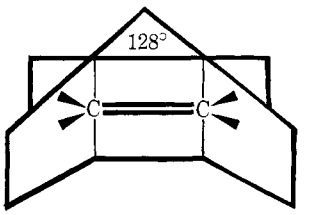
bonding in such complexes, a situation commented upon earlier by others.[12] A useful employment of the pmr data is, however, the calculation of bond angles from the ρ values obtained. If we regard the acetylene molecule, for example, as being perturbed (in some unspecified manner) upon coordination, with the observed reduction in s character of the carbon hybrid, then a simple calculation[13] shows that the angle between two equivalent hybrid orbitals, *i.e.*, the HCC bond angle, is 139°. This compares well with the 140° found[14] for the corresponding angle in the complex $(PPh_3)_2Pt(C_6H_5CCC_6H_5)$.

A similar calculation for the ethylene complex shows the angle between equivalent orbitals (HCH and HCC bond angles) to be 115° and the out-of-plane angle (I) to be 26° (assuming *cis* bending). This leads to a dihedral angle of 128°; the corresponding angle in the complex $(PPh_3)_2Ir(CO)(Br)[C_2(CN)_4]$ has a value of 110°.[15] The large difference (18°) is disappointing but perhaps not unexpected in view of the electronic dissimilarity of the two ligands[12] and the associated differences in the strengths of the two olefin–metal interactions.



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In addition to the use of coupling constant data for predicting molecular geometries of coordinated molecules, we anticipate[16] that the measurement of ^{195}Pt–^{13}C and ^{13}C–^{13}C coupling constants in these and related complexes will provide a more fruitful basis for discussion of the bonding in such complexes than has been available hitherto.

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Book Reviews

Structure and Mechanism in Organic Chemistry. Second Edition. By C. K. INGOLD, Professor of Chemistry, University College, University of London. Cornell University Press, 124 Roberts Place, Ithaca, N. Y. 1969. ix + 1266 pp. 16 × 24 cm. $32.50.

The first edition of this book was called "one of the few great books of organic chemistry" by its reviewer in this Journal [J. D. Roberts, *J. Amer. Chem. Soc.*, **75**, 6355 (1953)]. It is therefore a matter of considerable interest that it has been revised. The new edition is considerably expanded (from 828 to 1266 pages in size and, unfortunately, from $9.75 to $32.50 in price) and covers several areas previously not treated.

About two-thirds of the original text has been retained, with a part of the new material being devoted to clarifying or updating discussions by presenting evidence which has become available since the 1951 closing date for the first edition. For example, the discussion of "Unsaturated Rearrangements" has been elaborated by a treatment of "Valency Tautomerism" which introduces the concept of orbital symmetry as a stereochemistry-controlling factor. A later discussion of cycloaddition reactions unfortunately does not employ this concept, but does include a new section on addition of carbenes to olefins.

A threefold symmetry (electrophilic–nucleophilic–homolytic, or anion–cation–radical) is developed in several of the chapters which formerly treated only one of these sectors. For example, the detailed discussion of nucleophilic aliphatic substitution, one of the fields in which the author's contributions have occupied so prominent a position, is now supplemented by small sections on electrophilic aliphatic substitution and homolytic aliphatic substitution. Radical chemistry, which was not covered at all in the first edition, has been discussed in appropriately placed new sections throughout the text and in a new chapter on "Stable Radicals." A large section of the discussion in this chapter may have to be reinterpreted in view of recent evidence that triarylmethyl radical dimer is not hexaphenylethane but rather a dimer involving the *para* position of one of the phenyl rings.

A new chapter on "Polar Energy," placed late in the book, briefly discusses the theory and development of important linear free energy relationships. Many readers will lament the isolation of these concepts in a single chapter, with little use being made of the vast literature which describes their application in studies of mechanisms. It is not difficult to find arguments in earlier chapters which could have been stated more concisely, and, perhaps more convincingly, in terms of the concepts and the vocabulary of this chapter.

The book gives rather more emphasis to the historical development of ideas than is currently fashionable in textbook writing in this area. When one considers the central place which the author has held in the development of the field, however, it is clear that a book presenting his perspectives on structure and mechanism in organic chemistry represents a uniquely valuable contribution to the review literature.

It is an absorbing book which will provide the thoughtful reader with many rewarding insights.

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BOOKS RECEIVED, *February 1970*

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BENJAMIN CARROLL, Editor. "Physical Methods in Macromolecular Chemistry." Volume 1. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1969. 385 pp. $17.75.

ROBERT E. IRELAND. "Organic Synthesis." Prentice-Hall, Inc., Englewood Cliffs, N. J. 1969. 147 pp. $6.95.

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HUGH W. SALZBERG, JACK I. MORROW, STEPHEN R. COHEN, and MICHAEL E. GREEN. "Physical Chemistry, A Modern Laboratory Course." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 528 pp. $9.50.

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