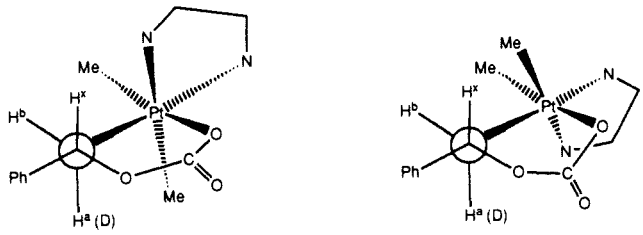
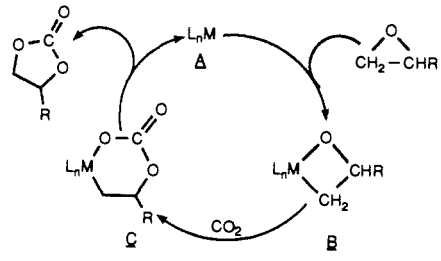


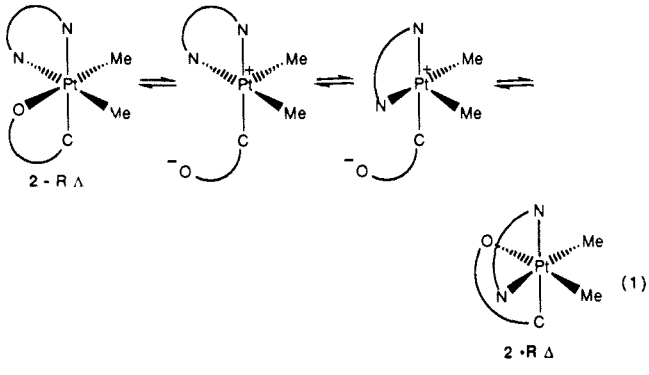
2 - R Λ 2 - R Δ

Figure 2. Diagram of the MMX minimized structures of **2**-RΛ and **2**-RΔ, showing a view down the CHPh–CH_2 bond. The optimized dihedral angles used in calculating the coupling constants ^3J(HH) were H^xCCH^b = 60 (5)° and 63 (2)°, H^xCH^a = 173 (4)° and 171 (2)° for the RΔ/SΛ and RΛ/SΔ diastereomers.

Scheme I



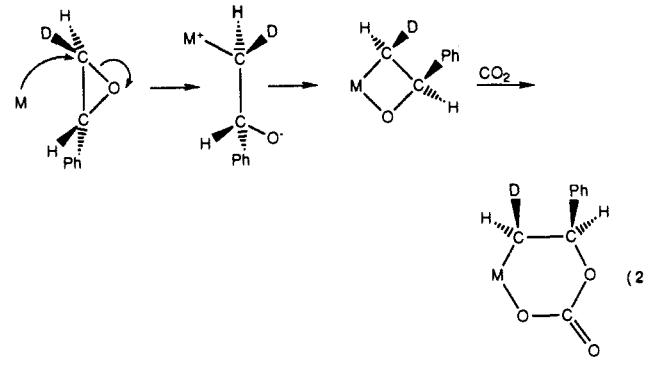
dissolved, the NMR spectrum indicated the presence of a mixture of diastereomers; hence interconversion between **2**-RΔ and **2**-RΛ is facile under these conditions. This probably occurs by dissociation of the Pt–O bond, followed by pseudorotation and recoordination as shown in eq 1.



