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Comparison of Minimal and Extended Basis Sets in Terms of Resonant Formulas. Application to 1,3 Dipoles

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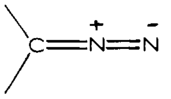
Abstract: The validity of weights of structural formulas derived from valence-bond wave functions is questionable, because these functions are, by necessity, calculated with minimal basis sets. To test this validity, we compare the structural weights, calculated in minimal and extended basis sets, for a series of 1,3 dipoles, one of the rare systems for which some kind of extended basis valence-bond function can be obtained. Both basis sets provide results in good agreement for the dipoles having no outer oxygen. The relevance of the calculated structural weights to chemical reactivity is discussed.

I. Introduction

Despite the wide, almost universal applicability of MO theory for the study of electronic properties of molecules, the merits of rigorous, nonempirical valence-bond calculations are far from negligible. Indeed, this type of calculation provides some information which is impossible to extract from a molecular orbital (MO) wave function, as it allows one to visualize the electronic states in terms of structural formulas which can be given rigorous, quantitative weights. This is particularly interesting in the case of excited states, or ground states of conjugated molecules, especially if some zwitterionic structures are expected to play a role. In addition to a better understanding of the relevant electronic states, the advantages of such an analysis are many. For example, weights of structural formulas are very useful for thermochemical estimations of the energetic features of reactions. Also, substituent effects on partly zwitterionic states are straightforwardly predicted.[1] Perhaps more importantly, valence-bond formulas can be very helpful for understanding reactivity. Indeed, the weights of octet zwitterionic structures are directly connected to the ambident nucleophilicity of some 1,3 dipoles.[2] As an example, a well-known ambident nucleophile, diazomethane, has as major structural formulas the two zwitterionic octets **1** and **2**. Moreover, the less pronounced, but still present ambident electrophilic character of some 1,3 dipoles may be predicted by the weights of zwitterionic sextet formulas. Zwitterionic structures are also expected to be able to polarize very easily under the approach of a charged reactant, thus accounting for very high reaction rates with charged species, in apparent contrast with the overall neutrality of the attacked molecule. Lastly, the influence of diradical structures of 1,3 dipoles onto the concertedness of cycloadditions to olefins has been studied by Harcourt.[3]



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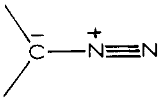

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Thus, it is not surprising that so many techniques have been utilized to get structural formulas for wave functions, including localization procedures,[4] the generalized valence-bond theory,[5] the "loge" theory,[6] etc. An ab initio valence-bond (VB) calculation is, of course, the most appropriate for that purpose, and we recently proposed a simplified method to project MO wave functions onto a basis of valence-bond functions,[7,8] thus getting the same result as that of an ab initio VB calculation but avoiding the costly evaluation of matrix elements between nonorthogonal determinants. Both pure VB calculations and MO projections have been frequently applied to small conjugated systems, particularly by Harcourt,[9-13] who has been first to stress the importance of diradical structures[12,13] in 1,3 dipoles.

A common feature inherent to both ab initio true VB calculations and MO projection calculations, if nonorthogonalized atomic orbitals (AO) are used, is that they are restricted to minimal basis sets. As we are interested in the description of the wave function's nature rather than in absolute or relative energies, one may wonder whether or not extraction of structural formulas, if it were possible, from double-ζ basis set wave functions would yield results significantly different from those obtained in minimal basis set. In other words, although minimal and double-ζ basis sets give quite different energies, do they provide wave functions which qualitatively differ by their types of bonding? It is essential to answer this question before interpreting minimal basis set VB functions, whatever the way, projection or ab initio calculation, they have been obtained. Fortunately, although this comparison of basis sets is impossible in the general case, it is conceivable for very small molecules, the biggest of which being the three-atom, four-electron system. The aim of this paper is to carry out such a comparison, in a way to get an insight on the validity of structural weights calculated from minimal basis set valence-bond functions. We have chosen a series of 1,3 dipoles for the following reason: (i) they have a wide importance in organic chemistry, (ii) their structural formulas have given rise to controversy, and (iii) they belong to the largest class of systems for which a comparison of basis sets can still be made.

