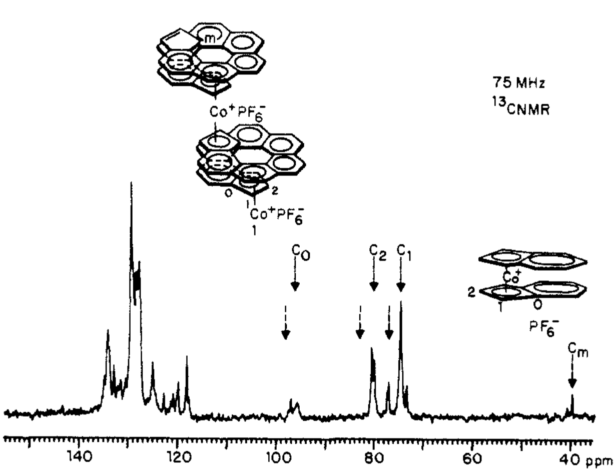

Figure 1. 75-MHz proton-noise-decoupled ^{13}C NMR spectrum of **2** in CD_3COCD_3. The spectrum, measured by using 90° pulses and no relaxation delay, is displayed with 5 Hz line broadening. The chemical shifts were measured assuming that of CD_3COCD_3 to be 29.8 ppm. Peaks assigned to metallocene carbons are pointed out, and the dotted arrows show where the corresponding resonances appear for the indene analogue (pictured). The peak marked C_m is attributed to the methylene carbon (labeled on the diagram).

it is racemic.[11] (3) The direction in which the helix winds is that favoring silyloxyls outside the helix.[12,13] Helicity is thus controlled by the stereochemistry of **5**.[5]

When the sample of helicene **1** in Scheme I is combined in tetrahydrofuran first with *tert*-butyllithium and then with $CoBr_2$·DME (DME = 1,2-dimethoxyethane) and the product is oxidized in aqueous HCl with $FeCl_3$, addition of NH_4PF_6 precipitates a red cobaltocenium salt (64% yield after washing with water and ether and drying).[5,14,15] It is soluble in acetone and acetonitrile and is unaffected by heating in air at 260 °C.

Evidence that this material is a short polymer of structure **2** ($M = Co^+PF_6^-$) is the following. The ^{13}C NMR spectrum (Figure 1) shows how metal and hydrocarbon are linked. The spectrum consists only of resonances characteristic of benzenoid helicenes (including **1**)[16] (135–118 ppm),[17] diindenylcobalt(III) salts (80–74 ppm),[18] and the methylene group of **1** (40 ppm, this last one small, corresponding to ca. two end groups for every three to four cobalts).[16,18] The shift of the cyclopentadienyl resonances 2 ppm to higher field than in diindenylcobalt(III) corresponds to the shift of the carbon-2 resonance in [7]helicene[17] (where this carbon is above another ring) from that in [4]helicene.[19] The absence of resonances around 51.3 ppm, characteristic of 1,1′-bi-1*H*-indene ["bi(3-indenyl)"], is also significant, showing that the transition-metal ions do not couple the carbanions by oxidation.

The fast atom bombardment (FAB) mass spectrum,[20] measured by S. Naylor and D. H. Williams in Cambridge, identifies the material as a mixture of oligomers. Thus the only prominent peaks correspond to oligomers with the following compositions:[21] $HArCo^+ArH$ (*m/e* 965), $HArCo^+ArCo^+ArH$ (*m/e* 1476), and $HArCo^+ArCo^+ArCo^+ArH$ (*m/e* 1987). The conclusion that two to four units are linked is also supported by elemental analyses, which correspond to 3.13 hydrocarbons, 2.13 $CoPF_6$'s, and 3.45 ± 1.4 H_2O's,[16] and therefore a number average molecular weight of ca. 1.9×10^3.

The optical activity is very large, $[\alpha]_D$ −26 000° for 100% enantiomeric excess (ee),[23] 4.1 (±0.6) times greater than that of **1**. The molar ellipticities of the CD peaks at 474 and 263 nm (-8.4×10^5 and -3.3×10^6, assuming the molecular weight to be 1.9×10^3) are 7.2 and 6.0 times larger than for the corresponding peaks in **4b**.[5]

Acknowledgment. We are grateful to the National Science Foundation (DMR-82-13794) and the National Institutes of Health (GM-34737) for support, to Christopher Turner and Michael Zagorski for assistance in measuring NMR spectra, and to D. H. Williams and S. Naylor for the FAB mass spectrum.

