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Exchange-Storage of a Guest Molecule in an Inclusion Crystal of 2,11,20,29-Tetramethyl-2,11,20,29-tetraaza [3.3.3.3]paracyclophane[1)]

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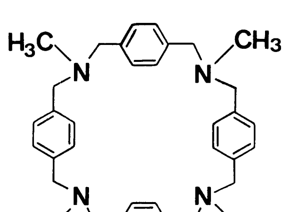
The $CHCl_3$ guest molecules of the 2,11,20,29-Tetramethyl-2,11,20,29-tetraaza[3.3.3.3]paracyclophane (**1**) inclusion complex were completely replaced by CH_2BrCl when [**1**·$CHCl_3$] powder simply made contact with gaseous CH_2BrCl molecules. This guest exchange in the crystalline phase was confirmed by ^{1}H NMR, GLPC, and X-ray analysis. The guest exchange was found to proceed in a biphasic manner, viz., (a) a "slow" exchange approaching a guest composition of 65% $CHCl_3$/35% CH_2BrCl followed by (b) a "rapid" exchange. The latter abrupt increase of the exchange rate was most reasonably attributed to a change of in crystal structure, based on the X-ray diffraction pattern of a fully guest-exchanged crystal (Type I) which was found to be very similar to that of a Type II crystal of [**1**·CH_2BrCl].

The application of molecular recognition to the crystal or solid phase has been successfully attempted, giving promise of a new field of chemistry. For example, the application of crystalline inclusion complexes to a chiral discrimination of inclusion guest molecules,[2,3)] control of organic reaction,[4,5)] or electronic devices[6)] has been reported in recent years.

2,11,20,29-Tetramethyl-2,11,20,29-tetraaza[3.3.3.3] paracyclophane (**1**) affords a 1 : 1 host–guest crystals.[7,8)] Crystal and molecular structures are highly sensitive to the size and/or shape of the guest molecules. Thus, chiral conformers, *R* and *S* of **1**, give a different packing of the host–guest pair $(R\text{-}\mathbf{1}\cdot G_I)_n$ or $(S\text{-}\mathbf{1}\cdot G_I)_n$(Type I, chiral crystal) or $[(R\text{-}\mathbf{1}\cdot G_{II})_n(S\text{-}\mathbf{1}\cdot G_{II})_n]$ (Type II, alternant racemic crystal), depending on the guest molecule, e.g., G_I=$CHCl_3$, G_{II}=CH_2BrCl. In this way, a weak host–guest interaction is remarkably "amplified" or "accumulated" in crystals, and the crystal structure may tend to retain the information "implanted" by the original guest molecule.



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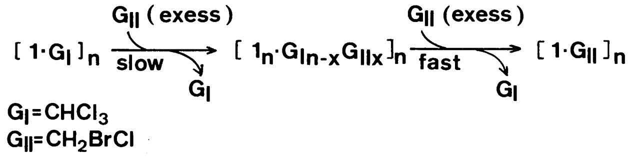
We report here that the $CHCl_3$ guest molecule (G_I) *included in the molecular cavity of a crystalline molecular inclusion comlplex*, $(R\text{-}\mathbf{1}\cdot G_I)_n$, is exchangeable by applying a second *gaseous* guest molecule (G_{II}). The $CHCl_3$ (G_I) exchange with CH_2BrCl (G_{II}) proceeded successfully and completely in the inclusion crystal under such a "crystal phase–gas phase" contact condition (Scheme 1). The formation of guest-free paracyclophane **1** did not precede or intervene in the exchange process. Further, the guest exchange was allowed with a retention of the main crystal structure of the original [**1**·$CHCl_3$] crystals. Interestingly, the kinetic process of the present guest exchange was found to be stepwise, i.e., the strain accumulated by the guest exchange during the process, (a) may reach a certain threshold value that overcomes the lattice stabilization (Type I), and (b) form defects in the crystal that had most probably accelerated the further exchange with CH_2BrCl.



Scheme 1.