2 - R Λ

2 - R Δ (1)

The reaction of *trans*-CHDCHPhO, CO_2, and **1** gave [$PtMe_2${*cis*-CHDCHPhOC(O)O}(phen)] (**2**-D). Investigations using NMR techniques have shown that the product has *cis*-1-D,2-Ph stereochemistry (Figure 2). On the basis of crystallographic data for the RΔ isomer (Figure 1) and MMX data for both the RΔ and RΛ isomers (Figure 2),[12] each isomer is expected to give $^3J(H^aH^x)$ = 11–13 Hz and $^3J(H^bH^x)$ = 0–3 Hz.[13] The observed coupling constants are in good agreement (see supplementary material, Table SX). Of critical importance to this investigation is the absence of the coupling constant $^3J(H^aH^x)$ in both isomers of **2**-D (Table SX). The stereochemistry is therefore determined with confidence, and the result shows that the reaction forming **2**-D occurs with inversion of stereochemistry at the CHD center. An S_N2 mechanism for the oxidative addition, in which the metal attacks at the less sterically hindered carbon atom, can be inferred as shown in eq 2, M = [$PtMe_2$(phen)].



(2)

Acknowledgment. The NSERC of Canada and the Academic Development Fund of the University of Western Ontario are thanked for financial support of this research. L.G. is grateful for the award of an NSERC postdoctoral scholarship.

Supplementary Material Available: Tables SI–SVII, SIX, and SX, comprising crystal data and experimental conditions, atomic positional and thermal parameters, bond distances and angles, weighted least-squares planes, selected torsion angles, selected friedel pairs, and ^{1}H NMR data for **2** (9 pages); Table SVIII, comprising structure amplitudes for **2** (16 pages). Ordering information is given on any current masthead page.

(11) This is not a trivial experiment since metallacycles undergo many types of rearrangements which could lead to racemization or inversion at that carbon center.[4-6] In particular, platinacyclobutanes undergo ready skeletal isomerization. Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(12) We cannot tell if the second crystalline form contains molecules in the RΛ configuration, but we can be confident that the chirality at the carbon is *R*. Similarly, because of the equilibration, we cannot tell if RΔ is the major diastereomer in solution. Molecular mechanics calculations suggest that RΛ is more stable by ≈0.8 kcal mol^{-1} than RΔ. This would give an equilibrium constant K = [RΛ]/[RΔ] ≈ 3.9 in the absence of differential solvation effects. The calculations were made by using the MMX force field developed by K. Gilbert and J. J. Gajewski (Indiana University). Good agreement was found by using starting structures based on the X-ray data for **2**-RΔ or using a "hand-drawn" structure. The metallacycle configuration with equatorial phenyl groups was found to be 1.5–2.5 kcal mol^{-1} more stable than that with axial phenyl groups for both diastereomers.

(13) Haasnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1981**, *36*, 2783. The extent of inversion at the CHD center is estimated to be at least 90%.

(14) The reductive elimination step in the catalytic cycle[2] would then also occur with inversion, that is by dissociation of the Pt–O bond followed by S_N2 attack by the O^- center on the Pt–CH_2 group, to give overall retention of stereochemistry.

Synthesis of Helical Poly-β-pyrroles. Multiple Atropisomerism Resulting in Helical Enantiomorphic Conformations

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We have been interested in designing large conformationally flexible molecular arrays that have a predictable secondary

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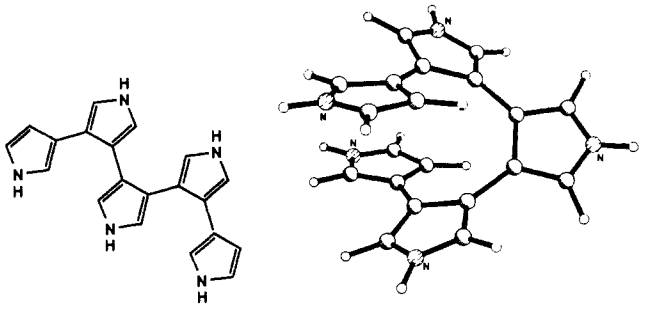


Figure 1. Computer-generated, energy-minimized β-linked pentapyrrole.

