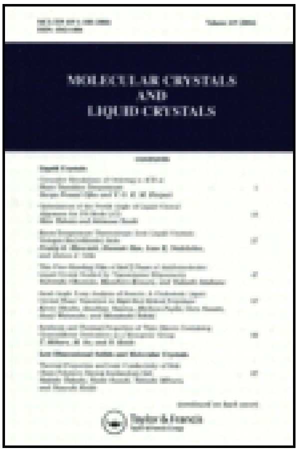

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Ab Initio Computation of the Spin Population of Substituted α-Nitronyl Nitroxide Radicals

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AB INITIO COMPUTATION OF THE SPIN POPULATION OF SUBSTITUTED α-NITRONYL NITROXIDE RADICALS

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Abstract The ability of various ab initio methods (UHF, ROHF, MCSCF, MP2, CISD, CCD) to reproduce the experimental information on the spin distribution over various substituted α-nitronyl nitroxide radicals was tested using various basis sets which range from single zeta to near Hartree-Fock limit quality.

INTRODUCTION

The free radical family of α–nitronyl nitroxides has attracted in the last few years much interest. Most of the purely organic molecular solids that present bulk ferromagnetism ordered states belong to this family of compounds.[1] The detailed knowledge of the spin distribution in the molecular radical seems to be necessary to for the understanding of the magnetic behavior of its crystals. It is for this reason that many efforts have been dedicated to determine this property by using several experimental techniques and various theoretical methods.[2] Among these studies, there has been a special interest in the determination of the spin density and the atomic spin population of various members of the nitronyl nitroxide family of free radicals,[3-5] whose general formula is presented in Figure 1, being X = CH_3. Outstanding members of this family of free radicals are the

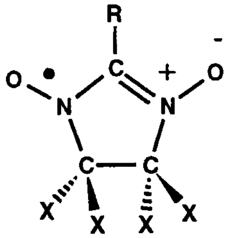

FIGURE 1. General formula of substituted α-nitronyl nitroxide radicals

phenyl (where R = phenyl) or just the H substituted (R = H) α-nitronyl nitroxide radicals, since both compounds are structurally simple and a great deal of experimental data are available elsewhere.

From previous experimental studies it is known that most of the spin density is equally distributed among the four atoms of the two N-O groups,[3,5] and that the bridge carbon atom of the five-member ring carries a significant negative spin density. Delocalization of the spin among the phenyl fragment is found to be weak, often at their limit of experimental accuracy, and sign alternation is found among the carbon atoms of the ring. There is also a report of ab initio calculations,[3] on the whole molecule using density functional theory (DFT), and on a truncated form of the nitronyl nitroxide shown in Figure 1 with X=H and R=H (hereafter, compound **1**) using the UHF, CI and MP2 methods. These ab initio results[3] show that the DFT calculations reproduce well the sign and magnitude of the spin populations, while the UHF/3-21G (i.e., the UHF method using a 3-21G basis set) and UHF/6-311G(d,p) computations give the correct sign for the spin population in the atoms but exaggerates the spin polarization on the phenyl ring. The CI/3-21G and MP2/3-21G computations give better atomic spin populations than the UHF method, but twice the experimental value.

The main goal of this work is to carry a systematic study of the performance of the ab initio methods in computing the spin density of the nitronyl nitroxides radicals. We are going to extend the scope of previous studies by employing more ab initio methods and better basis sets in a series of molecules which also includes compound **1**. In that process we will test the effect of the selected method, basis set, and the model to define the atomic spin population. The ab initio methods tested are the UHF, ROHF, MCSCF, MP2, CISD, and CCD.[6] On top of that, we have also tested the performance of the B-LYP nonlocal exchange and correlation density functional[7] (B-LYP identifies the exchange-correlation density functional employed, B being the nonlocal exchange functional of Becke,[8] and LYP being the nonlocal correlation functional of Lee, Yang and Parr).[9] These tests will be carried out with various basis set, to study the basis set truncation effect on our numbers, using basis which range from single zeta quality up to a very extended basis set of near Hartree-Fock limit quality. As models to compute the atomic spin populations, we will have a look at the result obtained using the Mulliken and Lowdin populations,[6] and then we will compare these with the values obtained from a numerical integration of the spin density.[10]

