Table II. First-Order Rate Constants ($10^5 k/s^{-1}$) and Activation Volumes ($cm^3\ mol^{-1}$) for Z-E Isomerization of 1 in Aqueous Methanol at 25 °C

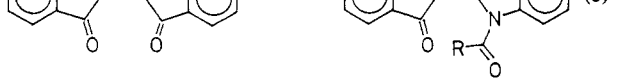
	P/MPa								
% MeOH	0.1	30.0	60.0	90.0	120.0	150.0	180.0	210.0	ΔV_0^*
20	18.4	14.5	12.0	9.49	7.64	6.40	5.35	4.46	19.1 ± 0.8
40	101	78.3	58.0	46.0	36.2	27.9	22.6	17.8	22.2 ± 0.8

activation volume at zero pressure estimated by eq 1[6] and 2. The values are in the range 16.5–20.0 $cm^3\ mol^{-1}$.

$$\ln k_P/k_{0.1} = aP + b \ln (1 + cP) \quad (1)$$

$$\Delta V_0^* = -(a + bc)RT \quad (2)$$

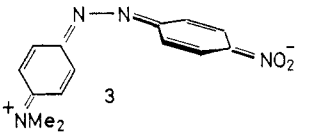
There are three probable factors that may cause an increase in partial molar volume in this reaction. The first two are the increase in the bond length in the central carbon–carbon bond and the increase in the freedom of motion. Both of them are expected because of the rupture of the central π-bond. The third factor is desolvation caused by the intramolecular neutralization of the opposite charges. A good example for the first and the second contributions is the isomerization of *N,N'*-diacylindigo dyes (eq 3).[7] In this isomerization, small positive (<4 $cm^3\ mol^{-1}$)



(3)

activation volumes were observed.[8] Since the reaction rate and the activation volume are almost independent of solvent polarity, the observed activation volumes must be the result of the first two contributions mentioned above. From these results, we can safely conclude that the major part of our activation volumes comes from desolvation caused by the charge neutralization in the activation step. In other words, the negatively charged oxygen and positively charged nitrogen atoms have their own solvation shell not only in the *E* but also in the *Z* configuration, and this solvational stabilization largely disappears in the transition state. The activation entropy calculated according to the Eyring theory (45 and 49 $J\ K^{-1}\ mol^{-1}$ at 0.1 and 180 MPa, respectively) is also in accordance with this conclusion. When solute–solvent interactions change greatly as in the present case, the accompanying volume change usually increases with rising temperatures. This is believed to derive mainly from the solvent polarity decrease by thermal expansion. The activation volumes in Table I clearly show this tendency. Furthermore, solvent effects on the rate and on the activation volume are also in accordance with desolvation in the activation step. If solvational stabilization is important in the *Z* configuration, the isomerization rate and its activation volume are expected to increase when less polar cosolvent is added to the reaction mixture. This assumption was examined by adding methanol at 25 °C. The results are shown in Table II. The rate constant increases from $5.74 \times 10^{-5}\ s^{-1}$ in water to 18.4 and $101 \times 10^{-5}\ s^{-1}$ in 20 and 40 wt % aqueous methanol, respectively; at the same time, the activation volume increased to 19.1 (20%) and 22.2 $cm^3\ mol^{-1}$ (40%), respectively. The larger retardation in less aqueous solvent can be seen in Figure 1. The short half-life prevented us from studying pressure effects in less polar solvents. However, the tendency is clear. All of the results obtained show the importance of desolvation in the activation step of the present isomerization.

In the *Z–E* isomerization of aminoazobenzenes, the strong solvational stabilization of a quinoid-type transition state such as **3** was proposed on the basis of a large negative activation volume and its dependence on temperature and solvent polarity.[3] If the strong solute–solvent interactions in the initial state disappear as the result of quinoid structure formation in the present inner salt, it is reasonable to assume an increase in solute–solvent interactions because of the appearance of formal charges in the rotational transition state of isomerization of aminoazobenzenes.



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Acknowledgment. We are grateful for valuable suggestions from Professor W. J. le Noble in manuscript preparation.

Registry No. 1, 67106-80-3.

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(8) Relatively large activation volumes (8–9 $cm^3\ mol^{-1}$) observed for *N,N'*-dibenzoylindigos are attributable to face-to-face interactions of the aromatic rings in the initial state.

