

***N*-Salicylideneamine Derivatives with TEMPO Substituents**

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Abstract: Three *N*-salicylideneamine derivatives bearing TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) substituents were prepared in order to study their structure and property relationships and to investigate the possibilities of the existence of heat and/or light responsive magnetic properties. Curie-Weiss behavior with weak ferromagnetic intermolecular spin-spin interactions was observed in one of the radicals, while antiferromagnetic interactions were predominant for the other radicals and the structure-property relationships were investigated for the radical compounds from their crystal structures obtained by X-ray analyses. Preliminary results of the examination of their responses towards light and heat are also described.

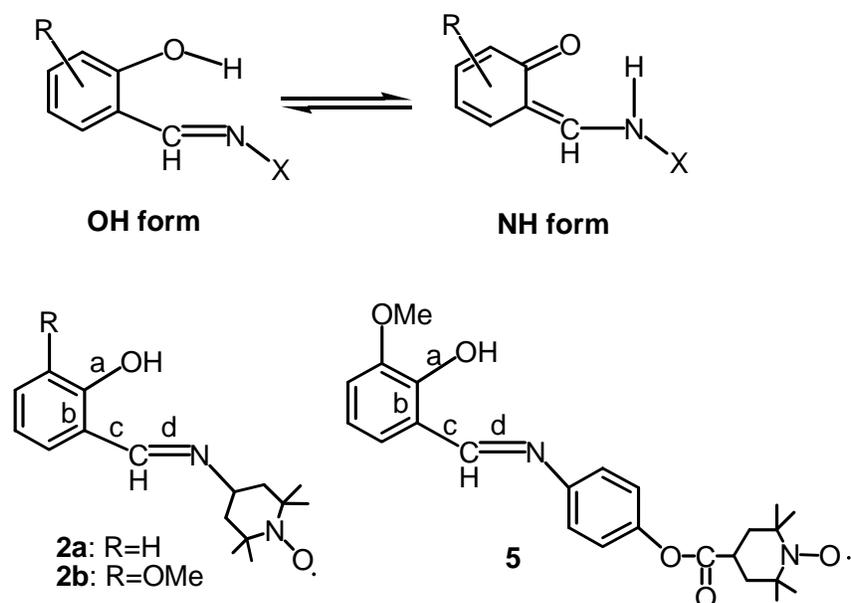
Keywords: Salicylideneamine, salicylideneaniline, TEMPO, magnetic property, crystal structure

Introduction

Considerable attention is now focused on the development of organic and molecular-based magnetic materials and a number of new spin systems have been prepared in recent years [1]. It is of current interests in the field of molecular-based magnetic and related materials to develop spin systems with multi-properties and the development of photo- or heat-responsive spin systems is paid particular attention among them. In the course of our studies for the development of novel spin systems, we have

been interested in preparing organic spin systems which respond to outer stimuli, such as light, heat, pressure, electron, etc. and tried to develop spin systems with multi-properties [2].

Some of the derivatives of *N*-salicylideneamine/aniline (the Schiff bases of salicylaldehydes with amines/anilines) are known to show photochromism and/or thermochromism in solution and even in the solid-state, owing mainly to the structural change based on enol-keto tautomerization of the hydroxy as well as imine groups, namely the isomerization between OH form and NH form as shown in the chart below, and in some cases, *Z-E* isomerization of the resulting keto-isomer [3]. We then have tried to introduce a radical substituent as a spin source in *N*-salicylideneamine/salicylideneaniline derivatives to see the possibilities of the existence of heat- and/or photo-responsive magnetic properties due to the structural changes based on the tautomerization. In this paper, we wish to report on the preparation of some *N*-salicylideneamine/aniline derivatives bearing TEMPO substituents (**2a**, **2b**, and **5**) and their structures obtained by X-ray analyses, together with their magnetic properties. Some preliminary observations of their photo- and heat-responsive properties are also briefly described.