Supplementary Material Available: Elemental analyses of **2**, ^{1}H and ^{13}C NMR spectra of **1**, and CD and UV spectra of **1** and **2** (5 pages). Ordering information is given on any current masthead page.

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[10] Sudhakar, A. Ph.D. Dissertation, Columbia University, New York, NY, 1985.

[11] Prepared from (*R*)-**5** [46–52% enantiomeric excess (ee)] and irradiated in the presence of traces of iodine, it gives helical bis(indene) (containing the bromine) whose $[\alpha]_D$ (+82°) corresponds to ca. 1% ee. The double bonds in this material are shifted from their position in **1**.[10]

[12] The absolute configurations of **1** and **5** and **1**'s ee were assigned as in ref 5.

[13] (*S*,*S*)-**6** gives 27% (*M*)-**7a** (recognized by the symmetry of the ^{1}H NMR after debromination), 12% **7b**, and no detectable (^{1}H NMR) endo,endo isomer. The major product cannot have the endo,endo structure since the *M* configuration requires more asymmetric carbons with R stereochemistry than are present in **6**.[10]

[14] Kölle, U.; Khouzami, F. *Chem. Ber.* **1981**, *114*, 2929.

[15] $FeCl_2$·2(THF) gives an elusive product. (Diindenyliron is similarly sensitive. See: Treichel, P. M.; Johnson, J. W.; Calabrese, J. C. *J. Organomet. Chem.* **1975**, *88*, 215.)

[16] See the supplementary material.

[17] Defay, N.; Zimmermann, D.; Martin, R. H. *Tetrahedron Lett.* **1971**, 1871.

[18] Köhler, F. H. *Chem. Ber.* **1974**, *107*, 570.

[19] The second protonated carbon in the first ring counting from the inside of the helix.

[20] (a) Barber, M.; Bordoli, R. S.; Elliott, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A. (b) Rinehart, K. L., Jr. *Science (Washington, D.C.)* **1982**, *218*, 254.

[21] 3-Nitrobenzyl alcohol matrix,[22] 8-keV Xe^+ beam. Ar is $C_{36}H_{20}$. It is the monocations, formed by reduction, that are detected.

[22] Meili, J.; Seibl, J. *Org. Mass Spectrom.* **1984**, *19*, 581.

[23] Measured by using a sample prepared from **1** whose ee was 60%.

Molecular Discrimination in the Formation of Mixed Crystals of Some Substituted Chlorocinnamic Acids

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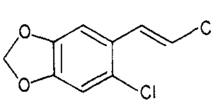
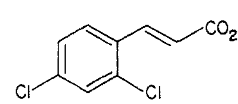
Received November 15, 1985

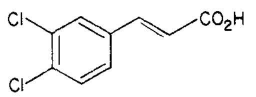
A study of the packing of mixed crystals is a valuable approach toward understanding weak intermolecular interactions in organic solids.[1] We have found that 6-chloro-3,4-(methylenedioxy)cinnamic acid (**1**) and 2,4-dichlorocinnamic acid (**1a**) form a



1



1a



1b

2a = $(\mathbf{1})_2(\mathbf{1a})$ **2b** = $(\mathbf{1})(\mathbf{1b})$

distinct 2:1 complex, **2a**, which is neither a solid solution nor a mixture of **1** and **1a**.[2] Yet, acid **1** and 3,4-dichlorocinnamic acid (**1b**) cocrystallize from EtOH not only as a 1:1 complex, **2b** (mp 217–218 °C), but also as variable-melting solids with compositions between 7:1 and 1:3 of **1** and **1b**. These differences between the closely related acids **1a** and **1b** may be used to monitor the im-

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[1] Kitaigorodskii, A. I. *Mixed Crystals*; Springer-Verlag: Berlin, Heidelberg, 1984.

[2] Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1984**, 145.