II. The Problem of Extended Basis Sets

Basically, the problem lies in the fact that an extended basis set has too many atomic orbitals compared with the number of electrons. In a true valence-bond function, each atomic orbital bears one electron, with the exceptions of the free pairs and the positive charges. Going from minimal basis set to extended basis set doubled the number of AOs while the number of electrons

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† The Laboratoire de Chimie Théorique is associated with the CNRS (ERA No. 549).

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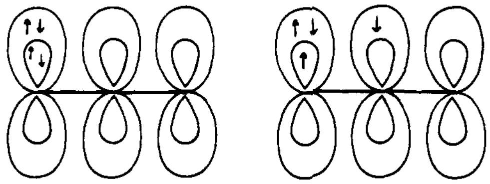

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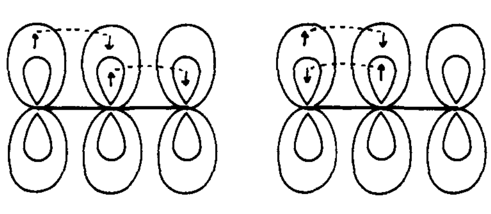

TYPE II

Figure 1. Some uninterpretable structures inherent to extended basis sets.

remains constant. An attractive solution would be to define an AO as the sum of its inner and outer parts, but the inadequancy of this definition is clearly seen if one gets the VB function by projection of MO wave functions; a simple examination of molecular orbitals would show that the inner:outer ratio of an AO differs from one MO to another, thus rending impossible such a definition of an AO. Of course, this inadequacy does not depend on the way, projection of variation, the VB function is obtained, since both methods are equivalent at the highest level of electronic correlation. The only solution is to consider the inner and outer components of each valence AO as two independent AOs, and to build a basis set of VB structures with this large set of AOs, but the difficulty now is that some of these structures are difficult or impossible to interpret in terms of chemical bond. There are two types of such structures, which we illustrate in Figure 1 using the example of 1,3 dipoles.

Structures of type I are particularly meaningless. Since each atom bears two π atomic orbitals, there are some structures in which an AO is doubly occupied, and the other AO on the *same* atom is singly or doubly occupied. Thus a single atom bears three or four π electrons, which violates Pauli's principle since two electrons of the same spin are located in very close regions. Fortunately, and because of this violation, any realistic wave function is expected to have essentially no such component; indeed, this is the case of all the calculations carried out in the present work.

Structures of type II are more reasonable in that the number of electrons per atom is never greater than two, but these electrons are coupled in a strange way, thus rending impossible the connection between structures and chemical bonding. Indeed, though the charges on each atom are reasonable, the number of bonds is not and the octet rule is violated. Of course, these structures are relatively minor, but they cannot be neglected since they represent typically 25% of the total wave function in our calculations. What kind of information can we extract from these structures? Strictly speaking, they do not represent chemical structures, but they give a distribution of electrons among atoms. So, for any molecule, minimal and extended basis sets VB calculations can be rigorously compared if one deals with electronic distributions rather than structural formulas. If one wants to compare structural formulas, one has to choose a system in which there is a one-to-one correspondence between these formulas and electronic distributions, or, in other words, a system in which the basis of VB structures is not overcomplete. Four-electron, three-atom systems are the biggest ones verifying this property, and as such are particularly adapted to a basis sets comparison.