Results and Discussion

[**1**·$CHCl_3$] crystals were prepared as described elsewhere.[7a)] Since heterocyclophane **1** in the inclusion crystalline state has no symmetry element, except for the C_2-axis, **1** exists as an optically active "*R*-" or "*S*-" conformer, even though the $R \rightleftarrows S$ conformer change is very rapid in the solution phase.[7a)]

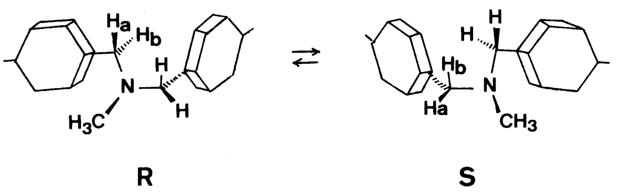


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Table 1. Included Ratio of the Exchanged Guest Molecules

G2	Time/h	Ratio G2/$CHCl_3$ in **1**	Method
CH_2BrCl	24	24/76	NMR
	48	90/10	NMR
	72	90/10	NMR
	120	92/8	NMR
	98	96/4	GLPC
CH_2Cl_2	59	52.3/47.7	NMR
CH_3CN	48	13.3/86.7	NMR
CH_3CHCl_2	48	0/100	NMR
1,4-Dioxane	48	0/100	NMR

The *R* (or *S*) conformers with the included $CHCl_3$ molecules (guest molecule) are stacked along the *b*-axis so as to produce a molecular column with a continuous hydrophobic cavity, where guest molecules are included one after another with host/guest=(1 : 1). Powder crystals of [**1**·$CHCl_3$] were placed in a thermostated closed vessel (3 cm diameter, 15 cm height) containing gaseous bromochloromethane (CH_2BrCl) of a partial pressure (P=183 mmHg, 1 mmHg=133.322Pa), which is equilibrated with 2 ml of liq.CH_2BrCl. The guest content in the inclusion crystals was determined by ^{1}H NMR and/or GLPC (Table 1). After 120 h of gas-crystal contact (in a typical experiment) the powder of **1** was dissolved into 1 ml of dioxane containing 1,2-dichloroethane as an internal standard. In the ^{1}H NMR of the product crystals dissolved in CCl_4, although no absorption due to $CHCl_3$ guest molecules (δ=7.30) was detected, instead, the absorption of a CH_2BrCl proton newly appeared at δ=5.13. The guest exchange proceeded similarly on [**1**·$CHCl_3$] powder, not only with CH_2BrCl, but also with other guest molecules, like CH_2Cl_2 or CH_3CN. For example, the exchange extent was 52.3% (30 °C, 59 h) for CH_2Cl_2 or 13.3% (30 °C, 48 h) for CH_3CN. On the contrary, CH_3CHCl_2 or 1,4-dioxane could not appreciably replace the $CHCl_3$ molecules from [**1**·$CHCl_3$], even after 48 h (Table 1).[10] Therefore, CH_3CHCl_2 or 1,4-dioxane was too slow to be exchanged with $CHCl_3$ in the crystalline state of [**1**·$CHCl_3$], indicating that the present guest exchange is accompanied by guest selectivity.

X-Ray Diffraction Observation. Figure 1 shows the powder diffraction patterns of the inclusion crystals of **1** before (Fig. 1a) and after (Fig. 1b) the exchange, when [**1**·$CHCl_3$] was applied to the gaseous molecule CH_2BrCl. Clearly, instead of an intense diffraction at 2θ=16.3 ° for [**1**·$CHCl_3$], two peaks of 2θ=16.6 ° and 17.0 ° were found. A strong diffraction peak newly appeared at 2θ=21.2 °. Further, the diffraction pattern between 2θ=17 °—20 ° was completely changed after the guest exchange,[11] strongly supporting the idea that the molecular packing in [**1**·$CHCl_3$] crystals had been completely changed. However, it is to be noted that the diffraction pattern after a guest exchange (Fig. 1b) is almost superimposable to that of intact [**1**·CH_2BrCl] inclusion crystals recrystallized from a CH_2BrCl solution of **1** (Fig. 1c), in which two intense diffractions at 2θ=21 ° are characteristically seen. Therefore, the guest-exchange phenomena due to the gas-solid phase contact was found to make a new type of the "molecular inclusion crystal".

