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Chiral High-Pressure Liquid Chromatographic Stationary Phases. 1. Separation of the Enantiomers of Sulfoxides, Amines, Amino Acids, Alcohols, Hydroxy Acids, Lactones, and Mercaptans

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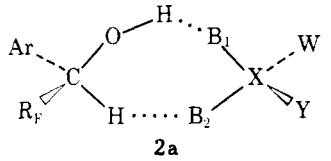
A silica gel bonded chiral fluoro alcoholic stationary phase has been prepared for the direct liquid chromatographic separation of the enantiomers of a wide assortment of solutes. The chiral fluoro alcohol utilized was selected on the basis of a rationally devised chiral recognition model that accounts for the origins of the observed separations and elution orders of the various enantiomers. More than 50 such resolutions are presented for sulfoxides, lactones, and derivatives of amines, amino acids, amino alcohols, alcohols, thiols, and hydroxy acids.

Owing to its conceptual simplicity and manifest utility, the direct liquid chromatographic separation of enantiomers upon chiral columns has been attempted many times. For most workers, the target has proven chimerical and, not withstanding the achievements of Gil-Av,[1] Lochmüller,[2] and Cram,[3] there has been little portent of the development of broad spectrum chiral stationary phases of extended scope and utility. While no single chiral stationary phase will ever suffice to separate all enantiomers, it is possible to rationally design chiral LC stationary phases that will separate the enantiomers of a wide assortment of solutes. The present paper describes one such stationary phase upon which we have to date separated the enantiomers of roughly 200 sulfoxides, lactones, amines, amino acids, amino alcohols, alcohols, hydroxy acids, and mercaptans. Insofar as this is our initial effort, we hardly consider this stationary phase to be perfected. Even so, from the high degree of latitude permissible in terms of structural variation, it is evident that literally thousands of racemic solutes can be resolved using the present stationary phase. We are confident that this is the first in a repertoire of rationally designed chiral LC stationary phases that will find widespread analytical and preparative applications.

If a chiral molecule (or stationary phase) is to have different affinities for enantiomers, it must have a minimum of three points of interaction with at least one of the enantiomers. Of these interactions, at least one must be stereochemically dependent and may be either bonding or repulsive.[4]

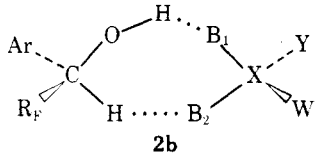
Prior NMR studies[6a–d] have shown that chiral type **1** fluoro alcohols afford two-point bonding to molecules bearing appropriate combinations of a wide variety of functional groups. Consequently, **1** interacts with enantiomers of an appropriate solute to afford diastereomeric chelate-like solvates, broadly depicted as **2a** and **2b**. These diastereomeric solvates differ in stability only if there is some mechanism whereby the alcohol substituents, R_F and W, "know" the relative locations of Y and Z. Momentarily neglecting interactions involving R_F and Y, it is obvious that a concomitant bonding interaction between W and Z will confer additional stability to **2a**, whereas repulsion between W and Z will cause **2a** to be of diminished stability. Obviously, R_F and Y are also involved in determining stability differences between solvates **2a** and **2b**. At present, these two groups seem to be relegated to rather minor roles and, as an *initial* simplifying assumption, we shall neglect whatever contributions these groups may make toward stability differences of the diastereomeric solvates. While virtually any kind of "third" interaction might be used to confer such stability differences, we initially have chosen to utilize an interaction differing in kind from the first two.

