#### **RESEARCH ARTICLE**



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### Influences of polarizability effect of alkyl group and homoring competition effect of substituents on the NMR spectra of salen-type Schiff base

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#### Abstract

Salen-type Schiff bases are a kind of important compounds and are widely used. In order to explore the effect of alkyl groups and substituents attached to aromatic ring on the chemical shifts, 63 title compounds were synthesized. Their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained; and the effects of the alkyl chain length and substituents on the chemical shifts ( $\delta_{\rm H}$ (CH=N),  $\delta_{\rm C}$ (CH=N),  $\delta_{\rm H}({\rm OH})$ , and  $\delta_{\rm C}({\rm C-OH})$ ) were studied. The results show that (1) the alkyl polarizability effect index (PEI) has an important influence on the chemical shifts of the above four atoms, with the increase of PEI, the values of  $\delta_{\rm H}$ (CH=N) and  $\delta_{\rm C}$ (CH=N) decrease, and the values of  $\delta_{\rm H}$ (OH) and  $\delta_{\rm C}$ (C–OH) increase. (2) The influence of substituent X attached to aromatic ring on the chemical shift is related to its position by taking OH or CH=N as reference. As for the effect of substituent on the chemical shifts, the effect of Hammett constant  $\sigma(X)_{-OH}$  and excited-state substituent parameter  $\sigma_{CC}^{ex}(X)_{-OH}$  with OH as reference are different from that  $of\sigma(X)_{-CH=N}$  and  $\sigma_{CC}^{ex}(X)_{-CH=N}$  with CH=N as reference, and there is a "homoring competition effect" of the substituent. (3) The effect of the cross-interaction between X and OH on the chemical shift is also significantly different due to the different position of X. Quantitative correlation equations against chemical shifts were built for the four atoms, and the stability and prediction ability of the obtained equations were confirmed by leave-one-out cross validation.

#### **KEYWORDS**

alkyl polarizability effect, homoring competition effect, NMR chemical shift, salen-type Schiff base, substituent effect

### **1** | INTRODUCTION

Salen-type Schiff bases refers to a class of compounds containing carbon-nitrogen double bond (C=N), condensated by salicylaldehyde derivative with diamine. Because the molecular central position contains four coordination atoms of O, N, N, and O, which can be used as a good ligand for certain metals, they were widely

applied to materials,<sup>[1,2]</sup> catalysis,<sup>[3–7]</sup> biomedicine,<sup>[8–10]</sup> and other fields.<sup>[11,12]</sup> For example, Zhang et al.<sup>[1]</sup> provided a comprehensive introduction for many salen-type Schiff bases metal complexes, to be used as soluble conjugated materials, as converters for light/electricity signals in organic light-emitting diodes and dye-sensitized solar cells, energy storage, and potential conductive thermoelectric materials. He pointed out that metal Schiff base

<sup>2</sup> WILEY-

chemistry can and will make important contribution to the global energy problem. Cozzi<sup>[5]</sup> pointed out that Schiff base ligands are able to coordinate many different metals, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Mahapatra et al.<sup>[6]</sup> synthesized a kind of salen-type Schiff base and its complex containing mononuclear copper, prepared two kinds of new trinuclear complexes, and investigated their catalytic activities, then proposed firstly the mechanisms of these biomimetic oxidase reactions involving any heterometallic catalyst. Damercheli et al.<sup>[8]</sup> indicated that it is possible to use bioactive salen-type Schiff bases transition metal complexes as anticancer agents. The work of Onami et al.<sup>[9]</sup> showed that the salen-type Schiff bases metal complexes can increase the degradation of protein.

In addition to metal ions and coordination modes, the structure and properties of ligands also have an important influence on the properties and applications of the complexes. Abu-Surrah et al.<sup>[13]</sup> synthesized a series of salen-type Schiff bases with different substituents and obtained some complexes with metals Fe(III) and Co(III). He further studied the catalytic activities of the obtained complexes. The obtained results showed that the iron(III) complexes catalysts bearing electron-withdrawing substituents on the salen ligands showed the highest catalytic activity under similar reaction conditions. Rao et al.<sup>[14]</sup> synthesized four Schiff bases which differ in the chain lengths of the substituents and their Pd(II) complexes, investigated the catalytic activity in Suzuki-Miyaura reaction, and found that the catalytic activity is related to the alkyl chain length of substituents. Gupta et al.<sup>[15]</sup> studied the effect of diamines with different chain lengths (carbon atom number n = 2, 3, 4) on the formation of complexes with salen-type Schiff bases and Co(III) and observed that the nature of the final product is sensitive to small changes in the length of the spacer in the initial diamine. Nathan et al.<sup>[16]</sup> designed and synthesized a series of salen-type Schiff bases with different diamine chain lengths and studied their coordination with copper. It was found that the coordination modes of salen-type Schiff bases with different diamine chain lengths were different. It can be seen that the substituent and the chain length of the diamine play an important role for the properties of salen-type Schiff bases.

Theoretically, the coordination ability of salen-type Schiff bases with metals depends on the charge density on the N and O atoms in the molecule. For a series of compounds with similar parent structures, the chemical shifts are an effective method to express the relative density of charges on the atoms of interest. A lot of salentype Schiff bases and their complexes have been investigated by researchers by changing substituent and chain length, but there is a lack of systematic study on the effect of substituent and carbon chain length on the charge density distribution of these Schiff bases, especially on the quantitative correlation analysis of NMR spectra. Studies of Cao et al.<sup>[17-19]</sup> showed that the electronic effect of substituents had an important effect on the NMR spectra of single Schiff bases and showed a good quantitative relationship. However, the effect of substituent on the NMR chemical shift of salen-type Schiff bases and the influence of diamine chain length on the NMR chemical shift of salen-type Schiff bases are still unclear. Therefore, a series of salen-type Schiff bases with different diamine chain length (carbon atom number n = 2-8) were designed and synthesized in this study. The change regularity of NMR chemical shifts was discussed in terms of both the electronic effect of substituents and the change of alkyl chain length, which may provide a reference for understanding the charge distribution of salen-type Schiff bases.

