tween a fast and somewhat unfavorable equilibrium (eq 6) followed by reaction of the CCH with the trap, or direct

$$\pi\text{C} \overset{k_6}{\rightleftharpoons} \text{CCH} \qquad (6)$$

reaction of πC with the trap. Skell has argued against the former on the basis that equilibration involving covalent bond formation (eq 6) should be slower than equilibration forming a π complex. This argument is unconvincing, since bond-forming reactions of Cl$^\bullet$ are often diffusion controlled (as here) and the only requirement here is that the equilibration in eq 6 be slower than the relatively slow dissociation of πC (k_4), i.e., that CCH be less stable than πC but more stable than the LSI. A more valid criticism is that if K_6 is small, rate constants for reaction of CCH with traps would have to be even faster than the k_7's calculated above. From his spectra Ingold estimated $K_6 < 0.1$ and, from the lack of effect of O_2 on the disappearance of the HSI, $K_6 < 0.01$. This latter estimate is complicated by the fact that Skell did observe competition between reactions of the chain carrier with O_2 and Cl_2 and could be too low.

Skell has objected to direct reaction of πC with maleic anhydride as being unprecedented and involving concerted formation of two σ bonds and the opening of a π bond. The same objection could be raised to his postulated reaction of CCH with DMB, which forms a σ and a π bond and breaks two σ bonds. It may be that this is another case where two models, πC and CCH, lie at the extremes of what is actually a continuum. The structures of only a few π complexes are known, and "πC" could be anything from a centrosymmetric species, to one which is quite asymmetric with the Cl approaching bonding to a single carbon although still showing a "charge-transfer-type" spectrum. What species it is that actually reacts with Cl_2 and MA, in short, remains unknown.

Optical Resolution of Phosphinates and Phosphine Oxides by Complex Formation with Optically Active 2,2′-Dihydroxy-1,1′-binaphthyl and Crystallographic Study of Two Diastereomeric Complexes with $(CH_3)(C_6H_5)(OCH_3)PO$

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Some [(alkyl-substituted)arene]phosphinates and -phosphine oxides have been resolved efficiently by crystalline complexation with optically active 2,2′-dihydroxy-1,1′-binaphthyl (**1**). Two diastereomeric 1:1 complexes of the latter with a representative phosphoric ester $(CH_3)(C_6H_5)(CH_3O)P{=}O$ (**2a**) were studied by X-ray diffraction methods in order to characterize the geometric pattern of intermolecular interaction. They form very similar crystal structures in space group $P2_1$ which consist of continuous chains of hydrogen-bonded species. Along the chains, **2a** is located between and bound (through its PO nucleophile) simultaneously to two adjacent molecules of **1**, while **1** donates its OH protons to two different molecules of **2a**. Steric forces that involve the lipophilic substituents and steric barriers on the interacting components play an important role in determining the crystal packing arrangements and effecting mutual recognition.

Introduction

Only a few preparative methods of optically active phosphinates and phosphine oxides have been reported so far. Menthane phosphinates derived from (−)-menthol were resolved by repeating recrystallization several times from hexane,[1] and the optically active species so obtained were converted into the corresponding optically active phosphine oxides by a stereoselective reaction with Grignard reagents.[1,2] Optically active phosphorous compounds derived from carbohydrates,[3] (−)-ephedrin,[4,5] and (−)-prolinol[6] have also been prepared by resolution, and their conversion into optically active phosphorus compounds by selective reactions with organometallic reagents is known. These methods, however, require natural products as a chiral source (menthol, carbohydrates, ephedrin, proline), and the selectivity of the conversion of diastereomeric phosphorus compounds derived from the natural product to phosphine oxides, phosphinates, and phosphonates is always limited to some extent.[1-6]

On the other hand, it has recently been reported that sulfoxides[7,8] and selenoxides[9] are easily resolved by complexation with optically active 2,2′-dihydroxy-1,1′-binaphthyl (**1**). This method is very simple and does not require natural products. It gives 100% optically pure compound since the resolution can easily be repeated, or the complex with **1** can be purified by recrystallization. Moreover, the enantiomeric derivatives of the compound can be resolved separately by complexation with the cor-

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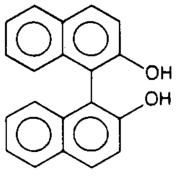
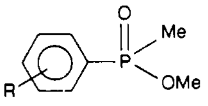
responding enantiomer of 1 (**1a** or **1b**).