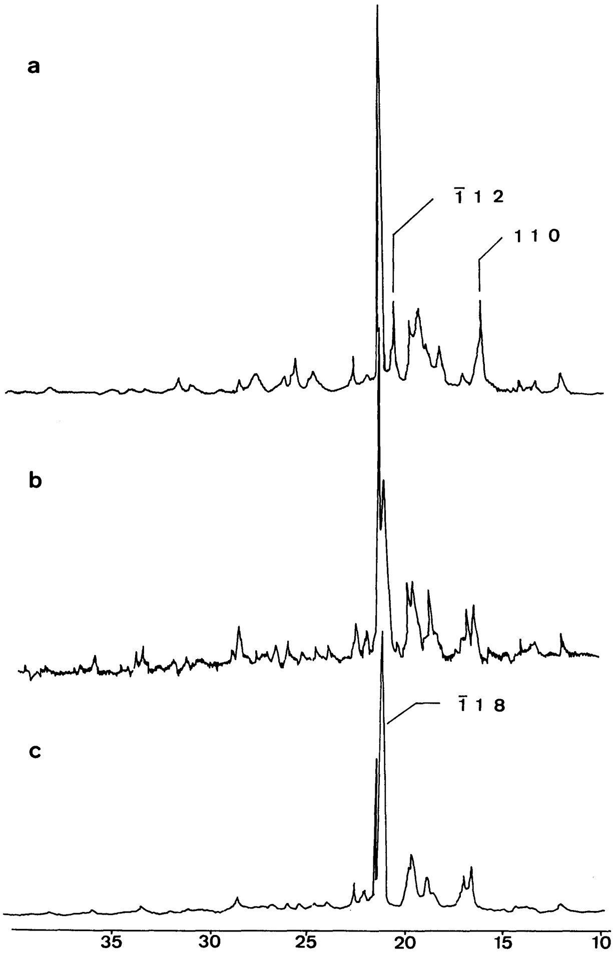

Fig. 1. X-Ray powder diffractions of a) [**1**·$CHCl_3$] crystal, b) CH_2BrCl guest-exchanged crystal, and c) [**1**·CH_2BrCl] crystal.

Column inclusion crystals, as observed for perhydrotriphenylene or deoxycholic acid, are also known to keep their lattice structures, even after the loss of guest molecules. The present inclusion crystal has a significant advantage over columnar inclusion in that more than two different packing patterns can be achieved by using different guest molecules. Six different packing patterns have been known by us for heterocyclophane **1** (Table 3).[7]

A 5 mg sample of the microcrystals of [**1**·$CHCl_3$], the size distribution of which is 500±100μm, was placed in the vessel mentioned above at 30 °C for several days, which was filled with a gaseous mixture of $CHCl_3$ and CH_2BrCl (P_{CHCl_3}=247 mmHg, P_{CH_2BrCl}=183 mmHg); the guest ratio of $CHCl_3$/CH_2BrCl in the host crystals (solid phase) was followed by the GLPC method. The above-

Table 2. Guest Ratio ($CH_2BrCl/CHCl_3$) and Powder Pattern of the [**1**·$CHCl_3$] Inclusion Complex Under the Guest-Exchange Process from [**1**·$CHCl_3$] to [**1**·CH_2BrCl]

GLPC		X-Ray powder diffraction	
Time/h	$CH_2BrCl/CHCl_3$ ratio	Time/h	Diffraction pattern
11	53.6/46.4	15	[**1**·$CHCl_3$] type (Fig. 3a)
80	83.6/16.4	83	[**1**·CH_2BrCl] type (Fig. 3b)
124	100/0	138	[**1**·CH_2BrCl] type (Fig. 1b)

Table 3. Crystal Data of Inclusion Complexes of **1**

Guest	a/Å	b/Å	c/Å	β/°	Space group	Z
$CHCl_3$[a)]	25.166	5.668	13.438	111.31	$C2$	2
Dioxane[b)]	25.091	5.691	13.440	112.06	$C2$	2
CH_2BrCl[c)]	25.314	5.536	53.508	111.07	$C2/c$	8
CH_2Cl_2[a)]	25.373	5.486	53.759	111.00	$C2/c$	8
CH_3CN[d)]	25.544	5.406	26.948	109.90	$C2/c$	4
CO_2[d)]	25.590	5.420	26.900	109.86	$C2/c$	4
Benzene[e)]	49.846	5.772	13.514	112.41	$P2_1$	4
Pyridine[e)]	12.694	5.712	13.496	111.84 α=90.15 γ=80.30	$P1$	1
None[d)]	21.457	15.097	10.013	97.370	$P2_1/a$	4

a) Ref. 7. b) Ref. 8i. c) This work. d) Ref. 7c. e) Unpublished results.