Efficient Optical Resolution of 2,2'-Dihydroxy-1,1'-binaphthyl and Related Compounds by Complex Formation with Novel Chiral Host Compounds Derived from Tartaric Acid

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Previously we reported that amide host compounds such as oxamide (**1**),[1,2] fumaramide (**2**),[3,4] methanetricarboxamide (**3**),[5] and 2,2'-biphenyldicarboxamide derivatives (**4**)[6] include a wide variety of organic compounds and form crystalline complexes of a stoichiometric host:guest ratio. Optical resolution of a guest compound by enantioselective inclusion is expected when an optically active amide host compound is used. We designed chiral amide host compounds, succinamide derivatives **7** and **10** and dioxolane-4,5-dicarboxamide **8**, by starting from the naturally occurring inexpensive chiral compound, (+)-tartaric acid.

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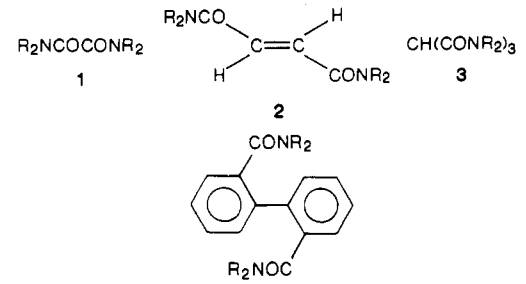
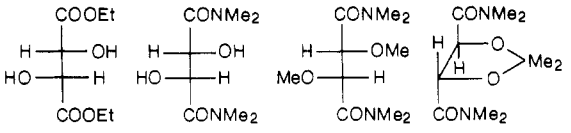
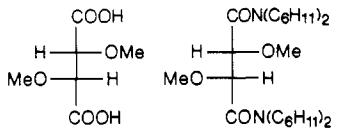
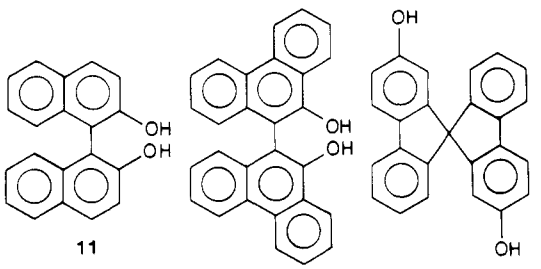


R = *i*-Pr, C_6H_{11}





These host compounds were found to be very useful for resolution of C_2 symmetrical chiral guest compounds such as 2,2′-dihydroxy-1,1′-binaphthyl (**11**), 10,10′-dihydroxy-9,9′-biphenanthryl (**12**), and 2,2′-dihydroxy-9,9′-spirobifluorene (**13**). Some optical resolution methods of **11** have



been reported so far, for example, resolution by inclusion complex formation with optically active methyl *m*-tolyl sulfoxide[7] and by fractional recrystallization of the cinchonine salt of the cyclic phosphoric acid derivative of **11**.[8] However, these are not efficient preparative methods for obtaining optically active **11** in bulk, because preparation of the optically active methyl *m*-tolyl sulfoxide is not easy and cinchonine is very expensive. Recently, the preparation of (*S*)-(−)-**11** by a stereoselective coupling of 2-naphthol in the presence of (*S*)-(+)-amphetamine copper(II) complex has also been reported.[9] This method is also not appropriate to prepare optically active **11** in bulk, because it is difficult to obtain optically active amphetamine.

Although a preparative method of optically active **12** by the enantioselective coupling of 9-hydroxyphenanthrene in the presence of optically active 1,2-diphenylethylamine has been reported,[10] this is not applicable to a large-scale production because of the difficulty in obtaining the resolved amine. Optical resolution of a large amount of **13** by a complexation method with sparteine[11] is also not appropriate because of a difficulty in obtaining the sparteine inexpensively.