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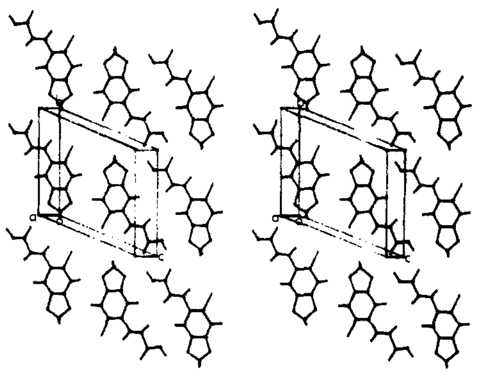
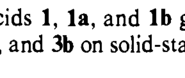


Figure 1. Stereoview of the crystal structure of acid **1**, (form I) to show the molecular sheet parallel to (102).

portance of directional forces vis-à-vis shape and size factors in the crystal stabilization of these complexes.

Acids **1**, **1a**, and **1b** were chosen for these experiments since they are all planar chloro-aromatic compounds which adopt the so-called "β-structure" with a cell edge of ca. 4 Å.[3,4] We have noted that such crystal structures are characterized by short in-plane Cl···Cl and C–H···O contacts.[5,6] Consequently it was expected that the complexes should also adopt the β-structure by optimizing such interactions. Indeed, the triclinic crystals of **2a** have a short axis of 3.79 Å.[4]

Acids **1**, **1a**, and **1b** gave the topochemical β-truxinic dimers **3**, **3a**, and **3b** on solid-state UV irradiation. Complex **2a**, however,



Ar₁, 6-chloro-3,4-(methylenedioxy)phenyl
Ar₂, 2,4-dichlorophenyl
Ar₃, 3,4-dichlorophenyl

3: X = Y = Ar$_1$; **3a**: X = Y = Ar$_2$; **3b**: X = Y = Ar$_3$; **3c**: X = Ar$_1$, Y = Ar$_2$; **3d**: X = Ar$_1$, Y = Ar$_3$

yielded diacids **3**, **3a**, and **3c** in a 4:1:4 ratio (maximum conversion) while complex **2b** gave, similarly, diacids **3**, **3b**, and **3d** in 1:1:2 ratio.[7] The formation of these symmetrical and pseudosymmetrical products indicates that **1** and **1a** (or **1b**) are related by 4-Å translation in the complexes. Additionally, the product distributions confirm a mixed molecular stacking.[3] These facts offer a convincing argument for a disordered stack structure for these complexes.

Crystals of **2a** and **2b** were not suitable for further study. However, it was felt that the structures of these complexes could also be understood by a model where **1a** or **1b** has been induced to cocrystallize in the structure of **1** because (i) **1** is the major constituent of **2a**, (ii) the cell dimensions of **2a** and **2b** are similar to those of **1** while pure **1a** and **1b** crystallize in a different system,[4] and (iii) the isomeric **1a** and **1b** do not cocrystallise yet each forms distinct complexes with **1**.[8]

The structure determination of **1** was therefore undertaken.[9,10]

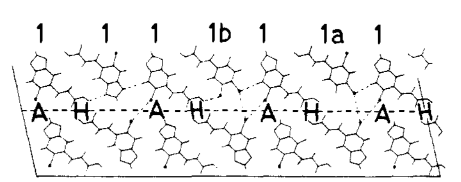


Figure 2. Mixed crystallization of acids **1**, **1a**, and **1b** on the (010) face (perpendicular to the page and intersecting it on the dotted line) of a nucleus crystal of **1**. For brevity **1**, **1a**, and **1b** are shown together but any experiment involves **1** with either **1a** or **1b**. A and H sites are indicated. Chlorine atoms are shown as heavy circles. Nonbonded C–H···O, O–H···O$>^{C}_{C}$, Cl···Cl, and C–H···Cl interactions are dotted. Note that **1** and **1b** are held somewhat better at the A sites when compared to **1a**.

Figure 1 shows that molecules lie as centrosymmetric hydrogen-bonded dimers in sheets which are further characterized by short C–H···O (2.44 and 2.58 Å), C–H···Cl (3.28 Å), and Cl···Cl (3.90 Å) contacts. These weak but directionally specific interactions stabilize the sheet structure and the β-crystal structure is generated by van der Waals stacking of sheets.[5]