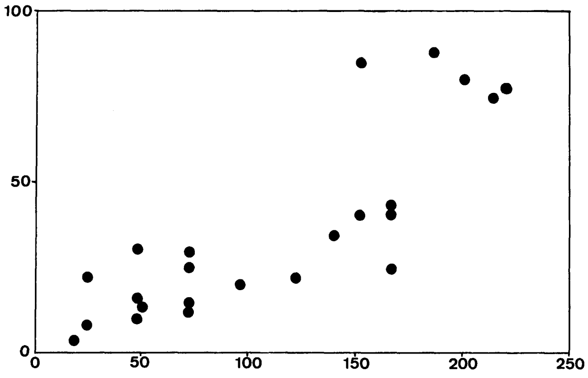

Fig. 2. Rate process of the guest-exchange in molecular inclusion of **1** in crystalline phase ($CHCl_3$/CH_2BrCl=50/50).

mentioned situation was very clearly illustrated by the guest content-time profile (Fig. 2). Clearly, in the early stage (0—150 h), the guest exchange was very sluggish, the CH_2BrCl content slowly approaching to 35%. However, the occupancy ratio of CH_2BrCl did not exceed 40%, even after 140 h. Interestingly, however, the guest ratio suddenly increased to the maximum value of $CHCl_3/CH_2BrCl$=80/20 during a 150—220 h time range, showing a catastrophic feature of the present guest exchange.

The X-ray powder diffraction pattern during an early stage (15 h) and the second stage after a catastrophic

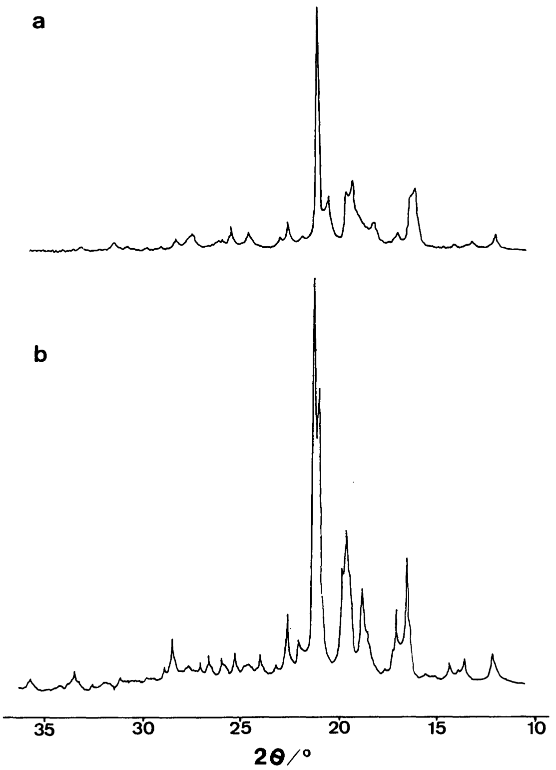

Fig. 3. X-Ray powder diffractions of [**1**·$CHCl_3$] under the guest-exchange process at a) 15 h ([**1**·$CHCl_3$] type crystal) and b) 83 h ([**1**·CH_2BrCl] type crystal).

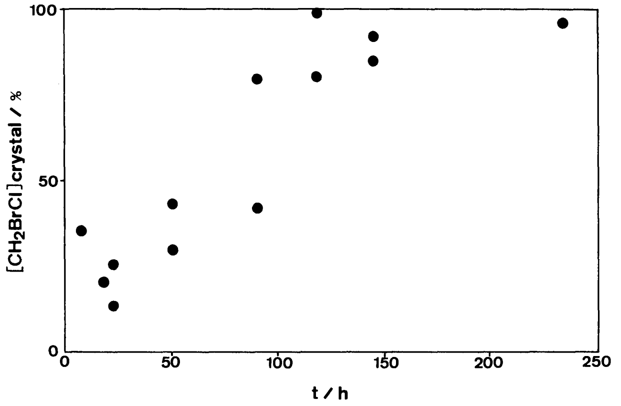

Fig. 4. Rate process of the guest-exchange in molecular inclusion complex of **1** in crystalline phase (100% CH_2BrCl vapor).

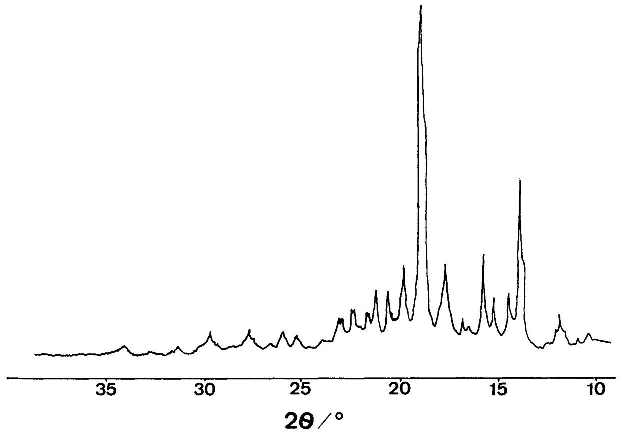

Fig. 5. X-Ray powder diffraction of guest-free **1** crystals.

guest exchange are shown in Figs. 3(a) and (b), respectively. Judging from the diffraction pattern of these two phases, the host structure of [**1**·$CHCl_3$] was maintained during "the early stage". However, the host structure changed to that of [**1**·CH_2BrCl] during the second stage after the catastrophic phenomena had occurred (Table 2).

