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NOTES ON VALENCE BOND THEORY, STRUCTURE-RESONANCE THEORY, AND GRAPH THEORY

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Summary. The relevance of earlier works an valence bond theory to structure-resonance theory and to current structure-reactivity problems is outlined. Graph-theoretical components of both types of calculations are delineated.

Introduction. The π-system properties of neutral π-hydrocarbons, ions, and radicals can be treated by Hückel MO and more advanced MO procedures, or by using valence bond theory. Structure-resonance theory,[1] which is an empirical valence bond theory with the structural basis set limited to principal structures,[2] has also been shown to be useful in this regard. Structure-resonance theory provides a simpler computational procedure, and in most cases gives quantitative numerical correlations with experimental results that go beyond HMO or perturbational MO methods. An algorithm for resonance energies[3] lnSC (a, constant; SC, structure count) further simplifies calculations and produces numerical results tantamount to those obtained using LCAO-MO-SCF methods.

The purpose of these notes is to point out several valence bond and graph theory studies bearing on structure-resonance theory, many of which predate more recent publications. These prior papers and others have not been consistently cited in our previous work for one of the following reasons: (a) the necessity for conciseness, (b) lack of direct pertinence, or (c) oversight due to an insufficiently detailed search of the literature. The results of these works are applicable to current structure-reactivity problems. Therefore short descriptions and references are given below.

Valence bond calculations on π-radicals. Highly approximate valence bond calculations in which the basis set was limited to principal resonance structures were carried out by Pauling and Wheland in 1933.[4] Mistakes in the original work were corrected, and the results were republished.[5] Some justification for the limited basis set assumption is provided by the fact that valence bond *ab initio* calculations for the ground state of allyl radical show that it is well described as the resonance hybrid of the two principal resonance structures.[6] The valence bond resonance energies for radicals derived from aromatic hydrocarbons and alkyl derivatives show a precise linear correlation with the lnSC algorithm.[7] This result is pertinent to discussions of thermal[8] and radical reactivities [9-11] of polycyclic aromatic hydrocarbons, and to evaluation of theoretical procedures for obtaining resonance energies of π-radicals.[7-14] In a recent example, the CC bond dissociation energies in 1-ethylnaphthalene and 9-ethylanthracene were predicted using structure-resonance theory, and the predictions were then found to be in excellent agreement with pyrolytic rate data.[15]

Benzenoid Hydrocarbons. The principal resonance structures for benzenoid hydorcarbons are the Kekule structures, and these are taken as the basis structures in structure-resonance theory calculations. The more usual assumption in early valence bond theory papers was to include all canonical structures (Kekule plus all formal long-bond structures). As examples, see the works of Svartholm,[16] the Daudels,[17] and the Pullmans[18] in which the valence bond definitions of bond orders and free valencies are discussed in relation to chemical reactivities and carcinogenicities.[19-21] The π-electronic spectra calculations of Sklar[22] also made use of all canonical structures. However, Förster[23] described calculations in which the various electronic states were obtained using only the Kekule structures for several benzenoids. Simpson[24] classified states of this type as N states, and showed how one can obtain resonance energies and symmetry species of the N states of benzene, azulene, and naphthalene from experimental spectra. Koenig[25] has carried out some additional development of this "structure-representation" method with applications to interpretations of photoelectron spectra. A resonance theory of polar excited π-electron states has been presented by Heilbronner.[26]

The bond lengths in alternant and nonalternant benzenoid hydrocarbons are accurately correlated[27] by the Pauling bond order, i.e. the number of Kekule structures in which a CC bond is a double bond divided by the total number of structures.[28] Detailed reviews of the Pauling bond order concept have been published,[27,29] and several simple graph theoretical procedures for the rapid calculation of the bond orders have been described.[29,30] Pauling recently used the more cumbrous method of drawing all Kekule structures to obtain bond orders,[31] and briefly described results in comparison with some of the older data and a newly determined structure[32] of tetrabenzo-[de,no,st,c,d]heptacene.

