Carbethoxynitrene. The Stereochemistry of the Intermolecular Singlet Carbon–Hydrogen Insertion [*J. Am. Chem. Soc.*, **91,** 5107 (1969)]. By JOSEPH M. SIMSON and WALTER LWOWSKI, Research Center, New Mexico State University, Las Cruces, New Mexico 88001, and the Department of Chemistry, Yale University, New Haven, Connecticut 06520.

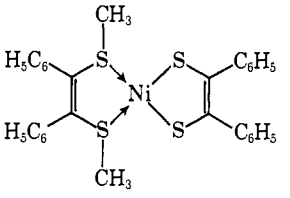
Professor S.-I. Yamada has kindly informed us of our error in calculating the retention of configuration in his work (our ref 25). The value is not 82% but 107%, as also detailed in his full paper: S. Terashima and S.-I. Yamada, *Chem. Pharm. Bull.* (Tokyo), **16,** 1953 (1968).

Chemistry of Metal Complexes with Polydentate Ligands. Complexes of N-Hydroxyethylethylenediamine [*J. Am. Chem. Soc.*, **91,** 5958 (1969)]. By B. DAS SARMA and JOHN C. BAILAR, JR., West Virginia State College, Institute, West Virginia, and the W. A. Noyes Laboratory of the University of Illinois, Urbana, Illinois.

On page 5960, column 1, line 9, IV should read II.

Stabilization of a Thioketocarbene through π-Complex Formation. Synthesis and Structure of *Trihapto*-1,2-diphenylthioketocarbene–Hexacarbonyldiiron [*J. Am. Chem. Soc.*, **92,** 212 (1970)]. By G. N. SCHRAUZER and H. N. RABINOWITZ, Department of Chemistry, University of California, San Diego, La Jolla, California 92037, and JO ANN K. FRANK and IAIN C. PAUL, W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

In eq 2, structure **4** should be

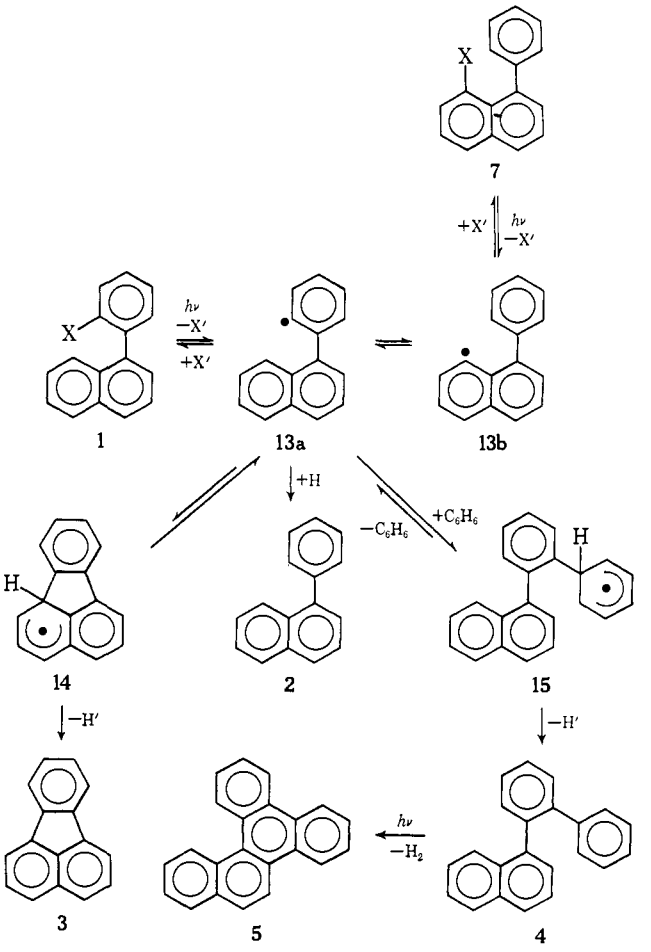


Stereoselective Interaction of Optically Active Amino Acids and Esters with (L-Valine-N-monoacetato)copper(II) [*J. Am. Chem. Soc.*, **91,** 6296 (1969)]. By B. E. LEACH and R. J. ANGELICI, Department of Chemistry, Iowa State University, Ames, Iowa 50010.

The last sentence in column 1 on page 6296 should read: Relative stabilities of analogous histidine complexes,[6] Co(L-Hist)$_2$ and Co(L-Hist)(D-Hist), have been shown to be different.