The interaction operating between host molecules seems to be sufficiently strong to absorb a rather small strain which is induced by the CH_2BrCl guest binding, until the strain reaches to a certain threshold value.

In the case of a guest ratio of CH_2BrCl 100% in the vapor phase, the guest content-time profile is depicted in Fig. 4. Compared to the previous guest exchange process, in which the guest ratio in the vapor phase was $CHCl_3/CH_2BrCl=50/50$ (Fig. 2), the slope of the curve of the CH_2BrCl content in the solid phase was slightly steep, and the period of the early stage was short; then, the guest content reached a maximum value of 80% after 100 h. The catastrophic guest exchange phenomenon was barely recognized in this case. Thus, the unique exchange process in the inclusion crystals was effected both by the difference in the vapor pressures of two guest molecules, and by guest stabilization in the crystal lattice.

In order to investigate the mechanism of the guest exchange, we prepared a guest-free host **1** powder crystal (host **1** crystal which includes no guest molecule) and compared the X-ray powder pattern of guest-free host **1** to that of the intermediates of "the guest-exchange process".

When [**1**·$CHCl_3$] crystals were heated at 80 °C for 4 h under a vacuum below 0.5 mmHg, the $CHCl_3$ guest molecule comlpletely disappeared, judging from the GLPC analysis, and a complete disappearance of the IR intensity of the C–Cl stretching (ν=760 cm^{-1}) of $CHCl_3$ occurred. Only absorption due to the host remained. The X-ray powder diffraction was measured in order to analyse the host structure, which is depicted in Fig. 5. The intense diffraction peaks at 2θ=16.4 °, 21.2 °, and 21.4 ° disappeared, and those at 2θ=13.8 °, and 18.9 ° appeared; they were completely different from the diffraction pattern of the inclusion complex shown in Figs.1a—c and 3a,b. This guest-exchange by gas–solid phase contact of [**1**·$CHCl_3$] with CH_2BrCl occurred not via the vacant host lattice from which the guest molecule was completely excluded, but via only diffusion of CH_2BrCl into crystals, and liberation of $CHCl_3$ from crystals. This is because the X-ray powder diffraction pattern of the "guest-free" host **1** was quite different from that of the inclusion crystalline complex of **1**, or guest-exchanged **1**. Therefore, this guest-exchange by gas–solid phase contact of [**1**·$CHCl_3$] with CH_2BrCl did not occurr via the vacant host lattice from which the guest molecule was completely excluded.

Crystal Structure of [1·CH_2BrCl] Inclusion Complex. The moleculer structure of [**1**·CH_2BrCl] was the same type as that of the [**1**·CH_2Cl_2] molecular inclusion complex[6a] (Fig.6a,b). The guest molecule, CH_2BrCl, is included in the molecular cavity of **1** in the ratio 1 : 1, and in molecular complex stacks vartically along the *b*-axis. As shown in Figs.6a and b, the CH_2BrCl molecule is disordered in the cavity of **1**: 65% of C37,Br1,Cl1, and 35% of C38,Br2,Cl2. Molecules of [**1**·CH_2BrCl] form racemic inclusion crystals, of which crystal data are given in Table 3 (Type II). The crystal structure of [**1**·CH_2BrCl] (Fig.6c) shows two *R* and two *S* columns appearing alternately in the *c*-axis direction. Molecular columns with the same chirality arrange along the *a*-axis to make a chiral layer. Thus, the molecular inclusion crystal of [**1**·CH_2BrCl] is displayed by the formula $[(R\text{-}\mathbf{1}\cdot G)_2(S\text{-}\mathbf{1}\cdot G)_2]_n$ (Type II).