Novel chiral host compounds **7**, **8**, and **10** were prepared by the following method. Treatment of (*R*,*R*)-(+)-2,3-dihydroxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide (**6**), which can easily be prepared from (*R*,*R*)-(+)-diethyl tartrate (**5**) and dimethylamine,[12] with dimethyl sulfate and 2,2-dimethoxypropane gave (*R*,*R*)-(+)-2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide (**7**) and (*R*,*R*)-(+)-*N*,*N*,*N*′,*N*′-tetramethyl-2,2-dimethyl-1,3-dioxolane-*trans*-4,5-dicarboxamide (**8**), respectively, in yields of more than 90%. Although (+)-**7** (mp 61–62 °C, $[\alpha]_D$ +115° (*c* 1.2, $CHCl_3$)) is a known compound,[12] its inclusion ability for guest compounds has never been reported. Treatment of (*R*,*R*)-(+)-2,3-dimethoxysuccinic acid (**9**)[13] by PCl_5 followed by dicyclohexylamine gave the tetracyclohexyl derivative of (+)-**7**, (*R*,*R*)-(+)-**10**, in 53% yield. By the same method, (*S*,*S*)-(−)-**7**, (*S*,*S*)-(−)-**8**, and (*S*,*S*)-(−)-**10** were prepared from non naturally occurring (−)-tartaric acid.

Optical resolution of **11**, **12**, and **13** was achieved very efficiently by complexation with **7**, **8** and **10**, respectively. By this simple complexation method, optically pure **11**, **12**, and **13** can easily be prepared in bulk. Procedures of the complexation are shown in the Experimental Section. This simple but efficient resolution method is valuable, because optically active **11**, **12**, and **13** are very useful compounds. For example, optically active **11** is useful not only as a chiral source to prepare chiral reagents such as BINAP[14] and chiral crown ethers[15,16] but also as a chiral host compound for optical resolution of various guest compounds[11] and a chiral shift reagent.[17] Optically active **12**[18] and **13**[11] are also useful for optical resolution of compounds.

Experimental Section

Reagents were obtained from commercial suppliers and used without purification. Infrared spectra were measured on a JASCO A-100 spectrometer in Nujol mulls. ^1H NMR spectra were measured on a JEOL PMX-60 spectrometer in $CDCl_3$. All $[\alpha]_D$ values were measured on a JASCO DIP-140 polarimeter.

(*R*,*R*)-(+)-*N*,*N*,*N*′,*N*′-Tetramethyl-2,2-dimethyl-1,3-dioxolane-*trans*-4,5-dicarboxamide (8). A solution of (*R*,*R*)-(+)-**6** (5.35 g, 26.2 mmol), 2,2-dimethoxypropane (5.5 g, 52.9 mmol), and *p*-toluenesulfonic acid monohydrate (0.1 g) in benzene (50 mL) was heated under reflux for 30 min. The reaction mixture was washed with 10% aqueous K_2CO_3 and water and dried (Na_2SO_4). Evaporation of the solvent gave crude **8**, which upon recrystallization from benzene–hexane gave (*R*,*R*)-(+)-**8** as colorless prisms (5.75 g, 90%): mp 86–88 °C; $[\alpha]_D$ +2.5° (*c* 1.4, $CHCl_3$); IR 1640 cm^{-1} (CO); ^1H NMR δ 1.47 (s, 6 H), 2.97 (s, 6 H), 3.17 (s, 6 H), 5.22 (s, 2 H). Anal. Calcd for $C_{11}H_{20}O_4N_2$: C, 54.08; H, 8.25; N, 11.47. Found: C, 54.22; H, 8.13; N, 11.21.

(*R*,*R*)-(+)-2,3-Dimethoxy-*N*,*N*,*N*′,*N*′-tetracyclohexylsuccinamide (10). A mixture of (*R*,*R*)-(+)-**9**[8] (16.8 g, 94.4 mmol), PCl_5 (42 g, 202 mmol), and $POCl_3$ (30 mL) was heated at 80 °C for 30 min. Evaporation of $POCl_3$ under reduced pressure gave the crude acid chloride of (*R*,*R*)-(+)-**9**. The crude acid chloride was added to an ice-cooled solution of dicyclohexylamine (72.4 g, 400 mmol) in benzene (300 mL), and the solution was stirred at room temperature for 12 h. The benzene solution left after separation of dicyclohexylamine HCl salt by filtration was washed with 10% aqueous $NaHCO_3$ and water and dried (Na_2SO_4).