COMPUTATIONAL DETAILS

Atomic spin population on each atom are computed in general using the Mulliken and Lowdin methods.[6] According to the Mulliken population method, the atomic population from a wavefunction is computed by adding the contributions of the diagonal elements of the **P*S** matrix for the elements associated to atomic orbitals centered in the atom of interest (**P** is the first order density matrix in the [nonorthogonal] atomic orbitals basis set, and **S** is the overlap matrix in the same basis). In a UHF wavefunction, where one computes separately the α and β spin electrons (i.e., there is a $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ matrix), one can compute the atomic spin population by substracting the α and β components of the population analysis. It is possible to show that the addition of all the diagonal elements of the **P*S** matrix (i.e., the trace of **P*S**, represented as Tr(**P*S**)) is equal to the N, the number of electrons in the molecule. A fundamental property of the **P*S** trace is that $\mathrm{Tr}(\mathbf{P}*\mathbf{S}) = \mathrm{Tr}(\mathbf{S}^{n} * \mathbf{P} * \mathbf{S}^{1-n}) = N$. In the case in which n=1/2, one obtains the so called Lowdin population analysis by adding the diagonal elements in the same way we did in the Mulliken population analysis. Obviously, there are an infinite number of choices for the value of n, each one providing a different value of the atomic spin (or also the atomic charge). This just reflects the fact that the atomic spin or the atomic charge within a molecule is not a physical observable property. Our results with the various methods show that the Lowdin and Mulliken populations analysis give very similar results, although Mulliken gives always higher (that is, more polarized) atomic spin populations. So, in the following we will discuss only the numbers from the Mulliken population analysis. We did the computation of the Mulliken atomic spin populations using the adequate option in the GAUSSIAN-92 [11] and GAUSSIAN-92/DFT [12] programs.

Another way of computing atomic charges and spin populations is by integrating the density (or substracting the integrated α and β components of the density) over the atomic volume. We can define the atomic volume following Bader's method.[10] In this way, each molecule can be splitted into non-overlapping atomic volumes. We used these volumes to integrate the spin density function as computed in the spin-natural orbital basis set (the eigenvectors of the spin density matrix). This method is probably the most physically meaningful way of computing any atomic property for the atoms of a molecule. So we have used the values from the numerical integration as a test to check the quality of the Mulliken atomic spin populations. The computation of the integrated atomic spin populations were carried out with a modified version of the PROAIM package.[13]

