derivatives for analytical reasons and because of the occurrence of dihydrouracil in tRNA.[17–19] A similar transformation is involved in the well-known photohydration reaction of uracil,[20,21] which has important consequences for the functioning of nucleic acids.[22,23]

In addition to its synthetic use in nucleotide chemistry, we believe that sodium bisulfite should be of value as a reference mutagen. It is the first reagent to be described that can *specifically* convert one common, naturally occurring nucleic acid heterocycle to another. It should finally be noted that sodium bisulfite is a food additive and sulfur dioxide is an atmospheric pollutant. It now seems probable that these substances may constitute a genetic hazard to living organisms.

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Carbon–Carbon and Carbon–Hydrogen Bond Length–Bond Overlap Correlations

Sir:

The well-known environmental changes in single carbon–carbon bond lengths have been attributed to differences in hybridization of carbon atoms.[1] The bonds have been classified into sp^n–sp^m types (n, m being 1, 2, 3) and a rule is found[2] that carbon–carbon single bond distance decreases by 0.04 Å when one of the participating carbon atoms changes the hybridization type from sp^3 to sp^2, or sp^2 to sp. However, there is sufficient evidence in the literature to indicate that useful correlations may be obtained when the hybridization in molecules is not restricted to the special cases sp, sp^2, and sp^3. For example, it has been found that J-(^{13}C–H), assumed to depend mainly on the percentage of s character in the bonds,[3] of the bridgehead carbon atom of norbornane is much larger than that of the usual sp^3–sp^3 bond.[4] Similarly, the enhanced acidity and reduced reactivity of aryl positions adjacent to fused strained rings toward electrophilic substitution indicate that the atomic orbitals of the fused aryl carbon used to construct the strained ring have higher p character than the simple sp^2 hybrids suggest.[5] The theoretical approaches also suggest models which do not restrict the hybridization parameters (exponent n in sp^n) to integers. Thus the hybrids calculated by the maximum overlap approximation,[6] which are of the general sp^n (n = a noninteger) form, lead to correlations of bond energy,[7] chemical shift,[8] or spin–spin coupling (^{13}C–H)[9] with hybridization. Other theoretical approaches, like local orbital prediction of the hybridization based on the CNDO/2 MO wave functions, also lead to noninteger hybrid parameters.[10] On the other hand, an estimate of the s:p ratio from experimental bond lengths, following the idea that hybrid radius is a function of hybridization,[11] was made, and noninteger hybrid parameters were suggested.[12] All this indicates that the restriction of hybridization parameters to integers is neither justified nor useful in approximate descriptions of the bonding in molecules.

Here we considered various single C–C and C–H bonds and established a correlation between the bond lengths and corresponding bond overlaps based on hybrids with noninteger values of the exponent n, m. It is found that hybridization characterized by noninteger exponents obtained by the maximum overlap approximation can account for C–C and C–H bond length variations and be useful in predictions of the environmental changes of single C–C bonds in molecules for which the experimental data are not complete or available. Bond overlaps depend on the amount of electron density in the region between the atoms forming the bond and are expected, therefore, to be a useful bond index, especially for similar bonds, when bonded electrons are approximately equally bound to their own atoms, and there is no high polarity of bonds.[13,14] This is, for example, a justification for Coulson's well-known definition of bond orders,[15] and is implied in various semiempirical methods in which overlap or integrals proportional to overlap are allowed to depend on the bond length.[16,17]

Bond overlap for some 20 hydrocarbons for which experimental bond lengths are known have been evaluated. Hybrid orbitals characterizing the bonds have been obtained by the method of maximum overlap. The method of calculation has been previously described in detail.[6] The computations were not directly based on the variational theorem in which an energy expression is minimized with respect to a set of parameters. Instead, a basis set consisting of local hybrid orbitals was assumed, and parameters specifying the hybridization were varied to maximize the total overlap. Briefly, in the method we search for optimal parameters a_i, b_i, of individual hybrids ψ_i =

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$a_i(s) + b_i(p_i) \equiv sp^n$, $n = (b_i/a_i)^2$, which maximize the sum

$$S = k_{CH}\sum S_{CH} + k_{CC}\sum S_{CC} \quad (1)$$

where S_{CH} and S_{CC} are overlaps of C–H and C–C bonds, respectively. The weighting factors $k_{CH} = 135.86$ and $k_{CC} = 121.17$ take into account the fact that the same overlap in different bonds corresponds to different bond energies. The coefficients a_i, b_i, are subject to the orthogonality relationship: $a_ia_j + b_ib_j \cos \theta_{ij} = \delta_{ij}$, where θ_{ij} is angle between the directions of hybrids ψ_i and ψ_j centered at the same atom. By systematic variation of independent parameters for an assumed initial hybrid composition the maximum bond overlaps and the best hybridizations were found. For atomic functions, those suggested by Clementi[18] have been adopted, assuming the experimental bond lengths. The necessary basic overlap integrals are taken from the available tables.[19] During the calculations the bond angles were allowed to follow the directions of hybrids freely, except in cyclic systems where necessarily bent bonds appear. The calculated C–C bond overlaps, experimental C–C bond lengths, and the corresponding maximum overlap hybrids associated with the bond for a selection of molecules are listed in Table I. The following linear relationship between C–C bond lengths and bond overlap is found.

