

A BOND INDEX DESCRIPTION OF BONDING IN
UNSATURATED MOLECULES CONTAINING gem-DIFLUOROGROUPS

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Unique chemical reactivity and other anomalous properties, due to the electronegativity of fluorine, place unsaturated compounds containing the terminal gem-difluorogroup, =CF₂, in a different class from their proton analogs; the electronic reasons for the enhanced reactivity of these compounds has only recently drawn theoretical attention.^{1/} The purpose of this work is to disclose the results of the application of the bond index method of Wiberg,^{2/} and Trindle and Sinanoglu,^{3/} which is based on the CNDO method of Pople^{4/} to several fluorinated compounds containing terminal CF₂ groups. In this work the bond index description has been applied to representatives of both polar and nonpolar fluorinated unsaturated compounds.

The bond index between two atomic orbitals is defined by $W_{ab} = P_{ab}^2$ ^{2,3c,d/} where P_{ab} is the Coulson bond order. When the bond indices between an orbital, a , and all of the other orbitals interacting with orbital a are summed, the result is given as $2q_a = \sum_b W_{ab}$ where q_a is the charge in orbital a . The amount of charge in orbital a , centered on atom A, which is involved in bonding in an A-B bond is expressed by $W_{ab} = \sum (b \text{ in } B) W_{ab}$ ^{3/}. A bond index figure, W_{AB} , of 1 corresponds to one valence bond.

The p character of a hybrid orbital on center A , projected toward B , is given by $X_p = (W_x + W_y + W_z) / (W_s + W_x + W_y + W_z)$, where the subscripts refer to S, P_x, P_y, P_z of an atom of the first row of the periodic table.^{3b/} (i.e., $W_x = W(2P_x, A-B)$ etc.)

If the molecular orbitals, used in definition of the bond indices, are highly localized, X_p gives the same values as the expression used in a full localization treatment for evaluation of

hybridization.^{3c/} A criterion of when X_p is a good definition of hybridization is given by D_1 , the localization defect. This parameter is given by $D_1 = \sum(a) [2 q_a - q_a^2] - \sum(b) W_{ab}$. When D_1 approaches zero, the system under description approaches complete localization.^{3b,c/}

A closed shell version of a CNDO program was written for the IBM 360/30 computer.^{5,6/} This program was used to calculate the CNDO wave functions and bond order-charge density matrix. The W_{ab} matrix was obtained by squaring each element in the charge density matrix. The values of W_{ab} for each bond in molecule were obtained by summing over the orbitals involved in that bond.

Three compounds, representing widely different types of unsaturated compounds containing terminal gem-difluorogroups, vinylidene fluoride, tetrafluoroethylene, and carbonyl fluoride, were chosen for this study. These compounds represent a polar fluorocarbon, a nonpolar fluorocarbon, and a polar heteroatomic compound. Thus, a wide representation of the types of compounds containing the CF_2 group provides a good indication of the scope of the bond index representation method in unsaturated compounds containing fluorine.

The results of the CNDO/2 calculations are summarized in Table I. The fact that these results closely agree with published results of dipole moments encourages confidence in the validity of the program. The charge densities in 10^3 units of charge, which were calculated, are shown in Figures 1-3.

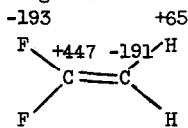


Figure 1

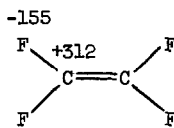


Figure 2

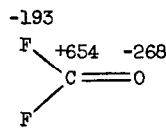


Figure 3

A point of interest is the size of the localization defects, D_1 , which have been entered in Table I according to each atomic center, and according to the orbitals traditionally described as contributing to a σ or π M.O. Neglect of lone pairs in summing up bond indices on the fluorine atoms gives rise to localization defects which are fairly large due to the amount of charge formally "delocalized" into lone pair orbitals. However, in every case with lone pair hybrids, the total molecular localization defect is less than 1.0, indicating that even if lone pair hybridization is neglected, the resultant structures are fairly well localized. Including the lone pair bond indices in the definition of hybridization gave much lower localization defects (footnotes to Table I) and better agreement with input geometries.

TABLE I
SUMMARY OF BOND INDEX CALCULATIONS FOR COMPOUNDS
CONTAINING THE CF₂ GROUP

	Dipole Moment (Debye)		Bond A-B	W _B	D _{LA} ^o	W _B ^π	D ^{πA}	D _L ^{Total}
	Calcd.	Observed						
1. Vinylidene Fluoride	1.37	1.37 ^a	C-C	1.0431	0.0968	0.8907	0.0001	0.0968
			F-C	0.9272	0.3424	0.0526	0.0439	0.3863 ^c
			C-H	0.9285	0.0264	--	0.0829	0.1093
2. Tetrafluoro-0.00 ethylene	0.00	0.00	C-C	0.9899	0.0112	0.8225	0.0829	0.0946
			F-C	0.9479	0.3790	0.0430	0.0496	0.4286 ^d
3. Carbonyl Fluoride	0.97 ^b	0.95 ^a	C-O	1.269	0.0106	0.7907	0.000	0.0106
			C-F	0.8815	0.3810	0.0819	0.0486	0.4296

a) Geometries used were experimental ones in each case. (Ref. 9, 10, 11)

b) This value agrees exactly with the dipole moment calculated by Segal and coworkers, Ref. 12.

c) This value becomes 0.0288 if the W(s,x), W(s,y) and W(x,y) values for hybridized lone pairs are included.

d) This value becomes 0.0852 if the lone pair bond indices W(s,x) etc. are included in the $\sum (B) W_{AB}$.

TABLE II
HYBRIDIZATION OF CARBON ATOMS IN TERMINAL UNSATURATED gem-DIFLUORO GROUPS

Compound	X _s of Hybrid or Orbital External to < FCF	λ ^{2a}		Geometry ^b	
		Observed	Calcd.	Input	Calcd.
CF ₂ CH ₂	49.36	3.03	3.08	109°18'	108°57'
CF ₂ CF ₂	46.38	2.92	2.83	110°	110°42'
CF ₂ O	39.68	2.56	2.52	113°	113°24'

a) Computed from $\lambda^2 \cos \theta = -1$ (see Refs. 7 and 8). b) The geometries used as input were as follows: Vinylidene fluoride, Ref. 9; Tetrafluoroethylene, Ref. 10; and Carbonyl fluoride, Ref. 11.

In Table II the hybridization results obtained by calculation of X_s are presented.

These results include the terms W_(s,x), W_(x,y), W_(s,y) etc., of orbital interaction on a single atomic center, which describes the lone pair hybridization on that center, in the calculation of W_x, W_y, W_z, etc. The hybridization indices were obtained from the well known stereochemical relationships^{7,8} $\lambda^2 \cos \theta + 1 = 0$, and where each bonding a.o. is S + λP.

The important points of this study are that the CNDO wave functions of the three representative fluorinated compounds may be analyzed into localized structures by means of this bond index treatment, and that description of the hybridization of each center by the Wiberg-Trindle-Sinanoglu method reasonably reflects the true molecular geometry. For example, the known high percentage of S character in the hybrid orbital directed toward the methylene carbon¹ in vinylidene fluoride is accurately shown in X_s for that orbital.

One may conclude that a bond index description of terminal unsaturated gem-difluorogroups of this study accurately depicts the input geometry of the compounds. Thus, the bond index method provides a means of exploring hybridization of unknown fluorine-containing structures.

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