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# Comparison of Crystal Structures of New Racemic Chiral Compounds Showing and Not Showing the Phenomenon of Preferential Enrichment\*

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The crystal structures of ( $\pm$ )-[2-[4-(3-ethoxy-2-hydroxypropoxy)phenylcarbamoyl]ethyl] trimethylammonium *p*-chlorobenzenesulfonate [( $\pm$ )-NCMe<sub>3</sub>] and its terminal methoxy derivative, ( $\pm$ )-NCMe<sub>3</sub>-OMe, are compared. The former racemate exhibited the phenomenon of Preferential Enrichment, whereas the latter failed to do so. Crystal data, ( $\pm$ )-NCMe<sub>3</sub>: CuK $\alpha$  radiation, space group *P*1, *Z* = 2, *a* = 9.848(5), *b* = 14.823(3), *c* = 9.147(1) Å,  $\alpha$  = 97.81(1),  $\beta$  = 92.68(3),  $\gamma$  = 105.92(2)°, *D*<sub>calc</sub> = 1.355 g/cm<sup>3</sup>, *R* = 0.056 for 3213 observed reflections; ( $\pm$ )-NCMe<sub>3</sub>-OMe: CuK $\alpha$  radiation, space group *P*1, *Z* = 2, *a* = 11.350(1), *b* = 14.568(2), *c* = 8.2981(4) Å,  $\alpha$  = 94.346(7),  $\beta$  = 112.376(5),  $\gamma$  = 78.622(9)°, *D*<sub>calc</sub> = 1.343 g/cm<sup>3</sup>, *R* = 0.069 for 1519 observed reflections.

**Keywords:** Preferential Enrichment; Enantiomeric resolution; Mixed crystal; Racemic compound; X-ray crystallography

## INTRODUCTION

Recently a new enantiomeric resolution phenomenon has been found to occur by simple

recrystallization of a series of certain racemic chiral compounds (( $\pm$ )-ST [1, 2], SC [3], SN [4], NNMe<sub>2</sub> [5], NCMe<sub>2</sub> [6] and NBMe<sub>3</sub> [7]) and has been referred to as "Preferential Enrichment". Preferential Enrichment has the following features: (1) Repeated recrystallization of the racemate and each crop of deposited crystals results in a remarkable alternating enrichment of the two enantiomers up to 100% *ee* in the mother liquors (*enantiomeric enrichment in the mother liquors*) with full reproducibility. (2) When nonracemic samples with low *ee* values are recrystallized, the resulting deposited crystals with low *ee* values (less than 10% *ee*) always display the opposite chirality (*reversal of chirality in the deposited crystals*) as shown in Scheme 1. (3) Only the racemates or nonracemates with low *ee* values have to be crystalline, since highly enantiomerically enriched materials are obtained from the mother liquor. These unique

\* Dedicated to Professor Fumio Toda on the occasion of his 67th birthday.

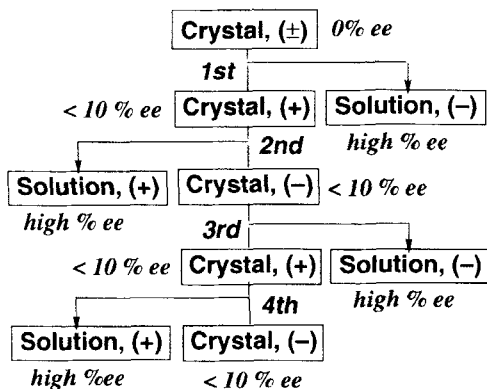
<sup>†</sup> Corresponding author.

features are quite different from those of the preferential crystallization of enantiomeric conglomerates in which considerable enantiomeric enrichment occurs in the deposited crystals [8].