### 2 | EXPERIMENTAL METHODS

#### 2.1 | Materials synthesis

Sixty-three samples of diamine-salicylaldehyde condensates (abbreviated as  $C_n$ -X) were synthesized according to You et al.<sup>[20]</sup> The ethanol solution (50 ml) of diamine compound  $H_2N(CH_2)_nNH_2$  (n = 2-8) (1.0 mmol) was slowly added into the ethanol solution (50 ml) of substituted salicylaldehyde (2.0 mmol). The mixture was stirred for 30 min at room temperature, and yellow precipitate appeared. Some of the solvent was evaporated and cooled until there was a great deal of the yellow precipitate. After filtering and recrystallizing with ethanol, the target products were obtained with yield of 90% to 95%. After vacuum drying, their molecular structures were confirmed. The synthetic route is as shown in Figure 1.

#### 2.2 | Spectroscopic measurement

Using CDCl<sub>3</sub> as solvent, NMR spectra of the target compound were recorded at 298 K by using a Bruker AV 500-MHz spectrometer and measured relative to the signals for residual chloroform (7.26 ppm for <sup>1</sup>H and 77.00 ppm for <sup>13</sup>C) in the deuterated solvent. And the chemical shifts were referenced to TMS (0.00 ppm). The acquisition parameters for the <sup>1</sup>H NMR were pulse sequence, zg30; spectral width, 13,020 Hz; number of scans, eight; and acquisition time, 1.50 s. The acquisition parameters for the <sup>13</sup>C NMR were pulse sequence, **FIGURE 1** Synthesis route of target compound C<sub>n</sub>-X

zgpg30; spectral width, 29,762 Hz; number of scans, 20-200; and acquisition time, 1.10 s. Data were processed by using Bruker's TOPSPIN-NMR software version 2.1 (Bruker, Germany). A total of 63 samples were characterized with <sup>1</sup>H and <sup>13</sup>C NMR. The chemical shift value of the hydrogen atom on the CH-N is expressed as  $\delta_{\rm H}$ (CH=N), and that of the carbon atom on the CH=N is expressed as  $\delta_{\rm C}$  (CH=N); the chemical shift value of the hydrogen atom of hydroxyl group (OH) connected to the benzene ring is expressed as  $\delta_{\rm H}({\rm OH})$ , and the chemical shift value of the carbon atom connected to the OH is expressed as  $\delta_{\rm C}$  (C–OH). The obtained chemical shift values of hydrogen atoms and carbon atoms are listed in Table 1. Additionally, mass spectra of some new compounds were performed with a Waters Xevo Q-TOF-electronic spray ion mass spectrometer. The NMR and mass spectra were presented in the Supporting Information.

### 2.3 | Parameters introduction

### 2.3.1 | Alkyl PEI

The alkyl polarizability effect index (*PEI*) was proposed by Cao and Li,<sup>[21]</sup> to quantify the relative magnitude of the polarizability effect of alkyl groups, and was extensively applied.<sup>[25–27]</sup> The *PEI* used in this paper was directly calculated by the method reported in Cao and Li,<sup>[21]</sup> listed in Table 1.

### 2.3.2 | Hammett parameter ( $\sigma$ )

Hammett parameter  $(\sigma)^{[22]}$  is a well-known substituent parameter characterizing the ground-state electronic effect, which has been extensively applied to the quantitative structure–property relationship (QSPR) studies.<sup>[18,22,28,29]</sup> The value of the Hammett constant of a substituent is related to its position on the aromatic ring. If a group is in *ortho* (*o*)-, *meta* (*m*)-, or *para* (*p*)-position, its Hammett constant is, expressed by  $\sigma_0$ ,  $\sigma_m$ , and  $\sigma_p$ , respectively. The molecular structure of the target compound, affected by the intramolecular hydrogen bonding, the benzene ring with substituent X, C=N bond and OH group can form a six-membered quasi-ring containing atoms HOCCCN, which has some aromaticity.<sup>[30-32]</sup> In this quasi-ring, there are lone pairs of electrons on atom of O and N. The electron transfer direction is shown in Figure 2. If the hydroxyl group OH is used as reference and X is at C-5 (Figure 2), it is in *para*-position to OH; and when it is at C-4, it is in *meta*-position to OH. However, if the reference is CH=N, X is at C-5 (Figure 2), it is in the *meta*-position to CH=N; and when it is at C-4, it is in the *meta*-position to CH=N; and when it is at C-4, it is in the *para*-position to CH=N. Therefore, we use both OH and CH=N as reference for locating X group. The Hammett constants values of the substituents X with about two locating methods are expressed as  $\sigma(X)_{-OH}$  and  $\sigma(X)_{-CH=N}$ , listed in Table 1.

# 2.3.3 | Excited-state substituent parameters ( $\sigma_{CC}^{ex}$ )

Excited-state substituent parameter ( $\sigma_{CC}^{ex}$ ) was proposed by Cao et al.<sup>[23]</sup> and is a molecular descriptor characterizing the stability of the excited state. It was extensively applied to the QSPR studies<sup>[29,33–35]</sup> and plays an important role in the study of the chemical shifts.<sup>[33,36,37]</sup> We use both OH and CH=N as reference and express the  $\sigma_{CC}^{ex}$ of the substituent X as  $\sigma_{CC}^{ex}(X)_{OH}$  and  $\sigma_{CC}^{ex}(X)_{CH=N}$  by adopting the locating method of substituent X in Section 2.3.2, listed in Table 1.

