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Synthesis and Characterization of Anils Exhibiting Thermochromism

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Several Schiff bases containing a hydroxy naphthyl moiety and substituted pyridyl groups were synthesized. The pyridyl substituted Schiff bases were isolated as a single stable tautomer at room temperature. High-resolution proton and carbon NMR spectroscopy showed that these compounds exist as keto tautomers. The Schiff bases showed extraordinary stability and did not convert to the enol tautomer, even at high temperatures. Most of the compounds exhibited thermochromic properties.

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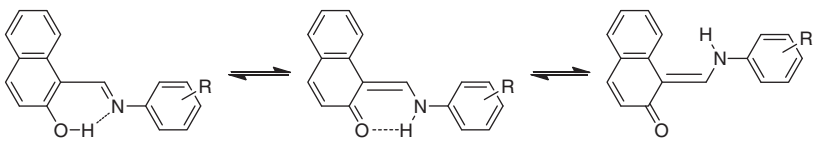
Introduction

Schiff bases containing hydroxyl groups have attracted attention because of their photochromic and thermochromic properties, which have been attributed to keto-enol tautomerism.[1–26] Photochromism is a reversible process in which a single chemical species exhibits two different absorption spectra in the presence of light, depending on its electronic state. Compounds exhibiting photochromism are present in an equilibrium state. Since the 1950s, it has been known that Schiff bases derived from salicylaldehyde and aniline derivatives (anils) are thermochromic, changing their colours from yellow to orange at different temperatures in solid state. The reversible thermochromic property associated with these anils has been attributed to keto-enol tautomerism, with proton transfer, as shown in Scheme 1.

The tautomers are in a temperature dependent equilibrium with proton transfer resulting either in the excited state or the ground state of the molecule. It has been postulated that in planar molecules the amine basicity is higher for the nitrogen atom in the molecule resulting in the lone electron pair not being involved with either ring. On the contrary, in non-planar molecules this overlap occurs with the ring. In other words, the OH···N bond is stronger in the ground state in planar molecules. An increase in temperature results in a high proportion of the keto form, thus resulting in a deepening of the colour of the crystal. Cohen et al.[27] have shown that the difference in the energy associated with such a thermochromic process is minimal (1.76 kcal mol^{-1}).

Recently, Asiri et al.[11] described the synthesis and characterization of new anils possessing a heterocyclic core. Ultraviolet and infrared spectroscopic studies of keto-enol formation of these pyridine based naphthyl anils, suggested the existence of both keto and enol forms in the solution state. Salaman et al.[13] used solution and solid-state ^{13}C NMR spectroscopic methods to demonstrate the tautomeric equilibrium of 2-hydroxy naphthaldehyde derived anils. Schilf et al.[14–16] studied the effects of deprotonation of Schiff bases using proton sponges and other strong nitrogen containing bases on tautomerism. ^{1}H and ^{13}C NMR spectroscopy was used to monitor the proton transfer, which only occurred under specific conditions with very strong bases ($pK_a > 18.18$).

Thermochromic compounds have found wide use and application in recent years. For example, thermochromic liquid crystals are routinely used in thermometers. Thermochromic dyes have been used in thermometric applications such as household battery state indicators as well as in inks, paints, papers, semiconductor devices, and in other temperature sensitive devices. Due to the wide application of thermochromic compounds, we attempted to synthesize and characterize certain anils possessing both a naphthyl and a pyridyl ring in their structures, and subsequently examine their thermochromic properties. In these compounds, substitution of the pyridyl ring with various electron-withdrawing or -donating groups resulted in the exclusive formation of the keto-tautomers.



Scheme 1.

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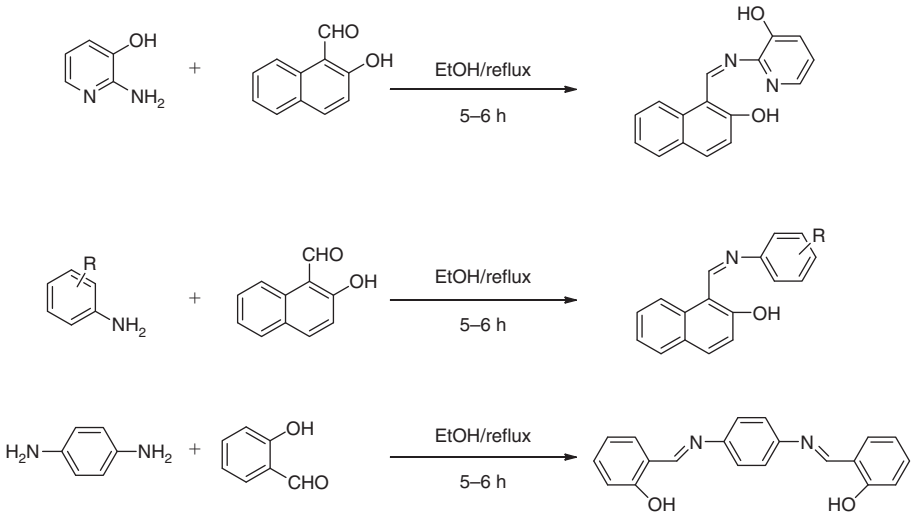


Scheme 2. Synthesis of various anils.

Results and Discussion

The synthesis of anils was accomplished using a general protocol shown in Scheme 2. In brief, appropriate amino compounds were condensed with 2-hydroxy naphthaldehyde, which was chosen specifically to retain the hydroxy moiety. This hydroxyl group can then be conveniently functionalized to obtain other substituted anils. The anils were obtained as crystalline materials with brilliant colours. Table 1 shows the structures of anils prepared in the present study and the colour of each compound at room temperature, which varied from bright orange to pale yellow. The UV spectra of these anils in both methanol and chloroform, showed an intense peak at ~400–460 nm. Additional absorption peaks were also observed at around 350 nm, in keeping with previous reports,[11] suggesting the existence of both enol and keto forms. This was irrespective of the substituents on the pyridine ring, which did not result in preferential formation of either tautomer.

The FT-IR spectra were similar for most of the anils, with the presence of a broad band between 3500 and 3200 cm^{-1}, and peaks between 1700 and 1600 cm^{-1}. In certain anils, the C=O stretching band was much stronger compared with other anils. Nonetheless, these data were consistent with the presence of both enol and keto tautomeric forms.

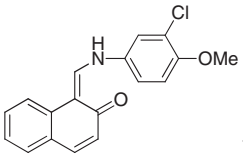
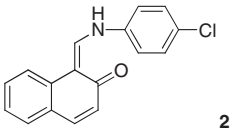
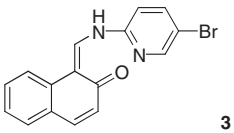
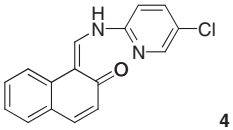
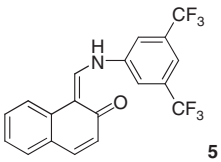
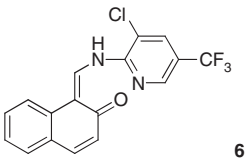
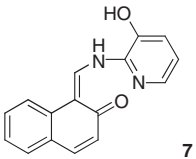
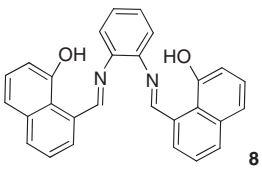
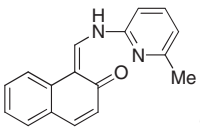
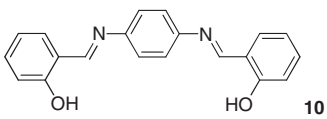
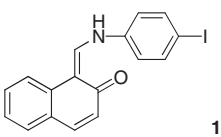
The NMR spectra were carefully analyzed for each of the compounds in the present study to thoroughly understand the structure of the compounds. Although there is an abundance of published literature on the structural determination of these anils, there are inconsistencies in the interpretation of the physical data. To overcome these discrepancies we have undertaken a detailed study to synthesize these anils and examine their NMR spectra using various techniques and to compare our data with published values. The proton NMR of compound **1** showed a doublet at 15.32 ppm with a coupling constant of ~2 Hz, which was assigned to the NH proton. We rationalize that the formation of this doublet is attributed to the coupling between the NH proton and the neighbouring CH proton. This is further substantiated by the fact that the CH=N proton also resonated as a doublet, with similar coupling constant (~2 Hz). The ^{13}C NMR spectrum showed a signal at 166.9 ppm, which was assigned as the C=O carbon, even though the signal is shifted upfield in comparison to typical C=O groups. However, the IR spectrum did not show a band at 3500 cm^{-1}, thus indicating the absence of the OH group. Based on the above result we tentatively assigned the structure of the compound as a keto tautomer. In the previous reports,[13–24] the presence of hydrogen bonding in the enol tautomer has been deduced from the chemical shift of the OH protons with a broad singlet at ~14 ppm. The chemical shift of the hydroxyl group in our compound is 1.42 ppm downfield of 14 ppm, leading us to conclude that it is due to the NH group of the keto tautomer. It is also interesting to note that Dudek et al.[7–10] postulated in 1963 that the proton on the NH in naphthalene derivatives might split into doublets, although they were not able to observe this phenomenon perhaps due to the low field of their spectrometers.