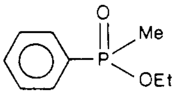
In fact, the method of inclusion-type crystalline complexation was found suitable for an effective resolution of phosphinates and phosphine oxides as well, and we now report the first resolution of phosphinates **2a–d** and phosphine oxides **5a** and **5c**. In addition, we describe in detail the crystal and molecular structures of two diastereomeric complexes I and II and relate the observed features of selectivity to structure: I, 1:1 **1a**:(+)-**2a**; II, 1:1 **1b**:(+)-**2a**.



1a:(−) enantiomer
b:(+) enantiomer



2a: R=H
b: R=*o*-Me
c: R=*m*-Me
d: R=*p*-Me



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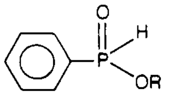
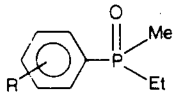
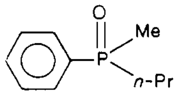


4a: R=Me
b: R=Et



5a: R=H
b: R=*o*-Me
c: R=*m*-Me
d: R=*p*-Me



6

Experimental Section

Materials. Phosphinates and phosphine oxides have been prepared according to a reported procedure.[10,11] Preparation of optically active 1 (**1a** and **1b**) has already been described in ref 7 and 8.

Optical Resolution of 2c by Complexation with 1a and 1b. When a solution of **2c** (4.5 g, 24 mmol) and **1a** (3.5 g, 12 mmol) in benzene (50 mL) was kept at room temperature overnight, a 1:1 complex of (+)-**2c** and **1a** was obtained as colorless plates (3.46 g, 60% yield). Two recrystallizations of the complex from benzene gave a pure complex of mp 140–142 °C (1.95 g, 34% yield, $[\alpha]_D$ +1.5°), which upon column chromatography on silica gel (benzene) gave 100% ee (+)-**2c** (0.70 g, 31% yield, $[\alpha]_D$ +46.3°). The filtrate left after the separation of the crude complex of (+)-**2c** and **1a** was evaporated to dryness, and the residue was chromatographed on silica gel (benzene) to give crude (−)-**2c** (2.7 g, $[\alpha]_D$ −11.5°). The crude (−)-**2c** and **1b** (4.1 g) were dissolved in benzene (30 mL) and the solution was kept at room temperature overnight to give a 1:1 complex of **1b** and (−)-**2c** as colorless plates (4.75 g, 82.6% yield). Two recrystallizations of the complex from benzene gave pure complex of mp 140–142 °C (3.10 g, 53.9% yield, $[\alpha]_D$ −1.5°), which upon column chromatography on silica gel (benzene) gave a 100% ee of (−)-**2c** (1.12 g, 50% yield, $[\alpha]_D$ −46.3°). In all cases 1 was recovered in almost quantitative yield. Other phosphorous compounds were resolved by the same procedure. Melting points and results of chemical analyses for the various complexes have been deposited in the supplementary material.

Crystal Structure Analyses. Single crystals of the diastereomers I and II were prepared by mixing the corresponding optically pure components; crystals obtained for the 1:1 complex between **1b** and (−)-**2c** were not suitable for X-ray diffraction experiments. Diffraction data of I and II were measured at ca. 18 °C on an CAD4 diffractometer equipped with a graphite monochromator, using Mo Kα (λ = 0.71069 Å) radiation. The unit cell constants were determined by least-squares from 25 accurately positioned reflections. The intensities of reflections within $0 < 2\theta < 54°$ ($(\sin\theta)/\lambda < 0.64$ Å^{-1}) were collected by the ω–2θ scan technique with a scan range of 1.1 + (0.3 tan θ)°. All data were recorded at a constant 3° min^{-1} scan rate. Possible deterioration of the analyzed crystals was tested by detecting frequently the intensities of standard reflections and was found negligible during the measurements. The data sets were not corrected for absorption or secondary extinction effects.

