

The correlation is perhaps surprising. The hydrogen-bonding hypothesis suggests that water should be pulled into the contact solvation shell of Cl^- on a preferential basis and that it should remain the dominating solvating species until bulk water activity has been reduced by a factor comparable to the activity change for transfer of the ion from protic aprotic solvent. The results indicate that, in fact, the immediate environment of Cl^- is related to the long-range structural aspects of solvent mixtures. We can imagine how this occurs if we look closely at the meaning of our numbers. The advantage of the chemical shift parameter as a solvation probe is that it reflects composition of the solvent layers in contact with Cl^- . The activities from vapor pressures characterize the solvent in the solution at a distance far enough from Cl^- to be unperturbed by the ions. Both of these regions are in equilibrium with an intervening region to which we have no experimental access. A reason why water is not strongly preferred over the aprotic solvent in the layer in contact with Cl^- might well be that a protic solvent molecule hydrogen

bonded to Cl^- is strongly polarized so that it presents a "lyate ion like" aspect to the middle solvent region and this "lyate ion like" species is poorly "solvated" by the aprotic solvent. Conversely, an aprotic molecule solvating Cl^- may interact less favorably with the Cl^- but much more favorably with the surrounding solvent layer. In this way, the short-range favorable or unfavorable effects are mitigated and the local environment of the ion comes to reflect long-range interactions.

A final point: lines in the mixed solvents were very wide. They imply a residual asymmetry in the field gradient at the nucleus that is not averaged by tumbling.

(12) Alfred P. Sloan Research Fellow 1968–1970.

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Additions and Corrections

The Mechanism of the Aminolysis of Methyl Formate [*J. Am. Chem. Soc.*, **90**, 2638 (1968)]. By G. M. BLACKBURN and W. P. JENCKS, Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02154.

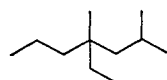
On page 2639, column 2, line 3, the rate constant for alkaline hydrolysis of methyl formate should read $1.95 \pm 0.1 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$.

Cyclopropyl Conjugation in Olefinic Esters. Conformational Effects on Ultraviolet Absorption [*J. Am. Chem. Soc.*, **90**, 3769 (1968)]. By MARGARET J. JORGENSON and TERESA LEUNG, Department of Chemistry, University of California, Berkeley, California.

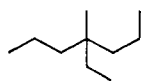
On page 3773, column 1, the second sentence of the third paragraph should read: The values determined for esters **1**, **5**, and **6**, are 9.4, 10.0, and 10.3 cps, respectively.

Biosynthesis of Indole Alkaloids. Vindoline [*J. Am. Chem. Soc.*, **90**, 4144 (1968)] by T. MONEY, I. G. WRIGHT, F. MCCAPRA, E. S. HALL, and A. I. SCOTT, Chemistry Department, University of British Columbia, Vancouver 8, Canada.

On page 4146, Figure 2, the schematic structure



should be replaced by



The Interpretation of Porphyrin and Metalloporphyrin Spectra [*J. Am. Chem. Soc.*, **90**, 6577 (1968)]. By ALSOPH H. CORWIN, ARTHUR B. CHIVVIS, ROBERT W. POOR, DAVID G. WHITTEN, and EARL W. BAKER, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland.

In Table I, column 6, the last value should be 24,530 instead of 24,360. On page 6580, Figures 2 and 3 should be interchanged.

The Acid-Catalyzed Hydrolysis of Acyl Phosphates [*J. Am. Chem. Soc.*, **90**, 6803 (1968)]. By DAVID R. PHILLIPS and THOMAS H. FIFE, Department of Biochemistry, University of Southern California, Los Angeles, California 90053.

In the abstract, the legend to Figure 6, and on page 6808 it should read: plots of $(\log k_{\text{obsd}} + H_0)$ vs. $(\log C_{\text{H}} + H_0)$. This expression appeared with the parentheses misplaced.

Spin-Delocalization Mechanisms in Some Paramagnetic Tris-2,2'-bipyridine Complexes of Nickel(II) [*J. Am. Chem. Soc.*, **90**, 6946 (1968)]. By M. WICHOLAS and R. S. DRAGO, William A. Noyes Laboratory, University of Illinois, Urbana, Illinois.

The first compound in Table I should be $\text{Ni}(\text{bipy})_3 \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$. On page 6950, the sentence beginning in column 2, line 37 should read: "The downfield resonance peak is due to either the *ortho* and *para* protons or the *meta* and *para* protons, and the upfield resonance peak is due to either the *ortho* or *meta* protons; however, of these only one assignment is reasonable." The last sentence should read: "If the assignments are correct, the contact shifts are consistent with

π delocalization of positive spin density involving ψ_4 and negative spin density involving ψ_7 or ψ_8 ."