Chiral 2,2,2-trifluoro-1-(9-anthryl)ethanol, **1a**, has previously been used as a chiral solvating agent for the NMR de-



2a

1



2b

R_F = Perfluoroalkyl
X = C, N, P, S, or a group of atoms
B_1 = hydrogen bond receptor
B_2 = carbinyl hydrogen bond receptor

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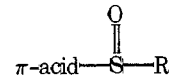
Table I. Separation of Sulfoxide Enantiomers upon Chiral Stationary Phase 3



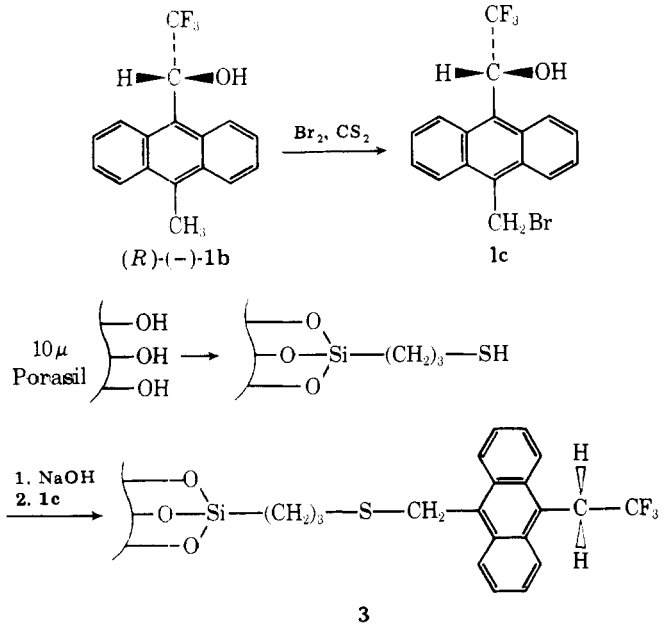
compd	R	π-acid	α	k'_1	k'_2	CD of first enantiomer
5[a]	methyl	2,4-DNP	1.12	13.05	14.61	+ at 293 nm
6	isopropyl	2,4-DNP	1.21	5.43	6.57	
7	*n*-butyl	2,4-DNP	1.19	6.32	7.53	+ at 296 nm
8	*n*-octyl	2,4-DNP	1.24	4.44	5.51	
9	*n*-dodecyl	2,4-DNP	1.26	3.33	4.20	+ at 297 nm
10	phenyl	2,4-DNP	1.23	6.82	8.38	+ at 296 nm
11	benzyl	2,4-DNP	1.22	7.70	9.43	+ at 206 nm
12	*n*-dodecyl	4-$NO_2C_6H_4$	1.09	2.78	3.03	
13	*n*-dodecyl	2,4,6-$(NO_2)_3$-5-CH_3C_6H	1.18	2.87	3.38	
14	*n*-dodecyl	2-CF_3-4-$NO_2C_6H_3$	1.08	1.82	1.97	
15	*n*-dodecyl	2,4-$(NO_2)_2C_6H_3CH_2$	1.38	6.39	8.79	+ at 263 nm
16[a]	*n*-dodecyl	4-ClC_6H_4	1.02	1.26	1.29	

[a] Chromatography of a partially resolved configurationally established sample established elution order.

termination of enantiomeric purity and absolute configuration.[6a-d] In addition to being a good chemical shift perturber, the anthryl substituent of **1a** is a π-base. Hence, solute enantiomers affording the types of solvates depicted in **2a** and **2b** seemed[7a-c] quite likely to separate upon a **1a**-derived chiral stationary phase provided one of the solute substituents, W, was a π-acceptor. In other words, we are intentionally incorporating a stereochemically dependent third interaction, in this instance a π–π donor–acceptor interaction. This simple concept not only gives a basis for anticipating *when* enantiomer separation might occur, it also predicts elution order. The enantiomer incorporated into solvate **2a** is expected to be the last eluted.