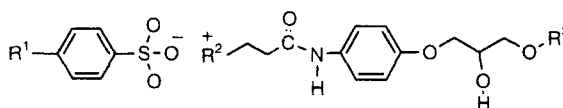
The investigation of the crystal properties of the racemate, nonracemate and pure enantiomer of ST [1,2] has indicated that the polymorphic transformation from a less ordered metastable crystal phase into a more ordered stable one during crystallization might be closely related to the phenomenon of Preferential Enrichment. In order to predict the mode of the polymorphic transformation associated closely with the mechanism of Preferential Enrichment, it is indispensable to elucidate each stable crystal structure of the compounds, which effect the phenomenon of Preferential Enrichment, as well as the molecular association mode in solution. We have compared three different crystal struc-

tures of three compounds (NNMe<sub>2</sub> [5], NCMe<sub>2</sub> [6] and NTMe<sub>2</sub> [5]) obtained by slight modification of the molecular structure; NNMe<sub>2</sub> was an ordered racemic compound crystal, NCMe<sub>2</sub> was a fairly ordered racemic mixed crystal, and NTMe<sub>2</sub> was a highly disordered racemic mixed crystal. The racemates of NNMe<sub>2</sub> and NCMe<sub>2</sub> successfully effected Preferential Enrichment, whereas that of NTMe<sub>2</sub> failed to do so. These results indicated the large electronic effects of the para substituent on the benzenesulfonate anion upon the crystal structure and thereby the occurrence of Preferential Enrichment.

In order to investigate other substituent effects, we prepared NNMe<sub>2</sub>-OMe, NCMe<sub>2</sub>-OMe and NTMe<sub>2</sub>-OMe, the terminal methoxy derivatives of NNMe<sub>2</sub>, NCMe<sub>2</sub> and NTMe<sub>2</sub>, respectively, and the racemates of these three new compounds were subjected to Preferential Enrichment conditions. Contrary to our expectation, only (●)-NNMe<sub>2</sub>-OMe exhibited the phenomenon of Preferential Enrichment. Since it is not clear why (±)-NCMe<sub>2</sub>-OMe failed to show the phenomenon, we tried to clarify this reason on the basis of the crystal structure of (±)-NCMe<sub>2</sub>-OMe. But due to its tendency to form polycrystalline powders, it was impossible to obtain a single crystal of (±)-NCMe<sub>2</sub>-OMe. Therefore, we have synthesized the racemates of NCMe<sub>3</sub> and NCMe<sub>3</sub>-OMe, the quarternary ammonium analogues of NCMe<sub>2</sub> and NCMe<sub>2</sub>-OMe, respectively, which might give single crystals of adequate quality for X-ray analysis like (±)-NBMe<sub>3</sub> [7]. As expected, (±)-NCMe<sub>3</sub> showed



SCHEME 1 Preferential Enrichment.



ST: R<sup>1</sup>=Me, R<sup>2</sup>=Me<sub>2</sub>S, R<sup>3</sup>=Et  
 SC: R<sup>1</sup>=Cl, R<sup>2</sup>=Me<sub>2</sub>S, R<sup>3</sup>=Et  
 SN: R<sup>1</sup>=NO<sub>2</sub>, R<sup>2</sup>=Me<sub>2</sub>S, R<sup>3</sup>=Et  
 NNMe<sub>2</sub>: R<sup>1</sup>=NO<sub>2</sub>, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Et  
 NCMe<sub>2</sub>: R<sup>1</sup>=Cl, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Et  
 NBMe<sub>3</sub>: R<sup>1</sup>=Br, R<sup>2</sup>=Me<sub>3</sub>N, R<sup>3</sup>=Et  
 NTMe<sub>2</sub>: R<sup>1</sup>=Me, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Et  
 NNMe<sub>2</sub>-OMe: R<sup>1</sup>=NO<sub>2</sub>, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Me  
 NCMe<sub>2</sub>-OMe: R<sup>1</sup>=Cl, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Me  
 NTMe<sub>2</sub>-OMe: R<sup>1</sup>=Me, R<sup>2</sup>=Me<sub>2</sub>HN, R<sup>3</sup>=Me  
 NCMe<sub>3</sub>: R<sup>1</sup>=Cl, R<sup>2</sup>=Me<sub>3</sub>N, R<sup>3</sup>=Et  
 NCMe<sub>3</sub>-OMe: R<sup>1</sup>=Cl, R<sup>2</sup>=Me<sub>3</sub>N, R<sup>3</sup>=Me

STRUCTURE

the phenomenon of Preferential Enrichment, whereas ( $\pm$ )-NCMe<sub>3</sub>-OMe failed to do so. Here we compare the crystal structures of ( $\pm$ )-NCMe<sub>3</sub> and ( $\pm$ )-NCMe<sub>3</sub>-OMe and describe why Preferential Enrichment was not observed for the latter compound.