The *RS* contact in a Type II crystal is characterized by the presence of a symmetry center, with the *S*-**1** host having an inverse configuration and orientation of the adjacent *R*-**1** host. By contrast, the *R*-**1** to *R*-**1** or *S*-**1** to *S*-**1** contact, related by the C_2-axis, closely resembles the all-*R* or all-*S* packing of the Type I crystal. The reason that the crystal structure of [**1**·$CHCl_3$] represents $(R\text{-}\mathbf{1})_n$

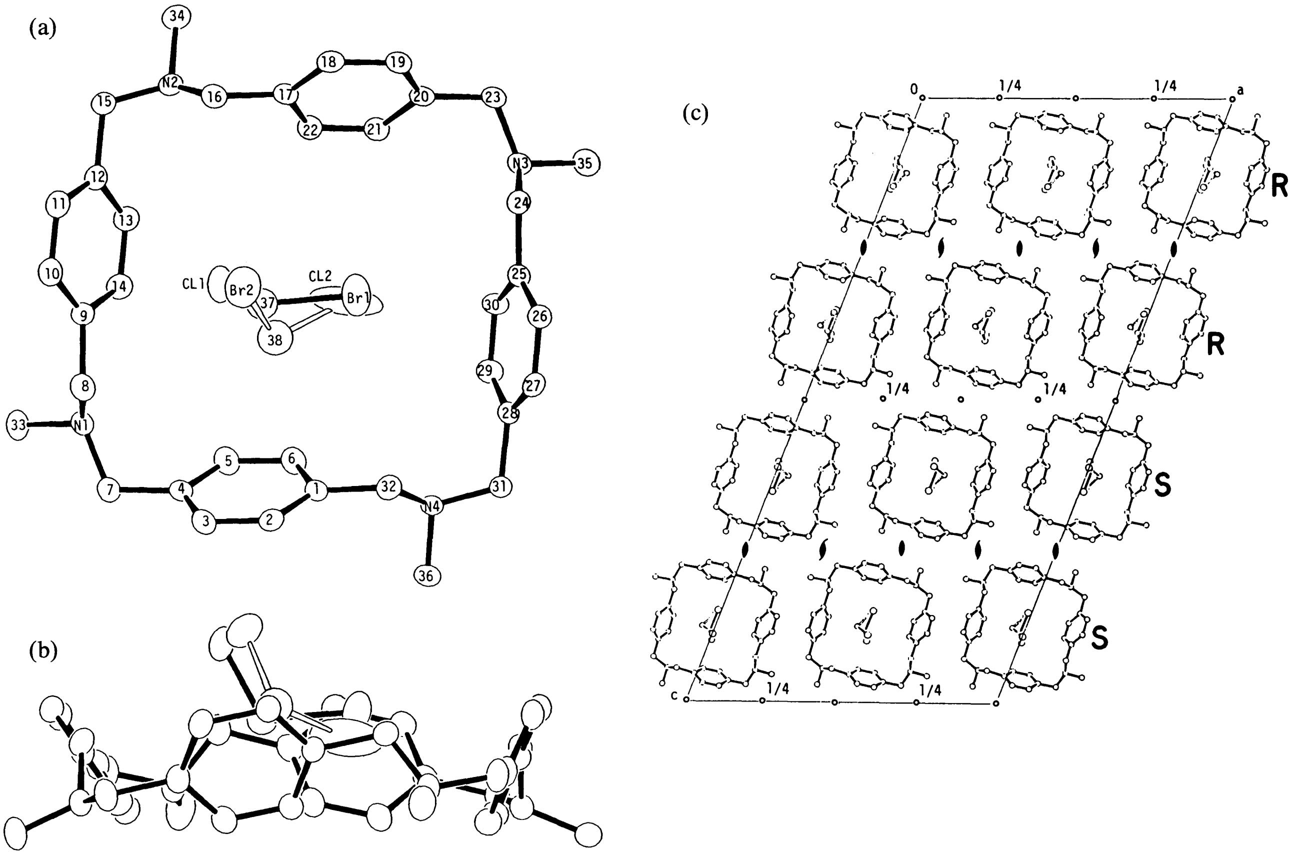

Fig. 6. View of molecular structure of [**1**·CH_2BrCl] a) perpendicular to the macrocycle and b) along the macrocycle. c) View of the crystal structure of [**1**·CH_2BrCl].