Table I. Optical Resolution of the Phosphorus Compounds 2, 4, and 5

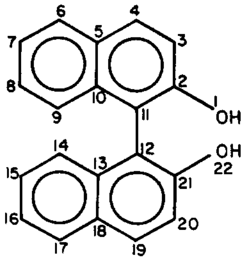
		100%[b] ee enantiomers obtained from		
		complex with **1a**		filtrate[c]
P compds[a]	mp (°C)	$[\alpha]_D$[d] (deg)	yield (%)	yield (%)
2a	188–192	+46.0	12	
2b	135–137	+45.5	47	14
2c	140–142	+46.3	31	50
2d	140–142	+47.1	32	14
4a	87–91	*e*		
4b	92–94	*f*		
5a	174–175	−23.1	60	30
5b	147–148	*g*		
5c	118–119	−24.0	33	16
5d	111–112	*g*		

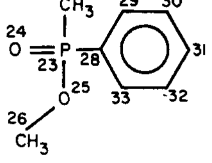
[a] Satisfactory combustion analytical data for C and H were reported for all of the compounds in this table. [b] Optical purity was determined by HPLC on Chiralcel. [c] Isolated by complexation with **1b**. [d] Measured in THF at the concentration of c 0.2. [e] (+) enantiomer of less than 10% ee was obtained after four recrystallizations of its complex with **1a** followed by decomposition. [f] A 1:1 complex with **1a** decomposed upon recrystallization. [g] No optical resolution occurred.

Both isomers of the 1:1 complex between the 2,2′-binaphthol host ($C_{20}H_{14}O_2$) and the phosphoric ester guest ($C_8H_{11}O_2P$) crystallize in the monoclinic chiral space group $P2_1$ with two entities of the complex (M_r = 456.5) in the unit cell [$F(000)$ = 480 e]. The crystal data are as follows. Isomer **I**: a = 9.132 (5), b = 11.809 (6), and c = 11.708 (2) Å, β = 112.50 (2)°, V = 1166.5 Å^3, d_c = 1.300 g cm^{-3}, μ(Mo Kα) = 1.44 cm^{-1}. Isomer **II**: a = 9.384 (2), b = 11.809 (2), and c = 11.462 (5) Å, β = 111.44 (2)°, V = 1182.3 Å^3, d_c = 1.282 g cm^{-3}, μ(Mo Kα) = 1.42 cm^{-1}.

The two structures were solved by a combination of direct methods and Fourier techniques (MULTAN80).[12] Their refinements were carried our by large block least-squares (SHELX76),[13] including the positional and anisotropic thermal parameters of all the non-hydrogen atoms. Most hydrogens were included in the structure factor computations in calculated positions (the methyl groups being treated as rigid groups); those involved in hydrogen bonds were located directly in difference-Fourier maps. The final refinements were based only on those observations that satisfied the condition $F^2 > 3\sigma(F^2)$, using experimental weights [$w = \sigma^{-2}(F_o)$] and minimizing $w(\Delta F)^2$. The final difference-Fourier maps showed no indication of incorrectly placed or missing atoms, the highest peak and deepest trough generally not exceeding 0.3 e Å^{-3}; slightly higher peaks (0.4 and 0.5 e Å^{-3}) appeared only in the vicinity of the second-row phosphorous atom. At convergence the discrepancy factors are as follows. For isomer **I**: R = 0.057 and wR = 0.058 for 1392 reflections above the intensity threshold (out of 2429 unique data above zero), goodness-of-fit = 1.09 e. For isomer **II**: R = 0.063 and wR = 0.069 for 1407 observations (out of 2397 unique data), g.o.f. = 1.14 e.

The crystallographic atom labeling scheme used is shown below:





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Results

Optical Resolution Study. The results of the optical resolution experiments are summarized in Table I. The simplicity of the method used is illustrated by the main stages of the reaction between **1** and **2**: Treatment of the racemic phosphinate **2** with **1a** in benzene led to the formation of a 1:1 complex of (+)-**2** with **1a**. Two crystallizations of the complex from benzene gave a pure compound. Column chromatography of the complex on silica gel gave optically pure (+)-phosphinate in the yield shown in Table I. A similar treatment with **1b** of the filtrate left after the separation of the complex between (+)-**2** and **1a** gave finally the optically pure (–)-**2** isomer (see Experimental Section).

The efficiency of the optical resolution of alkylaryl-substituted sulfoxides[7,8] and selenoxides[9] was found to depend on the type of substitution on the aryl group, and it is best in a meta substitution. A similar observation applies to phosphine oxide **5**; **5a** and **5c** were resolved efficiently, but no satisfactory resolution could be obtained for **5b** and **5d**. In the case of phosphinate **2**, however, all isomers **2a–d** could be well-resolved irrespective of the position of R on the aryl substituent. On the other hand, the resolution efficiency appears to be rather sensitive to the size of the alkyl substituents on P. For example, **3** does not form a complex with **1**. Similarly, no complexation has been observed between oxide **6** and **1**. In the case of **4a**, an optical isomer of less than 10% ee has been obtained after four recrystallizations of its complex with **1** from benzene. The complex of **4b** and **1** is labile and decomposes when recrystallized from benzene.