Compound **2** showed doublets at 15.27and 9.34 ppm in the ^{1}H NMR spectrum, corresponding to the NH and CH=N protons, respectively (Fig. 1). These values are consistent with the data obtained by Sosa et al.[28] Similarly, the ^{13}C NMR spectrum showed a signal at 168.4 ppm in $CDCl_3$, which was assigned to the C=O carbon in the keto tautomer (Fig. 2). This value was also similar to that obtained by Sosa et al. (169.4 ppm in DMSO-d_6), who suggested that this Schiff base exists as the keto tautomer in solution. These authors reported that the infrared spectral data gave evidence for an enol tautomer in solid state due to the absence of a carbonyl stretching band. In contrast, our infrared spectral data provided the carbonyl-stretching band at 1631 cm^{-1}, suggesting that it is likely that the keto tautomer exists in the solid state. This is further substantiated by the X-ray crystal structure data (unpublished results) for compound **2** which showed a keto tautomeric structure in the solid state.

Examination of the proton NMR spectrum of compound **3** revealed similar findings with doublets for the NH and CH=N protons, corroborating the existence of a keto tautomeric form for this compound. Our ^{13}C NMR spectral data also provided evidence for a keto tautomeric form of **3**, with a signal at 176.7 ppm for the C=O carbon atom. Gusev et al.[29] have prepared the lead complex of this compound using lead nitrate, although no NMR data were published.

Ranganathan et al.[30,31] reported that the proton NMR spectrum of compound **4** showed a doublet at 15.40 ppm, which was assigned to a hydroxyl group in the structure. These authors also observed a doublet for the CH=N proton. Our findings were similar, however we assigned these doublets to the coupling of

Table 1. Characteristics of compounds

Structure	Colour	Thermochromic
 **1**	Orange yellow crystals	Changes to bright yellow at −40°C and deep orange at 50°C
 **2**	Greenish yellow crystals	Changes colour to crimson green at −40°C
 **3**	Orange yellow crystals	Converts to yellow at −40°C. Becomes red at 50°C
 **4**	Orange yellow	Converts to deep yellowish green at −40°C. Becomes orange at 50°C
 **5**	Crimson yellow	Crimson green at −40°C. Higher temperatures gave slight orange tinge
 **6**	Pale yellow crystals	Changes to bright yellow at −40°C and light orange at 50°C
 **7**	Orange powder	Converts to yellow powder at −40°C. Becomes dark orange at 50°C
 **8**	Deep orange crystals	Changes to yellow at −40°C. At higher temperatures it remains orange
 **9**	Yellow crystals	Does not change colour at −40°C. When the temperature is increased to 50°C, a slight orange colour is observed
 **10**	Pale yellow	Does not change colour at −40°C. Changes to darker yellow at 50°C
 **11**	Olive green crystals	Changes to light yellow green on −40°C. Remains olive green at 50°C

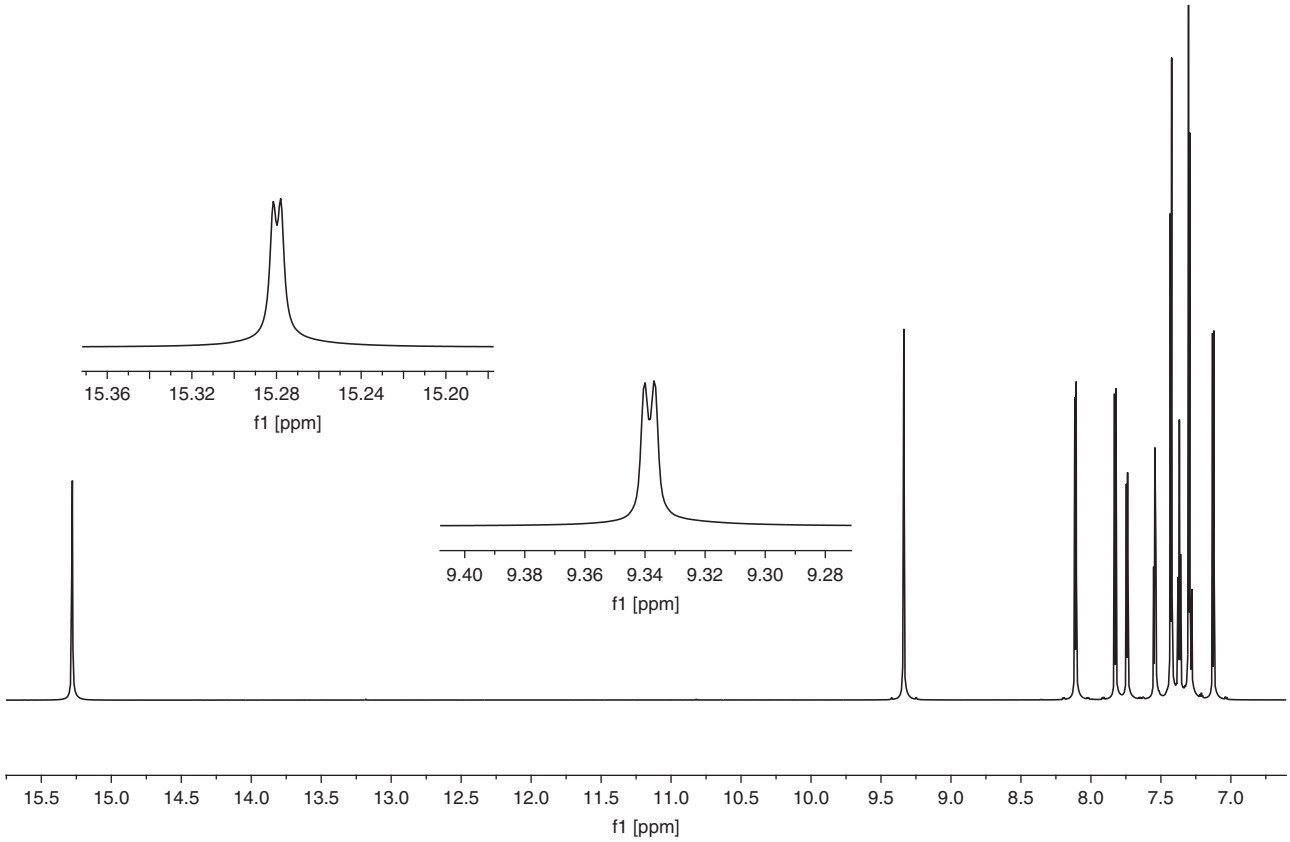


Fig. 1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at room temperature (only the NH doublet and the CH doublet are shown in the spectrum).

