sets were contracted using the Raffenetti scheme in a similar way as for the first-row metals. For the second-row metals, however, the core orbitals 4s and 4p have to be described by a double-ζ basis to reproduce the relativistic effects,[25] leading to a [7s, 6p, 4d] contraction. For palladium one extra contracted s function and one extra contracted p function was added in the 3s and 3p regions, respectively, leading to a [8s, 7p, 4d] contraction. In Table VI the splittings between the lowest atomic states of the metals are given, calculated at the Hartree–Fock level. It can be seen that the basis sets used here give results close to the Hartree–Fock limit. For carbon the primitive (9s, 5p) basis by Huzinaga[26] was used, contracted according to the Raffenetti scheme to [3s, 2p]. In some calculations one d function with exponent 0.63 was added on carbon. For the active hydrogen the primitive (5s) basis from ref 26 was used, augmented with one p function with exponent 0.8 and contracted to [3s, 1p]. The inactive methyl hydrogens were described by the (4s) basis from ref 26 contracted to [2s] and with the exponents scaled by a factor 1.2.

In the large basis set calculations a primitive (20s, 15p, 10d, 6f) basis was used for nickel,[27] ANO contracted to [7s, 6p, 4d, 2f]. This basis set gives a nonrelativistic splitting between the ^{3}D(d^{9}s) and the ^{3}F(d^8 s^2) states of the nickel atom of −0.11 eV, correlating the 10 valence electrons in a one-reference scheme. It turned out that the ANO contracted basis set on nickel did not give reasonable relativistic energies, and the relativistic contributions to the energies for the nickel reactions were therefore taken from the calculations using the standard basis set. The relativistic effect on the ^{3}D to ^{3}F splitting of the nickel atom is −0.26 eV using the standard basis set, yielding an estimated splitting for the large basis of −0.37 eV, compared to the experimental value of 0.03 eV. For palladium the primitive Huzinaga basis[24] was extended by replacing the four outermost d exponents by five and by adding four f functions, yielding a (17s, 13p, 10d, 4f) basis. The d and f functions were ANO contracted giving a [8s, 7p, 5d, 2f] contracted basis. This basis set gives a splitting between the ^{1}S(d^{10}) and the ^{3}D(d^{9}s) states of 0.93 eV including relativistic effects and valence correlation, to be compared to the experimental value of 0.95 eV. For carbon a primitive (13s, 8p, 6d) basis[28] was used, ANO contracted to [4s, 3p, 2d]. For the active hydrogen a primitive (7s, 4p) basis contracted to [4s, 3p][29] was used. The inactive methyl hydrogens were described by the [3s, 1p] contracted basis used for the active hydrogen in the standard basis set described above.

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Valence Bonds in the Main Group Elements. Generalized Valence Bond Description

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Abstract: The generalized valence bond (GVB) theory provides an ideal framework to test ideas regarding bonding in hypervalent molecules as it provides the *most general* orbital picture and at the same time it provides *unique orbitals*. However, it is very difficult to implement computationally and as a consequence the results presented here employ the usual strong orthogonality and perfect-pairing (SOPP) restrictions. Nonetheless the method is a substantial improvement beyond Hartree–Fock theory and provides a new perspective on back-bonding, participation of d-orbitals, multiple bonds, and the validity of the Octet rule. The ONF$_3$ and OPF$_3$ molecules are studied and the NO bond in the former is found to be composed of a single bond and *three back-bonds*, while the OP bond of the latter is a *triple bond*. Some general deductions regarding the nature of the bonding description in the full GVB method are made, leading to the qualitative scheme for discussing bonding which is applied to several examples.

Introduction

Much of the theoretical understanding of the chemical bond, both qualitative and quantitative, is based on the use of a single set of valence s, p, and d atomic orbitals at each atomic site in a molecule.[1] The concepts of π-bonds and δ-bonds arise from considering the interaction of atomic p or d orbitals, respectively, on adjoining atoms. The concept of hybrid orbitals makes use of linear combinations among a single set of valence atomic s, p, and d orbitals at a given nuclear site. The *linear combination of atomic orbitals* (LCAO) approximation forms the basis of modern computational quantum chemistry, whether the approach is semiempirical molecular orbital theory,[2] ab initio molecular orbital theory,[3] ab initio valence bond theory,[4] or more general approaches such as configuration interaction (CI) or multiconfiguration self consistent field (MCSCF).[5] Even in the ab initio

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calculations where basis sets beyond a minimum basis set (MBS) are employed, the additional functions are frequently considered to provide radial flexibility to the MBS s and p orbitals and allow for polarization of these orbitals.

In spite of the widespread acceptance of this simple atomic orbital perspective and the LCAO approximation, it is worthwhile to recall that for general molecular and solid-state systems there are no fundamental theoretical reasons to suggest one should focus so exclusively on this particular approach.[6] In fact the restriction to atomic orbitals may implicitly carry with it a restriction in concepts available for describing the chemical bond. For example, in the case of hypervalent molecules (those that do not conform to the Octet rule) the usual molecular orbital and valence bond approaches based on simple atomic orbital arguments have not been entirely successful in describing the bonding and structure. In particular, the concepts of $p\pi$–$d\pi$ bonding and dsp^3 and d^2sp^3 hybrids as models for the structure and bonding of these molecules are now known to be inadequate.[7,8]

On the other hand, the many successes of the atomic orbital and hybrid orbital concepts speak favorably of their ability to capture a significant measure of physical content within an orbital approximation to electronic structure. Hence, it would seem of some interest to explore computationally the limits of orbital concepts for hypervalent molecules.

