

Conformational Study of Isobutenylene Chains in Tandem Claisen Rearrangement Products. Insights from X-ray Crystallography and ^{1}H NMR for Salicylideneaniline Derivatives

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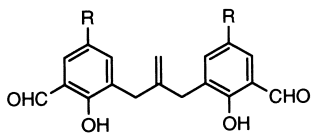
A new variety of salicylideneaniline derivatives were prepared from a substituted aniline and a bis(hydroxybenzaldehyde) which has been synthesized through a tandem Claisen rearrangement reaction. X-ray crystal structures were obtained for many of the products. With respect to the conformation of their isobutenylene chain, the crystal structures can be classified into three groups: i.e., skew–skew (I), *syn*–skew (II), and *syn–syn* (III) conformers. The ^{1}H NMR spectra were significantly different among these compounds, especially for the isobutenylene moiety. The set of the chemical shifts, ($\delta(H^a)$, $\delta(H^b)$), of exo-methylene (H^a) and benzylic methylene (H^b) is a good index for classifying the NMR spectra, and these values also reflect the conformation of the isobutenylene chain found in the crystal state. Namely, each conformer of I, II, and III corresponds to the ($\delta(H^a)$, $\delta(H^b)$) values (ppm) around (5.10, 3.43), (4.86, 3.43), and (4.74, 3.56), respectively. This result is verified by the complexation study of a 15-crown-5 derivative with alkali metal ions. The chemical shift change caused by the complexation is successfully explained by the conformation changes among I, II, and III.

Macrocyclic compounds with various functional groups have attracted much attention in the field of supramolecular chemistry.[1] During these years, Hiratani et al. have developed a number of compounds by utilizing tandem Claisen rearrangement reaction.[2] This reaction simultaneously introduces multiple phenolic groups and an isobutenylene (2-methyleneпropane-1,3-diyl; $–CH_2–C(=CH_2)–CH_2–$) linkage between two aryl groups. This enables us to prepare various types of macrocyclic host compounds having phenolic groups in the main frame. For example, a crownophane composed of isobutenylene-linked phenols and oligoethylene glycol chain captures a water molecule inside its cavity by taking advantage of multiple hydrogen bonding.[3,4] For this molecule, the conformation of isobutenylene moiety forces the –OH (hydrogen bond donor) and –O– (hydrogen bond acceptor) groups into tetrahedral arrangement, which is responsible for the stable binding with the water molecule. In view of the crystal structures of a series of the crownophanes,[3] one may conclude that the isobutenylene chain plays an important role in regulating the shape of the molecule.

Theoretical calculations have revealed three stable conformers, i.e., *syn–syn*, *syn*–skew, and skew–skew forms, within a energy range of 3 kcal/mol for isobutenylene moiety.[5] However, there are no experimental studies on the preferable conformation of the isobutenylene-linked compounds in solution. X-ray crystallography is a powerful tool to obtain a molecular structure in solid state, and also to suggest a molecular structure in solution. On the other hand, there are several NMR techniques to obtain structural information as a thermodynamical average in a solution state. Above all, the chemical shift value is most easily available, and can be used to obtain structural information related to the electronic states.[6] Accordingly, a combination of these two sources of information would strengthen the insight into a molecular conformation, if their correlation is clearly established.

In this paper, we present a conformation-chemical shift relationship found in a series of salicylideneaniline derivatives prepared by Schiff base formation of a bis(hydroxybenzaldehyde) (**1a–c**)[7,8] (Chart 1) and a variety of diamines. Salicylideneanilines are known to exhibit interesting types of photochemical behavior, such as photochromism, thermochromism, and fluorescence.[9–14] These photochemical properties largely depend on the molecular structure, including the distance, orientation, and spatial arrangement of the functional groups. In addition, the salicylideneaniline derivatives are widely applied as polydentate ligands in the area of coordination chemistry.[15] To obtain the fundamental information on the molecular structure, we examined twenty Schiff base compounds by means of X-ray crystallography and NMR spectroscopy. Based on the conformation-chemical shift relation, we will show the trajectory



1a: R = H
1b: R = Me
1c: R = t-Bu

Chart 1.

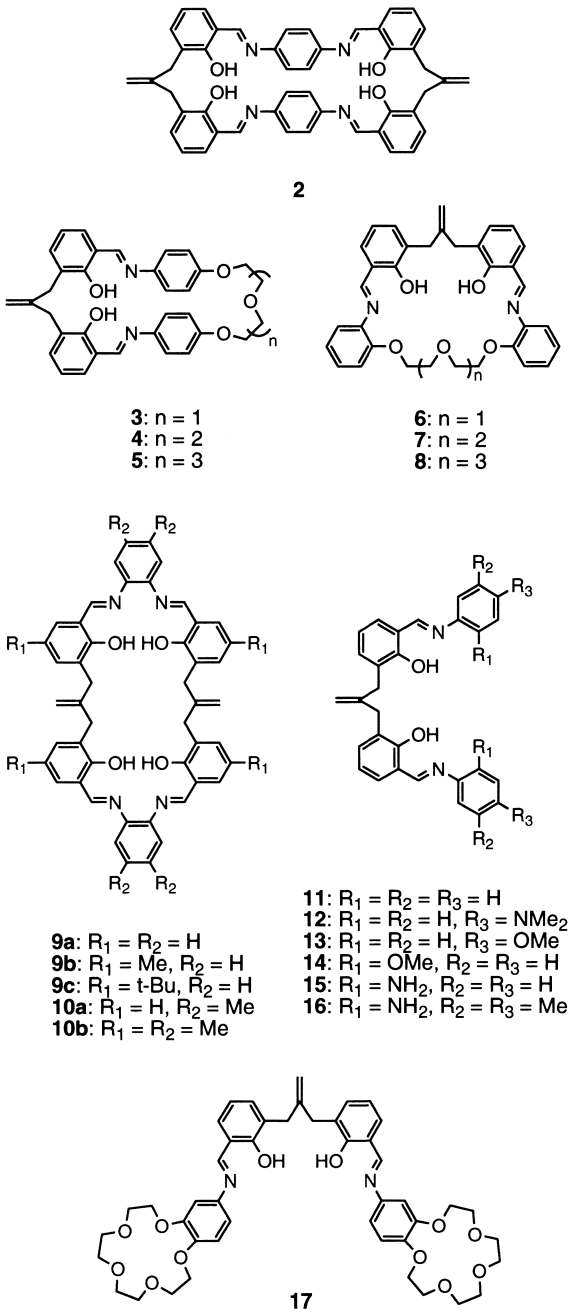


Fig. 1. The structures of the Schiff base compounds studied.

of structural change caused by molecular complexation.

Results

Figure 1 shows the chemical structures of the Schiff base compounds studied. The compounds include cyclic (**2**–**10**) and acyclic (**11**–**17**) ones. The cyclic Schiff bases are further classified into two groups, *p*-substituted aniline derivatives (**2**–**5**) and *o*-substituted ones (**6**–**10**).

Crystal Structure of the Schiff Bases. The X-ray single crystal structures of eleven compounds were successfully obtained. As can be seen from the chemical structure of salicylideneaniline moiety, there are two possible tautomeric forms, i.e., OH- and NH-forms, for the O–C–C–N framework.[9–14] For some compounds, the hydrogen atoms concerned with this tautomerization could not be found by differential Fourier transformation process. By comparison with the reported values of the bond length of the salicylideneaniline moiety,[16] we finally judged that each moiety adopts the OH-form for all the cases examined.

