1,2 + 1,3 in a ratio of 4/1. The first two mixtures could be rejected quite confidently. The 1,2 + 1,3 mixture in the ratio 4/1 gave spectra scarcely distinguishable from those for pure 1,2 shifts, and the mixture must be considered to provide an acceptable explanation for the observed spectra. For an equal mixture of 1,2 and 1,3 shifts, the spectra shown in Figure 3 are obtained. We think that these spectra are slightly but definitely less satisfactory than those given by pure 1,2 shifts and feel that the proportion of 1,3 shifts cannot be as high as 50%. However, the reader may inspect Figure 3 and make his own judgment.

In summary, comparison of computed and observed spectral changes shows that the latter can only be accounted for by a rearrangement pathway which either consists exclusively of 1,2 shifts or consists mainly of 1,2 shifts with 1,3 shifts occurring no oftener than about 40% of the time.

If we make the reasonable assumption that rotation of the C_7H_7 ring occurs without significant movement of the metal atoms relative to each other, then the points obtained by dropping a perpendicular from each metal atom onto the mean C_7H_7 ring plane will trace out circles concentric with the heptagon approximating to the time-average ring conformation. It would then be impossible for a 1,3 shift (or a 1,4 shift either) to occur as distinct from two (or three) 1,2 shifts. On this basis, we would come to the final conclusion that the overwhelmingly predominant intramolecular rearrangement process in this molecule is the 1,2 shift and that the averaging of proton resonance signals may be attributed to a rapid sequence of 1,2 shifts.

By choosing residence times which permit the closest practical match of a computed spectrum (for 1,2 shifts) to each of several observed spectra (specifically, those at 0, −3, −8, −12, −18, and −22°; see Figure 1 for the goodness of fit), a set of rate constants at various temperatures was obtained. These data gave a good Arrhenius plot from which the following activation parameters were extracted: $E_a = 13 \pm 1$ kcal/mole; $\log A = 12.7 \pm 0.8$; $\Delta S^* = -2$ eu at 273° and +2 eu at 251°.

Local Orbital and Bond Index Characterization of Hybridization

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Abstract: Hybridization, a local property of the wave function, is discussed in terms of the molecular orbital theory. Two methods for prediction of hybridization are introduced, one based on orbital localization and the other on an extension of Wiberg's bond index. When a localized description of the wave function is possible, a situation which allows unambiguous definition of hibridization, the two methods give indistinguishable results. Calculations employing the complete neglect of differential overlap approximation for a variety of molecules, including alkanes, alkenes, ethers, alcohols, and carboxylic acids, give a reliable qualitative account of trends in hybridization. Agreement between the calculated p character X_p and estimates of X_p from nmr coupling constants is good. Correspondingly, a local orbital estimate of the hybridization can be used to predict the coupling between carbon-13 nuclei and directly bound protons in molecules for which the experimental data are not available.

The valence-bond treatment of the molecular charge distribution provided an intuitively appealing description of bonds in terms of ionic character, hybridization, and resonance.[2a] Many molecular properties, including dipole moments, bond lengths, force constants, quadrupole coupling constants, and certain nuclear magnetic resonance shifts, could be understood using these ideas.[2b] It is desirable to define intuitively meaningful quantities parallel to these earlier ideas in terms of the molecular orbitals.

In this report we consider the notion of hybridization.[3] Several particular problems are examined: conditions requisite to the unambiguous definition of hybridization are sought. Two methods affording numerical characterization of hybridization, expressed in terms of the molecular orbitals, are introduced. Finally the reliability of predictions of hybridization based on semiempirical wave functions is indicated by comparison to an experimental reference, the carbon-13–proton coupling, for a variety of molecules including alkanes, alkenes, alcohols, ethers, and carboxylic acids.

Definition of Hybridization

The idea of hybridization is the result of an assumption that an atom retains its identity within a molecule and makes only slight adjustments to the molecular environment. This assumption has two main implications. First, the total wave function may be represented in terms of orbitals formed by combination of atomic functions. Since each atom then has s, p, etc., orbitals unambiguously associated with it, it is possible to define atomic s and p populations. Such a definition is essential for any discussion of hybridization. Wave functions expressed in terms of floating Gaussian

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[1] National Science Foundation Postdoctoral Fellow, 1967–1968.

[2] (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960—of course; (b) W. Kauzman, "Quantum Chemistry," Academic Press, New York, N. Y., 1957.

[3] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

orbitals or a one-center expansion, for example, cannot be understood by specifying hybridization at individual atoms.

A second consequence of the assumption that molecules are composed of slightly distorted atoms is that the distortion is at least qualitatively described by perturbation theory. The perturbation on an atom (that is, the field at an atom due to nearby atoms) leads to a mixing of the atomic orbitals, producing the distortion of that atom which maximizes its overlap with the charge of the neighboring atoms. In first-row atoms the nearly degenerate 2s and 2p orbitals will contribute predominantly to the mixed (*i.e.*, hybridized) orbitals. This is the reason behind the formation of sp^n hybrid orbitals in first-row atoms.