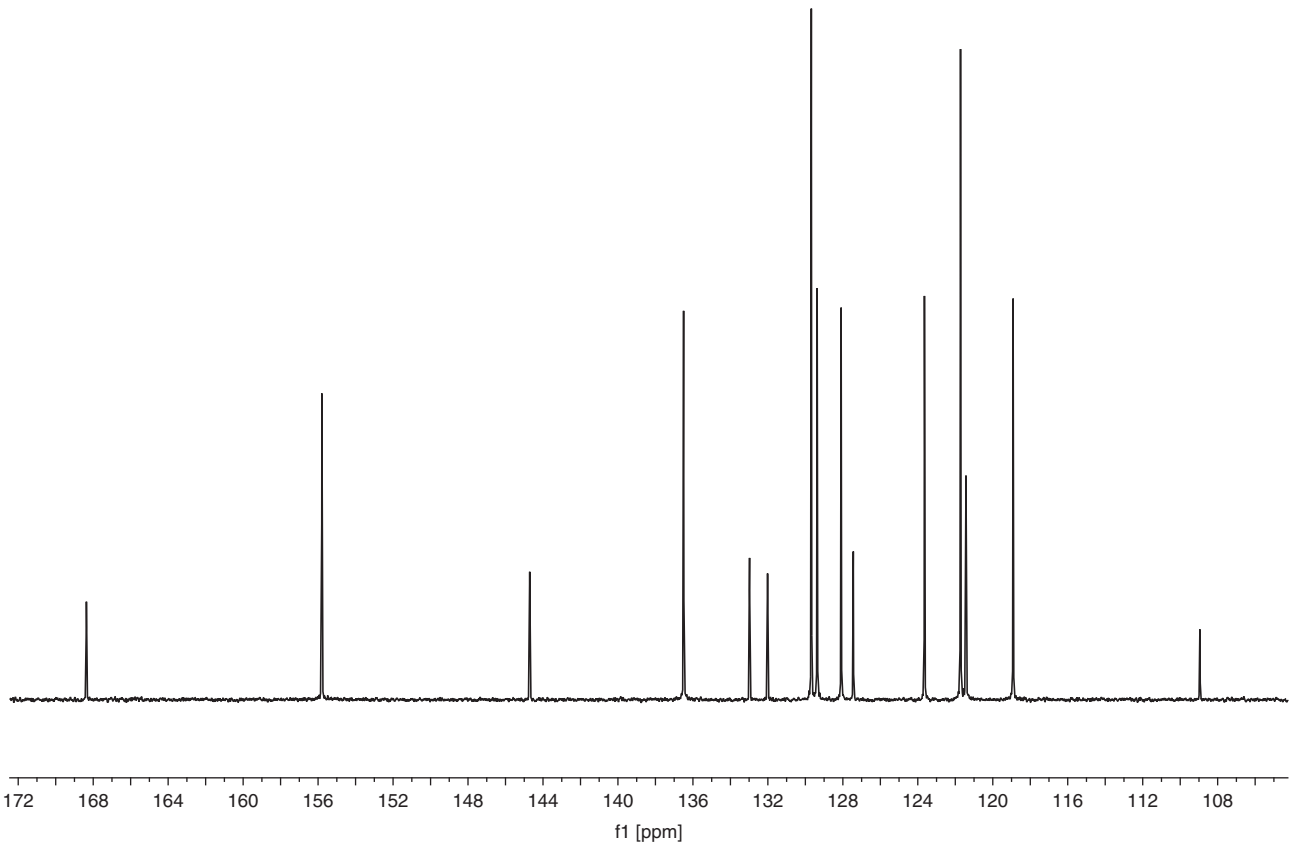


Fig. 2. ^{13}C NMR spectrum of compound **2** in $CDCl_3$ at room temperature (note the peak at 169 ppm corresponding to the C=O of the keto-enamine tautomer).

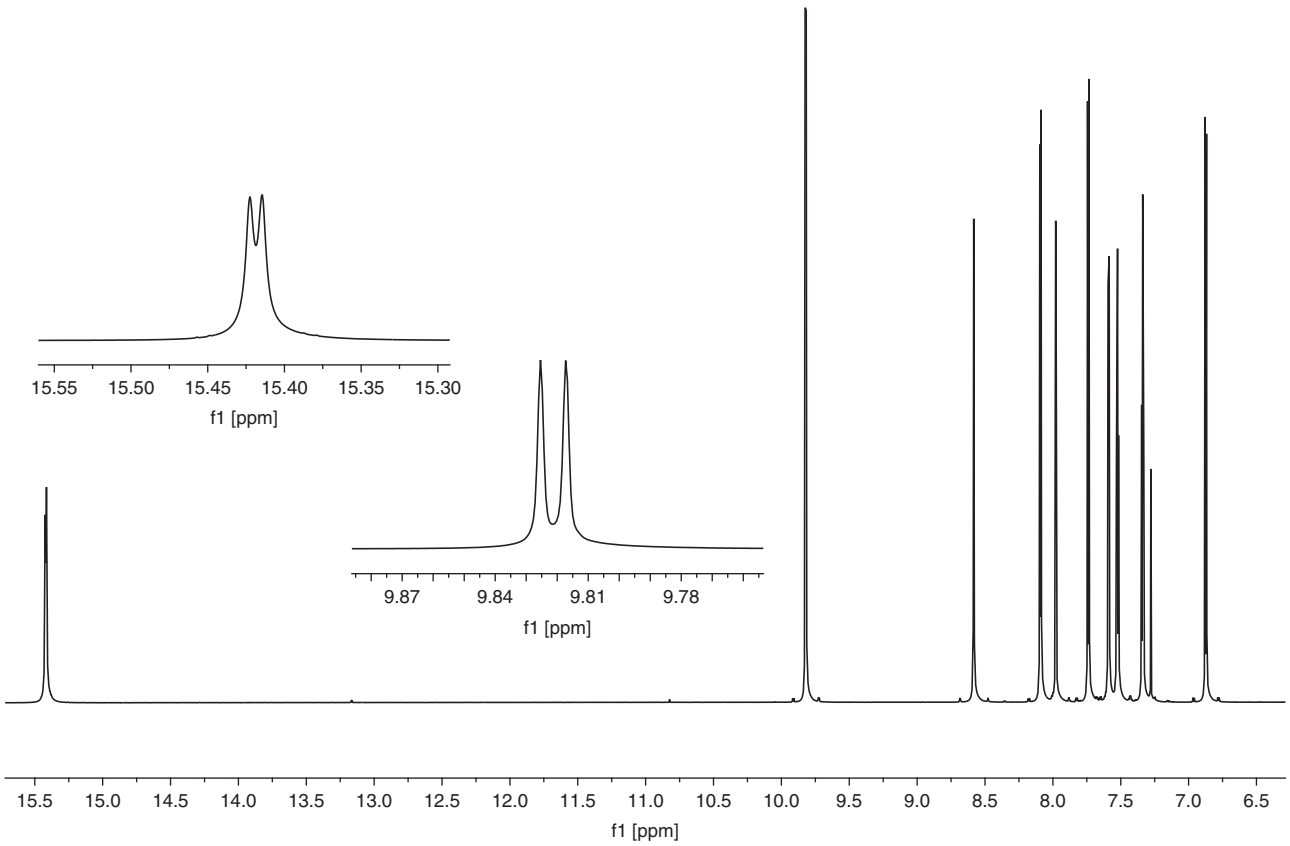


Fig. 3. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at room temperature (only the doublets are shown for NH and CH protons).

the NH proton with the CH=N proton. The ^{13}C NMR spectrum showed a signal at 176.4 ppm corresponding to the carbon of the C=O group. Additional evidence for the keto tautomeric structure was derived from the IR spectral data, which lacked the 3500 cm^{-1} band typical of the OH functional group. Ranganathan et al.[30,31] also suggested that electron-withdrawing groups on the pyridyl moiety would tend to favour a keto tautomer, which is consistent with our notion for a keto tautomeric structure for this compound. Our UV spectral data provide a strong absorption peak at 466 nm, which is consistent with the quinanoid structure of compound **4**.