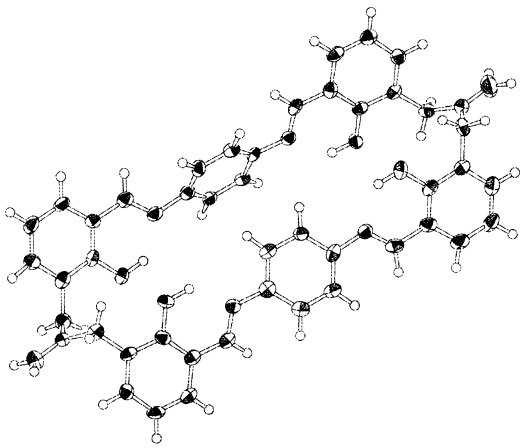


Fig. 2. The crystal structure of **2**. The solvent of crystalization is omitted for clarity.

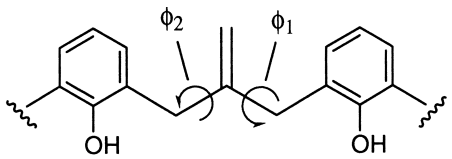


Fig. 3. Definition of ϕ_1 and ϕ_2, the torsion angle of a C=C–C–C(Ar) moiety. The angles ϕ_1 and ϕ_2 are 0°, when the C=C–C–C(Ar) moiety takes *syn* conformation.

Figure 2 shows an ORTEP drawing of **2**, the 2:2 adduct of **1a** and *p*-phenylenediamine. Since the disalicylidene-*p*-phenylenediamine moieties have a relatively rigid structure, the conformation of the isobutenylene chain is the predominant factor regulating the shape of the molecule. For the conformation change of isobutenylene linkage, there are mainly two degrees of freedom, i.e., the torsion angles of two C=C–C–C(Ar) moieties. Here we denote a set of the angles (°) as (ϕ_1, ϕ_2), where ϕ is defined to be 0°, when a C=C–C–C(Ar) moiety takes *syn* conformation (Fig. 3). For **2**, there are two sets of isobutenylene linkage, and the (ϕ_1, ϕ_2) values were (105.0, 116.0) and (−107.5, −116.0), respectively. Consequently, the isobutenylene moiety adopts approximately C_2 symmetry with respect to the C=C bond. The values of (ϕ_1, ϕ_2) for all the compounds examined are listed in Table 1.

Compounds **3**–**5** are 4-aminophenol derivatives having di-, tri-, and tetraethylene glycol moieties, respectively. Figure 4 shows an ORTEP drawing of **4**. As can be understood from the figure, the conformation of the isobutenylene chain is quite similar to that of **2**. The values of (ϕ_1, ϕ_2) are (108.5, 115.6), indicating the similarity from a quantitative aspect (see Table 1). The crystal structures of both **3** and **5** have shown a conformation similar to **4** with respect to the isobutenylene chain (drawings are not shown). As shown in Table 1, both ϕ_1 and ϕ_2 are in the range of 100–120°. Namely, differences in the

Table 1. Torsion Angles (ϕ_1, ϕ_2) Found in the Crystal Structure of Schiff Base Compounds

Compounds	(ϕ_1, ϕ_2)	Class[a)]
2	(105.0, 116.0)	I
	(−107.5, −116.0)	I
3	(108.4, 118.7)	I
4	(108.5, 115.6)	I
5	(111.6, 115.3)	I
9a	(4.2, 109.6)[b)]	II
9c	(−15.0, 108.3)	II
10a	(5.4, 116.1)	II
10b	(2.4, 112.1)	II
12	(3.5, 7.0)	III
13	(10.0, 10.0)	III
16	(8.4, 8.4)[b)]	III

a) Based on the classification shown in Fig. 9.
b) From Ref. 8.

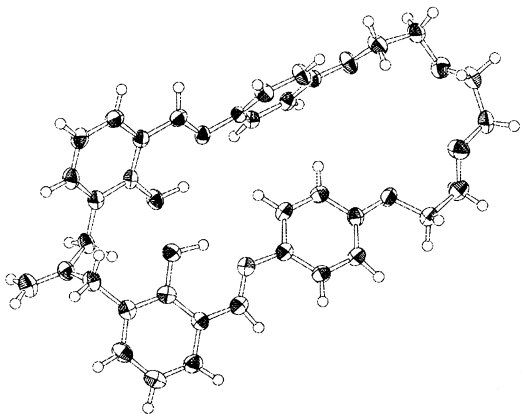


Fig. 4. The crystal structure of **4**.

length of ethylene glycol chain hardly affect the overall shape of the molecules.

The *o*-substituted aniline derivatives are further divided into two groups. The compounds **6–8** are 2-aminophenol derivatives having di-, tri-, and tetraethylene glycol moieties. Unfortunately, the crystal structures of these compounds have not been revealed. The compounds **9a–c** and **10a–b** are composed of 2:2 ratios of a bis(hydroxybenzaldehyde) (**1a**, **b**, or **c**) and an *o*-phenylenediamine. The crystal structures of this group are similar to each other. In the crystal structure, they have an inversion point of symmetry in the molecule; thus the two sets of isobutenylene moiety are crystallographically equivalent. As a typical example, the crystal structure of **10a** is shown in Fig. 5. The values of (ϕ_1, ϕ_2) are (5.4, 116.1), indicating a significant displacement from the C_2 symmetry with respect to the C=C bond. For all the compounds in this group, ϕ_1 is in the −15–15° range whereas ϕ_2 is in the 100–120° range (Table 1).

Compounds **11–17** are acyclic Schiff bases composed of **1a** and two molar amounts of a substituted aniline. The crystal structures were obtained for **12**, **13**, and **16**. Figure 6 shows an ORTEP drawing of **13** as a representative. In the crystal, the molecule has the C_2 axis coincident with the C=C bond. Thus, the values of ϕ_1 and ϕ_2 equal each other, that is, (ϕ_1, ϕ_2) = (10.0, 10.0). The compound **16** also has the C_2 axis, while **12**

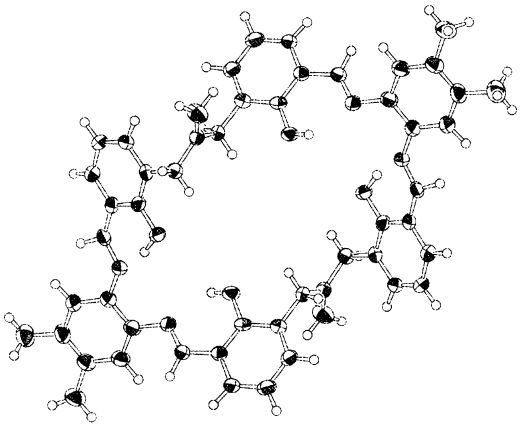


Fig. 5. The crystal structure of **10a**. The solvent of crystalization is omitted for clarity.

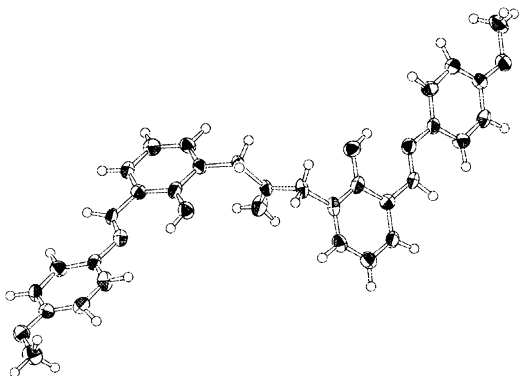


Fig. 6. The crystal structure of **13.**

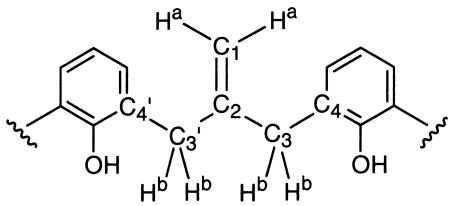


Fig. 7. The atomic labels of isobutenylene-linked phenol moiety used in this study.

is slightly unsymmetric with respect to the torsion angles of two 4-dimethylaminophenyl groups, causing a slight difference between ϕ_1 (3.5°) and ϕ_2 (7.0°). Consequently, for these compounds we can summarize that the values of ϕ_1 and ϕ_2 fall into the 0–15° range.