or (S-**1**)$_n$, and that of [**1**·CH_2BrCl] does [(R-**1**)$_2$(S-**1**)$_2$]$_n$ is shown as follows. The difference between 'R-**1** to R-**1**(or S-**1** to S-**1**) contact' and 'R-**1** to S-**1** contact' is assumed to depend on the inclination of the benzene ring of **1**, which contacts that of the neighbor layer. The smaller is the inclination of the benzene ring (to 90 °), the greater is the 'R-**1** to R-**1** contact' stabilized. 'R-**1** to R-**1** contact' is taken in the [**1**·$CHCl_3$] crystal lattice in which the benzene ring of **1** has an inclination of 28 °. In the case of a [**1**·CH_2BrCl] crystal lattice, 'R-**1** to R-**1** contact' is taken in the case of 28 °, while 'R-**1** to S-**1** contact' is taken when the benzene ring has an inclination of 36 °. This is also supported from the inclination of the benzene ring of **1** if the crystal lattice is 32 ° in either [**1**·CH_3CN] or [**1**·CO_2] inclusion crystals, which have only 'R-**1** to S-**1** contact'.

The mechanism of the guest-exchange reaction in the molecular inclusion crystals of [**1**·$CHCl_3$], which were contacted to a gaseous mixture of $CHCl_3/CH_2BrCl=1/1$ was assumed to be as follows. In the exchange of the crystal structure from the [**1**·$CHCl_3$] (Type I) to [**1**·CH_2BrCl] (Type II) molecular inclusion complex, half of the R-**1** conformers should inverse their conformation to the S-**1**, and R to S intercolumn contact should form in the crystal (Fig.7). When [**1**·$CHCl_3$] powder was left in the vapor of a $CHCl_3$ and CH_2BrCl (1 : 1) mixture, CH_2BrCl diffused into the crystalline lattice of [**1**·$CHCl_3$]; the guest molecules of $CHCl_3$ were then gradualy replaced with CH_2BrCl molecules without forming a part of the crystal structure of [**1**·CH_2BrCl] (Type II). Therefore, the crystal structure of [**1**·$CHCl_3$] was maintained until 40% of the $CHCl_3$ contents in inclusion crystals were replaced with CH_2BrCl molecules, followed by a catastrophic exchange by the accumulated strain energy under the first exchange process. This accumulated strain energy was caused mainly by the reduction of the 'R-**1** to R-**1** contact' interaction energy by a change of the orientation of the benzene ring. Half of the R (or S) conformers should invert to S (or R) conformers having an antidirected column structure, followed by a catastrophic guest exchange to reach the 90% content of the new guest molecules.

In the case of CH_2BrCl 100% in the vapor phase, the exchange reaction should occur rapidly and the phase transition be performed as exchanging from the [**1**·$CHCl_3$] to the [**1**·CH_2BrCl] (Type I to Type II) crystal structure.

This unique guest-exchange phenomena is the first example in which the crystal structure of the inclusion complex is changed by different guest molecules. This

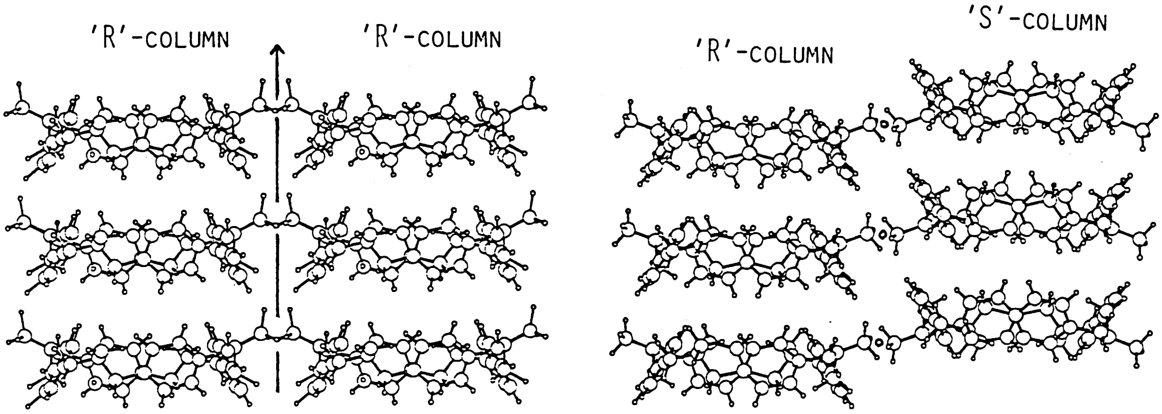

Fig. 7. '*R*'-Column to '*R*'-Column contact and '*R*'-column to '*S*'-column contact.

may provide a storage method of molecular memory in inclusion crystals by implanting specific guest binding and stabilizing by a column-to-column interaction, if the different packing modes are related to certain macroscopic physical properties.[12)]

Experimental

Materials. 2,11,20,29-Tetramethyl-2,11,20,29-tetraaza-[3.3.3.3] paracyclophane **1** was prepared as described in our previous paper.[13)] Inclusion crystals of **1** were obtained by slow evaporation of a solvent ($CHCl_3$,CH_2Cl_2,CH_2BrCl, or CH_3CN) from a solution of **1** of the solvent in a vial.