Table I. Calculated C–C Bond Overlaps and Bond Lengths According to the Maximum Overlap Approximation

Molecule	Overlap	Exptl bond length, Å	Hybrids	Calcd bond length, Å
Diacetylene	0.7889	1.379	$sp^{1.15}$–$sp^{1.15}$	1.378
Vinylacetylene	0.7370	1.448	$sp^{1.20}$–$sp^{2.23}$	1.439
Methylacetylene	0.7184	1.459	$sp^{1.18}$–$sp^{3.01}$	1.460
Cyclooctatetraene	0.7139	1.462	$sp^{2.10}$–$sp^{2.10}$	1.466
1,3-Butadiene	0.7062	1.483	$sp^{2.23}$–$sp^{2.23}$	1.475
Diphenyl	0.7015	1.492	$sp^{2.19}$–$sp^{2.19}$	1.480
Propylene	0.6847	1.501	$sp^{2.18}$–$sp^{3.01}$	1.500
Isobutylene	0.6775	1.507	$sp^{2.22}$–$sp^{3.22}$	1.508
Isobutane	0.6566	1.525	$sp^{3.00}$–$sp^{3.15}$	1.532
Neopentane	0.6514	1.540	$sp^{3.00}$–$sp^{3.22}$	1.538
Ethane	0.6476	1.543	$sp^{3.20}$–$sp^{3.20}$	1.543

$$\text{C–C (Å)} = -1.166S_{CC} + 2.298 \quad (2)$$

This relationship is used to reproduce the bond lengths in the last column of Table I. A similar relationship was found for C–H bond lengths.

$$\text{C–H (Å)} = -0.869S_{CH} + 1.726 \quad (3)$$

A selection of molecules on which the evaluation of the above linear relationship between C–H bond overlap and bond length was based together with the corresponding values of C–H bond overlaps, experimental C–H bond lengths used, and the maximum overlap hybrids found are listed in Table II. The last column gives the calculated bond lengths. The bond length–bond overlap correlations can be used in an iterative procedure and applied to systems for which the variations in C–C bonds are not known. One starts by assuming a standard value for C–C and C–H bond lengths. Then by calculating the maximum overlap hybrids the new bond lengths are deduced from the corresponding bond overlaps, and the process is repeated until the input and the output bond lengths are equal. For example, if we assume deliberately long C–C and C–H bond lengths in diacetylene (1.54 and 1.08 Å, respectively) after eight iterative steps they are reduced to the expected values: 1.38 Å for an sp–sp single C–C bond and 1.065 Å for an sp C–H bond. This is in full agreement with the experimental values of Craine and Thompson,[20] not used in obtaining the correlations. The convergence could be considerably improved if one starts with bond lengths which are close to the values corresponding to various sp^n–sp^m (n, m = 1, 2, 3) types.

Table II. Calculated C–H Bond Overlaps and Bond Lengths According to the Maximum Overlap Approximation

Molecule	Overlap	Exptl bond length, Å	Hybrids	Calcd bond length, Å
Acetylene	0.7686	1.059	$sp^{1.30}$	1.058
Benzene	0.7412	1.084	$sp^{2.18}$	1.082
Ethylene	0.7403	1.085	$sp^{2.17}$	1.083
Cyclopropane	0.7328	1.089	$sp^{2.50}$	1.089
Cyclooctatetraene	0.7356	1.090	$sp^{2.32}$	1.087
Cyclobutane	0.7287	1.092	$sp^{2.65}$	1.093
Ethane	0.7196	1.102	$sp^{2.94}$	1.101

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Synthetic Studies on Insect Hormones. IX.[1,2] Stereoselective Total Synthesis of a Racemic Boll Weevil Pheromone

Sir:

Recent isolation[3] of the sex attractant of the male boll weevil (*Anthonomus grandis* Boheman) followed a most difficult phase of insect pheromone research[4] and allowed structure elucidation[4] of the essential components as the monoterpenes **1**, **2**, and **3** or **4**, which have recently been synthesized by nonselective routes.[5]

We wish to report the first stereoselective synthesis of racemic **1** which now defines unambiguously the stereochemistry of the natural product and provides a practical route to material for experimental evaluation in insect control.

Since the stereochemistry of the pheromone **1** was unknown at the outset, it was planned to derive the iso-

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(1) Part VIII: see J. B. Siddall, M. Biskup, and J. H. Fried, *J. Amer. Chem. Soc.*, **91**, 1853 (1969).

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