^{1}H NMR Chemical Shifts. The ^{1}H NMR chemical shifts of the compounds studied showed a characteristic distribution, especially for the methylene protons, H^a and H^b (Fig. 7). Figure 8 plots the set of $\delta(H^a)$ and $\delta(H^b)$ values against the horizontal and vertical axes, respectively. Hereafter, this set is written as ($\delta(H^a)$, $\delta(H^b)$) after the model of the plane coordinate. From this figure, we can see that the ($\delta(H^a)$, $\delta(H^b)$) can be divided into several groups. The data localized around (5.10, 3.43) (region A: shown by a square) are the data from **2–5**, which are the cyclic compounds containing *p*-substituted aniline. The data around (4.74, 3.56) (region B: shown by an

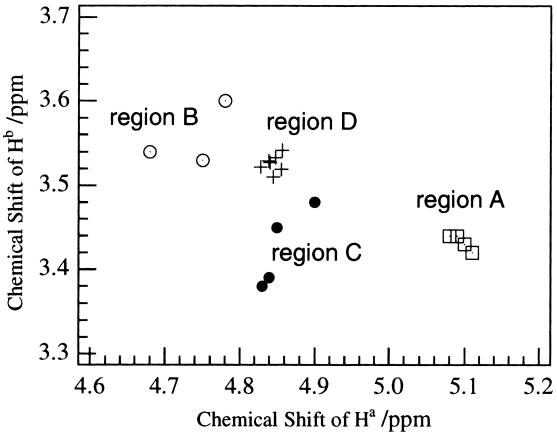


Fig. 8. The plot of the ($\delta(H^a)$, $\delta(H^b)$) values of **2**–**5** (□), **6**–**8** (○), **9a**–**10b** (●), and **11**–**17** (+). The annotations, regions A–D, are shown to classify their distribution.

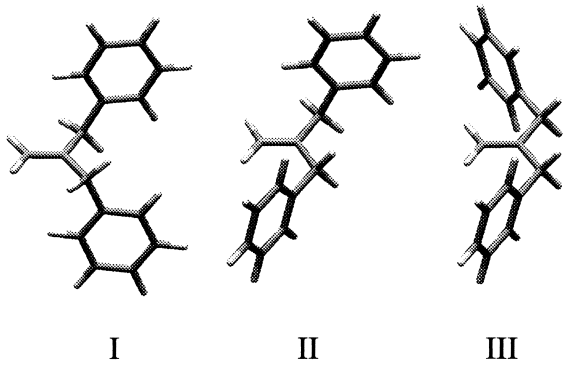


Fig. 9. The illustrative drawings of the comformers I (skew–skew), II (*syn*–skew), and III (*syn*–*syn*) of 2-benzyl-3-phenyl-1-propene as a model of isobutenylene-linked compounds.

open circle) are from **6**–**8**, which are cyclic compounds containing the *o*-aminophenoxy component. The data around (4.86, 3.43) (region C: shown by a closed circle) are from **9a**–**10c**, which are cyclic compounds composed of 2:2 ratio of a bis(hydroxybenzaldehyde) and a *o*-phenylenediamine. Finally, the data localized around (4.84, 3.53) (region D: shown by a cross) are from **11**–**17**, which are acyclic Schiff bases including *p*- and *o*-substituted anilines.

On considering that the ($\delta(H^a)$, $\delta(H^b)$) values of **11**–**17** are almost independent of the substituents on an aniline ring, we assume that their change is attributed to the conformation change, especially around the isobutenylene moiety. Since there is no π-conjugation between ethylene and phenyl groups, steric (through-space) effects can affect the chemical shift more largely than inductive (through-bond) effects do.

Interestingly, we found that our classification of the ($\delta(H^a)$, $\delta(H^b)$) data is in agreement with the conformations of the isobutenylene moiety that were observed for the X-ray crystal structures. Namely, the compounds in the region A (**2**–**5**) gave both ϕ_1 and ϕ_2 values of 100–120°, those in the region C (**9a**–**10b**) gave ϕ_1 of −15–15° and ϕ_2 of 100–120°, and those in the region D (**11**–**17**) gave both ϕ_1 and ϕ_2 of 0–15°. Although the crystal structures of the compounds in the region B (**6**–**8**) have not been obtained, we can expect that the isobutenylene moieties take similar conformations to each other among these compounds that have a similar chemical structure, except for the length of the ethylene glycol chain. This agreement between crystal structures and ^{1}H NMR chemical shifts suggests that, even though the molecules move continually in solution, the thermodynamical average of their conformation reflects their crystal structure to some extent. This may partly result from the rigidity of the salicylideneaniline moiety, which forms a strong intramolecular hydrogen bond between –OH and =N– groups to reduce the number of degrees of freedom of motion.

Discussion

Conformation-Chemical Shift Relationship in Isobutenylene Linkage. As described above, the Schiff base compounds studied here can be classified into three groups in terms of the conformation of their isobutenylene moiety in crystal state. Furthermore, this classification is also applicable to the distribution of the chemical shift ($\delta(H^a)$, $\delta(H^b)$) data. Figure 9 illustrates the classified conformers, I, II, and III, for a model compound (2-benzyl-3-phenyl-1-propene). Conformer I, where both C=C–C–C(Ar) chains take skewed anti conformation ($\phi_1 = \phi_2 = 110°$), corresponds to the isobutenylene moiety of **2**–**5**. Conformer II, where one C=C–C–C(Ar) chain takes *syn* and the other takes skewed *anti* conformation ($\phi_1 = 0°$, $\phi_2 = 110°$), is found in **9a**–**10b** in Table 1. Conformer III, where both C=C–C–C(Ar) chains take *syn* conformation ($\phi_1 = \phi_2 = 0°$), is a model for **11**–**17** in solid state. Importantly, these three conformers correspond to the stable conformers predicted by *ab initio* molecular orbital calculation, that is, skew–skew, *syn*–*skew*, and *syn*–*syn* forms.[5]

Differences in conformation among I–III can cause differences in NMR chemical shifts of ^{1}H and ^{13}C mainly by steric effects. If a C=C–C–C(Ar) chain changes its conformation from skewed *anti* to *syn*, the relative separation between the phenyl ring and the exo-methylene group is drastically changed. For example, the distance between the exo-methylene carbon (C_1 in Fig. 7) and the ipso-carbon of the phenyl ring (C_4 in Fig. 7) for **4** is 3.50 Å on average, whereas that for **13** is 2.91 Å. These two carbons are in γ-position for each other, and thereby are expected to exert γ-steric effect on the shieldings of both ^{1}H and ^{13}C, especially when they are arranged in syn conformation. In addition, in *syn* conformation the phenyl group may cause the ring current effect on the shielding of exo-methylene protons (H^a). Consequently, the exo-methylene protons can be upfield shifted when the C=C–C–C(Ar) moiety takes *syn* conformation. This explains the difference in the chemical shift between **4** ($\delta(H^a)$ = 5.09 ppm) and **13** ($\delta(H^a)$ = 4.84 ppm). As for ^{13}C NMR chemical shift, we can see the same tendency between **4** ($\delta(C_1)$ = 114.1 ppm) and **13** ($\delta(C_4)$ = 112.4 ppm). This difference (114.1−112.4 = 1.7 ppm) is in moderate agreement with a theoretical estimation of the γ-steric effect on olefinic carbons.[17]

Since C_3 and C_4' are also in the γ-position of each other (Fig. 7), a methylene group attached to a phenyl ring (benzylic methylene, H^b) will receive both γ-steric and ring current effects when a C=C–C–C(Ar) chain takes skewed *trans* conformation. Namely, H^a and H^b show a quite opposite chemical

shift change to each other during the conformation change. This assumption is again supported by the experimental results of **4** ($\delta(H^b)$ = 3.44 ppm) and **13** ($\delta(H^b)$ = 3.53 ppm). ^{13}C NMR spectra also showed the same tendency for **4** ($\delta(C_3)$ = 34.1 ppm) and **13** ($\delta(C_3)$ = 35.7 ppm). Therefore, we can reach a hypothesis that, on going from conformer I to III through II, protons and carbons of exo-methylene group undergo upfield shift, whereas those of benzylic methylene experience downfield shift.

