



Fig. 2.—(a) Resonance structures for C₂B₄H₈ in which C atoms are adjacent. (b) Valence structure for C₂B₄H₈ in which C atoms are not adjacent. One H atom is to be added to each B and C atom.

mations, including the possibility of racemization of an optical isomer, provided that the driving force is present.

Another possibility of rearrangement is presented by C₂B₄H₈ (C_s). The valence structure proposed⁹ for C₂B₄H₈ does not satisfy the valency rules.¹⁰ However, a resonance hybrid type of three-center bond description can be written which does indeed have as satisfactory bond angles as those present in the known hydrides and derivatives (Fig. 2a). It also is possible to formulate an alternative bonding description based upon a different molecular geometry which also seems to be compatible with the nuclear magnetic resonance spectrum⁹; an isomerization is required inasmuch as the C atoms are not bonded (Fig. 2b). A structure determination by X-ray diffraction methods may settle this point.

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Kinetics of Iodination of 8-Quinolinol-5-sulfonic Acid and its Metal Chelates¹

Sir:

From a series of studies on the halogenation products obtained from certain aromatic amines, 8-quinolinol, and their metal coordination complexes,²⁻⁴ it was concluded that metal coordination has very little effect on the reactivity of these ligands. In contrast, our studies of the kinetics of iodination of 8-quinolinol-5-sulfonic acid and certain of its divalent transition metal chelates show that the coordinated metal ion has a profound effect on the rate of iodination of the ligand.

(1) This work was supported by a grant from the National Institutes of Health.

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The rate at which iodine (electrogenerated, using a direct current, at a known, constant rate from KI) reacted with 8-quinolinol-5-sulfonic acid or its metal chelate in an appropriately buffered solution was determined by recording the decrease in the diffusion current of the iodine-iodide system as a function of time.⁵

The iodination of 8-quinolinol-5-sulfonic acid in aqueous buffered solution at constant iodide ion concentration is first order in both 8-quinolinol-5-sulfonic acid and iodine (Table I). The apparent second order

TABLE I

IODINATION OF 8-QUINOLINOL-5-SULFONIC ACID AT 20°					
pH = 7.0 ^a ; [I ⁻] = 0.05 M		pH = 7.0 ^a ; [I ⁻] = 0.10 M		pH = 9.0 ^b ; [I ⁻] = 0.10 M	
[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹
0.500	2.27	1.005	1.08	0.503	27.5
1.005	2.31	1.510	1.09	1.005	26.2
1.510	2.27			1.510	29.2
2.510	2.40				
5.000	2.27				

^a Runs at pH 7.0 were in a phosphate buffer with total phosphate = 0.10 M. ^b Runs at pH 9.0 were in a carbonate buffer with total carbonate = 0.10 M.

rate constant is inversely proportional to the iodide concentration and increases with increasing pH as well as with increasing concentrations of the buffer components. This behavior is similar to that observed previously for the iodination of phenol⁶⁻⁸ and suggests that the same mechanism may be operating in both cases, *i.e.*, the general base-catalyzed removal of the proton from the addition product of the phenolate anion of 8-quinolinol-5-sulfonic acid and I⁺.

When the iodination reaction was carried out with metal chelates of 8-quinolinol-5-sulfonic acid, formed in solution by the addition of a stoichiometric ratio (1:2) of metal ion to ligand, the same general rate expression found in the absence of metal ion was obeyed. Table II lists the observed apparent second order rate constants.

TABLE II

1:2 Metal chelate ^a	IODINATION OF METAL CHELATES OF 8-QUINOLINOL-5-SULFONIC ACID AT 20°	
	pH = 7.0; [I ⁻] = 0.05 M k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	pH = 9.0; [I ⁻] = 0.10 M k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹
Mn ⁺⁺	1.86	7.96
Zn ⁺⁺	0.506	1.64
Fe ⁺⁺	0.482	2.05
Co ⁺⁺	0.375	~1.0 ^b
Ni ⁺⁺	~0.15 ^b	... ^c
Cu ⁺⁺	... ^c	1.3 ^b

^a The concentration of the metal chelate = 5.0 × 10⁻⁵ M. ^b Followed to <15% completion. ^c No reaction was observed under the conditions of the experiment.