However, this objective has been handicapped somewhat because the computational studies of hypervalent molecules used to judge the efficacy of proposed bonding concepts have employed molecular orbital methods almost universally.[7-9] A notable exception is the early contribution of Hay.[10] Molecular orbital theory, as is well-known, provides an orbital interpretational scheme because of its independent particle nature. Nonetheless it is *not* the most general independent particle model (IPM), and furthermore because the Hartree–Fock wave function is a single Slater determinant, the orbitals are not unique. As discussed over 20 years ago,[11] the most general independent particle model takes the form of a generalization of classical valence bond theory *and* provides a *unique* set of orbitals with which to interpret the bonding. In this and other recent work, the nature of bonding in hypervalent molecules has been explored within this valence bond framework.[12]

A general *N*-electron wave function may always be expressed as a resonating valence bond (RVB) expansion given by

$$\psi_{\mathrm{RVB}} = \sum_r c_r \mathcal{A}[\prod_i^N (\varphi_i^r)\Theta_r] \tag{1}$$

where $\mathcal{A}$ is the antisymmetrization operator, r is the index over resonance structures, c_r is the coefficient for the rth resonance structure, φ_i^r is the ith single-particle orbital of the rth resonance structure, and Θ_r is the spin function for the rth resonance structure. When the wave function above can be approximated by a single term (i.e., a single valence bond structure) and the optimal forms of the single-particle functions and the spin coupling are determined variationally, one arrives at the most general form of the *independent particle model*. This electronic wave function for a system has come to be called the generalized valence bond (GVB) wave function.[11] It can be written as

$$\Phi^{\mathrm{GVB}} = \mathcal{A}[\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\varphi_3(\mathbf{r}_3)\varphi_4(\mathbf{r}_4)...\varphi_N(\mathbf{r}_N)\Theta(\sigma_1,\sigma_2,\sigma_3,\sigma_4...\sigma_N)] \tag{2}$$

where the spatial functions $\varphi_i(\mathbf{r})$ describe the spatial probability amplitude of single electrons and the spin function Θ of the spin coordinates σ_i is of the most general form which guarantees a well-defined spin symmetry (i.e., Φ^{GVB} is an eigenfunction of the $\mathbf{S}^2$ and $\mathbf{S}_z$ operators). In fact, very few calculations have been performed which employ this general form. Most calculations have invoked two simplifying assumptions: the strong orthogonality (SO) approximation and the perfect pairing (PP) approximation. The perfect pairing approximation assumes the molecule can be described by a set of generalized Heitler–London like valence bonds, where pairs of φ_i are singlet coupled into bonds.[4] The strong orthogonality approximation assumes that the generalized Heitler–London pairs are mutually orthogonal, although the functions within a pair are overlapping.[4c] These approximations greatly simplify the calculations—but they may also introduce artifacts into the concepts derived from such calculations.

Recently it has been demonstrated[13] that the strongly orthogonal perfect pairing (SOPP) version of the GVB model leads to a different description of multiple bonds than the full GVB model. In particular, the full GVB model leads to Ω-bonds (bent multiple bonds) for double and triple bonds in molecules, whereas the SOPP approximation usually leads to σ,π-bonds. There are, however, some important cases[14] where the SOPP approximation also leads to the Ω-bond description found for the full GVB model. These results are important for two reasons: first, they show that approximations to the independent particle model (IPM) may lead to different conclusions and concepts than the full implementation of the IPM, and second, the consequences of full IPM calculations can suggest new avenues of investigation.

Here the question is explored: can a more accurate independent particle model (GVB with SOPP restrictions) than the Hartree–Fock molecular orbital (HF–MO) method give different conclusions regarding bonding in hypervalent molecules? For the molecules treated here the answer is affirmative and the bonding description contrasts rather dramatically with the recent molecular orbital study of Reed and Schleyer.[9e] In the discussion section below, the question of how the description obtained here might be altered by the full implementation of GVB (the most general IPM) is addressed.

Computational Results for ONF_3, ONH_3, and OPF_3

ONF_3. The GVB method with the SOPP approximations is employed to obtain the numerical results presented.[4a] In Figure 1 contour plots of the calculated orbitals of ONF_3 are shown. At the top of the figure there is a schematic of the bonding in the molecule with orbitals labeled to correspond to the contour plots

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(6) (a) From a mathematical viewpoint, one could argue that if the atomic orbital (AO) basis set at each site is large enough that the basis set is saturated, then the AO basis is as good as any other basis one might propose. However, in practical applications this situation never occurs and it is therefore meaningful to inquire about the best basis set for a fixed number of basis functions. Furthermore, the simple bonding concepts used to describe computational results are derived from very restricted AO expansions (usually minimum basis sets). (b) In solid-state applications based on band theory, plane wave basis sets, augmented plane wave basis sets, and mixed atomic orbital/plane wave basis sets have been used for years as alternatives to the LCAO method.

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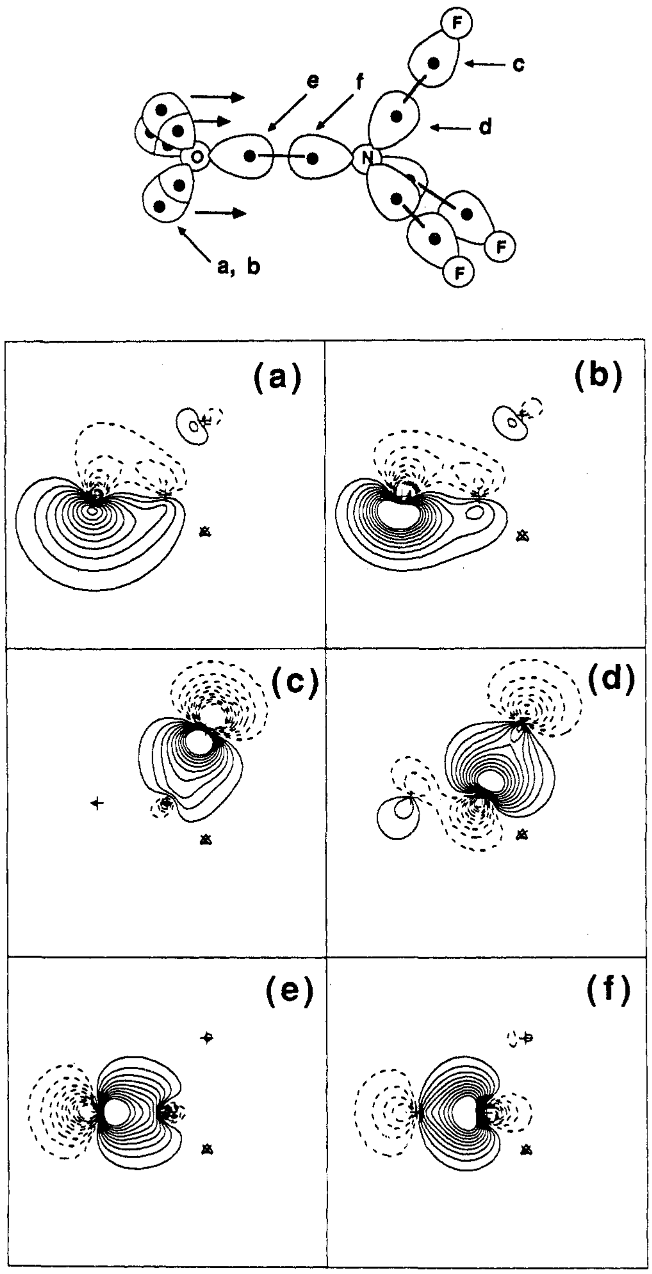