## RESULTS AND DISCUSSION

The single crystals of ( $\pm$ )-NCMe<sub>3</sub> and ( $\pm$ )-NCMe<sub>3</sub>-OMe were prepared by recrystallization from the twofold supersaturated solutions in 2-propanol, followed by slow evaporation of the solvent at 25°C, and subjected to X-ray crystal structure analysis (Tab. I).

The crystal structure of ( $\pm$ )-NCMe<sub>3</sub> is shown in Figure 1. The stable crystalline form of ( $\pm$ )-NBMe<sub>3</sub> is not a racemic compound, but a fairly ordered racemic mixed crystal composed of the two enantiomers. This crystal structure is similar to that of ( $\pm$ )-NCMe<sub>2</sub> [6] and essentially identical to that of ( $\pm$ )-NBMe<sub>3</sub> (Fig. 2) [7]. The orientational disorder was observed at the position of the hydroxy group on an asymmetric carbon atom. Constrained refinement of these two positions gave occupancy factors of 0.771 and 0.229 for O2a and O2b, respectively, for ( $\pm$ )-NCMe<sub>3</sub>. Hence, either the *R* or the *S* enantiomer can be located at the same site in the crystal lattice. The corresponding occupancy factors were 0.737 and 0.263 for O2a and O2b of ( $\pm$ )-NCMe<sub>2</sub> [6], and 0.684 and 0.316 for those of ( $\pm$ )-NBMe<sub>3</sub> [7], respectively. The crystal structure of ( $\pm$ )-NCMe<sub>3</sub> is characterized by hydrogen bonds between the hydroxy group and the amide carbonyl oxygen atom of the long-chain cation to give the minor dimer structure (type I) (O2b...O4' and O2b'...O4 2.73(1) Å) and between the hydroxy group and the ethoxy oxygen atom to give the major dimer structure (type II) (O2a...O1' and O2a'...O1 2.8806(4) Å, O2b...O1' and O2b'...O1 3.17(1) Å). From the occupancy factors for O2a and O2b, the contents of the type I and type II dimer

TABLE I Crystallographic data

	( $\pm$ )-NCMe <sub>3</sub>	( $\pm$ )-NCMe <sub>3</sub> -OMe
Crystal habit	prism	plate
Crystal size	0.30 × 0.05 × 0.20	0.35 × 0.25 × 0.01
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> [Å]	9.848(5)	11.350(1)
<i>b</i> [Å]	14.823(3)	14.568(2)
<i>c</i> [Å]	9.147(1)	8.2981(4)
$\alpha$ [°]	97.81(1)	94.346(7)
$\beta$ [°]	92.68(3)	112.376(5)
$\gamma$ [°]	105.92(2)	78.622(9)
<i>V</i> [Å <sup>3</sup> ]	1267.2(7)	1243.7(2)
<i>Z</i>	2	2
<i>F</i> (000)	548	530
<i>D</i> <sub>calc</sub> [g cm <sup>-3</sup> ]	1.355	1.343
2 $\theta$ max	120.1°	135.9°
Total data	4018	3997
Collected		
Independent reflections	3763	3781
Observed reflections	3213	1519
[ <i>I</i> > 2.00 $\sigma$ ( <i>I</i> )]		
Godness of fit	2.95	0.98
<i>R</i> / <i>R</i> <sub>w</sub> <sup>a</sup>	0.056/0.097	0.069/0.245
$\rho$ max[e Å <sup>-3</sup> ]	0.39	0.76
$\rho$ min[e Å <sup>-3</sup> ]	-0.36	-0.25

<sup>a</sup>  $R_I = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  for  $I > 2.00\sigma(I)$  data,  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$ ; Weighting  $w = [\sigma^2(F_o) + (pF_o/2)]^{-1}$ , where  $p = (F_o^2 + 2F_c^2)/3$ .

