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A VALENCE CRITERION FOR DIRADICALS AND ZWITTERIONS

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Abstract: A new criterion for the determination of diradicals and zwitterions is presented. An application of typical systems is given and the differences to existing criteria are discussed.

Diradical and zwitterion are common concepts in organic chemistry. A diradical is considered as an electronic state of a molecule with two lone electrons either at one atom or at two distant atoms. The organic chemist deduces the existence of a diradical from the loss of stereospecificity in a chemical reaction. A neutral molecule described by an ionic electronic structure is called a zwitterion. Salem and Rowland /1/ have given these two concepts a common basis. A diradical as defined by these authors is characterized by singlet-triplet degeneracy. A pair of diradical electronic states is accompanied by a pair of zwitterionic states. Döhnert and Koutecky /2/ have modified this criterion through the introduction of natural orbital occupation numbers. In particular, they point out that there exist diradicals without singlet-triplet degeneracy. Recent interest in diradicals is documented trough the book by Borden /3/.

The present workt suggests an alternative to Salem /1/ and Koutecky /2/. Both methods make global statements on diradicals and zwitterions referring to the whole molecule, whereas we present a criterion which not only identifies diradicals and zwitterions, but also the diradical and zwitterionic centers.

For such a local criterion the atomic valence number recently advanced by us on SCF (self-consistent-field) /4/ and CI (configuration interaction) level /5/ is most appropriate. The atomic valence number is related to Wiberg's bond index /6/ and represents a measure of the actually used covalent bonding of an atom in a molecule. The sum of such bond indices of a reference atom with all other atoms in a molecule can be considered as valence /7,8/. The normal valence is 4 for carbon, 3 for nitrogen, 2 for oxygen etc. By a comparison of the actually calculated valence number with the normal valence number one can determine a subvalent of hypervalent atom in a molecule. A quantum chemical calculation with the semiempirical method SINDO1 /9/ yield subvalent carbon with $V = 2.99$ in CH_3 and hypervalent nitrogen with $V = 3.64$ in NH_4^+ /4/.

The two lone electrons of a diradical do not contribute to covalent bonding. Therefore the valence numbers of corresponding atoms are reduced compared to the normal valence numbers. If there are two lone electrons distributed over the atoms of a molecule, the sum of atomic valence numbers should be reduced by approximately 2. This definition is more general than Berson's /10/ who considers a molecule with an even number of electrons as a diradical if it contains one bond less than allowed by the standard rules of valence.

In a zwitterion a donor atom should transfer one electron to an acceptor atom. This influences the covalent bonding of these atoms. The donor atom should be subvalent and the acceptor atom hypervalent. However, for carbon as an acceptor we can find only subvalence since the maximal valence of carbon in valence orbital calculations is 4. The charge transfer increases the dipole moments drastically. Therefore we must consider also the dipole moment. However, for high molecular symmetry there might be zwitterionic electronic states without a dipole moment.

To demonstrate the efficiency of the method, various electronic states and structures of some simple molecules were optimized with SINDO1 /7/ and the valence numbers calculated. For ethylene S_0 was optimized in D_{2h}. The geometry of D_{2d} was obtained by rotation of D_{2h} and of C_s by bending from D_{2h} for all further states T_1, S_1, S_2. Table 1 presents the valence reductions for some states of ethylene, trimethylenemethane, cyclobutadiene and benzene. Atomic valency means the actual valence number of an atom in a molecule based on an SCF or CI calculation with the SINDO1 method. Valency reduction is defined as a sum over all atoms of differences between normal (V_A^{normal}) and actual (V_A^{actual}) atomic valence numbers.

$$\Delta V = \sum_{A}^{\text{atoms}} (V_A^{\text{normal}} - V_A^{\text{actual}})$$

The number of diradical centers is here 2, 3 and 4 due to symmetry. For all diradical states the total actual valency is reduced by about 2 compared to the normal valency. For instance, in the orthogonal triplet state of ethylene (T_1, D_{2d}) the actual valence numbers are 3.11 for the carbon atoms and 1.00 for the hydrogen atoms. The total actual valency is 10.22. Since the normal valency is 4 for carbon and 1 for hydrogen, the total normal valency for two carbons and four hydrogens is 12. So the valency reduction from normal is 1.78 for C_2H_4 in this state. Similarly the total actual valency for trimethylenemethane (T_1, D_{3h}) is 19.44, namely the sum of 3.75 for the central carbon, three times 3.23 for the outer carbons and six times 1.00 for the hydrogens. The total normal valency of four carbons and six hydrogens is 22. Here the total actual valency is reduced by 2.56 compared to the total normal valency.