Figure 1. GVB orbitals obtained by using the SOPP approximations for the ONF_3 molecule. The labels on the schematic at the top correspond to the contour plots of the orbitals below. Panels a and b show one of the three equivalent lone pairs on the oxygen atom (note the back-bonding to nitrogen). Panels c and d show one of the N–F bonds, and panels e and f show the oxygen-nitrogen bond.

in the panels below. Panels a and b show the orbitals of one of the three equivalent lone pairs on the oxygen atom. Note that they are significantly polarized toward the nitrogen atom, yielding three equivalent back-bonds from O to N. Together these amount to a "second bond" between O and N. In panels c and d one of the three equivalent N–F bonds is shown, with panel d exhibiting a very strong polarization of one of the N orbitals toward the F atom to which it is bonded. Thus the fluorine atoms polarize the three orbitals on N toward themselves, leaving an unscreened positive charge on the N atom. The lone pair orbitals on the oxygen atom respond by polarizing onto the N atom so as to screen the induced positive charge. Note how they avoid the orbitals involved in N–F bonds while performing the screening. Although the orbitals are very similar to tetrahedral hybrids qualitatively, quantitatively they are rather different. In this particular example, only the familiar VDZ basis is used on N, O, and F with a single set of d functions on N.[15] The calculated NO bond length is 1.20 Å as compared to the experimental value of 1.16 Å.[16]

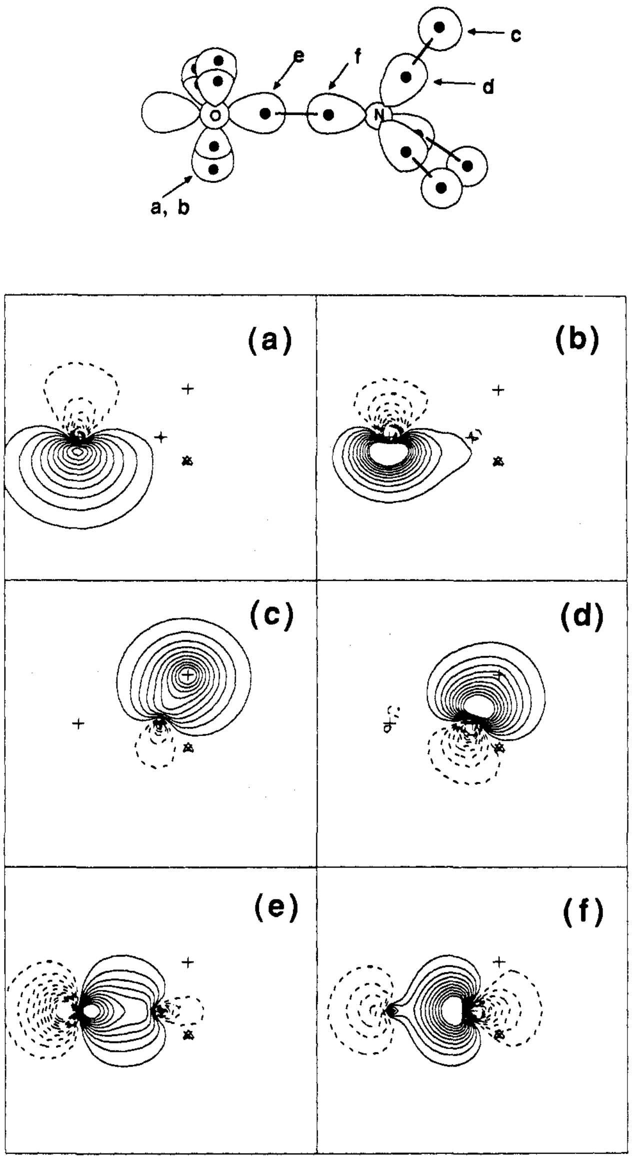

Figure 2. GVB orbitals obtained by using the SOPP approximations for the ONH_3 molecule. The labels on the schematic at the top correspond to the contour plots of the orbitals below. Panels a and b show one of the three equivalent lone pairs on the oxygen atom (note the difference in back-bonding to nitrogen as compared to the previous figure). Panels c and d show one of the N–H bonds, and panels e and f show the oxygen-nitrogen bond.

ONH_3. In order to check the effect of the F atom's electronegativity in allowing the oxygen lone pairs to participate in back-bonding to nitrogen, it is instructive to carry out a calculation on the molecule H_3NO with the same geometry as the F_3NO molecule. In fact, a molecule with this combination of atoms and geometry does not exist—hence this calculation is strictly a theoretical experiment to gain some insight. In Figure 2 the contour plots of the orbitals of H_3NO are shown. Panels a and b show one of the three equivalent lone pairs on the oxygen atom. Note there is relatively little interaction with the N atom in comparison to the situation for F_3NO. Panels c and d show one of the three equivalent N–H bonds. The hydrogen causes little polarization of the N orbitals as compared to the case in the previous figure. Finally, panels e and f describe the O–N bond. The schematic at the top of the figure summarizes the bonding.