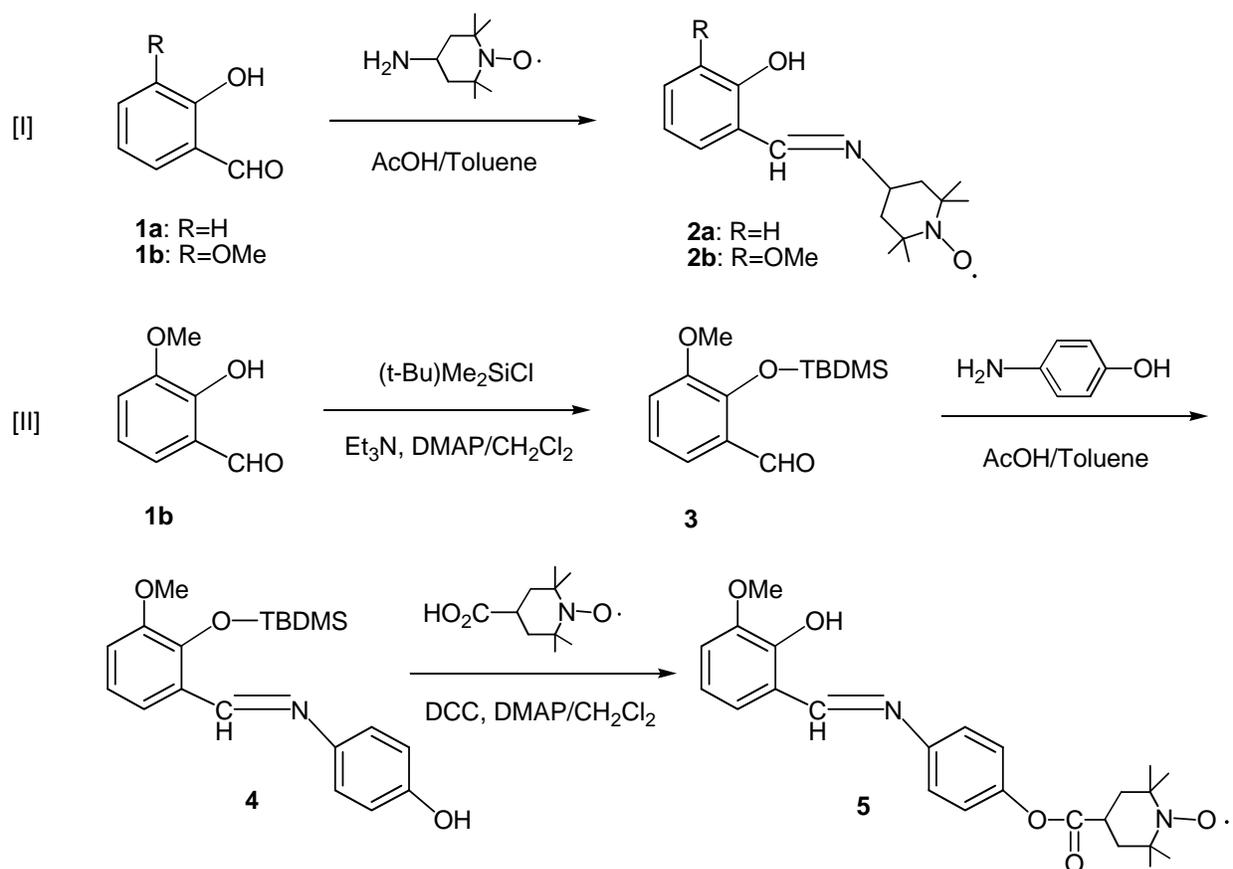


Results and Discussion

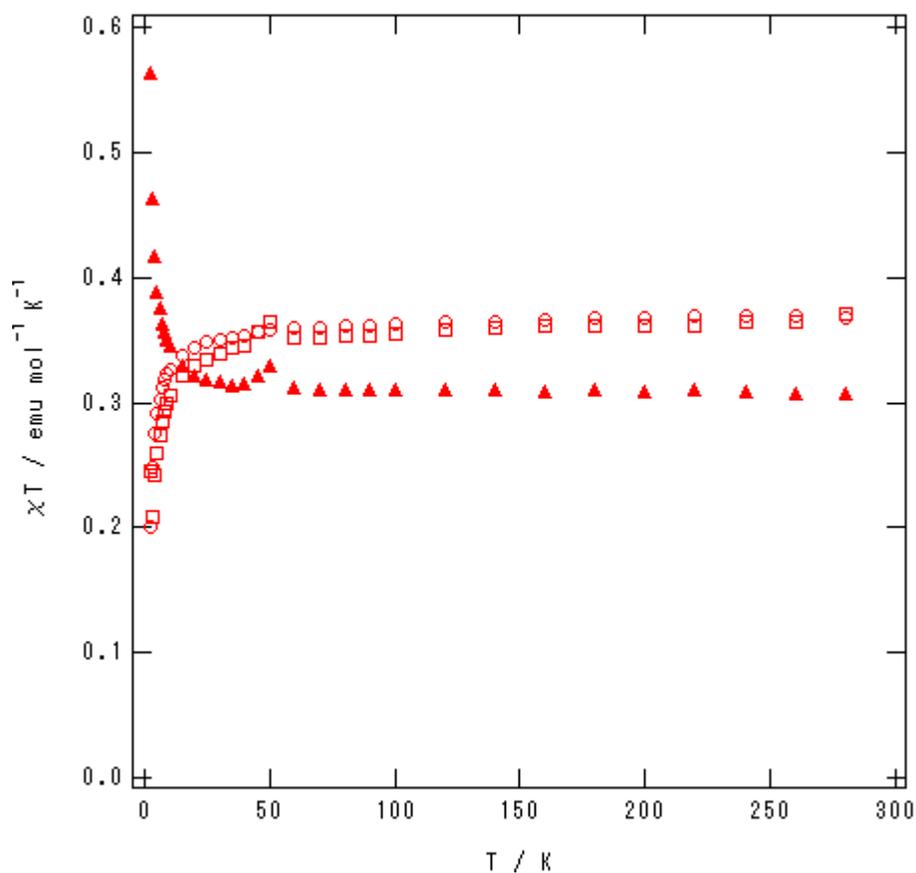
The preparation of the *N*-salicylideneamine/aniline derivatives with TEMPO substituents was carried out as shown in Scheme 1. Condensation of salicylaldehyde (**1a**) or *o*-methoxysalicylaldehyde (**1b**) with 4-amino-TEMPO in toluene solution gave the corresponding Schiff bases **2a** [4] and **2b** in moderate yields (reaction [I]). The salicylideneaniline derivative **5** was prepared from *o*-methoxysalicylaldehyde (**1b**) according to reaction [II]. The hydroxy group in **1b** was at first protected with a TBDMS (*tert*-butyldimethylsilyl) group to avoid the anticipated self-condensation reaction in the subsequent step to give the derivative **3** in 52% yield, which was then condensed with *p*-aminophenol to

afford the phenol derivative **4** in low yield (10%). The phenol **4** was finally condensed with 4-carboxy-TEMPO using DCC (1,3-dicyclohexylcarbodiimide) and DMAP [4-(dimethylamino)-pyridine] in dichloromethane solution, with concomitant deprotection of the TBDMS group, to give the desired salicylideneaniline derivative **5** in 38% yield. A similar approach to the unsubstituted derivative starting from salicylaldehyde (**1a**) has so far been unsuccessful because of the failure of the reaction with *p*-aminophenol in this case.

Scheme 1



The temperature dependence data of their magnetic susceptibilities were obtained by the SQUID measurements from 2 to 300 K and the results are shown in Figure 1. Curie-Weiss behaviour with weak intermolecular magnetic interactions are observed in all three radical compounds and ferromagnetic interactions with Weiss temperature of ca. 1 K are found, among them, only for **2b**, while antiferromagnetic interactions are predominant in the other two radicals with apparently larger Weiss temperature for **5** (-2.06 K) than for **2a** (-1.34 K, lit. -1.4 K [4]). The Curie constants are reasonable values as $S=+1/2$ spin ($0.37 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) for **2a** and **5** but it is apparently less than the anticipated value for **2b** ($0.31 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$), indicating the existence of some diamagnetic species in the radical.

Figure 1. Temperature dependence data of χT for **2a** (○), **2b** (▲), and **5** (□).

Single crystals of the compounds could be obtained by recrystallization of the radicals and their X-ray diffraction data are summarized in Table 1.

