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ORIGINAL PAPER

Synthesis and Structural Characterization of (Z)-3-[(4-Chlorophenylamino) Methylene] Naphthalene-2(3H)-One: An Enol, Keto or Zwitterionic Tautomer?

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Abstract The structure of the title compound was determined using X-ray crystallography at both 173 and 293 K. The molecular structure and packing did not change significantly with temperature and a disordered structure was identified comprising a keto and enol tautomeric form. Analysis of the bond lengths in the vicinity of the C=O group suggested the keto form was predominantly in its zwitterionic form structure. ^{1}H NMR spectroscopy showed the presence of a single compound in solution with two diagnostic doublets demonstrating the compound had an NH group next to a CH group resembling the zwitterionic form of the compound.

Keywords Synthesis · Schiff base · NMR · X-ray · Crystallography · Keto–enol tautomer

Introduction

The study of keto–enol tautomerism in Schiff bases is an active area of research due to the uncertainty regarding the structure of these types of compounds. Although many reports have appeared in the literature regarding the structure of enol/keto tautomeric forms [1–40] there appears to be controversy regarding the structure of Schiff bases in solution and solid state. To investigate this puzzle, Ogawa et al. [25] conducted an X-ray crystallographic study on a salicylidene Schiff base. By varying the temperature the authors came to the conclusion that at lower temperatures (90 K) the Schiff base exists as a keto tautomer (90%). Similarly, Pavlovic [27] examined both the X-ray crystal structure and solution NMR of 3-chlorophenyl-2-hydroxyl-1-naphthalidimine and concluded that in solution the compound exists as the keto tautomer while in the solid state the enolic form predominates. In all cases described above, both the enol and keto tautomeric forms were observed. We were interested in using these Schiff bases as ligands to complex copper and synthesized the titled Schiff base, which exhibited thermochromism. It is also well known that many Schiff bases exhibit this property, which has been proposed to be due to one of four mechanisms: proton transfer, zwitterionic formation, electron delocalization or alterations in crystal packing geometry [19]. In light of the uncertainty in the literature regarding the structure of Schiff bases, we conducted a detailed study on this compound. In the following sections we will discuss the results obtained for both solution and solid state for the titled compound.

Results and Discussion

The Schiff bases derived from the naphthaldehyde possess extraordinary properties with potential applications in nonlinear optics, as sensors and as conductors. The titled molecule was synthesized by condensing 2-hydroxy naphthaldehyde with 4-chloroaniline in ethanol and the solid product material was further purified by recrystallization.

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The UV/visible spectrum of the compound showed peaks at 460 and 440 nm along with additional shoulders at 380 and 340 nm. The long wavelength absorption peaks indicate an extensive conjugation in the molecule. The infrared spectrum of the compound had a band at 3400 cm^{-1} followed by strong bands at 1631, 1611, and 1548 cm^{-1}, respectively. The band at 3400 cm^{-1} was assigned preliminarily to the presence of NH or OH groups in the molecule. The intense bands at 1631 and 1611 cm^{-1} were assigned to the C=O or C=N stretching frequency. The proton NMR spectrum of the compound showed a single conformation in solution (Fig. 1).

A doublet peak, centered at 15.25 ppm, had a coupling constant of 3 Hz and was assigned to a NH group. The extreme down field shift shown by this proton was attributed to a hydrogen bond with a hydrogen bond acceptor. Further examination of the peak at 15.25 ppm found it was coupled to a peak at 9.34 ppm. A cross peak in the COSY spectrum confirmed the presence of a HN–CH fragment. These doublets suggest a keto tautomeric structure for the compound. There was no evidence of an OH peak in the NMR spectrum of the compound and all other aromatic protons showed the expected coupling patterns consistent with a keto structure for the compound.