III. Method and Results

The calculations presented here have been made for a series of 17 1,3 dipoles. The valence-bond wave functions have been obtained by projection (see the description of the method in ref 7) from an SCF calculation followed by configuration interaction (CI). The molecular orbitals have been calculated with the Gaussian 70 series of programs,[14] using the 4-31G extended basis set[15] of contracted Gaussian functions. The minimal basis set structural weights of these 1,3 dipoles have already been published,[7] and we kept the same geometries for our calculations in extended basis set. With both basis sets, we made a CI calculation in the SD interacting space for π electrons, i.e., including all single and double excitations among π orbitals. The structural weights have been calculated by means of eq[16] 1, where W_m is the weight

$$W_m = K_m^2 + \sum_{n\neq m} K_m K_n \langle V_m | V_n \rangle \qquad (1)$$

of a structural formula, $|V_m\rangle$ its corresponding function, and K_m its coefficient in the total wave function of the molecule.

This is not the only way to perform a population analysis in valence-bond theory; in particular, Gallup has developed the so-called "inverse overlap population analysis" (IOPA).[17] Briefly, the IOPA analysis allows one to measure, for each structure V_m, the part of the total wave function which is orthogonal to the other structures V_n, or, in other words, the part of the wave function which is unique to V_m and unduplicated in the other V_n's. The structural weights resulting from this analysis have two advantages: (i) they cannot be negative or greater than unity; (ii) they reflect the ability of a basis function V_m to lower the total electronic energy when incorporated in the variational procedure.[17] Nevertheless, we have chosen, in this work, formula 1, mainly because it has been shown[16b] that this population analysis is strictly equivalent to Mulliken's one in MO theory.[18] Our experience in using this definition always showed that negative weights, although possibly present in principle, were in fact negligible. Note that, strictly speaking, we have compared electronic distributions rather than structural formulas. Nevertheless, the results are displayed in Tables I and II in the form of weights of structural formulas, for the sake of clarity, and because both these properties are equivalent in minimal basis set for the systems under investigation (see previous section).

The results are displayed in Tables I and II respectively for the allyl-like 1,3 dipoles (ozone through azomethine ylide) and the propargyl-allenyl-like 1,3 dipoles (nitrous oxide through nitrile ylide).

(a) Allyl-Like 1,3 Dipoles. All these 1,3 dipoles have the following common features: the three heavy atoms are connected by two single σ bonds, and the four π electrons can be distributed into three π atomic orbitals, possibly creating a π bond and a doublet, thus making the dipole resemble an allyl anion. The bond lengths have been optimized[7] in minimal basis set after inclusion of correlation for π electron, and the bond angles, which we assumed to be unimportant as far as structural weights are concerned, were all kept[19] equal to 120°.

For this kind of dipoles one could expect a priori two opposite tendencies as one goes from minimal to extended basis sets. First, the terminal π atomic orbitals (i.e., the two p orbitals, perpendicular to the molecular plane, which are not located on the central atom) have a much larger overlap in the extended basis set than

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Table I. Structural Weights of Allyl-Like 1,3 Dipoles, Calculated in Minimal and Extended Basis Sets