Table 1. Summary of crystal data for **2a**, **2b** and **5**

Parameter	2a	2b	5
Formula	$C_{16}H_{23}N_2O_2$	$C_{17}H_{25}N_2O_3$	$C_{24}H_{29}N_2O_5$
Formula weight	275.37	305.40	425.50
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pca2_1$	$P2_1/a$	$P2_1/c$
$a/\text{\AA}$	15.6355(9)	11.287(2)	7.755(1)
$b/\text{\AA}$	8.2552(3)	11.121(2)	27.707(1)
$c/\text{\AA}$	24.276(2)	13.823(2)	11.038(1)
$\alpha/\text{degrees}$	90	90	90

β /degrees	90	103.17(1)	107.66(1)
γ /degrees	90	90	90
$V/\text{\AA}^3$	3133.4(4)	1690.1(5)	2260.0(4)
Z	8	4	4
D (calc)/gcm ⁻³	1.167	1.200	1.250
No. of measured reflections	13559	4292	4969
No. of independent reflections	6690	4094	4858
No. of used reflections in refinement $F > 2\sigma$	4138	1392	1957 ¹
No. of parameters refined	407	199	280
R	0.069	0.057	0.068
R_w	0.070	0.031	0.046

¹ $F > 4\sigma$

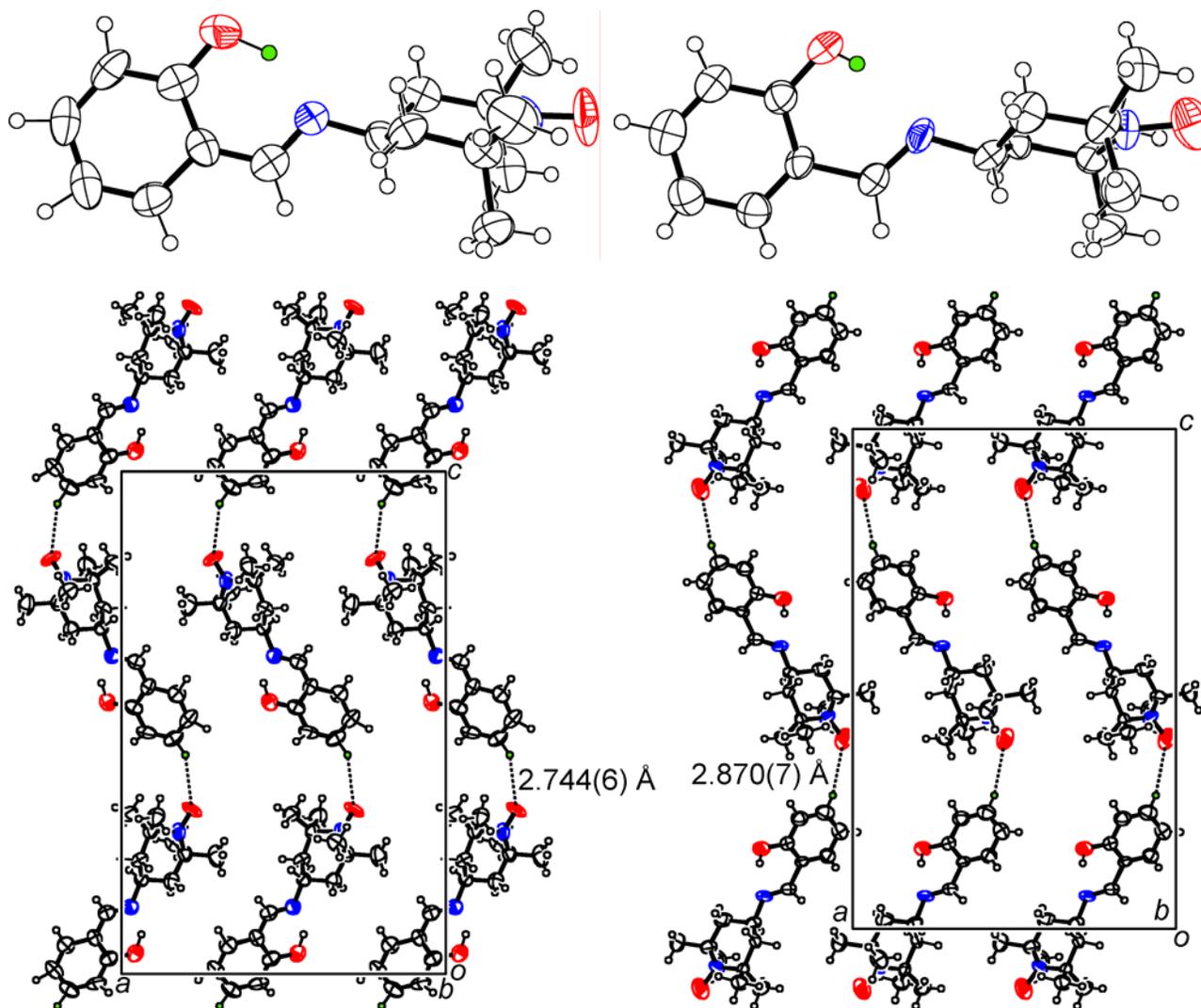
There are two crystallographically independent molecules in the crystal of **2a** (molecule A and molecule B) as shown in Figure 2 (upper). Inspection of the bond lengths in the molecules about the four bonds concerning the salicylideneamine moieties (see the chart above and Table 2) indicates that the molecule A has some tendency towards the NH form whilst the predominance of the OH form is suggested in the molecule B, taking the difference of their bond alternations into consideration [5]. The molecules of molecule A are found to form sheet-like structures on the *ac*-plane and the similar sheet-like structures formed on the *ac*-plane by the molecules of molecule B are stacked along the *b*-axis to form an alternated columnar structure of sheets along the *b*-axis (Figure 2, lower).

