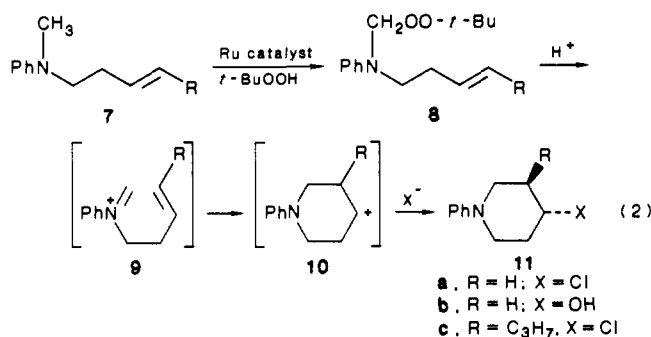


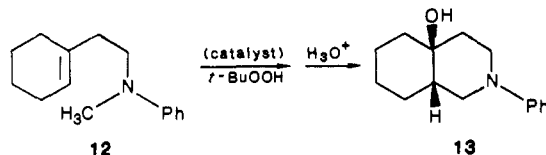
would give Ru(II)OOBu-*t*, which undergoes cleavage of the O—O bond to give Ru(IV)=O.¹² Tertiary amines would undergo oxidation with Ru(IV)=O species to give **2** similar to the formation of R¹R²NCH₂OH in the P-450 induced demethylation reactions.¹⁰

Selective N-demethylation of tertiary methylamines is performed by the present ruthenium-catalyzed oxidation and subsequent hydrolysis with an aqueous HCl solution (eq 1). This is the first synthetically practical method for the N-demethylation of tertiary methylamines although few catalytic^{2,3} and stoichiometric reactions¹³ have been reported. The representative results of the N-demethylation are listed in Table II. Methyl groups are removed chemoselectively in the presence of various alkyl groups.

The present reaction provides a novel, biomimetic method¹⁴ for the construction of piperidine skeletons from *N*-methylhomallylamine **7** via olefin-iminium ion cyclization reactions (eq 2).



The reported olefin-iminium ion cyclizations are limited to the reactions of the iminium ions which are derived from the condensation of primary or secondary amines with carbonyl compounds,¹⁵ the reaction of imines with acetyl chloride,¹⁶ and the protonolysis of reduced cyclic imides.¹⁷ The ruthenium-catalyzed oxidation of *N*-methyl-*N*-(3-butenyl)aniline (**7a**) gave the peroxide **8a** (87%), which was converted to 1-phenyl-4-chloropiperidine (**11a**) (77%) upon treatment with a 2 N HCl solution at room temperature. Similar treatment of **7a** with a 0.4 N aqueous CF₃CO₂H solution gave 1-phenyl-4-hydroxypiperidine (**11b**) (50%). Cyclization of the peroxides **8** bearing a substituted 3-butenyl group gave *trans*-3,4-disubstituted piperidines stereoselectively. Thus, *trans*-1-phenyl-3-propyl-4-chloropiperidine (**11c**) has been obtained stereoselectively from *N*-methyl-*N*-(3-heptenyl)aniline (**7c**) (oxidation 76%; cyclization 55%). The reaction of cyclic amines gives only *cis* fused bicyclic amines. Thus, *cis*-4a-hydroxy-2-phenyldecahydroisoquinoline (**13**) was obtained from



N-methyl-*N*-2-(1-cyclohexenyl)ethylaniline (**12**) (85%; 44%) selectively upon treatment of the corresponding peroxide with an

aqueous CF₃CO₂H solution. These cyclizations can be rationalized by assuming the formation of iminium ion **9** by protonation of **8** and subsequent elimination of *t*-BuOOH. Nucleophilic attack of an alkene gives carbonium ion **10**, which is trapped by nucleophile X⁻ from the less hindered side. It is noteworthy that recovered *t*-BuOOH can be used again.

Work is in progress to provide definitive mechanistic information and to apply our method to other systems.

Supplementary Material Available: Spectral data of the product peroxides, **11** and **13** (4 pages). Ordering information is given on any current masthead page.

Generalized Valence Bond Description of Multiple Bonds

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Recently, we have reported on a number of generalized valence bond (GVB) calculations¹⁻⁴ for multiple bonds which have employed the standard strongly orthogonal and perfect-pairing (SOPP) approximations,⁵ i.e., the GVB-PP method. In these calculations for CO₂, C₂F₂, benzene, and CO, we have found that the usual description of multiple bonds in terms of σ and π bonds is energetically less favorable than a description in terms of "bent bonds".