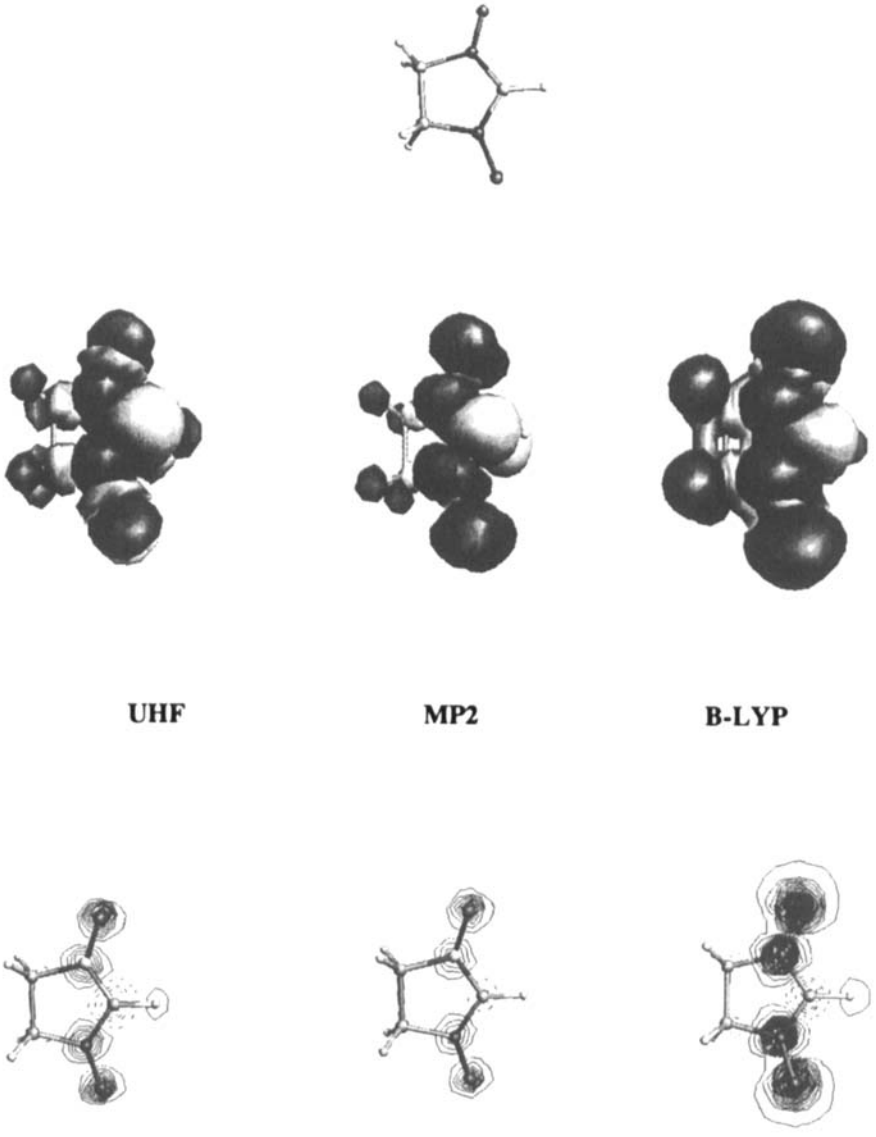

FIGURE 2 Distribution of the spin density for compound 1. Its chemical structure is shown in the first row, the spatial distribution of the 0.001 (dark) and -0.001 (light) e/$Å^3$ contours is shown in the second row, and the counter map with the variation of the spin distribution in the O-N-C-N-O molecular plane (continuous dark lines = positive, broken dark lines = negative, lighter lines = zero; increment = 0.01 e/$Å^3$) is shown in the third row.

RESULTS AND DISCUSSION

We started our tests by looking at the effect on the atomic population of the various ab initio methods. For this set of tests we selected compound **1** at its optimum energy structure, as computed at the UHF/D95V(d) level. At this geometry, to have an idea of how the spin density is distributed on the molecule, we computed the spin density density on the space surrounding the molecule with the UHF, MP2 and the B-LYP functional. We used the 6-31G(2d,2p) basis set for the UHF and MP2 computations. The B-LYP was computed using DGAUSS [14,15] employing the DFT optimized DZP basis set (double zeta plus polarization basis set optimized for DFT computations) and the A1 auxiliary basis set. The distribution of spin density computed with these three methods is plotted in Figure 2. From the theoretical point of view, the MP2 and B-LYP methods are the ones giving the best results. MCSCF computations show that the wavefunction for this molecule can be very well described by a Hartree-Fock determinant and, in a monoreference computation like this one, the MP2 method recover most of the electron correlation not included in the UHF wavefunction. The B-LYP can be considered as an approximation using functionals to the exact computation which is well reproduced by the MP2 method. One expects that the CISD, and CCSD spin density will be very close to the MP2 .

A look at Figure 2 shows that the main features of the spin density distribution are similarly reproduced by the three methods. Thus, they predict that most of the spin density is concentrated on the two N-O groups and there is a significative amount of negative spin density on the region of the C(sp^2) atom. However, they differ in the amount of spin predicted on the C(sp^2) atom, on the H atom attached to C(sp^2), or on the C(sp^3) atoms and the H atoms bonded to them.