Table 2. Selected bond lengths in the molecules of **2a**, **2b** and **5**

bond ¹	2a	2b	5
a	1.344(6) ² 1.359(5) ³	1.355(4)	1.341(4)
b	1.419(7) ² 1.391(6) ³	1.385(4)	1.404(5)
c	1.423(8) ² 1.488(7) ³	1.465(5)	1.440(5)
d	1.240(6) ² 1.293(6) ³	1.259(4)	1.279(4)

¹see the chart for the bond assignments; ²data for the molecule A; ³ data for the molecule B.

Figure 2. Upper: molecular structures of **2a** (left: molecule A, right: molecule B). Lower: sheet-like structures in the crystal structure of **2a** (left: a sheet from molecules A, right: a sheet from molecules B).

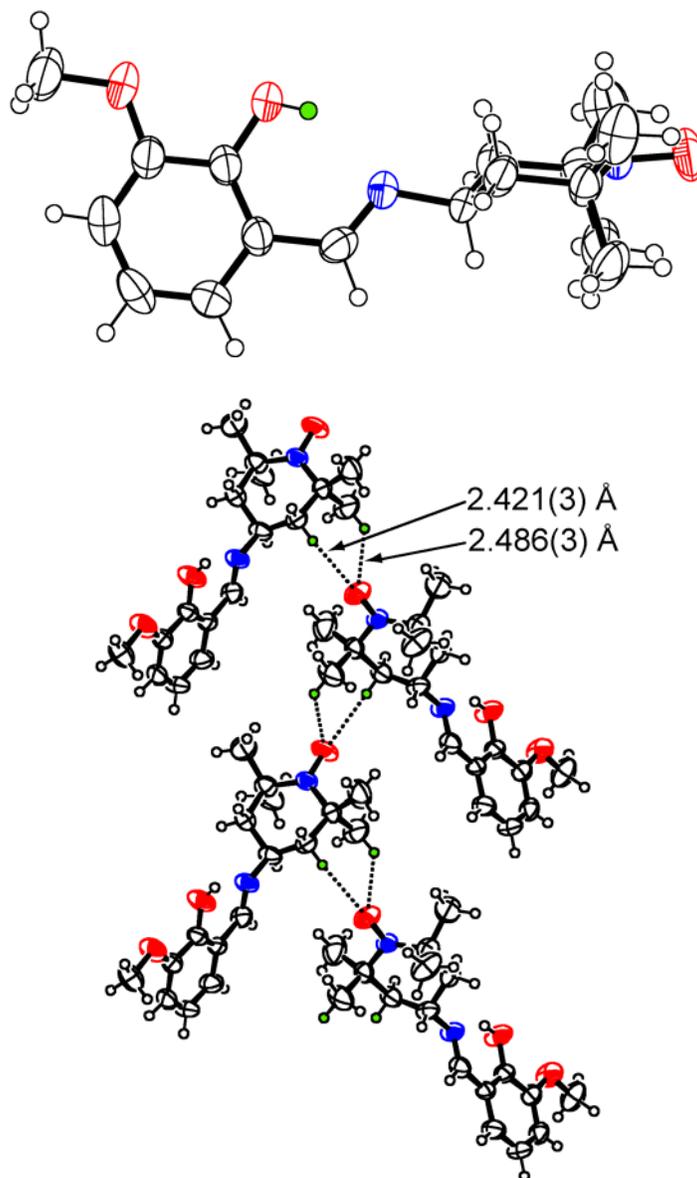


The nearest oxygen-oxygen distance of the spin centers amounts to 5.50 Å and is observed between a molecule of A and a molecule of B in the neighboring sheet along the *b*-axis, which appears to be well separated to afford sufficient intermolecular magnetic interactions and, although it is