Acids **1**, **1a**, and **1b** are related crystallographically, topochemically, and also geometrically; the volumes of the respective molecules in their native crystal structures are 232, 230, and 235 Å.[3] Further, the shape of the **1** molecule closely matches that of **1a** at the carboxylic end and that of **1b** at the aromatic end.[12] The stoichiometric incorporation of **1a** or **1b** in a disordered stack fashion in the sheet-based crystal structure of **1** may therefore be considered according to any of the following possibilities: (i) The acids are disordered over all sites in a sheet in a 2:1 or a 1:1 ratio. The stacking is necessarily disordered and explains the reaction products. (ii) Any sheet contains only one type of molecule but there are, respectively, twice as many or just as many **1** sheets as **1a** or **1b** ones and stacking is disordered. (iii) Each sheet is ordered with 2:1 or 1:1 stoichiometry but the stacking is disordered. The former situations explain neither the differences in behavior between **1a** and **1b** nor the particular stoichiometries obtained. However, the final possibility is reasonable; while the major intrastack interactions are the C···C ones which are not particularly molecule specific, the intrasheet ones are directionally specific and more likely to lead to sheet ordering. Further, the experimental stoichiometries for different samples of complex **2a** vary slightly (1:2.03; 1:2.05; 1:2.08), a fact that is consistent with a disorder mechanism.

A realistic model for mixed crystallization considers the attachment of individual **1** and **1a** (or **1b**) molecules to an embryonic crystal of **1**.[11] Although detailed comment would be speculative, the differences in the complex-forming abilities of **1a** and **1b** should depend on the relative ease with which they crystallize onto the face where fastest sheet growth occurs. This is (010) and Figure 2 shows that, in the nucleus crystal, alternate inversion related **1** molecules present their carboxyl and hydrocarbon ends to define distinct growth sites, H (hydrogen-bonded) and A (aromatic). Since O–H···O interactions at H are unlikely to be very discriminating, either **1** or **1a** (**1** or **1b**) will probably be accommodated equally well. However, at A it is conceivable that **1** and **1b** molecules fit better than **1a**. While molecule **1** is held by two fairly specific C–H···O and O–H···O$<^{C}_{C}$ bonds (Figure 2), the molecular shape of **1b** in the crucial 3- and 4-substituted aromatic region is sufficiently similar to that of **1** to permit it to mimic its

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(3) Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2014.

(4) Cell parameters (all crystals from EtOH): acid **1**, form I, $P\bar{1}$, $Z = 2$, $a = 3.875$ Å, $b = 9.574$ Å, $c = 13.047$ Å, $\alpha = 106.39°$, $\beta = 91.97°$, $\gamma = 91.3°$; form II, $P\bar{1}$, $Z = 2$, $a = 9.05$ Å, $b = 12.94$ Å, $c = 4.10$ Å, $\alpha = 93.3°$, $\beta = 95.5°$, $\gamma = 74.4°$; **1a**, $P2_1/c$, $Z = 4$, $a = 3.88$ Å, $b = 6.44$ Å, $c = 36.8$ Å; $\beta = 90.5°$; **1b** plates, $P2_1/c$, $Z = 4$, $a = 14.2$ Å, $b = 3.92$ Å, $c = 17.0$ Å, $\beta = 92°$; needles, $P2_1/c$, $Z = 4$, $a = 3.9$ Å, $b = 6.56$ Å, $c = 36.84$ Å, $\beta = 91.5°$; complex **2a**, triclinic, $a = 3.79$ Å, $b^* = 0.1215$ Å, $c^* = 0.1794$ Å, $V = 452$ Å^3.

(5) Sarma, J. A. R. P.; Desiraju, G. R. *Chem. Phys. Lett.* **1985**, *117*, 160.

(6) Desiraju, G. R. *Proc.—Indian Acad. Sci., Chem. Sci.* **1984**, *93*, 407.

(7) The products were characterized as diesters. For example, 3-(3,4-(methylenedioxy)-6-chlorophenyl)-4-(2,4-dichlorophenyl)cyclobutane-1,2-dicarboxylic acid dimethyl ester: obtained from **3c** is a white solid, mp 76 °C; NMR ($CDCl_3$) δ 3.74, 4.82 (m, 4 H), 3.80 (s, 6 H), 5.96–6.0 (q, 2 H), 6.58 (d, $J_{AX} = 3$ Hz, 1 H), 6.76 (d, $J_{XA} = 3$ Hz, 1 H), 7.06 (q, $J_{AB} = 8$ Hz, 2 H), 7.24 (d, $J_{AX} = 1$ Hz, 1 H); MS (70 eV) *m/z* (%), 470 (1.5), 472 (1.5), 474 (0.5), 476 (0.07) all $M^{+\cdot}$; 326 (0.6), 328 (0.6), 330 (0.25), 332 (not detected) all $(M - C_6H_8O_4)^{+\cdot}$; 240 (100), 242(34) both $(C_{11}H_9ClO_4)^{+\cdot}$; 230 (10), 232 (7), 234 (2) all $(C_{10}H_8Cl_2O_2)^{+\cdot}$; 113 (47) $(C_5H_5O_3)^+$.