A limitation implicit in the preceding discussion is that hybridization is primarily a local response to a local perturbation of the atom. Individual hybrids are associated with local bonds; whenever delocalization vitiates the idea of localized bonding, the value of the concept of hybridization is reduced.

From these remarks we see that a definition of hybridization is feasible if the wave function is represented by combinations of atomic orbitals. It is meaningful if a localized description of the charge distribution is possible. The problem of numerical characterization of the local property, hybridization, in terms of the fundamentally delocalized molecular orbitals occupies the next section.

Theoretical Description of Hybridization in Molecular Orbitals

A. Local Molecular Orbitals. The most direct description of molecular orbitals in terms of the individual hybrids is obtained by a unitary transform of the symmetry-adapted molecular orbitals to localized orbitals identifiable with bonds, cores, and lone pairs.[4] The invariance of the expectation values (the physically meaningful quantities) to such unitary transform justifies this trade of mathematical convenience for conceptual clarity. We[5] have suggested a simple procedure for the application of the physical localization criterion of Lennard-Jones and coworkers[6,7] that an electron in a localized orbital interacts maximally with the electron sharing that orbital. To illustrate the results of a localization transform we have reproduced the transformation matrix **T** and the local orbitals **L** for a sample localizable system, $C_2H_5NH_2$ (Tables I and II). The original molecular orbitals **C** were obtained by a Pole-type CNDO-II calculation,[8] since this is the simplest σ MO theory which obeys the requirement that expectation values are invariant to a unitary transform of the orbitals. These symmetry-adapted orbitals may be obtained by the relation $\mathbf{C} = \mathbf{T}^t\mathbf{L}$, where $\mathbf{T}^t$ is the transpose (and the inverse) of **T**.

An estimate of the hybridization of the nitrogen atomic orbitals toward a hydrogen atom in ethylamine may be obtained from an inspection of the rightmost local orbital in Table II, which corresponds to a NH bond. The p character X_p is given by

$$X_p = \frac{C(\mathrm{N2p}_x)^2 + C(\mathrm{N2p}_y)^2 + C(\mathrm{N2p}_z)^2}{C(\mathrm{N2s})^2 + C(\mathrm{N2p}_x)^2 + C(\mathrm{N2p}_x)^2 + C(\mathrm{N2p}_z)^2}$$

Similar simple calculations describe specific hybrids in any local orbital.

B. Bond Index. An alternate approach to the determination of p character in individual hybrids is provided by the bond index of Wiberg.[9] The bond index is defined as the square of the bond order, P_{ab}, familiar from the simple MO theory of π systems.[10]

$$P_{ab} = 2\sum(i)c_{ia}c_{ib} \qquad (2)$$

The sum extends over occupied MO's i, and the c's are the LCAO expansion coefficients in an orthogonalized atomic orbital basis. The square of the bond order, $P_{ab}{}^2 = W_{ab}$, as is shown in the Appendix, measures the amount of charge in the AO a which is involved in bonding to the AO b. Let us sum W_{ab} over a set of orbitals V_B on atom B which are expected to participate in an A–B bond; the AO a is assumed to be on atom A.

$$W_{aB} = \sum(b \text{ in } V_B)W_{ab} \qquad (3)$$

The result is the amount of charge in orbital a which is involved in the A–B bond. More concretely, if center B is a carbon atom, the set V_B contains the 2s and 2p orbitals of that carbon. If we define $W_s = W(\mathrm{2sA{-}B})$, $W_x = W(\mathrm{2p_xA{-}B})$, $W_y = W(\mathrm{2p_yA{-}B})$, and $W_z = W(\mathrm{2p_zA{-}B})$, the p character X_p of the hybrid on center A which is directed toward atom B is given by

$$X_p = (W_x + W_y + W_z)/(W_s + W_x + W_y + W_z) \qquad (4)$$

For the special case that A–B is a CH bond, the set V_B contains only the hydrogen 1s orbital; $W_{aB} = P^2(a - \mathrm{1sH})$. This is the quantity used by Wiberg to estimate hybridization in CH bonds.[9]

We show in the Appendix that, if the set of molecular orbitals is highly localized, the bond index estimate of X_p reduces to the expression used in the direct

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(4) D. Peters (*J. Chem. Soc.*, 2003, 4017 (1963)) has analyzed hybridization in small molecules by localization of rigorously determined SCF–LCAO–MO's. Peters demands that localized orbitals have no contribution from atomic orbitals removed from the bond or lone pair represented by the local orbital. For example, a fluorine lone-pair orbital would have no lithium 2s component, in LiF. While analysis based on this type of localization is enlightening in many ways, the detailed results may be questioned. In the symmetry-determined local orbitals of the valence shell of CH_4, each CH bond orbital contains nonnegligible contributions[4] from the other protons. This result is not consistent with the demand that off-bond orbitals make no impact on the bond function. A further objection is that the choice of the localization condition is not unique in many cases. Different conditions will in general lead to different localized orbitals: the problem is illustrated by Peters' results for H_2O.

