where $\gamma \equiv b/a$. For the values $a = 2.42$ Å, $b = 0.486$ Å, λ 5000 Å, and $|\kappa| = 0.18$ (for 6328 Å),[11] the CID components are found to be $\Delta_z \sim 0.62 \times 10^{-3}$ and $\Delta_x \sim 0.41 \times 10^{-4}$. These estimates apply only to gaseous samples; in liquids a significant reduction in Rayleigh scattering occurs through interference, the isotropic contribution being suppressed much more than the anisotropic contribution.

These Rayleigh CID components of hexahelicene are disappointingly small; in solution they will be even smaller due to the Rayleigh intensity from the solvent and could probably not be detected at present. The calculated Rayleigh CID of a biphenyl twisted at 45° is rather larger ($\Delta_z \sim 1.3 \times 10^{-3}$, $\Delta_x \sim 0.6 \times 10^{-4}$).[5] In contrast, the calculated specific rotation (using the dynamic coupling model) of the twisted biphenyl (863°) is rather smaller than that of hexahelicene (2650°).[9] This is because each pairwise CID contribution is "weighted" by a corresponding polarizability, whereas each pairwise optical rotation contribution is purely additive. Thus a molecule with a large specific rotation will not necessarily show a large Rayleigh CID. Raman CID's associated with certain normal vibrational coordinates of hexahelicene should be rather larger than the Rayleigh CID, but a detailed analysis will take some time.

Acknowledgment. I thank Professor A. D. Buckingham for discussion.

(11) N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **295**, 334 (1966).

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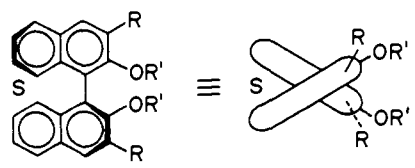
Models for Chiral Recognition in Molecular Complexation[1]

Sir:

Optically pure host compounds **5**[2] and **8** have been examined for their abilities to complex selectively and make extractable from water into chloroform the enantiomers of α-amino ester hexafluorophosphate salts as guest compounds. Racemic 3,3′-bishydroxymethyl-2,2′-dihydroxy-1,1′-binaphthyl (**2**)[3] with hydrogen bromide in glacial acetic acid gave (90%) 3,3′-bisbromomethyl-2,2′-dihydroxy-1,1′-binaphthyl, mp 211–213° dec.[4] With LAH, the bromo compound gave (87%) (±)-**3**,[4] mp 204–205°. Optically pure (*R*)-**3**[4] was obtained (25% overall) by resolution of the cinchonine salt of the phosphoric acid diester[4] of (±)-**3**.[5] From dihydropyran and 2-(2′-chloroethoxy)-ethanol was produced (96%) 2-(2′-chloroethoxy)ethyl 2′-tetrahydropyranyl ether,[4] bp 87–88° (0.5 mm), which with sodium hydroxide, butanol, and optically pure (*S*)- and (*R*)-2,2′-dihydroxy-1,1′-binaphthyl[2] (**1**) at reflux for 20 hr gave pyranyl ethers that by conventional procedures were converted to ditosylates, (*S*)-**4** and (*R*)-**4**, respectively (Chart I). Treatment

Chart I

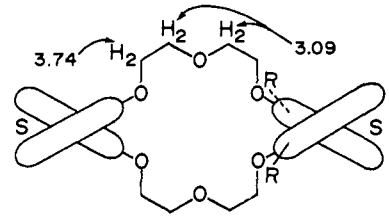


Compd no.	R	R′	Mp, °C	$[\alpha]^{25}_{578}$, deg	Solvent[a]	Yield, %
(*S*)-**1**[2]	H	H	207–208	−34.3[b]	$(CH_2)_4O$	Ref 2
(*R*)-**1**[2]	H	H	207–208	+34.1[b]	$(CH_2)_4O$	Ref 2
(*R*)-**2**[3]	CH_2OH	H	192–195	+64.1	$(CH_2)_4O$	Ref 3
(*R*)-**3**[4]	CH_3	H	202–204	+30.2	$CHCl_3$	25
(*S*)-**4**[4]	H	$(CH_2CH_2O)_2Ts$	Oil	−30.7	$(CH_2)_4O$	70
(*R*)-**4**	H	$(CH_2CH_2O)_2Ts$	Oil	+31	$(CH_2)_4O$	68

[a] *c*, 1.0. [b] Sodium D line.

