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RESOLUTION OF AROMATIC COMPOUNDS ON A *Λ*-Ru(1,10-PHENANTHROLINE)$_3^{2+}$–MONTMORILLONITE COLUMN

AKIHIKO YAMAGISHI
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)
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SUMMARY

The chromatographic resolution of aromatic molecules was investigated on a 2 cm × 1.2 cm O.D. *Λ*-Ru-tris(1,10-phenanthroline)$^{2+}$ [*Λ*-Ru(phen)$_3^{2+}$]–montmorillonite column. The following three groups of compounds were resolved partially when they were eluted with methanol–water mixtures: (A) 2,2′-dihydroxy-1,1′-binaphthyl, 2,2′-dimethyl-1,1′-binaphthyl and 2,2′-diamino-1,1′-binaphthyl; (B) 2,3-dihydro-2-methyl-5,6-diphenylpyrazine and *trans*-2,3-diphenyl-5,6,7,8,9,10-hexahydroquinoxaline; and (C) benzoin, hydrobenzoin and 1,2-diphenylethanol. In contrast, the following compounds were not resolved, although they seemed to belong to the indicated groups: (A) 2,2′-dibromo-1,1′-binaphthyl; (B) 2,3-dihydro-2-methyl-5,6-dimethylpyrazine; and (C) 1-phenylethanol. These results suggest that a resolved molecule was adsorbed by the column material with its two aromatic groups interacting with *Λ*-Ru(phen)$_3^{2+}$. For a preferred enantiomer, the molecular planes of the aromatic groups would be preferably stacked with the two phenanthroline ligands in *Λ*-Ru(phen)$_3^{2+}$.

INTRODUCTION

Sodium ions in sodium montmorillonite are exchanged quantitatively with the optically active tris(1,10-phenanthroline) complexes of bivalent metal ions [M(phen)$_3^{2+}$][1]. In the resultant compound, *Λ*-M(phen)$_3^{2+}$–montmorillonite, for example, the chiral centres due to pre-adsorbed *Λ*-M(phen)$_3^{2+}$ are distributed two-dimensionally on the silicate sheet of a clay. Previous studies revealed that these chiral centres are effective in recognizing the absolute configuration of an approaching molecule[1]. Based on this, liquid column chromatography on a *Δ*- or *Λ*-M(phen)$_3^{2+}$–montmorillonite (M = Ni and Ru) was successful in resolving various inorganic metal complexes[2]. Resolution was achieved by the intermolecular interaction of a resolved molecule with a pre-adsorbed optically active M(phen)$_3^{2+}$ ion. The phenanthroline ligands in M(phen)$_3^{2+}$ would stack with the ligands of a resolved chelate in selecting the more preferable partner with M(phen)$_3^{2+}$.

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If the intermolecular force between phenanthroline ligands and a resolved molecule is responsible for the achievement of resolution, the same column would be expected to resolve also an organic molecule, if some parts of the molecule stack with the phenanthroline ligands in a similar manner to the ligands of a metal complex. Such stacking would be particularly likely when the molecules have bulky functional groups such as benzene rings. These expectations prompted an investigation of the chromatographic resolution of aromatic molecules on a column of *Λ*-$Ru(phen)_3^{2+}$–montmorillonite. This column was found to resolve organic molecules when these molecules possess two aromatic groups at adjacent positions (cyclic aliphatic molecules were also resolved on this column[3]).

EXPERIMENTAL

Solid *Λ*-$Ru(phen)_3^{2+}$–montmorillonite (< 70 mesh) was prepared as described previously[2]. About 67% of the Na^+ in sodium montmorillonite was replaced with *Λ*-$Ru(phen)_3^{2+}$. A 1.5-g amount of the material was used to form a 2 × 1.2 cm O.D. column in wet conditions.

2,2′-Dihydroxy-1,1′-binaphthyl (Tokyo, Kasei, Japan), benzoin (Wako, Japan), 1,2-diphenylethanol (Tokyo, Kasei) and 1-phenylethanol (Tokyo Kasei) were commercially available and used without further purifications. 2,3-Dihydro-2-methyl-5,6-diphenylpyrazine, *trans*-2,3-diphenyl-5,6,7,8,9,10-hexahydroquinoxaline and 2,3-dihydro-2-methyl-5,6-dimethylpyrazine were prepared according to the literature[4]. 2,2′-Dimethyl-1,1′-binaphthyl, 2,2′-diamino-1,1′-binaphthyl and 2,2′-dibromo-1,1′-binaphthyl were donated by Prof. R. Noyori (Nagoya University, Japan) and hydrobenzoin by Prof. T. Matsumoto (Hokkaido University, Japan).