Del Re and others [G. Del Re, U. Esposito, and M. Carpentieri, *Theoret. Chim. Acta*, **6**, 36 (1966); A. Veillard and G. Del Re, *ibid.*, **2**, 55 (1964)] have considered hybridization as described by local orbitals determined by requiring that hybrids on different atoms have minimal overlap unless they participate in the same bond. These authors are mainly concerned with the relation of s character in hybrids to bond angles, *i.e.*, the question of "bent bonds." Different basis sets and different localization criteria give various views of this question. The problem will be discussed more fully by us in a forthcoming report.

(5) C. Trindle and O. Sinanoğlu, *J. Chem. Phys.*, **49**, 65 (1968).

(6) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.* (London), **A220** 446 (1950); **A210**, 190 (1951).

(7) C. Edmiston and K. Reudenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); *J. Chem. Phys.*, 43, S97 (1965).

(8) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965); G. A. Segal and J. A. Pople, **43**, S136 (1965); **44**, 3289 (1966).

(9) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968). The relation of the 1s–2s bond index to the $J(^{13}\mathrm{CH})$ coupling constant is pointed out in this report.

(10) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961; L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

Table I. The Localization Transform Matrix **T** for Ethylamine[a]

	1a′	2a′	3a′	1a″	4a′	5a′	2a″	6a′	3a″	7a′
C(1)C(2)	0.4480	0.3611	0.0642	0.0000	0.2390	−0.6063	0.0000	0.1332	0.0000	0.4715
C(2)H(3)[b]	0.2432	−0.3148	−0.3660	0.3589	0.1731	0.3181	−0.4872	0.2759	0.3658	−0.0232
NC(1)	0.4906	−0.3128	0.1326	0.0000	0.3934	0.3658	0.0000	0.5800	0.0000	−0.1375
C(2)H(2)[b]	0.2431	0.3148	−0.3661	0.3588	0.1732	0.3181	−0.4872	−0.2757	−0.3660	−0.0231
N1p	−0.1359	0.2647	−0.0252	0.0000	0.3770	−0.3900	0.0000	0.0683	0.0000	−0.7822
C(1)H(4)[c]	−0.2816	−0.0977	−0.5193	0.4703	0.1282	−0.0790	−0.0484	0.3051	0.5257	0.1604
C(2)H(1)	−0.1684	−0.4518	0.1216	0.0000	0.6795	−0.0725	0.0000	−0.4986	0.0000	0.1926
C(1)H(5)[c]	0.2817	0.0978	0.592	0.4704	−0.1281	0.0791	−0.0485	−0.3051	0.5257	−0.1604
NH(6)[d]	0.3427	−0.3743	−0.2789	0.3873	−0.2137	−0.2513	0.5102	−0.1647	−0.2995	−0.1693
NH(7)[d]	0.3427	−0.3743	−0.2789	−0.3872	−0.2137	−0.2513	−0.5102	−0.1647	0.2995	−0.1693

[a] $L = TC$, where C contains the coefficients of the MO's in order of increasing energy. The bonds or lone pairs by which the localized orbitals are labeled are listed at the left. Note that equivalent bonds (*i.e.*, those permuted by symmetry operations) are associated with equivalent rows in the localization transform matrix. [b–d] Bonds with like letter superscripts are equivalent.

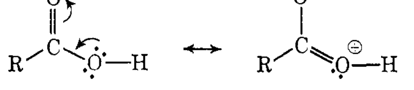
Table II. Local Orbital Coefficients for Ethylamine[a]