### 2.3.4 | The cross-interaction parameter between substituents ( $\Delta \sigma^2$ )

The cross-interaction parameter between substituents  $(\Delta\sigma^2)$  is a parameter used to express the cross-interaction effect between two or more substituents in an organic molecule. In this study, the cross-interaction parameter between substituents is directly calculated by the method reported in Cao et al.<sup>[38]</sup> The cross-interaction parameter between hydroxyl group (OH) and substituent (X) has two expressions  $\Delta\sigma_p^2$  and  $\Delta\sigma_m^2$ , that is,  $\Delta\sigma_p^2 = [\sigma_p(X)_{-OH} - \sigma_p(OH)]^2$  and  $\Delta\sigma_m^2 = [\sigma_m(X)_{-OH} - \sigma_m(OH)]^2$ .



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	$\sigma^{ex}_{CC}(\mathbf{X})_{-CH=N}^{c}$	0.00	0.02	0.02	-0.03	-0.03	0.10	0.06	-0.22	-0.33	-0.17	-0.50	-1.81	0.00	0.02	0.02	-0.03	-0.03	0.10	0.06	-0.22	-0.33	-0.17	-0.50	-1.81	0.00	0.02	0.02	-0.03	-0.03	0.10
	$\sigma_{CC}^{ex}(X)_{\longrightarrow OH}{}^{c}$	00.00	0.06	-0.22	-0.33	-0.17	-0.50	0.02	0.02	-0.03	-0.03	0.10	0.17	00.00	0.06	-0.22	-0.33	-0.17	-0.50	0.02	0.02	-0.03	-0.03	0.10	0.17	00.00	0.06	-0.22	-0.33	-0.17	-0.50
	$\sigma(\mathbf{X})_{-\mathrm{CH}=\mathrm{N}}^{\mathrm{b}}$	0.00	0.34	0.37	0.39	-0.07	0.12	0.06	0.23	0.23	-0.17	-0.27	-0.83	0.00	0.34	0.37	0.39	-0.07	0.12	0.06	0.23	0.23	-0.17	-0.27	-0.83	0.00	0.34	0.37	0.39	-0.07	0.12
	$\sigma(X)_{-OH}^{b}$	0.00	0.06	0.23	0.23	-0.17	-0.27	0.34	0.37	0.39	-0.07	0.12	-0.16	0.00	0.06	0.23	0.23	-0.17	-0.27	0.34	0.37	0.39	-0.07	0.12	-0.16	0.00	0.06	0.23	0.23	-0.17	-0.27
umeters	$PEI^{a}$	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1405	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.1887	1.2122	1.2122	1.2122	1.2122	1.2122	1.2122
l substituent para	δ <sub>C</sub> (COH)	160.94	157.06	159.54	160.02	158.65	155.06	163.66	161.95	161.89	161.02	164.71	165.02	161.08	157.10	159.62	160.11	158.76	155.12	164.11	162.22	162.14	161.13	165.50	165.97	161.14	157.15	159.74	160.24	158.82	155.18
ounds C <sub>n</sub> -X and	$\delta_{\rm H}({ m OH})$	13.22	12.88	13.12	13.15	12.98	12.73	13.73	13.50	13.47	13.24	13.73	13.69	13.45	13.11	13.36	13.39	13.20	12.94	14.01	13.77	13.74	13.47	13.95	13.87	13.55	13.20	13.48	13.51	13.26	13.01
shifts of title comp	δc(CH=N)	166.45	165.51	165.40	165.31	166.39	166.21	165.66	165.76	165.91	166.09	165.36	164.68	165.42	164.40	164.32	164.24	165.37	165.12	164.57	164.65	164.79	165.02	164.28	163.54	164.87	163.88	163.81	163.73	164.85	164.58
tal NMR chemical	δ <sub>H</sub> (CH=N)	8.35	8.30	8.29	8.28	8.29	8.30	8.30	8.31	8.30	8.29	8.19	8.05	8.38	8.31	8.30	8.29	8.32	8.33	8.32	8.32	8.31	8.31	8.19	8.05	8.34	8.29	8.28	8.27	8.29	8.30
The experiment	Compounds	C <sub>2</sub> -5-H	C <sub>2</sub> -5-F	C <sub>2</sub> -5-Cl	C <sub>2</sub> -5-Br	C <sub>2</sub> -5-Me	C <sub>2</sub> -5-OMe	C <sub>2</sub> -4-F	C <sub>2</sub> -4-Cl	C <sub>2</sub> -4-Br	C <sub>2</sub> -4-Me	C <sub>2</sub> -4-OMe	C <sub>2</sub> -4-NMe <sub>2</sub>	C <sub>3</sub> -5-H	C <sub>3</sub> -5-F	C <sub>3</sub> -5-Cl	C <sub>3</sub> -5-Br	C <sub>3</sub> -5-Me	C <sub>3</sub> -5-OMe	C <sub>3</sub> -4-F	C <sub>3</sub> -4-Cl	C <sub>3</sub> -4-Br	C <sub>3</sub> -4-Me	C <sub>3</sub> -4-0Me	C <sub>3</sub> -4-NMe <sub>2</sub>	C4-5-H	C4-5-F	C <sub>4</sub> -5-Cl	C <sub>4</sub> -5-Br	C <sub>4</sub> -5-Me	C <sub>4</sub> -5-OMe
TABLE 1	No.	1	2	3	4	5	9	7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