Unver et al.[32] reported the synthesis and characterization of the trifluoromethyl-substituted compound **5**, including its NMR and X-ray crystal data. According to the authors, the proton NMR spectrum for this compound showed a singlet at 14.91 ppm as well as another singlet at 9.74 ppm, for the OH and CH=N protons, respectively. In their ^{13}C NMR spectral study, they assigned the peak at 167.8 ppm for the CH=N carbon, and the signal at 160.8 ppm for the C-OH carbon. The infrared spectral data showed a band at 3448 cm^{-1}, which was attributed to the OH group in the enol tautomer. These authors also obtained a crystal structure that demonstrates an enol tautomeric form for this compound. Our ^{1}H NMR data for this compound showed a doublet at 14.62 ppm as well as a broad singlet at 9.49 ppm for the NH and CH=N protons, respectively. Our IR data did not show a peak at 3448 cm^{-1}, which indicates the absence of an OH group. The origin of the doublet obtained in the present study is unclear in the absence of X-ray data. It is possible that the differences in the findings are due to differences between the solvents used, DMSO-d_6 versus $CDCl_3$, which may affect hydrogen bonding characteristics considerably. Unver et al. found that in DMSO-d_6, the percentage of keto tautomer is 35%, while in acidic $CDCl_3$ it was 64%.

The trifluoromethyl-chloro substituted pyridyl Schiff base (compound **6**) showed a doublet at 15.42 ppm with a coupling constant of ~6 Hz (Fig. 3). This doublet is assigned to the NH proton coupling with CH. We observed another doublet at 9.83 ppm corresponding to the CH=N proton. The chemical shifts of all other aromatic protons were consistent with the assigned structure of the compound. This is further substantiated by the ^{13}C NMR spectral data in which the C=O resonance appeared at 180.3 ppm (Fig. 4). Further confirmation of the keto tautomeric structure for this compound is obtained using TOCSY NMR spectroscopy (see Fig. 5).

Compound **7** possesses a pyridyl moiety and a hydroxy group in its structure and was reported by Issa et al.[33] These authors assigned the peak at 8.50 ppm to the CH=N proton and singlets at 9.70 and 9.75 ppm were ascribed to the free OH in the pyridyl moiety and the hydrogen-bonded OH group of the naphthalene ring, respectively. This is contrary to our interpretation of proton NMR data that showed a doublet at 15.14 ppm corresponding to the NH proton. Additionally we observed a broad singlet at 10.93 ppm, which is attributed to the hydroxyl group associated with the pryidyl moiety. We did, however, observe a doublet at 9.72 ppm for the CH=N proton. Furthermore, we observed a signal at 181.2 ppm in the ^{13}C NMR spectrum which demonstrates the presence of a C=O group. Our experimental result adds support to the formation of the keto tautomer, while the one reported by Issa et al. perhaps accounts for an enol tautomer. Additionally, we present the ^{15}N HMBC NMR spectrum, which further substantiates the keto tautomeric structure for this compound (Fig. 6). We conclude that the compound exists in its keto

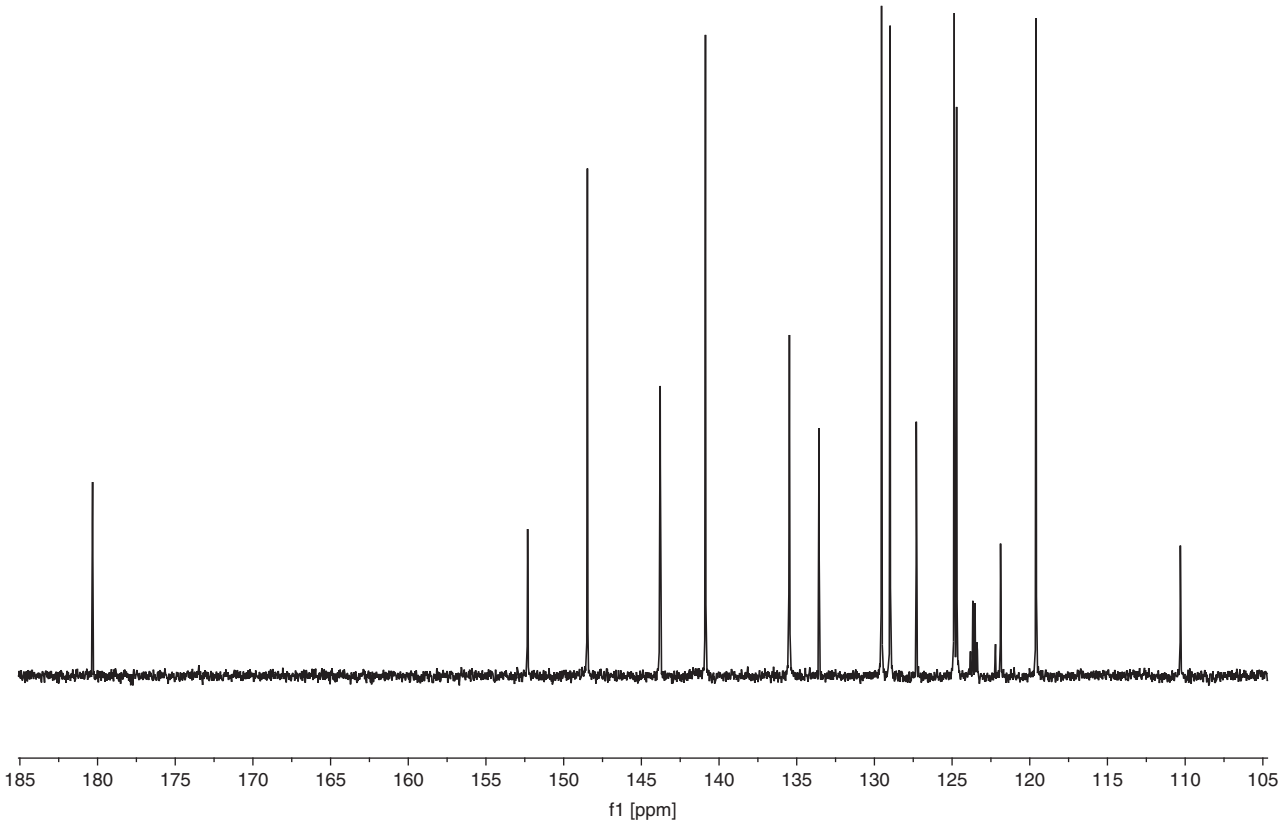


Fig. 4. ^{13}C NMR spectrum of compound **6** in $CDCl_3$ at room temperature (note the peak at 180 ppm corresponding to the C=O group of the keto-enamine tautomer).

