Furthermore the ease of formation and high chemical stability of compound **1** indicates that more examples of such complexes may exist.

Acknowledgment. I am indebted to Prof. L. M. Venanzi for valuable suggestions and discussion and to Prof. B. Magyar for the molecular weight measurement.

Supplementary Material Available: (a) Experimental details including synthesis, elemental analyses, molecular weight measurement, and magnetic measurements, and (b) tables of final atomic coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

(13) $Ir(H)_2(Cl)_2(P\text{-}i\text{-}Pr_3)_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.191$ (3) Å, $b = 8.982$ (4) Å, $c = 16.447$ (4) Å, $\beta = 93.30$ (2)°, $V = 1208.0$ (7) Å^3, ρ(calcd) = 1.61, ρ(meas) = 1.60 (1) g cm^{-3} (measured by flotation in $CdCl_2$ aqueous solution) for $Z = 2$ and $M = 585.66$. Iridium occupies a special position, that of crystallographic symmetry $\bar{1}$; the symmetric unit contains half of the molecule. Data collection was made by an automatic diffractometer Nicolet P3m (room temperature); the residuals for the 5237 data, corrected as described in ref 15 ($2\theta_{max} = 90°$; $I > 3\sigma I$; crystal size 0.13 × 0.23 × 0.68 mm) are $R = 3.12$ and $R_w = 3.60$. All the heavy atoms together with the 21 hydrogen atoms of the P-*i*-Pr_3 group were located and refined, hydrido hydrogen[16] contribution fixed.

(14) A full paper on this and related chemistry: Mura, P.; Segre, A. L., manuscript in preparation.

(15) Bachechi, F.; Zambonelli, L.; Marcotrigiano, G. *J. Cryst. Mol. Struct.* **1977**, *7*, 11-20.

(16) A difference-Fourier synthesis based on low-angle reflections[17] (with 458 reflections maximum sin $\theta/\lambda = 0.36$ Å^{-1}) clearly revealed the hydrido hydrogen position. Full-matrix refinement of all heavy atoms (anisotropic t.f.) and hydrido hydrogen (isotropic t.f.) with fixed contribution of 21 H atoms of the P-*i*-Pr_3 group gives $R = 1.58$ and $R_w = 1.80$ with Ir-H(111) 1.90 (7) Å and $B_{iso} = 1.7$ (2.1) Å^2.

(17) Bau, R.; Chiang, M. Y.; Ho, D. M.; Gibbons, S. G.; Emge, T. J.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 2823-2829 and references cited therein.

A New, Easily Accessible Reciprocal Chiral Stationary Phase for the Chromatographic Separation of Enantiomers

W. H. Pirkle* and Thomas C. Pochapsky

School of Chemical Sciences
University of Illinois at Urbana-Champaign
Roger Adams Laboratory, Urbana, Illinois 61801

Received September 26, 1985

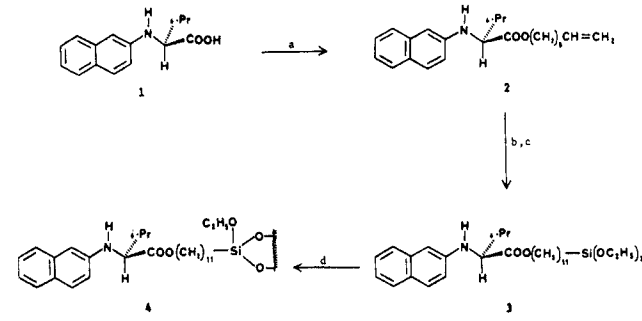
N-Aryl-α-amino acids (and their ester and amide counterparts) contain a combination of π-donor, basic and acidic sites spatially arranged so as to afford unusually efficient chiral recognition upon interaction with the complementary π-acceptor, acidic and basic sites of *N*-(3,5-dinitrobenzoyl)-α-amino acids.[1,2] For example, the enantiomeric ω-undecenyl esters of *N*-(2-naphthyl)alanine are separable by HPLC on columns packed with a silica-bonded chiral stationary phase (CSP) derived from (*S*)-*N*-(3,5-dinitrobenzoyl)leucine, exhibiting an enantiomeric separability factor[4] of 10.4, an unusually large value. In view of the reciprocal aspect of chiral recognition, CSPs derived from *N*-(2-naphthyl)-α-amino acids were expected to afford facile separations of the enantiomers of *N*-(3,5-dinitrobenzoyl) derivatives of α-amino acids. Additionally, such CSPs were expected to separate the enantiomers of appropriately derivatized amines, amino alcohols, amino phosphonates, alcohols, and thiols. Appropriate derivatization consists of N, O, or S acylation with 3,5-dinitrobenzoyl chloride or 3,5-dinitrophenyl isocyanate.[6,7]

(1) Pirkle, W. H.; Hyun, M. H.; Bank, B. *J. Chromatogr.* **1984**, *316*, 585-604.