The ^{13}C NMR spectrum of compound **1** was examined and illustrated in Fig. 2. From this figure, the signal at 168.4 ppm was tentatively assigned to a C=O group in spite of its upfield shift and the previous evidence indicating the keto tautomer for another Schiff base [26]. This is in agreement with the literature reported value for the 3-chloro substituted analog in DMSO-d_6 (169.5 ppm, [26]. Analyzing the COSY, TOCSY, HSQC, and HMBC experiments, we fully assigned the proton and carbon chemical shifts (Table 1). Figure 3 shows the TOCSY spectrum of the compound **1** which confirmed the relationship between the HN proton and the olefinic proton. Interestingly the NH proton had a cross peak with the residual water from the solvent implying that this proton is in slow exchange with the water.

Although we assigned the protons and the carbon chemical shift values for the compound and tentatively proposed a keto/zwitterionic tautomeric structure for this compound, we were uncertain about the tautomeric configuration of the compound. Our uncertainty was motivated by an earlier report that the 3-chlorophenyl substituted compound existed in the enol form in the solid state and in the keto form in solution [26]. A D_2O exchange experiment was performed by adding D_2O directly to the NMR tube and resulted in the peak at 15.27 ppm almost completely disappearing and the doublet at 9.33 ppm collapsing to a singlet. The ^{13}C NMR spectrum was also acquired and confirmed the presence of a peak at 168 ppm which was tentatively assigned to the C=O group.

It is well established that Schiff bases exhibit thermochromism [4, 6, 8–11, 13–15, 17–20, 32–40]. This has been attributed to the equilibrium between the enol and keto tautomer (see Scheme 1) where the proton from the hydroxyl group is transferred to the nitrogen atom forming a keto tautomer. Single crystal X-ray crystallography suggests that an intramolecular bond exists between the