Crystallographic Study. Final atomic coordinates of I and II are listed in Tables III and IV (in supplementary material). Molecular dimensions obtained for the various molecules are in good agreement with the values of such bonds and angles in other molecules. The observed bond lengths (uncorrected for thermal motion effects) for $P{=}O$, $P{-}O$, $P{-}C(sp^2)$, $P{-}C(sp^3)$, and $C(sp^2){-}OH$ vary within 1.476–1.484, 1.501–1.531, 1.753–1.795, 1.808–1.853, and 1.346–1.366 Å, respectively. The distortions from an ideal tetrahedral arrangement around P is best reflected in large $O{-}P{=}O$ angles (mainly due to electrostatic repulsions) 117.5–119.8° and small $Me{-}P{-}OMe$ angles 92.6–96.9°. The two naphthyl fragments in the host moiety are nearly at right angles to each other, the dihedral angles between their mean planes being 92.7° and 97.7° in isomers I and II, respectively. Lists of anisotropic thermal parameters, H atom coordinates, bond lengths, and bond angles are in the supplementary material section.

Discussion

The crystal structures of the two compounds are characterized by similar features. They consist of continuous chains of hydrogen-bonded species which are aligned along the *b* axis of the crystal; Figure 1 illustrates the association mode between the constituent molecules. Along the chains, adjacent binaphthol hosts, related to each other by the 2_1 screw symmetry are bridged through their hydroxyl groups by the phosphoric ester guest. The polar $P{=}O$ nucleophile of the latter acts as a proton acceptor from two different hosts. Correspondingly, each one of the hosts donates its two hydroxyl protons to different guests located on opposite sides of the chain. The geometric parameters of this main interaction are summarized in Table II. The close similarity of the above pattern in the two structures is associated with the same length of the polar *b* axis (11.809 Å).