Hence, it is reasonable to presume that the compounds belonging to region B predominantly adopt a conformation like III, since the compounds corresponding to region C are **9a–10b** that prefer the conformation II, and those corresponding to region A are **2–5** that prefer the conformation I. From Fig. 8, we notice that the region D is located between the regions B and C. This can be interpreted by assuming that the NMR data of the region D are averages of thermodynamical distribution of several conformers including II and III. In solution, it seems natural that the conformation change between II and III easily occurs on acyclic molecules like **13** due to thermal motion.

In summary, the distributions of the ($\delta(H^a)$, $\delta(H^b)$) values are interpreted from the conformation change of isobutenylene moiety. The compounds **2–5** maintain a conformation like I even in solution, resulting in the ($\delta(H^a)$, $\delta(H^b)$) values in the region A. Similarly, **6–8** and **9a–10b** are present in a conformation like III and II, respectively, resulting in the ($\delta(H^a)$, $\delta(H^b)$) values in the regions B and C, respectively. The compounds **11–17** are in equilibrium between conformers II and III, resulting in the ($\delta(H^a)$, $\delta(H^b)$) values in the region D.

Conformation Change by Host–Guest Interaction. Based on the above consideration, we examined the conformation change of **17** upon complexation with alkali metal ions. As is well known, a crown ether captures an alkali metal ion inside its cavity to form a complex.[1] Benzo-15-crown-5 prefers the 2:1 complexation with potassium ion in a sandwich fashion, because the ion radius is large compared to the cavity size.[18] There have been several reports on 'pincers-type' compounds having two or more benzo-15-crown-5 moieties.[19] Such compounds are expected to show a kind of allostericity for large structural changes due to potassium ion as an effector.

Figure 10(a) shows a selected region of ^1H NMR spectrum for **17** in chloroform (ca. 10 mM) without additives. Under this condition, the ($\delta(H^a)$, $\delta(H^b)$) values (ppm) are (4.83, 3.52), appearing in region D. On addition of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Na·TFPB) to this solution, the spectrum showed significant changes (Fig. 10(b)). On going from 0.5 to 1.0 equivalents' addition, the ($\delta(H^a)$, $\delta(H^b)$) values move from (4.98, 3.48) to (5.11, 3.45). This is a transfer from the region D to the region A, indicating that the conformation of the isobutenylene moiety changed from the equilibrated state between II and III toward I. When **17** takes a conformation like I, the two crown ether rings can approach each other (the averaged distance between the center of the aniline ring is 4.9 Å among **2–5**). Thus, at this stage, probably the sodium ion is bound by two benzo-15-crown-5 moieties (Fig. 11(a)).

By further addition of Na·TFPB, the chemical shifts were changed toward the opposite side. On going from 1.0 to 3.0 through 2.0 equivalents addition, the ($\delta(H^a)$, $\delta(H^b)$) values

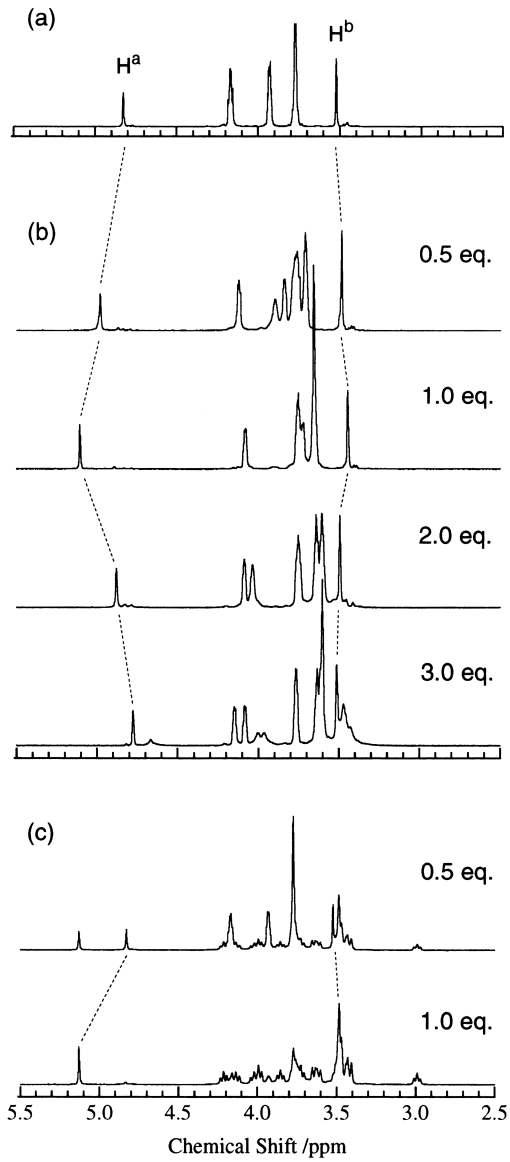


Fig. 10. The selected region of the ^1H NMR spectra of (a) **17** in chloroform, (b) **17** with various equivalents of Na·TFPB, and (c) **17** with various equivalents of K·TFPB. The dotted lines indicate the change of the peaks of H^a and H^b, respectively.

moved from (5.11, 3.45) to (4.78, 3.51) through (4.88, 3.49). This change corresponds to a transfer from region A to region B, indicating that the molecular structure changed from I to III. Thus, at this stage, each benzo-15-crown-5 accommodates one sodium ion to form the structure shown in Fig. 11(b). No further material was added because the solution became cloudy after adding 3.0 equivalents.

Figure 10(c) shows the ^1H NMR spectra of **17** when TFPB salt of potassium ion (K·TFPB) was added to the solution. When we added 0.5 equivalents, a new set of peaks have appeared in addition to the original peak set of **17**. After addition of 0.5 more equivalents of K·TFPB, the new peak set was mainly observed. The ($\delta(H^a)$, $\delta(H^b)$) values are (5.13, 3.48), quite similar to those of **17**–Na·TFPB 1:1 complex, indicating that **17** and potassium ion form a sandwich type complex as

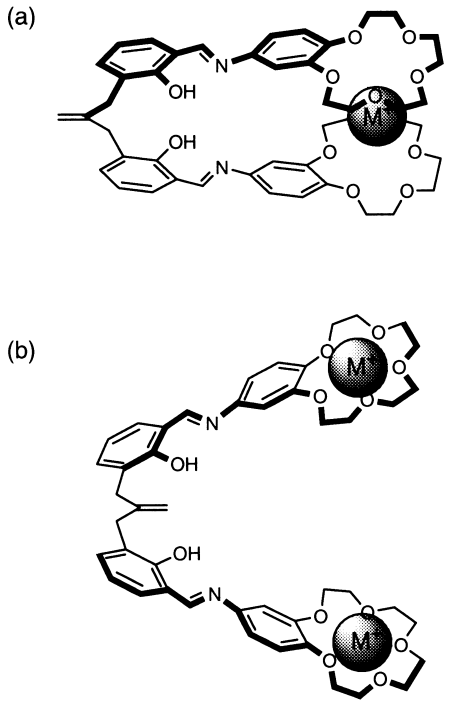


Fig. 11. Schematic representation of the complex of **17** and alkali metal ion (M^+). (a) A sandwich-type 1:1 complex presumed for sodium and potassium ions, and (b) a 1:2 complex presumed for sodium ion.

shown in Fig. 11(a). In contrast to Na·TFPB, more K·TFPB was not dissolved when an excess amount was added to the solution. This indicates that in this condition **17** cannot form a dipotassium complex like Fig. 11(b) because of a size-mismatch between benzo-15-crown-5 and potassium ion. As can be seen in the spectra, the complexation is almost quantitative, and the exchange between complexed and uncomplexed forms is relatively slow. Furthermore, all the methylene protons of the crown ether moiety appear to be magnetically nonequivalent, implying that the degree of freedom of their motion is reduced due to the complexation.