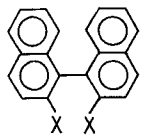
Chromatography was carried out at room temperature. Usually 1–2 mg of a compound in 1 ml of methanol–water was placed on a column. The eluent flow-rate was 0.1–0.3 ml min^{-1} under a pressure of 1–2 kg cm^{-2} of helium. The UV spectra and optical rotatory dispersion (ORD) curves of the collected fractions were recorded on a JEOL Model ORD/CD-5 optical rotatory spectrometer.

The solubilities of the compounds in methanol–water solvent were determined by measuring the UV spectra of the supernatant solution after centrifuging a mixture of the solvent and a large excess of the solid compound.

RESULTS

Resolution of 2,2′-dihydroxy-1,1′-binaphthyl (I) and its analogues

The compound first investigated was 2,2′-dihydroxy-1,1′-binaphthyl (I) (Fig.



X = (I) OH, (II) CH_3, (III) NH_3, and (IV) Br

Fig. 1. 1,1′-Binaphthyl derivatives.

1). I has C_2 symmetry and its chirality originates from the two naphthyl groups twisted around the C_2 axis. Such a propeller-like structure might allow molecules of I to stack with Λ-Ru(phen)$_3^{2+}$ stereoselectively on a clay surface. According to previous studies on the resolution of metal complexes, it was desirable for the eluent to contain as much water as possible[2]. A methanol-water mixture was therefore selected as the eluent and Fig. 2 shows the solubility of I in methanol–water at 20°C. Fig. 2 indicates that elution was possible when the mixture contained 0–70 vol.-% of water.

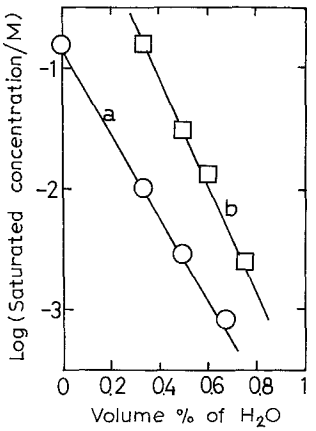


Fig. 2. Solubility of (a) 2,2′-dihydroxy-1,1′-binaphthyl (I) and (b) 2,3-dihydro-2-methyl-5,6-diphenylpyrazine (V) in methanol–water at 20°C.

Table I gives the chromatographic results when I was placed on a 2 × 1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$–montmorillonite column and eluted with 1:1 (v/v) methanol–water. About 60% of I was recovered after the passage of 40 ml of the eluent. After this stage, the eluate contained less than $2 \cdot 10^{-5}$ M of I. When pure methanol was used thereafter, the remaining I was recovered within 20 ml. By measuring the UV and ORD spectra of the collected fractions, the optical purity of each fraction, R, was determined. R is defined as $R = [M]_{310}/[M]^{\circ}_{310}$, where $[M]_{310}$ and $[M]^{\circ}_{310}$ are the molecular rotations of a given fraction and a solution of pure enantiomer at 310 nm, respectively. $[M]^{\circ}_{310}$ was taken to be $2.2 \cdot 10^4$ and $-2.2 \cdot 10^4$ for the S- and R-forms of I, respectively[5]. Based on these values, the initial 6-ml fractions contained more than 90% of the R-enantiomer, and the final 30-ml fractions obtained with the methanol eluent contained 100% of the S-enantiomer. By constructing the elution curves of the R- and S-enantiomers from the above data, the separation factor (f_s), defined as the ratio of the peak positions of the finally and initially recovered enantiomers, was determined to be 4.4 ± 1. In spite of the large value of f_s, the separation of the enantiomers was not complete, mainly because the initially eluted R-enantiomer tailed greatly, as shown in Fig. 3a.