(2) Pirkle, W. H.; Pochapsky, T. C.; Mahler, G. S.; Field, R. M. *J. Chromatogr.* **1985**, *348*, 89-96.

(3) Pirkle, W. H.; Welch, C. J. *J. Org. Chem.* **1984**, *49*, 138-140.

Scheme I[a]



[a] (a) $CH_2{=}CH(CH_2)_9OH$ (1.1 equiv), CH_3SO_3H, toluene at reflux, azeotropic removal of water. (b) 1.5 g of **2**, 20 mL of $HSiCl_3$, 0.01 g of H_2PtCl_6 dissolved in 0.5 mL of 2-propanol, 5 h at reflux. (c) Distillation of excess $HSiCl_3$, 20 mL of 1:1 CH_3CH_2OH-$(CH_3CH_2)_3N$, concentration in vacuo, flash chromatography on silica using 1:1 hexane-CH_2Cl_2 eluent. (d) 5 g of 5-μm silica, 0.05 torr, 110 °C, 14 h.

We now describe a broadly applicable CSP derived from (*S*)-(-)-*N*-(2-naphthyl)valine which, owing to its performance and ease of preparation, will almost certainly see early commercialization.[12]

(*S*)-(-)-*N*-(2-Naphthyl)valine **1**, prepared from L-valine and β-naphthol using a variation of the Bucherer reaction,[8] was esterified with 10-undecen-1-ol in the presence of an acid catalyst. Ester **2** was hydrosilylated with trichlorosilane–chloroplatinic acid to afford the chiral trichlorosilane which was converted, without purification, to the less reactive triethoxysilane **3**, by the action of ethanol–triethylamine. This silane was purified by flash chromatography on silica, fully characterized, and bonded to dried 5-μm Spherisorb silica by heating in a Kugelrohr apparatus under vacuum at 110 °C for 14 h. This sequence is shown in Scheme I. Elemental analysis of washed and dried CSP **4** indicates that a loading of 0.3 mmol/g (based on C and N analysis) was achieved. The material was slurry-packed (methanol) into a 4.6 mm × 250 mm stainless steel column.

Table I provides data pertinent to the chromatographic separation of the enantiomers of a representative assortment of analyte classes. In each instance, the analyte has been derivatized with either 3,5-dinitrobenzoyl chloride or 3,5-dinitrophenyl isocyanate. Derivatization incorporates functionality essential to chiral recognition and facilitates detection.

One notes separability factors (e.g., 17.7, 18.7) larger than any yet reported for enantiomer separation for amide derivatives of *N*-(3,5-dinitrobenzoyl)-α-amino acids regardless of whether a simple amine or another amino acid is used in making the amide derivative. Perusal of Table I shows examples of enantiomer separation of the derivatives of secondary and tertiary alcohols,

(4) The separability factor is the ratio of retention times measured from the time of elution of a nonretained solute. This ratio is related to the difference in energy of the diastereomeric adsorbates formed when the enantiomers interact with the CSP.

(5) Pirkle, W. H.; House, D. W.; Finn, J. M. *J. Chromatogr.* **1980**, *192*, 143-158.

(6) Ôi, N.; Nagase, M.; Doi, T. *J. Chromatogr.* **1983**, *265*, 111.

(7) Pirkle, W. H.; Mahler, G. S.; Hyun, M. H. *J. Liq. Chromatogr.*, in press.

(8) Pirkle, W. H.; Pochapsky, T. C. *J. Org. Chem.*, in press.

(9) The capacity ratio, k_1', is the number of void volumes of mobile phase beyond the initial void volume needed to elute the first enantiomer.

(10) The resolution, R_S, of the two enantiomers is a measure of the chromatographic efficiency of the separation. An $R_S \geq 1$ indicates effectively complete band separation. R_S is defined by the equation

$$R_S = 2(t_2' - t_1')/(w_2 + w_1)$$

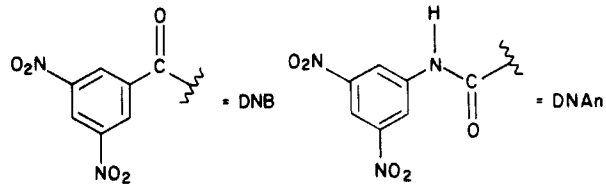
where the t_i's are the corrected retention times of the enantiomers, and the w_i are the widths of the peaks at their bases.

