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Menschutkin-Type Reaction of Substituted Benzyl Arenesulfonates with Substituted N,N-Dimethylanilines

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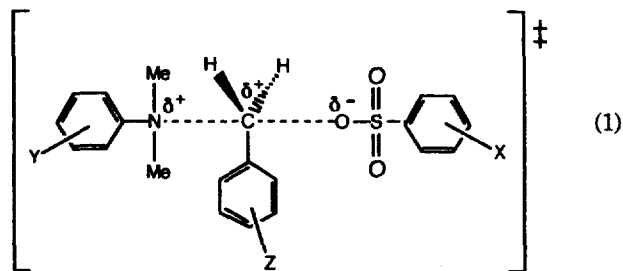
The substituent effects in the second-order reaction of Z-substituted benzyl tosylates and benzyl X-benzenesulfonates with Y-substituted N,N-dimethylanilines (DMAs) were studied in acetonitrile at 35 °C. Rate constants for the reaction of Z-benzyl tosylates with DMAs exhibited a curved Hammett plots, and the apparent ρ_Z values increased negatively in the following sequence $Y=m\text{-NO}_2 > \text{H} > p\text{-MeO} > p\text{-NMe}_2$. This means that the weaker nucleophile magnifies the effect of the benzyl substituent Z. The plot of ρ_Y against $\log(k_Z/k_H)_{Y=H}$ showed good linear relation with a slope of 0.57 and it was discussed that the change in transition state structure was mainly attributed to C-N bond formation. The $|\rho_Y|$ value, determined by introducing of electron-withdrawing substituent in the leaving group, was decreased from -1.75 (X=p-Me) to -1.58 (X=p-NO₂). This result indicates that a poor leaving group requires more nucleophilic assistance.

Introduction

Curved Hammett plot is one of the most characteristic feature of substituent effect in nucleophilic displacement reaction of substituted benzyl system. Although various interpretation have been offered for this borderline behavior,¹⁻¹¹ the way of mechanistic shift for the curvature in the Hammett plot has not been resolved completely. In order to investigate the variation of the structure of S_N2 transition state for benzyl reaction, it is important to evaluate the contribution between the bond formation of nucleophile-benzyl carbon (C_a) and the bond fission of C_a -leaving group. However, variations in the structure of either the nucleophile or the leaving group would change several properties of the reactant, which could not explain how the structure of the reactants affects the structure of a S_N2 transition state.

The Menschutkin-type reaction of benzyl benzenesulfonates with DMAs is a typical S_N2 displacement reaction and accompanies a considerable change in mechanism with substituent changes. Furthermore, this system is highly appropriate to describe the shift of mechanism in terms of the substituent effects for three variables, X, Y, and Z, in three aryl moieties which are capable of monitoring the degree of bond formation, bond fission, and central charge development, respectively, without any steric change in the fundamental framework of the transition state.

In the foregoing paper,¹ we have analyzed the substituent effect on the reactions of substituted Z-benzyl tosylates with DMA, and pointed out a remarkable mechanistic change with substituent Z in the benzyl substrate. Electron-donating sub-



stituents prompted the reaction, indicating positive charge development at the benzyl reaction center in the transition state. The negative ρ_Z values for the whole range of benzyl Z substituents indicate the dominance of the bond fission in the transition state, which becomes looser (or tighter) as the substituent Z becomes more electron donating (or attracting). In this paper, we will concern mainly with the reactions between typical benzyl tosylates and Y-substituted DMAs and an elucidation of the relation between benzyl substituent Z and the contribution to C-N bond formation. The effect of the leaving group on the transition state structure is also discussed.