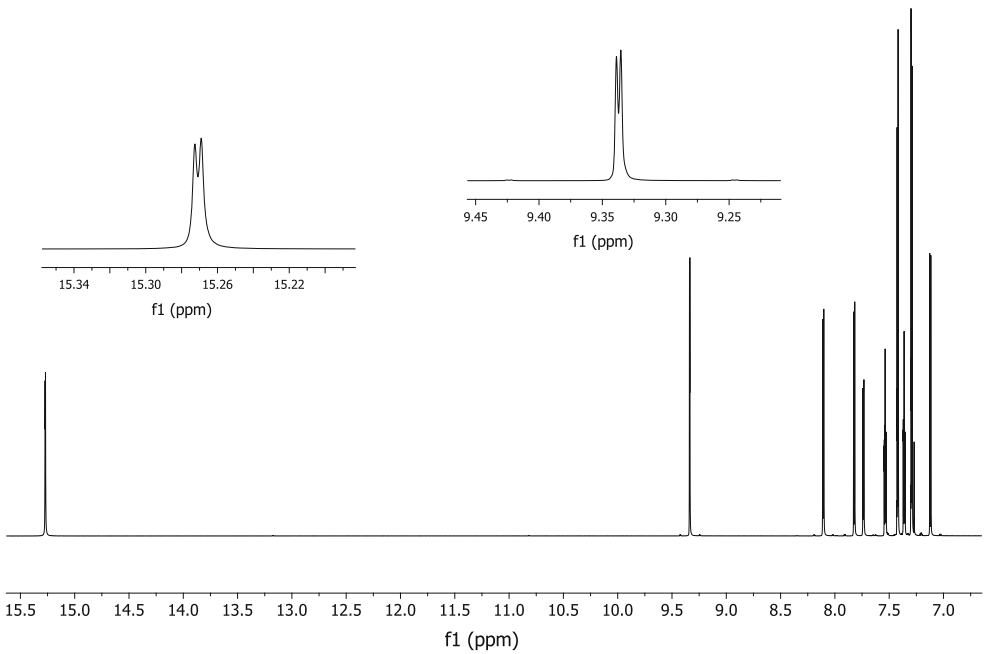


Fig. 1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at 298 K

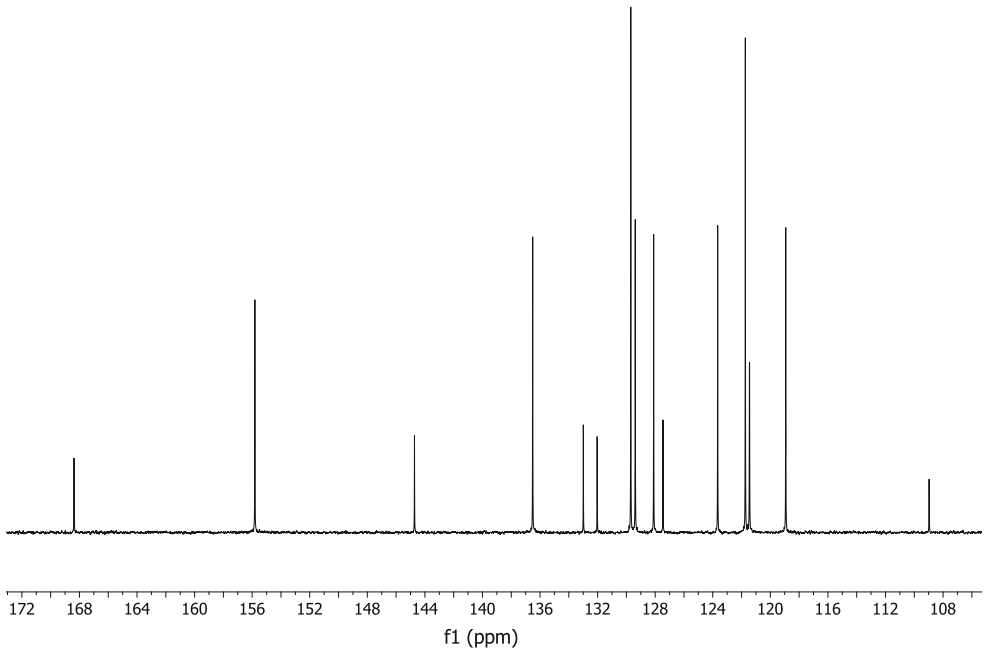
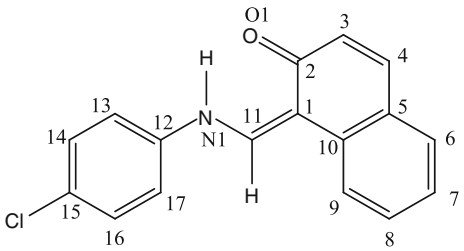


Fig. 2 ^{13}C NMR spectrum of compound **1** in $CDCl_3$ at 298 K

Table 1 Chemical shift assignments for compound **1**



Atom	Proton	Carbon	Atom	Proton	Carbon
1	–	109.0	10	–	132.9
2	–	168.4	11	9.33	155.8
3	7.11	121.5	12	–	144.7
4	7.82	136.5	13	7.29	121.7
5	–	127.5	14	7.42	129.7
6	7.73	128.4	15	–	132.0
7	7.35	123.6	16	7.42	129.7
8	7.54	128.1	17	7.29	121.7
9	8.11	118.9	N–H	15.27	–

The spectra were referenced to the residual solvent signal at 7.27 and 77.0 ppm for proton and carbon, respectively

hydroxyl proton and the nitrogen lone pair and vice versa for the keto tautomer. Another possibility is that there are two configurations for the keto tautomers, a *cis*- and a trans-keto in equilibrium. However, caution should be exercised in dealing with a trans-keto form since the intramolecular hydrogen bond in Schiff bases can be broken only in extreme circumstances. It has also been postulated that electron delocalization and crystal packing characteristics contribute to thermochromism [19].

We evaluated the solid state structural aspects for compound **1**. Crystals of compound **1** were examined by changing the temperature (Fig. 4). The color changed from yellow at −40 °C to an orange color at 50 °C.