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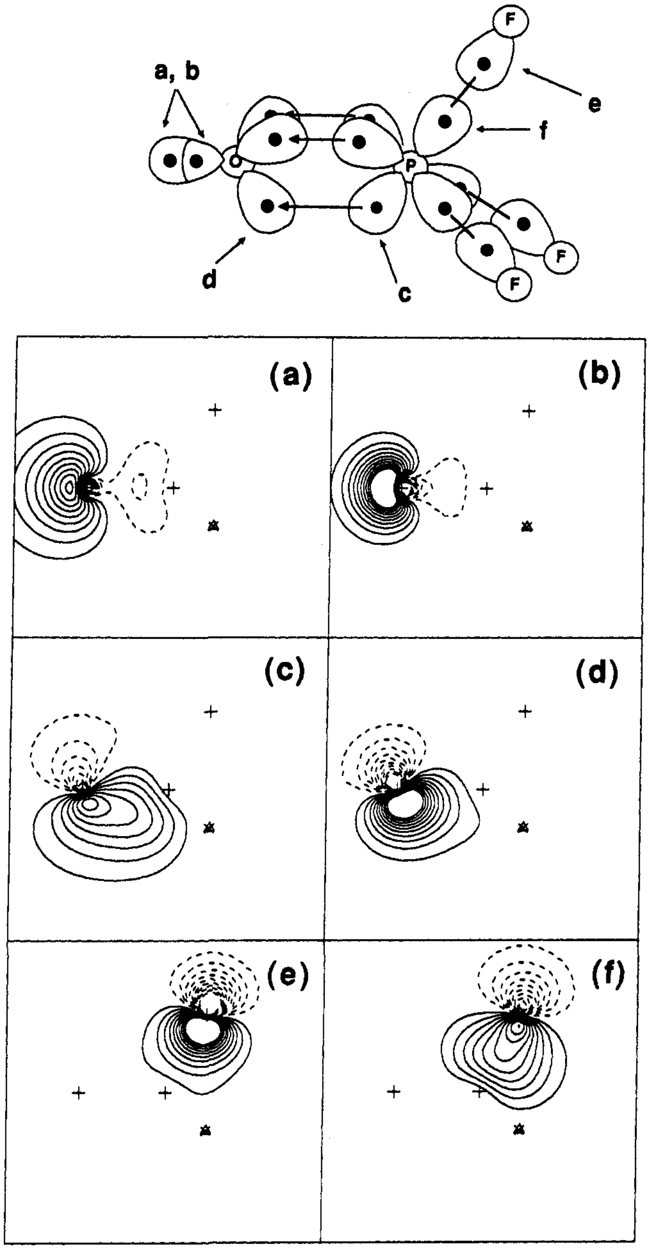

Figure 3. GVB orbitals obtained by using the SOPP approximations for the OPF_3 molecule. The labels on the schematic at the top correspond to the contour plots of the orbitals below. Panels a and b show the oxygen lone pair; panels c and d show one of the three equivalent oxygen–phosphorus bonds; panels e and f show one of the three equivalent phosphorus–fluorine bonds.

In contrast to the situation for F_3NO, here the lone pairs on the O atom appear to make little contribution to the bonding—there is essentially no back-bonding in the H_3NO case. This is supported by the results of calculating the equilibrium N–O distance for this assumed geometry of H_3NO, which turns out to be 1.42 Å. This is very similar to known N–O *single* bond lengths for other molecules and is over 0.2 Å longer than the N–O bond length in F_3NO. The polarization of the N orbitals by the F atoms is obviously a crucial feature in allowing back-bonding of the O lone pairs. Without the back-bonding the molecule is very much $O^-N^+H_3$, which has a lower energy configuration if a proton moves over to the oxygen ion to form the stable hydroxylamine molecule.

OPF_3. It is instructive to compare the bonding in the OPF_3 molecule to that in ONF_3 in order to assess the differences between first- and second-row atoms. The results for OPF_3 are shown in Figure 3. The schematic diagram at the top of the figure summarizes the bonding. It is clear that there is a significant difference between the ON bonding in ONF_3 and the OP bonding in OPF_3.

In the OPF_3 case the oxygen atom forms a triple bond to the phosphorus atom and the latter assumes a pseudooctahedral distribution of orbitals about its core. As can be seen from Figure 3, the orbitals about phosphorus are rather strongly polarized toward the surrounding atoms. For the PF bonds the situation is completely analogous to that for the NF bonds of ONF_3, cf. panels e and f in Figure 3 and panels c and d in Figure 1. In the calculation a similar level of theoretical treatment to that of ONF_3 was employed: valence double-ζ basis for O and F; effective potential[17] for P with valence DZ basis and a single set of d functions. The calculated PO bond length is 1.47 Å as compared to the experimental value[18] of 1.44 Å.

For the PO bond, a formal triple bond is obtained. Contour plots of the oxygen lone-pair orbitals are shown in panels a and b and contour plots of one of the three equivalent phosphorus–oxygen bonds are shown in panels c and d. This difference in the bonding for ONF_3 and OPF_3 illustrates an important point regarding first- and second-row atoms. The nitrogen atom in ONF_3 prefers to form *four primary bonds* (oriented in roughly tetrahedral directions). The ON bonding consists of a primary bond between oxygen and nitrogen and three secondary bonds to nitrogen (the back bonds). However, the phosphorus atom in OPF_3 prefers to form *six primary bonds* (oriented in roughly octahedral directions). The ability of phosphorus to form six primary bonds is a consequence of the greater core size in the second row which is also the source of hypervalency (e.g., PF_5 and PF_6^- are known to exist, NF_5 and NF_6^- are not known).

Discussion

Comparison with Previous Work. The bonding results just described for F_3NO and F_3PO from generalized valence bond calculations contrast rather markedly with the bonding descriptions recently deduced from molecular orbital theory.[9e] It was concluded that the bonding in F_3CO^- (isoelectronic to F_3NO), F_3PO, SO_4^{2-}, and SO_2Cl_2, among others, was quite analogous.[9e] Namely, about the central atom there are four "partially ionic σ-bonds and partial π-bonding through strong $n \rightarrow \sigma^*$ negative hyperconjugation". The "$n \rightarrow \sigma^*$ negative hyperconjugation" is described as ligand lone pairs donating into the σ-antibonding orbitals which are concentrated between the central atom and adjacent ligands.

The generalized valence bond descriptions of F_3NO and F_3PO are not analogous, and furthermore the GVB descriptions of SO_4^{2-} and SO_2Cl_2 are quite different and not at all analogous to F_3NO or F_3PO. The bonding in SO_4^{2-} and $SO_2(OH)_2$ (which is isoelectronic to SO_2Cl_2) is described elsewhere.[12b] For F_3NO and F_3PO there is no evidence for the lone pairs of the oxygen atom to donate into N–F or P–F antibonding orbitals (see Figures 1 and 3). Rather, in the case of F_3NO, the donation of the oxygen lone pairs is staggered with respect to the N–F bonds as would be expected on the basis of the Pauli exclusion principle. In addition, the unscreened regions of N core will be anisotropic and precisely in the directions where other electronic orbitals are not concentrated—again the lone pairs will "see" the N core more effectively if they are staggered with respect to the N–F bonds.