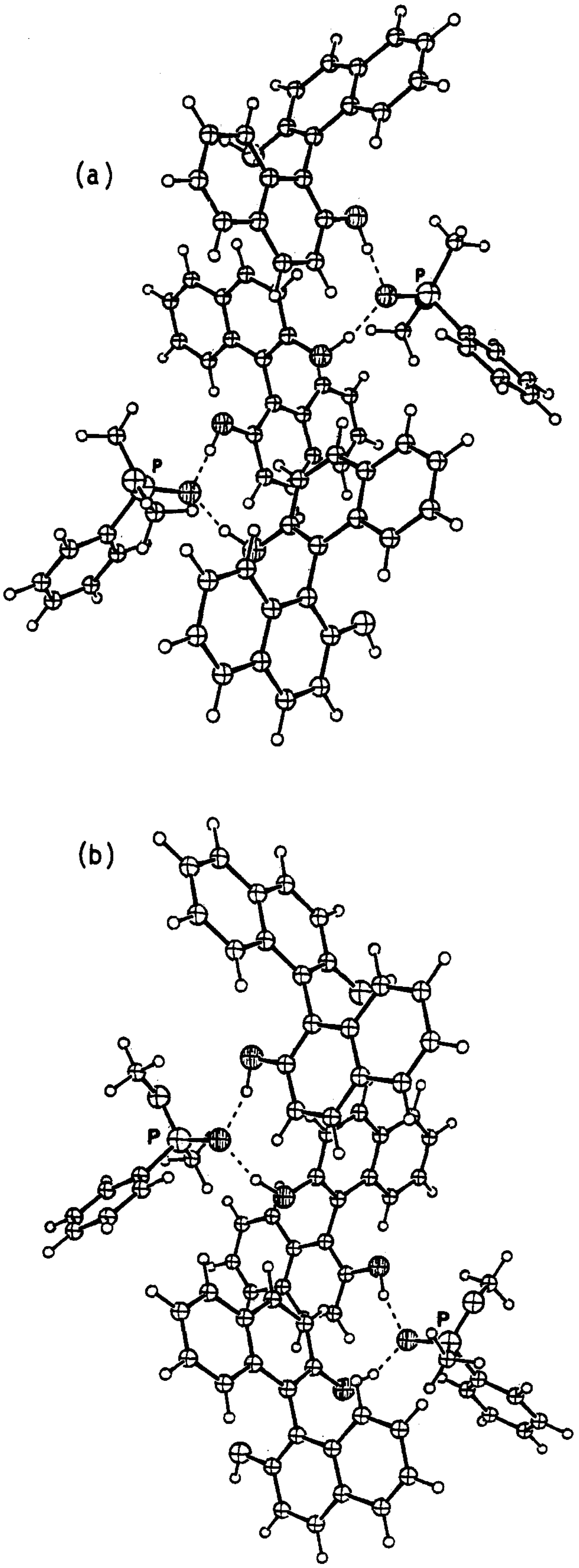

Figure 1. Views of the hydrogen-bonding interactions between host and guest in isomer I (a) and isomer II (b).

Side packing of the H-bonded chains along the *a* and *c* directions is stabilized by weaker van der Waals forces (hydrophobic interactions between host and guest, partial overlap of the aromatic fragments), thus being more sensitive to structural variations. Figure 2 illustrates the

Table II. Geometry of the Hydrogen Bonds in Isomers I and II

	I	II
Bond Lengths (Å)		
O(1)···O(24)	2.696 (7)	2.740 (8)
O(1)–H(1)	1.04	1.06
H(1)···O(24)	1.65	1.72
O(22)···O(24)	2.761 (6)	2.753 (6)
O(22)–H(22)	1.05	1.06
H(22)···O(24)	1.75	1.72
Bond Angles (Degrees)		
O(1)–H(1)···O(24)	179.5	159.2
O(22)–H(22)···O(24)	160.5	163.0

crystalline environment of the phosphinate guest species in the two enantiomerically related host lattices; each phosphinate is surrounded by and in contact with two adjacent guests and four dinaphthol hosts. In addition to the hydrogen bonds the most significant nonbonding interactions of the guest with the surrounding molecules, having a considerable influence on the prefered arrangement of the molecular entities in the crystal, involve the OMe and Me substituents on P. The $CH_3(26)\cdots CH_3(27)$ nonbonding distances between guests located in adjacent chains of the H-bonded species, and related to each other by the screw axis of symmetry at 0, y, 1 (Figure 3), are 3.648 Å in I and 3.670 Å in II, considerably shorter than the corresponding sum of van der Waals radii (4.0 Å).[14] Most of the methyl-to-naphthyl nonbonding distances are larger than 3.6 Å. The only exceptions involve the bulkier methoxy substituent: within the chains in I, C(26)···C(9) at $1 - x, y - {}^1/_2, 2 - z$ 3.390 Å and C(26)···C(8) at $1 - x, y - {}^1/_2, 2 - z$ 3.501 Å, and between adjacent chains in II, C(26)···C(5) at $x - 1, y, z$ 3.556 Å. The methoxy oxygen is not involved in any specific interaction.

The crystal packing arrangement in complexes I and II is clearly dominated by a characteristic pattern of hydrogen bonds around the twofold screw axes. The possibility to resolve the two enantiomers of **2** by crystalline complexation with optically active **1** is due to differences in topological complementarity between the hydrogen-bonded chains of host and guest molecules. Evidently, the configurational relationships between the constituents in the crystal of II are noncomplementary: (a) Complex II is less densly packed than complex I; while the methoxy group is turned inward (with respect to the H-bonding site) in I, it is turned outward in II, "pushing" away the neighboring chains. (b) As a result, the substituents on P exhibit considerably larger amplitudes of thermal motion in II than in I. (c) The dihedral angle of the binaphthyl unit in II (97.3°) is significantly larger than that in structure I (92.3°), reflecting on a strained arrangement. In less strained derivatives of 2,2′-substituted binaphthyls the corresponding values are generally lower: 89° for the uncomplexed **1**,[15] 85° for 2,2′-diamino-1,1′-binaphthyl,[15] and 87° for 2,2′-dicarboxy-1,1′-binaphthyl.[16] The high value of 111° observed in the crystal structure of 2,2′-dimethoxy-1,1′-binaphthyl has also been related to imperfect steric fit between the molecular entities.[17] Comparable observations were made in related compounds possessing 1,1′-diaryl units with oxygens attached at the 2,2′-positions.[18]