Fig. 3d, b and c show similar elution curves for I when pure methanol and 2:1 and 1:2 (v/v) methanol–water, respectively, were used as the eluent. The results indicate that as the methanol content in the methanol–water mixture increased, compound I was recovered more rapidly with a concomitant decrease in the separation

TABLE I

CHROMATOGRAPHIC RESULTS FOR RESOLUTION OF 2,2'-DIHYDROXY-1,1'-BINAPHTHYL (I) ON A 2 × 1.2 cm O.D. COLUMN

$6 \cdot 10^{-6}$ mole of I was placed on the column.

No.	*Volume of eluent (ml)**	*Concentration (10^{-4} M)*	$[M]_{310} \times 10^{4}$***	*R (%)****
1	2	0	0	0
2	2	1.70	−2.2	100
3	2	2.26	−2.0	90
4	2	2.04	−1.6	80
5	2	1.32	−1.1	60
6	2	1.12	0.0	0
7	2	0.94	+0.5	25
8	2	0.73	+0.8	40
9	2	0.63	+1.1	55
10	2	0.55	+1.4	70
11	2	0.48	+1.5	80
12	2	0.41	+1.8	90
13	4	0.33	+2.2	100
14	4	0.22	+2.2	100
15	4	0.17	+2.2	100
16	4	0.14	+2.2	100
17	4	0.70	+2.2	100
18	4	0.50	+2.2	100
19	4	0.18	+2.2	100
20	8	0.15	+2.2	100

* Eluent: 1:1 (v/v) methanol–water for Nos. 1–16 and methanol for Nos. 17–20.

** Molecular rotation at 310 nm.

*** Optical purity defined by $R = [M]_{310}/[M]^{\circ}_{310}$ with $[M]^{\circ}_{310} = +22{,}000$ and $-22{,}000$ for *S*- and *R*-enantiomers, respectively [the absolute configuration and molecular rotation of the main compounds investigated were determined on the basis of refs. 5 (compound I), 4 (compound V), 6 (compound VIII), 7 (compound IX) and 8 (compound X)].

factor. The results show the importance of the role of water in the eluent for the achievement of a high resolution efficiency. The same tendency has already been noted in the resolution of metal complexes[2].

In the above experiments, the amount of compound I taken was about $4 \cdot 10^{-6}$ mole (1.1 mg). When $2 \cdot 10^{-4}$ mole (56 mg) of I were placed on the same 2 × 1.2 cm O.D. column and eluted with 1:1 (v/v) methanol–water, the maximum optical purities attained were only 0.2 and 0.3 for the *R*- and *S*-isomers, respectively. In order to extend the operating range to about $2 \cdot 10^{-4}$ mole (56 mg), the following column was prepared: 6 g of *Λ*-Ru(phen)$_3^{2+}$–montmorillonite were mixed in a slurry with 30 g of silica gel (Wako Gel-Q-50; Wako, Japan) and poured over a 3G17 glass filter to form a 2 × 6.5 cm O.D. column in wet conditions. Table II gives the results when $2 \cdot 10^{-4}$ mole (56 mg) of I were placed on this column and eluted with 1:1 (v/v) methanol–water. The initial 90 ml of eluate contained $12 \cdot 10^{-5}$ mole (34 mg) of the *R*-isomer with 85% purity, and the final 110 ml contained $6 \cdot 10^{-5}$ mole (16 mg) of the *S*-isomer with 80% purity. The results indicate the possibility of utilizing the present material for the preparative resolution of I (compound I is a ligand used for asymmetric syntheses[9].