difficult to assign the origin of the magnetic interactions exactly, the antiferromagnetic intermolecular interactions of this radical might be due to the spatial arrangements of the aryl groups within each sheet [6].

The short contacts between the oxygen atoms of the spin centers and the *p*-hydrogen atoms on the benzene rings of the neighboring molecules are shown in dotted lines in Figure 2 (lower) and that are assumed to be one of the possible origins for the antiferromagnetic interactions observed in this radical.

It is apparent from the bond lengths in Table 2 that the molecular structure of the radical **2b** has predominantly OH form and the mean plane of the six-membered ring of TEMPO moiety is oriented almost perpendicular from that of the benzene ring (Figure 3, upper).

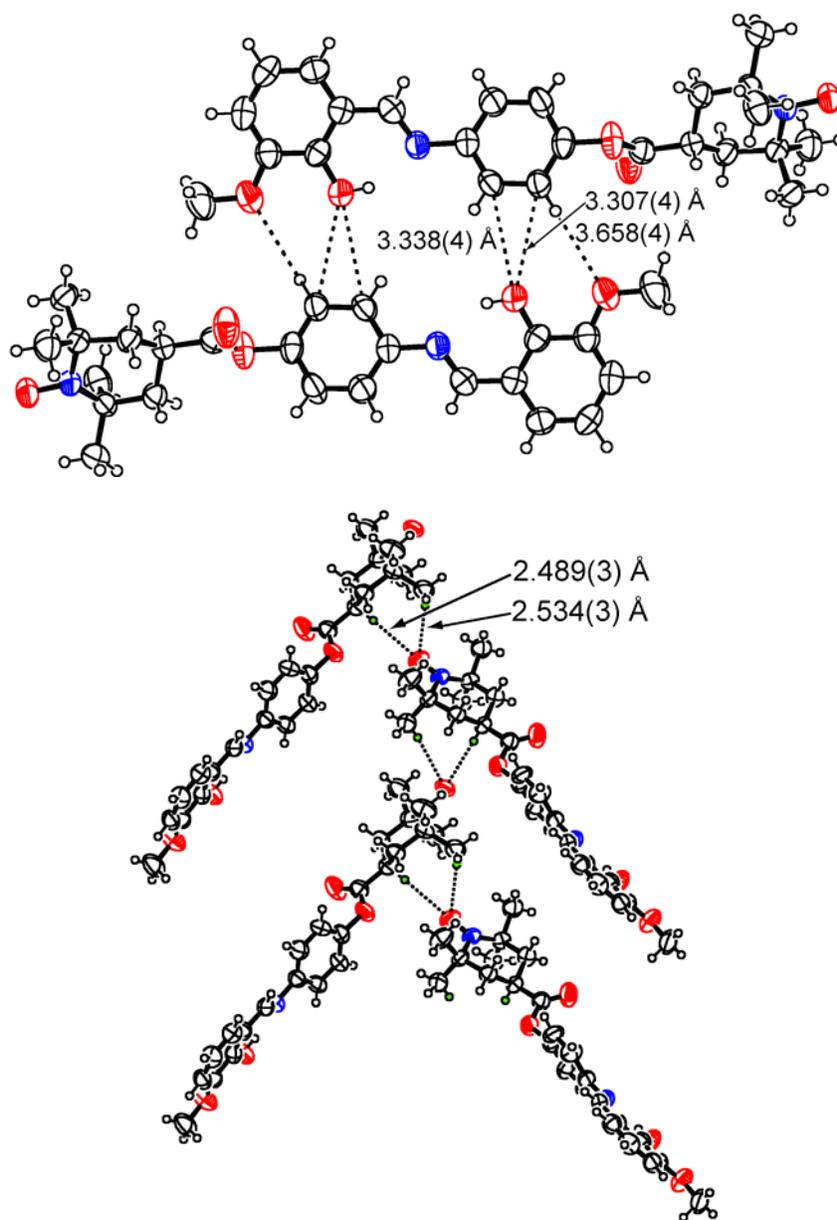
Figure 3. Molecular (upper) and crystal structure (lower) of **2b**.



