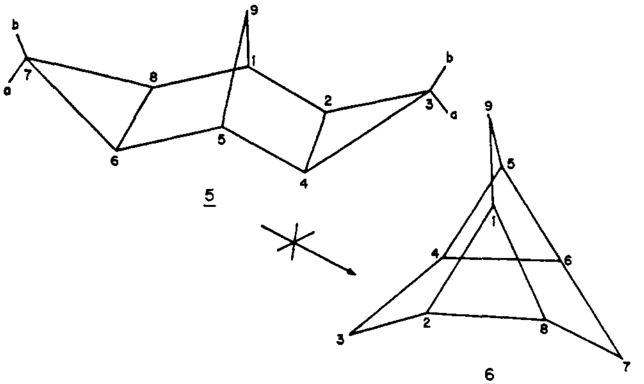

The absence of *exo-endo* isomerization of **5** in the presence of $Rh_2(CO)_4Cl_2$ makes the occurrence of an equilibration between **5** and **6** unlikely. The failure of the valence isomerization of **5** may be due to greater changes in geometry necessary to effect the conversion.

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Bond Index Description of Delocalization

Sir:

A study of nonclassical behavior in carbonium ions[1] and strained ring systems[2] made apparent the desirability of a simple method for determining whether a localized description of a molecule is feasible, given approximate molecular orbital coefficients.[3,4] Extant methods are not suitable; in nonplanar systems, the definition of "delocalization energy" loses its simplicity. The bond order also becomes difficult to interpret for these systems. In this report we describe an interpretation of Wiberg's bond index,[5] which makes possible a detailed description of delocalization, by partitioning the charge into various valence-bond (VB) structures.

The bond index is simply the square of the bond order: $W_{ab} = (P_{ab})^2 = 4\Sigma(i,j \text{ occupied})C_{ia}C_{ib}C_{ja}C_{jb}$; i and j label the doubly occupied molecular orbitals of a closed-shell molecule, and a and b label atomic orbitals in the LCAO expansion. The sum of W_{ab} over all atomic orbitals b, since we assume $\Sigma(b)C_{ib}C_{jb} = \delta_{ij}$, is a dimensionless quantity proportional to the charge in orbital a: $\Sigma(b)W_{ab} = 4\Sigma(i)C_{ia}{}^2 = 2q_a$. The sum may be partitioned into terms as follows.

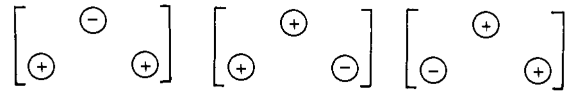
$$q_a = \frac{1}{2}W_{aa} + \frac{1}{2}\sum(K)\sum(b \text{ in } B_K)W_{ab}$$

The first term on the right may be considered the charge in orbital a which is not involved in bonding to other orbitals. The difference $[q_a - (W_{aa}/2)]$ will be referred to as the "active charge" in orbital a and is separated into charges participating in covalent valence bond structures B_K. These statements will be given some clarity by the examples below.

Consider the (definitely delocalized) π system in allyl cation: the doubly occupied Hückel π orbital is

$$\Phi = \frac{1}{2}[\phi_1 + \sqrt{2}\phi_2 + \phi_3]$$

The active charges are (A_1, A_2, A_3) = (0.375, 0.500, 0.375). Note that the total active charge, 1.250 electrons, falls short of the total charge of 2.000 electrons. The remaining charge is involved in ionic structures shown below.

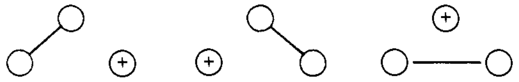


(q_2 = 0.500) (q_3 = 0.125) (q_1 = 0.125)

I_1 I_2 I_3

The overemphasis of ionic structures is a property of the simplest molecular orbital theory, which takes no account of electron interaction. A direct valence-bond calculation would have assigned smaller weight to the ionic forms above.

Of more interest is the relative weights of the valence-bond structures of greater covalency. Consider the structure B_1 in which C_1 is bound to C_2.



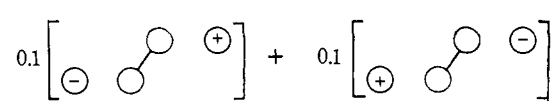
B_1 B_2 B_3

The bond indices predict that the charges involved in B_1 are ($^1/_2W_{12}$, $^1/_2W_{21}$, 0.00), which equals (0.25, 0.25, 0.00). The mirror valence-bond structure accounts for (0.00, 0.25, 0.25) electrons. Finally, the valence-bond structure B_3 in which C_1 is bound to C_3 comprises the remaining active charge, (0.125, 0.000, 0.125). Therefore, the π charge in allyl cation can be viewed as consisting of the three covalent structures and the three ionic structures, in this way

$$q^{\pi}(CH_2CHCH_2{}^+) = {}^1/_4(B_1 + B_2) + {}^1/_8(B_3) + {}^1/_4(I_1) + {}^1/_{16}(I_2 + I_3)$$

This partitioning of charge into VB structures is unambiguous only if the wave functions corresponding to the structures are orthonormal. The structures are not orthogonal in general, but the assumption of an orthogonalized atomic orbital basis set as in most simple π-electron theories and the CNDO method[4] assures the essential orthogonality.