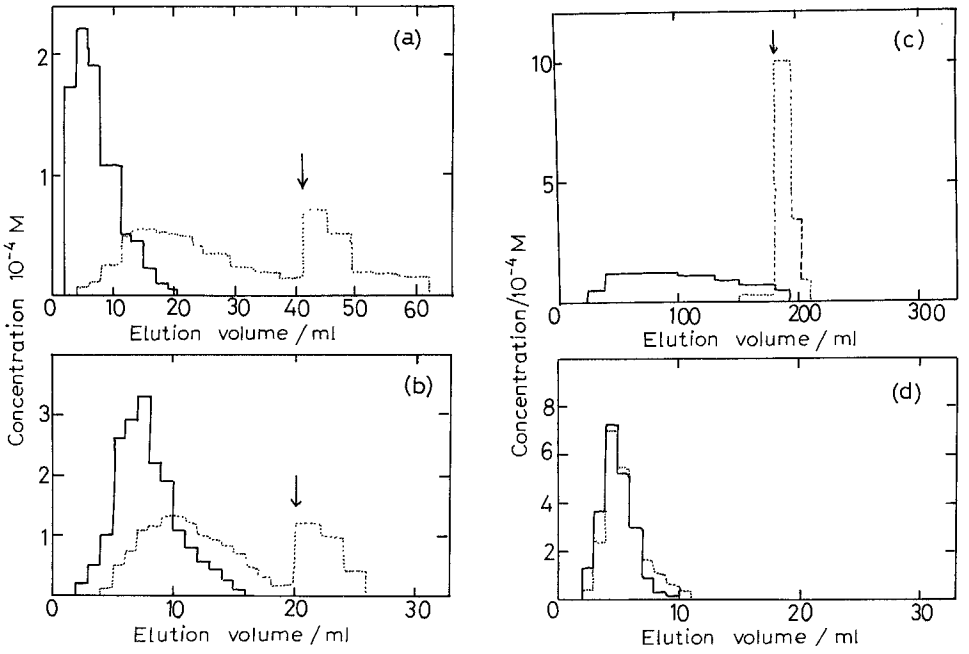


Fig. 3. Chromatographic results for resolution of 2,2′-dihydroxy-1,1′-binaphthyl (I); *R*-isomer (——) and *S*-isomer (– – –). Initial eluent: (a) 1:1, (b) 2:1, (c) 1:2 and (d) 1:0 (v/v) methanol–water. For (a)–(c) the eluent was replaced with methanol at the position indicated by the arrow.

TABLE II

CHROMATOGRAPHIC RESULTS FOR RESOLUTION OF 2,2′-DIHYDROXY-1,1′-BINAPHTHYL (I) ON A 2 × 6.5 cm O.D. COLUMN

$2 \cdot 10^{-4}$ mole of I was placed on the column.

No.	*Volume of eluent (ml)**	*Concentration (10^{-4} M)*	*R (%)***
1	30	12	80 (*R*)
2	30	20	70 (*R*)
3	30	7.5	30 (*R*)
4	30	5.5	30 (*S*)
5	30	5.5	65 (*S*)
6	50	4.5	90 (*S*)

* Eluent: 1:1 (v/v) methanol–water for Nos. 1–5 and methanol for No. 6.
** Optical purity as defined in Table I. The enantiomer in excess is indicated in parentheses.

The following analogues of I were placed on the 2 × 1.2 cm O.D. column: 2,2′-dimethyl-1,1′-binaphthyl (II), 2,2′-diamino-1,1′-binaphthyl (III) and 2,2′-dibromo-1,1′-binaphthyl (IV) (Fig. 1). In each instance about 1 mg of the compound in 1 ml of methanol was placed on the column and eluted with 1:1 (v/v) methanol–water as the initial eluent. At the stage when the eluate contained less than $2 \cdot 10^{-5}$ *M* of

TABLE III

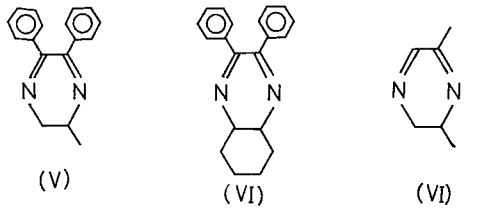
CHROMATOGRAPHIC RESULTS FOR RESOLUTION OF 1,1'-BINAPHTHYL DERIVATIVES ON A 2 × 1.2 cm O.D. COLUMN

Compound	*No.*	*Eluent*	*Volume of eluent (ml)*	*Concentration* $(10^{-4}\ M)$	$[M]_{240}$
2,2'-Dimethyl-1,1'-binaphthyl (II)	1	Methanol–water	2	0	0
	2	(1:1, v/v)	4	0.90	$-10 \cdot 10^4$
	3		4	0.30	$-6 \cdot 10^4$
	4		4	0.08	0
	5		4	0.05	0
	6	Methanol	4	1.17	$+15 \cdot 10^4$
2,2'-Diamino-1,1'-binaphthyl (III)	1	Methanol–water	2	0	0
	2	(1:1, v/v)	4	0.25	$-16 \cdot 10^4$
	3		4	0.78	$-14 \cdot 10^4$
	4		4	0.16	$-10 \cdot 10^4$
	5		4	0.10	0
	6	Methanol	4	0.10	0
	7		4	1.05	$+11 \cdot 10^4$
	8		4	0.81	$+15 \cdot 10^4$
2,2'-Dibromo-1,1'-binaphthyl (IV)	1	Methanol–water	2	0	0
	2	(1:1, v/v)	4	0.30	0
	3		4	0.25	0
	4		4	0.10	0
	5	Methanol	8	1.90	0

the compound, the eluent was changed to pure methanol in order to recover the remainder of the compound. The results are given in Table III, and indicate that II and III were partially resolved, whereas IV was not resolved at all. The implications of the results are discussed below.