	STO-3G	4-31G		STO-3G	4-31G		STO-3G	4-31G
ozone								
$^-O-O^+=O$	0.184	0.231	$\dot{O}-O-\dot{O}$	0.593	0.476	$^+O-O-O^-$	0.008	0.009
$O=O^+-O^-$	0.184	0.231	$^-O-{}^+O^+-O^-$	0.023	0.044	$^-O-O-O^+$	0.008	0.009
nitroso oxides								
$-\bar{N}-O^+=O$	0.134	0.079	$-\dot{N}-O-\dot{O}$	0.551	0.430	$-\underline{N}^+-O-O^-$	0.021	0.061
$-N=O^+-O^-$	0.264	0.400	$-\bar{N}-{}^+O^+-O^-$	0.025	0.026	$-\bar{N}-O-O^+$	0.005	0.003
nitrosimines								
$-\bar{N}-O=\underline{N}-$	0.182	0.180	$-\dot{N}-O-\dot{N}-$	0.538	0.586	$-\underline{N}^+-O-\bar{N}-$	0.008	0.017
$-N=O^+-\bar{N}-$	0.182	0.180	$-\bar{N}-{}^+O^+-\bar{N}-$	0.080	0.020	$-\bar{N}-O-N^+-$	0.008	0.017
carbonyl oxides								
$>\bar{C}-O^+=O$	0.059	0.039	$>\dot{C}-O-\dot{O}$	0.434	0.339	$>\underline{C}^+-O-O^-$	0.105	0.130
$>C=O^+-O^-$	0.326	0.472	$>\bar{C}-{}^+O^+-O^-$	0.071	0.019	$>\bar{C}-O-O^+$	0.005	0.0
carbonyl imines								
$>\bar{C}-O^+=\underline{N}-$	0.144	0.088	$>\dot{C}-O-\dot{N}-$	0.531	0.522	$>\underline{C}^+-O-\bar{N}-$	0.027	0.062
$>C=O^+-\bar{N}-$	0.264	0.303	$>\bar{C}-{}^+O^+-\bar{N}-$	0.026	0.018	$>\bar{C}-O-N^+-$	0.007	0.006
carbonyl ylides								
$>\bar{C}-O^+=\underline{C}<$	0.197	0.161	$>\dot{C}-O-\dot{C}<$	0.552	0.622	$>\underline{C}^+-O-\bar{C}<$	0.015	0.020
$>C=O^+-\bar{C}<$	0.197	0.161	$>\bar{C}-{}^+O^+-\bar{C}<$	0.025	0.016	$>\bar{C}-O-C^+<$	0.015	0.020
nitro compounds								
$^-O-\overset{\vert}{N^+}=O$	0.205	0.266	$\dot{O}-\overset{\vert}{N}-\dot{O}$	0.527	0.354	$^+O-\overset{\vert}{N}-O^-$	0.012	0.016
$O=\overset{\vert}{N^+}-O^-$	0.205	0.266	$^-O-{}^+\overset{\vert}{N}{}^+-O^-$	0.038	0.082	$^-O-\overset{\vert}{N}-O^+$	0.012	0.016
azoxy compounds								
$\diagdown\bar{N}-\overset{\vert}{N^+}=O$	0.167	0.134	$\diagdown\dot{N}-\overset{\vert}{N}-\dot{O}$	0.523	0.371	$\diagdown\bar{N}-\overset{\vert}{N}-O^+$	0.009	0.007
$\diagdown N=\overset{\vert}{N^+}-O^-$	0.247	0.390	$\diagdown\bar{N}-{}^+\overset{\vert}{N}{}^+-O^-$	0.036	0.056	$\diagdown\overset{+}{N}-\overset{\vert}{N}-O^-$	0.019	0.043
azimines								
$\diagdown\bar{N}-\overset{\vert}{N^+}=N\diagup$	0.200	0.227	$\diagdown\dot{N}-\overset{\vert}{N}-\dot{N}\diagup$	0.540	0.470	$\diagdown\bar{N}-\overset{\vert}{N}-\overset{+}{N}\diagup$	0.014	0.017
$\diagdown N=\overset{\vert}{N^+}-\bar{N}\diagup$	0.200	0.227	$\diagdown N-{}^+\overset{\vert}{N}{}^+-N\diagup$	0.032	0.041	$\diagdown\overset{+}{N}-\overset{\vert}{N}-\bar{N}\diagup$	0.014	0.017
nitrones								
$>\bar{C}-\overset{\vert}{N^+}=O$	0.148	0.074	$>\dot{C}-\overset{\vert}{N}-\dot{O}$	0.444	0.304	$>\bar{C}-\overset{\vert}{N}-O^+$	0.004	0.003
$>C=\overset{\vert}{N^+}-O^-$	0.268	0.482	$>\bar{C}-{}^+\overset{\vert}{N}{}^+-O^-$	0.104	0.044	$>\overset{+}{C}-\overset{\vert}{N}-O^-$	0.034	0.093
azomethine imines								
$>\bar{C}-\overset{\vert}{N^+}=N\diagup$	0.168	0.140	$>\dot{C}-\overset{\vert}{N}-\dot{N}\diagup$	0.509	0.448	$>\bar{C}-\overset{\vert}{N}-\overset{+}{N}\diagup$	0.012	0.011
$>C=\overset{\vert}{N^+}-\bar{N}\diagup$	0.253	0.319	$>\bar{C}-{}^+\overset{\vert}{N}{}^+-\bar{N}\diagup$	0.034	0.037	$>\overset{+}{C}-\overset{\vert}{N}-\bar{N}\diagup$	0.024	0.046
azomethine ylides								
$>\bar{C}-\overset{\vert}{N^+}=C<$	0.209	0.215	$>\dot{C}-\overset{\vert}{N}-\dot{C}<$	0.514	0.491	$>\bar{C}-\overset{\vert}{N}-\overset{+}{C}<$	0.017	0.023
$>C=\overset{\vert}{N^+}-\bar{C}<$	0.209	0.215	$>\bar{C}-{}^+\overset{\vert}{N}{}^+-\bar{C}<$	0.033	0.033	$>\overset{+}{C}-\overset{\vert}{N}-\bar{C}<$	0.017	0.023