Table 1: Atomic valence numbers for carbon atoms, total valency reduction and dipole moments (Debye) of diradical (D) and zwitterionic (Z) states

molecule	state	symmetry	type	atomic valencies	valency reduction	dipole moment
C_2H_4	T_1	D_{2h}	D	2.99	2.01	0
	S_o	D_{2d}	D	3.11	1.78	0
	T_1	D_{2d}	D	3.11	1.78	0
	S_o	C_s	D	3.10, 3.13	1.77	1.07
	T_1	C_s	D	3.10, 3.13	1.77	1.07
	S_1	C_s	Z	3.24, 3.40	1.36	2.21
	S_2	C_s	Z	3.26, 3.15	1.59	4.36
$C(CH_2)_3$	T_1	D_{3h}	D	3.75, 3.23	2.56	0
C_4H_4	T_1	D_{4h}	D	3.46	2.16	0
	S_o	D_{4h}	D	3.46	2.16	0
C_6H_6	T_1	D_{2h}	D	3.27, 3.80	2.26	0

For the zwitterionic states of ethylene the valencies are not so drastically reduced, but more different for the two atoms than for the diradical states and have large dipole moments. For C_s symmetry the bond angles at on carbon atom were different by less than 1°, but keeping the CH_2 group orthogonal. The valence numbers show the effect of sudden polarization /11/.

For cyclobutadiene not only the triplet, but also the square singlet is a diradical, a fact not explained by the octet rule. We must consider T_1 of benzene also as a diradical due to its quinoidal structure /12/, the reduced valency of atoms in para position and the small atomic net charges of less than 0.04. Since there is no singlet-triplet degeneracy in this case, this explanation is contrast to Salem /1/.

Table 2 compares normal and zwitterionic isomers. All zwitterions are characterized by a pair of hyper- and subvalent atoms and large dipole moments in agreement with our criterion. For the hypothetical methane oxide H_4CO, which is experimentally unknown, an ab initio calculation was performed in addition. Table 3 suggests an equilibrium, but it is thermally quite unfavorable with respect to dissociation into H_2 and H_2CO. H_4CO is characterized by a polar weakened CO double bond and weakened CH single bonds, but also some HH ring bonding.

We are presently engaged in an application of the method to concerted and nonconcerted reactions. The change of valence numbers during a reaction can be used to understand alternative reaction pathways.

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Table 2: Atomic valence numbers and dipole moments (Debye) of normal (N) and zwitterionic (Z) isomeric molecules

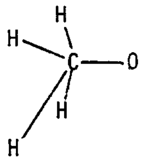
molecule	type	atomic valencies	dipole moment
H_2NCH_3	N	3.00 (N), 3.98 (C)	2.02 (1.30^a, 1.62^b)
H_3NCH_2	Z	3.59 (N), 2.72 (C)	5.77 (5.53^b)
H_2NNH_2	N	3.00 (N), 3.00 (N)	1.60 (1.75^a, 2.22^b)
H_3NNH	Z	3.62 (N), 1.76 (N)	5.07 (5.01^b)
H_2NOH	N	2.99 (N), 2.01 (O)	0.56 (0.41^b)
H_3NO	Z	3.67 (N), 0.85 (O)	4.80 (4.48^b)
H_3COH	N	3.95 (C), 2.02 (O)	1.67 (1.70^a, 1.51^b)
H_4CO	Z	3.92 (C), 1.72 (O)	5.56
H_2BCHO	N	3.04 (B), 3.91 (C)	1.23 (1.77^a)
H_3BCO	Z	3.60 (B), 3.28 (C)	3.78

a) A.L. McClellan, Tables of Experimental Dipole Moments, Vol. I. W.H. Freeman, San Francisco 1963; Vol. II, Rahara Enterprises, El Cerrito 1973.

b) J.A. Pople et al., STO-3G calculations, Carnegie-Mellon Quant.Chem. Arch. 1980.

Table 3: Properties of H_4CO (C_{4v})

		SINDO1	6-31G**
Bond length (Å)	CO	1.297	1.263
	CH	1.181	1.153
Bond angle	OCH	117.0	124.1
Dipole moment (Debye)		5.56	5.88
Dissociation energy (kcal/mol)		313.6	233.4
Fragmentation energy (H_2CO+H_2)		-156.8	-107.4



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