The Orbital Phase Continuity Principle and Selection Rules for Concerted Reactions

Sir:

In recent years the GI method[1] for electronic wavefunctions has been used to improve upon Hartree–Fock and yet retain the orbital interpretation. In the GI method we allow every orbital to be different (no double occupation restriction) and yet retain the correct spin symmetry.[2] The result is one electron per orbital and two orbitals per bond, with the orbitals generally localized near one or two nuclei (for nonaromatic systems). These orbitals are solved for self-consistentcy; however, we find that for many molecules the orbitals tend to be qualitatively similar to the familiar valence-bond functions. For example, the π orbitals of *trans*-1,3 butadiene are shown[2] in Figure 1. Orbitals ϕ_{1a} and ϕ_{1b} form one bonding pair and ϕ_{2a} and ϕ_{2b} form a symmetrically related bonding pair.

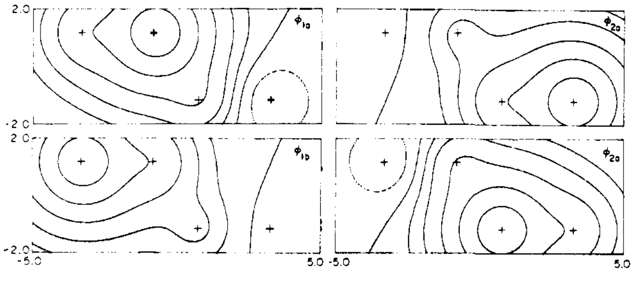

Figure 1. The GI orbitals for *trans*-1,3-butadiene. (The plot is for 1.06 bohrs above the molecular plane. The dashed line represents negative amplitude and the first solid contour is the nodal line. The other contours correspond to amplitudes of 0.01, 0.021, 0.0441, 0.0926, and 0.1945; thus a purely exponential function would have equal spacings between the contours.) The crosses represent projections of the nuclei.

From consideration of *ab initio* GI calculations on reactions of small molecules, we have found that paired bonding orbitals remain paired and nonbonding orbitals change phase as the orbitals and bonds interchange centers during the reaction.[3] For reactions involving the π electrons of molecules, this principle implies that as the bond between A and B is transferred to B–C, the π orbital concentrated on C must change phase as it is transferred to A. Using this *orbital phase continuity principle* (OPCP), we obtain selection rules for chemical reactions in general agreement with both the Woodward–Hoffmann rules[4,5] and experiment. The details of the calculations leading to the basis of OPCP will be presented elsewhere. The principles are simple to use and can be applied to systems with symmetry too low for the Woodward–Hoffmann approach, and hence we will illustrate the use of OPCP with some simple examples.

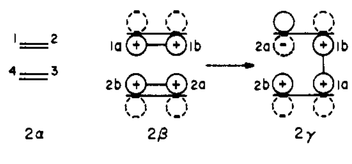

Figure 2. 2 + 2 cycloaddition.

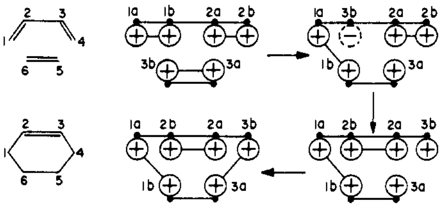

Figure 3. 4 + 2 cycloaddition.

Consider first the 2 + 2 addition reaction of Figure 2. (Here we schematically represent the GI orbitals by a simplified contour plot; a bonding pair is indicated by a line connecting two GI orbitals.) In Figure 2β we show the plane of the two ethylenes and the schematic contours of the four occupied π orbitals. To obtain the product, Figure 2γ, we transfer the 1a–1b bond from centers 1–2 to centers 2–3, but we see that according to OPCP, orbital ϕ_{2a} must simultaneously move from 3 to 1 *and change phase*. But now in the product the phase of ϕ_{2a} is not consistent with retaining the 2a–2b bond (*i.e.*, ϕ_{2a} and ϕ_{2b} have opposite phases) and hence the thermal reaction is unfavored (*i.e.*, it should require a large activation energy; a twist of the top ethylene would be required to match the phases of 2a and 2b).[6]

Now consider the 4 + 2 addition of Figure 3. Here we have illustrated the recouplings of the bonding orbitals by moving one bond at a time. As we move the 1a–1b and 2a–2b bonds, orbital 3a moves first to center 2 and then to center 4, changing phase twice; hence, in the product, 3a and 3b are adjacent and have the same phase. Thus the phase changes required to preserve the 1a–1b and 2a–2b bonds are in this case consistent with retaining the 3a–3b bond and the reaction is favored. Of course, in the real reaction the changes in all bonds occur simultaneously. We have examined these changes one at a time in order to determine if they are all consistent, and find that they are. Note that these considerations do *not* depend upon the exact geometry of the transition state (TS) and do *not* require the preservation of, say, a C_2 axis during the reaction.[7]

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(1) W. A. Goddard III, *Phys. Rev.*, **157**, 81 (1967); *J. Chem. Phys.*, **48**, 5337 (1968); W. E. Palke and W. A. Goddard III, *ibid.*, **50**, 4524 (1969); R. C. Ladner and W. A. Goddard III, *ibid.*, **51**, 1073 (1969); R. J. Blint, W. A. Goddard III, R. C. Ladner, and W. E. Palke, *Chem. Phys. Lett.*, **5**, 302 (1970); R. C. Ladner and W. A. Goddard III, manuscript in preparation.

(2) G. Levin, W. J. Hunt, W. A. Goddard III, and T. H. Dunning, manuscript in preparation. These orbitals were obtained using the SOGI method (ref 1).