The physical significance of the results of C₂F₂ has been challenged^{6,7} however on two grounds. The first criticism is that conclusions based upon the results of GVB-PP calculations may not be valid because the restrictive nature of the SOPP approximation to the full GVB wave function,⁸ the most general wave function interpretable within an independent particle (IP) picture, may produce artifacts. A second criticism is that the valence bond approach itself is too restrictive and that a more general wave function may demonstrate that the σ, π description is the "correct" description of multiple bonds.

These are certainly important points which must be addressed before the validity and utility of the "bent bond" (or Ω -bond) description can be fully assessed. In order to resolve the first point, we carry out the *first* full GVB calculations for multiple bonds (i.e., IP calculations which do not invoke either the perfect pairing or strong orthogonality restrictions). We deal with the second criticism immediately, because it is the easier to examine.

For a wave function more general than the valence bond wave functions above, the question of whether the "bent bond (Ω -bond)" or the σ, π bond description is better is not even meaningful. GVB-CI calculations⁶ on C₅F₄ or full valence CI (FVCI) calculations⁷ on C₂F₂ cannot address this question because the wave functions cannot be interpreted unambiguously in terms of either

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Table I. Calculated Energies for C₂F₄ Using Single-Particle Interpretable Wave Functions^a

method	total energies (hartrees)		$E_{\Omega} - E_{\sigma,\pi}^b$ (eV)	ΔE_{Ω}^c (eV)
	σ,π bonds	bent bonds		
HF	-473.488 80	-473.488 80	0.000	0.000
SOPP	-473.528 70	-473.528 64	+0.002	-1.084
PP ^d	-473.528 70	-473.539 19	-0.285	-1.371
GVB	-473.533 84	-473.539 40	-0.145	-1.377

^aVDZD basis for C and VDZ basis for F (ref 6). ^bEnergetic favorability of bent bonds (negative values). ^cEnergy lowering of theory with respect to HF result for the bent bond description. ^dThe PP approximation (i.e., no SO restrictions) for the case of the σ,π description is identical with SOPP because the σ and π orbitals are orthogonal by symmetry.

a σ,π or Ω bond model, but only as complicated combinations of both descriptions. The best one can hope for in this regard is that a consensus on a criterion for measuring the weights of the two descriptions in the general wave function be adopted. If for example the overlap of Φ_{Ω} and $\Phi_{\sigma,\pi}$ with the more general wave function Ψ_G is used as the criterion, one would have a measure of the more appropriate bonding model.

With this situation for general wave functions, it is fair to ask why one should bother with attempting a simple description of the bonding. Our reasons for pursuing the GVB description of multiple bonds, even though it clearly results in an inferior total energy with respect to more general wave functions, are that (1) simple physical models traditionally have provided insight and concepts useful in understanding more complex problems; (2) the GVB model represents a simple model for understanding electron correlation; (3) it provides the most general "independent particle interpretation" possible (i.e., the most general wave function which has each spatial orbital occupied by a single electron); and hence (4) the question of whether σ,π or bent bonds are more appropriate is well-posed and meaningful; and (5) no full GVB calculations for multiple bonds have been published, and hence it is of interest to investigate the consequences of this aspect of the GVB model.

To investigate the consequences of the GVB model with respect to the description of multiple bonds, the answer in the general case cannot be deduced analytically. It is necessary to carry out a series of calculations on representative molecules and find if there is a trend which might be argued to be characteristic of the generic situation. We have obtained results for about 15 molecules in our attempt to assess the GVB model of multiple bonds.⁹ These results present a consistent picture and will be presented in detail elsewhere.^{10,11} In the present contribution, we focus on the GVB results for the C=C double bond in tetrafluoroethylene, as this molecule has been the subject of some speculation in a recent communication.⁶

The form of the single particle interpretable wave function used in our calculations for C₂F₄ is given by

$$\Phi = \det \{[\text{core}] \varphi_{1a} \varphi_{1b} \varphi_{2a} \varphi_{2b} \Theta\} \quad (1)$$

where {core} describes a set of doubly occupied orbitals not relevant to the active space, and the remainder describes the singly occupied spatial orbitals φ_{μ} , along with a singlet four-electron spin eigenfunction Θ , associated with the multiple bond. This form of the