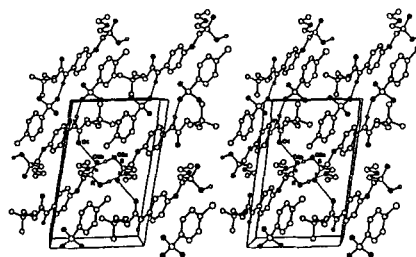


FIGURE 1 Crystal structure of ( $\pm$ )-NCMe<sub>3</sub> viewed down the *a* axis (stereoview). The *b* axis is vertical, and the *c* axis is horizontal. The oxygen atoms are represented by black circles. Hydrogen atoms are omitted for clarity except for those of hydroxy groups. Hydrogen bonds are indicated by thin lines. *R* and *r* represent the more and less highly occupied sites of the *R* enantiomers, and *S* and *s* the corresponding sites of the *S* enantiomer.

structures in the crystal were estimated to be 0.052 (0.229 × 0.229) or less and 0.594 (0.771 × 0.771) or less, respectively. Thus, the overall content of these two cyclic dimers in

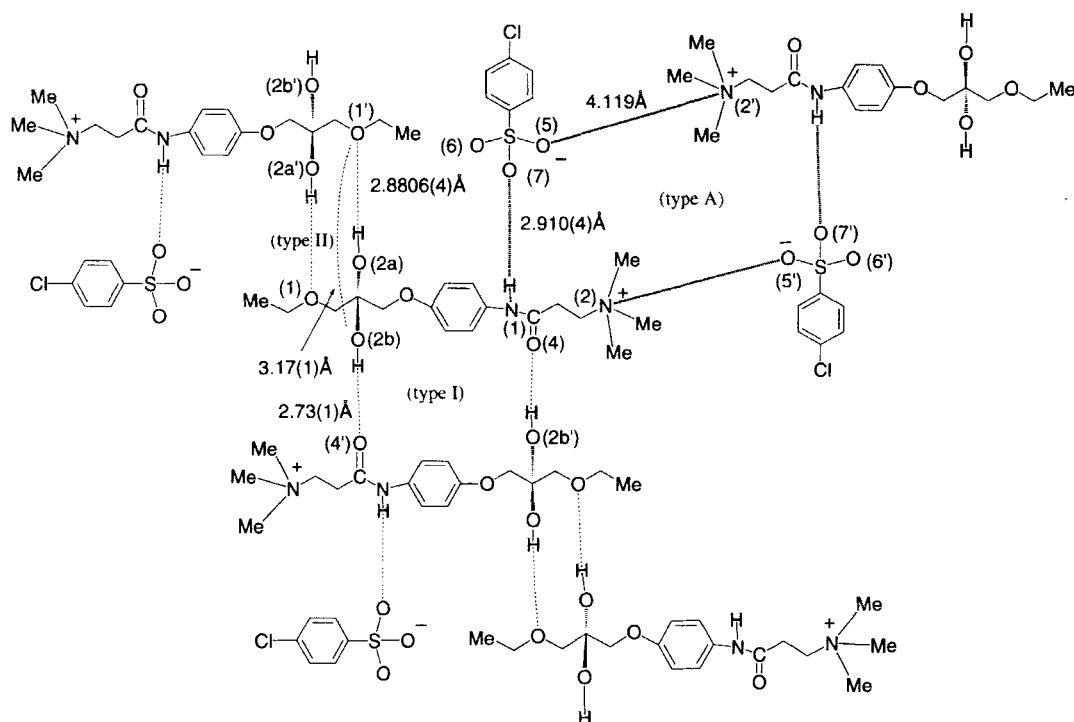


FIGURE 2 Schematic representation of the intermolecular interactions (types I, II and A) in the crystal of  $(\pm)$ -NCMe<sub>3</sub>.