Reed and Schleyer[9e] note three interesting trends in the bond lengths of molecules they studied. First, on going from $(CH_3)_2SO_2$ to CH_3SO_2Cl to SO_2Cl_2, the SO bond lengths decrease from 1.435 to 1.424 to 1.404 Å. Second, F_3CO^- and F_3NO have *increased* bond lengths with respect to CF_4 and F_3N, respectively. Third, in the F_3PO and F_3PS molecules the FP bonds are *shortened* with respect to the PF_3 molecule. They explain the first two trends by invoking "negative hyperconjugation" but cannot explain the third trend—merely stating that other factors must influence the bond lengths besides negative hyperconjugation. With the framework established above it is quite natural to explain all three trends as a consequence of some simple principles.

The most important physical principle determining the distribution of orbitals is the Pauli exclusion principle. A second

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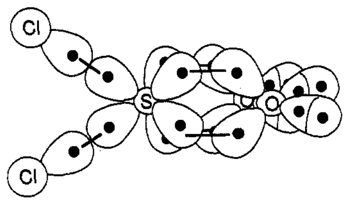

Figure 4. Schematic representation of the expected GVB bonding description of SO_2Cl_2 based on results for the isoelectronic molecule $SO_2(OH)_2$ described in ref 12b.

important feature is the electron donating or withdrawing capability of the ligands, and a third aspect is the size of the ion core about which the orbitals must distribute themselves in accord with the first two effects.

In the case of SO_2Cl_2 the bonding is shown schematically in Figure 4. Here the Cl atoms polarize the orbitals of sulfur, to which they are bonded (singlet spin-coupled), toward themselves; the other four orbitals on S form two sets of double bonds with the oxygen atoms. In CH_3SO_2Cl, the replacement of Cl by CH_3 does not polarize the bond as much as a consequence the electrons of the H_3C–S bond are closer to the sulfur atom. This results in larger Pauli repulsions with the other bonds thereby producing a lengthening of the SO bonds. The introduction of the second CH_3 group to replace the other Cl only accentuates this effect.

In going from the F_3N to the F_3NO molecule, the added oxygen contributes polarizable lone pairs which may contribute electron density to screen the N core. When the lone pairs get closer to the small N core, the resulting increased Pauli repulsions with the N–F bonds produce a lengthening in the N–F bonds. The same reasoning holds for the comparison between F_4C and F_3CO^-.

What is different in the case of going from F_3P to F_3PO is that P is a second-row element capable of forming more than four primary bonds, due to its much larger core size in comparison to first-row N. Thus the P atom has no difficulty forming six bonds with electronegative ligands. Furthermore, because the oxygen polarizes orbitals away from P there is a reduction in Pauli repulsions with the PF bonds (see Figure 3) resulting in the shortening of these bonds.

A central problem in the use of molecular orbital theory to describe bonding is the myriad ways in which this may be done. An interesting example of this has been discussed for H_3PO.[9b] The authors[9b] show that two different localization schemes[19] produce two rather different sets of localized molecular orbitals. The Boys method gives orbitals that suggest a PO triple bond, while the Ruedenberg method gives a PO single bond with some back-donation of oxygen lone pairs. Of course the Hartree–Fock wave functions and total energies of the two descriptions are identical. This lack of uniqueness of orbitals provides a constant source of debate about the nature of the bonding. The fact that one can analyze a Hartree–Fock calculation and arrive at many different orbital descriptions of the bonding depending on one's approach is quite unsatisfactory. It is curious therefore that one finds in a discussion[9c] of phosphine oxide bonding that one set of localized MOs is "clearly superior" to another. What criterion other than personal aesthetics can one use to make such a judgement?

This arbitrariness in orbitals may be contrasted with the GVB approach used here. GVB with the SOPP restrictions, as well as the most general independent particle model—full GVB (see, eq 2), yield *unique* orbitals that are variationally determined. Any change in the variationally determined orbitals raises the total energy! Hence, whether one likes the orbitals or not they are the *only* orbitals one may use to describe the bonding. In the case of F_3NO and F_3PO the lowest energy is obtained with the orbitals shown in Figure 1 and 3, respectively. Mere inspection of the orbitals describes the bonding, and one has no other choice than to conclude that (within the SOPP approximations) the NO bond of F_3NO is best described as a single bond with considerable back-bonding from the O lone pairs, while the PO bond in F_3PO is a triple bond. Of course, it is quite possible that the GVB approximation is inadequate to give a reasonable representation of the many-electron wave function of the molecule. (If this is the case then the molecular orbital wave function, which is an approximation to GVB, would also be inadequate.) In such a case one would not find the orbitals very instructive. However, there are likely very large classes of molecules for which an IPM description beyond MO theory constitutes a very reasonable approximation.

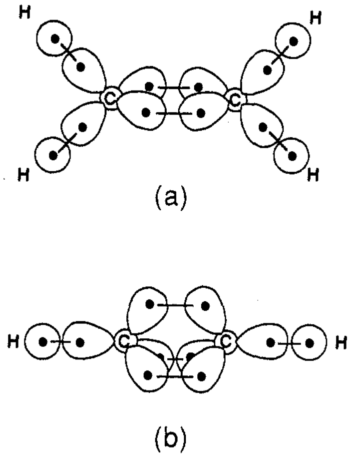

Figure 5. Schematic representation of the bonding obtained from generalized valence bond calculations that do not invoke the strong orthogonality or perfect-pairing assumptions for the multiple bonds of (a) ethylene and (b) acetylene.

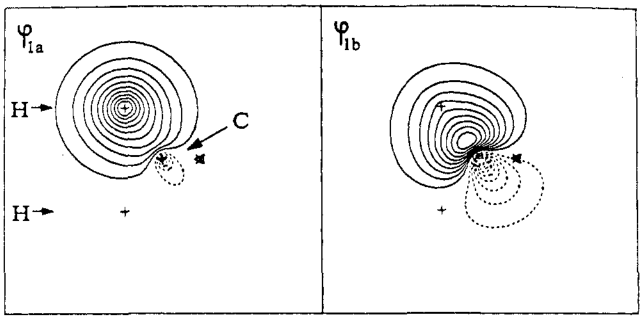

Figure 6. GVB orbitals obtained by using the strong orthogonality and perfect pairing (SOPP) approximations for one of the four equivalent bonds in the methane molecule. The orbital at the left is centered on a hydrogen atom and the one at the right is a valence orbital of the carbon atom.