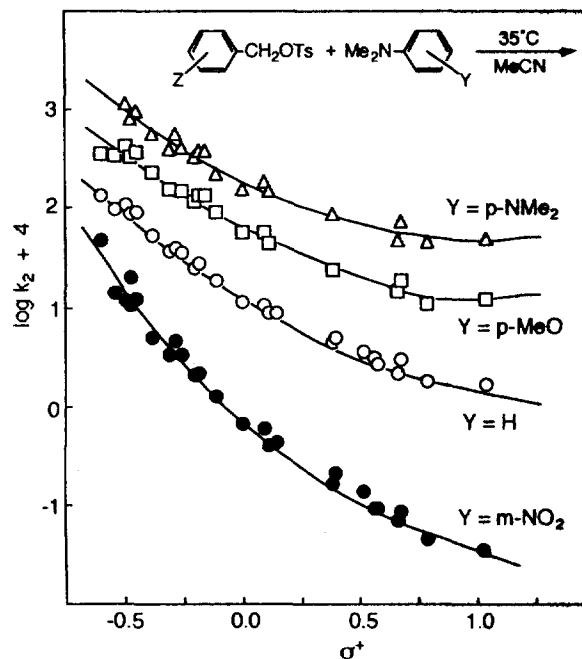
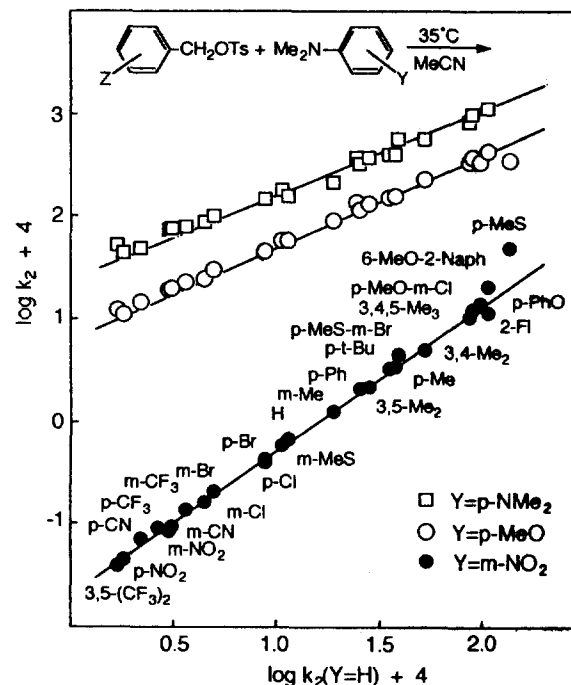
Results and Discussion

The reaction rates of Z-substituted benzyl tosylates with Y-substituted DMAs were measured in acetonitrile at 35 °C by the increase of the conductance of the quaternary anilinium salts at initial concentration of ester 0.0005 M (M = mol dm⁻³) and DMAs 0.1 to 0.25 M as described in the

Table 1. Second-Order Rate Constants ($k_2 \times 10^4$, $\text{L s}^{-1} \text{M}^{-1}$) for the Reactions of *Z*-Substituted Benzyl Tosylates with *Y*-Substituted *N,N*-Dimethylanilines at 35 °C in Acetonitrile

Z	Y= <i>p</i> -NMe ₂	<i>p</i> -MeO	H	<i>m</i> -NO ₂	ρ_Y
<i>p</i> -MeS		351	137	48.3	-0.64
6-MeO-2Naph		499	131	35.6	-0.78
<i>p</i> -PhO		337	98.1	14.2	-1.18
2-Fluorenyl	1140	431	107	11.6	-1.36
<i>p</i> -MeO- <i>m</i> -Cl	825	337	86.8	10.4	-1.30
3,4,5-Me ₃	977	375	90.1	11.8	-1.22
3,4-Me ₂	576	228	52.9	5.05	-1.44
<i>p</i> -MeS- <i>m</i> -Br	560		39.3	4.55	-1.32
<i>p</i> -Me	396	158	37.6	3.39	-1.47
<i>p</i> - <i>t</i> -Bu	409	153	35.1	3.34	-1.44
<i>p</i> -Ph	332	117	25.3	2.09	-1.53
3,5-Me ₂	377	133	28.1	2.20	-1.56
<i>m</i> -Me	219	91.0	18.8	1.27	-1.65
H	159	57.3	11.5	0.684	-1.73
<i>m</i> -MeS	184	57.9	10.6	0.596	-1.76
<i>p</i> -Cl	149	44.6	8.77	0.402	-1.89
<i>p</i> -Br	147	46.3	8.82	0.428	-1.85
<i>m</i> -Cl	88.9	24.3	4.42	0.167	-2.01
<i>m</i> -Br	101	30.2	4.99	0.211	-1.94
<i>m</i> -CF ₃	80.5	23.1	3.68	0.139	-2.01
<i>p</i> -CF ₃			2.60	0.0912	-2.05
<i>m</i> -CN	77.5	20.2	3.117	0.0941	-2.14
<i>p</i> -CN	48.4	14.6	2.184	0.0705	-2.10
<i>m</i> -NO ₂	74.5	19.0	3.005	0.0847	-2.19
<i>p</i> -NO ₂	44.1	11.3	1.820	0.0458	-2.27
3,5-(CF ₃) ₂	53.1	12.5	1.680	0.0404	-2.28