Resolution of 2,3-dihydro-2-methyl-5,6-diphenylpyrazine (V) and its analogues

The next group of compounds investigated were substituted 2,3-dihydropyrazines (Fig. 4), prepared by condensation of a 1,2-diketone and a diamine. Chirality arises from the asymmetric carbon atom in the diamine. It was expected that the compounds might stack with Λ-$Ru(phen)_3^{2+}$ with their dihydropyrazine rings facing the phenanthroline ligands. Such a tendency would be enhanced if the phenyl groups were attached to the dihydropyrazine rings and interact with the phenanthroline ligands. Based on these expectations, the resolution of compounds V, VI and VII was examined.



(V) (VI) (VI)

Fig. 4. Substituted 2,3-dihydropyrazines.

The solubility of V in methanol–water is shown in Fig. 2. It dissolved in 1:0–1:3 (v/v) methanol–water mixtures to a measurable extent, and the eluent used was therefore methanol–water, as with of I. V was placed on the 2 × 1.2 cm O.D. column and eluted with 1:2 (v/v) methanol–water. The results are given in Table IV. Based on these results, we constructed the elution curves of the *R*- and *S*-enantiomers of V (Fig. 5c). Fig. 5 also includes the results when 2:1 and 1:1 (v/v) methanol–water were used as the eluent. The initial eluates contained the *R*-isomer in excess and the final eluates the *S*-isomer. The optical purity of these isomers was lower than that of I with identical eluents. The reason might be that V dissolved to a greater extent than I in the methanol–water. As already noted with I, an increase in the methanol content resulted in a decrease in resolution.

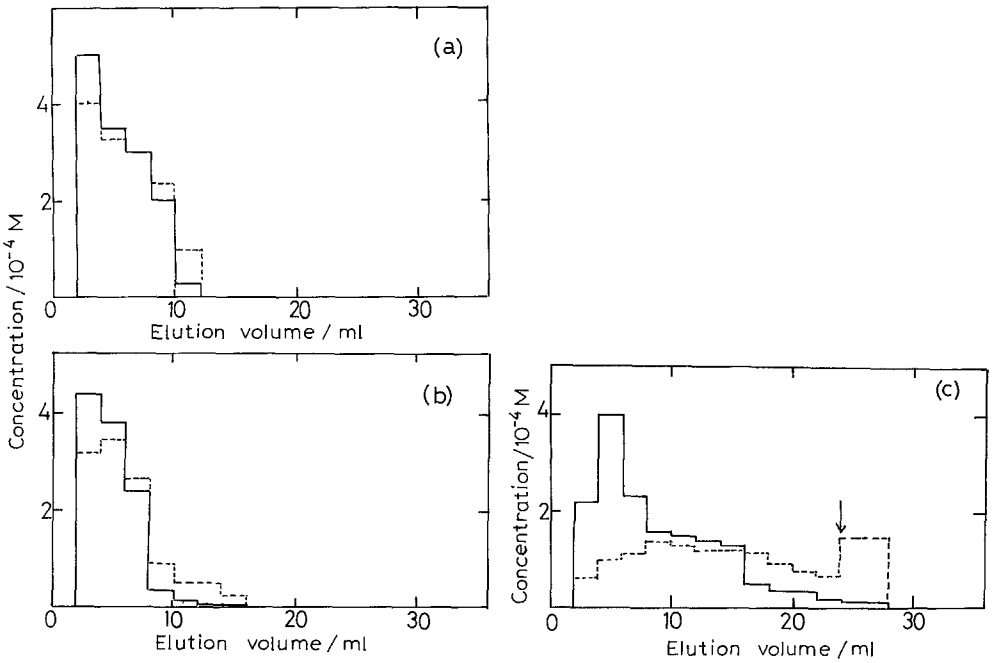


Fig. 5. Chromatographic results for resolution of 2,3-dihydro-2-methyl-5,6-diphenylpyrazine (V); *S*-isomer (——) and *R*-isomer (– – –). Initial eluent: (a) 2:1, (b) 1:1 and (c) 1:2 (v/v) methanol–water. For (c), the eluent was replaced with methanol at the position indicated by the arrow.