In the following examples we discuss only the distribution of the active charge in various molecules, since the ionic structures are not of immense importance. The active charge in butadiene is composed of three structures



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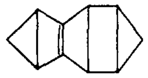
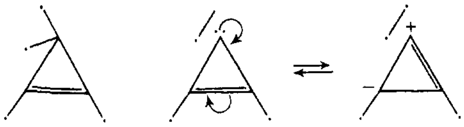
According to this method, 89% of the active π charge in benzene is represented by the two Kekulé structures: the remainder must be described by Dewar structures, implying some cross-ring binding. Only 81% of the π charge in azulene is accounted for by Kekulé structures. The Dewar form



is quite important; over 10% of the active π charge is involved in cross-ring bonding.

Systems expected to be highly localized are also unambiguously characterized by this method. The familiar structure of ethane embraces 99.5% of the active charge, according to the bond index analysis of the CNDO–MO function. The remainder of the active charge is involved in H–H bonding.

The most interesting use of the bond index analysis is the diagnosis of delocalization (and hence, nonclassical character) in carbonium ions and strained-ring systems. We give a single example here, reserving others for more leisurely discussion. In cyclopropene, 97% of the active charge is represented by the usual valence bond structure V_1. About two-thirds of the remaining active



V_1 V_2 V_2'

charge is delocalized in the plane of the ring ("σ delocalization") and one-third is "π delocalized." The latter is predominantly due to a structure V_2 in which the apical protons are bonded, and the resulting carbon lone pair can roam about the ring. The σ delocalization involves a number of open-ring structures.

According to these examples, the bond index can be used to analyze the charge distribution into intuitively significant structures with, insofar as the wave function is accurate, meaningful numerical weights. This device should increase our understanding of MO treatments of molecules.

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The Circular Dichroism of β-Poly-L-lysine[1]

Sir:

Recently, reports have appeared upon the optical rotary dispersion (ORD)[2,3] and circular dichroism (CD)[3,4] of poly-L-lysine (Lys)$_n$ solutions which had been heated to 50° at alkaline pH before analysis. Theoretical and experimental considerations suggest that (Lys)$_n$ solutions treated in such a manner are in the pleated β conformation.[2–7] Such data have therefore been used as a basis for evaluating the β structure present in proteins.[5,8] However, up to the present time, such attempts have been unsuccessful.

The minimum in the CD of previously heated (Lys)$_n$ solutions at around 216 mμ coincides with those of the polarized spectra of oriented (Lys)$_n$ films[7] which have been shown by uv and infrared spectroscopy as well as by X-ray diffraction[9] to be in the β conformation. However, different values in the magnitude of the molar residue ellipticity at the minimum have been reported, ranging from $-19{,}000$[4] to $-23{,}000$[3] deg cm^2/dmol. Furthermore, kinetic experiments[2] and ultracentrifugational[3] analyses of the heated (Lys)$_n$ solution have led to different conclusions concerning whether the β structure is within or between polypeptide chains.

In our laboratory, difficulties were encountered in analyzing the CD of lens α-crystallin[10] by the method of curve fitting,[11] using (Lys)$_n$ heated to 50° at pH 11.5 as the reference for β structure. Because of such difficulties, an investigation of the effect of heating upon the (Lys)$_n$ was undertaken.

Curve 1 in Figure 1 represents the CD between 200 and 250 mμ of a heated solution of (Lys)$_n$ (LY-87-10, New England Nuclear Corp., Boston Mass.), prepared in *exactly* the same manner as reported by Greenfield, *et al.*[2] Based on such data, a mean molar residue ellipticity $[\theta]$ ranging from -16×10^3 to -25×10^3 deg cm^2/(dmol) could be calculated. Amino acid analysis after hydrolysis in 6 *N* HCl indicated the presence of no other amino acid. Before heating, the sample appeared homogeneous by equilibrium centrifugation, giving a molecular weight of 40,700 ± 1200. However, after heating, a molecular weight could no longer be determined since a fine suspension had formed. This was demonstrated in the following manner. The heated solution, after cooling to room temperature, was immediately centrifuged in a Spinco Model L centrifuge at 26,400*g* (20,000 rpm) for 15 min at 20°. The CD of the supernatant (curve 3 of Figure 1) shows a typical double minima of an unheated (Lys)$_n$ solution at pH 11. Thus, the soluble (Lys)$_n$ appears to be in the α-helical form. By comparing the magnitude of the ellipticity of the supernatant with that of the original alkaline solution prior to heating, the amount of soluble (Lys)$_n$ left in the supernatant is about 12%. Resuspending the precipitate in alkaline KOH yielded curve 2 of Figure 1, again characteristic of the β conformation. This suspension was then fil-

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