foregoing paper.¹ The second-order rate constants are summarized in Table 1. The rate enhancement with a more electron-donating benzyl substituent indicates that the positive charge developed on benzyl carbon is stabilized by the electron-donating substituents in the transition state as described previously.¹ The change in the benzyl *Z* substituent from *p*-MeS to *p*-NO₂ produces a 32-fold rate decrease with a fixed nucleophile, Y=*p*-MeO, while gives a 1055-fold rate decrease with Y=*m*-NO₂. In other words, the weaker nucleophile magnifies more remarkably the effect of the benzyl substituent *Z*. On the other hand, the rate ratio for the substituent effect of nucleophile Y, ($k_{Y=H}/k_{Y=m\text{-NO}_2}$), varies from 2.8 for *p*-MeS benzyl tosylate to 37 of *p*-NO₂ one. This indicates that the less electron-donating substituent *Z* becomes, the larger contribution from the effect of DMAs is required. The logarithmic rates of substituted benzyl tosylates are plotted against σ^+ in Figure 1 for the Y=*p*-NMe₂, *p*-MeO, H and *m*-NO₂ DMA. The magnitude of the $|\rho_Z|$ values increase as the substituent in the DMA is changed from Y=*p*-NMe₂ to *m*-NO₂ (slope more negative). This fact suggests that the greater positive charge is accumulated at the benzyl carbon by a weaker nucleophile in the transition state. The transition state structure of S_N2 reaction becomes more carbocationic as the nucleophile becomes less nucleophilic. It is worth noting that the reaction of 3,5-bis(trifluoromethyl)benzyl

**Figure 1.** Hammett plots for the reactions of *Z*-substituted benzyl tosylates with *Y*-substituted *N,N*-dimethylanilines in acetonitrile at 35 °C.**Figure 2.** Logarithmic rate plots for the reactions of *Z*-substituted benzyl tosylates with Y=*p*-NMe₂, *p*-MeO, unsubstituted and *m*-NO₂ *N,N*-dimethylanilines.

tosylate with strong nucleophile, Y=*p*-MeO and *p*-NMe₂-DMAs give a rate increase compared with *p*-NO₂ one. In general, the reaction between anionic nucleophile and substituted benzyl derivatives shows a U-shaped Hammett plot with a minimum rate for the unsubstituted compound.⁶⁻¹²

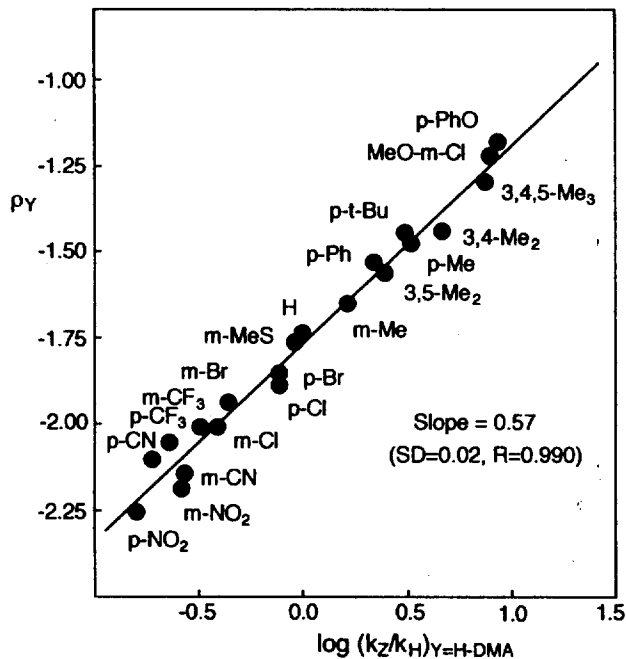


Figure 3. Plot of ρ_Y against $\log(k_Z/k_H)_{Y=H}$.