c)—CH=N <sup>c</sup>																															
$\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathbf{X}$	0.06	-0.22	-0.33	-0.17	-0.50	-1.81	0.00	0.02	0.02	-0.03	-0.03	0.10	0.06	-0.22	-0.33	-0.17	-0.50	0.00	0.02	-0.03	-0.03	-0.22	-0.17	00.0	0.02	-0.03	-0.22	-0.17	00.0	0.02	
$\sigma_{CC}^{ex}(\mathbf{X})_{OH}^{c}$	0.02	0.02	-0.03	-0.03	0.10	0.17	0.00	0.06	-0.22	-0.33	-0.17	-0.50	0.02	0.02	-0.03	-0.03	0.10	0.00	-0.22	-0.33	-0.17	0.02	-0.03	0.00	-0.22	-0.17	0.02	-0.03	0.00	-0.22	
$\sigma(X)_{-CH=N}^{b}$	0.06	0.23	0.23	-0.17	-0.27	-0.83	0.00	0.34	0.37	0.39	-0.07	0.12	0.06	0.23	0.23	-0.17	-0.27	0.00	0.37	0.39	-0.07	0.23	-0.17	0.00	0.37	-0.07	0.23	-0.17	0.00	0.37	
σ(X)_OH <sup>b</sup>	0.34	0.37	0.39	-0.07	0.12	-0.16	0.00	0.06	0.23	0.23	-0.17	-0.27	0.34	0.37	0.39	-0.07	0.12	0.00	0.23	0.23	-0.17	0.37	-0.07	0.00	0.23	-0.17	0.37	-0.07	0.00	0.23	
$PEI^{a}$	1.2122	1.2122	1.2122	1.2122	1.2122	1.2122	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2260	1.2350	1.2350	1.2350	1.2350	1.2350	1.2350	1.2414	1.2414	1.2414	1.2414	1.2414	1.2461	1.2461	
δ <sub>c</sub> (c—0H)	164.52	162.53	162.45	161.26	166.30	166.81	161.23	157.21	159.84	160.33	158.86	155.20	164.90	162.80	162.72	161.40	166.96	161.26	159.90	160.41	158.90	162.99	161.49	161.31	159.96	158.95	163.10	161.53	161.34	159.99	
$\delta_{\rm H}({ m OH})$	14.12	13.90	13.87	13.55	14.03	13.91	13.65	13.31	13.58	13.63	13.39	13.09	14.24	14.01	13.98	13.65	14.10	13.69	13.64	13.68	13.42	14.07	13.69	13.70	13.66	13.43	14.10	13.70	13.72	13.68	
δc(CH=N)	164.06	164.14	164.27	164.50	163.71	162.90	164.66	163.66	163.59	163.49	164.61	164.34	163.84	163.91	164.05	164.30	163.44	164.54	163.45	163.36	164.51	163.79	164.20	164.46	163.36	164.43	163.70	164.12	164.42	163.30	
δ <sub>H</sub> (CH=N)	8.27	8.29	8.28	8.29	8.14	7.99	8.33	8.26	8.25	8.24	8.27	8.29	8.25	8.26	8.25	8.27	8.11	8.33	8.26	8.25	8.27	8.26	8.27	8.32	8.25	8.27	8.26	8.27	8.33	8.25	
Compounds	$C_4$ -4-F	C <sub>4</sub> -4-Cl	$C_4$ -4-Br	C <sub>4</sub> -4-Me	C <sub>4</sub> -4-OMe	$C_{4}$ -4- $NMe_{2}$	C <sub>5</sub> -5-H	C <sub>5</sub> -5-F	C <sub>5</sub> -5-Cl	C <sub>5</sub> -5-Br	C <sub>5</sub> -5-Me	C <sub>5</sub> -5-OMe	С <sub>5</sub> -4-F	C <sub>5</sub> -4-Cl	C <sub>5</sub> -4-Br	C <sub>5</sub> -4-Me	C <sub>5</sub> -4-OMe	C <sub>6</sub> -5-H	C <sub>6</sub> -5-Cl	C <sub>6</sub> -5-Br	C <sub>6</sub> -5-Me	C <sub>6</sub> -4-Cl	C <sub>6</sub> -4-Me	$C_{7}$ -5-H	C <sub>7</sub> -5-Cl	C <sub>7</sub> -5-Me	C <sub>7</sub> -4-Cl	C <sub>7</sub> -4-Me	C <sub>8</sub> -5-H	C <sub>8</sub> -5-Cl	
No.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	

WEI ET AL.

TABLE 1 (Continued)

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TABLE 1 (Continued)

No.	Compounds	δ <sub>H</sub> (CH=N)	δc(CH=N)	$\delta_{\rm H}({ m OH})$	δ <sub>C</sub> (C—OH)	$PEI^{a}$	$\sigma(X)_{-OH}^{b}$	$\sigma(X)_{-CH=N}^{b}$	$\sigma_{CC}^{ex}(X)_{\!\!-\!OH}^{c}$	$\sigma_{CC}^{ex}(X)_{-CH=N}^{c}$
61	C <sub>8</sub> -5-Me	8.27	164.39	13.45	158.96	1.2461	-0.17	-0.07	-0.17	-0.03
62	C <sub>8</sub> -4-Cl	8.26	163.65	14.13	163.19	1.2461	0.37	0.23	0.02	-0.22
63	C <sub>8</sub> -4-Me	8.27	164.07	13.73	161.56	1.2461	-0.07	-0.17	-0.03	-0.17
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<sup>a</sup>The alkyl polarizability effect index (*PEI*) was taken from Cao and Li.<sup>[21]</sup> <sup>b</sup>Hammett parameter ( $\sigma$ ) was taken from Hansch et al.<sup>[22]</sup> <sup>c</sup>The excited-state substituent parameters ( $\sigma_{CC}^{ex}$ ) were taken from Cao et al.<sup>[23]</sup> and Zhu et al.<sup>[24]</sup>

### <sup>6</sup> \_\_\_\_\_WILEY-



FIGURE 2 Electron transfer diagram of the target compounds

#### **3** | **RESULTS AND DISCUSSION**

# 3.1 | Influence of alkyl chain length on the chemical shift

It was found that the NMR chemical shifts of salentype Schiff bases with the same substituent X and different alkyl chain length are different. In order to investigate the relationship between the chemical shift and the alkyl chain length, we took  $\delta_{\rm H}(\rm OH)$  and  $\delta_{\rm C}(\rm CH=N)$  and plotted the chemical shift values of  $\delta_{\rm H}(\rm OH)$  and  $\delta_{\rm C}(\rm CH=N)$  against the chain length *n* (Figure 3).