	C(1)C(2)	C(2)H(3)	NC(1)	C(2)H(2)	N1p	C(1)H(4)	C(2)H(1)	C(1)H(5)	NH(6)	NH(7)
2s N	0.0112	−0.0106	0.3593	−0.0106	0.5141	−0.0126	0.0187	−0.0126	0.3849	0.3849
C(1)	0.3532	0.0047	0.3243	0.0046	−0.0167	0.3649	0.0012	0.3649	0.0040	0.0040
C(2)	0.3487	0.3654	0.0020	0.3654	0.0244	0.0001	0.3481	0.0000	−0.0086	−0.0086
$2p_x$ N	0.0000	0.0057	0.0000	−0.0057	0.0000	−0.0253	0.0000	0.0252	0.5122	−0.5122
C(1)	0.0000	−0.0432	0.0000	0.0431	0.0000	−0.4851	0.0000	0.4851	0.0476	−0.0476
C(2)	0.0000	−0.4931	0.0000	0.4931	0.0000	−0.0423	0.0000	0.0425	−0.0030	0.0030
$2p_y$ N	−0.0004	0.0079	−0.1783	0.0079	0.8504	0.0037	−0.0133	0.0037	−0.1963	−0.1963
C(1)	−0.6068	−0.0148	0.1984	−0.0149	0.0458	0.2167	−0.0162	0.2167	−0.0111	−0.0111
C(2)	0.6203	−0.2156	0.0139	−0.2156	0.0288	0.0123	−0.2118	0.0122	−0.0069	−0.0069
$2p_z$ N	−0.0105	−0.0093	0.6148	−0.0093	−0.0161	0.0127	0.0287	0.0127	−0.2987	−0.2987
C(1)	0.0022	−0.0241	−0.5586	−0.0242	0.0480	0.2754	0.0478	0.2754	−0.0289	−0.0289
C(2)	0.0042	−0.2779	−0.0428	−0.2779	0.0181	0.0222	0.5768	0.0222	−0.0052	−0.0052
1s H(1)	−0.0043	0.0010	0.0410	0.0010	−0.0178	−0.0147	0.7046	−0.0146	0.0065	0.0066
H(2)	−0.0041	−0.0085	−0.0150	0.7033	0.0052	0.0418	−0.0165	−0.0171	−0.0011	0.0001
H(3)	−0.0041	0.7033	−0.0150	−0.0085	0.0052	−0.0173	−0.0165	0.0418	0.0001	−0.0011
H(4)	−0.0070	−0.0167	−0.0117	0.0404	−0.0188	0.7079	−0.0139	−0.0122	0.0384	−0.0154
H(5)	−0.0071	0.0404	−0.0117	−0.0169	−0.0188	−0.0122	−0.0139	0.7079	−0.0154	0.0384
H(6)	−0.0122	0.0016	−0.0076	0.0053	−0.0491	0.0401	0.0003	−0.0084	0.6757	−0.0084
H(7)	−0.0122	0.0053	−0.0076	0.0015	−0.0491	−0.0085	0.0003	0.0401	−0.0084	0.6757

[a] Orbitals are labeled as bonds or lone pairs horizontally; basis functions are labeled vertically at left.

evaluation of hybridization in a local orbital, eq 1. From this demonstration we deduce that one reason for disagreement between bond index and local orbital estimates of p character would be incomplete localization, due either to early termination of the iterative localization procedure or to the presence of a truly mobile charge distribution. Highly delocalized systems such as the π orbitals in benzene produce paradoxes if localization is attempted; small delocalizations can be diagnosed from the disageement of the two estimates of X_p.

We have performed localization and bond-index-type calculations of hybridization for a variety of molecules, representing some of the important organic functional groups. The results are summarized in Table III. Most of the disagreement between the bond index and local orbital predictions of p character can be traced to small amounts of delocalization, obvious in the local orbital coefficients. For example, in the carboxylic acids the importance of an ionic structure shown below is apparent from the local orbital coefficients (Table IV). The O′ lone pairs are clearly delocalized onto the central carbon atom. This delocalization makes ambiguous the definition of the oxygen lone-pair hybridization and affects all the other hybrids as well. The O′ hybrid in the CO′ bond would be diminshed in p character relative to the analogous hybrid in an alcohol, which is involved in a purely single bond. The expected decrease is observed in the formic acid–methanol and acetic acid–ethanol pairs.



A similar situation is found in cyclopropene. The deviations between the bond index and local orbital predictions of hybridization are due to delocalization in both the σ and π systems of the molecule. The local orbital coefficients show the delocalization plainly (Table V).

A local orbital analysis will always make clear the presence of delocalization; the feasibility of defining individual hybrids is then easy to judge. However, if the bond index estimates of hybridization are to be relied upon, a localized description of the charge distribution must be possible. A simple method for determining the validity of a localized picture of the charge, given the bond indices, has been discussed by one of us (C. T.) elsewhere.[11] If more than one valence-bond structure is necessary to account for all the charge in the molecule, hybridization is not definable for the parts of the molecule where the structures differ. As a

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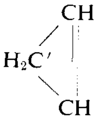
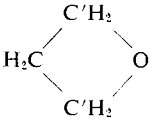
(11) C. Trindle, *J. Am. Chem. Soc.*, in press.