structure, in particular, one that could potentially mimic the topology of the α-helical domains of proteins. The single structural feature that distinguishes biopolymers (and certain polymers) from small molecules is their ability to adopt helical conformations due to nonbonding interactions.[2] Here we describe the systematic construction of poly-β-linked pyrroles **1** whose conformation(s) are determined by the atropisomerism of the adjacent pyrrole rings. If one makes a model of a sequence of β-linked pyrrole rings, the twist between each flat ring imparts a helical secondary structure to the overall array if the twist between each pyrrole ring is in the same direction. Figure 1 shows an energy-minimized, computer-generated β-linked pentapyrrole.[3] After considerable experimentation with respect to pyrrole protecting groups and

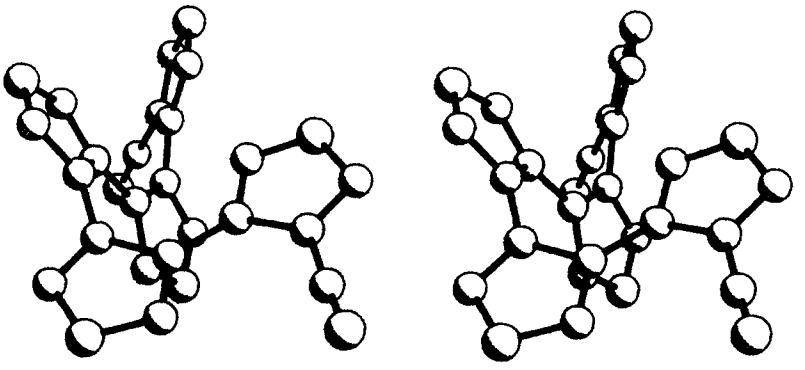
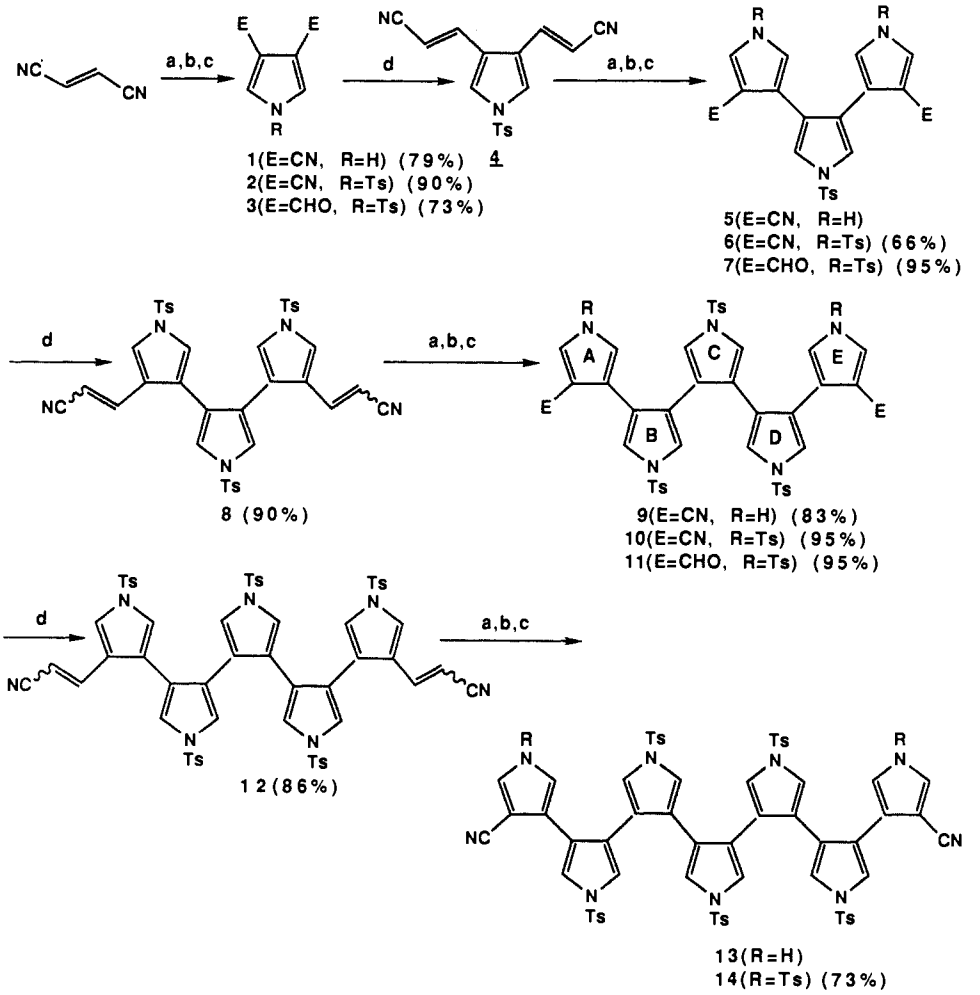


