interconnection that is in the former with the graph set motif $C_2^2(7)$ achieved through the single N–H...O hydrogen bond only and the binding [N22–H...O21ⁱⁱⁱ 2.994 Å; (iii): $x, -y, z+\frac{1}{2}$ and N2–H...O1^v 2.985 Å; (v): $x-\frac{1}{2}, -y+1.5, z$]. Due to the difference in space group symmetry the columns in polymorph [2] spread along [100] direction. The efficient packing of the columns is accomplished by the internal symmetry: in the crystals of polymorph [1] with single column shifting for a quarter of the a -period (Fig. 5), while the columns shift in the crystals of polymorph [2] is for a period along z -axis. The packing motif in polymorph [2] is essentially the same as shown for polymorph [1] in Fig. 5.

The motif of molecular interconnection brings the molecules inside of each column in such a position that generates offset π - π stacking mode of interaction between aromatic rings of the fused rings fragment.^{18,19} In both cases geometry parameters relating neighbouring aromatic offset, parallel displaced rings predict the interactions as slightly attractive as was in detail described in Ref. 19. At centroid contacts being in range of 3.87 to 3.91 Å and the displacement angle of approx. 21° the horizontal shifting corresponds to almost one C–C bond length. Due to the ring plane offset, $Cn1$ atom from a $Cn1$ -to- $Cn6$ ring lies nearly over the centre of almost parallel, adjacent symmetry related $Cn1$ -to- $Cn6$ ring and *vice versa* – the $Cn6$ atom from the latter ring lies in projection roughly above the middle of the former ring. Ring offset ranging from ap-

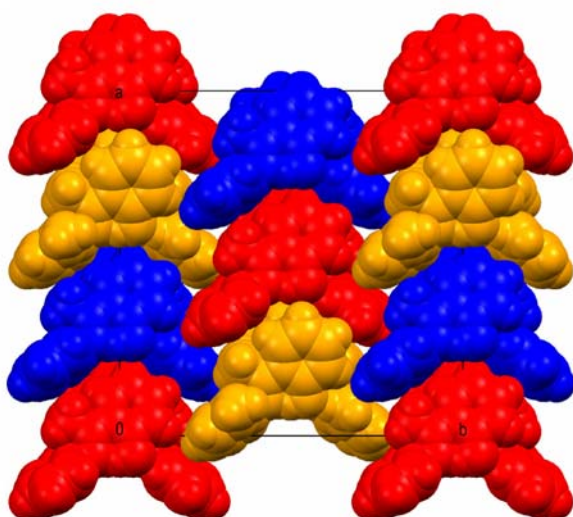


Figure 5. Unit cell packing diagram of polymorph [1] viewed along the [001] direction showing the scheme of stacking the red molecules (1), the blue molecules (2) and the orange molecules (3), respectively.

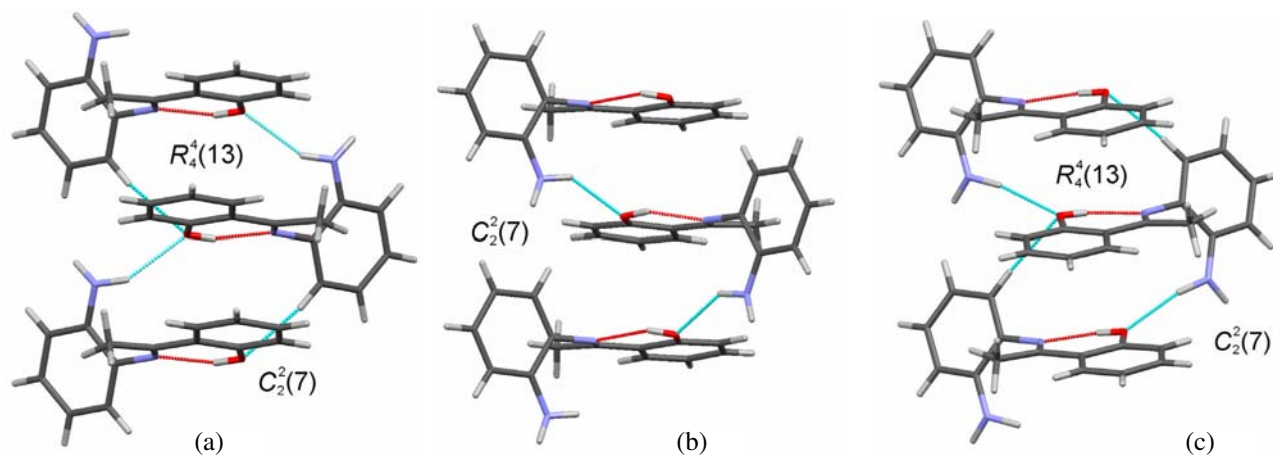


Figure 6. The connecting mode of the polymorph [1] molecules (1), (2) and (3), respectively. The $C_2^2(7)$ motif is present as a basic way of interlinking the molecules in [001] infinite columns in all three cases. Conformers (1) and (3), respectively achieve an additional fastening through the $R_4^4(13)$ graph set motif (Figures 6(a) and 6(c)). The supramolecular architecture in polymorph [2] is essentially the same as in the Fig. 6(b) illustrating the intermolecular linkage of molecule (2) in polymorph [1].