(3) This phase change would not occur if electrons were Bosons or if they had an intrinsic spin larger than one-half; hence the phase relationships can be considered a consequence of the basic properties of electronic systems. The orbital flips can also be discussed approximately in terms of changes in the spin coupling angles. Further details will be presented in a subsequent paper.

(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(6) In the transition state of the 2 + 2 cycloaddition, the ϕ_{2a} and ϕ_{2b} orbitals become essentially orthogonal; thus we have essentially broken one bond, obtaining the diradical (in this case the phases between the orbitals of the products need not be related to the phases of the reactants). An alternative concerted path could be obtained by displacing center 4 above the plane and twisting by 180° during the reaction, which would allow orbitals ϕ_{2a} and ϕ_{2b} to retain their phases during the reaction. It would appear that the diradical path predominates.

(7) In competition with the 4 + 2 concerted cycloaddition is the 2 + 2 cycloaddition.[6] The latter reaction involves a diradical intermediate and requires about 7 kcal/mol greater activation energy. However,

We see that the selection rule for such addition reactions depends on whether an even or odd number of phase changes are made, and thus such *addition reactions are favored where there are an odd number of* π *bonds in the relevant segments.* This is the same rule obtained by Woodward and Hoffmann[4] from a completely different type of analysis using correlation diagrams for Hartree–Fock orbitals. An application of this same orbital phase continuity principle (OPCP) to electrocyclic and hydrogen-migration reactions again leads to the rules found by Woodward and Hoffmann for thermal reactions.[4,5]

In the Woodward–Hoffmann approach one determines the symmetries of the bonding and antibonding molecular orbitals (essentially minimum basis set Hartree–Fock orbitals) and constructs a correlation diagram. In this approach molecular and orbital symmetry are crucial. In the OPCP approach we use just the bonding GI orbitals (for many cases these are very much like valence-bond orbitals). Here molecular and orbital symmetry are irrelevant. Thus the OPCP approach may be useful even for reactions along low-symmetry reaction paths and involving molecules of low symmetry and may provide a convenient means of predicting and discussing such reactions.

Woodward and Hoffmann[5] have generalized their rules to cases for which correlation diagrams would be difficult or impossible to construct. For thermal reactions these rules are in general agreement with the predictions from OPCP. Trindle[8] has proposed a way of using the nodal structure of MO's to analyze low-symmetry reactions. Since OPCP is based upon GI-type wave functions, it is more akin to valence-bond wave functions than to MO's, and there is no direct connection between these MO approaches and OPCP. More significant differences result for excited states, where the GI wave function can lead to descriptions quite different from the MO or Hartree–Fock wave functions.

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for C_2F_4 plus butadiene the energy of the diradical intermediate is much lower and 2 + 2 cycloaddition dominates: P. D. Bartlett, *Science*, **159**, 833 (1968).

[8] C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970).

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Book Reviews

Organic Fluorine Chemistry. By WILLIAM A. SHEPPARD, Central Research Department, E. I. du Pont de Nemours and Co., and CLAY M. SHARTS, San Diego State College. W. A. Benjamin, Inc., 2 Park Ave., New York, N. Y. 1969. xvi + 602 pp. 16 × 23.5 cm. $30.00.

This book is a "must" for any organic chemist who has any interest in the field of fluorine chemistry, and even for the average organic chemist who wants to comprehend the effect of fluorine substitution in organic compounds.

Critical discussion of the theory of the carbon–fluorine bond adds to the importance of the book as a standard desk reference, since it compiles into one volume a thorough compilation of fluorine chemistry reviews. This book is an excellent example of the effectiveness of collaboration between industrial library organizations, which can compile all the available literature, with authors who are active in the field. The bibliography compiled by the library organization is faultless, and this is by itself enough to make this volume worthwhile. There should be more of this type of collaboration in the future.

This book is a welcome addition to the rather broad but specialized field of fluorine chemistry. The authors have done an excellent job, on the whole, in discussing the classical (pre-1960) methods of fluorination. This book should be a welcome complement to Hudlicky's earlier book in giving a critical evaluation of the various synthetic methods for introducing fluorine into the organic molecule.

There are some general criticisms, however. The typography could be better; it is quite difficult to read the printed material for any length of time and the tables are too compact.

The authors have not always given primary references, but in many instances have referred to another general review (*e.g.*, Table 1-6, p 7) without giving proper credit to the people who actually carried out the work.

In referring to bond dissociation energies, the authors at one point refer to them as B(C–X) (see p 3) and later as D(C–X) (see p 16). One or the other should be used, not both.

The reviewer also is quite surprised that the critical character of this book seems to have lapsed in the discussion of the "Freon" process (p 77), which is described as operating at 30–40 atm. This process is as old and outmoded as the Model T. Another shortcoming is found in the section in which the authors describe the perfluorinated epoxides and their polymers. Very little mention is made of the outstanding contribution of Du Pont chemists in this field. Modesty may be a virtue; in this instance it is carried too far.

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Nitrenes. Edited by WALTER LWOWSKI, Research Center, New Mexico State University, Las Cruces, N. M. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1970. xi + 457 pp. 16 × 23 cm. $23.50.

The definition of a nitrene is stated in the introductory chapter to the book: "the name nitrene stands for the electron-deficient, electroneutral molecule NH and its derivatives. The derivatives are formally produced by substitution of the hydrogens in NH. . . . The definition is based on the structure of the molecule, and not on any particular chemical property." The latter sentence is quite pertinent in that the chemistry of a particular derivative is markedly influenced by the nature of the group substituted for H in NH. While the name nitrene strongly resembles the name carbene, the chemistry of these two species is only mildly analogous, the strong-