In light of this observation, we performed X-ray crystallography on the compound at room temperature and at low temperature (293 and 173 K) and solid state NMR at room temperature and at high temperature (296, 313, and 333 K). These combined temperatures cover the temperature range shown in Fig. 4.

The solid state NMR spectra (100–180 ppm) for the variable temperature study are shown in Fig. 5. As can be seen, the spectra were similar at all temperatures. Solid state NMR did not give any evidence for a temperature dependent structural change. The key feature is that the carbonyl at 171 ppm does not change with temperature but there appears to be a slight shoulder, which does change shape although insignificantly. However, there was a 3 ppm difference between the solid state NMR and the solution NMR for the C=O carbon. This down field shift in the solid state NMR may be due to the equilibrium shifting towards the NH tautomer in solid state compared to solution state or a change in electron delocalization with temperature. A contribution from differences in the instrumental parameters used is also plausible but is likely to be small. The aromatic carbons showed little or no change in their chemical shift. Solid state NMR was conducted at higher

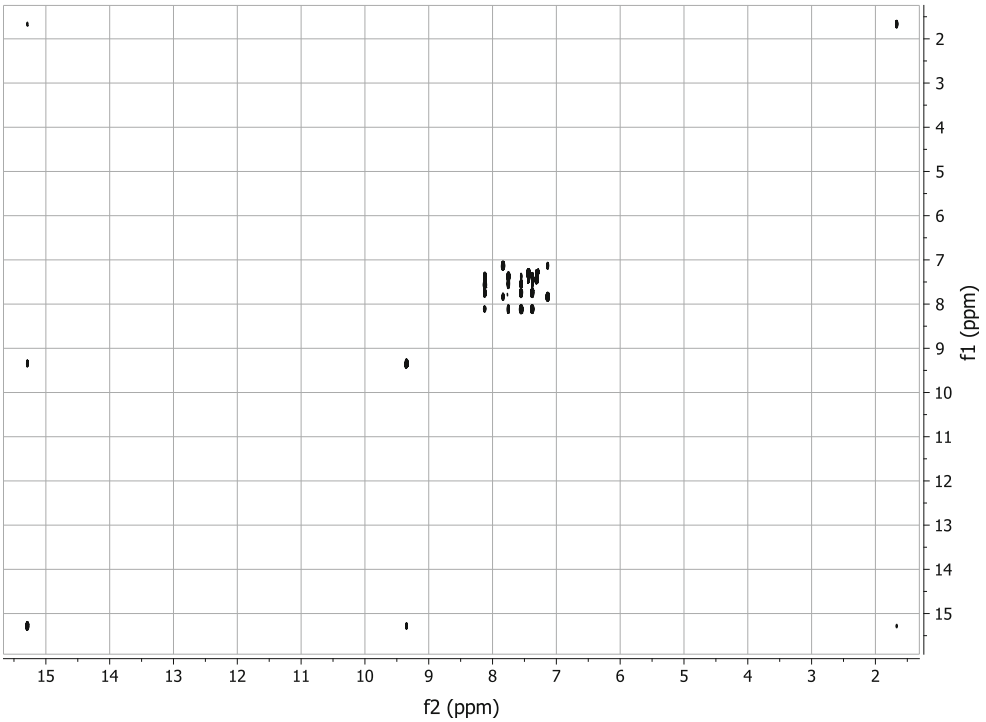


Fig. 3 TOCSY spectrum of compound **1** in $CDCl_3$ at 298 K

Scheme 1 Scheme showing the keto–enol tautomeric equilibrium in compound **1**

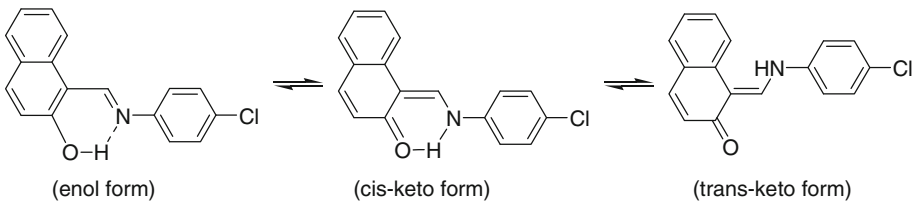
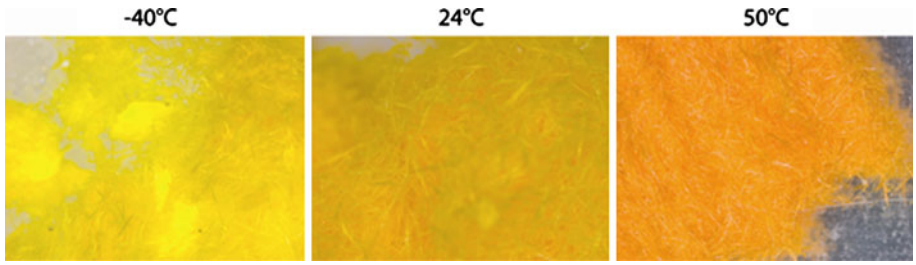


Fig. 4 Observed thermochromism at various temperatures for the Schiff base



temperatures (>50 °C), at which a color change had already been observed (Fig. 4) but even at these temperatures no change in NMR results was observed.

X-ray crystallography studies were undertaken on crystals grown by slow evaporation of a chloroform solution at room temperature. The same crystal was used in both a high (293 K) and low temperature (173 K) data collection. In both cases the structures were isomorphous (monoclinic, space group $P2_1/n$, see Table 2). The changes in cell dimensions as a function of temperature were insignificant, which is quite surprising given the large change in temperature. There was also no significant change in the bond lengths and angles at high and low temperature (Table 3).

Of most relevance to this study was the tautomeric form of compound **1**. During refinement, and after assignment of all non-H atoms plus all aromatic protons, the largest residual electron density peak appeared equidistant between N1 and O1. Constraining this H-atom to either N1 or O1 led to the appearance of a new electron density peak next to the other potential H acceptor. This indicated that the single electron density peak equidistant from O1 and N1 was in