of (*R*)-**3** with (*R*)-**4** and potassium hydroxide in THF and water at reflux for 100 hr gave (*RR*)-**8**. Similarly, (*S*)-**4** and (*S*)-**1** gave (*SS*)-**5**, and (*R*)-**4** and (*R*)-**1** gave (*R,R*)-**5**. Reaction of (*R*)-**4** with optically pure (*R*)-**2**[3] gave (*R,R*)-**6**, which with $SOCl_2$ gave (*R,R*)-**7**, which with LAH gave (*R,R*)-**8** (Chart II). The known absolute

Chart II



Compd no.	R	Mp, °C	$[\alpha]^{25}_{578}$, deg	Solvent[a]	Yield, %
(*S,S*)-**5**[2]	H	123–126 (solvate)[2]	−221	CH_2Cl_2	31[b]
(*R,R*)-**5**[2]	H	123–126 (solvate)[2]	+221	CH_2Cl_2	22[b]
(*R,R*)-**6**[4]	CH_2OH	Oil	+170	$CHCl_3$	28[b]
(*R,R*)-**7**[4]	CH_2Cl	Oil	+122	$CHCl_3$	76
(*R,R*)-**8**[4]	CH_3	Oil	+152	$CHCl_3$	80
(*R,R*)-**8**[4]	CH_3	Oil	+152	$CHCl_3$	32[b]

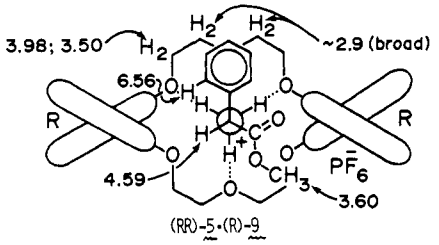
[a] *c*, 0.8–1.0. [b] Yields on ring closure.

configurations of **2**[3b] and **1**[2] indicate the absolute configurations of **5**–**8**.

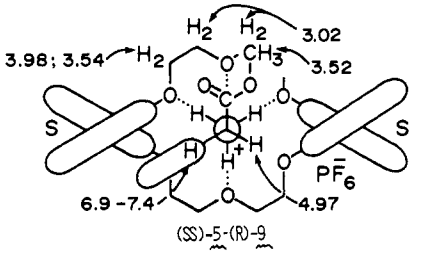
Optically pure diastereomeric complexes, (*R,R*)-**5**·(*R*)-**9** and (*S,S*)-**5**·(*R*)-**9**, were prepared by extracting at −3° a 1.25 *M* solution of the hexafluorophosphate salt of 6 equiv of (*R*)-phenylglycine methyl ester ((*R*)-**9**) in D_2O (1.25 *M* in $NaPF_6$) with a 0.16 *M* solution (1-equiv) of each enantiomeric cycle in $CDCl_3$.[6] The pmr spectra of the solutions were taken, and indicated [guest]/[host] = 0.8. Comparisons of the chemical shifts (δ) of **5** alone (CH_2OCH_2, 3.09; $ArOCH_2$, 3.74) and of each

(1) This work was supported by a grant from the National Science Foundation, GP33533X, and by the U. S. Public Health Service, Research Grant No. GM12640-10 from the Department of Health, Education and Welfare.
(2) E. P. Kyba, K. Koga, L. R. Sousa, M. G. Siegel, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 2692 (1973).
(3) (a) R. C. Helgeson, J. M. Timko, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 3023 (1973); (b) R. C. Helgeson, K. Koga, J. M. Timko, and D. J. Cram, *ibid.*, **95**, 3021 (1973).
(4) (a) Carbon and hydrogen analyses were within 0.30% of theory. Pmr spectra were consistent with assigned structures. (b) Mass spectra exhibited molecular ions.
(5) The procedure resembled that applied to 2,2′-dihydroxy-1,1′-binaphthyl: J. Jacques and C. Fouquay, *Tetrahedron Lett.*, 4617 (1971).
(6) In the absence of cycle, no detectable ester salt was extracted.

diastereomer support the structures written for (*R,R*)-**5**·(*R*)-**9** and (*S,S*)-**5**·(*R*)-**9**, which are also arrived at by examination of CPK molecular models. The upfield shifts (0.19–0.38 ppm) of those protons shielded by the ring currents of the naphthalene and benzene rings are particularly informative. Their magnitudes indicate fairly rigid structures. The ortho proton of the phenyl and the CH_2OCH_2 protons in (*R,R*)-**5**·(*R*)-**9** would have moved much further upfield, had they not been averaging. Complex (*S,S*)**5**·(*R*)-**9** crystallized with 1 mol of chloroform.[4a]