Table III. Local Orbital and Bond Index Estimates of Hybridization[a]

	Bond A–B	W_A	W_B	LO_A	... LO_B
	Alkanes				
CH_4	CH	75.1	...	74.0	...
CH_3CH_3	CH	75.4	...	75.2	...
	CC	74.0	74.0	75.8	75.8
$CH_2(C'H_3)_2$	C'H	75.3	...	74.8	...
	CH	77.0	...	76.0	...
	C'C	74.0	73.2	74.8	74.1
Cyclopropane	CH	69.5	...	66.8	...
	CC	80.3	80.3	82.0	82.0
	Amines				
CH_3NH_2	NH	69.8	...	67.3	...
	CH	73.4	...	71.5	...
	NC	78.8	63.8	80.2	62.5
$CH_3C'H_2NH_2$	NH	73.4	...	71.2	...
	CH	75.3	...	76.1	...
	C'H	74.7	...	72.9	...
	C'C	73.7	73.7	74.9	75.0
	NC'	80.7	77.1	79.0	77.0
$(CH_3)_2NH$	NH	64.8	...	61.8	...
	CH	73.9	...	72.0	...
	CN	78.2	69.4	76.9	70.9
	Alcohols				
CH_3OH	CH	73.4	...	71.3	...
	OH	82.2	...	86.8	...
	CO	79.5	82.5	78.9	84.8
$CH_3C'H_2OH$	CH	75.2	...	74.4	...
	C'H	73.7	...	71.7	...
	OH	83.1	...	85.9	...
	CC'	74.5	72.1	74.4	72.5
	C'O	80.1	82.1	78.2	84.6
$(CH_3)_2C'HOH$	CH	75.7	...	74.7	...
	C'H	74.9	...	75.1	...
	OH	85.9	...	82.5	...
	C'O	80.1	79.5	78.6	77.7
	CC'	74.2	72.6	71.8	71.5
	Carbonyls				
$CH_3C'HO$	CH	75.3	...	74.5	...
	C'H	69.3	...	64.3	...
	CC'	74.4	65.1	75.9	61.6
$(CH_3)_2C'O$	CH	75.2	...	74.7	...
	CC'	74.7	67.2	74.2	65.9
	C'O	68.6	73.6	67.0	75.1
	Carboxylic Acids				
$HCO(O'H)$	CH	61.8	...	57.1	...
	O'H	83.6	...	81.7	...
	O'C	79.3	70.0	75.7	66.8
	OC	70.8	64.4	73.2	62.8
$C'H_3CO(O'H)$	C'H	75.1	...	75.1	...
	O'H	82.7	...	79.6	...
	O'C	81.7	74.0	74.5	68.4
	OC	75.1	65.0	75.8	63.1
	C'C	75.0	65.0	75.6	58.8
	Alkenes				
C_2H_4	CH	69.0	...	71.2	...
	CC	62.5	62.5	62.2	62.2
trans-$CH_3C'HC'HCH_3$	C'H	69.6	...	67.8	...
	CH	74.9	...	74.4	...
	C'C	69.9	74.9	66.8	74.8
	C'C'	62.1	62.1	62.4	62.4
cis-$CH_3C'HC'HCH_3$	C'H	70.3	...	68.3	...
	CH	75.0	...	75.5	...
	C'C	69.2	74.8	66.1	75.2
	C'C'	62.2	62.2	62.5	62.6
$C''H_2C(CH_3)_2$	C''C'	62.1	62.8	61.3	64.4
	C'C	69.9	74.8	67.6	74.7
	C''H	69.2	...	66.3	...
	CH	75.1	...	74.5	...
	C'C	80.8	75.6	85.6	79.7
	CC	66.5	66.5	65.8	65.8
	C'H	68.2	...	65.7	...
	CH	62.3	...	54.5	...
	Ethers				
$(CH_3)_2O$	CO	77.7	74.8	77.8	74.0
	CH	73.2	...	71.5	...
	OC'	83.1	81.3	81.7	80.7
	C'C	75.4	75.2	77.0	76.3
	C'H	71.5	...	69.6	...
	CH	74.4	...	73.8	...

[a] Molecules are classified by functional group in the leftmost column: the bond A–B is identified in the next column. The bond index value for the p character of the A hybrid participating in the A–B bond (W_A) and the value for the p character in the corresponding B hybrid (W_B) are given in the third and fourth columns. The parallel quantities obtained by a local orbital (LO) analysis (LO_A and LO_B) are presented in the last two columns.

Table IV. Local Orbital Coefficients for Formic Acid[a]