It can be seen from Figure 3 that as the number *n* of carbon atoms in the alkyl chain changes, the chemical shift value also changes, but there is no linear relationship. The alkyl group is nonpolar, in which each C atom of  $-CH_2$ — is in sp<sup>3</sup> hybrid state and cannot transfer the conjugation effect. Under the action of the hydrogen bond O—H…N and the partial charge of the nitrogen atom, the alkyl group is polaeized, which affect the chemical shift. Therefore, we plotted the  $\delta_{\rm H}(\rm OH)$  and  $\delta_{\rm C}(\rm CH=N)$  in Figure 3 against the *PEI* of the alkyl group and obtained Figure 4.

It can be seen from Figure 4 that the chemical shifts show a good linear relationship with *PEI*. Therefore, it is preliminarily judged that the alkyl *PEI* has a direct influence on the NMR chemical shift value.

# 3.2 | The effect of substituent X on chemical shift

As shown in Table 1, compounds with alkyl chains with equal number of carbon atoms but different substituents have different chemical shift values. The type of substituent on the aromatic ring and their relative position on the aromatic ring have an important influence on the NMR chemical shift value.

### 3.3 | Quantitative correlation of the chemical shift

We used the alkyl *PEI*; the substituent electronic effect parameters  $\sigma(X)_{-OH}$ ,  $\sigma(X)_{-CH=N}$ ,  $\sigma_{CC}^{ex}(X)_{-OH}$ , and  $\sigma_{CC}^{ex}(X)_{-CH=N}$ ; and the cross-interaction parameter between substituents  $\Delta \sigma_p^2$  and  $\Delta \sigma_m^2$  as variables and performed regression analysis for  $\delta_H(CH=N)$ ,  $\delta_C(CH=N)$ ,  $\delta_H(OH)$ , and  $\delta_C(C-OH)$  values (Table 1). The obtained QSPR models are shown in Table 2. Leave-one-out cross validation is also carried out to test the stability and predictive ability for each model and its performances, marked by "cv," were also listed in Table 2. That is,  $R_{CV}$  and  $S_{CV}$  represent the correlation coefficient and standard deviation of the leave-one-out.

For  $\delta_{\rm H}(\rm CH=N)$ ,  $\delta_{\rm C}(\rm CH=N)$ ,  $\delta_{\rm H}(\rm OH)$ , and  $\delta_{\rm C}(\rm C-OH)$ discussed in this work, we established QSPR models (Table 2) by carrying out regression analysis and employing different parameters. In order to investigate the contribution of each parameter to the chemical shift, we calculated the parameter contributions to each model according to Equations 5 and 6.<sup>[27,39]</sup>  $\Psi_{\gamma}$  and  $\Psi_{\rm f}$  are the relative and fractional contributions of the parameter to the model. In Equations 5 and 6,  $m_i$  and  $\overline{X}_i$  are the regression coefficient and the average value of each parameter



FIGURE 3 Plot of the NMR chemical sift value versus the number of carbon atoms n



FIGURE 4 Plot of the NMR chemical shift value versus the alkyl polarizability effect index (PEI)

in the QSPR model, respectively, and *R* is the correlation coefficient. The physical meanings of each model will be discussed in the following sections.

$$\Psi_{\gamma}(i) = m_i \overline{X}_i$$
$$\Psi_{\rm f}(i) = \frac{R^2 |\Psi_{\gamma}(i)|}{\sum_i |\Psi_{\gamma}(i)|} \times 100\%.$$

# 3.3.1 | Influence of alkyl *PEI* and various substituent parameters on $\delta_{\rm H}$ (CH=N)

From Equation (1), we can see that  $\delta_{\rm H}(\rm CH=N)$  of the target compound have good correlations with alkyl  $PEI, \ \sigma(X)_{-OH}, \ \sigma(X)_{-CH=N}, \ \sigma_{CC}^{ex}(X)_{-OH}, \ \sigma_{CC}^{ex}(X)_{-CH=N},$  $\Delta \sigma_{\rm p}^2$ , and  $\Delta \sigma_{\rm m}^2$ , the correlation coefficient R is 0.9244, and the standard error S is 0.03 ppm. The leave-one-out cross validation gives similar result. It indicates that Equation (1) can quantitatively describe the change of  $\delta_{\rm H}$ (CH=N). Equation (1) shows that  $\delta_{\rm H}$ (CH=N) decreases as PEI increases (i.e., the alkyl chain increases). The  $\delta_{\rm H}$  (CH=N) is mainly affected by the Hammett constant  $\sigma(X)_{-OH}$  with hydroxyl (OH) as reference positioning group, and the  $\delta_{\rm H}(\rm CH=N)$  decreases as  $\sigma(\rm X)_{-\rm OH}$ increases. Different from the influence of Hammett constant, the  $\delta_{\rm H}$ (CH=N) was simultaneously affected by the excited-state substituent parameters with OH and CH=N as reference positioning group  $\sigma_{CC}^{ex}(X)_{OH}$ and  $\sigma_{CC}^{ex}(X)$ \_\_\_\_\_N, and  $\delta_{H}(CH=N)$  increases as  $\sigma_{CC}^{ex}(X)$ \_\_\_\_\_ and  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm CH=N}$  increase. The cross-interaction parameter between substituent X and OH, the  $\delta_{\rm H}$ (CH=N) was affected by  $\Delta \sigma_p^2$  and  $\Delta \sigma_m^2$ , and  $\delta_H$ (CH=N) increases as  $\Delta \sigma_p^2$  and  $\Delta \sigma_m^2$  increase. In summary, the effect of substituent X on  $\delta_{\rm H}$ (CH=N) can play a role by different ways via OH and CH=N groups, which shows the complexity of substituent effect. In order to discuss the contribution of each parameter in Equation (1) to  $\delta_{\rm H}$ (CH=N), we calculated the parameter contributions and fractional contributions to Equation (1) according to Equations 5 and 6 and listed in Table 3.