(11) The absolute configuration of the most-retained enantiomer is determined from chromatography of samples enriched in one enantiomer of known configuration.

(12) **Note Added in Proof**: Columns of this type, derived from valine and from alanine are available in (*R*), (*S*), and (*RS*) forms from Regis Chemical Co., 8210 Austin Av., Morton Grove, IL 60053.

0002-7863/86/1508-0352$01.50/0

Table I. Representative Separations of Enantiomers on CSP **4**



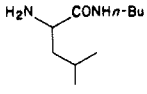
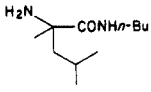
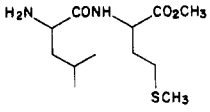
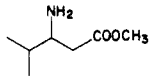
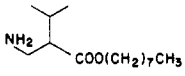
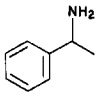
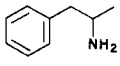
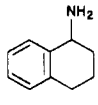
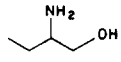
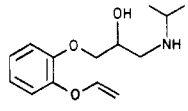
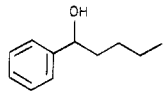
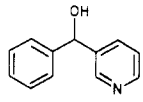
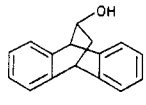
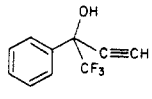
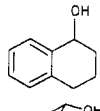
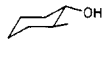
compound	derivative	separability factor (α)	k_1'[9]	R_S[10]	eluent, % v/v 2-propanol in hexane	most retained enantiomer[11]
		α- and β-Amino Acid Derivatives				
	DNB	17.66	0.38	10.5	10%	*S*
	DNB	1.45	7.97	4.2	5%	
	DNB	18.66	1.87	18.3	20%	*S,S*
	DNB	1.97	0.93	2.2	5%	*R*
	DNB	1.25	7.33	2.1	5%	
		Derivatives of Amines and Amino Alcohols				
	DNAn	1.19	5.87	1.5	5%	*R*
	DNAn	1.33	3.27	2.8	20%	*S*
	DNAn	1.19	6.37	2.1	5%	
	DNAn	2.42	14.87	10.6	5%	
	DNAn	4.53	1.35	7.7	20%	*S*
	bis-DNAn	1.41	13.2	3.6	20%	
		Derivatives of Alcohols and Thiols				
	DNAn	1.24	3.19	1.8	5%	*S*
	DNAn	2.51	4.87	10.6	5%	
	DNAn	1.20	8.71	2.0	5%	
	DNAn	1.47	4.87	3.2	5%	
	DNAn	1.22	5.35	2.5	5%	*S*
	DNAn	1.10	4.07	0.7	5%	

Table I (Continued)

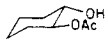
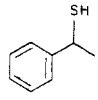
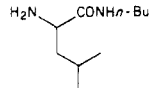
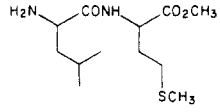
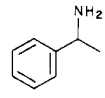
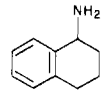
compound	derivative	separability factor (α)	k_1'[9]	R_S[10]	eluent, % v/v 2-propanol in hexane	most retained enantiomer[11]
	DNAn	1.49	3.87	3.7	5%	
	DNAn	1.50	2.94	2.7	5%	
	DNAn	1.40	9.40	3.5	5%	

Table II. Reverse-Phase Separations of Enantiomers on CSP 4[a]

compound	derivative	separability factor (α)	k_1'	R_S	most retained enantiomer
	DNB	2.61	9.0	5.0	S
	DNB	3.71	9.0	5.8	S,S
	DNB	no separation			
	DNAn	1.19	12.8	0.6	

[a] In all cases, the mobile phase used was 50% methanol–water.

diols, acyclic and cyclic primary amines, and thiols (expected to behave much as the corresponding alcohols) as well as derivatives of α- and β-amino acids. We have observed that column efficiencies of CSP **4** are comparable to those of typical silica-bonded-phase HPLC columns. CSP **4** may be used with either normal or reverse-phase eluents. However, enantiomer selectivities are typically reduced in polar eluents relative to those observed in nonpolar eluents (Table II). This may in certain cases be an advantage, however, where very large separation factors are unnecessary.

In view of the great scope of this easily prepared CSP, it should be of utility to those engaged in asymmetric synthesis or other stereochemical studies and to those wishing to monitor the enantiomeric composition of drugs or metabolites in body fluids.

Acknowledgment. This work has been supported by a grant from the National Science Foundation.