(8) For instance, the solid obtained from an EtOH solution of **1a** (mp 229 °C) and **1b** (mp 218 °C) has a melting range 208–215 °C.

(9) Structure determination of acid **1**, form I CAD-4 (IIT, Madras), Mo Kα, 761 nonzero (3σ) reflections out of 1367 collected with 3° ≤ θ ≤ 28°, solution with MULTAN80, $R = 0.045$ and $R_w = 0.045$, hydrogens isotropic, all other atoms anisotropic. For a full report see ref 12.

(10) Both forms of acid **1** are obtained from EtOH but are visually indistinguishable. Form II crystals were not satisfactory for diffractometer work and a possible structure has been obtained by using packing considerations (Kearsley, S. K.; Desiraju, G. R., unpublished results) and closely resembles the solved structure of form I. Both polymorphs are expected to give the same topochemical product. The cell parameters of **2a**[4] seem to be based on form I of acid **1**. No crystal of **2a** was found with a short axis around 4.10 Å.

(11) Addadi, L.; Weinstein, S.; Gati, E.; Weissbuch, I.; Lahav, M. *J. Am. Chem. Soc.* **1982**, *104*, 4610.

(12) Sarma, J. A. R. P.; Desiraju, G. R., unpublished results.

behavior and enter these sites. In contrast, shape differences between **1** and **1a** in the aromatic extremities are probably different enough for effective molecular discrimination. Analogous arguments when applied to all growth faces lead to an overall 1:1a stoichiometry of nearly 2:1 for **2a**, while the **1–1b** system appears to be a substitutional solid solution.[12]

It is noteworthy that minor geometrical differences between **1a** and **1b** result in a considerable amplification of the structural differences between **2a** and **2b**. Weak but nontrivial forces may discriminate between subtle shape variations and include molecules of the "right" shape or contour with a high degree of selectivity. These studies have implications in the deliberate design or crystal engineering of organic crystal structures stabilized by C–H···O and Cl···Cl interactions and also in the kinetics of solid-state topochemical processes.

Acknowledgment. We thank the DST (SERC), New Delhi, for financial support.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, F_o/F_c values, and intramolecular bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

Book Reviews

Basic Organometallic Chemistry. By I. Haiduc (Babes—Bolyai University, Romania) and J. J. Zuckerman (University of Oklahoma). Walter de Gruyter: Berlin, New York. 1985. XXVIII + 488 pp. $64.90 (Hardcover). Student edition: XXVIII + 376 pp. $29.90 (Paperback). ISBN 3-11-007184-3.

The purpose of this book is to provide a textbook for the neophyte organometallic chemist. It is published in both a Professor's edition, which contains an appended bibliography of secondary literature references, and a paperback student edition, without the bibliography and at a much lower price.

The text is divided into three parts: Part I is an introduction to general concepts and techniques of organometallic chemistry, including chapters on the scope and history of organometallic chemistry, the metal–carbon bond, laboratory techniques, and literature; Part II contains a descriptive listing of the synthesis, structures, and reactions of the organometallics of the non-transition elements including boron and silicon but not phosphorus; and Part III starts with an introduction to the electronic nature of transition-metal organometallics and continues with a listing of transition-metal organometallics based on ligand type. The emphasis throughout is on preparation and structure, reactions are only briefly covered, and mechanistic and spectroscopic aspects are not covered at all. There are few references to the primary literature, but the bibliography of reviews, texts, and monographs is extensive.

The text is a rewrite of I. Haiduc's 1974 Romanian-language work and attempts have been made to include updated information (to 1984).

Because of the lack of reaction, mechanistic, and spectroscopic content, this book may not be suitable as the sole source for a survey course in organometallic chemistry; however, the detailed structural and preparative listings would be of use to the advanced student.