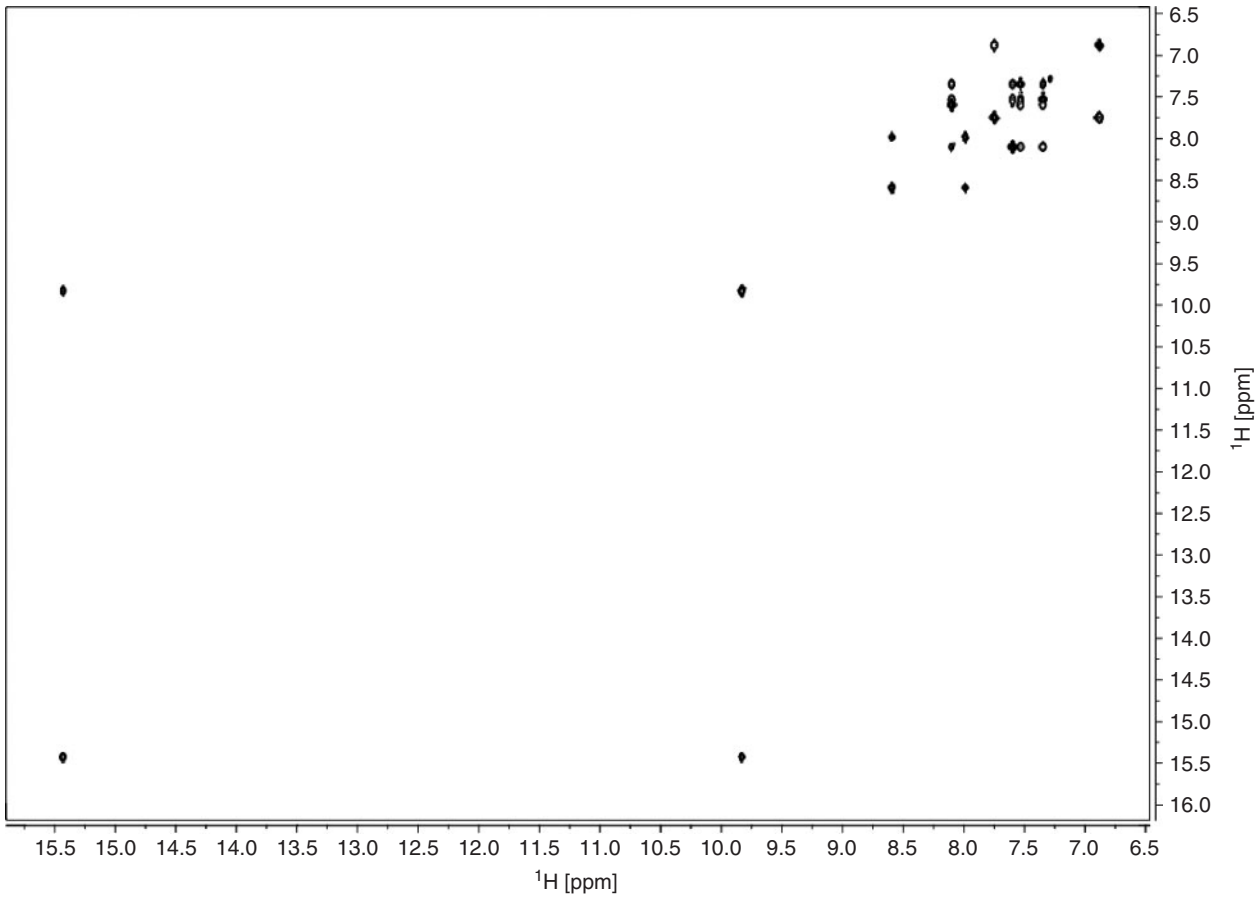


Fig. 5. TOCSY spectrum of compound **6** in $CDCl_3$ at room temperature.

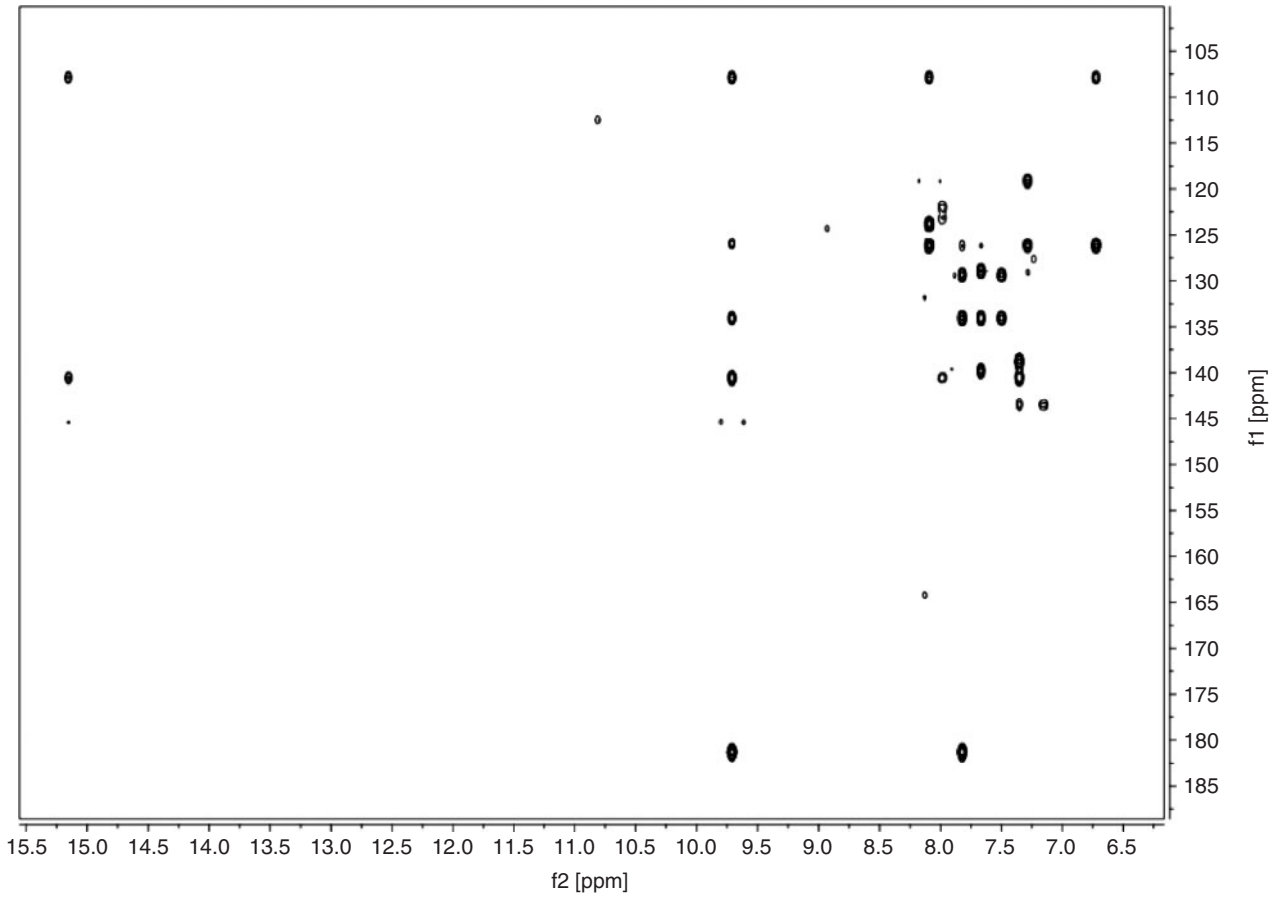
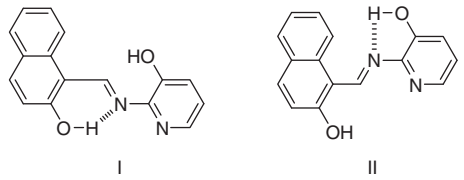


Fig. 6. HMBC spectrum for compound **6** in $CDCl_3$.



Scheme 3.

tautomeric form both in solution and in the solid state. The X-ray crystal structure for compound **7** published Ozek et al.[34] also suggested a keto tautomer with a C=O bond length of 1.29 Å.

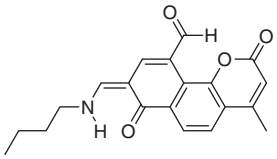
Compound **7** contains two hydroxyl groups; one associated with the pyridyl ring and the other with the naphthyl ring. Theoretically, a hydrogen bond can be formed with the N=C in two ways (Scheme 3). In structure (I) the proton from the hydroxyl group of the naphthalene ring participates in hydrogen bonding, resulting in the formation of a stabilized six-membered ring. In structure (II), the proton from the hydroxyl group associated with the pyridine ring is involved in a hydrogen bonded five-membered ring.

The X-ray crystal structure reported by Meng et al.[35] for compound **8** showed an enol tautomer with a C=O bond length of 1.340 Å, which is in accordance to the known bond lengths of enols. The proton and carbon NMR data of our compound confirms the enol tautomeric form for this compound. The CH=N proton appeared as a singlet at 9.69 ppm. Furthermore the IR spectrum showed a strong stretching vibration band at 3416 cm^{-1} for the free hydroxyl group in the structure.