	CH(1)	O(1)H(2)	O(1)C	O(2)C^{σ}	O(1)–1p	O(1)–1p	O(2)C_{π}	O(2)–1p	O(2)–1p
2s O(1)	−0.0232	0.3775	0.3796	−0.0010	0.5191	0.5184	0.0000	−0.0276	0.0293
O(2)	−0.0009	−0.0145	−0.0002	0.3773	0.0101	0.0102	0.0000	0.6003	0.6012
C	0.4631	0.0148	0.3667	0.4166	−0.0165	−0.0166	0.0000	−0.0029	−0.0186
$2p_x$ O(1)	0.0002	−0.0001	−0.0001	−0.0002	0.6892	−0.0899	−0.0418	0.0006	−0.0002
O(2)	0.0000	−0.0001	0.0001	0.0000	−0.0698	0.0699	0.7960	−0.0001	0.0000
C	0.0000	−0.0001	0.0000	0.0000	0.1399	−0.1400	0.6039	0.0001	0.0000
$2p_y$ O(1)	0.0040	0.4879	−0.6036	0.0122	0.0838	0.0838	0.0001	0.0190	−0.0366
O(2)	0.0174	−0.0076	−0.0305	−0.0001	0.0030	0.0030	0.0001	0.6925	−0.6929
C	−0.4422	0.0679	0.4483	0.0116	−0.0234	0.0234	0.0000	0.1244	−0.1244
$2p_z$ O(1)	−0.0218	0.4500	0.2895	−0.0101	−0.4701	−0.4698	0.0000	−0.0306	0.0288
O(2)	0.0096	0.0204	0.0097	−0.6242	−0.0153	−0.0150	0.0000	0.3719	0.3719
C	−0.2998	0.0385	−0.2633	0.5414	−0.0224	−0.0225	0.0000	0.0125	0.0261
1s H(1)	0.7051	0.0363	−0.0459	−0.0266	−0.0092	−0.0090	0.0000	0.0610	−0.0376
H(2)	0.0403	0.6391	−0.0058	−0.0152	−0.0341	−0.0341	0.0000	0.0160	−0.0022

[a] Localized molecular orbitals are labeled as bonds or lone pairs horizontally; atomic orbitals are labeled vertically at left. O(1) is O′ of Table III.

rule, hybridization is definable throughout a molecule if the sum of all the bond indices used in the definition of hybrids is equal to $\Sigma(a)[2q_a - q_a^2]$, where q_a is the charge in orbital a.

Table V. Local Orbital Coefficients for Cyclopropene[a]

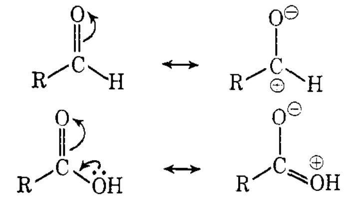
	C(1)C(2)	C(1)C(3)	C(2)C(3)	C(1)H(2)	C(1)H(1)	C(3)H(4)	C(2)H(3)	C(2)C(3)(π)
2s C(1)	0.2676	0.2674	0.0404	0.4105	0.4103	0.0102	−0.0034	−0.0001
C(2)	0.3094	0.0406	0.4108	0.0103	0.0006	−0.0131	0.4874	−0.0001
C(3)	0.0407	0.3095	0.4109	0.0004	−0.0061	0.4873	−0.0131	−0.0001
$2p_x$ C(1)	0.0001	0.0001	0.0000	−0.4697	0.4697	0.0065	0.0095	0.1456
C(2)	0.0003	0.0001	0.0000	0.0144	−0.0144	−0.0001	−0.0001	0.6965
C(3)	0.0003	0.0001	0.0000	0.0144	−0.0144	−0.0001	−0.0001	0.6965
$2p_y$ C(1)	0.5672	−0.5671	0.0000	−0.0008	−0.0005	0.0249	−0.0248	−0.0002
C(2)	0.0544	−0.1068	−0.4870	−0.0078	−0.0022	0.0137	0.4856	−0.0001
C(3)	0.1067	−0.0545	0.4869	0.0016	0.0085	−0.4857	−0.0134	0.0000
$2p_z$ C(1)	−0.3231	−0.3234	−0.1040	0.3186	0.3188	0.0018	−0.0091	0.0002
C(2)	0.6110	0.1118	−0.2954	−0.0103	−0.0060	0.0123	−0.2198	−0.0003
C(3)	0.1117	0.6109	−0.2954	−0.0053	−0.0027	−0.2201	0.0127	−0.0001
1s H(1)	−0.0042	−0.0044	0.0160	−0.0344	0.7125	0.0080	−0.0009	−0.0646
H(2)	−0.0042	−0.0045	0.0160	0.7124	−0.0344	−0.0022	−0.0161	0.0646
H(3)	−0.0442	0.0525	−0.0193	0.0133	−0.0008	0.0043	0.6905	0.0001
H(4)	0.0525	−0.0442	−0.0194	−0.0006	−0.0102	0.6905	0.0040	0.0001

[a] Atomic orbitals are listed vertically; LO's are labeled horizontally.

An interesting feature of the reliable predictions of hybridization (those where the bond index and local orbital values agree) is that considerable deviation from sp^3 (X_p = 75%) and sp^2 (X_p = 66.7%) hybridizations is predicted. Many of the deviations can be understood when it is recalled that hybridization is essentially a response of the atomic orbitals to the field due to the neighboring atoms in the molecule. True sp^3 or sp^2 hybrids would be expected only for atoms in strictly tetrahedral or trigonal fields. Consider a carbon atom in ethylene; presumably the neighboring carbon atom exerts a strong axial perturbation on an otherwise trigonal field. It should then be no surprise that the p character of the CC hybrids is shifted from the trigonal value (66.7%) toward the linear value (50.0%). The CH hybrids must compensate for this decrease in X_p, and consequently increase in p character.