The Spectra of Dyes. Both qualitative and quantitative discussions of ionic dye spectra have made use of a structure-resonance theory formulism limited to principal resonance structures. Theoretical developments are due to Pauling,[33] Sklar and Herzfield,[34] Lewis,[35] Platt,[36] and Simpson.[37] Useful older reviews are by Brooker[38] and Wheland,[39] and a modern idiosyncratic viewpoint has been summarized by Dähne.[40] A graph- theoretical structural study of polymethine dyes has recently appeared.[41]

Reactivity and the lnSC Algorithm. The logarithm of the ratio SC(intermediate)/SC(reactant) or SC(product)/SC(reactant) has proved to be an excellent reactivity index for several types of organic reactions.[1,6,42] A recent example[43] involved kinetic studies of the Diels-Alder reactions of 46 polycylic aromatic hydrocarbons. The rates spanned a factor of 10^7, and were precisely correlated by the ln[SC(product)/SC(reactant)] algorithm. From the theoretical viewpoint, several groups have explored the relationships of HMO π-energies, the logarithm of the number of Kekule structures, and graph-theoretical properties of π-molecular graphs.[44]

Both the structure-resonance theory and the graph-theoretical results are predated by the work of Carter,[45] published posthumously in 1949. He correlated the reduction potential of quinones with an empirical linear equation in which N_H and H_Q are the numbers of Kekule structures for reduced

$$E^\circ = a_o + a_1 \ln(N_H/N_Q)$$

hydroquinone and quinone respectively. This equation still gives a reasonable account of more recently available data,[46] and it was justified by using the same kind of arguments advanced later by Swinbourne-Sheldrake, Herndon, and Gutman.[3] Carter also showed that the HMO π-energy of a benzenoid hydrocarbon could be expressed with a 3-term linear equation where $N = SC$ and D is the

$$\pi E = b_o + b_1 D + b_2 \ln N$$

number of double bonds. The similarity of this equation to graph-theoretically derived equations recently published[44] is striking, and it is also of interest that applications of the equation to elucidation of aromatic hydrocarbon reactivities (indluding Diels-Alder reactions, see above paragraph) were carried out but evidently never published.

In the older literature one also finds valence bond calculation on heterocycles[47,48] and valence bond discussions of aromatic substitutions[49] that are still apropos to modern problems. Finally, Bartell[50] has shown how to obtain π-energies from Pauling bond orders derivable by inspection of the Kekule resonance structures. The procedure was applied to π-hydrocarbon systems and to the calculations of resonance effects in substitution and cycloaddition reactions, radical stabilities, ionization potentials, and electronic spectra.[51] The agreement with the results of MO calculations was substantial, but no further developments of this promising valence bond approach are extant.

Procedures. The general procedures necessary to carry out the types of calculations considered here are described in lucid expositions by Sandorfy (valence bond)[52] and McGlynn, et al. (structure-resonance theory).[53] Valuable discussions of valence bond theory have been given by McWeeney,[54] and Simonetta and co-workers.[55] The valence bond treatments of orbitally degenerate anions, cations, and radicals have been considered at both a simplified[56,57] and the ab initio level.[58]

A graph-theoretical concept of "conjugated circuits" in aromatic hydrocarbons has been developed by Randić,[59] and a parameterization that allows resonance energies to be calculated by counting conjugated circuits was established[59,60] by reference to LCAO-MO-SCF calculations.[61] Randić has pointed out that the mathematical formulations of structure-resonance theory and the conjugated circuit approach are practically identical,[60] since resonance integrals are enumerated by a procedure that involves a sequential deletion of each conjugated circuit from the molecular π graph of the molecule under consideration.[62] The relationship of both methods to the "islands" or "cycles" procedures of Eyring, *et al*.[63] and Pauling[64] which enabled one to write valence bond Hamiltonian matrix elements by inspection of pairs of valence bond structures is also apparent.

The principal eigenvalue (ground state) of the parameterized structure-resonance theory Hamiltonian matrix can be obtained by using standard MO computer programs. In some cases it is more convenient to use graph theory to write the secular equation for the graph that corresponds to the resonance theory matrix, and to extract the desired eigenvalue by algebraic techniques. Procedures given by Hosoya,[65] Graovac, *et al*.,[66] and Aihara[67] were summarized and reformulated by Herndon and Ellzey.[68] In our work, the virtually equivalent procedure outlined by Daudel, Lefebvre, and Moser (1959)[69] based on work of Samuel[70] and Coulson[71] is not cited for reason (c) given in the introduction.

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