Concluding Remarks

We synthesized a series of Schiff base compounds containing isobutenylene linkage, and revealed the crystal structures of the major part of them. We have discovered that the crystal structure can be classified into three groups with respect to the conformation of isobutenylene moiety, and that the ($\delta(H^a)$, $\delta(H^b)$) values can be a good index for identifying the molecular structure in solution. The validity of this index was verified by the complexation study of the benzo-15-crown-5 derivative and alkali metal ions. We have succeeded in following the change in molecular structure based on the change in ^{1}H NMR chemical shift. This work provides a good example of clarifying the physical meaning of the chemical shift change by molecular complexation.

Experimental

The aldehydes **1a–c** were prepared similarly to the method explained in the previous report.[7] The anilines used (aniline, *p*-phenylenediamine, *p*-anisidine, *o*-phenylenediamine, 4,5-dimethyl-*o*-phenylenediamine, *o*-anisidine, *N*,*N*-dimethyl-*p*-phenylenediamine, and 4′-aminobenzo-15-crown 5-ether) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. For the synthesis of **3**, diethylene glycol bis(4-aminophenyl) ether was prepared by a reaction of *N*-benzylidene-*p*-aminopenol and diethylene glycol di-*p*-tosylate in the presence of sodium hydride in DMF, followed by the deprotection. Similarly, combinations of 2- or 4-aminophenol and di-, tri-, or tetraethylene glycol unit were carried out for the syntheses of **4–8**, respectively.

The Schiff base compounds **2–17** were synthesized from the corresponding bis-hydroxybenzaldehyde (**1a–c**) and aniline by the following three methods A–C. Method A: the starting materials were dissolved in chloroform, to which methanol was gradually added over several days (a method modified from a reported procedure).[7] Method B: the starting materials were allowed to react in methanol. Method C: The starting aldehyde was firstly reacted with an excess amount of diamine, and then the product was converted to a macrocyclic compound by recombination of a Schiff base linkage in a slow diffusion system.[8] For all the compounds except for **11** and **14**, the resultant precipitate was collected by filtration and purified either by column chromatography (eluted with chloroform on silica gel) or by recrystallization (with chloroform-methanol system, unless otherwise noted) as need arose. For **11** and **14**, which were obtained as viscous liquids, the reaction mixture was heated at 110 °C under reduced pressure after the completion of the reaction. The chemical structure of the compounds was confirmed by ^{1}H and ^{13}C NMR, ESI MS, elemental analysis, and X-ray crystallography. The compounds **9a**, **15**, and **16** have been already reported elsewhere.[8]

***p*-Phenylenediamine Schiff Base of 1a (2).** Prepared by method A, orange crystalline solid, 76%. ^{1}H NMR δ 3.42 (s, –C*H*$_2$–(C=CH$_2$)–, 8H), 5.11 (s, –(C=C*H*$_2$)–, 4H), 6.80 (t, J = 7.3 Hz, Ar*H*–OH, 4H), 7.03 (s, =N–Ar*H*–N=, 8H), 7.17 (d, J = 7.4 Hz, Ar*H*–OH, 4H), 7.27 (d (coupling constant undetermined), Ar*H*–OH, 4H), 8.57 (s, Ar–C*H*=N-, 4H), 13.31 (s, Ar–O*H*, 4H). ^{13}C NMR spectrum was not measured due to low solubility. ESI MS m/z 737.1 ($M + Na^+$). Elemental Analysis Found: C, 78.02; H, 5.39; N, 7.53%. Calcd for $C_{48}H_{40}N_4O_4$: C, 78.24; H, 5.47; N, 7.61%. Crystal Data: $C_{48}H_{40}N_4O_4$·$(CHCl_3)_2$ MW = 975.62, crystal system = triclinic, space group $P\bar{1}$(#2), Z = 2 in a cell of dimensions: a = 15.7086(4), b = 16.6372(2), c = 10.2754(1) Å, α = 95.1457(8), β = 107.042(1), γ = 63.5514(9)°, V = 2296.17(8) Å^3, D_{calcd} = 1.411 g/cm^3. μ = 4.24/cm, 21938 measured and 10279 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.048). R_1 = 0.089, R_w = 0.075.

Diethylene Glycol Bis(4-aminophenyl) Ether Schiff Base of 1a (3). Prepared by method B, yellow crystalline solid, 23%. ^{1}H NMR δ 3.42 (s, Ar–C*H*$_2$–C(=CH$_2$)–, 4H), 3.88 (t, J = 4.2 Hz, Ar–O–CH$_2$–C*H*$_2$–O–, 4H), 4.20 (t, J = 4.1 Hz, Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 5.10 (s, –C(=C*H*$_2$)–, 2H), 6.71–74 (m, Ar*H*, 6H), 6.93 (d, J = 8.7 Hz, =N–Ar*H*–O–, 4H), 7.08 (d, J = 7.3 Hz, Ar*H*–OH, 2H), 7.17 (d, J = 7.2 Hz, Ar*H*–OH, 2H), 8.45 (s, Ar–C*H*=N–, 2H), 13.50 (s, Ar–O*H*, 2H). ^{13}C NMR δ 34.1, 68.6, 69.8, 114.1, 115.7, 118.1, 118.5, 121.9, 127.8, 129.8, 132.7, 141.0, 148.5, 157.5, 159.2, 159.7. ESI MS m/z 549.2 ($M + H^+$). Elemental Analysis Found: C, 73.72; H, 5.78; N, 4.94%. Calcd for $C_{34}H_{32}N_2O_5$·$(H_2O)_{0.25}$: C, 73.82; H, 5.92; N, 5.07%. Crystal Data: $C_{34}H_{32}N_2O_5$ MW = 548.64, crystal system = triclinic, space group $P\bar{1}$(#2), Z = 2 in a cell of dimensions: a = 11.811(2), b = 13.725(2), c = 9.541(1) Å, α = 104.147(7), β = 95.819(4), γ = 66.298(9)°, V =

1373.1(4) Å^3, D_{calcd} = 1.327 g/cm^3. μ = 0.89/cm, 10697 measured and 5897 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.051). R_1 = 0.077, R_w = 0.125.

Triethylene Glycol Bis(4-aminophenyl) Ether Schiff Base of 1a (4). Prepared by method B, yellow crystalline solid, 28%. ^{1}H NMR δ 3.44 (s, –C*H*$_2$–(C=CH$_2$)–, 4H), 3.78 (s, –O–C*H*$_2$–C*H*$_2$–O–, 4H), 3.90 (t, J = 4.8 Hz, Ar–O–CH$_2$–C*H*$_2$–O–, 4H), 4.07 (t, J = 4.9 Hz, Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 5.09 (s, –(C=C*H*$_2$)–, 2H), 6.70 (d, J = 6.9 Hz, =N–Ar*H*–O–, 4H), 6.74 (t, J = 7.5 Hz, Ar*H*–OH, 2H), 6.99 (d, J = 6.7 Hz, =N–Ar*H*–O–, 4H), 7.10 (d, J = 7.6 Hz, Ar*H*–OH, 2H), 7.19 (d, J = 7.4 Hz, Ar*H*–OH, 2H), 8.47 (s, Ar–C*H*=N–, 2H), 13.50 (s, Ar–O*H*, 2H). ^{13}C NMR δ 34.2, 67.8, 69.7, 71.3, 114.1, 115.1, 118.0, 118.6, 122.1, 127.9, 129.8, 132.7, 141.2, 148.4, 157.8, 159.2, 160.1. ESI MS m/z 615.3 (M + Na$^+$). Elemental Analysis Found: C, 72.30; H, 6.05; N, 4.67%. Calcd for $C_{36}H_{36}N_2O_6\cdot(H_2O)_{0.25}$: C, 72.40; H, 6.16; N, 4.69%. Crystal Data: $C_{36}H_{36}N_2O_6$ MW = 592.69, crystal system = triclinic, space group $P\bar{1}$(#2), Z = 2 in a cell of dimensions: a = 10.0965(5), b = 16.591(1), c = 9.5682(6) Å, α = 92.640(3), β = 108.707(3), γ = 85.265(3)°, V = 1512.6(2) Å^3, D_{calcd} = 1.301 g/cm^3. μ = 0.89/cm, 16176 measured and 6832 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.043). R_1=0.067, R_w = 0.100.