The preceding argument helps to explain the predictions of X_p for the hydrocarbons. A restatement of it, known as the rule of Bent,[3] accounts for the variation in hybridization of carbon atoms in molecules containing heteroatoms. The rule states that s character is concentrated in the carbon hybrid directed toward the most electropositive substituent.[12] The tendency can be seen in the amines, alcohols, ethers, and carbonyl compounds. In the carboxylic acids, it would appear that the O'H group is less electronegative and/or more electron donating than the carbonyl oxygen. This suggestion is consistent with our chemical intuition and with the form of the local orbitals.

From the entries of Table III, it would be inferred that the carbonyl oxygen in a carboxylic acid is not so efficient at withdrawing charge from its carbon atom as is a carbonyl oxygen in an aldehyde. This conclusion is made plausible by an inspection of the valence-bond structures below. Resonance as shown withdraws charge from the carbon atom in the aldehyde, but not in the carboxyl compound.



Comparison with "Experimental" Hybridization from ^{13}CH Coupling Constants

It appears that qualitative trends in hybridization are described in a reasonable way by a local orbital analysis of CNDO wave functions and, where it can be relied on, by the bond index. The value of these analyses would be enhanced if we could place some faith in their quantitative validity. There is some reason to be skeptical of the accuracy of hybridization predicted by calculations employing the assumption of complete neglect of differential overlap. As Pople makes clear,[8] reconciliation of this assumption with the demand of transformational invariance requires that Coulomb integrals be dependent only on the principle quantum numbers of the orbitals involved. That is, Coulomb integrals containing p orbitals are not distinguished from Coulomb integrals containing s orbitals only.

The predictions of hybridization based on CNDO wave functions may be checked by comparison to results of analysis of wave functions obtained more rigorously. Such wave functions are becoming available[13] for polyatomic molecules, of interest here. It would be interesting to apply the methods discussed above for the prediction of hybridization to these more exact wave functions as a test of the quality of the semiempirical wave functions. However, in this report we shall compare the hybridizations deduced from CNDO wave functions with an experimental measure.

The constant $J(^{13}\text{CH})$, measuring the coupling between a carbon-13 nucleus and a proton directly bound to it, is linearly dependent on the s character of the carbon hybrid directed toward the proton, according to Juan and Gutowsky.[14] Certain approximations

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[12] Qualitative rationalizations for this rule invoking differences in the tightness of binding of s and p orbitals are reasonable, but the calculations we do make no explicit provision for these differences. The trends in hybridization found in this work, which are consistent with the predictions of Bent's rule, arise from the assumption that H_{ab} is proportional to S_{ab}, where H_{ab} is the off-diagonal matrix element of the one-electron part of the Hamiltonian, and S_{ab} is the corresponding element of the overlap matrix.

[13] W. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966), and many others; see A. Golebiewski and H. S. Taylor, *Ann. Rev. Phys. Chem.*, **18**, 353 (1967).

[14] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 37, 2198 (1962).

made in their theory demand that the perfect-pairing valence-bond structure be a useful description of the ground state of the molecule (at least in the region of the CH bond).[15] In other words, the ground-state function must be highly localizable. Since this is also the condition for the definition of hybridization, we restrict our attention to localizable systems.

The linear dependence of $J(^{13}CH)$ on the s character X_s $(=1 - X_p)$ allows us to compare the local orbital and bond index predictions of hybridization with an empirical estimate.[9] Figure 1[16] illustrates the comparison for CH bonds in a variety of molecules, indicating a substantial agreement among the three sets of values. The general agreement indicates that the CNDO wave function gives an adequate account of hybridization. One case of serious disagreement, the CH bond in formic acid, involves a localizable subsystem of a molecule possessing some delocalization. One of the atoms in the local bond also participates in the delocalization. It is interesting to note in this case where we may expect some discord between the theoretical estimates, the LO value is more consistent with experiment. Whether this is a general phenomenon is not discernible from the data available. A series of calculations on strained ring systems, which may be expected to show some delocalization, coupled with measurements of their $J(^{13}CH)$ values could answer this question.

Conclusion

The possibility of an essentially completely localized description of the charge distribution is the condition for an unambiguous definition of hybridization. Both methods for determination of p character in an individual hybrid reveal the presence of delocalization. The bond index must be subjected to a detailed analysis, while the less readily obtained local orbitals make the degree and range of the delocalization immediately apparent. Where localization is nearly complete, the two methods give indistinguishable estimates of the p character.

Approximate molecular orbital wave functions obtained with the complete neglect of differential overlap give an adequate account of hybridization. Calculations on a wide variety of molecules support the qualitative rule of Bent; they also agree with experimental estimates based on the magnitude of nuclear magnetic coupling between a carbon-13 nucleus and a directly bound proton. The qualitative and quantitative reliability of these MO predictions of hybridization allow the conclusion that the idea of hybridization is useful outside the context of a valence-bond description of the molecular charge distribution.