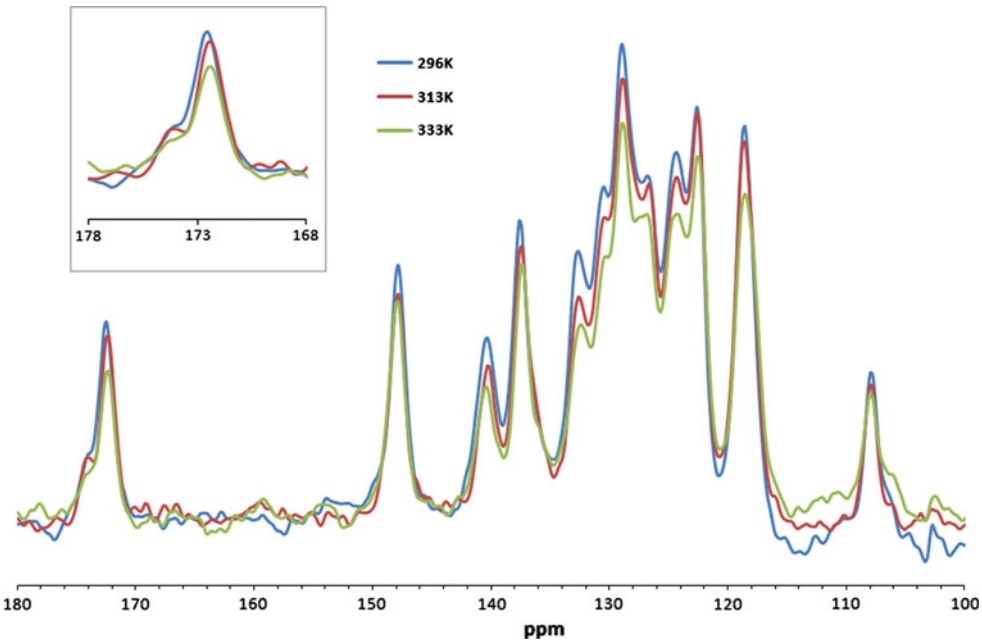


Fig. 5 Solid state ^{13}C NMR of compound **1** at various temperatures

Table 2 Crystal data for compound **1**

	173 K structure	293 K structure
Empirical formula	$C_{17}H_{12}ClNO$	$C_{17}H_{12}ClNO$
Formula weight	281.73	281.73
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$p2_1/n$	$p2_1/n$
Unit cell dimensions	$a = 4.7277(2)$ Å	$a = 4.7293(2)$ Å
	$b = 20.3385(7)$ Å	$b = 20.3378(6)$ Å
	$c = 13.6076(7)$ Å	$c = 13.6124(7)$ Å
	$\beta = 93.514(4)°$	$\beta = 93.535(3)°$
Volume (Å^3)	1306.0(1)	1306.8(1)
Z	4	4
Density (calculated) (Mg/m^3)	1.433	1.432
Absorption coefficient (mm^{-1})	0.286	0.286
F(000)	584	584
Crystal size (mm^3)	0.3 × 0.1 × 0.1	0.3 × 0.1 × 0.1
Index ranges	$-5 \le h \le 5$, $-24 \le k \le 23$,	$-5 \le h \le 5$, $-22 \le k \le 24$,
	$-12 \le l \le 16$	$-6 \le l \le 16$
Reflections collected	4972	4710
Independent reflections	2304 [R(int) = 0.0357]	2304 [R(int) = 0.0332]
Completeness to $\theta = 25.00°$ (%)	99.7	99.7
Data/restraints/parameters	2304/0/183	2304/0/183
Goodness-of-fit on F^2	0.773	0.769
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, $wR_2 = 0.0485$	$R_1 = 0.0356$, $wR_2 = 0.0512$
R indices (all data)	$R_1 = 0.0820$, $wR_2 = 0.0532$	$R_1 = 0.0805$, $wR_2 = 0.0559$
Largest diff. peak and hole (e Å^{-3})	0.22 and −0.21	0.24 and −0.20

fact due to two partially occupied H-atoms from the NH (keto) and OH (enol) forms of the compound. These were each constrained with a riding model and only their occupancies were refined complementarily. The occupancies of the keto and enol forms were 0.54(3):0.46(3) at 173 K and 0.49(3):0.51(3) at 293 K, respectively. No

Table 3 Selected bond lengths of compound **1** at various temperatures

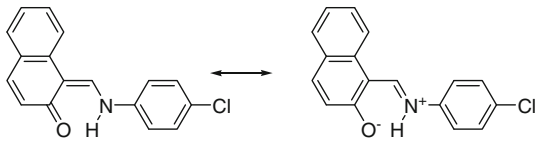
Bond	173 K	293 K
O1–C2	1.311(2)	1.308(2)
C2–C1	1.410(3)	1.412(3)
C1–C11	1.415(2)	1.419(2)
C11–N1	1.307(2)	1.310(2)
N1–C12	1.416(2)	1.416(2)

changes in the remaining bond lengths and angles were apparent as a function of temperature.

Interpretation of the structure of the keto form leads to the conclusion that it is predominantly in its zwitterionic resonance form. The bond lengths for C2–O1 are considerably longer than one would expect for a regular C=O group (1.23 Å, Table 4) and shorter than a single bond (1.43 Å). Similarly the C11–N1 bond (1.30 Å) is shorter than the expected for a single C–N bond (1.47 Å) and closer to that of a double bond (1.28 Å). The expected bond orders of the C–C, C–N, and C–O bonds should be the same in the conventional enol (Scheme 1) and dominantly zwitterionic keto form (Scheme 2) and disorder due to proton transfer appears to best describe the present structure of compound **1**. Intramolecular H-bonds are seen in both the keto and enol forms as the proton moves from one donor to the other.