Keeping Figure 2 in mind, we can analyze the atomic spin density computed by the Mulliken and numerical integration methods (in just some of the cases) when applied to the spin density distribution obtained using the UHF, ROHF, MCSCF, MP2, CISD, CCD methods and the B-LYP density functional. We carried out these computations using the D95V(d) basis set in all the cases. The atomic spin computed on each atom is collected in Table I, where C_2 and C_3 identifies the C(sp^2) and C(sp^3) atoms in **1**, and H_2 and H_3 are the hydrogens attached to the C(sp^2) and C(sp^3) atoms, respectively. A look at the Mulliken atomic spin populations shows that they are strongly localized on the N-O bonds and the C(sp^2) atom, as expected from Figure 2 plots. At the same time, the values on these atoms present a strong dependence in the computational method employed, being the most sensitive result that for the C(sp^2) atom. Its value is maximum for the UHF method, and decreases when the electronic correlation is included. This tendency is clearly seen when we compare the MCSCF(3,3) and MCSCF(7,7), whose difference is just the number of determinants in the computation (larger in the MCSCF(7,7) computation). These computation are a complete CI for the 3 and 7 orbital valence spaces and can be taken as a reference for the other correlation results. The numerical integration and Mulliken methods show the same general trend, but with smaller values for the numerical method.

When compared to the experimental values, the Mulliken or numerical integration B-LYP results are the closest ones. The MP2 values are the next in quality, although there the Mulliken method overestimates the population on the C(sp^2) atom, while the CISD and CCD give larger values at a much higher computational cost. Finally, the B-LYP functional gives results which are too small when compared to any of the other results from the correlational methods. Finally, the UHF method grossly overestimates the spin population of the C(sp2) atom by a large number with Mulliken and a smaller number with the numerical integration. The other atoms presents similar trend but with smaller differences.

TABLE I Atomic spin populations for compound 1 computed using the D95V(d) basis set. First row results are from Mulliken's method and second row (when given) are from the numerical integration method.

Method	Atom					
	C_2	N	O	C_3	H_2	H_3
UHF	-0.84	0.45	0.45	-0.06	0.08	0.02
	-0.55	0.36	0.41	-0.03	0.02	0.01
ROHF	0.01	0.25	0.23	0.00	0.00	0.01
MCSCF(3,3)	-0.47	0.34	0.38	0.01	0.00	0.01
MCSCF(7,7)	-0.41	0.33	0.36	0.01	0.00	0.00
MP2	-0.34	0.33	0.33	-0.03	0.01	0.02
	-0.23	0.28	0.32	-0.01	-0.01	0.01
CISD	-0.67	0.37	0.45	-0.05	0.05	0.02
CCD	-0.54	0.37	0.39	-0.04	0.03	0.02
B-LYP	-0.12	0.23	0.33	-0.02	0.01	0.01
	-0.09	0.22	0.31	-0.01	0.00	0.01
exp. (ref 3)	-0.121	0.278	0.262	-0.025	0.009	---

After the previous results, we decided to tested the basis set effect on the atomic spin populations, that is, how the atomic spin population values computed with one method depend on the basis set employed in the calculation. We concentrated this study in the UHF and MP2 ab initio methods and in the B-LYP density functional. For these three methods, we computed the atomic spin population on compound 1 using the

TABLE II Mulliken atomic spin populations for compound **1** computed using the UHF, MP2 and B-LYP methods (first, second, and third row, respectively) using the indicated basis set.