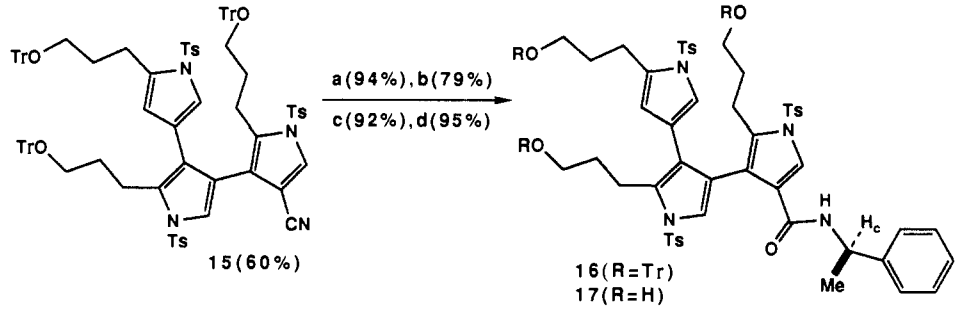
Figure 2. Stereotopic representation of **10** with the Ts groups removed for clarity.

Scheme I[a]



[a] (a) TOSMIC/DMF/NaH/0 °C. (b) NaH/DMF/TsCl. (c) DIBAL/PhMe/−30 °C. (d) $(EtO)_2P(O)CH_2CN$/NaH/−30 °C.

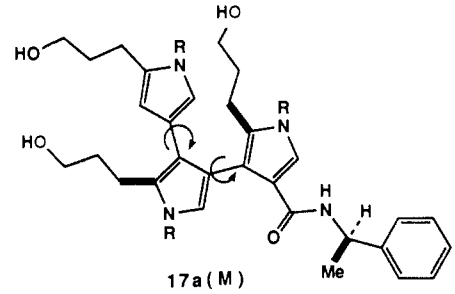
Scheme II[a]

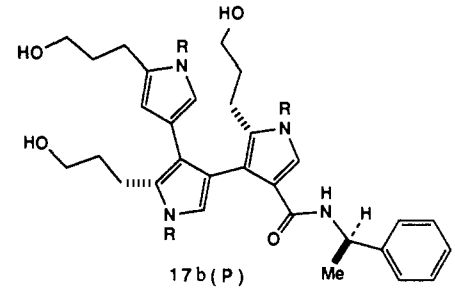


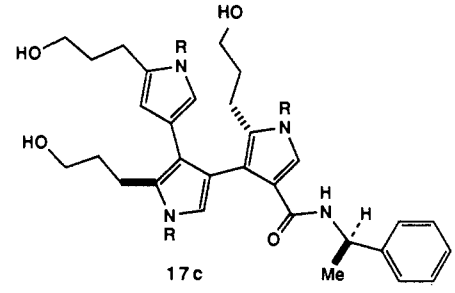
[a](a) DIBAL/THF. (b) $NaClO_2/NaH_2PO_4/DMSO/H_2O$. (c) (*R*)-α-Methylbenzylamine, $Ph_2P(O)Cl/THF$. (d) *p*-TsOH/$CHCl_3$/MeOH.