the crystal of  $(\pm)$ -NCMe<sub>3</sub> is 0.646 or less and the rest of the crystal is composed of equal amounts of *R* and *S* enantiomers that do not give cyclic dimers containing the asymmetric center. Similarly to  $(\pm)$ -NCMe<sub>2</sub> and  $(\pm)$ -NCMe<sub>3</sub>, the electrostatic interactions and hydrogen bonds among the ammonium nitrogen atoms, the sulfonate oxygen atoms and the amido NH groups were observed in the crystal structure of  $(\pm)$ -NCMe<sub>3</sub>, forming the third head-to-head cyclic dimer (type A) which is not directly affected by the asymmetric center as shown in Figure 2 (bold dotted lines). Furthermore, the electrostatic interactions between the ammonium nitrogen atoms and the sulfonate oxygen atoms (O6···N2 4.038(6) Å and O6···N2' 3.804(5) Å) formed the fourth head-to-head cyclic dimer (type B) (bold dotted lines in Fig. 3) in the crystal of  $(\pm)$ -NCMe<sub>3</sub>, which was also observed in that of  $(\pm)$ -NBMe<sub>3</sub> but not in that of  $(\pm)$ -NCMe<sub>2</sub>. This dimer was connected to the

neighboring same one through weak electrostatic interactions between another sulfonate oxygen atom and the neighboring ammonium nitrogen atoms (O5···N2 and O5'···N2' 4.119 Å, Fig. 3). Consequently, these interactions form a two-dimensional sheet structure on the [110] plane.

The crystal structure of  $(\pm)$ -NCMe<sub>3</sub>-OMe is shown in Figure 4. The crystalline form of  $(\pm)$ -NCMe<sub>3</sub>-OMe is a racemic compound; no orientational disorder was observed at the position of the hydroxy group on an asymmetric carbon atom. This crystal structure has a very similar part to  $(\pm)$ -NCMe<sub>3</sub> as well as a very different one. The formation of two cyclic dimer structures of types II and A owing to hydrogen bonds and electrostatic interactions were again observed in the crystal of  $(\pm)$ -NCMe<sub>3</sub>-OMe, resulting in the formation of a one-dimensional network (Fig. 5). Noteworthy is the fact that there are two unique intermolecular interactions in the crystal of  $(\pm)$ -NCMe<sub>3</sub>-OMe; one is the

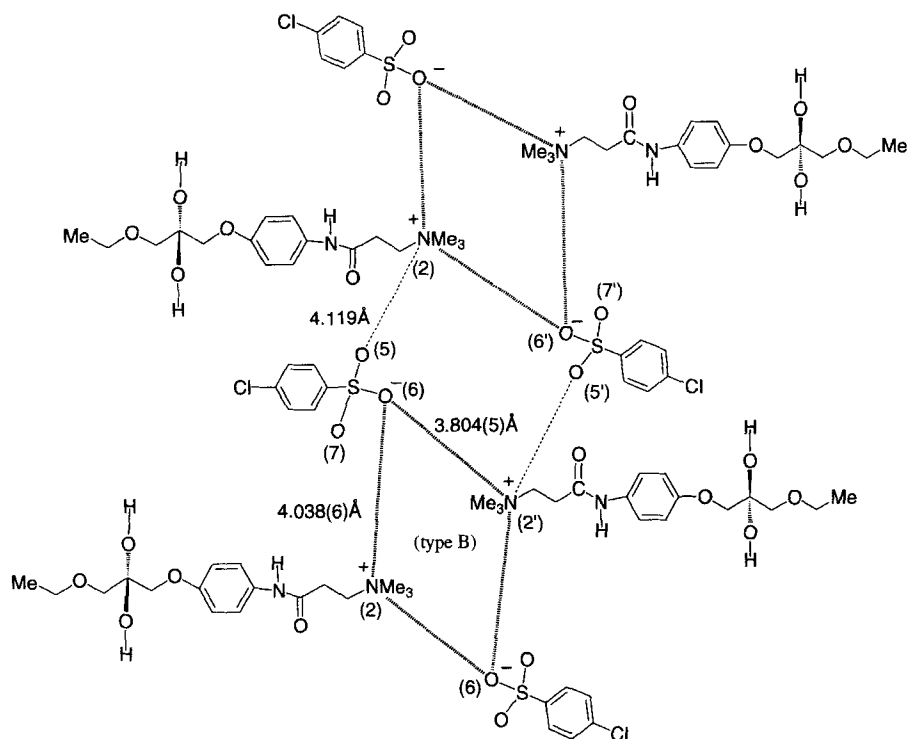


FIGURE 3 Schematic representation of the intermolecular interactions (type B) in the crystal of  $(\pm)$ -NCMe<sub>3</sub>.