Tetraethylene Glycol Bis(4-aminophenyl) Ether Schiff Base of 1a (5). Prepared by method B, yellow crystalline solid, 30%. ^{1}H NMR δ 3.44 (s, –C*H*$_2$–(C=CH$_2$)–, 4H), 3.76 (m, –O–C*H*$_2$-C*H*$_2$–O–, 8H), 3.94 (t, J = 4.7 Hz, Ar–O–CH$_2$–C*H*$_2$–O–, 4H), 4.06 (t, J = 4.7 Hz, Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 5.08 (s, –(C=C*H*$_2$)–, 2H), 6.72 (d, J = 6.7 Hz, =N–Ar*H*–O–, 4H), 6.74 (t, J = 7.5 Hz, Ar*H*–OH, 2H), 7.03 (d, J = 6.7 Hz, =N–Ar*H*–O–, 4H), 7.10 (d, J = 7.6 Hz, Ar*H*–OH, 2H), 7.19 (d, J = 7.5 Hz, Ar*H*–OH, 2H), 8.46 (s, Ar–C*H*=N–, 2H), 13.49 (s, Ar–O*H*, 2H). ^{13}C NMR δ 34.3, 67.7, 69.6, 70.4, 70.9, 114.0, 114.9, 118.0, 118.6, 122.2, 127.8, 129.9, 132.7, 141.2, 148.4, 157.8, 159.2, 160.2. ESI MS m/z 659.1 (M + Na$^+$). Elemental Analysis Found: C, 71.50; H, 6.28; N, 4.31%. Calcd for $C_{38}H_{40}N_2O_7$: C, 71.68; H, 6.33; N, 4.40%. Crystal Data: $C_{38}H_{40}N_2O_7$ MW = 636.74, crystal system = triclinic, space group $P\bar{1}$(#2), Z = 2 in a cell of dimensions: a = 11.8768(3), b = 14.4156(3), c = 11.2434(2) Å, α = 101.658(2), β = 114.023(2), γ = 99.2913(8)°, V = 1656.84(7) Å^3, D_{calcd} = 1.276 g/cm^3. μ = 0.88/cm, 15253 measured and 7384 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.044). R_1 = 0.074, R_w = 0.083.

Diethylene Glycol Bis(2-aminophenyl) Ether Schiff Base of 1a (6). Prepared by method A, orange crystalline solid, 97%. ^{1}H NMR δ 3.60 (s, Ar–C*H*$_2$–C(=CH$_2$)–, 4H), 4.09 (t, J = 4.9 Hz, Ar–O–CH$_2$-C*H*$_2$–O–, 4H), 4.19 (t, J = 4.9 Hz, Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 4.78 (s, –C(=C*H*$_2$)–, 2H), 6.85 (t, J = 7.5 Hz, Ar*H*, 2H), 7.00–7.03 (m, Ar*H*, 4H), 7.22 (t, J = 7.2 Hz, Ar*H*, 2H), 7.23–7.28 (m, Ar*H*, 6H), 8.69 (s, Ar–C*H*=N–, 2H), 14.22 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.9, 69.6, 70.6, 111.5, 114.7, 118.0, 118.1, 119.0, 121.7, 127.9, 128.5, 130.0, 133.9, 148.2, 152.8, 160.2, 160.8. ESI MS m/z 571.2 (M + Na$^+$). Elemental Analysis Found: C, 74.26; H, 5.79; N, 5.10%. Calcd for $C_{34}H_{32}N_2O_5$: C, 74.43; H, 5.88; N, 5.11%.

Triethylene Glycol Bis(2-aminophenyl) Ether Schiff Base of 1a (7). Prepared by method A, orange crystalline solid, 86%. ^{1}H NMR δ 3.54 (s, –C*H*$_2$–(C=CH$_2$)–, 4H), 3.94 (s, –O–C*H*$_2$–C*H*$_2$–O–, 4H), 3.94 (t, J = 3.9 Hz, Ar–O–CH$_2$–C*H*$_2$–O–, 4H), 4.18 (t, J = 4.0 Hz), Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 4.68 (s, –(C=C*H*$_2$)–, 2H), 6.87 (t, J = 7.6 Hz, Ar*H*, 2H), 6.93 (d, J = 8.1 Hz, Ar*H*, 2H), 6.99 (t, J = 7.1 Hz, Ar*H*, 2H), 7.20–7.29 (m, Ar*H*, 8H), 8.70 (s, Ar–C*H*=N–, 2H), 14.26 (s, Ar–O*H*, 2*H*). ^{13}C NMR δ 35.9, 69.5, 69.9, 72.0, 110.6, 112.6, 117.8, 118.0, 119.1, 121.0, 127.9, 128.1, 130.1, 134.1, 136.9, 148.5, 152.8, 160.0, 160.7. ESI MS m/z 615.3 (M + Na$^+$). Elemental Analysis Found: C, 72.89; H, 6.08; N, 4.68%. Calcd for $C_{36}H_{36}N_2O_6$: C, 72.95; H, 6.12; N, 4.73%.

Tetraethylene Glycol Bis(2-aminophenyl) Ether Schiff Base of 1a (8). Prepared by method A, orange crystalline solid, 59%. ^{1}H NMR δ 3.53 (s, –C*H*$_2$–(C=CH$_2$)–, 4H), 3.71 (t, J = 5.0 Hz, –O–CH$_2$–C*H*$_2$–O–, 4H), 3.82 (t, J = 5.0 Hz, –O–C*H*$_2$–CH$_2$–O–, 4H), 3.92 (t, J = 4.2 Hz, Ar–O–CH$_2$–C*H*$_2$–O–, 4H), 4.17 (t, J = 4.1 Hz, Ar–O–C*H*$_2$–CH$_2$–O–, 4H), 4.75 (s, –(C=C*H*$_2$)–, 2H), 6.88 (t, J = 7.0 Hz, Ar*H*, 2H), 6.94 (d, J = 8.0 Hz, Ar*H*, 4H), 6.99 (t, J = 7.8 Hz, Ar*H*, 2H), 7.20–7.29 (m, Ar*H*, 8H), 8.71 (s, Ar–C*H*=N–, 2H), 14.11 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.6, 69.1, 69.7, 70.5, 71.0, 111.8, 112.8, 118.2, 118.6, 119.1, 121.1, 127.8, 130.2, 133.9, 137.3, 152.5, 159.9, 161.5. ESI MS m/z 637.2 (M + H$^+$). Elemental Analysis Found: C, 71.43; H, 6.28; N, 4.36%. Calcd for $C_{38}H_{40}N_2O_7$: C, 71.68; H, 6.33; N, 4.40%.