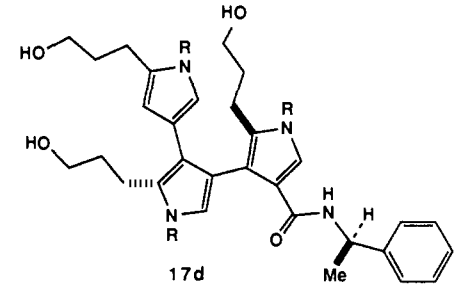
Michael acceptors, the sequence shown below provided a convenient and reasonably rapid way for making gram quantities of β-oligopyrroles, Scheme I.

Treatment of fumaronitrile with (*p*-tolylsulfonyl)methyl isocyanide[4] (TOSMIC)/DMF/NaH (2 equiv) at 0–5 °C for 15 min gave 3,4-dicyanopyrrole **1** (79%). N-Tosylation of **1** (NaH/DMF/TsCl) gave **2** (90%). While it might be expected that in situ tosylation of the sodium salt of **1** would give **2**, thus avoiding a separate protection step, it was found that superior yields of **2** were possible if the N-tosylation was conducted as a separate step. Both nitriles in **2** can be reduced with DIBAL/PhMe/−30 °C to give **3** (73%). Treatment of the dialdehyde **3** with diethyl (cyanomethyl)phosphonate/NaH/−30 °C gave **4** [77%, isomer ratio 52(*E*,*E*):49(*E*,*Z*):27(*Z*,*Z*)]. The above mixture was treated with TOSMIC/DMF/NaH at 0–5 °C and the resulting tripyrrole **5** N-tosylated (TsCl/CH_2Cl_2/DMAP) to give **6** (66% from **4**). DIBAL reduction of the dinitrile **6** in toluene at −30 °C gave the dialdehyde **7** (95%). Repetition of the same sequence of transformation, Horner–Wittig reaction, TOSMIC treatment, and N-tosylation, gave respectively **8** (90%), **9** (83%), and **10** (95%). Similarly, the penta-β-pyrrole **10** was converted into the hepta-β-pyrrole **14** (65%). The penta-β-pyrrole **10** gave crystals suitable for X-ray diffraction (DMF–H_2O diffusion). Figure 2 is a stereotopic representation with the Ts groups removed for clarity. The dihedral angles between each pyrrole ring are AB (−11.83°), BC (−115.15°), CD (25.98°), and DE (45.24°), respectively. There are two molecules of **10** per unit cell, and two molecules of DMF. Interestingly, they are antipodal due to the right-handed (P) and left-handed (M) forms of the helical secondary structure. In order to examine whether or not β-polypyrroles adopt helical conformations in solution, we have made the tripyrrole **17** by the sequence of transformations shown in Scheme II. Compound **17** can exist in four diastereomeric forms, **17a–d**, which can interconvert if rotation about the adjacent β-linked pyrrole rings is possible. If the rotational barrier is high (>17 kcal mol^{-1}), it should be possible to observe by NMR all four compounds; but if the tri-β-pyrrole adopts a helical secondary structure, only two diastereomers, **17a**(P) and **17b**(M), will be present. The ^1H NMR









(300 MHz) spectrum of **17** shows doubling (1:1) of all the signals, and no change in the spectrum from 0–100 °C. Thus only two diastereomeric conformers are present rather than four. While this does not prove that they are **17a** and **17b**, taken together with the X-ray data, it is most likely that the diastereomers are the right-handed (M) **17a** and left-handed (P) **17b** helical conformers. It should be noted that **15** does not show any doubling of its ^1H NMR resonances. The NTs groups in compounds such as **10** can be removed by treatment with 2 N EtONa/EtOH. The unprotected poly-β-linked pyrroles are extremely acid sensitive as ex-