Table II. Structural Weights of Propargyl-Allenyl-Like 1,3 Dipoles, Calculated in Minimal and Extended Basis Sets

	STO-3G	4-31G		STO-3G	4-31G		STO-3G	4-31G
nitrous oxide								
$^-O-N^+\equiv N$	0.378	0.541	$\dot{O}-N=\dot{N}$	0.167	0.187	$^+O-N=N^-$	0.0	0.002
$O=N^+=N^-$	0.191	0.076	$^-O-{}^+N^+=N^-$	0.135	0.090	$^-O-N=N^+$	0.130	0.104
azides								
$-^-N-N^+\equiv N$	0.293	0.337	$-\dot{N}-N=\dot{N}$	0.316	0.304	$-N^--N=N$	0.029	0.041
$-N=N^+=N^-$	0.252	0.211	$-N^--{}^+N^+=N^-$	0.093	0.094	$-N^+-N=N^-$	0.015	0.013
diazoalkanes								
$>C^--N^+\equiv N$	0.164	0.162	$>\dot{C}-N=\dot{N}$	0.281	0.303	$>C^--N=N^+$	0.010	0.011
$>C=N^+\equiv N^-$	0.414	0.396	$>C^--{}^+N^+=N^-$	0.089	0.078	$>C^+-N=N^-$	0.042	0.050
nitrile imines								
$-N^--N^+\equiv C-$	0.372	0.406	$-\dot{N}-N=\dot{C}-$	0.287	0.282	$-N^--N=C^+-$	0.052	0.067
$-N=N^+=C^--$	0.189	0.155	$-N^--{}^+N^+=C^--$	0.090	0.093	$-N^+-N=C^--$	0.009	0.008
nitrile ylides								
$>C^--N^+\equiv C-$	0.247	0.245	$>\dot{C}-N=\dot{C}-$	0.297	0.324	$>C^--N=C^+-$	0.023	0.024
$>C=N^+=C^--$	0.316	0.301	$>C^--{}^+N^+=C^--$	0.092	0.078	$>C^+-N=C^--$	0.025	0.028

in the minimal one, because the outer part of the split orbitals are quite diffuse. Typically, the overlap between these outer terminal AOs is about 0.13, while the overlap between the corresponding AOs in minimal basis set is only 0.02–0.03. As a consequence, the singlet diradical structures, sometimes called "long-bond" structures, should be more stabilized in extended basis set, and should have a larger contribution to the ground states. On the other hand, diffuse orbitals are also more appropriate for locating negative charges, and this should increase the weights of zwitterionic structures in the extended basis set ground states. Table I shows that these two effects may or may not counterbalance, depending on the molecule. They nearly compensate one another for the dipoles which have no terminal oxygen. Indeed, the agreement between both basis sets is rather good for these dipoles, and the general preponderance of diradical structures is confirmed. Also, in both basis the sextet structures are found definitely minor.