Basis set	Atom					
	C_2	N	O	C_3	H_2	H_3
STO-3G	-0.93	0.15	0.79	-0.02	0.08	0.01
	-0.73	0.02	0.62	-0.03	0.05	0.01
	-	-	-	-	-	-
STO-3G(d,p)	-0.86	0.17	0.74	-0.02	0.06	0.01
	-0.58	0.24	0.54	-0.02	0.02	0.01
	-	-	-	-	-	-
D95V(d)	-0.84	0.45	0.45	-0.06	0.08	0.02
	-0.34	0.33	0.33	-0.03	0.01	0.02
	-0.12	0.23	0.33	-0.02	0.01	0.01
D95V(2d,2p)	-0.79	0.46	0.43	-0.06	0.05	0.02
	-0.31	0.31	0.34	-0.02	0.00	0.01
	-	-	-	-	-	-
D95V+(2df,2pd)	-0.80	0.47	0.43	-0.05	0.05	0.02
	-0.29	0.31	0.32	-0.01	0.00	0.01
	-0.12	0.23	0.31	-0.01	0.00	0.01

TABLE III Numerically integrated atomic spin populations for compound **1** computed using the UHF, MP2 and B-LYP methods (first, second, and third row, respectively) using the indicated basis set.

Basis set	Atom					
	C_2	N	O	C_3	H_2	H_3
STO-3G	-0.73	0.10	0.75	-0.01	0.03	0.01
	-0.58	0.18	0.60	-0.02	0.02	0.01
	-	-	-	-	-	-
STO-3G(d,p)	-0.67	0.13	0.70	-0.01	0.02	0.01
	-0.46	0.21	0.52	-0.01	0.00	0.01
	-	-	-	-	-	-
D95V(d)	-0.55	0.36	0.41	-0.03	0.02	0.01
	-0.23	0.28	0.32	-0.01	-0.01	0.01
	-0.09	0.22	0.31	-0.01	0.00	0.01
D95V(2d,2p)	-0.55	0.37	0.40	-0.03	0.01	0.01
	-0.21	0.27	0.32	-0.01	-0.01	0.01
	-	-	-	-	-	-
D95V+(2df,2pd)	-0.54	0.36	0.41	-0.03	0.01	0.01
	-0.20	0.28	0.31	0.00	-0.01	0.01
	-0.08	0.23	0.31	-0.01	0.00	0.01