Compounds VI and VII were placed on the 2 × 1.2 cm O.D. column and eluted with 1:2 (v/v) methanol–water. The results for VI are given in Table IV, and indicate that it was resolved with a similar efficiency to V. With VII, however, all of the compound was eluted within 50 ml of eluate and no optical activity appeared in any fraction. Hence it was concluded that VII was not resolved on the column used. The results indicate that two phenyl groups attached to a dihydropyrazine ring are essential for resolution.

Resolution of substituted 1,2-diphenylethanes

The third group compounds investigated were substituted diphenylethanes

TABLE IV

CHROMATOGRAPHIC RESULTS FOR RESOLUTION OF COMPOUNDS V AND VI (FIG. 4) ON A 2 × 1.2 cm O.D. COLUMN

$7 \cdot 10^{-6}$ mole of V was placed on the column.

Compound	*No.*	*Volume of eluent (ml)**	*Concentration* $(10^{-4}\ M)$	$[M]_{400}$	*R (%)***
2,3-Dihydro-2-methyl-5,6-diphenylpyrazine (V)	1	2	0	0	0
	2	2	2.8	−1400	60
	3	2	6.6	−1400	60
	4	2	3.4	−880	36
	5	2	3.0	−220	9
	6	2	2.8	−220	9
	7	2	2.6	−130	5
	8	2	2.3	−80	6
	9	2	1.7	+600	25
	10	2	1.4	+800	33
	11	2	1.1	+1000	42
	12	2	0.75	+1800	77
	13	4	1.5	+2000	83
trans-2,3-Diphenyl-5,6,7,8,9,10-hexahydroquinoxaline (VI)	1	2	0	0	0
	2	4	3.3	+1400	51
	3	4	2.5	+1300	43
	4	4	1.7	+1000	36
	5	4	1.3	+370	12
	6	4	0.85	−400	13
	7	4	0.67	−1200	40
	8	4	0.60	−1700	57
	9	4	0.50	−2200	73
	10	4	0.40	−2200	73
	11	10	1.17	−2400	87

* Eluent: 1:2 (v/v) methanol–water for Nos. 1–12 and methanol for No. 13 for V and 1:1 (v/v) methanol–water for Nos. 1–10 and methanol for No. 11 for VI.

** R was estimated on the basis of $[M]^{\pm}_{400} = +2400$ and -2400 for R- and S-enantiomers of V, respectively[4], and $+2750$ and -2750 for R- and S-enantiomers of VI, respectively.

(Fig. 6). These compounds have asymmetric carbon atoms with two phenyl groups at the 1- and 2-positions. Although carbon atoms 1 and 2 are connected by a C–C single bond, two substituted methyl groups are not likely to rotate freely around the C–C bond but may have potential minima at certain rotation angles[10]. Owing to such hindered rotation, the asymmetry around a C-1 and/or C-2 atom may induce chirality in the relative orientation of two phenyl groups.

If this were so, it would be expected that compounds VIII–X might interact

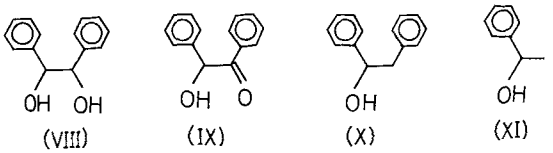


Fig. 6. 1,2-Diphenylethane derivatives.

with Λ-Ru(phen)$_3^{2+}$ stereoselectively, having their phenyl groups facing the phenanthroline ligands in Λ-Ru(phen)$_3^{2+}$.

Accurate solubility data could not be obtained for these compounds owing to a lack of sufficient materials. Based on the previous experiments, 1:1 (V/V) methanol–water was selected as the eluent. Table V gives the results for VIII, IX and X. All three compounds were resolved on the column used, $[M]^\circ$ has been reported in the literature only for VIII[6], so the resolution efficiency was calculated only for this compound. Fig. 7 shows the elution curves of the *RR*- and *SS*-enantiomers of VIII.