Notably Ogawa et al. [25] have reported the bond length for the C=O (keto) salicylendemine Schiff base at 90 K as 1.310 Å, which is very similar to our compound at both temperatures. It is important to bear in mind that in our case the temperatures used were 173 and 293 K. The abnormal bond length may be rationalized as being due to a zwitterionic species. In the literature of X-ray crystal structures for related 'keto' tautomers, the C=O bond lengths range from 1.257 to 1.308 Å [41–46]. Our bond lengths are at the top of this range being 1.310 and 1.307 Å for 173 and 293 K, respectively.

The goodness-of-fit on F^2 for compound **1** were 0.773 at 173 K and 0.769 at 293 K. The low factor can mean a good model or over-fit refinement according to the literature [47, 48]. It is known that over fitting can occur due to the following reasons: (i) the number of model parameters far exceeds data, and (ii) too much freedom to model. Several other authors have observed even lower goodness-of-fit values in the range of 0.60–0.81 [49–52].



Scheme 2 Neutral and zwitterionic resonance structures of the keto tautomer

Table 5 Observed cell dimensions at various temperatures for compound **1**

Unit cell dimension ID	173 K (Å (SD))	293 K (Å (SD))	Difference (Å)
a	4.7277(2)	4.7293(2)	0.0016
b	20.3385(7)	20.3378(6)	0.0007
c	13.6076(7)	13.6124(7)	0.0480

Our observations are pertinent to the proposed mechanisms to explain the phenomenon of thermochromism in these compounds. The mechanism involving a shift in the keto-enol equilibrium as a function of temperature was absent from the X-ray crystal structure of compound **1**, although both forms were identified. Another possible explanation may be a change of electron delocalization with temperature but again this was not supported by any changes in the C–C, C–N, or C–O bond lengths with temperature. The crystal packing geometry was also insensitive to temperature as indeed were the unit cell dimensions, which is remarkable (Table 5). It is unclear at present why the structure is resistant to change. Finally we note that Filarowski et al. [46] have presented a related structure where the labile proton is shared equally between the two potential H-bond donors in a so-called 'low barrier' hydrogen bond. In principle compound **1** could be refined similarly but the appearance of distinct electron density next to both N1 and O1 leads us to the present disorder model rather than one where a single proton is shared between two potential H-bond acceptors.

Table 4 Reported bond length of single, double, and partial double bonds

Bond type	Carbon–oxygen (Å)[b]	Carbon–carbon (Å)[b]	Carbon–nitrogen (Å)[a]
Single	1.43 ± 0.01	1.541 ± 0.003	1.465 ± 0.011
Double	1.23 ± 0.01 (ketone, aldehyde)	1.337 ± 0.006	1.279 ± 0.008
Partial	1.36 ± 0.01 (salicylic acid)	1.395 ± 0.003 (aromatic)	1.339 ± 0.016 (2° amide)

[a] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen. Tables of bond Lengths determined by X-ray and neutron diffraction. Part I. Bond lengths in organic compounds. *J. Chem. Soc. Perkin Trans. II* **1987**, S1–S19

[b] CRC handbook of chemistry and physics 1990

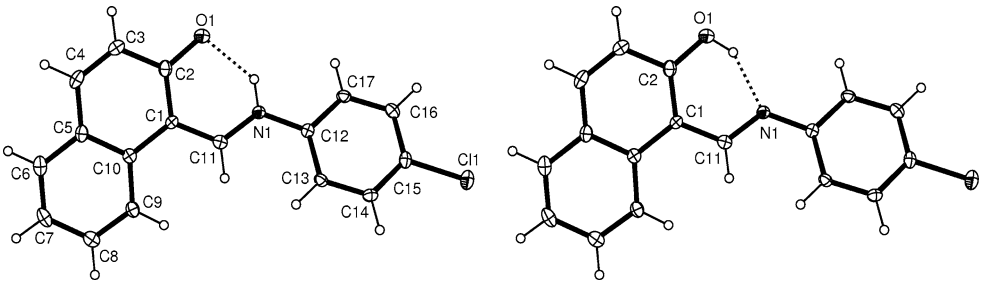


Fig. 6 The keto and enol contributors to disorder in the structure compound **1** at 173 K (30% probability ellipsoids)