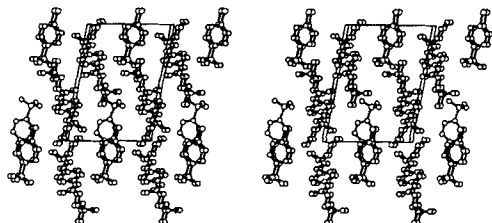


FIGURE 4 Crystal structure of  $(\pm)$ -NCMe<sub>3</sub>-OMe viewed down the  $c$  axis (stereoview). The  $b$  axis is vertical, and the  $a$  axis is horizontal. Hydrogen atoms are omitted for clarity.

weak  $\pi$ - $\pi$  stacking (plane distance 3.54 Å) between the benzene rings of the nearest two *p*-chlorobenzenesulfonate groups along the  $a$  axis, which are aligned in an antiparallel manner to each other, and the other is the weak C(sp<sup>2</sup>)H $\cdots$ Cl contacts (H $\cdots$ Cl distances 3.105(1) and 3.115(1) Å) between one chlorine atom of the *p*-chlorobenzenesulfonate group and vicinal two hydrogen atoms on the benzene ring

of the long chain cation (Fig. 5), resulting in connections among the above one-dimensional networks to form two-dimensional networks. The cyclic dimers of types I and B were not observed in this crystal. Instead, there are one-dimensional intermolecular interactions between ammonium nitrogen atoms through the intermediary of one sulfonate group (N2 $\cdots$ O6' and N2' $\cdots$ O6 distance 4.003(9) Å, N2 $\cdots$ O5' and N2' $\cdots$ O5 distance 3.787(6) Å) (bold dotted lines in Fig. 6). The interplay of these intermolecular interactions shown in Figures 5 and 6 defines the crystal structure of  $(\pm)$ -NCMe<sub>3</sub>-OMe, leading to the formation of the more rigid three-dimensional network structure.

In summary, by comparison of the molecular structure of  $(\pm)$ -NCMe<sub>3</sub>-OMe with that of  $(\pm)$ -NCMe<sub>3</sub>, it can be understood that the slight change in the size of the terminal alkoxy groups largely affects the crystal