Similarly, the reaction of benzyl bromides with pyridine showed U-shaped Hammett plot with a minimum rate for *p*-nitro benzyl one.¹³ These results are in agreement with the rate increase for the reaction of 3,5-bis(trifluoromethyl) benzyl tosylate with strong nucleophile as shown in Figure 1, and it can be interpreted that bond formation is ahead of bond fission in the transition state. Figure 1 shows that the transition state should become more S_N1 -like when the substituent of *N,N*-dimethylaniline becomes more electron-attracting. Nevertheless, we see that a good linear free energy relationship (Figure 2) exists among the logarithmic rates for the reaction with different nucleophile,

$$\log(k_Z/k_H)_{Y=p-NMe_2} = 0.75 \log(k_Z/k_H)_{Y=H}; \quad (2)$$

(SD=0.02, R=0.995)

$$\log(k_Z/k_H)_{Y=p-MeO} = 0.85 \log(k_Z/k_H)_{Y=H}; \quad (3)$$

(SD=0.01, R=0.997)

$$\log(k_Z/k_H)_{Y=m-NO_2} = 1.46 \log(k_Z/k_H)_{Y=H}; \quad (4)$$

(SD=0.03, R=0.995).

Thus, the mechanistic shift toward S_N1 induced by the reaction of the benzyl substituent with a weaker nucleophile must occur in a quite similar manner to the change with a relatively stronger nucleophile even if the degree of change is magnified with the weaker nucleophile. Based on the reactivity change with $Y=H$ and $m-NO_2$, ρ_Y value can be estimated for a series of *Z*-substituted benzyl tosylates. The ρ_Y values listed in the last column of Table 1 can be regarded as a relative measure of the degree of C-N bond formation in the transition state. The ρ_Y values change widely and steadily from -2.3 to -0.64 as the benzyl substituent *Z* changes from *p*- NO_2 to *p*-MeS. The degree of bond formation in the reaction of *p*-MeO benzyl tosylate may be a quarter that of *p*- NO_2 one. As reported before,¹ the effect of the benzyl-*Z*-substituents can not be linearly described by any substituent constants, but only as a monotonically curved plot agai-

Table 2. Second-Order Rate Constants ($k_2 \times 10^4$, $s^{-1}M^{-1}$) for the Reactions of Benzyl-X-Benzenesulfonates with *Y*-Substituted *N,N*-Dimethylanilines in Acetonitrile at 35 °C

X	Y=H	<i>m</i> - NO_2	ρ_Y
<i>p</i> -Me	11.5	0.678	-1.75
H	20.8	1.24	-1.73
<i>p</i> -Cl	65.2	3.89	-1.72
<i>p</i> -Br	68.4	4.15	-1.72
<i>m</i> -Cl	110	7.60	-1.64
<i>m</i> - NO_2	473	33.3	-1.62
<i>p</i> - NO_2	459	34.8	-1.58

nst σ^+ . In order to investigate the quantitative relation between C-N bond formation and the electron density of benzyl carbon, the ρ_Y values are plotted against $\log(k_Z/k_H)_{Y=H}$ values in place of σ_Z as shown in Figure 3. The $|\rho_Y|$ values increase linearly with the decrease in electron density at the benzyl carbon. This means that the transition state shifts to loose state (tight) with an increase in the electron-donating (withdrawing) ability of the benzyl *Z*-substituent.

The same discussion can be applied to the ρ_X values¹ which indicates the degree of C-O bond-breaking, and we obtained the slope of 0.07 with correlation coefficient, 0.998. It is worthy of note, the magnitude of slope. The great sensitivity (slope=0.57) of ρ_Y to the change of charge distribution on benzyl carbon can be rationalized in terms of the variation of the relative importance of bond-formation and bond-breaking in the transition state.