For comparison with the above compounds, the resolution of XI was examined

TABLE V

CHROMATOGRAPHIC RESULTS FOR RESOLUTION OF 1,2-DIPHENYLETHANE DERIVATIVES ON A 2 × 1.2 cm O.D. COLUMN

Eluent: 1:1 (v/v) methanol–water, except where methanol alone is indicated.

Compound	*Amount placed on column (mole)*	*No.*	*Volume of eluent (ml)*	*Concentration [M]* (10^{-4} M)*	*R (%)***
Hydrobenzoin (VIII)	$5 \cdot 10^{-5}$	1	2	0	0
		2	2	12	+2000	74
		3	2	41	+1500	56
		4	2	18	+890	33
		5	2	14	+730	27
		6	2	9.7	+160	6.1
		7	2	6.6	−550	20
		8	4	5.8	−900	33
		9	4	4.1	−1000	40
		10	4	2.6	−1100	56
		11	4	2.2	−1500	56
		12	4 (methanol)	2.5	−2000	74
Benzoin (IX)	$4 \cdot 10^{-6}$	1	0	0	0	
		2	2	0.66	+4200	
		3	2	1.7	+2900	
		4	2	3.3	+1500	
		5	2	3.9	+1100	
		6	2	3.9	+200	
		7	2	3.1	−1600	
		8	2	1.9	−2700	
		9	2	0.83	−3400	
1,2-Diphenylethanol (X)	$8 \cdot 10^{-6}$	1	2	0	0	
		2	2	0.70	+1000	
		3	2	7.0	+860	
		4	2	12.0	+500	
		5	2	4.6	−1900	
		6	4 (methanol)	2.04	−2400	

* $[M]_{300}$ for VIII, $[M]_{335}$ for IX and $[M]_{250}$ for X.

** R was estimated on the basis of $[M]^\circ_{300} = +2750$ and -2750 for the *S*- and *R*-enantiomers, respectively[6].

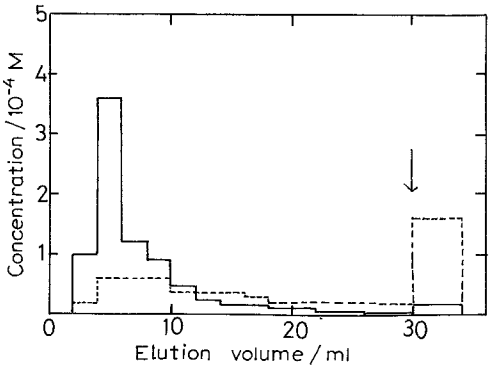


Fig. 7. Chromatographic results for resolution of hydrobenzoin (VIII); *SS*-isomer (——) and *RR*-isomer (----). Eluent: 1:1 (v/v) methanol–water for 0–30 ml and methanol for 30–38 ml.

on the same column. XI has a single phenyl group attached in contrast to VIII–X. When XI was placed on the column and eluted with 1:1 (v/v) methanol–water, the compound was recovered within 40 ml of the eluate. No optical activity appeared in any of the fractions, indicating that XI was not resolved under the conditions used. The results indicate that two phenyl groups at the 1 and 2 positions are essential for resolution.

DISCUSSION

From a comparison of the molecules successfully resolved (I, II, III, V, VI, VIII, IX and X) with those not resolved (IV, VII and XI), the following points are considered to be required for resolution.

(1) Binaphthyl compounds are resolved when they are attached to electron-donating groups. Resolution is difficult for a naphthyl compound bearing electron-withdrawing groups.

(2) 2,3-Dihydropyrazine compounds are resolved when they are attached to two phenyl groups at the 5- and 6-positions. Resolution is difficult when the phenyl groups are replaced by methyl groups.

(3) 1,2-Diphenylethane derivatives are resolved. When one of the two phenyl groups is replaced by a hydrogen atom, resolution is not achieved.