Beyond the SOPP Approximations of GVB. As the GVB method with SOPP restrictions yields an orbital description of hypervalent bonding which is quite different from that obtained in molecular orbital studies, is it possible that the bonding description will change again if one were to use the full GVB method? As mentioned in the introduction the GVB method with the SOPP approximations leads to a description of the carbon–carbon bonds of ethylene and acetylene in terms of σ- and π-bonds, much the same as molecular orbital theory. However, the results of full GVB calculations (for the multiple bonds only) of ethylene and acetylene give an explanation[13] of the bonding shown schematically in Figure 5. This suggests that the carbon atoms in ethane, ethylene, and acetylene have local electronic structures nearly the same. That is, they have four orbitals distributed nearly tetrahedrally about their cores. One may choose to analyze this result in terms of atomic s and p orbitals on carbon or sp^3 hybrids, but this is not necessary—it is equally possible to analyze the result in terms of wave packets whose centers do not coincide with the atomic nuclei. For the present discussion the latter approach is taken. It is essential in working from this perspective, however, to recall a few basic principles. The nodal properties of carbon orbitals in a bond which result from GVB calculations with the

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usual SOPP approximations, such as shown in Figure 6 for a methane bond, do not necessarily arise because of the mixing of s and p *atomic* orbitals, they may arise because of the strong orthogonality between the orbitals involved in different singlet pairs. The same nodal properties can be readily generated, for example, by using wave packets whose centers are *not* on the carbon atom and are made up of only spherical gaussians. Thus, atomic-centered orbitals are usually sufficient but not necessary to interpret the results of the calculations. Nodeless wave packets not centered on atoms but forced to satisfy SO constraints can lead to the same results. Hence, the likely major change in the orbitals in going from GVB-SOPP to full GVB is that they will appear less atomic-like in the latter method.

This leads one to ask the question: if carbon has four wave packets symmetrically distributed about its core when forming four covalent bonds, why does nitrogen not have five packets and oxygen six wave packets forming five and six covalent bonds, respectively? Is it that under normal circumstances first-row atoms can only accommodate four wave packets symmetrically distributed about their cores? What happens in that case to the fifth valence electron of nitrogen? The additional nuclear charge will strongly attract the first four wave packets in addition to the fifth one added. This nuclear attraction brings all the wave packets closer to the nucleus making them overlap more strongly. But this leads to strong Pauli repulsions that can be reduced by having the fifth wave packet singlet-coupled to one of the original four. This forms an intra-atomic bond (a lone pair) and only allows three two-center two-electron bonds (as in ammonia) to form; e.g., $NH_4^+ + e^- \rightarrow NH_3 + H$. The same stratagem can be applied to neutral oxygen and fluorine to explain their capacity for forming two and one covalent bonds, respectively.

The full GVB method may thus lead to orbitals that are nodeless or contain fewer nodes than the corresponding GVB orbitals obtained with the strong orthogonality condition. This situation may be emphasized as in the discussion above by referring to the GVB single particle functions as "wave packets" rather than as "orbitals"—as the latter term tends to carry atomic connotations. In a qualitative discussion about what one *might expect* to arise from a full GVB calculation, it is not appropriate to refer to the orbitals or wave packets as "GVB orbitals". Hence it is important to introduce a terminology which differentiates between the actual GVB results and the qualitative aspects that are presently understood about such orbitals. As full GVB calculations on hypervalent molecules become available these qualitative ideas can be tested and refined to reflect the actual situation. Thus, a qualitative systematization is introduced which is referred to as the *extended valence bond orbital* (EVBO) scheme. It is "extended" because it goes beyond the classic valence bond model which assumes atomic orbitals and hybrid atomic orbitals (but of course this extension is inherent in the GVB method with SOPP restrictions), but it is also "extended" because it makes use of the limited experience[11a,13,20] from calculations that have removed the strong orthogonality and perfect-pairing restrictions. The basic qualitative features of this scheme, relevant for hypervalent molecules, are the following: (1) the Pauli exclusion effect together with the correlations in the motions of valence electrons around atomic cores in a molecule result in the valence electrons becoming localized in wave packets that surround the core; (2) the number of bonds an atom can form is governed by the amount of angular space available to the wave packets; (3) the space available to the wave packets about a given atom can be dramatically affected by the electronegativities of the atoms bonded to the given atom; (4) normal two center–two electron covalent bonds consist of two significantly overlapping wave packets, whose shapes are largely transferable from molecule to molecule containing the "same bond"; (5) "oxidation" of a lone pair consists of (a) allowing a lone pair to "angularly correlate" by supplying electronegative ligands and (b) unpairing the spins of the electrons in the lone pair and recoupling them to spins of electronic wave packets on other atoms.

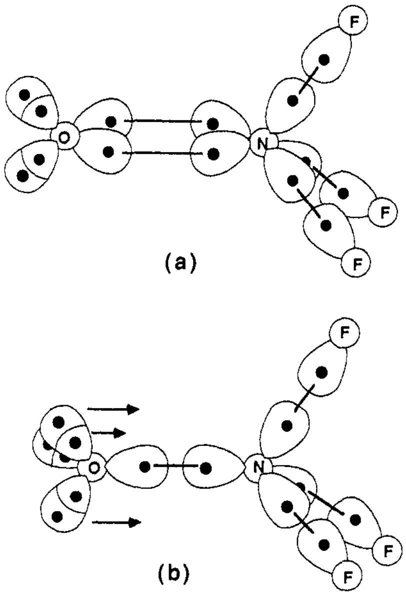

Figure 7. Schematic representations of two valence bond descriptions of the ONF_3 molecule. In (a) one of the resonance structures of a N atom with five bonds is shown. In (b) a single VB structure description is shown which involves three back-bonding contributions from the oxygen lone pairs to the nitrogen atom.