Compound **9** showed keto tautomeric structural features with the NH and CH=N protons resonating as doublets. In the carbon NMR spectrum, the peak at 179.3 ppm was assigned to the carbon of the C=O group. The keto tautomeric structure of the compound is further substantiated by the X-ray crystal structure reported by Holeck et al.,[36] with a reported C=O bond length of 1.26 Å, which is close to the normal value for a carbon-oxygen double bond (1.22 Å). The slight increase in the bond length observed in the X-ray crystallographic studies might be due to a zwitter ionic species.

In the case of compound **10**, the proton and carbon NMR chemical shifts pointed towards an enol tautomer. For example, there was no doublet at ~15.0 ppm as seen in previous keto compounds. A singlet resonance at 13.19 ppm was observed, indicating an OH group hydrogen bonded to the nitrogen on the CH=N group. In addition we obtained another singlet at 8.68 ppm corresponding to the CH=N proton. The IR spectrum also showed a band at 3502 cm^{-1} consistent with the enol tautomeric form. Recently Kai et al.[37] reported the electronic structure and nonlinear optical properties of Bis(salicylaldiminatio) schiff base compounds and their Ni(II) complexes, thus supporting an enol tautomer.

Finally our data support a keto tautomeric structure for the iodo-substituted compound **11**. Gundazvez et al.[38] reported a broad singlet at 15.25 ppm for this compound, which they attributed to an OH group, suggesting the existence of an enol tautomeric form. However, their ^{13}C NMR chemical shifts



Scheme 4. Structure of Schiff base derived from chromene based aldehydes.

were identical to those that we observed for the compound in the present study. Unver et al.[39] reported the X-ray crystallographic studies of 1-[*N*-(4-iodophenyl)]aminomethylidene-2(*H*)naphthalenone. Our IR spectrum did not show the free hydroxyl group (lack of 3500 cm^{-1} band) in contrast to reports in the literature.[38] We obtained a doublet for both the NH and CH=N protons, unlike earlier reports.

Recently, Sashidhara et al.[40] regioselectively synthesized and characterized the keto-amines derived from chromene derivatives, consisting of fused benzopyranones, and concluded that these Schiff bases existed only as keto-enamine structures. The reported proton NMR spectrum showed a signal at 13.5 ppm, which they assumed to be due to the hydrogen bonding characteristics of NH protons. They also observed an ^{13}C NMR resonance at 179 ppm, which they attributed to the C=O group in the keto-enamine product. Further evidence for the presence of a keto-enamine tautomer was provided using HSQC, COSY, and HMBC spectroscopy. The structure of the chromene-based Schiff base synthesized by Sashidhara et al. is shown in Scheme 4 for clarity.

Effect of the Pyridyl and Benzyl Moieties

We compared the chemical shift observed in the ^{13}C NMR spectra for anils that contained the C=O signal. All anils containing the pyridyl group showed peaks between 176.5 ppm and 181.5 ppm. Anils containing the benzyl group showed peaks in the considerably upfield range of 165.7–168.8 ppm. However, the latter compounds also showed a clear doublet for the NH protons as well as for the CH protons in the ^1H NMR spectra. This can only be possible if the compounds existed as keto-tautomers, because the hydrogen bonded OH of the enolic form would only result in a broad singlet with a chemical shift <15 ppm, which was not observed here. Although these compounds also contained doublets for the NH as well as CH protons in the proton NMR spectra, the coupling constants were relatively small, in the range of 2–3 Hz, unlike those observed for the pyridyl substituted anils (6–8 Hz). At present, the more upfield chemical shift for the carbon associated with C=O in anils containing a benzene ring remains to be explained. The trifluoro-substituted compound and the hydroxy-substituted compound showed the highest chemical shift value for the C=O carbon in these anils. In the phenyl compounds, introduction of iodo- and chloro-substituents shifted the carbonyl carbon signals to ~168 ppm. We examined the effect that varying the solvent had on the chemical shift of individual protons of selected anils. In both $CDCl_3$ and DMSO-d_6, we observed the doublets for the NH and CH protons demonstrating that the polarity of the solvent did not affect the chemical shift of these protons.

The challenge in identifying the correct structural features of these anils is reflected in the inconsistencies in interpretation of their spectral data. In this regard, in the present study, the solution and solid-state spectral characteristics match for most of the compounds, allowing a convergent interpretation of the structures of the compounds.

Thermochromism

Many Schiff bases exhibit thermochromism. Ogawa et al.[41] studied the properties of crystalline forms of certain anils exhibiting thermochromism using X-ray crystallography. There was a mixture of keto and enol tautomers in the solid state and the proportion of each tautomer varied with temperature. The highest proportion (90%) of the keto form was observed at 90 K. Carles et al.[42] showed that salicylidene Schiff bases exhibit thermochromism in the solid state. Thermochromism was observed in most of our anils, which changed colour when the temperature was altered (Table 1, Fig. 7). For example, compound **2** converted from orange red to deep yellow when cooled to −40°C with dry ice.

In summary, we have synthesized anils which possess thermochromism. ^1H and ^{13}C NMR spectroscopy suggests that only the keto-enamine structure is formed at room temperature in several of the compounds. We observed a doublet for the coupling of the NH proton with the neighbouring CH proton, providing additional insight into the keto-enamine structure of these anils.

Experimental

All chemicals were obtained from Sigma Aldrich and were used without further purification. NMR spectra were recorded in both $CDCl_3$ as well as DMSO-d_6 and the chemical shifts are reported relative to the chloroform peak at 7.27 ppm or DMSO at 2.54 ppm, respectively. The NMR data was acquired on a Bruker 900 MHz NMR spectrometer equipped with a cryoprobe. The proton NMR spectra where acquired with a sweep width of 18 ppm centred at 7 ppm. The carbon NMR spectra were acquired with a sweep width of 220 ppm centred at 110 ppm. The DQCOSY and TOCSY experiments were also acquired with a sweep width of 18 ppm using a 90° pulse of 9 μs with 256 and 350 increments, respectively. The ^{15}N HSQC spectrum was acquired with sweep widths of 18 and 45 ppm for proton and nitrogen, respectively, and the nitrogen centred at 118 ppm. The ^{15}N chemical shifts were not referenced, since spectra were run to qualitatively identify whether the proton is directly attached to the nitrogen atom in the molecule. The raw data was usually multiplied by an exponential or shifted sine squared function before performing the Fourier transform. UV-vis spectra were obtained from a Lambda UV spectrometer using either methanol or chloroform as the solvent. Infrared spectra were taken as KBr discs on a Lambda FTIR spectrometer.

General Procedure for Synthesis of Anil Derivatives

The appropriate amine compound (0.05 mol) and the respective aldehyde (0.05 mol) and 50 mL of absolute ethanol were added to a 100 mL round-bottom flask, the contents stirred, and the resulting solution refluxed over an oil bath for 5 h. The precipitated anils were filtered under vacuum and washed with copious amount of ethanol and dried under vacuum. Some of the compounds reported in the present study have been reported previously.[28–38] However, for many of the compounds, their NMR and IR data does not match with the data reported in the present study. A detailed discussion on this aspect is included in the results and discussion section of the manuscript.