The Acid-Catalyzed and Mercuric Ion Catalyzed Hydrolysis of 2-(para-Substituted phenyl)-1,3-oxathiolanes [*J. Am. Chem. Soc.*, **90**, 7266 (1968)]. By NIMAI C. DE and LEO R. FEDOR, Department of Medicinal Chemistry, School of Pharmacy, State University of New York at Buffalo, Buffalo, New York 14214.

The rate constant for the acid-catalyzed hydrolysis of 2-(*p*-nitrophenyl)-1,3-oxathiolane (**5**), Table III, is $0.0025 M^{-1} \text{ min}^{-1}$. Accordingly, for the acid-catalyzed reaction $\rho = -2.82 \pm 0.13$.

Synthetic Spectroscopic Models Related to Coenzymes and Base Pairs. II. Evidence for Intramolecular Base-Base Interactions in Dinucleotide Analogs [*J. Am. Chem. Soc.*, **90**, 7302 (1968)]. By DOUGLAS T. BROWNE, J. EISINGER, and NELSON J. LEONARD, Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801, and Bell Telephone Laboratories, Inc., Murray Hill, New Jersey 07974.

On page 7309, column 1, line 15, Ad-C₃-Ad should be Ad-C_n-Ad.

On page 7313, column 1, line 24, Ad-C_n should be Ad-C_n-Ad.

On page 7320, column 1, compound **35**, O₁₆ in formula should be O_e.

Polarized Electronic Spectroscopy of Molecules Oriented by a Nematic Liquid Crystal [*J. Am. Chem. Soc.*, **91**,

191 (1969)]. By GERALD P. CEASAR and HARRY B. GRAY, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

The name *p*-(*p*'-ethoxybenzoxy)phenyl butyl carbonate as used in the paper is incorrect. The correct name is butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate.

A Large Deuterium Solvent Isotope Effect on a Photochemical Reaction [*J. Am. Chem. Soc.*, **91**, 198 (1969)]. By MARGARET J. JORGENSEN, Department of Chemistry, University of California, Berkeley, California.

On page 199, column 1, the last sentence should read as follows: The low *d*₂ content of **2** and **3** (Table I) argues for a negligible rate of γ deuteration of dienols **5** and **6** (**5a** and **6a** to **1a** and **5b** and **6b** to **1b**).

Polarized Infrared Spectroscopy of Molecules Oriented in a Nematic Liquid Crystal. Application to Mn₂(CO)₁₀ and Re₂(CO)₁₀ [*J. Am. Chem. Soc.*, **91**, 772 (1969)]. By GERALD P. CEASAR, ROBERT A. LEVENSON, and HARRY B. GRAY, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

The name *p*-(*p*'-ethoxybenzoxy)phenyl butyl carbonate as used in the paper is incorrect. The correct name is butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenyl carbonate.

Book Reviews

Molecular Orbital Theories of Bonding in Organic Molecules. By ROBERT L. FLURRY, JR., Department of Chemistry, Louisiana State University, New Orleans, La. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1968. x + 334 pp. 16 × 23 cm. \$17.95.

The object of this book is to provide the reader with "a conceptual knowledge of the principles of chemical bonding, as explained by molecular orbital theory" and "a *working* knowledge of the methods in common usage for applying molecular orbital theory to moderately large molecules." After a brief introduction to MO theory, successive chapters deal with the free electron theory, LCAO theory, perturbation methods, the HMO method, group theory and symmetry orbitals, atomic structure, SCF MO methods, and bonds, with a very brief final chapter (19 pp) on application to specific problems.

The author's general approach is to state theoretical results with little or nothing by way of derivation, and to illustrate their use by detailed discussions of their application to specific simple problems. Thus in Chapter III, the HMO method is illustrated by a detailed discussion of H₂, and of the π electrons in butadiene, following empirical rules for constructing the MO equations, and in Chapter 5 the solution of such equations is discussed in great detail; however, neither the basic principles of the HMO method nor the approximations implicit in it are discussed at all. Similar comments apply to the rest of the book, and indeed it is clear that the author has set out with the object of training chemists to use MO theory as a kind of black box without their understanding in the least the basic principles involved.

Those who consider such an approach satisfactory will find this an admirable text for their courses; it is clearly written, well produced, and reasonable in price.

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Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry. By C. A. PARKER, Ph.D., D.Sc., F.R.M.S., F.R.I.C., Royal Navy Scientific Service, Admiralty Materials Laboratory, Holton Heath, Poole, Dorset, England. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave, New York, N. Y. 1968. xvi + 544 pp. 15.5 × 23 cm. \$30.00.

Advances in the understanding of molecular electronic processes in conjunction with simultaneous advances in chemical instrumentation have increased the number of chemists engaged in synthetic and analytical studies involving excited states. For a long time no suitable texts were available for this field. Recently, the relationship between absorption spectra and the geometry of excited molecules has been adequately covered by several authors. This left a conspicuous need for a companion volume on solution photoluminescence. C. A. Parker is a recognized spectroscopist who has published papers dealing with almost every branch of this field. He is exceedingly well qualified to write on such a topic and his book fulfills this need.