Chiral stationary phase **3** was prepared as shown in Scheme I and bonded onto 10μ Porasil. A 10 × 254 mm LC column packed with this material affords ~4000 theoretical plates for an unretained sample (durene) and retains simple nitroaromatics in order of increasing π-acidity. More interestingly, it separates the enantiomers of a variety of solutes that contain π-acid substituents. To facilitate direct comparison, all separations discussed herein employed 4:1 hexane–2-propanol, a mixture not necessarily optimal for any given solute. Figure 1 shows a typical resolution of a racemic solute. Although a

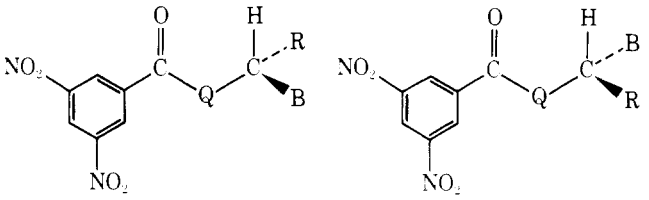
Scheme I



3

more extensive compilation of examples and chromatographic data will appear elsewhere, Table I provides sufficient data to illustrate the scope of the sulfoxide resolutions. Elution orders appear to be consistent (judged from the signs of CD adsorption of the separated enantiomers), and the actual elution orders appear to be those expected.

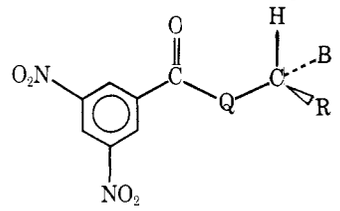
The ability to incorporate π-acid functionality into many solutes considerably extends the scope of stationary phase **3**. General representation **4** depicts 3,5-dinitrobenzoyl derivatives of the enantiomers of amines, amino acids, amino alcohols, alcohols, hydroxy acids, and mercaptans. The conformation shown in **4** is heavily populated in solution[8] and affords a ready means for understanding the origin of the enantiomeric separation and the elution orders observed. In instances where B is less basic than the carbonyl oxygen of the dinitrobenzoyl group, the latter serves as B_1 (see **2a,b**), the site of strong hydrogen bonding by the hydroxyl of **3**. The secondary interaction at B affords a chelate-like solvate that, with respect to the chelate ring, places the 3,5-dinitrophenyl substituent either cis (most stable and strongly retained) or trans to the anthryl group, depending upon the stereochemistry of the solute.



Q = NH, O, S
B = Ar, CH_2Ar, COOR', CH_2COOR', CONHR'
R = alkyl, perhaloalkyl, $(CH_2)_nAr$

Table II provides the chromatographic data pertinent to a number of chromatographic resolutions upon stationary phase **3**. Chromatography of partially resolved samples of known absolute configuration shows the observed elution orders to be consistent with the aforementioned model. Structural complexities beyond those evident from representation **4** may be tolerated. For example, the R group need not be a simple alkyl group and B can be a group other than those indicated. It should be evident, however, that additional basic sites (or π-acid groups) might introduce complications into the simplistic model just presented. When B is more basic than the carbonyl oxygen in **4**, elution orders are reversed as the solvation mode "flip-flops". That is, B groups such as COOR, CH_2COOR, and CONHR serve as B_1 and the carbonyl