On the contrary, structural weights of dipoles containing one or two terminal oxygens are very sensitive to the basis set. Table I shows that all such dipoles have their diradical weights decreased by some 20–30% from minimal to extended basis set, for the benefit of the octet zwitterionic structures, especially the ones whose negative charges are located on the oxygen atoms. Clearly, the diffuse orbitals of the extended basis set stabilize much more the negative charge than the "long-bond" diradical structure, for this category of dipoles. The reason why it is not so for the other dipoles is very simple: all their terminal heavy atoms are sp^2 hybridized, a necessary condition for the stabilization of the molecule by resonance; thus the negative charge can only be located in a pure p orbital, while it is well known that it would be much more stabilized by a sp^3 orbital. For example, a CH_3 anion is definitely pyramidal, while the methyl radical is nearly planar.[21] This problem is meaningless, of course, for a terminal oxygen atom for which no pyramidalization can be defined.

(b) **Propargyl-Allenyl-Like 1,3 Dipoles.** These dipoles differ from the previous ones in that they have one additional double bond. There are now, strictly speaking, more than four π electrons, but what we consider as π electrons, in what follows, are the electrons located in p orbitals perpendicular to the plane of the molecule, if it is not linear. In other words, the calculation is restricted to electrons which can significantly delocalize.

The case of nitrous oxide is special, in that it is completely linear; as a consequence, it contains two perpendicular sets of three p orbitals, each of which bearing four electrons. These two sets are strictly equivalent, and, according to the above criterion, the VB calculation should be carried out for both of them at the same time. For clarity, we chose to analyze only one set of π orbitals, freezing the other set like the σ orbitals.

If we were dealing with a single determinant wave function, the 36 structural weights that would result from a full 8π electron VB projection could be obtained very easily by simple products of structural weights given by the 4π electron study. Unfortunately, this property does not hold true for wave functions calculated by configuration interaction, which renders questionable the validity of our 4π electron study. In other words, our approximation does not allow one π set of electrons to influence the other one. Nevertheless, the SCF configuration is still very largely preponderant after the configuration interaction, with a weight of 0.94, thus making the final wave function very similar to a single determinant. Consequently, a 4π electron study should be reasonably reliable in this particular case, but this cannot be generalized to all molecules of this type. The structures displayed in Table II have been drawn assuming the following distribution for the frozen set of π electrons: a doublet on oxygen and a π bond between both nitrogens, which corresponds to the major structure of the nonfrozen set. The 4π electron treatment is again certainly valid for the remaining dipoles, for the following reasons. (i) The SCF configuration is largely predominant in the wave functions of both azide and nitrile imine, with weights of 0.94 and 0.93, respectively; (ii) there can be no delocalization among the in-plane π orbitals of diazoalkane and nitrile ylide.

Similarly to the other category of dipoles, only the bond lengths between heavy atoms have been optimized,[7] and the bond angles are standard, 120 or 180°.

Table II shows, again, a very good agreement between structural weights calculated in minimal and extended basis sets, for dipoles bearing no terminal oxygen. The extended basis set, as expected, dramatically favors the zwitterionic octet structure of nitrous oxide involving a negatively charged oxygen, making this 1,3 dipole the most zwitterionic of the series, with a diradical contribution of only 19%.

Discussion

Our results confirm the importance of the diradical structures in allyl-like dipoles, in agreement with Harcourt[9,12,13] and Goddard.[22] These structures are even the major ones if the dipoles have no terminal oxygen. On the contrary, we find that propargyl-allenyl-like dipoles are best described as zwitterions. Carbonyl oxide is the more zwitterionic of the series, with the octet structure $H_2C{=}O^+{-}O^-$ contributing by 47% to the ground state, in good agreement with the 32-kcal rotational barrier, as estimated by Cremer[23] after rather sophisticated calculations.