It can be seen from Table 3 that the alkyl *PEI* is the most important parameter in Equation (1) with fractional contribution of 70.10%. The second is the excited-state substituent parameters  $\sigma_{CC}^{ex}(X)$ \_<u>CH=N</u> which is located by the reference group of CH=N. By comparing the contributions of parameters  $\sigma_{CC}^{ex}(X)$ \_OH with that of  $\sigma_{CC}^{ex}(X)$ \_CH=N, as well as the contributions of parameters  $\Delta \sigma_p^2$  with that of  $\Delta \sigma_m^2$ , it can be preliminarily considered that, for the influence of X group on the  $\delta_{H}(CH=N)$ , there is a competitive effect when using OH and CH=N as reference groups.

# 3.3.2 | Influence of alkyl *PEI* and various substituent parameters on $\delta_{\rm H}$ (OH)

From Equation (2), we can see that  $\delta_{\rm H}(\rm OH)$  is mainly affected by *PEI*,  $\sigma(\rm X)_{-\rm OH}$ ,  $\sigma(\rm X)_{-\rm CH=N}$ ,  $\sigma_{\rm CC}^{\rm ex}(\rm X)_{--\rm OH}$ ,  $\sigma_{\rm CC}^{\rm ex}(\rm X)_{--\rm CH=N}$ ,  $\Delta \sigma_{\rm p}^2$ , and  $\Delta \sigma_{\rm m}^2$ . The correlation is good, the correlation coefficient *R* is 0.9931, and the standard error *S* is 0.04 ppm. The leave-one-out cross validation gives similar result. It indicates that Equation (2) can quantitatively describe the  $\delta_{\rm H}(\rm CH=N)$  change. The  $\delta_{\rm H}(\rm CH=N)$  increases as *PEI* increases, the  $\delta_{\rm H}(\rm OH)$  is simultaneously affected by  $\sigma(\rm X)_{-\rm OH}$  and  $\sigma(\rm X)_{-\rm CH=N}$ , but the effect of the two parameters on  $\delta_{\rm H}(\rm OH)$  are just opposite. The  $\delta_{\rm H}(\rm OH)$  is affected by both  $\sigma_{\rm CC}^{\rm ex}(\rm X)_{--\rm OH}$  and  $\sigma_{\rm CC}^{\rm ex}(\rm X)_{--\rm CH=N}$ , and the effects of the two parameters on  $\delta_{\rm H}(\rm OH)$  are also opposite. The  $\delta_{\rm H}(\rm CH=N)$  is affected by

NMR chemical shift	Quantitative equation				Equation No.
δH(CH=N)	$\delta_{H(CH=N)} = 8.75 - 0.38PEI - 0.13\sigma(X)_{OH} +$	$0.09\sigma^{ex}_{CC}(X)_{-OH} + 0.22\sigma^{ex}_{CC}(X)_{-CH=h}$	$_{N}$ + 0.13 $\Delta\sigma_{p}^{2}$ + 1.37 $\Delta\sigma_{m}^{2}$		(1)
	R = 0.9244	S = 0.03	F = 54.78	N = 63	
	$R_{ m CV}=0.8975$	$S_{\rm CV} = 0.03$			
δc(cH=N)	$\delta_{H(OH)} = 7.55 + 4.97 \text{PEI} + 1.93 \sigma(X)_{OH} - 1.$	$22\sigma(X)_{-CH=N}-0.19\sigma_{CC}^{ex}(X)_{-OH}+0.$	$10\sigma_{CC}^{ex}(X)_{-CH=N} - 0.23\Delta\sigma_{p}^{2} - 1.24_{L}$	$\Delta \sigma_m^2$	(2)
	R = 0.9931	S = 0.04	F = 563.85	N = 63	
	$R_{ m CV}=0.9904$	$S_{\rm CV} = 0.05$			
δ <sub>C</sub> (cH=N)	$\delta_{\rm C(CH=N)} = 188.35 - 19.63PEI - 1.03\sigma(X)_{\rm OH}$	$-0.93\sigma(X)_{-CH=N} + 1.62\sigma_{CC}^{ex}(X)_{-CH=N}$	$=_{\rm N} + 8.07 \Delta \sigma_{\rm m}^2$		(3)
	R = 0.9447	S = 0.28	F = 94.66	N = 63	
	$R_{ m CV}=0.9284$	$S_{\rm CV} = 0.30$			
$\delta_{C(C-OH)}$	$\delta_{C(C-OH)} = 151.17 + 8.03PEI + 16.61\sigma(X)_{-OH}$	$_{ m H}$ - 13.09 $\sigma({\rm X})_{ m CH=N}$ - 0.84 $\sigma_{ m CC}^{ m ex}({\rm X})_{ m OH}$	$_{ m I}$ + 0.57 $\sigma^{ m ex}_{ m CC}({\rm X})_{ m CH=N}$ – 21.67 $\Delta\sigma^2_{ m m}$		(4)
	R = 0.9926	S = 0.36	F = 623.35	N = 63	
	$R_{\rm CV} = 0.9895$	$S_{\rm CV} = 0.40$			