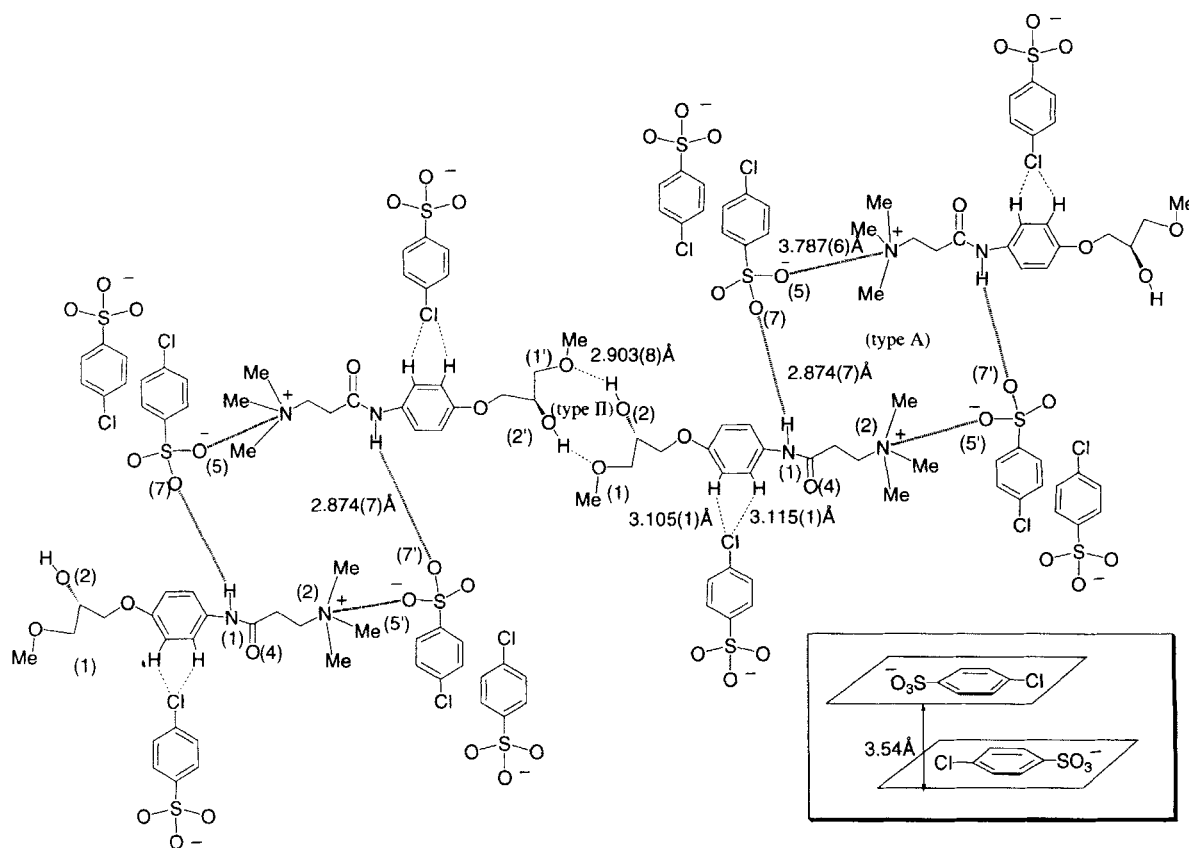


FIGURE 5 Schematic representation of the intermolecular interactions (types II and A,  $\pi$ - $\pi$ , and H $\cdots$ Cl) in the crystal of ( $\pm$ )-NCMe<sub>3</sub>-OMe.

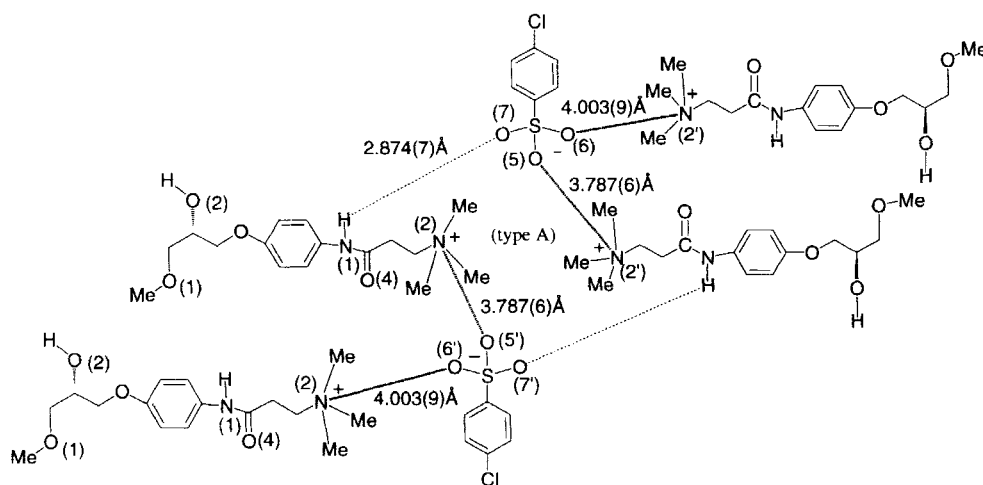


FIGURE 6 Schematic representation of additional intermolecular interactions in the crystal of ( $\pm$ )-NCMe<sub>3</sub>-OMe.

structure and eventually controls the occurrence of Preferential Enrichment. Since ( $\pm$ )-NCMe<sub>3</sub>-OMe cannot accommodate excess enantiomers in the crystal lattice, the deposition of the crystals with low *ee* values, which is a unique feature of Preferential Enrichment, cannot occur. Probably this would be the main reason why Preferential Enrichment did not occur for NCMe<sub>3</sub>-OMe.