Table II. Separation of Derivatized Enantiomers upon Chiral Stationary Phase 3



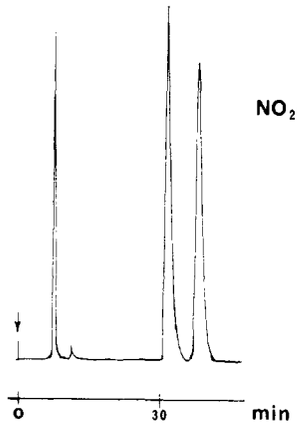
compd	Q	B	R	α	k_1'	k_2'
17[a]	NH	C_6H_5	CH_3	1.19	3.01	3.57
18[a]	NH	C_6H_5	C_2H_5	1.29	2.63	3.40
19[a]	NH	C_6H_5	i-C_3H_7	1.26	2.29	2.89
20[a]	NH	α-thienyl	CH_3	1.14	3.04	3.45
21[a]	NH	p-$CH_3OC_6H_4$	CH_3	1.18	5.19	6.13
22	NH	p-$CF_3C_6H_4$	CH_3	1.11	2.03	2.25
23[a]	NH	CO_2CH_3	CH_3	1.08	4.16	4.48
24[a]	NH	CO_2CH_3	$CH_2C_6H_5$	1.10	4.00	4.41
25[a]	NH	CO_2CH_3	i-C_3H_7	1.05	2.75	2.89
26[a]	NH	CO_2CH_3	$CH_3S(CH_2)_2$	1.04	4.81	5.03
27[a]	NH	CO_2CH_3	C_6H_5	1.19	4.17	4.48
28[a]	NH	CONH n-C_4H_9	CH_3	1.30	2.10	2.61
29[a]	NH	CONH n-C_4H_9	i-C_3H_7	1.33	0.82	1.10
30[a]	NH	CONH n-C_4H_9	$CH_2C_6H_5$	1.56	1.22	1.90
31[a]	NH	CONH n-C_4H_9	$(CH_2)_2SCH_3$	1.37	1.66	2.30
32[a]	NH	CONH n-C_4H_9	C_6H_5	1.78	0.75	1.33
33[a]	NH	CH_2OH	C_6H_5	1.38	2.36	3.30
34[a]	NH	CH_2OOCCH_3	C_6H_5	1.18	5.30	6.20
35	O	CO_2CH_3	2,5-$(CH_3)_2C_6H_3$	1.05	2.51	2.63
36[a]	O	CO_2CH_3	CCl_3	1.06	1.88	2.00
37[a]	O	CO_2CH_3	CH_3	1.05	3.39	3.57
38[a]	O	CO_2CH_3	$CH_3O_2CCH_2$	1.12	6.95	7.81
39[a]	O	C_6H_5	CH_3	1.08	1.56	1.68
40[a]	O	C_6H_5	C_2H_5	1.10	1.23	1.35
41[a]	O	C_6H_5	C_3H_7	1.12	1.09	1.23
42[a]	O	C_6H_5	i-C_3H_7	1.14	0.81	0.93
43[a]	O	C_6H_5	t-C_4H_9	1.13	0.81	0.92
44[a]	O	α-naphthyl	CH_3	1.04	2.21	2.29
45	O	9-anthryl	CH_3	1.06	2.53	2.67
46	O	2-phenanthryl	CH_3	1.07	3.13	3.36
47	O	p-$CH_3SC_6H_4$	C_3H_7	1.10	1.56	1.72
48	O	p-$CH_3OC_6H_4$	C_3H_7	1.12	1.60	1.79
49	S	C_6H_5	CH_3	1.07	1.47	1.57
50	S	α-naphthyl	i-C_3H_7	1.16	1.05	1.21
51				1.29	1.93	2.49
52				1.40	1.51	2.11
53				1.14	5.17	5.93
54[a]				1.06	4.90	5.20
55[a]				1.08	4.16	4.50
56				1.38	1.70	2.35
57[a]				1.17	11.00	12.90

[a] Chromatography of a partially resolved configurationally established sample established elution order.

oxygen of the 3,5-dinitrobenzoyl group serves as B_2 in **2a,b**. Table II provides chromatographic data for a number of such examples.

Cyclic compounds can also fall into the purview of **3**. For example, as the *N*-3,5-dinitrobenzoyl derivatives, the enantiomers of *cis*- (**51**) or *trans*-2-phenylcyclohexylamine (**52**), *cis*- (**53**) or *trans*-2-phenylcyclopropylamine (**54**), *trans*-3-amino-4-hydroxycyclopentene (**55**), and *cis*-2-amino-1-methylcyclobutanol (**56**) are separated (Table II). The enantiomers of γ-(2,4-dinitrophenyl)butyrolactone, **57**, can be separated. The restricted conformation freedom of cyclic solutes does not necessarily facilitate chiral recognition; conformation rigidity may either aid or prevent the simultaneous occurrence of the multiple interactions essential to chiral recognition.