The above features indicate that the column used recognizes the absolute configuration of the adsorbate in terms of the intermolecular interaction of the phenanthroline ligands in Λ-Ru(phen)$_3^{2+}$ with the two aromatic groups of the adsorbate. With binaphthyl compounds, the column prefers the *S*-enantiomers for all three compounds resolved. When an *S*-binaphthyl molecule is placed over the head of a Λ-Ru(phen)$_3^{2+}$ moiety with its C_2 axis parallel with the C_3 axis of Λ-Ru(phen)$_3^{2+}$, the two naphthyl groups of the former face the two phenanthroline ligands (Fig. 8b). Such a fit does not occur with an *R*-binaphthyl molecule, as the two naphthyl groups and the two phenanthroline ligands project into space in the same direction, interfering sterically with each other. Hence the results for the resolution of the binaphthyl compounds are consistent with above stacking models. It should be noted,

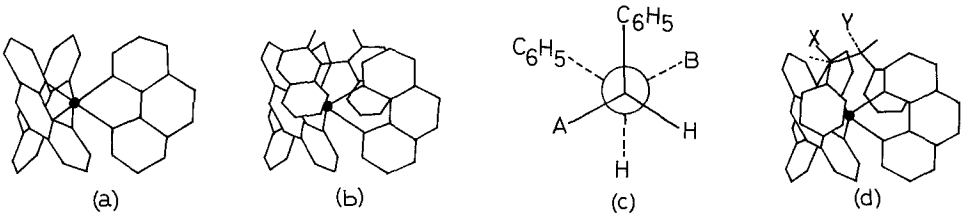


Fig. 8. (a) Structure of bound Λ-Ru(phen)$_3^{2+}$ on a clay surface. Note that the C_3 axis of the molecule is perpendicular to the surface. (b) Proposed structure of the bound state of 2,2′-dihydroxy-1,1′-binaphthyl with Λ-Ru(phen)$_3^{2+}$. (c) Conformation of 1,2-disubstituted-1,2-diphenylethylene in the -*SC* state[10]. (d) Proposed structure of the bound *RR*-hydrobenzoin (X, Y = OH) or *S*-1,2-diphenylthylene (X = OH, Y = H) with Λ-Ru(phen)$_3^{2+}$.

however, that IV is not resolved on the column used, although it also belongs to the binaphthyl group. The failure to resolve IV may indicate that a charge-transfer interaction operates between a naphthyl group as an electron donor and a phenanthroline ligand as an electron acceptor. The presence of bromine in IV decreases the electron-donating property of the naphthyl group.

With 2,3-dihydropyrazine compounds, the column prefers the *R*-enantiomer of V, whereas it prefers the *SS*-enantiomer of VI. The results indicate that the aliphatic group bound to an asymmetric carbon atom plays a decisive role in recognizing the absolute configuration of the adsorbent, although the phenyl groups at the 5- and 6-positions are also important. One possibility is that the cyclohexane ring in VI may have a tendency to face the phenanthroline ligand, whereas the interactions of the two phenyl groups at the 5- and 6-positions with Λ-Ru(phen)$_3^{2+}$ are a dominant factor in binding V to the column.

With the 1,2-diphenylethane derivatives, the column prefers the *RR*- or *R*-enantiomers of VIII and IX, whereas it prefers the *S*-enantiomers of X. According to a theoretical analysis of the conformational equilibria[10], these 1,2-disubstituted-1,2-diphenylethanes have the -*SC* conformation as the most stable one (Fig. 8c). In the -*SC* conformation, the two phenyl groups are located in the *gauche*-position. Therefore, the theoretical conclusions support the present view of the resolution mechanism that the chirality of a molecule is recognized owing to the concomitant interaction of the two phenyl groups with the phenanthroline ligands in Λ-Ru(phen)$_3^{2+}$. However, which of the enantiomers realizes the preferred stacking with the phenanthroline ligands in Λ-Ru(phen)$_3^{2+}$ depends on the relative orientation of the two phenyl groups at the 1- and 2-positions. For example, if one assumes that the enantiomers preferred by the column used have their phenyl groups facing the phenanthroline ligands in Λ-Ru(phen)$_3^{2+}$, *RR*-VIII and *S*-X would take the conformations shown in Fig. 8d. It is noted that the stability of such conformations would be greatly dependent on the subtle intramolecular interactions such as the interaction between the OH group and the phenyl group on the same asymmetric carbon atom. Any detailed theoretical calculations would be of interest in judging the validity of the possible stable conformations as given in Fig. 8.

From the practical point of view, the results are interesting because some of the resolved compounds, such as I are used as optically active reagents for synthetic purposes[9]. At present, both the resolution efficiency and the operational scale of the

present method are inferior to those of known chemical and chromatographic methods[11]. However, Λ-Ru(phen)$_3^{2+}$–montmorillonite has the great advantage over other methods that it can be easily prepared from inexpensive compounds.

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