**TABLE 2** The quantitative equation of NMR chemical shift

Parameters	PEI	$\sigma(X)_{-OH}$	$\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathbf{X})_{\mathrm{OH}}$	$\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm -CH==N}$	$\Delta \sigma_{ m p}^2$	$\Delta \sigma_{ m m}^2$	<b>TABLE 3</b> The relative and fractional contributions of parameters
$\Psi_{\gamma}$	-0.4633	-0.0121	0.0073	0.0386	0.0128	0.0307	in Equation (1)
$\Psi_{\rm f}$ (%)	70.10	1.82	1.10	5.84	1.94	4.65	

**TABLE 4** The relative and fractional contributions of parameters in Equation (2)

Parameters	PEI	$\sigma(X)_{-OH}$	$\sigma(X)_{-CH = N}$	$\sigma^{\rm ex}_{\rm CC}({\rm X})_{\rm {}OH}$	$\sigma^{ex}_{CC}(X)_{-CH=N}$	$\Delta \sigma_{ m p}^2$	$\Delta \sigma_{ m m}^2$
$\Psi_{\gamma}$	5.9800	0.1765	-0.0757	0.0161	-0.0176	-0.0235	-0.0277
$\Psi_{\rm f}$ (%)	93.36	2.76	1.18	0.25	0.27	0.37	0.43

 $\Delta \sigma_{\rm p}^2$  and  $\Delta \sigma_{\rm m}^2$  and decreases as  $\Delta \sigma_{\rm p}^2$  and  $\Delta \sigma_{\rm m}^2$  increase. The parameter contributions and fractional contributions of Equation (2) were listed in Table 4.

10

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Table 4 shows that the alkyl *PEI* contributes 93.36% to  $\delta_{\rm H}({\rm OH})$ , which is the main contribution. The second contribution is  $\sigma({\rm X})_{-{\rm OH}}$ . By comparing the contributions of parameters  $\sigma({\rm X})_{-{\rm OH}}$  with that of  $\sigma({\rm X})_{-{\rm CH}={\rm N}}$ , we can see that, for the influence of substituent X on the  $\delta_{\rm H}({\rm CH}={\rm N})$ , there is also a competitive effect between the  $\sigma({\rm X})_{-{\rm OH}}$  and  $\sigma({\rm X})_{-{\rm CH}={\rm N}}$ .

### 3.3.3 | Influence of alkyl *PEI* and various substituent parameters on $\delta_{\rm C}$ (CH=N)

The result of Equation (3) shows that  $\delta_{\rm C}(\rm CH=N)$  of the compound is mainly affected by *PEI*,  $\sigma(X)_{-OH}$ ,  $\sigma(X)_{-CH=N}$ ,  $\sigma_{CC}^{ex}(X)_{-CH=N}$ , and  $\Delta \sigma_{m}^{2}$ . The correlation is good, the correlation coefficient R is 0.9447, and the standard error S is 0.28 ppm. The leave-one-out cross validation gives similar result. It indicates that Equation (3) can quantitatively describe the change of  $\delta_{\rm C}$  (CH=N). From Equation (3), it can be seen that  $\delta_{\rm C}(\rm CH=N)$  decreases as *PEI* increases. The  $\delta_{\rm C}(\rm CH=N)$  is affected not only by  $\sigma(X)_{-OH}$  but also by  $\sigma(X)_{-CH=N}$ , which is negatively correlated with  $\sigma(X)_{-OH}$  and  $\sigma(X)_{-CH=N}$ . The  $\delta_{C}(CH=N)$  is only affected by  $\sigma_{CC}^{ex}(X)$ —<sub>CH=N</sub>, whereas the influence of  $\sigma_{CC}^{ex}(X)_{OH}$  on the  $\delta_{C}(CH=N)$  can be ignored. When  $\sigma_{CC}^{ex}(X)_{CH=N}$  increases,  $\delta_{C}(CH=N)$  also increases. The  $\delta_{\rm C}({\rm CH}\!\!=\!\!{\rm N})$  is mainly affected by  $\Delta\sigma_{\rm m}^2$  and increases as  $\Delta\sigma_{\mathrm{m}}^2$  increases. The parameter contributions and fractional contributions of Equation (3) were listed in Table 5.

It can be seen from Table 5 that the alkyl *PEI* is the most important parameter in Equation (3) with the fractional contribution of 86.99%. For the influence of the substituent on the  $\delta_{\rm C}$ (CH=N), there is also a competitive effect between  $\sigma$ (X)<sub>-OH</sub> and  $\sigma$ (X)<sub>-CH=N</sub> (Table 5).

# 3.3.4 | Influence of alkyl *PEI* and various substituent parameters on $\delta_{\rm C}$ (C–OH)

It can be seen from Equation (4) that  $\delta_{\rm C}({\rm C-OH})$  of the compound is mainly affected by *PEI*,  $\sigma(X)_{-OH}$ ,  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm OH}$ ,  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm CH=N}$ , and  $\Delta \sigma_{\rm m}^2$  $\sigma(X)_{-CH=N},$ together. The correlation is good, the correlation coefficient R is 0.9926, and the standard error S is 0.36 ppm. The leave-one-out cross validation gives similar result. This indicates that Equation (4) can quantitatively describe the change of  $\delta_{\rm C}$ (C–OH). The  $\delta_{\rm C}$ (C–OH) increases as *PEI* increases. The  $\delta_{\rm C}$ (C–OH) is affected not only by  $\sigma(X)_{-OH}$  but also by  $\sigma(X)_{-CH=N}$ , and the effects of the two parameters on  $\delta_{\rm C}({\rm C-OH})$  are just opposite. The  $\delta_{\rm C}$ (C–OH) is simultaneously affected by  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm OH}$  and  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm CH=N}$ , the effects of the two parameters are also opposite. For the cross-interaction between substituents, the  $\delta_{\rm C}({\rm C=OH})$  is mainly affected by  $\Delta \sigma_{\rm m}^2$ . The parameter contributions and fractional contributions of Equation (4) were listed in Table 6.