The crystal structure of the radical **2b** is shown in the lower side of Figure 3, in which ferromagnetic intermolecular interactions were uniquely observed within the radicals prepared in this work. There exist a couple of short contacts (3.29 Å and 3.31 Å) between the oxygen atom of the aminoxyl moiety in a molecule and one of the methyl as well as one of the methylene carbon atoms in the neighboring molecule and a closer look indicates the existence of the short contacts between the oxygen atom and the

β -hydrogen atoms on the methyl as well as the methylene group of the neighboring molecule, amounting to 2.49 Å and 2.42 Å, respectively. The ferromagnetic interactions observed in this radical crystal may be understood on the basis of the spin polarization effect through the hydrogen bonds between the spin centers and the β -hydrogen atoms [4].

Figure 4. Molecular structures of **5** (two molecules are depicted) with indication of the short contacts found between the molecules (upper) and the crystal structure of **5** (lower).



From the bond length data in Table 2 the molecular structure of the radical **5** is also thought to correspond to that of the OH form and the corresponding structure is shown in Figure 4 (upper). It is of

some interest from the viewpoint of crystal structure formation that there are several side-by-side interactions between the molecules through the oxygen atoms of a molecule and the hydrogen atoms and/or the carbon atoms of the neighboring molecule to form such a side-by-side structure as depicted in Figure 4 (upper). It is anticipated at the same time that the intramolecular hydrogen bonds are surpassing the intermolecular ones around the salicylidene aniline moieties. In the radical crystal, short contacts are found between the oxygen atoms of the spin centers and the β -hydrogen atoms of one of the methyl groups and the γ -hydrogen atoms on the methine carbon atoms in the neighboring molecules to form one-dimensional zigzag chains (Figure 4, lower). The antiferromagnetic interactions observed in this radical suggest that the magnetic interactions are controlled mainly by the spin-spin interactions through the hydrogen bond found between the oxygen atom of a spin center and the γ -hydrogen atom on the methine carbon atom in the neighboring molecule.

Insofar as we have determined in our preliminary investigations, no distinct photochromic properties of these three radicals could be discerned upon irradiation with ultraviolet light, nor was any apparent thermochromic behaviour detected for the radicals **2a** and **2b**. On the other hand, an appreciable color change was observed for the crystals of **5**, *i.e.*, the original brownish yellow color of the crystals turned first to deep orange when they were heated over 160°C, then gradually to deep red up to 168°C, and finally they melted. The behavior suggests the existence of thermochromic properties in the radical compound and according a study on the magnetic properties of the radical with heating is now under way.

Conclusions

Three kinds of *N*-salicylideneamine/aniline derivatives with TEMPO substituents, *i. e.*, **2a**, **2b**, and **5**, were prepared and their structure/magnetic property relationships were investigated. Two crystallographically independent molecules were found to exist in the crystal of the radical **2a**, forming sheet-like structures and the antiferromagnetic interactions observed in the radical are supposed to be due to the spatial arrangements of the aryl groups built in this radical. Based on the crystal structure of the radical **2b**, the ferromagnetic interactions observed in the radical are understandable considering the spin polarization effect through the hydrogen bonds between the spin centers and the β -hydrogen atoms on a methyl and a methylene group of the neighboring molecule. The hydrogen bond formed in the radical **5** between the oxygen atom of a spin center and the γ -hydrogen atom on the methine carbon atom in the neighboring molecule could afford the antiferromagnetic interactions in the radical. Preliminary examination of their photo- and heat-responsive properties revealed that the radical **5** could exhibit some thermochromic property when heated over 160°C.