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Appendix: Mathematical Properties of the Bond Index

Consider the bond index $W_{ab} = P_{ab}^2$.

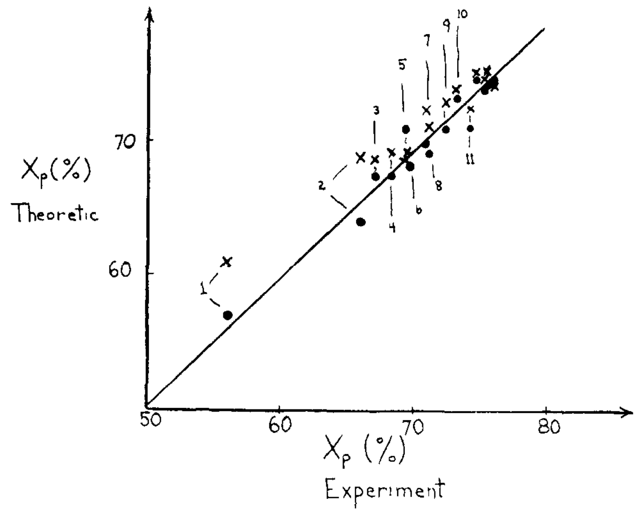

Figure 1. Comparison of experimental and theoretical predictions of the per cent p character, X_p, of the carbon hybrid in CH bonds. Experimental X is deduced from the nmr coupling constants $J(^{13}CH)$, ref 16 (see text). Circles represent local orbital values, crosses bond index values of X_p. The straight line would result from perfect agreement of the experimental and theoretical estimates of X_p. Labeled points are (1) formic acid,[16a] (2) acetaldehyde (aldehydic proton),[16a,b] (3) ethylenimine,[16c] (4) cyclopropane,[16a] (5) ethylene,[16a] (6) isobutylene,[16b] (7) trimethylene oxide (α-H),[16c] (8) fluoromethane,[16a] (9) methanol,[16a,b] (10) methylamine,[16a] (11) trimethylene oxide (β-H).[16a] Unlabeled points clustering about $X_p = 75$ are various methyl CH hybrids.

$$W_{ab} = 4\sum(ij)c_{ia}c_{ib}c_{ja}c_{jb} \tag{A1}$$

Here the sum over i and j spans the set of occupied molecular orbitals. We assume an orthogonalized basis set, so $\Sigma(b)c_{jb}c_{ib} = \delta_{ij}$; then if we sum W_{ab} over all atomic orbitals b, we find

$$\sum(b)W_{ab} = 4\sum(ij)\delta_{ij}c_{ja}c_{ia} = 4\sum(j)c_{ja}^2 = 2q_a \tag{A2}$$

The sum is proportional to the charge in orbital a, q_a. Let orbital a be placed on center A. If we restrict the sum in eq A2 to a subset V_B containing orbitals associated with atom B, the result W_{aB} may be considered the charge in orbital a which participates in an A–B bond.

$$W_{aB} = \sum(b \text{ in } V_B)W_{ab} \tag{A3}$$

W_{aB} can be expressed as a sum of two terms.

$$W_{aB} = 4\sum(b \text{ in } V_B)\left[\sum(i)c_{ia}^2c_{ib}^2 + 2\sum(i > j)c_{ia}c_{ja}c_{ib}c_{jb}\right] \tag{A4}$$

The second term is a measure of the product of charge densities in different MO's; the first is the square of the density in a single MO. For well-localized systems, the second term will be small relative to the first, and the first term will be dominated by the contribution from the local orbital which describes the A–B bond (call that local orbital k). Therefore, for a highly localized set of orbitals, $W_{aB} \simeq \Sigma(b \text{ in } V_B)c_{ka}^2c_{kb}^2$, and the bond index estimate of the p character X_p becomes

$$X_p \simeq \frac{[c_{kp_x}^2 + x_{kp_y}^2 + c_{kp_z}^2]4\sum(b \text{ in } V_B)c_{kb}^2}{[c_{ks}^2 + c_{kp_x}^2 + c_{kp_y}^2 + c_{kp_z}^2]4\sum(b \text{ in } V_B)c_{kb}^2}$$

which reduces to the local orbital expression in the text, eq 1.

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(15) M. Karplus, *J. Chem. Phys.*, **33**, 941 (1960).

(16) (a) N. Muller and D. Pritchard, *ibid.*, **31**, 768, 1471 (1959); N. Muller, *ibid.*, **36**, 359 (1962); (b) H. Dreeskamp and E. Sackmann, *Z. Phys. Chem.* (Frankfurt am Main), **34**, 273 (1962); (c) E. Lippert and H. Prigge, *Ber. Bunsenges. Phys. Chem.*, **67**, 415 (1963).