1: ν_{max}(KBr)/cm^{-1} 3341, 1625, 1609 (s), 1569 (w), 1498 (vs), 1438, 1334, 1301, 1261 (s), 1184, 1066, 1026, 979, 919, 829, 758. λ_{max} ($CHCl_3$)/nm 460, 454, 388, 342. δ_H ($CDCl_3$,

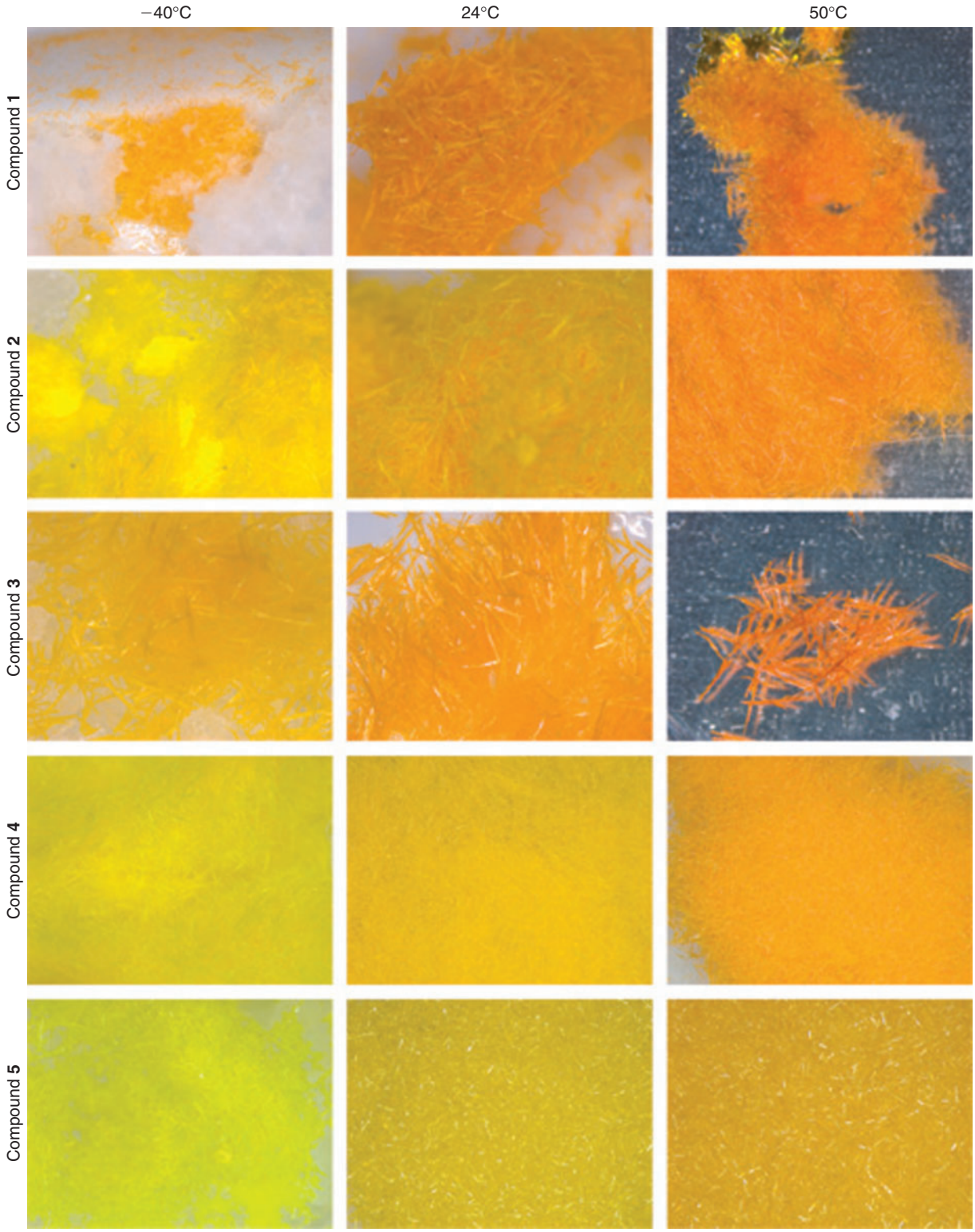


Fig. 7. Appearance of crystals of selected anils at various temperatures in the solid state.

900 MHz) 15.32 (d, *J* 2.3 Hz, 1H), 9.35 (d, *J* 2.0 Hz, 1H), 8.15–8.14 (d, *J* 9.0 Hz, 1H), 7.83–7.82 (d, *J* 9.0 Hz, 1H), 7.76–7.75 (d, *J* 9.0 Hz, 1H), 7.55–7.54 (t, 1H), 7.45–7.44 (d, *J* 9.0 Hz, 1H), 7.36 (s, 1H), 7.26–7.25 (t, 1H), 7.15–7.14 (d, *J* 9.0 Hz, 1H), 7.01–7.00 (d, *J* 9.0 Hz, 1H), 3.6 (s, 3H). δ_H ($CDCl_3$, 225 MHz) 166.9, 155.6, 153.8, 140.2, 135.9, 132.9, 129.3, 128.0, 127.53, 127.5, 122.1, 122.0, 121.0, 119.1, 112.6, 109.1, 56.4.

2: ν_{max}(KBr)/cm^{-1} 3001, 1631, 1611 (vs), 1558, 1488, 1422, 1329, 1180, 1084, 1007, 968, 836, 759. λ_{max} ($CHCl_3$)/nm 460, 440, 380, 340. δ_H ($CDCl_3$, 900 MHz) 15.27 (d, *J* 3.0 Hz, 1H), 9.34 (d, *J* 3.0 Hz, 1H), 8.11–8.10 (d, *J* 9.0 Hz, 1H), 7.83–7.82 (d, *J* 9.0 Hz, 1H), 7.74–7.73 (d, *J* 9.0 Hz, 1H), 7.55–7.53 (t, 1H), 7.42–7.41 (d, *J* 9.0 Hz, 2H), 7.36–7.35 (t, 1H), 7.30–7.29 (d, *J* 9.0 Hz, 2H), 7.13–7.12 (d, *J* 9.0 Hz, 1H). δ_C ($CDCl_3$, 225 MHz)

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.

3: ν_{max}(KBr)/cm^{-1} 3119, 2606, 1629, 1548, 1480, 1450, 1312, 1255, 1192, 1144, 1120, 1033, 981, 848, 818, 741. λ_{max} (MeOH)/nm 461, 438, 316, 298, 276. δ_H ($CDCl_3$, 900 MHz) 15.36–15.35 (d, *J* 9.0 Hz, 1H), 9.93–9.92 (d, *J* 9.0 Hz, 1H), 8.51 (s, 1H), 8.14–8.13 (d, *J* 9.0 Hz, 1H), 7.84–7.83 (d, *J* 9.0 Hz, 1H), 7.77–7.76 (d, *J* 9.0 Hz, 1H), 7.63–7.62 (d, *J* 9.0 Hz, 1H), 7.52–7.51 (t, 1H), 7.33–7.32 (t, 1H), 7.08–7.07 (d, *J* 9.0 Hz, 1H), 6.94–6.93 (d, *J* 9.0 Hz, 1H). δ_C ($CDCl_3$, 225 MHz) 176.7, 152.2, 151.3, 149.9, 141.0, 133.8, 129.4, 128.6, 128.2, 127.2, 124.1, 123.9, 119.4, 117.6, 116.9, 109.1.

4: ν_{max}(KBr)/cm^{-1} 3207, 2729, 1620 (vs), 1606, 1588, 1548, 1475, 1402, 1375, 1319, 1294, 1218, 1133, 1107, 972, 835, 765. λ_{max}($CHCl_3$)/nm 466, 441, 378, 344, 310. δ_H ($CDCl_3$, 900 MHz) 15.38 (d, *J* 2.0 Hz, 1H), 9.93 (d, *J* 3.0 Hz, 1H), 8.42–8.41 (d, *J* 9.0 Hz, 1H), 8.14–8.13 (d, *J* 9.0 Hz, 1H), 7.77–7.76 (d, *J* 9.0 Hz, 1H), 7.70–7.69 (d, *J* 9.0 Hz, 1H), 7.64–7.63 (d, *J* 9.0 Hz, 1H), 7.53–7.51 (t, 1H), 7.33–7.32 (t, 1H), 7.13–7.12 (d, *J* 9.0 Hz, 1H), 6.95–6.94 (d, *J* 9.0 Hz, 1H). δ_C ($CDCl_3$, 225 MHz) 176.4, 151.9, 151.7, 139.0, 138.2, 133.8, 129.3, 128.8, 128.5, 127.2, 124.0, 123.8, 119.4, 117.2, 109.0.