Acknowledgements

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Experimental

General

4-amino-TEMPO and 4-carboxy-TEMPO are commercially available (Tokyo Kasei Kogyo Co.) and were used without further purification. Melting points were measured on a YAMATO MP-21 apparatus and were uncorrected. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. ESR spectra were obtained on a JEOL JES-FE3XG spectrometer and each g-value was determined using Mn^{2+}/MgO maker as internal standard. Magnetic susceptibility measurements were carried out on a QUNTUM DESIGN MPMS-5 SQUID susceptometer using *ca.* 10 mg for each powdered sample in the usual way [7]. X-ray diffraction data were recorded using a Quantum CCD area detector on a Rigaku AFC-7R diffractometer at room temperature. CCDC deposition numbers 236979 – 236981 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Preparation of TEMPO-substituted salicylideneimine derivatives **2a** and **2b**.

The typical procedure, exemplified for **2b**, is as follows: a stirred solution of 3-methoxysalicylaldehyde (**1b**, 0.18 g, 1.2 mmol) and 4-amino-TEMPO (0.20 g, 1.2 mmol) in toluene (30 mL) was heated to reflux and heating was continued for 3 h. The resulting reaction mixture was cooled and concentrated to give a precipitate, which was filtrated and recrystallized from 1:1 diethylether-dichloromethane to give orange yellow crystals of **2b** (0.24 g, 67%). M.p. 148-150°C; EPR (benzene): triplet, $g=2.006$, $a=1.60$ mT; FAB-HRMS calcd for $C_{17}H_{26}N_2O_3$ (M+1) 306.1943, found m/z 306.1968. In the similar manner, **2a** was prepared in 75% yield and its data are as follows: m.p. 155°C; EPR (benzene): triplet, $g=2.007$, $a=1.55$ mT; FAB-HRMS calcd for $C_{16}H_{24}N_2O_2$ (M+1) 276.1838, found m/z 276.1792.

Preparation of TEMPO-substituted salicylideneaniline derivative **5**.

To a stirred solution of 3-methoxysalicylaldehyde (**1b**) (0.18 g, 1.2 mmol) in dichloromethane (10 mL) was added at ambient temperature *tert*-butyldimethylsilyl chloride (2.4 g, 5.1 mmol), followed by triethylamine (0.33 g, 5.6 mmol) and DMAP (0.04 g) and the reaction mixture was then stirred for 48 h at the same temperature. The reaction mixture was treated successively with aqueous sodium bicarbonate and aqueous ammonium chloride solutions and the separated organic layer was dried over anhydrous magnesium sulfate to give **3** as yellowish solid (0.65 g, 52%). The formation of this compound was checked by MS [m/z 267 (M+1)] and it was used for the next reaction without further purification. The protected benzaldehyde derivative **3** (0.10 g, 0.40 mmol) was mixed with *p*-aminophenol (0.043 g, 0.40 mmol) in toluene (10 mL), the mixture was heated to reflux and the heating was continued for 1 day. The

reaction mixture was then concentrated and purified by column chromatography on silica gel using benzene and diethylether as eluents to give the Schiff base **4** (0.13 g, 88%) as a yellow viscous oil, which could not be crystallized and its formation was confirmed by MS data [m/z 358 (M+1)]. The Schiff base **4** (0.13 g, 0.35 mmol) was then reacted with 4-carboxy-TEMPO (0.070 g, 0.35 mmol) together with DCC (0.080 g, 0.42 mmol) and DMAP (0.050 g, 0.42 mmol) in dichloromethane (20 mL) and the reaction mixture was stirred at ambient temperature for 6 days. The resulting mixture was filtered to remove white powdery solid and then concentrated under reduced pressure to give a dark brown oily material, which gave a brownish powdery solid when triturated with small amount of diethylether. The resulting solid was recrystallized from methanol and a small amount of dichloromethane to give brownish yellow plates (0.056 g, 38%). M.p. ca. 168°C (see text); EPR (benzene): triplet, $g=2.007$, $a=1.55$ mT; FAB-HRMS calcd for $C_{24}H_{30}N_2O_5$ (M+1) 426.2155, found m/z 426.2183.

References and Notes

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Sample availability: Samples of compounds **2a**, **2b** and **5** are available from the authors.