Three-point binding model



Four-point binding model

Racemic amine hexafluorophosphates dissolved (~1 *M*) in D_2O (1.0–4.0 *M* in $LiPF_6$ at pH ~4) were shaken at the desired temperature with solutions of optically pure host (~0.2 *M*) in $CDCl_3$. The pmr spectra indicated that in the $CDCl_3$ layer, [guest]/[host] = 0.7–1.0.[6] The layers were separated, the amines were isolated from each layer, and their optical purities and configurations were determined. The results provided *enantiomer distribution constants*, EDC = D_A/D_B, where D_A is the distribution coefficient of the enantiomer more complexed in $CDCl_3$ and D_B is that of the enantiomer less complexed (Table I).

Table I

Run no.	—RR′CHNH$_3^+$PF$_6^-$— R	R′	Host	*T*, °C	EDC (D_A/D_B)	More stable complex
1	C_6H_5	CH_3	(*S,S*)-**5**	0	1.8	3-Point
2	C_6H_5	CO_2CH_3	(*R,R*)-**5**	−15	3	3-Point
3	C_6H_5	CO_2CH_3	(*R,R*)-**5**	24	2.5	3-Point
4	*p*-HOC_6H_4	CO_2CH_3	(*R,R*)-**5**	−15	5	3-Point
5	$C_6H_5CH_2$	CO_2CH_3	(*R,R*)-**5**	−1	1.8	4-Point
6	$(CH_3)_2CH$	CO_2CH_3	(*R,R*)-**5**	−10	1.5	4-Point
7	$CH_3S(CH_2)_2$	CO_2CH_3	(*R,R*)-**5**	−5	1.7	4-Point
8	C_6H_5	CO_2CH_3	(*R,R*)-**8**	24	12	3-Point
9	*p*-HOC_6H_4	CO_2CH_3	(*R,R*)-**8**	24	18	3-Point
10	$CH_3S(CH_2)_2$	CO_2CH_3	(*R,R*)-**8**	−5	2.2	3-Point

With no ester group present (run 1), the 3-point binding complex was more stable. *In all of the more crowded complexes* (runs 1, 2, 3, 4, and 8–10), *the 3-point binding model applies.* The methyl groups of **8** extended the chiral barrier, and increased the value of EDC from 2.5 (run 3) to 12 (run 8). Introduction of a para-hydroxyl group into the phenyl of the guest in run 4 increased the EDC from 3 (run 2) to 5 (run 4). Possibly the π–π repulsions between the phenyl and naphthalene in (*S,S*)-**5**·(*R*)-**9** increased upon introduction of the para-hydroxyl group, and this diastereomer was relatively destabilized. In the less crowded complexes of runs 5–7, the 4-point binding diastereomers were the more stable. A comparison of runs 7 and 10 indicates that the methyl groups of host (*R,R*)-**8** crowded the complex enough to cause a switch in model stability.

These results demonstrate the feasibility of designing host compounds for optically resolving amino esters by selective complexation. A molecular basis has been provided for building an amino ester resolving machine.

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Structure of the Dimer of Diphenylantimony Trichloride

Sir:

Diphenylantimony trichloride was first prepared by Michaelis and Reese[1] who obtained it as a monohydrate following recrystallization from dilute hydrochloric acid. The anhydrous compound was readily obtained by heating the hydrate to 100°. Although diphenylantimony trichloride has been frequently reported in the chemical literature,[2] a clear distinction between the hydrated and anhydrous material has not always been made.

In a preliminary paper in 1961 Polynova and Porai-Koshits,[3] on the basis of X-ray determination, concluded that the compound was a trigonal bipyramid with two equatorial phenyl groups. Although this paper clearly stated that $(C_6H_5)_2SbCl_3$ was used, the method cited for its preparation[4] should have yielded the monohydrate. Somewhat later, in a review paper,[5] these same authors state that the compound exists as a monohydrate with octahedral geometry but cite their earlier paper as the reference for this result. The issue has been further confused by a recent paper by Gukasyan and coworkers[6] who conclude, on the basis of the ^{121}Sb Mössbauer spectrum, that the compound exists as a trigonal bipyramid with three chlorine atoms in equatorial positions. Again it is unclear as to whether they used the hydrated or the anhydrous material.

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(5) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **7**, 742 (1966).
(6) S. E. Gukasyan, V. P. Gor'kov, P. N. Zaikin, and V. S. Shpinel, *Zh. Strukt. Khim.*, **14**, 650 (1973).