(2) For references to both the general description of helical molecules and more specifically α-helical peptide domains, see: Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 21. Farina, M. *Top. Stereochem.* **1987**, *17*, 1. Mislow, K.; Bickart, P. *Isr. J. Chem.* **1977**, *15*, 1. Morawetz, H. *Macromolecules in Solution*; Wiley: New York, 1975. Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 10. Brewster, J. H. *Top. Curr. Chem.* **1974**, *47*, 29. Schlögl, K. Planar Chiral Molecular Structures. *Top. Curr. Chem.* **1984**, *125*, 27. Laarhoven, W. H.; Prinsen, W. J. C. Carbohelicenes and Heterohelicenes. *Top. Curr. Chem.* **1984**, *125*, 63. Poland, D.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic Press: New York, 1970. For references to α-helical domains of peptides, see: Creighton, T. E. *Proteins* W. H. Freeman and Company: New York, 1984. Sueki, M.; Lee, S.; Powers, S. P.; Denton, J. B.; Konishi, Y.; Scheraga, H. A. *Macromolecules* **1984**, *17*, 148. Scheraga, H. A. *Acc. Chem. Res.* **1978**, *12*, 7.

(3) Dr. Regina Bohacek of Ciba-Geigy Corporation is thanked for the molecular modeling studies.

(4) van Leusen, A. M.; Possel, O. *Heterocycles* **1977**, *7*, 77. For the synthesis of 3,3′-bipyrroles, see: Magnus, P.; Gallagher, T.; Schultz, J.; Or, Y.-S.; Ananthanarayan, T. P. *J. Am. Chem. Soc.* **1987**, *109*, 2706. Alkylation of TOSMIC: van Leusen, A. M.; Bouma, R. J.; Possel, O. *Tetrahedron Lett.* **1975**, 3487.

pected. With a flexible route to these new structural types available, we are examining the many possible and varied uses these molecules might exhibit.[5,6] In a general sense, the iterative process depicted herein should enable an array of molecules with predictable secondary structure to become available.

Acknowledgment. The National Science Foundation and the Robert A. Welch Foundation are thanked for their financial support of this research. Dr. Douglas A. Gage, Michigan State University—NIH Mass Spectrometry Facility, is thanked for mass spectral data. Dr. Jan Wasley, Ciba-Geigy Corporation, is thanked for discussions concerning pyrrole chemistry.

Supplementary Material Available: Spectral data for compounds **1–3**, **6**, **7**, **10**, **14**, **15**, and **17** (2 pages). Ordering information is given on any current masthead page.

(5) α-Linked polymeric pyrroles have useful semiconducting properties: Bryce, M. R. *Nature* **1988**, *335*, 12. Cowan, D. O.; Wlygul, F. M. The Organic Solid State. *Chem. Eng. News* **1986**, *64*, 28. Munn, R. W. Molecular Electronics. *Chem. Br.* **1984**, 518. Bryce, M. R. Organic Conductors. *Chem. Br.* **1988**, 781.

(6) For details of the single-crystal X-ray crystallographic structure determination of **10**, please write to Dr. J. C. Huffman, Molecular Structure Center, Indiana University, Bloomington, IN 47405. Request report no. 88158.

Additions and Corrections

Carbonylation Chemistry of the Tantalum Silyl (η^5-C_5Me_5)-$Cl_3TaSiMe_3$. Synthesis, Characterization, and Reaction Chemistry of (η^5-C_5Me_5)$Cl_3Ta(\eta^2$-COSiMe$_3$) and Derivatives [*J. Am. Chem. Soc.* **1989**, *111*, 149–164]. JOHN ARNOLD, T. DON TILLEY,* ARNOLD L. RHEINGOLD,* STEVEN J. GEIB, and ATTA M. ARIF

The crystal structure of Cp*$Cl_3Ta[\eta^2$-OC(PEt$_3$)SiMe$_3$] (**6**) was originally reported as a fully mirror-plane disordered structure in the orthorhombic space group *Pcam* (R = 6.77%). A reexamination of the structure reveals that the correct space group is $Pca2_1$ (R = 2.85%) and that an ordered and chemically more reasonable structure is obtained, although all significant features of the earlier report remain unchanged. A set of the redetermined data may be obtained from one of us (A.L.R.) or from the complete disclosure that has been submitted for publication (Rheingold, A. L. *Acta Crystallogr., Sect. C*).