Photolytic Rearrangement and Halogen-Dependent Photocyclization of Halophenylnaphthalenes. II [*J. Am. Chem. Soc.*, **91,** 6049 (1969)]. By WILLIAM A. HENDERSON, JR., R. LOPRESTI, and ARNOLD ZWEIG, Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut.

In the structures on page 6054 three dots denoting radical electrons in structures **13a**, **13b**, and **14** were deleted by the engraver. The correct structures appear below.



Book Reviews

Statistical Mechanics of Chain Molecules. By PAUL J. FLORY, J. G. Jackson–C. J. Wood Professor of Chemistry, Stanford University, Stanford, Calif. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. xix + 432 pp. 16 × 23.5 cm. $17.50.

This is a complete account of a limited field, a true monograph. The field is that of the exact relation of the measurable properties of molecular chains to the known or surmised characteristics of the chemical bonds that compose them. The title might easily be misconstrued; Professor Flory does not attempt to discuss all that has been done with chain molecules under the name of statistical mechanics, but limits himself to those equilibrium properties that can be derived from the bond characteristics by the rigorous use of mathematics, mostly matrix algebra. Such properties are the mean-square end-to-end distance and the mean-square radius about the center of mass, the dipole moment and the electric polarizability, higher moments of these quantities, and their distribution functions as well. Solution thermodynamics and viscoelasticity are excluded, as are sedimentation and diffusion.

Books of this kind are successful only when a science has grown to maturity. A corpus of knowledge must have been built up that

is reliable and at the same time closely knit and extensive. Such is the case here, even though some four-fifths of the book is the work of the past ten years only. The idea that the properties of a chain may be accurately calculated from those of its constituent bonds is not a new idea, but its extensive application is. Although Eyring in 1932 first showed how to use matrix methods for such calculations, it was not until 1959 that Volkenshtein and coworkers in Russia, Lifson in Israel, Nagai in Japan, and Flory in the United States began the systematic application of such methods. Probably the long delay arose from the lack of the necessary input data on the characteristics chemical bonds. Most of these data, obtained by microwave spectroscopy, X-ray and electron diffraction, calorimetry, and nmr, were taken during the decade following World War II. Thus, it is natural that the great flowering of the subject of this book has occurred in the 1960's.

In the old days, polymer scientists got along fairly well using for the most part the simple random-flights model for the polymer chain. For this model the necessary two parameters, the length and the number of flights, were evaluated from measurements on the polymer, rather than being predicted from the characteristics of the chemical bonds.

The new method leads to deeper insights. We can quote two examples from the book. A very long chain of polymethylene, $(CH_2)_n$, has an end-to-end mean-square distance that is about 6.8 times the value that it would have if all the carbon–carbon bonds were joined by freely rotating universal joints. If one fixes the bond angle at 109°, but leaves the rotation free, the ratio is calculated to be 2, Eyring's 1932 result. With a realistic potential of 400 cal $mole^{-1}$ favoring the *trans* position, the ratio rises to about 3.5. To bring the value up to 6.8 one must take into account the "pentane effect," the collisions of two methylene groups separated by four bonds. Thus rather distant interactions have a strong influence on the chain conformation. Of similar interest is the discovery that the silicone chain, polydimethylsiloxane, has a preferred conformation that is a rather flat helix of six residues per turn with all backbone bonds slightly off the *trans* conformation. The breakdown of this helix with increase of temperature leads to an increase of the end-to-end distance with temperature, unlike the decrease found with polymethylene. The fundamental reason for the existence of this helix is the inequality of the bond angles at silicon (110°) and oxygen (143°), so that the all-*trans* conformation is not a straight zig-zag. The matrix-based calculations not only reproduce the chain dimensions and temperature coefficients quantitatively, they are also consistent with the observed high frequencies of rings of various sizes in the equilibrium silicone polymer.

There is much that remains to be done. Apparently the origin of the pronounced differences between the properties of the hydrocarbon and fluorocarbon polymers is still speculative. The asymmetric centers in vinyl polymers introduce serious complications. Polypeptides are simplified by the fact that the peptide group is coplanar, but the number of permutations is vast. The fundamental data on bond properties are still lacking for polynucleotides.

Flory's book contains a mine of material on the subject. It is too monographic and too detailed to be attractive for a general course or for introductory reading by those not already familiar with polymer science, but it can hardly be ignored by any research worker or teacher in the polymer field, and for many it will be indispensable.

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BOOKS RECEIVED, *January 1970*

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