Table 3. Hydrogen bond geometrical parameters for polymorph [1] and [2], respectively.¹

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
Polymorph [1]-molecule (1)				
O11-H11...N11	0.840	1.791	2.537(4)	147
N12-H11...N11	0.926	2.425	2.819(5)	106
C114-H114...O11 ⁱ	0.950	2.596	3.508(5)	161
N12-HBN1...O11 ⁱⁱ	0.926	2.269	3.109(5)	151
Polymorph [1]-molecule (2)				
O21-H21...N21	0.840	1.801	2.530(4)	144
N22-HAN2...N21	0.928	2.352	2.804(6)	110
N22-HAN2...O21 ⁱⁱⁱ	0.928	2.203	2.994(5)	143
C25-H25...O31 ⁱⁱⁱⁱ	0.950	2.749	3.490(6)	135
Polymorph [1]-molecule (3)				
O31-H31...N31	0.840	1.795	2.530(4)	145
C35-H35...O11	0.950	2.745	3.472(5)	134
N32-HBN3...O31 ⁱ	0.948	2.140	3.070(5)	166
C314-H314...O31 ⁱⁱ	0.950	2.553	3.469(5)	162
Polymorph [2]				
O1-H1 N1	0.837	1.746	2.536(4)	157
N2-H2A...O1 ^v	0.879	2.141	2.985(4)	161
C5-H5 O1 ^{vi}	0.930	2.746	3.420(5)	130

¹ Symmetry transformations used to generate the equivalent atoms (i) $x, -y+1, z-1/2$; (ii) $x, -y+1, z+1/2$; (iii) $x, -y, z+1/2$; (iv) $x+1/2, -y+1/2, z-1/2$; (v) $x-1/2, -y+1.5, z$; (vi) $x, y, z+1$.

prox. 1.37 to 1.42 Å with previously defined $Cn6$ position brings its $Hn6$ hydrogen atom on the top of $Cn4$ carbon atom of the nearby ring.

3. 2. IR and NMR Spectral Analysis

The IR spectrum of the title compound shows a broad absorption band of medium intensity with two distinct maxima at 3337 and 3450 cm^{-1} , respectively. They were assigned to the combination of $\nu(\text{NH}_2)$ and $\nu(\text{OH})$. The phenolic $\nu(\text{CO})$ and imino $\nu(\text{C}=\text{N})$ stretching vibra-

tions are observed as strong bands at 1260 and 1610 cm^{-1} , respectively. Their presence was taken as an evidence for the existence of the enol-imino tautomeric form in the solid state. The ring skeletal $\nu(\text{C}=\text{C})$ vibrations are observed in the region of 1453–1492 cm^{-1} .

Chemical shift positions are given in ppm using TMS as internal standard. ^1H NMR (CDCl_3) δ/ppm : 14.83 (s, 1H, OH), 6.69–7.65 (m, 8H, Ar), 3.64 (s, 2H, NH_2), 2.36 (s, 3H, CH_3). ^{13}C NMR (CDCl_3) δ/ppm : 173.51 (1C, $\text{C}=\text{N}$); 115.60, 118.07, 118.11, 118.31, 118.31, 119.57, 121.40, 126.01, 128.89, 133.06, 138.07, 161.97 (12C, Ar); 17.02 (1C, CH_3).

3.3 Thermal Analysis

The thermal decomposition of 2-{1-[(2-aminophenyl)imino]ethyl}phenol occurs in one degradation stage at a maximum temperature of 275 °C. The decomposition begins at 122 °C continuing up to 448 °C. Weight loss for this single step is 77.5%. Compound (**1**) melts at 95.81 °C as determined by the DSC measurement.

4. Conclusions

Prepared ketimine Schiff base 2-{1-[(2-aminophenyl)imino]ethyl}phenol showed to be a tridentate instead of a tetradentate with only one primary amino group of *ortho*-phenylenediamine converted to the imino group by a condensation reaction from 2:1 molar ratio of ketone and diamine. Recrystallization by different methods from different solvents yielded two polymorphic modifications, a monoclinic form, polymorph [**1**] and an orthorhombic one, polymorph [**2**]. The stereochemistry of three crystallographic independent molecules in polymorph [**1**] differs significantly. Conversely, there is large similarity between the shape of molecule (**2**) of polymorph [**1**] and the polymorph [**2**] molecule. There are two similar ways in which the molecules link in the solid state. The intermolecular binding is based on the moderately strong N–H...O hydrogen bonds and very weak C–H...O van der Waals attractions stacking the molecules into infinite columns spreading along the crystallographic direction [001] in polymorph [**1**] and [100] in polymorph [**2**], respectively. No interactions different than the standard van der Waals attraction forces occur in both polymorphs.

5. Acknowledgements

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Povzetek

Predstavljamo dve polimorfni strukturi Schiffove baze 2-{1-[(2-aminofenil)imino]etil}fenol, spojina (**1**), C₁₄H₁₄N₂O. Glede na topilo, uporabljeno pri prekrystalizaciji, je kristaliziral bodisi monoklinski bodisi ortorombski polimorf. Monoklinska oblika, polimorf [**1**], v asimetrični enoti vsebuje tri, ortorombski polimorf [**2**] pa le eno molekulo. V obeh polimorfih je zaradi stereokemijskih zahtev rigidnega kelatnega obroča prisotna močna intramolekularna O–H...N vodikova vez. Šibke intermolekularne interakcije N–H...O, ki se pojavljajo v obeh strukturah, povezujejo molekule v neskončne verige z graf-set motivom C₂²(7).

6. References

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