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Evaporation of the solvent gave crude **10**, which upon recrystallization from benzene–petroleum ether gave (*R,R*)-(+)-**10** as colorless prisms (25 g, 53%): mp 138–140 °C; $[\alpha]_D$ +57.7° (*c* 4.0, $CHCl_3$); IR 1630 cm^{-1} (CO); 0.83–2.67 (br, 44 H), 3.40 (s, 6 H), 4.53 (s, 2 H). Anal. Calcd for $C_{30}H_{52}O_4N_2$: C, 71.38; H, 10.38; N, 5.55. Found: C, 71.44; H, 10.13; N, 5.51.

Optical Resolution of 11 by Complexation with Optically Active 7. When a solution of (*R,R*)-(+)-**7** (4.06 g, 17.5 mmol) and *rac*-**11** (5.0 g, 17.5 mmol) in benzene (20 mL)–hexane (5 mL) was kept at room temperature for 12 h, a 1:1 complex of (*R,R*)-(+)-**7** and (−)-**11** (4.1 g) was formed, which upon recrystallization from benzene gave a pure complex as colorless prisms (3.70 g, 82%): mp 149–150 °C; $[\alpha]_D$ +61.5° (*c* 1.0, $CHCl_3$)). Column chromatography of the complex on silica gel using benzene as a solvent gave (*S*)-(−)-**11** of 100% ee[19] (1.8 g, 72%);[20] $[\alpha]_D$ −33.2° (*c* 1.1, THF). The filtrate left after separation of a 1:1 complex of (*R,R*)-(+)-**7** and (−)-**11** was chromatographed on silica gel to give (+)-**11** (2.7 g, $[\alpha]_D$ +21° (*c* 1.1, THF)). Complexation of the crude (+)-**11** (2.7 g) with (*S,S*)-(−)-**7** (2.19 g) followed by recrystallization gave a 1:1 complex of (*S,S*)-(−)-**7** and (+)-**11** as colorless prisms (2.70 g, 60%): mp 150–151 °C; $[\alpha]_D$ −43.9° (*c* 1.0, $CHCl_3$). Column chromatography of the complex on silica gel using benzene as a solvent gave (*R*)-(+)-**11** of 100% ee (1.48 g, 59%); $[\alpha]_D$ +33.2° (*c* 1.1, THF).

Decomposition of a 1:1 Complex of 7 and 11 with Hydrazine. For example, when a solution of a 1:1 complex of (*S,S*)-(−)-**7** and (*R*)-(+)-**11** (3.15 g) in benzene (20 mL) was treated with 64% aqueous NH_2NH_2 (5 mL) at room temperature for 5 min, a 1:1 complex of (*R*)-(+)-**11** and NH_2NH_2 was formed as colorless needles (1.78 g), mp 135–142 °C. Decomposition of the complex with dilute HCl gave (*R*)-(+)-**11** (1.7 g, 98%).

Optical Resolution of 12 by Complexation with Optically Active 8. When a solution of (*R,R*)-(+)-**8** (1.26 g, 5.16 mmol) and *rac*-**12** (1.0 g, 2.59 mmol) in EtOH (20 mL) was kept at room temperature for 12 h, a 2:1 complex of (*R,R*)-(+)-**8** and (−)-**12** (1.03 g) was formed, which upon recrystallization from EtOH gave a pure complex as colorless prisms (0.85 g, 75%): mp 178–180 °C; $[\alpha]_D$ −23.9° (*c* 1.0, $CHCl_3$). Column chromatography of the complex on silica gel using benzene as a solvent gave (*S*)-(−)-**12** of 100% ee (0.37 g, 74%); $[\alpha]_D$ −81.1° (*c* 1.2, $CHCl_3$). The filtrate left after separation of a 2:1 complex of (*R,R*)-(+)-**8** and (−)-**12** was concentrated to half-volume to give a 1:1 complex of (*R,R*)-(+)-**8** and (+)-**12** (0.8 g). The complex was recrystallized from EtOH, and chromatography on silica gel using benzene as a solvent gave (*R*)-(+)-**12** of 100% ee (0.4 g, 80%); $[\alpha]_D$ +81.1° (*c* 1.2, $CHCl_3$).

Decomposition of a 2:1 Complex of 8 and 12 with Ammonia. For example, when NH_3 gas was bubbled for 30 min at room temperature through a solution of a 2:1 complex of (*R,R*)-(+)-**8** and (*S*)-(−)-**12** (4.0 g) in MeOH (20 mL), a 2:2:1 coplex of (*S*)-(−)-**12**, NH_3, and MeOH was obtained as colorless prisms (1.6 g). Heating of the complex in vacuo gave (*S*)-(−)-**12** (1.48 g, 84%).