Dennis D. Davis, *New Mexico State University*

Higher Excited States of Polyatomic Molecules. Volume III. By Melvin B. Robin (AT&T Bell Laboratories). Academic Press: Orlando, FL. 1985. xv + 465 pp. $49.50. ISBN 0-12-589903-3.

In the last decade since the publishing of the first two volumes, significant advances have been made in the study of the electronic states of molecules above 60 000 cm^{-1}, both in the volume of research and in the introduction of new techniques. Dr. Robin attempts to place both the mass of data and the changes in this field of the last decade into the context of a closely reasoned review and discussion. This volume should be used in conjunction with his first two volumes, which have now become part of the standard reading for anyone interested in the electronics of molecules, including graduate students and researchers in other fields who want to gain quick access to the work done on electronic spectroscopy of molecules. Theoreticians have found this work especially helpful in guiding them through the experimental literature; experimentalists have found the presentation in the context of molecular orbitals and the comparison with current calculations a way to organize otherwise disparate information. The present volume will certainly be used in the same manner.

Dr. Robin focuses his attention on the question of at what energies electronic states occur. He writes as a chemist to chemists. This is not a handbook in spectroscopy; very little vibrational or rotational spectroscopy will be found. Arguments for state assignments are presented only when there is an active controversy or the author feels that the method of an assignment would illustrate a point under discussion. These topics are covered in Herzberg's "Polyatomics", which with the publication date of 1966 is no longer complete as an entree into the current literature on particular molecules.

In this third volume, Robin concentrates on the literature, and this book must be read with a research library nearby. New material of the author primarily consists of interpretations. His understanding and presentation of halogenated organic compounds is masterly, and his discussion of SF_6 has been completely reworked to bring order to the study of this molecule. The discussion of polyene spectroscopy is less complete, and heavy reliance has been placed upon the work of others, taken at face value, in writing this section, but Robin again is able to present a complex topic with cohesion and his own thoughts in the section on polyethylene. There is no section on polyacetylene. Other than main group hydrides, oxides, and halides, inorganic and organometallic chemistry is sparsely represented, probably a defect in the field and not in the book.

The techniques of Temporary-Negative Ion resonances (TNI) and MultiPhoton Ionization (MPI) are briefly presented. The data presented rely heavily upon these two new techniques and on both electron energy loss and optical spectroscopies. This emphasis represents the research of the last decade. Little is mentioned of currently available techniques of mostly future value: e.g., UV Raman spectroscopy, two-color, double-resonance laser techniques, and molecular jet cooling.

Overall, Dr. Robin writes enthusiastically and to the reader personally. Occasionally an expression will stiffen the reader's spine: Rydberg "progressions" or "series" or even "sequences", pass without particular notice, but a Rydberg "parade" brings me right to attention! Nor can I accustom myself to "exhaltation" or "elevation" as synonyms for "increase" in a scientific discussion. Yet, these terms will probably become endearing to those who need to become acquainted with this field and to workers in this field, who will probably buy, read, and reread this essential volume written with both enthusiasm and care.

Paul C. Engelking, *University of Oregon*

Soil Chemistry. Second Edition. By Hinrich L. Bohn (University of Arizona), Brian L. McNeal (University of Florida), and George A. O'Connor (New Mexico State University). John Wiley and Sons: New York. 1985. XIV + 341 pp. $29.95. ISBN 0471-82217-5.

This is the second edition of a text designed for soil scientists at the advanced undergraduate or beginning graduate level. It presumes only a basic freshman course in chemistry. Although this book is not written for chemistry majors, those readers of this journal who are interested, as I am, in the applications of chemistry to soil science will find this book useful. It discusses the major aspects of this subject in an informative way, with many example plots and tables taken from the soil-chemistry literature. In keeping with its primary objective as a textbook, all chapters have problem assignments attached and most of these have been expanded in this new edition. Sections of a number of chapters have been substantially revised and the discussion of organic components of soil has been expanded to a new, separate chapter for this edition.

The other major revision has been to use S.I. units throughout, following the standards of the Soil Science Society of America. This conversion has been made rather hurriedly, it appears—the table of S.I. units in Chapter 2 has a number of errors, the conversion to kJ of the heats of hydration rounds off −1090 to −10 kJ mol^{-1} for H^+, and although the Debye–Hückel closest approach, *a*, in the same chapter was converted