For the curvature of the Hammett plot, three possible explanations have been proposed:^{7,14} (i) a mechanistic change from S_N2 to S_N1 as electron-withdrawing substituents are changed to electron-donating ones;^{6,15-17} (ii) a change in the relative importance of bond formation and bond fission in transition state;^{4,8,9,18,19} (iii) a variable resonance effect of the substituents.^{7,14}

The first mechanism can be ruled out because the present Menshutkin reaction displays clean second-order kinetics and is first-order in the substrate and nucleophile, respectively, as far as we treated here. The third possibility can be also excluded because the meta substituent which is absent the resonance effect correlates with the single concave Hammett plot along with the para substituent. Experimental results of the present study support the second explanation and thus the concave Hammett plot in Figure 1 are explained by that greater slope (more carbocationic) for strongly electron donating benzyl substituent should arise as a result of the decrease in the C-N bond formation. The more important contribution by C-N bond formation to the mechanistic change obtained here is compatible with the result of the ^{14}C kinetic isotope effect. Yamataka and Ando²¹ have determined the ^{14}C kinetic isotope effect for the Menshutkin-type reaction between *Y*-DMAs and benzyl *X*-arenesulfonates. They found that substituent *Y* has a large effect of the k^{12}/k^{14} than substituent *X*. This may be characteristic of a typical S_N2 reaction in which the bond formation is relatively more important rather than the bond breaking in the rate-determining step.

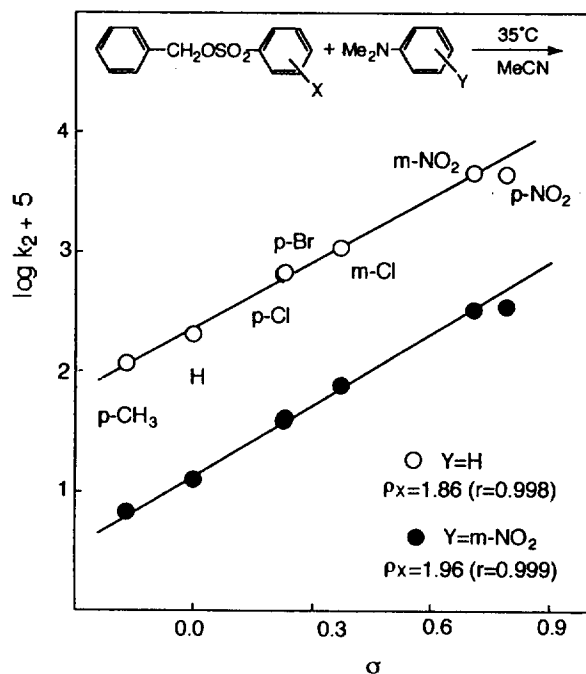


Figure 4. Hammett plots for the reactions of benzyl X-benzenesulfonates with *N,N*-dimethylanilines in acetonitrile at 35 °C.

To study the transition state variation by the leaving group, the second-order rate constants for the reactions of benzyl (X)-substituted benzenesulfonates with DMAs are determined and summarized in Table 2. The Hammett plots of the rate data in Table 2 show good linearity except the *p*-nitro substituent (Figure 4). The anomalous behavior of *p*-nitro substituent along with all para +R groups has been revealed in solvolytic or nucleophilic displacement reaction of the benzene sulfonate systems.^{22,23} The π -delocalization from aryl π -system to the NO₂ group is saturated because of repulsive interaction of charge produced at adjacent position with positive charge at the sulfur atom.²³ The downward deviation of *p*-nitro substituent in Figure 4, thus, can be explained in terms of the diminution of π -acceptor resonance. In Figure 4, the ρ_X value increases from 1.86 (Y=H) to 1.96 (Y=*m*-NO₂), which means that the bond breaking is more progressed as the nucleophile becomes weaker.

The relationships between bond formation and nucleofuge in benzyl reaction can not be explained clearly. Ballisteri *et al.* have reported the Hammett ρ_Y values for the reactions of benzyl halides with Y-anilines;³ the ρ_Y value decreased from -1.46 to -0.87 when the leaving group changed from iodide to chloride. Furthermore, Westway and Ali measured the ρ_Y value and isotope effect for the reaction between Y-thiophenoxide ion and aryl benzyl dimethylammonium ion, and concluded that more nucleophilic assistance is required to displace a better leaving group given.²⁵ These results suggest that changing to a better leaving group leads to product-like transition state structure. However, Table 2 shows that the $|\rho_Y|$ values decrease gradually as the substituent in the leaving moiety is changed from *p*-Me to *p*-NO₂, which means that C-N bond formation decreases progressively with a better leaving group. This is in complete agreement with the result of the Brønsted treatment for present reaction in ace-

tone.²⁴ In the case of present reaction system, thus, the better leaving group do not yield a "product-like" transition state but a "loose" one. This suggestion agrees with the prediction of More O'Ferrall diagram for the effect of leaving group variation on S_N2 transition state structure.²⁶