***o*-Phenylenediamine Schiff Base of 1b (cyclic) (9b).** Prepared by method A, orange crystalline solid, 48%. ^{1}H NMR δ 2.24 (s, Ar(OH)–C*H*$_3$, 12H), 3.38 (s, –C*H*$_2$–(C=CH$_2$)–, 8H), 4.83 (s, –(C=C*H*$_2$)–, 4H), 7.02 (s, Ar*H*–OH, 4H), 7.09 (s, Ar*H*–OH, 4H), 7.25–7.32 (m, =N–Ar*H*–N=, 8H), 8.58 (s, Ar–C*H*=N–, 4H), 13.15 (s, Ar–O*H*, 4H). ^{13}C NMR spectrum was not measured due to low solubility. ESI MS m/z 793.2 (M + H$^+$). Elemental Analysis Found: C, 78.43; H, 6.02; N, 6.98%. Calcd for $C_{52}H_{48}N_4O_4$: C, 78.76; H, 6.10; N, 7.07%.

***o*-Phenylenediamine Schiff Base of 1c (cyclic) (9c).** Prepared by method C, yellow crystalline solid (recrystallized from benzene), 54%. ^{1}H NMR δ 1.32 (s, Ar(OH)–C(C*H*$_3$)$_3$, 12H), 3.48 (s, –C*H*$_2$–(C=CH$_2$)–, 8H), 4.90 (s, –(C=C*H*$_2$)–, 4H), 7.24–7.35 (mult, Ar*H*, 16H), 8.66 (s, Ar–C*H*=N–, 4H), 13.26 (s, Ar–O*H*, 4H), ^{13}C NMR δ 31.4, 33.9, 35.5, 113.1, 118.2, 118.9, 126.7, 127.4, 127.5, 131.8, 140.8, 143.0, 146.6, 157.8, 163.6. ESI MS m/z 983.4 (M + Na$^+$). Elemental Analysis Found: C, 79.53; H, 7.47; N, 5.76%. Calcd for $C_{64}H_{72}N_4O_4\cdot(H_2O)_{0.25}$: C, 79.59; H, 7.57; N, 5.80%. Crystal Data: $C_{64}H_{72}N_4O_4\cdot C_6H_6$ MW = 1039.41, crystal system = triclinic, space group $P\bar{1}$ (#2), Z = 1 in a cell of dimensions: a = 12.4752(7), b = 14.420(2), c = 9.0653(5) Å, α = 101.082(3), β = 92.132(2), γ = 114.854(2)°, V = 1439.3(2) Å^3, D_{calcd} = 1.199 g/cm^3. μ = 0.74/cm, 12815 measured and 6362 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.076). R_1 = 0.103, R_w = 0.170.

4,5-Dimethyl-*o*-Phenylenediamine Schiff Base of 1a (cyclic) (10a). Prepared by method A, orange crystalline solid (recrystallized from DMF), 73%. ^{1}H NMR δ 2.34 (s, =N–Ar(C*H*$_3$)$_2$–N=, 12H), 3.45 (s, –C*H*$_2$–(C=CH$_2$)–, 8H), 4.85 (s, –(C=C*H*$_2$)–, 4H), 6.81 (t, J = 7.6 Hz, Ar*H*–OH, 4H), 7.08 (s, =N–Ar*H*–N=, 4H), 7.22–35 (m, Ar*H*–OH, 4H), 8.64 (s, Ar–C*H*=N–, 4H), 13.53 (s, Ar–O*H*, 4H). ^{13}C NMR spectrum was not measured due to low solubility. ESI MS m/z 815.2 (M + Na$^+$). Elemental Analysis Found: C, 78.19; H, 5.98; N, 6.91%. Calcd for $C_{52}H_{48}N_4O_4\cdot(H_2O)_{0.25}$: C, 78.32; H, 6.13; N, 7.03%. Crystal Data: $C_{52}H_{48}N_4O_4\cdot(C_3H_7NO)_2$ MW = 939.16, crystal system = triclinic, space group $P\bar{1}$ (#2), Z = 1 in a cell of dimensions: a = 11.787(1), b = 15.860(1), c = 7.1779(5) Å, α = 97.598(3), β = 98.194(6), γ = 70.047(4)°, V = 1439.3(2) Å^3, D_{calcd} = 1.254 g/cm^3. μ = 0.82/cm, 10958 measured and 5404 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.046). R_1 = 0.094, R_w = 0.166.

4,5-Dimethyl-*o*-phenylenediamine Schiff Base of 1b (cyclic) (10b). Prepared by method A, yellow crystalline solid, 63%. ^{1}H NMR δ 2.23 (s, Ar(OH)–C*H*$_3$, 12H) 2.33 (s, =N–Ar(C*H*$_3$)$_2$–N=,

12H), 3.39 (s, –CH_2–(C=CH_2)–, 8H), 4.84 (s, –(C=CH_2)–, 4H), 7.01 (s, Ar*H*–OH, 4H), 7.05 (s, =N–ArH–N=, 4H), 7.08 (s, Ar*H*–OH, 4H), 8.56 (s, Ar–C*H*=N–, 4H), 13.27 (s, Ar–O*H*, 4H). ^{13}C NMR spectrum was not measured due to low solubility. ESI MS *m*/*z* 849.3 (M + H^+). Elemental Analysis Found: C, 77.75; H, 6.54; N, 6.24%. Calcd for $C_{52}H_{48}N_4O_4\cdot H_2O$: C, 77.57; H, 6.74; N, 6.46%.

Aniline Schiff Base of 1a (11). Prepared by method B, yellow liquid, quantitative. ^{1}H NMR δ 3.53 (s, –CH_2–(C=CH_2)–, 4H), 4.85 (s, –(C=CH_2)–, 2H), 6.91 (t, J = 7.5 Hz, Ar*H*–OH, 2H), 7.25–29 (m, Ar*H*, 8H), 7.33 (d, J = 7.5 Hz, Ar*H*, 2H), 7.41 (m, Ar*H*, 4H), 8.62 (s, Ar–C*H*=N–, 2H), 13.56 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.7, 112.4, 118.7, 118.7, 121.1, 126.7, 127.7, 129.3, 130.6, 134.3, 146.9, 148.5, 159.4, 162.8. ESI MS *m*/*z* 447.2 (M + H^+). Elemental Analysis Found: C, 80.67; H, 5.82; N, 6.10%. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.69; H, 5.87; N, 6.28%.

***N*,*N*-Dimethyl-*p*-phenylenediamine Schiff Base of 1a (12).** Prepared by method B, orange crystalline solid, 88%. ^{1}H NMR δ 2.99 (s, –N(CH_3)$_2$, 12H), 3.53 (s, –CH_2–(C=CH_2)–, 4H), 4.84 (s, –(C=CH_2)–, 2H), 6.74 (d, J = 6.9 Hz, =N–Ar*H*–N<, 4H), 6.87 (t, J = 7.6 Hz, Ar*H*–OH, 2H), 7.24 (d, J = 7.8 Hz, Ar*H*–OH, 2H), 7.26–28 (m, Ar*H*, 6H), 8.62 (s, Ar–C*H*=N–, 2H), 14.02 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.8, 40.6, 112.2, 112.7, 118.4, 119.2, 122.1, 127.5, 129.8, 133.2, 137.2, 147.2, 149.7, 157.9, 159.2. ESI MS *m*/*z* 555.3 (M + Na^+). Elemental Analysis Found: C, 75.95; H, 6.73; N, 10.39%. Calcd for $C_{34}H_{36}N_4O_2\cdot(H_2O)_{0.25}$: C, 76.02; H, 6.85; N, 10.43%. Crystal Data: $C_{34}H_{36}N_4O_2$ MW= 532.68, crystal system = monoclinic, space group *C*2/*c* (#15), Z = 8 in a cell of dimensions: a = 16.3327(4), b = 12.1368(3), c = 29.8421(7) Å, β = 107.5331(8)°, V = 2581.9(5) Å^3, D_{calcd} = 1.254 g/cm^3. μ = 0.79/cm, 20481 measured and 6214 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.060). R_1 = 0.063, R_w = 0.064.