5: ν_{max}(KBr)/cm^{-1} 3158, 1633 (vs), 1610 (vs), 1572 (s), 1471, 1404, 1373, 1338, 1293, 1184, 1128, 1002, 983, 885, 832, 756. λ_{max} ($CHCl_3$)/nm 451, 384, 340. δ_H ($CDCl_3$, 900 MHz) 14.62 (d, *J* 1.5 Hz, 1H), 9.49 (bs, 1H), 8.19–8.18 (d, *J* 9.0 Hz, 1H), 7.91–7.90 (d, *J* 9.0 Hz, 1H), 7.81–7.79 (m, 2H), 7.76 (s, 2H), 7.61–7.59 (t, 1H), 7.43–7.41 (t, 1H), 7.21–7.20 (d, *J* 9.0 Hz, 1H). δ_C ($CDCl_3$, 225 MHz) 165.7, 159.8, 149.4, 136.9, 133.3, 133.1, 132.9, 132.8, 132.7, 129.5, 128.4, 127.8, 124.1, 123.6, 122.4, 121.2, 120.2, 119.7, 119.2, 109.2.

6: ν_{max}(KBr)/cm^{-1} 3240 (b), 1634, 1591, 1541, 1477, 1335, 1286, 1229, 1213, 1168, 1129, 1097, 1060, 967, 914, 837, 753. λ_{max}(MeOH)/nm 461, 440, 315, 296, 228. δ_H ($CDCl_3$, 900 MHz) 15.42–1541 (d, *J* 9.0 Hz, 1H), 9.83–9.82 (d, *J* 9.0 Hz, 1H), 8.58 (s, 1H), 8.10–8.09 (d, *J* 9.0 Hz, 1H), 7.98 (s, 1H), 7.74–7.73 (d, *J* 9.0 Hz, 1H), 7.59–7.58 (d, *J* 9.0 Hz, 1H), 7.53–7.51 (t, 1H), 7.35–7.33 (t, 1H), 6.88–6.87 (d, *J* 9.0 Hz, 1H). δ_C ($CDCl_3$, 225 MHz) 180.3, 152.3, 148.5, 143.8, 140.9, 135.5, 133.6, 129.5, 128.9, 127.3, 124.9, 124.8, 123.7–125.5 (q), 121.9, 119.6, 110.3.

7: ν_{max}(KBr)/cm^{-1} 3500–3300 (b), 1633, 1610 (s), 1577, 1482, 1471, 1404, 1373, 1338, 1293, 1217, 1193, 1136, 1020, 990, 885, 832, 756. λ_{max} (MeOH)/nm 471, 416, 351, 327, 230. δ_H (DMSO-d_6, 900 MHz) 15.14–15.15 (d, *J* 9.0 Hz, 1H), 10.93 (bs, 1H), 9.72–9.71 (d, *J* 6.3 Hz, 1H), 8.10–8.09 (d, *J* 9.0 Hz, 1H), 7.99–7.98 (d, *J* 9.0 Hz, 1H), 7.83–7.82 (d, *J* 9.0 Hz, 1H), 7.67–7.66 (d, *J* 9.0 Hz, 1H), 7.51–7.49 (t, 1H), 7.36–7.35 (d, *J* 9.0 Hz, 1H), 7.28–7.27 (t, 1H), 7.16–7.15 (m, 1H), 6.73–6.72 (d, *J* 9.0 Hz, 1H). δ_C (DMSO-d_6, 225 MHz) 181.5, 145.8, 143.8, 140.9, 140.1, 139.1, 134.4, 129.8, 129.3, 126.5, 126.3, 124.2, 123.6, 122.4, 119.5.

8: ν_{max}(KBr)/cm^{-1} 3416, 3026, 1615, 1573, 1496, 1459, 1432, 1372, 1321, 1286, 1218, 1193, 1168, 1130, 761. δ_C (DMSO-d_6, 900 MHz) no NH peak due to exchange in DMSO, 9.69 (s, 1H), 8.55–8.54 (d, *J* 9.0 Hz, 2H), 7.97–7.96 (d, *J* 9.0 Hz, 1H), 7.83–7.82 (d, *J* 9.0 Hz, 3H), 7.55–7.54 (t, 1H), 7.45–7.44 (d, *J* 9.0 Hz, 1H), 7.38–7.37 (t, 1H), 7.07–7.06 (d, *J* 9.0 Hz, 1H). δ_C (DMSO-d_6, 225 MHz) 168.6, 157.4, 138.5, 136.8, 133.0, 129.0, 128.2, 127.4, 126.9, 123.6, 121.5, 120.7, 119.7, 109.3.

9: ν_{max}(KBr)/cm^{-1} 3341, 3061, 1626, 1606, 1567, 1542, 1462, 1400, 1301, 1211, 1160, 1134, 1028, 992, 853, 795. λ_{max} ($CHCl_3$)/nm 464, 440, 371, 342, 332. δ_H ($CDCl_3$, 900 MHz) 15.41 (d, *J* 7.0 Hz, 1H), 9.92–9.91 (d, *J* 9.0 Hz, 1H), 8.12 (8.11 (d, *J* 9.0 Hz, 1H), 7.72–7.71 (d, *J* 9.0 Hz, 1H), 7.61–7.59 (m, 2H), 7.50–7.50 (t, 1H), 7.30–7.28 (t, 1H), 7.00–6.99 (d, *J* 9.0 Hz, 1H), 6.94–6.93 (d, *J* 9.0 Hz, 1H), 6.90–6.89 (d, *J* 9.0 Hz, 1H), 2.60 (s, 3H). δ_C ($CDCl_3$, 225 MHz) 179.6, 158.4, 151.5, 149.3, 139.3, 138.7, 134.2, 129.3, 128.4, 126,8, 123.7, 120.5, 119.2, 112.3, 108.5, 24.4.

10: ν_{max}(KBr)/cm^{-1} 3502 (b), 3063, 1615, 1573, 1496, 1459, 1372, 1286, 1218, 1193, 1161, 1148, 1130, 907, 828, 761. λ_{max} ($CHCl_3$)/nm 451, 379, 372, 336, 271. δ_H ($CDCl_3$, 900 MHz) Enol tautomer and no keto tautomer: 13.19 (s, 1H, hydrogen bonded OH), 8.68 (s, 1H), 7.43–7.37 (m, 5H), 7.05–7.04 (d, *J* 9.0 Hz, 1H), 6.98–6.96 (t, 2H). δ_C ($CDCl_3$, 225 MHz) 162.3, 161.1, 147.1, 133.3, 132.2, 122.2, 119.1, 117.3.

11: ν_{max}(KBr)/cm^{-1} 3385, 3158 3061, 1628, 1605, 1564, 1483, 1389, 1331, 1180, 1141, 1009, 970, 829, 767. λ_{max} ($CHCl_3$)/nm 464, 451, 384, 340, 323. δ_H ($CDCl_3$, 900 MHz) 15.24 (d, *J* 2.8 Hz, 1H), 9.33–9.33 (d, *J* 2.9 Hz, 1H), 8.10–8.09 (d, *J* 9.0 Hz, 1H), 7.82–7.81 (d, *J* 9.0 Hz, 1H), 7.77–7.76 (d, *J* 9.0 Hz, 2H), 7.74–7.73 (d, *J* 9.0 Hz, 1H), 7.54–7.53 (t, 1H), 7.37–7.35 (t, 1H), 7.11–7.10 (d, *J* 9.0 Hz, 3H). δ_C ($CDCl_3$, 225 MHz) 168.8, 155.5, 145.7, 138.6, 136.7, 133.0, 129.4, 128.1, 127.4, 123.7, 122.4, 121.6, 118.9, 108.9, 90.8.

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