Optical Resolution of 13 by Complexation with Optically Active 10. When a solution of (*R,R*)-(+)-**10** (0.58 g, 1.15 mmol) and *rac*-**13** (0.4 g, 1.15 mmol) in EtOH (5 mL) was kept at room temperature for 12 h, a 1:1 complex of (*R,R*)-(+)-**10** and (+)-**13** was obtained (0.51 g), which upon recrystallization from EtOH gave a pure complex as colorless prisms (0.45 g, 92%), mp 238–243 °C. Treatment of a solution of the complex in benzene with 3% aqueous NaOH gave an aqueous NaOH solution of (+)-**13**, which on acidification with dilute HCl gave (+)-**13** of 100% ee (0.18 g, 90%); $[\alpha]_D$ +27.1° (*c* 0.88, MeOH).

Registry No. **5**, 87-91-2; (+)-**6**, 26549-65-5; (−)-**6**, 63126-52-3; (+)-**7**, 26549-29-1; (*R,R*)-(+)-**7**·(−)-**11**, 114596-73-5; (−)-**7**, 63126-53-4; (*S,S*)-(−)-**7**·(+)-**11**, 114596-76-8; (*R,R*)-(+)-**8**, 63126-29-4; (*R,R*)-(+)-**8**·(+)-**12**, 114596-74-6; 2(*R,R*)-(+)-**8**·(−)-**12**, 114614-19-6; (*S,S*)-(−)-**8**, 111828-49-0; (*R,R*)-(+)-**9**, 7305-62-6; (*R,R*)-(+)-**9** (acid chloride), 114596-70-2; (*S,S*)-(−)-**9**, 6984-37-8; (+)-**10**, 114596-71-3; (+)-**10**·(+)-**13**, 114596-75-7; (−)-**10**, 114596-72-4; *rac*-**11**, 41024-90-2; (+)-**11**, 18531-94-7; (−)-**11**, 18531-99-2; *rac*-**12**, 95119-70-3; (+)-**12**, 95033-75-3; (−)-**12**, 95033-74-2; *rac*-**13**, 73100-16-0; (+)-**13**, 107955-86-2; (−)-diethyl tartrate, 13811-71-7; dimethylamine, 124-40-3; 2,2-dimethoxypropane, 77-76-9; dicyclohexylamine, 101-83-7.

(19) The optical purities (% ee) of **11**, **12**, and **13** were determined by HPLC using columns containing optically active solid phases, Chiralcel OC and OT(+), respectively, which are available from Daicel Chemical Industries, Ltd., Himeji, Japan. Accuracy of values of the % ee is more than 0.5%.

(20) All yields of the optical resolution were calculated on the basis of the theoretical amount of the optical isomer contained in the initial (±) compound.

Conformation of 2-(Diphenylphosphinoyl)-5,5-dimethyl-1,3-dioxane. A Contrasting Conformational Behavior of 2-Phosphoryl-Substituted 1,3-Dithianes and 1,3-Dioxanes

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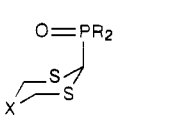
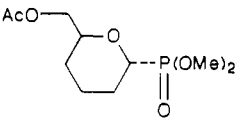
Received December 7, 1987

As part of our ongoing interest in the chemistry and stereochemistry of α-heterosubstituted phosphonates and related compounds,[1,2] we have undertaken a systematic investigation of the conformational preferences of various types of organophosphorus substituents in the 1,3-di- and 1,3,5-trithiane rings.[3] The first evidence that the 2-diphenylphosphinoyl group is axial in the 1,3-dithiane **1** was provided by Juaristi et al.[4] As a result of our investigations, a strong axial preference of the dimethoxyphosphoryl group in the 1,3,5-trithiane **2**[5] and 1,3-dithiane **3**[6] has also been found.



1, X=CH_2, R=Ph
2, X=S, R=MeO
3, X=CH_2, R=MeO



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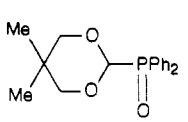

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Very recently, on the basis of the accumulated spectroscopic and X-ray analysis data as well as theoretical calculations, we proposed[3,7] a new explanation for a strong

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