Book Reviews *

Flow Injection Atomic Spectroscopy. Practical Spectroscopy Series. Volume 7. Edited by José Luis Burguera (University of Los Andes, Venezuela). Marcel Dekker: New York and Basel. 1989. xii + 353 pp. $125.00. ISBN 0-8247-8059-0.

More than 10 years has passed since the publication of the first papers on flow injection analysis (FIA), and the technique has now been clearly shown to have many widespread applications in analytical chemistry. One of these important applications, of course, is atomic spectroscopy, and therefore, this book comes along at a very appropriate time. This book provides a wealth of information for a basic understanding of the flow injection analysis-atomic spectroscopy (FIA-AS) technique. The book consists of a Foreword written by the originator of the FIA technique, Professor Jaromir Růžička, a Preface written by the Editor, eight chapters written by a variety of authors, and two very useful appendices. There is also an author and a subject index.

The first chapter, written by Kent K. Stewart, gives a general introduction to the technique and describes some basic components of FIA-AS systems. Various types of FIA-AS assay systems are described. In the second chapter, William E. van der Linden discusses some theoretical aspects of the technique, including some specific aspects related to the use of a flame atomic-absorption spectrophotometer as a detector. In Chapter 3, Jacobus F. van Staden describes basic components including sampling, pumping, manifold, and nebulizer-burner systems. Chapter 4, by Khaolun Fang, discusses various analytical methods and techniques, including hydride generation methods and cold vapor methods for mercury; and Chapter 5, by Miguel Valcárcel and Mercedes Gallego, describes separation techniques including continuous precipitation, liquid extraction and ion exchange. Chapter 6, by Elias A. G. Zagatto and co-workers, describes some selected applications of FIA-AS in agricultural and environmental analysis; and Chapter 7, by Roy A. Sherwood and Bernard F. Rocks, describes applications of the technique in clinical chemistry. Some specialized applications involving graphite furnaces, chromatography, and inductively coupled plasma (ICP) atomic emission spectrometry are discussed. The final chapter, by Marcela Burguera, José Luis Burguera, and Gilbert E. Pacey, provides some useful information as to "current trends" in FIA-AS including instrumental developments such as speciation, conversion, automation, and miniaturized FIA systems. Some recent applications are also considered. There is also a somewhat subjective discussion of the present and the future of the technique. The book concludes with two useful appendices. Appendix A is a list of symbols, and Appendix B is an FIA-AS bibliography. Overall, this book is highly recommended.

Peter N. Kellher, *Villanova University*

Introduction to Microscale High-Performance Liquid Chromatography. Edited by Daido Ishii (Nagoya University). VCH: New York and Weinheim. 1988. xii + 208 pp. $59.95. ISBN 0-89573-309-9.

This book consists of 7 chapters written by different contributors and 10 appendices which list the available packing materials for the preparation of packed and microcolumns. The editor, D. Ishii, is the co-author on four of the seven chapters. Chapter 1 gives a brief introduction on microcolumn HPLC (~5 pages), Chapter 2 describes the instrumental requirement in microcolumn HPLC (24 pages), Chapter 3 covers the characteristics of microcolumns (34 pages), Chapter 4 describes the use of different common LC detectors (UV, fluorescence, and electrochemical) in microcolumn HPLC experiment (23 pages), while chapter 5 (17 pages) covers the hyphenated systems (microcolumns with IR and MS detection). Chapter 6 is focused on the use of postcolumn derivatization in microcolumn HPLC mostly on the band broadening due to the use of different postcolumn reactors. Finally in Chapter 7 different applications of microcolumn HPLC is described rather extensively as compared to the first six chapters (52 pages).

All chapters are well written, and there seems to be no typographical errors.

*Unsigned book reviews are by the Book Review Editor.