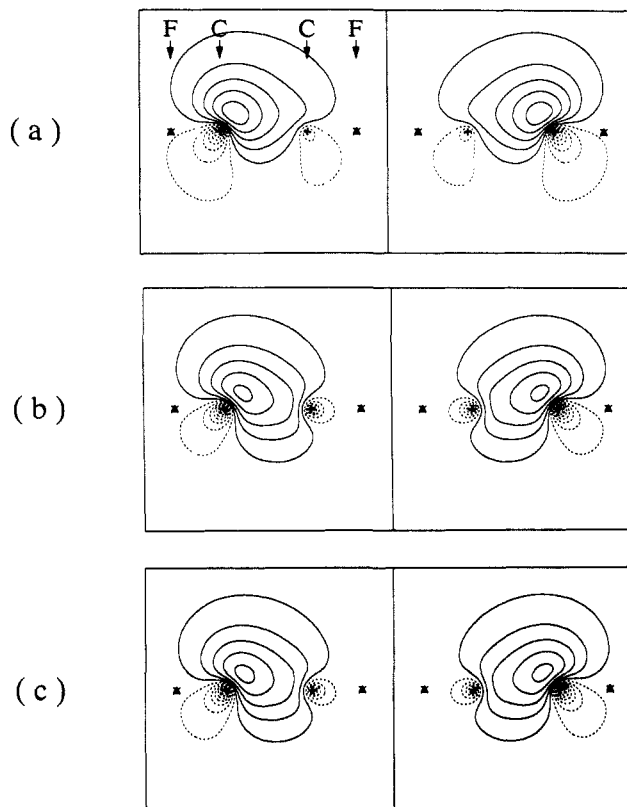


Figure 1. One of the two equivalent bent bonds for the C₂F₄ molecule. Each pair of orbitals forms a bond and was obtained on the basis of the following methods: (a) the GVB-PP method (with strong orthogonality and perfect-pairing restrictions); (b) PP method (with no strong orthogonality restriction but with the perfect pairing restriction); (c) GVB method (no SO or PP restrictions).

wave function can be rigorously interpreted within the bonding models.

Table I presents the total energies of the calculations using eq 1 when (1) φ_{μ} and Θ are simultaneously variationally optimized, giving the full GVB wave function; (2) Θ is restricted to the PP form $\Theta_{pp} = 1/2(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$; (3) additionally, strong orthogonality of orbitals in different pairs is enforced (SOPP); and (4) the orbitals with each pair are forced to take the same form yielding the HF result. The GVB-PP method (SOPP) favors the σ,π description by 0.002 eV, but the full GVB result clearly favors the symmetric bent bond description.¹² This appears to be characteristic of many cases of multiple bonds.^{9,10} The orbitals of the bent bonds for the SOPP, PP, and GVB approximations are shown in Figure 1.

In conclusion, we have reported the first full GVB results for a double bond (i.e., no strong orthogonality or perfect-pairing restrictions) with C₂F₄ as an example. The GVB description of the double bond in this molecule is *not* the traditional picture of σ and π bonds but rather a representation in terms of two bent bonds.

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(11) An important contribution to the understanding of the GVB model of multiple bonds was made by Palke (Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543) for the case of the ethylene molecule. In this work the strong orthogonality restriction was removed (the perfect-pairing restriction was still invoked however), and it was discovered that the bent-bond description was lower in energy than the σ,π description. This is just the reverse of the situation found when the usual strong orthogonality assumption is made. However, the fact that the perfect-pairing restriction was employed leaves open the possibility that the full GVB model might give a σ,π description. Our results^{9,10} for the double bond of the ethylene molecule with the full GVB model confirm the results of the Palke and suggest that the perfect-pairing restriction is not as important a limitation to the wave function as the strong orthogonality restriction (at the equilibrium internuclear separation).

(12) Previous GVB-PP calculations for C₂F₄ (ref 6) using a different polarization function for C ($\zeta^d = 0.64$ vs 0.75 in our calculations) find the symmetric bent bond description to be lower in energy than the σ,π description by 0.002 eV. The skewed σ,π description of ref 6, although found to be 0.004 eV lower in energy than the bent bond description, cannot be considered a legitimate approximation to the ground-state wave function as it does not have the correct symmetry. Furthermore, we find the overlap of the GVB-CI wave functions of ref 6 with our GVB (bent bond) wave function to be greater than with our GVB (σ,π) wave function. If one accepts the overlap criterion as a measure of the appropriateness of the bonding description for a general wave function, then the GVB-CI wave function is better described by bent bonds. This is contrary to the conclusions of ref 6.