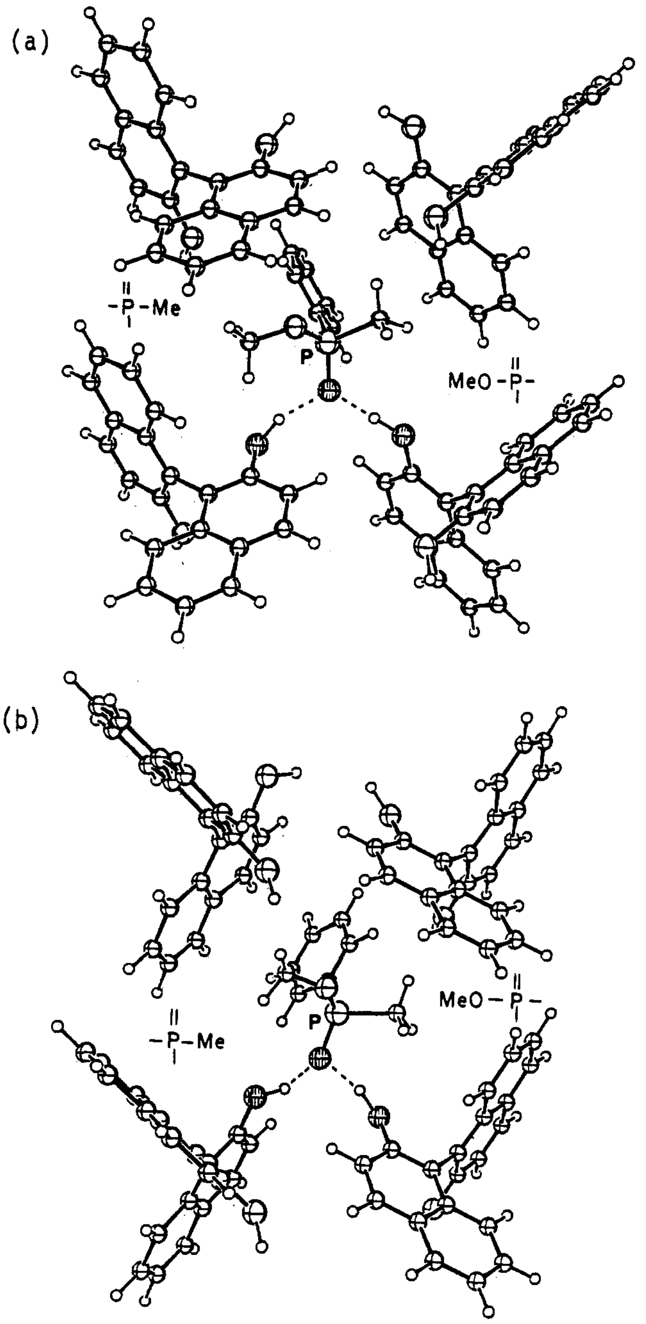

Figure 2. Views of the crystalline environment around the phosphoric ester guest in isomer I (a) and isomer II (b). For clarity, the positions of the two adjacent guest moieties are shown schematically.

Finally, the structural results described above provide a possible explanation of our findings that phosphorous guests with larger substituents on P (e.g., **3** and **6**) did not form complexes with **1** and could not be resolved (see above). It appears that in the observed crystal structure type, which consists of closely packed hydrogen-bonded chains of the complexed molecules (Figure 3), there is not enough space to accommodate a three-atom (or larger) residue attached to P without a severe distortion of the crystal lattice. In fact the Me···MeO nonbonding distances between guest species located in adjacent chains are already rather short (3.65–3.67 Å; see above). Effective complexation of **3** and **6** could probably be achieved by the formation of a different phase, and further study is needed

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to design a suitable host system for this aim. No reasonable account can be offered at this point for the effect of substitution on the guest aryl group on the resolution. In conclusion, it appears that the spatial relationships that affect optical resolution in the above described *coordination-assisted clathrates* are similar to those characterizing some optically resolved *molecular complexes*.[19] This should encourage additional applications of the lattice inclusion phenomena to problems of chiral recognition.