***p*-Anisidine Schiff Base of 1a (13).** Prepared by method B, yellow crystalline solid, 83%. ^{1}H NMR δ 3.52 (s, –CH_2–(C=CH_2)–, 4H), 3.84 (s, –O–CH_3, 6H), 4.84 (s, –(C=CH_2)–, 2H), 6.89 (t, J = 7.6 Hz, Ar*H*–OH, 2H), 6.93 (d, J = 6.7 Hz, =N–Ar*H*–O–, 4H), 7.26–27 (m, Ar*H*, 6H), 7.30 (d, J = 7.5 Hz, Ar*H*–OH, 2H), 8.61 (s, Ar–C*H*=N–, 2H), 13.71 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.7, 55.5, 112.4, 114.6, 118.6, 118.9, 122.2, 127.6, 130.2, 133.8, 141.4, 147.0, 158.7, 159.2, 160.6. ESI MS *m*/*z* 529.2 (M + Na^+). Elemental Analysis Found: C, 75.41; H, 5.88; N, 5.38%. Calcd for $C_{32}H_{30}N_2O_4\cdot(H_2O)_{0.25}$: C, 75.20; H, 6.02; N, 5.48%. Crystal Data: $C_{32}H_{30}N_2O_4$ MW= 506.60, crystal system = monoclinic, space group *C*2/*c* (#15), Z = 4 in a cell of dimensions: a = 25.894(3), b = 15.815(2), c = 6.4546(8) Å, β = 102.361(4)°, V = 2581.9(5) Å^3, D_{calcd} = 1.303 g/cm^3. μ = 0.86/cm, 14390 measured and 2948 unique reflections ($2\theta_{max}$ = 55.0°, R_{int} = 0.081). R_1 = 0.062, R_w = 0.091.

***o*-Anisidine Schiff Base of 1a (14).** Prepared by method B, orange liquid, quantitative. ^{1}H NMR δ 3.55 (s, –CH_2–(C=CH_2)–, 4H), 3.89 (s, –O–CH_3, 6H), 4.86 (s, –(C=CH_2)–, 2H), 6.88 (t, J = 7.6 Hz, Ar*H*–OH, 2H), 6.97–7.00 (m, =N–Ar*H*–O–, 4H), 7.19 (d, J = 7.7 Hz, =N–Ar*H*–O–, 2H), 7.23 (t, J = 7.9 Hz, =N–Ar*H*–O–, 2H), 7.27 (d, J = 8.1 Hz, Ar*H*–OH, 2H), 7.32 (d, J = 7.4 Hz, Ar*H*–OH, 2H), 8.70 (s, Ar–C*H*=N–, 2H), 13.98 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.6, 55.8, 112.4, 114.6, 118.6, 118.9, 122.2, 127.6, 130.2, 133.8, 141.4, 147.0, 158.7, 159.2, 160.6. ESI MS *m*/*z* 507.2 (M + H^+). Elemental Analysis Found: C, 75.67; H, 5.90; N, 5.42%. Calcd for $C_{32}H_{30}N_2O_4$: C, 75.87; H, 5.97; N, 5.53%.

***o*-Phenylenediamine Schiff Base of 1a (acyclic) (15).** Prepared by method B (with using 6 equiv. of *o*-phenylenediamine), yellow crystalline solid, 86%. ^{1}H NMR δ 3.52 (s, –CH_2–(C=CH_2)–, 4H), 4.01 (s, Ar–N*H*, 4H), 4.86 (s, –(C=CH_2)–, 2H), 6.76–80 (m, =N–Ar*H*–NH_2, 4H), 6.91 (t, J = 7.6 Hz, Ar*H*–OH, 2H), 7.03 (d, J = 7.7 Hz, =N–Ar*H*–NH_2, 2H), 7.09 (t, J = 7.7 Hz, =N–Ar*H*–NH_2, 2H), 7.29 (d, J = 7.7 Hz, Ar*H*–OH, 2H), 7.32 (d, J = 7.5 Hz, Ar*H*–OH, 2H), 8.61 (s, Ar–C*H*=N–, 2H), 13.22 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.5, 112.8, 115.7, 118.4, 118.8, 118.8, 119.1, 127.6, 128.0, 130.6, 134.2, 135.4, 140.8, 146.8, 159.0, 162.4. ESI MS *m*/*z* 499.2 (M + Na^+).

4,5-Dimethyl-*o*-phenylenediamine Schiff Base of 1a (acyclic) (16). Prepared by method B (using 6 equiv. of *o*-phenylenediamine), yellow crystalline solid, 90% yield. ^{1}H NMR δ 2.19 (s, =N–Ar–CH_3, 12H), 3.51 (s, –CH_2–(C=CH_2)–, 4H), 3.84 (s, Ar–N*H*, 4H), 4.85 (s, –(C=CH_2)–, 2H), 6.59 (s, =N–Ar*H*–NH_2, 2H), 6.84 (s, =N–Ar*H*–NH_2, 2H), 6.89 (t, J = 7.6 Hz, Ar*H*–OH, 2H), 7.26–29 (m, Ar*H*–OH, 4H), 8.59 (s, Ar–C*H*=N–, 2H), 13.37 (s, Ar–O*H*, 2H). ^{13}C NMR δ 18.9, 19.5, 35.5, 112.7, 117.4, 118.7, 119.1, 119.2, 126.8, 127.5, 130.3, 133.0, 133.8, 136.6, 138.6, 146.9, 158.9, 160.9. ESI MS *m*/*z* 555.3 (M + Na^+).

4′-Aminobenzo-15-crown 5-Ether Schiff Base of 1a (17). Prepared by method B, yellow crystalline solid, 91% yield. ^{1}H NMR δ 3.52 (s, –CH_2–(C=CH_2)–, 4H), 3.76 (s, –O–CH_2–CH_2–O–, 16H), 3.92–94 (m, Ar–O–CH_2–CH_2–O–, 8H), 4.16–19 (m, Ar–O–CH_2–CH_2–O–, 8H), 4.83 (s, –(C=CH_2)–, 2H), 6.85–91 (d, J = 6.7 Hz, Ar*H*, 8H), 7.27 (d, J = 7.9 Hz, Ar*H*–OH, 2H), 7.29 (d, J = 7.3 Hz, Ar*H*–OH, 2H), 8.60 (s, Ar–C*H*=N–, 2H), 13.68 (s, Ar–O*H*, 2H). ^{13}C NMR δ 35.8, 68.9, 69.3, 69.5, 70.4, 70.5, 71.0, 71.1, 107.6, 112.3, 113.1, 114.3, 118.6, 118.8, 127.6, 129.9, 130.3, 133.9, 142.1, 147.0, 148.3, 149.7, 159.3, 160.8. ESI MS *m*/*z* 827.2 (M + H^+). Elemental Analysis Found: C, 66.54; H, 6.51; N, 3.30%. Calcd for $C_{46}H_{54}N_2O_{12}$: C, 66.81; H, 6.58; N, 3.39%.

Measurement. For X-ray diffraction of a single crystal, the data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer, λ(Mo-$K\alpha$) = 0.7107 Å, at −80 °C. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms' coordinates were refined, but their isotropic B's were held fixed. The final cycle of full-matrix least-squares refinement was based on the observed reflections of $I > 1.5\sigma(I)$ and the variable parameters and converged with unweighted and weighted agreement factors, R_1 and R_w. All calculations were performed using the teXsan[20] crystallographic software package of Molecular Structure Corporation.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 178116–178124. The data are also deposited as Document No. 75021 at the Office of the Editor of Bull. Chem. Soc. Jpn.

NMR spectra were measured using a Brucker AVANCE500 (500 MHz for ^{1}H nuclei) system at 25 °C. The samples were dissolved in $CDCl_3$, and TMS was used as an internal standard.

Electrospray ionization (ESI) mass spectra were measured using a Micromass Platform LCZ system. The samples were dissolved in minimum amount of chloroform and then diluted with acetonitrile. All the data were measured in positive mode (cone voltage of 40 V for ionization).

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