Knowledge of solute structure should arm one for thoughtful assessment of the actual solvation mode. Significantly, no inversion of elution order has been found to occur



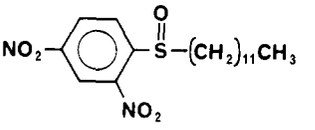


Figure 1. Separation of the enantiomers of racemic *n*-dodecyl 2,4-dinitrophenyl sulfoxide. The first peak is durene, added as a retention marker.

with solvent change, *including aqueous solvents*.

Although the present column is essentially analytical in scale, it has afforded total enantiomeric separation for 5-mg samples of racemates. It has also afforded accurate enantiomeric purity assays, even on highly enriched (99%) material. Practical applications for this and other related chiral fluoro alcoholic stationary phases should be apparent. For example, large versions of the present column will allow the automated resolution of multigram amounts of a variety of racemic solutes.

It should also be noted that a chiral stationary phase prepared from a single enantiomer of a racemate separable on **3** should allow separation of the enantiomers of **1a** and related fluoro alcohols. In this manner, the suitability of a variety of fluoro alcohols for incorporation into a chiral stationary phase can be rapidly ascertained and still more efficient chiral stationary phases devised.

Experimental Section

(*R*)-(−)-2,2,2-Trifluoro-1-[9-(10-α-bromomethyl)anthryl]-ethanol, 1c. This alcohol was prepared by the method of Pavlin[9] from (*R*)-(−)-**1b**. The preparation and resolution of **1b** has been described[9] and proceeds along the same lines as those reported for **1a**.[10a,b]

Preparation of Chiral Stationary Phase 3. Porasil [10μ, 21 g, dried 24 h at 160 °C (0.01 torr)] was treated under a nitrogen blanket with 84 mL of freshly distilled (3-mercaptopropyl)trimethoxysilane dissolved in 75 mL of 1:1 dry benzene–dry pyridine to afford a slurry stirrable with a magnetic bar. The slurry was heated to 80 °C for 24 h with occasional stirring. After cooling, the supernatant was decanted and the wet silica was thrice washed with benzene using centrifugation–decantation. The silica was thoroughly washed (fine pore sintered glass funnel) with acetone, ether, and pentane and dried for 12 h at 0.01 torr.

Anal. Found: C, 4.64; H, 1.22; Si, 42.54; S, 2.69.

The above silica (21 g) was suspended in 75 mL of absolute ethanol (nitrogen blanket) and stirred magnetically. After addition of a twofold excess of solid sodium hydroxide (1.54 g), the slurry was heated to ~75 °C for 3 h with occasional stirring. A twofold excess of (*R*)-(−)-2,2,2-trifluoro-1-[9-(10-α-bromomethyl)anthryl]-ethanol, **1c** (14.21 g), dissolved in 15 mL of absolute ethanol was added and heating was continued for 48 h under nitrogen with occasional stirring. After cooling, the modified silica was collected, washed exhaustively with methanol, acetone, ether, and pentane, and dried as before to afford 24.05 g of light yellow solid.

Anal. Found: C, 11.90; H, 1.40; F, 2.20; Si, 37.81; S, 1.84.

The 10 × 254 mm column was slurry packed (CCl_4) using conventional techniques.

Solutes. Most of the solutes utilized herein are either trivial derivatives of, or are themselves, well known compounds. Most are commercially available or were available in these laboratories from prior studies. Characterization of the solutes is described elsewhere.[11] Precautions were taken to ensure that the chromatographic peaks attributed to the solute enantiomers actually were those of the enantiomers.