Physical and Analytical Measurement. Infrared spectra were obtained in KBr pellets by using a Hitachi 215 spectrometer. ^{1}H NMR measurements were performed with JEOL PMX-60 and Varian HA100-D spectrometers. Quantitative determination of the included guest molecules was made by the method described in our previous paper.[7a)] X-Ray powder diffraction data were collected by a Rigaku powder diffractometer with Cu $K\alpha$ radiation (1.5418 Å), and the sample was placed on a Germanium plate.

Powder of the Inclusion Complex. The powder of [**1**·$CHCl_3$], the size distribution of which is 500±100 μm, was obtained by mortaring a large crystal of **1**·$CHCl_3$, followed by sifting through the meshes. The crystal sizes were measured using a microscope equipped with a micrometer; we determined the average size by the mean value of 576 number of the crystal size. These powder crystals were stored in a dessicator full of chloroform vapor for several hours before use.

Guest Exchange Experiment. A 100 ml of closed vessel (i.d.,3 cm, 15 cm height) which contained 2 ml of liq. CH_2BrCl was immersed in a water bath thermostated at 30 °C (±0.1 °C). Gaseous CH_2BrCl filled the vessel and then was allowed contact with 5 mg of [**1**·$CHCl_3$] microcrystals, thus obtained. In the case of a 1 : 1 mixture of gaseous $CHCl_3$ and CH_2BrCl (P=247 and 183 mmHg, respectively at 30 °C), a mixture of liq. $CHCl_3$ and liq. CH_2BrCl in a ratio of 0.41 : 0.59(w/w) was placed in a closed vessel and equilibrated. The ratio of these molecules in the vapor phase was checked by sampling of 2 ml of the gas with a syringe through a septum rubber cap, and was measured by GLPC analysis. Each point in both Fig. 2 and 4 was obtained from an independent experiment; the order of these experiments was random.

Crystal Structure Analysis. Inclusion crystals of [**1**·CH_2BrCl] suitable for X-ray analysis were obtained by programmed slow cooling from 25 to 2 °C of a solution using a thermostat. A crystal with an approximate dimension of (0.42×0.20×0.18 mm) sealed in a glass capillary so as to avoid any crystal degradation was used for X-ray measurements on a Rigaku AFC-6A diffractometer. Crystal data for [**1**·CH_2BrCl] monoclinic, space group $C2/c$, a=25.314(5), b=5.536(1), c=53.508(8) Å, β=111.07(2)°, Z=8, D_C=1.26 g cm^{-3}, μ(Mo-$K\alpha$)=12.7 cm^{-1}. 5754 Independent reflections [3521 with $|F|>3\sigma(F)$] were collected up to 50° in 2θ, using Mo-$K\alpha$ radiation at room temperature. The ω-scan mode was applied because of the long c-axis. The structure was solved with the aid of the structure of [**1**·CH_2Cl_2] which is isomorphous with that of [**1**·CH_2BrCl]. A crystallographic refinement shows a disordering of the guest molecule (CH_2BrCl), which was successfully resolved into two positions. The structure was refined to R=0.088 for 3521 observed data by a full-matrix least-squares method, with the refined occupancy factors of 0.65 and 0.35 for two components of disordered CH_2BrCl molecules. The hydrogen positions of the guest molecules were not determined.

Supplementary Material Available. Tables of atomic coordinates with thermal parameters, bond distances and angles, and structure factors for [**1**·CH_2BrCl] (21pages). The complete data are deposited as Document No.8980 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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11) X-Ray diffraction peaks at $2\theta=16.3°$ and $20.7°$ correspond to diffractions from the $(1\,1\,0)$ and the $(\bar{1}\,1\,2)$ planes, respectively, of the [**1**·$CHCl_3$] inclusion crystal. The diffraction peaks at $2\theta=21.2°$ which newly appeared after the guest exchange, corresponds to that from the $(\bar{1}\,1\,8)$ plane of [**1**·CH_2BrCl] inclusion crystal. Eighty-one % of diffraction intensity of this peak at $2\theta=21.2°$ were contributed by the host **1**.

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