Conclusion

In summary, we have synthesized (Z)-3-((4-chlorophenylamino) methylene) naphthalene-2(3H)-one and examined its X-ray crystal structure with varying temperature. The result shows that the compound exists as a disorder between a keto tautomer in its zwitterionic form and an enol tautomer. There was no change in crystal packing geometry or the non-H interatomic distances with temperature. The compound showed thermochromic behavior. Based on the results we propose that the thermochromism exhibited by Schiff bases does not involve a structural change but is linked to a more subtle temperature dependent change in electron delocalization. Similar effects in other compounds may well depend on the nature of substituents associated in the molecular framework.

Supporting Information Available

X-ray crystallographic data in CIF format is available from the Cambridge Crystallographic Data Center #CCDC 753759 and 753760.

Experimental

The title compound was prepared by refluxing a mixture of 4-chloro aniline and 2-hydroxy naphthaldehyde in ethanol for 8 h. The yellow precipitated product was washed thoroughly with ethanol and further purified by crystallization. UV/vis spectra were taken using a Lambda instruments. A Bruker 900 MHz NMR machine was used to acquire NMR data and $CDCl_3$ was used as a solvent. The chemical shifts are reported relative to residual chloroform signal at 7.27 ppm for the proton NMR and 77.0 ppm for ^{13}C NMR. The splitting patterns are designated as: *s* singlet, *d* doublet, *t* triplet, *m* multiplets.

Physical data for compound 1: ^{1}H NMR ($CDCl_3$, 900 MHz) δ ppm 15.27 (d, $J = 3.0$ Hz, 1H), 9.34 (d, $J = 3.0$ Hz, 1H), 8.11 (d, $J = 9.0$ Hz, 1H), 7.82 (d, $J = 9.0$ Hz, 1H), 7.74 (d, $J = 9.0$ Hz, 1H), 7.54 (t, 1H), 7.41 (d, $J = 9.0$ Hz, 2H), 7.36 (t, 1H), 7.29 (d, $J = 9.0$ Hz, 2H), 7.13 (d, $J = 9.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 225 MHz) δ ppm 168.4, 155.8, 144.7, 136.5, 132.9, 132.0, 129.7, 129.4, 128.1, 127.4, 123.6, 121.7, 121.4, 118.9, 108.9; UV ($CHCl_3$): 460, 440, 380, 340 nm; 3400, 1631, 1611 (vs.) 1558, 1488, 1422, 1329, 1180, 1084, 1007, 968, 836, 759 cm^{-1}. IR (KBr): 3400, 1631, 1611 (vs.) 1558, 1488, 1422, 1329, 1180, 1084, 1007, 968, 836, 759 cm^{-1}.

Crystallography

Single crystal intensity data were collected on an Oxford Diffraction Gemini S Ultra CCD diffractometer using graphite monochromated Mo-Kα radiation (λ 0.71073 Å) operating in the ω-scan mode. Data reduction and empirical absorption corrections were performed with the Chrysalis program (Oxford Diffraction, vers. 171.33.34d) while all other computations were performed with the WinGX suite of programs [53] (1998)].Structures were solved by direct methods with SHELXS and refined by full matrix least squares analysis with SHELXL97 [54]. All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were constrained at estimated positions using a riding model. The atomic nomenclature is defined in Fig. 6 drawn with ORTEP3 [55].

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