From Table 6, it can be seen that the alkyl *PEI* is the most important parameter in Equation (4) with fractional contribution of 75.30%, and the second is  $\sigma(X)_{-OH}$ , with fractional contribution of 11.81%. Comparing the contributions of  $\sigma(X)_{-OH}$  versus  $\sigma(X)_{-CH=N}$  and  $\sigma_{CC}^{ex}(X)_{-OH}$  versus  $\sigma_{CC}^{ex}(X)_{-CH=N}$  to  $\delta_{C}(C-OH)$ , it can also be

Parameters	PEI	$\sigma(X)_{-OH}$	$\sigma(X)_{-CH = N}$	$\sigma^{\rm ex}_{\rm CC}({\rm X})_{\rm -\!-\!CH\!=\!-\!N}$	$\Delta \sigma_{ m m}^2$
$\Psi_{\gamma}$	-23.6295	-0.0943	-0.0576	-0.2818	0.1807
$\Psi_{\rm f}$ (%)	86.99	0.35	0.21	1.04	0.67

**TABLE 5** The relative and fractional contributions of parameters in Equation (3)

Parameters	PEI	$\sigma(X)_{-OH}$	$\sigma(X)_{-CH = N}$	$\sigma^{\mathrm{ex}}_{\mathrm{CC}}(\mathbf{X})_{\mathrm{OH}}$	$\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm {\rm CH}=-{\rm N}}$	$\Delta \sigma_{ m m}^2$
$\Psi_{\gamma}$	9.6693	1.5160	-0.8105	0.0713	-0.0987	-0.4851
$\Psi_{\rm f}$ (%)	75.30	11.81	6.31	0.56	0.77	3.78



**FIGURE 5** Plot of the calculated chemical shifts versus the experimental ones of target compound. (a) The  $\delta_{H}(CH=N)$  ( $\triangle$ ) and  $\delta_{H}(OH)$  ( $\square$ ) of the hydrogen atoms and (b) the  $\delta_{C}(CH=N)$  ( $\circ$ ) and  $\delta_{C}(C-OH)$  ( $\Rightarrow$ ) of the carbon atom

concluded that for the influence of substituent on  $\delta_{\rm C}({\rm C-OH})$ , there are competitive effects among the  $\sigma({\rm X})_{\rm -OH}$  versus  $\sigma({\rm X})_{\rm -CH=N}$  and  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm -OH}$  versus  $\sigma_{\rm CC}^{\rm ex}({\rm X})_{\rm -CH=N}$ .

Through the analysis of the above four regression equations, it can be found that the influence of the substituents on the chemical shift values of the four atoms of the target compound in this work is different, but they have one thing in common. That is, if X group is located with OH or CH-N as reference, it shows different electronic effect and different influence intensity on the chemical shifts, and there appears a competitive effect. The above results show that in conjugated organic molecules with multiple substituents in the same aromatic ring, if the position of a substituent on the aromatic ring can be designated with two ways, such as to designate as para- or meta-position, the electronic effect of the substituent can show the electronic effect of para-substituent and meta-substituent. The intensities of the two electronic effects are different, and there is competition with each other. We name this phenomenon as "homoring competition effect."

In order to further exhibit the relationship between the calculated chemical shifts and the experimental ones, we plotted the calculated values against the experimental ones for the  $\delta_{\rm H}(\rm CH=N)$ ,  $\delta_{\rm C}(\rm CH=N)$ ,  $\delta_{\rm H}(\rm OH)$ , and  $\delta_{\rm C}(\rm C-OH)$ , as shown in Figure 5. It can be seen that the calculated chemical shifts are in good agreement with the experimental ones.

#### 4 | CONCLUSION

In summary:

- 1. The alkyl *PEI* has an important influence on the chemical shift of the mentioned four atoms. The  $\delta_{\rm H}(\rm CH=N)$  and  $\delta_{\rm C}(\rm CH=N)$  decrease with the increase of *PEI* (the alkyl chain increases); and  $\delta_{\rm H}(\rm OH)$  and  $\delta_{\rm C}(\rm C-OH)$  increase with the increase of *PEI*.
- 2. The chemical shift values of different atoms are affected by the different electron effect parameters of substituent X. Regression analysis were performed on the chemical shift values  $\delta_{\rm H}(\rm CH=N)$ ,  $\delta_{\rm C}(\rm CH=N)$ ,  $\delta_{\rm H}(\rm OH)$ , and  $\delta_{\rm C}(\rm C-OH)$  by using five to seven parameters, and good quantitative correlation equations were obtained. The leave-one-out cross validation shows that these quantitative equations have good stability and predictability and can be used to predict chemical shift values of the title compounds.
- 3. When the substituent X attached to the aromatic ring can be located by two reference groups, there are two ways of expressing its electronic effect. The two expressions may increase or decrease the chemical shift value of the specified atom and show different influence intensity on the chemical shift. We name this phenomenon "homoring competition effect" of the substituent.

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The phenomenon observed in this paper is of significance in terms of analysis of the chemical shift for salen-type Schiff bases and can be used to discuss the distribution of atomic charge density in this kind of compounds. In addition, the discovery of "homoring competition effect" provides a new perspective for understanding the substituents effect in-deep.

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### SUPPORTING INFORMATION

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