Our results may also be compared with experimentally observed reactivity trends of 1,3 dipoles. As mentioned above, the octet zwitterions are expected to be responsible for ambident nucleophilicity, while ambident electrophilicity should be due to sextet zwitterions. Two typically ambident nucleophiles, the azides and the diazoalkanes,[2] are indeed best described as octet zwitterions (Table II). Also, interestingly, the rarely observed sextet zwitterion structure is precisely found in 1,3 dipoles having some electrophilic character:[2] nitrous oxides (Table II), nitrone (Table I), and nitrile oxides.[24]

Lastly, McGarrity and Smyth have recently observed an extremely high rate of protonation of diazomethane by the hydronium ion,[25] which cannot be explained on the basis of exothermicity alone. They have suggested that "very little energy expanditure is necessary to localize all the negative charge prior to electron transfer". Again, this can be related to the large weight of zwitterionic structures in diazomethane, as zwitterionic states may polarize very easily under a small perturbation (sudden polarization phenomenon[26]). Thus, despite the overall neutrality of diazomethane, a hydronium ion may create an important negative charge at either end of the molecule.[27]

Conclusion

The results presented here bring encouraging support to the qualitative interpretation of minimal basis set valence-bond functions. Indeed, there are no significant discrepancies between the structural weights obtained with both minimal and extended basis sets, apart from a notable exception: the molecules in which a negative charge may locate into an appropriately hybridized atomic orbital, i.e., typically, for the conjugated molecules, those bearing a terminal oxygen. Then the minimal basis set systematically underestimates the weight of the corresponding zwitterionic structure. Interestingly, our calculated structural weights for

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carbonyl oxide account for a rotational barrier which is only correctly predicted at the highest level of sophistication, suggesting that a function calculated in relatively small basis set provides a qualitatively correct electronic description, even if its energy lacks reliability. Finally, the agreement between our results and reactivity trends emphasizes the usefulness of the still up-to-date valence-bond theory as a tool providing some unique and easily interpretable information.

Registry No. Ozone, 10028-15-6; nitrous oxide, 10024-97-2.

Ab Initio Quantum Mechanical Calculations of the Magnetic Shielding Constants of the Different Nuclei of Cytosine

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Abstract: The magnetic shielding constants of the different nuclei of cytosine are calculated by an ab initio self-consistent perturbation method utilizing gauge invariant atomic orbitals and a "split valence shell" basis set of Gaussian functions. The comparison of the results obtained with experimental data shows that for each of the four different types of nuclei present in the molecule (H, C, N, O) the theory reproduces correctly the qualitative trends observed and, in many cases, the numerical values of the measured chemical shifts.

In order to be able to carry out reliable calculations on the variation of the chemical shifts of the different nuclei of a nucleoside, a nucleotide, or a nucleic acid, due to conformational changes in that entity and/or to molecular interactions, it is necessary, in the first place, to be able to calculate with a fair degree of accuracy the magnetic shielding constants of these nuclei in the isolated molecules which are the building blocks of the biological entity of interest. For the nucleic acids there are three different units to be considered, namely the phosphate group, the ribose, and the purine and pyrimidine bases.

The semiempirical calculations of magnetic shielding constants, which have been carried out for nucleic acid bases,[1,2] nucleosides,[3] nucleotides,[4] and nucleic acids[5,7] have been concerned only with proton resonances. Moreover, if there is some evidence that such calculations take into account satisfactorily the "through space" or "geometric" effects[8] due to the ring currents[2a,b,9] and the anisotropy of the atomic susceptibility tensors,[9,10] the calculation of the "chemical" contributions,[8] such as the polarization effect, which has to be taken into account in conformational as well as in intermolecular problems,[2c,d,3,4] appears to be more delicate to carry out, even for protons.

Since it is now currently possible to study the ^{31}P, ^{17}O, ^{15}N, ^{14}N, and ^{13}C as well as ^{1}H nuclear magnetic resonance spectra of nucleosides or nucleotides,[11-14] oligo or polynucleotides,[11e,15,16]

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