Registry No. **1a**:(+)-**2b**, 111469-58-0; **1a**:(+)-**2c**, 111469-47-7; **1a**:(+)-**2d**, 111469-60-4; **1a**:(+)-**5a**, 111555-51-2; **1a**:(+)-**5c**, 111469-62-6; **1b**:(−)-**2a**, 111469-63-7; **1b**:(−)-**2b**, 111469-65-9; **1b**:(−)-**2c**, 111469-67-1; **1b**:(−)-**2d**, 111469-69-3; **1b**:(−)-**5a**, 111555-52-3; **1b**:(−)-**5c**, 111469-71-7; (±)-**2a**, 90458-69-8; (+)-**2a**, 34647-07-9; (−)-**2a**, 34647-06-8; (±)-**2b**, 111469-72-8; (+)-**2b**, 111469-57-9; (−)-**2b**, 111469-64-8; (±)-**2c**, 111469-73-9; (+)-**2c**, 111469-79-5; (−)-**2c**, 111469-66-0; (±)-**2d**, 111469-74-0; (+)-**2d**, 111469-59-1; (−)-**3d**, 111469-68-2; (±)-**4a**, 111469-75-1; (±)-**4b**, 111611-87-1; (±)-**5a**, 99396-67-5; (+)-**5a**, 17045-47-5; (−)-**5a**, 26515-05-9; (±)-**5b**, 111469-76-2; (±)-**5c**, 111469-77-3; (+)-**5c**, 111469-61-5; (−)-**5c**, 111469-70-6; (±)-**5d**, 111469-78-4; I, 111469-56-8; II, 111469-80-8.

Supplementary Material Available: Tables of atomic coordinates, lists of anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, bond angles, melting points, and results of chemical analyses, and Figure 3 (10 pages). Ordering information is given on any current masthead page.

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Solvent Effects on the Basicity of Alkyl-Substituted Dimethylamines

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Received May 13, 1987

The basicity of alkyl-substituted dimethylamines in various solvents is dictated largely by specific solvation of the ammonium ion. Solvent attenuation factors, which reflect the extent to which solvents solvate ions, are directly proportional to the solvent's hydrogen bond acceptor ability, β. Substituent polarizability attenuation factors indicate that charge-induced stabilization varies in different solvents.

Solvents play an important role in the equilibrium position of various proton-transfer reactions.[2,3] The position of equilibrium 1, where X represents any substituent, G some rigid framework, and B is the protonation site, can be altered depending on the solvent.[4-7] Solvation of ions offers stability not available in the gas phase. A comparison of proton-transfer reactions in the gas phase and various solutions demonstrates this fact. Various methods have been developed that attempt to define and quantify parameters that determine how solvents alter various equilibria.[8-11]

$$\text{X–G–B} + \text{H–G–BH}^+ \rightleftharpoons \text{X–G–BH}^+ + \text{H–G–B} \qquad (1)$$

Equilibrium 1 can also be altered by changing the substituent X. Brauman and Blair[12] observed that the basicities of amines, alcohols, and ethers increased with branching alkyl substituents. Mercaptans[13] and phenols[14] show a similar behavior. Substituents that do not form chelates with the reaction site may affect equilibrium 1 by any combination of three generalized kinds of inherent substituent effects: resonance, field/inductive, or polarizability effect.[15]

Table I. Relative Basicity of Alkyl-Substituted Dimethylamines in Various Media at 298 K, $\delta\Delta G^\circ_{298}$ in kcal mol^{-1}

X	$\delta\Delta G^\circ$-(gas)[26]	$\delta\Delta G^\circ$-(H_2O)[31,32]	$\delta\Delta G^\circ$-(DMSO)	$\delta\Delta G^\circ$-(AN)
CH_3	0.0	0.0	0.0	0.0
C_2H_5	−2.3	−0.6	−0.3	−0.6
n-C_3H_7	−3.0	−0.6	−0.4	−0.7
n-C_4H_9	−4.4	−0.6	−0.5	−1.1
i-C_3H_7	−4.7	−1.0	−0.6	−1.2
sec-C_4H_9	−5.9	−1.1	−0.6	−1.4[a]
t-C_4H_9	−6.5	−1.4	−0.8	−1.5
c-C_6H_{11}	−7.3	−1.6	−0.9	−1.8
t-C_5H_{11}	−7.9	−1.8	−0.9	−1.9[a]

[a] Calculated with eq 4.

Experimental Section

Dimethyl sulfoxide (DMSO)[16] and acetonitrile (AN)[17] were purified as described elsewhere.

Potentiometry. Potentiometric titrations of DMSO and AN solutions of dimethylamines were carried out at 25 °C in a glovebox under a dry nitrogen atmosphere with CF_3SO_3H in DMSO and AN, respectively. Constant ionic strength was maintained with 0.100 M Et_4NI. The electrodes used were an

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