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

Registry No.—**1c**, 69632-09-3; (+)-**5**, 69743-66-4; (−)-**5**, 56942-42-8; (+)-**6**, 69632-10-6; (−)-**6**, 69668-46-8; (+)-**7**, 69632-11-7; (−)-**7**, 69632-12-8; (+)-**8**, 69632-13-9; (−)-**8**, 69632-14-0; (+)-**9**, 69632-15-1; (−)-**9**, 69632-16-2; (+)-**10**, 69632-17-3; (−)-**10**, 69632-18-4; (+)-**11**, 69632-19-5; (−)-**11**, 69632-20-8; (+)-**12**, 69632-21-9; (−)-**12**, 69632-22-0; (+)-**13**, 69632-23-1; (−)-**13**, 69632-24-2; (+)-**14**, 69632-25-3; (−)-**14**, 69632-26-4; (+)-**15**, 69632-27-5; (−)-**15**, 69632-28-6; (+)-**16**, 69632-29-7; (−)-**16**, 69632-30-0; (+)-**17**, 69632-31-1; (−)-**17**, 69632-32-2; (+)-**18**, 69632-33-3; (−)-**18**, 69632-34-4; (+)-**19**, 69632-35-5; (−)-**19**, 69632-36-6; (+)-**20**, 69632-37-7; (−)-**20**, 69632-38-8; (+)-**21**, 69668-47-9; (−)-**21**, 69668-48-0; (+)-**22**, 69632-39-9; (−)-**22**, 69632-40-2; (D)-**23**, 69632-41-3; (L)-**23**, 69632-42-4; (D)-**24**, 69632-43-5; (L)-**24**, 69632-44-6; (D)-**25**, 69632-45-7; (L)-**25**, 69632-46-8; (D)-**26**, 69632-47-9; (L)-**26**, 69632-48-0; (+)-**27**, 69632-49-1; (−)-**27**, 69632-50-4; (+)-**28**, 69632-51-5; (−)-**28**, 69632-52-6; (+)-**29**, 69632-53-7; (−)-**29**, 69632-54-8; (+)-**30**, 69632-55-9; (−)-**30**, 69632-56-0; (+)-**31**, 69632-57-1; (−)-**31**, 69632-58-2; (+)-**32**, 69632-59-3; (−)-**32**, 69653-37-8; (+)-**33**, 69632-60-6; (−)-**33**, 69632-61-7; (+)-**34**, 69632-62-8; (−)-**34**, 69632-63-9; (+)-**35**, 69632-64-0; (−)-**35**, 69632-65-1; (+)-**36**, 69668-49-1; (−)-**36**, 69668-50-4; (+)-**37**, 69632-66-2; (−)-**37**, 69632-67-3; (+)-**38**, 69632-68-4; (−)-**38**, 69632-69-5; (+)-**39**, 3205-33-2; (−)-**39**, 3205-18-3; (+)-**40**, 69632-70-8; (−)-**40**, 69632-71-9; (+)-**41**, 69632-72-0; (−)-**41**, 69632-73-1; (+)-**42**, 69632-74-2; (−)-**42**, 69632-75-3; (+)-**43**, 69632-76-4; (−)-**43**, 69632-77-5; (+)-**44**, 69632-78-6; (−)-**44**, 69632-79-7; (+)-**45**, 69632-80-0; (−)-**45**, 69632-81-1; (+)-**46**, 69653-27-6; (−)-**46**, 69685-63-8; (+)-**47**, 69632-82-2; (−)-**47**, 69632-83-3; (+)-**48**, 69632-84-4; (−)-**48**, 69632-85-5; (+)-**49**, 69632-86-6; (−)-**49**, 69632-87-7; (+)-**50**, 69632-88-8; (−)-**50**, 69632-89-9; (+)-**50**, 37982-29-9; (−)-**50**, 37982-28-8; (+)-**50**, 37982-23-3; (−)-**52**, 69743-67-5; (+)-**53**, 69684-88-4; (−)-**53**, 69684-89-5; (+)-**53**, 3721-28-6; (−)-**54**, 3721-26-4; (+)-**55**, 69668-51-5; (−)-**55**, 69668-52-6; (+)-**56**, 69632-90-2; (−)-**56**, 69632-91-3; (+)-**57**, 61520-98-7; (−)-**57**, 61520-97-6; (3-mercaptopropyl)-trimethoxysilane, 4420-74-0.

References and Notes

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