It is instructive to apply this qualitative GVB reasoning to several molecules. Consider again the ONF_3 molecule and the possibility that five wave packets might be distributed symmetrically about the nitrogen atom, as it has characteristics which suggest that the bond between N and O is a double bond.[21] In Figure 7a, a valence bond structure for the molecule is suggested. Such a picture might make more sense than it appears to at first glance. For example, the three fluorine atoms will distort the orbitals of the nitrogen atom toward themselves and the lone pair of electrons might be able to separate because of the decreased electronic charge density on the N atom. However, from a pragmatic viewpoint the structure proposed in Figure 7a suffers from the fact that it does not have the proper C_{3v} symmetry of the molecule and thus additional "resonance structures" will be required. An alternative valence bond description of the molecule is given in Figure 7b, which shows that the molecule can be described with only a single VB structure, where the nitrogen has a formal charge of +1 and the oxygen atom has a formal charge of −1. However in this case the "second bond" would arise from the delocalization of the three lone pairs of the oxygen atom onto the nitrogen atom. This is possible because the highly polar N–F bonds have left the N atom descreened. Such a "back-bonding" mechanism is of course not new. What is different from the traditional version of the concept is that it is not based on atomic orbitals. Thus, in order for electrons on one atom to back-bond to another atom there is no need to invoke *vacant atomic orbitals* on the acceptor atom. In the traditional version (especially applied to the main group elements outside the first row), empty atomic d orbitals are invoked to allow "π back-bonding" to take place. In the first-row elements the argument is made that only empty p orbitals can be used to allow "π back-bonding" because "the d orbitals are far too high in energy to participate". This certainly leaves a dilemma as regards describing the ONF_3 molecule from the traditional viewpoint and probably is the origin of the comment that it is "curious that F_3NO is an isolable compound".[21] By contrast, the EVBO perspective suggests that the oxygen lone pairs can back-bond to the N atom if there is sufficient space for them. The energetic importance of d-functions in the basis sets of hypervalent molecules for Hartree–Fock or GVB (SOPP) calculations arises from their importance in *reducing the Pauli repulsions*

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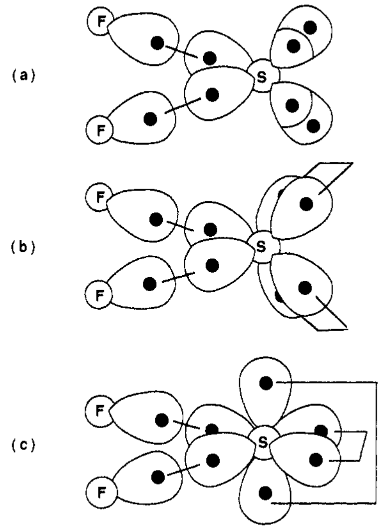

Figure 8. Schematic of possible alternative VB descriptions of the SF_2 molecule. In (a) the lone pairs on sulfur are in–out correlated; in (b) the lone pairs are angularly correlated and the orbitals about the sulfur are distributed in an approximately trigonal prismatic arrangement; and in (c) the lone pairs of sulfur are also angularly correlated, but are distributed in an approximately octahedral arrangement.

between bonds not in providing empty atomic d-orbitals for back-donation.[12] Thus this qualitative scheme allows one to interpret the calculations and make connections among them as well as anticipating the results of molecules for which no calculations have been performed. Although such a qualitative scheme may be appealing, its main advantage is that it can be tested by a full GVB computational study. This contrasts to the qualitative schemes of describing bonding in molecular orbital calculations, which because of the lack of uniqueness of MOs cannot really be proved or disproved.

The main group elements outside the first row have a much larger core around which to distribute the electron wave packets of the atom. This leads to some interesting possibilities which are briefly discussed here in qualitative terms. The true test, however, will be the computations that can probe the validity of the qualitative ideas suggested. Consider the SF_2 molecule to have a description in terms of wave packets, such as shown in Figure 8a. This is analogous to what one would expect for H_2O and F_2O. However, as sulfur has a larger core and fluorine atoms can polarize the sulfur wave packets to which they are bonded, the remaining sulfur wave packets may spread out around the core. That is, the remaining sulfur wave packets may become angularly correlated (instead of in–out correlated), increasing their nuclear attraction and lowering the energy of the system. One might imagine two especially symmetric ways to arrange the angularly correlated wave packets. These are shown in Figure 8, parts b and c. In the first case (b) the wave packets are roughly distributed in a trigonal prismatic arrangement, whereas in the second case (c) they are roughly distributed in an octahedral arrangement. This latter arrangement for SF_2 was in fact found by Hay in his early GVB (SOPP) study[10] of SF_2, SF_4, and SF_6.

The consequences of these arrangements of electron wave packets can be explored. It should be clear that for case a, just as for oxygen lone pairs, the individual wave packets of the lone pairs cannot form bonds. This is because there would be four electrons in the same region of space—which is forbidden by the Pauli principle. However, for the case of the angularly correlated lone pairs, such as in (b) and (c), there is now sufficient space that new covalent bonds can be formed to these angularly correlated wave packets. As examples of novel molecules based on the distribution of wave packets shown in Figure 8c, it is instructive to consider the cases of R_2CSF_4 and $RCSF_3$.[22] These appear to be the first instances of CS double and triple bonds and have properties very different from the usual sulfonium ylides known for many years.[23] The extended valence bond orbital description of these molecules is shown schematically in Figure 9, parts a and b.

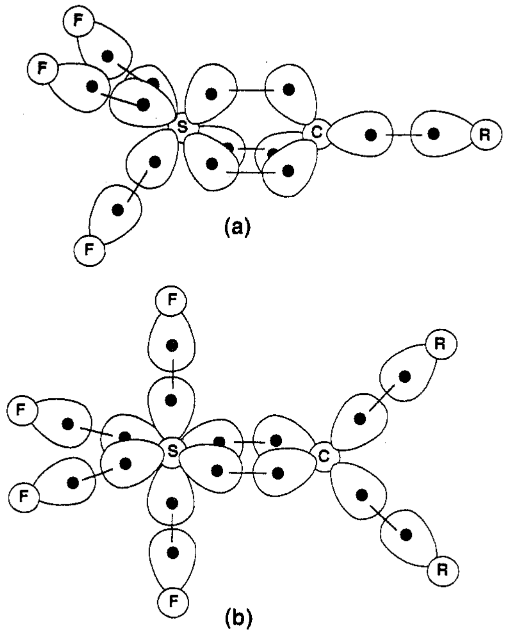

Figure 9. Schematic representation of bonding expected in the molecules (a) $RCSF_3$ and (b) R_2CSF_4. These expectations are based on the results described in the text of the paper.