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The presence of the metal ion significantly reduced the rate of iodination in all cases (Table II). Moreover, these rates can be attributed almost entirely to the reaction of the uncomplexed ligand formed by the partial dissociation of the metal chelate. This indicates that one important way in which the metal ion affects the reactivity of a ligand is by reducing its effective concentration in solution. Our results show that the rate of iodination of the metal chelate itself (since it is present in much higher concentration than the free ligand) must be very much smaller than that of the free

ligand. Hence the metal ion is seen to have a far greater effect on the rate of iodination of the ligand to which it is coordinated, because of its ability to affect the over-all electron distribution in the chelate molecule. Work is now in progress on the measurement of the reaction rates of the undissociated metal chelates.

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Book Reviews

Structural Principles in Inorganic Compounds. By W. E. ADDISON. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y., 1961. 183 pp. 21.5 × 14 cm. Price, \$3.25.

In the preface to this excellent little volume, the author states that the book is based on a lecture course which he has given to first year classes at Nottingham University. The book could be understood and appreciated by the better freshmen students in an American university, but, in general, the subject matter is somewhat more advanced than that in most American courses in general chemistry. It might well be used as a supplement to a standard American text.

Although this book is based on a course of college lectures, it is not written in the form of a textbook, but rather as a general survey of structural principles. It will be useful to students, but even more so to practicing chemists who want to review the modern theories of inorganic chemistry. It is well organized and is written in a clear, interesting manner. Although paper-bound, it is well printed on good paper. The type is a little smaller than in most textbooks, so the book contains more material than the number of pages would lead one to expect.

After a brief review of atomic structure and the different types of chemical bonding, the author describes some of the commoner methods used in the determination of structure, and then discusses the structures of the elements, factors which influence the crystal structure of three dimensional lattices, and the structures of representative covalent compounds. The book closes with a very interesting chapter on the defect solid state. The principles involved and the application of modern theory are stressed throughout, as is the relationship between the structures of inorganic compounds and their properties.

This book is not intended to be an exhaustive or advanced treatise, but rather, a fairly elementary review of a most important subject. As such, it will be useful to a large number of chemists who have fallen behind on their study of basic principles.

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Molecular Orbital Theory for Organic Chemists. By ANDREW STREITWIESER, JR. John Wiley and Sons, Inc., 440 Park Avenue South, New York, N. Y., 1961. 460 pp. 6 × 9 cm. Price, \$13.00.

It seems, at last, that organic chemistry, even the whole of chemistry, has entered that golden age when chemists in all fields

can begin to make effective use of quantum mechanics. That molecular quantum mechanics has provided quantitative correlations between chemical phenomena and simple electronic models is well established. Most chemists also probably would agree that from these correlations there have come some useful insights into microscopic chemical phenomena, and some very challenging new chemistry. Moreover, most of the applications of quantum mechanics in chemistry have been based on methods which are fundamentally straightforward—the Hückel model for organic chemistry and ligand field theory in its varied forms for inorganic chemistry. The general use of Hückel theory is much older than the corresponding wide application of ligand field methods; yet its acceptance among organic chemists has required a very long time, in contrast to the fiery love affair between inorganic chemistry and ligand fields. Finally, the past dozen years have seen π -electron theory, once the exclusive plaything of physicists and physical chemists, used as a guide for essentially every field of organic chemistry. Hückel theory, with its many refinements, is without question the only approach which has yet come from quantum mechanics that has the simplicity, generality, and semiquantitative validity to become a standard computational tool of the laboratory organic chemist.

Professor Streitwieser has written a book to fulfil exactly this function—to give to the organic chemist the operating tools and a full scale of results, so that he can use the methods and have considerable feeling for the range of their validity. The need for such a book has been very great and has been increasing rapidly. The list of more than a thousand footnotes makes this obvious at once. Moreover, the recent "Quantum Chemistry" of Daudel, Lefebvre, and Moser has a very different function, of presenting the variety and basis of quantum methods for extensive calculations. "Molecular Orbital Theory for Organic Chemists" deals, in three parts, with the mechanics of simple calculations of complicated systems and then, in great detail, with how these have been applied to computation of physical properties of molecules and of the directions and rates of reactions. It is this reviewer's opinion that the book could have been given the alternative title of "Modern Organic Chemistry for Physical Chemists"; the impressive quantity of material covered in its second and third divisions is assembled in a coherent, reasonable way, with careful consideration of the validity of alternative sets of assumptions and occasional skepticism toward data which, in context, seems appropriate.

By and large, the book seems to achieve its objective. The large number of examples worked out must inevitably make the book a pedagogic success. The only section about which I have any misgivings is the discussion of group theory in sections 3.5 and 3.6. I suspected when I read these sections that the discussion might be too brief to give a novice much intuitive feeling