Experimental

Materials. Purification of acetonitrile, substrate preparation, and product analysis have been previously described.¹ *N,N*-dimethylaniline and its *p*-NMe₂ and *m*-NO₂ derivatives were commercially available and were further purified by distillation or recrystallization before use. *N,N*-Dimethyl-*p*-methoxyaniline was synthesized²⁷ by the reduction of *N,N,N*-trimethyl-*p*-methoxyphenyl ammoniumiodide with LiAlH₄ which was prepared from *p*-anisidine and methyl iodide by Sandler's method,²⁸ mp 45.2-45.9 °C (lit. mp²⁹ 47 °C, 48-49 °C).³⁰

Kinetic Measurements. Rates were measured conductimetrically as described before.¹ The pseudo-first-order rate constants were determined by the least-squares computer program. The precision of the fit to pseudo-first-order kinetics was generally satisfactory, with correlation coefficient > 0.99995 over 2.5 half-lives of the reaction. For more reactive substrate than *p*-methylbenzyl tosylate, second-order rate constants were determined from the linear part with correlation coefficients ≥ 0.999 of the plot of k_{obs} vs. amine concentration. Second-order rate constants of other substrates were determined by dividing pseudo-first-order rate constants by the initial amine concentration.

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Resolution of Amide Derivatives of Naproxen on Pirkle-Type π -Acidic Chiral Stationary Phases

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A chiral recognition model which explains the chiral resolution behavior of N-alkyl amide derivatives of naproxen on the Pirkle type π -acidic CSPs derived from N-(3,5-dinitrobenzoyl)-(R)-phenylglycine and N-(3,5-dinitrobenzoyl)-(S)-leucine has been proposed. Based on the proposed model, an effort to improve the resolution of racemic naproxen derivatives on the CSP has been devoted and consequently, N-alkyl N-aryl amides of naproxen or N-alkyl N-cyclohexyl amides of naproxen have been found to be resolved quite well on a Pirkle type π -acidic CSP. Based on the reciprocity conception of chiral recognition, CSPs which might show excellent resolving ability for π -acidic racemic compounds have been suggested.

Introduction

Enantiomers of chiral drugs often show different biological activities¹ and, in consequence, the enantiomeric composition of chiral drugs has been an important issue in developing and using them.² The nonsteroidal anti-inflammatory drugs (NSAIDs) related to α -arylpropionic acids are one class of pharmaceutical compounds which exhibit the contrasting behavior of the two enantiomers. In general, the (S)-enantiomers of NSAIDs are more active for the desired therapeutic effect than the corresponding (R)-enantiomers and the (R)-enantiomers undergo metabolic inversion of configuration *in vivo*.³ In this instance, accurate and convenient means of measuring the enantiomeric purity of chiral drugs including NSAIDs has been sought.⁴

Chiral liquid chromatography based on chiral stationary phases (CSPs) has been most successfully applied to separate the two enantiomers of NSAIDs related to α -arylpropionic acids.⁵ Among others, the alkyl amide derivatives of racemic

NSAIDs have been resolved on CSP **1** derived from (R)-N-(3,5-dinitrobenzoyl)phenylglycine.^{5a-e} To rationalize the chromatographic resolution results of the alkyl amide derivatives of NSAIDs on CSP **1**, Wainer and Doyle proposed a chiral recognition model utilizing the dipole stacking of amide dipoles and the π - π interaction between the dinitrobenzoyl group of the CSP and the aryl substituent of the analyte.^{5a} Subsequently, this chiral recognition model was recognized by Pirkle as a "head-to-head" chiral recognition model.^{5e} However, resolving a homologous series of alkyl amide derivatives of racemic naproxen on CSP **2** derived from (S)-N-(3,5-dinitrobenzoyl)leucine, we found that the chromatographic resolution results are somewhat different from those on CSP **1**. To rationalize the differences between the chromatographic resolution results on CSP **1** and **2**, we herein propose an improved chiral recognition model utilizing the face-to-edge π - π interaction which has attracted considerable attention as an associative force between aromatic rings in the recent studies⁶ and the hydrogen bonding interaction