## EXPERIMENTAL

### Synthesis

( $\pm$ )-NCMe<sub>3</sub>: ( $\pm$ )-[2-[4-(3-Ethoxy-2-hydroxypropoxy)phenylcarbamoyl] - ethyl]dimethylamine [( $\pm$ )-1] was prepared according to the published procedure [4]. To a solution of ( $\pm$ )-1 (2.95 g, 9.51 mmol) in acetone (25 ml) was added methyl *p*-chlorobenzenesulfonate (2.96 g, 10.4 mmol). The mixture was stirred for 4 h at 55°C, then cooled to 25°C, and the deposited crystals were filtered and washed successively with cold acetone and ether to give 3.51 g (6.85 mmol, 72%) of ( $\pm$ )-NCMe<sub>3</sub> as colorless crystals. IR (KBr)  $\nu$  3396, 3145, 3035, 2927, 2869, 1685, 1612, 1556, 1513, 1245, 1189, 1105 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  1.18(3H, *t*, *J*=7.0 Hz), 2.94(2H, *t*, *J*=7.3 Hz), 3.16(9H, *s*), 3.50–3.62(4H, *m*), 3.73(2H, *t*, *J*=7.3 Hz), 3.94–4.06(3H, *m*), 6.90(2H, *d*, *J*=8.9 Hz), 7.41(2H, *d*, *J*=8.5 Hz), 7.44(2H, *d*, *J*=8.9 Hz), 7.78(2H, *d*, *J*=8.5 Hz); <sup>13</sup>C NMR (CD<sub>3</sub>OD)  $\delta$  15.4, 31.0, 53.7, 65.5, 67.9, 70.2, 70.8, 72.7, 115.8, 122.9, 122.7, 129.4, 132.7, 137.1, 145.2, 157.3, 168.4. Anal. Calcd. for C<sub>23</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>7</sub>S: C, 53.43%; H, 6.43%; N, 5.42%. Found: C, 53.04%; H, 6.23%; N, 5.27%.

( $\pm$ )-NCMe<sub>3</sub>-OMe: ( $\pm$ )-[2-[4-(3-Methoxy-2-hydroxypropoxy)phenylcarbamoyl]ethyl]dimethylamine [( $\pm$ )-2] was similarly prepared according to the published procedure [4]. To a solution of ( $\pm$ )-2 (0.111 g, 0.37 mmol) in acetone (25 ml) was added methyl *p*-chlorobenzenesulfonate (0.083 g, 0.40 mmol). The mixture was

stirred for 26 h at 55°C, then cooled to 25°C, and the deposited crystals were filtered and washed with cold ether to give 0.164 g (0.33 mmol, 88%) of ( $\pm$ )-NCMe<sub>3</sub>-OMe as colorless crystals. IR (KBr)  $\nu$  3420, 3134, 2936, 1682, 1607, 1510, 1481, 1418, 1229, 1184, 1087, 1038, 1010 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  2.91(2H, *m*), 3.15(9H, *s*), 3.28(3H, *s*), 3.48(2H, *m*), 3.69(2H, *m*), 3.95(3H, *m*), 6.87(2H, *d*, *J*=8.9 Hz), 7.38(2H, *d*, *J*=8.2 Hz), 7.40(2H, *d*, *J*=8.9 Hz), 7.75(2H, *d*, *J*=8.2 Hz); <sup>13</sup>C NMR (CD<sub>3</sub>OD)  $\delta$  31.1, 53.8, 63.6, 70.2, 70.8, 72.8, 74.2, 115.7, 122.8, 128.5, 129.3, 132.5, 137.0, 145.0, 157.0, 168.2. Anal. Calcd. for C<sub>22</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>7</sub>S: C, 52.53%; H, 6.19%; N, 5.57%. Found: C, 52.32%; H, 6.17%; N, 5.59%.

### Crystallography

For the X-ray crystallographic analysis, the single crystals were mounted in a glass capillary. The crystal data for all compounds are listed in Table I. The data collections were performed at 293K (CuK $\alpha$   $\lambda$ =1.5418 Å, graphite monochromator) on a Rigaku AFC7R for ( $\pm$ )-NCMe<sub>3</sub> and an Enraf-Nonius CAD4 diffractometer for ( $\pm$ )-NCMe<sub>3</sub>-OMe by the  $\omega$ -2 $\theta$  scans method. The structures were solved by the direct methods (SIR92 or SAPI91), and refined full-matrix least-squares against  $|F|^2$ , with all non-hydrogen atoms anisotropic thermal parameters and all hydrogen atoms fixed at calculated positions. Empirical absorption corrections were applied for both crystals. All calculations were performed with the crystallographic software package teXsan [9].

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