Comparison of Figure 9a with the schematic at the top of Figure 3 shows the close relationship between the expected bonding in $RCSF_3$ and that in OPF_3. Generalizing the meaning from its usual molecular orbital context to the present valence bond context one could call the SF_3 fragment in Figure 8a and the PF_3^- fragment in Figure 3 "isolobal".[24] Likewise, the CR fragment of Figure 9a, the O^+ fragment of Figure 3, and the CH fragment of Figure 5b are all isolobal in the extended valence bond sense. The $R_2C{=}SF_2$ molecule is derived from the SF_2 molecule in Figure 8c. SF_4 is obtained from the SF_4 molecule by forming SF bonds to the two lobes of SF_2 (Figure 8c) which are perpendicular to the plane of the molecule. This results in a fragment that can bond to the CR_2 fragment (which is isolobal to the CH_2 fragments of Figure 5a). The insight that P can form six bonds can also be used to understand a number of apparent bond length anomalies in phosphorothioate anions.[25]

Computational results which explore these simple ideas for sulfur-containing molecules have demonstrated[12] that sulfur in the SO_2 and SO_3 molecules has *six* wave packets oriented in a trigonal prismatic fashion and that the SO_4^{2-} anion has four "normal" S–O single bonds with each O atom having three back-bonds to the sulfur atom (for a total of *twelve*!).

Thus the extension of traditional ideas of orbitals provided by the GVB method integrates considerable known information and experience.[26] It allows for directional orientation of orbitals (such as suggested by hybrids) without imposing constraints that are too rigid (e.g., hybrids can only be oriented in specific directions and because they are orthogonal to one another on a given atom, they require too large an energy penalty—"promotion energy"). The GVB method also allows for back-bonding (as suggested by molecular orbitals) but without the restriction to "$d\pi$–$p\pi$" in-

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teractions. Very importantly, the derived qualitative conceptual scheme is not isolated from computational analysis. It can be tested, modified, and extended within the context of generalized valence bond theory as more accurate GVB calculations become available. For example, the full impact on bonding concepts of the strong orthogonality approximation (which is almost universally assumed) is yet to be thoroughly explored.

Summary. A generalization and extension of the classic valence bond ideas of Linus Pauling, first articulated nearly 60 years ago[1a] provide a natural framework to discuss hypervalent molecules. The valence bond method has been discredited as an approach to understanding hypervalent molecules because of too strict an adherance to the original concepts of atomic hybrid orbitals and resonance structures arising from various distributions of electrons among atomic orbitals. As seen here the use of GVB calculations (with SOPP restrictions) allows for a generalization of the original framework which achieves a consistent valence bond description. The extension to the full GVB method should retain much of what has been learned with GVB-SOPP; however, the orbitals will look less like atomic or hybrid orbitals and more like wave packets associated with one or more atomic cores. As the calculations for the full GVB method on hypervalent molecules do not exist yet, general arguments have been proferred which suggest the nature of the results. The resulting interpretational scheme has been used to discuss bonding in molecules for which calculations are not yet available.

Contrary to much previous discussion based on molecular orbital theory, generalized valence bond calculations exhibit *six bonds* to P and S atoms in the presence of electronegative ligands. One must conclude that this is strong evidence that such molecules violate the Lewis–Langmuir Octet rule.

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Electrochemistry and Electrochromic Behavior of Langmuir–Blodgett Films of Octakis-Substituted Rare-Earth Metal Diphthalocyanines

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Contribution from the Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan. Received May 1, 1990

Abstract: Heavy rare-earth metal diphthalocyanine complexes with alkoxy or alkyl substituents dissolved in common organic solvents formed stable Langmuir–Blodgett (L–B) films. The cyclic voltammogram of L–B films on indium–tin oxide Nesa glass electrodes showed smaller peak splitting and more symmetrical shape than those of corresponding solvent-cast films. The multicolor electrochromism was found both in L–B film and cast film systems in contact with an aqueous HCl–KCl electrolyte. For the completion of the color change, different potentials should be applied with different substituents. More than 1 V (versus SCE) was necesary for the *tert*-butyl-substituted complexes and less than 0.8 V for the propoxy-substituted ones. After about 7 h of repetitive cycling at 100 mV/s between 0 and $0.6\sim0.9$ V, the relative Q-band intensity decreased by 2–5%, demonstrating good electrochemical stability.

Multicolor electrochromic devices have potential applications in man–machine interface and display systems. Heavy rare-earth metal diphthalocyanine complexes (Pc_2M, M = Lu, Yb, Er, Ho, Dy, Gd, etc.) exhibit green, red-brown, blue, and purple colors by changing the potential of Pc_2M-coated electrodes. Although many papers have been published in this area, most earlier reports[1-7] focused on the unsubstituted diphthalocyanine complexes.

Pc_2M is soluble in common organic solvents, such as chloroform and benzene, only in very low concentration, and therefore the preparation of homogeneous films on an electrode is difficult either by casting or the Langmuir–Blodgett (LB) technique. The resulting inhomogeneous film may exhibit rather slow response (of color change) to the potential change and also easier separation from the electrode surface. It seems to us that these may be the major reasons the lack of long-time reversibility and stability of Pc_2M films.

In addition, our previous work[8] showed that cast films of $R^2{}_8Pc_2M$ (where R^2 = *tert*-butyl, M = Er, Lu) on an indium–tin oxide glass exhibited better color change, but its redox wave II is too close to the chloride oxidation potential Cl^-/Cl. On the other hand, the second oxidation potential of $R^1{}_8Pc_2M$ (R^1 = propoxy) is far more negative than that of $R^2{}_8Pc_2M$, but its color change is not satisfactory.

The purpose of this report is 4-fold. First, to combine the better color change that appears in $R^2{}_8Pc_2M$ with the less positive oxidation potential possessed by $R^1{}_8Pc_2M$, new substituted diphthalocyanine complexes were prepared. Second, using the L–B technique, homogeneous films of these complexes were fabricated. Third, the electrochemical properties and electrochromic behavior in relation to the kinds of substitutents were examined. Lastly, the electrochemical stability under repetitive cycling was also investigated by measuring the relative Q-band intensity.

Experimental Section

Chemicals. 4-Nitrophthalonitrile with 96% purity was a donation from Toyo Ink Co. Ltd. Other chemicals were of reagent grade and used without further purification. Solvents were distilled twice and used immediately.

Octakis[propoxy(R^1)/*tert*-butyl(R^2)]diphthalocyanatoerbium/lutetium (R_8Pc_2M) was prepared using methods that have been described

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