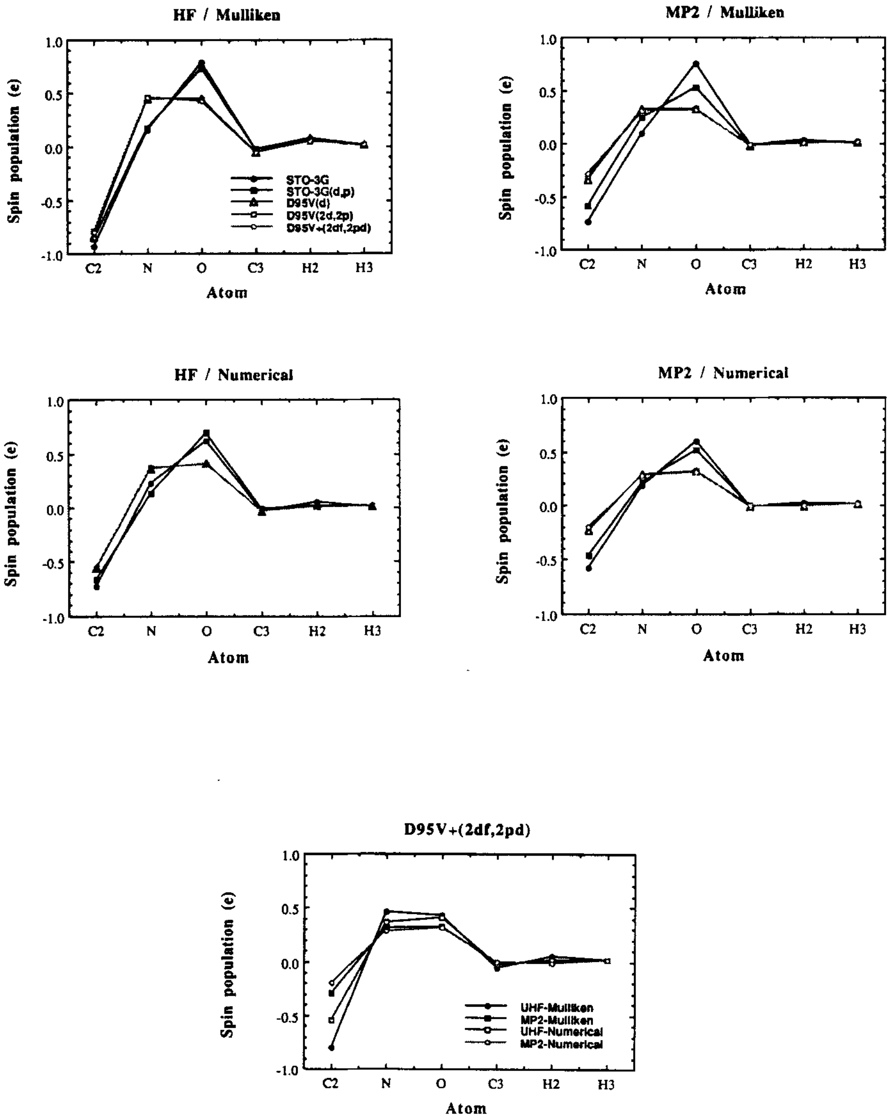

FIGURE 3 Variation of the atomic spin population for the non-symmetry related atoms of compound 1. First row shows the variation with the basis of the UHF and MP2 results computed using Mulliken population analysis. Second row show the same variation for the numerical integration values. Third row shows the results obtained using the D95V+(2df,2pd) basis set with the two methods at the UHF and MP2 levels.

following basis set, in an increasing order of quality: STO-3G, STO-3G(d,p), D95V(d) (the one used before in Table I), D95V(2d,2p), and D95V+(2df,2pd). The last basis set includes diffuse functions on the heavy atoms (indicated by a + in its name), two sets of d and one set of f polarization functions on the heavy atoms, and two sets of p and one set of d polarization functions on the hydrogens. Increasing the size of the basis set beyond these basis sets becomes too demanding computationally at the MP2. level. The atomicspin populations computed using the Mulliken population analysis, and the numerical integration method, are included in Tables II and III, respectively.

A representation of Tables II and III results (see Figure 3) shows that the effect of improving the basis set is very small on all the atoms except the two NO groups and the C(sp^2) carbon, where most of the spin density is located. In the later group of atoms, the main effect is the internal contraction of the basis set (i.e., STO-3G versus D95V) and almost no effect is seen by improving the polarization part. The main effect of increasing the basis set quality is to make the spin on the N and O atoms similar, decreasing the spin polarization provided by the STO-3G basis set. The trend is the same for the UHF and MP2 methods, and is independent on whether the spin population was computed by the Mulliken or numerical integration methods. We would like to mention here that a similar trend was also reported in the literature for the UHF results of compound **1** computed using the 3-21G and 6-311G(d,p) basis sets. Although the results will not be discussed here, a similar trend is obtained using a truncated version of compound **1** where the two C(sp^3) atoms are substituted by hydrogen atoms (compound **2**). In this smaller molecule we have been able to carry out MP2 calculations using a near Hartree-Fock limit basis set, that is, a basis set which is capable of reproducing the analytical results for the UHF method. The results obtained in this system at the UHF and MP2 level indicate that the spin populations computed at the D95V(d) level are very close to these obtained with the near-Hartree-Fock limit basis (the variations are smaller than 0.1 for the C(sp^2) atom, which is also the most basis set dependent atomic spin population in compound **2**).

We have finished our study by looking at the effect on the atomic spin populations of substituting atom H_2 of compound **1** by a F, Cl, Br or I atom. We did the computation at the UHF and MP2 levels, using the D95V(d) basis set on the F-substituted compound. For the Cl, Br, and I compounds there is no D95V(d) basis set available in the literature. In consequence, we used basis sets of similar quality for them: the 6-31G(d) basis set for the Cl compound, and the LANL2DZ for the valence electrons of the Br and I compounds, in conjunction with effective core potentials for the core electrons.[16] All the computations were carried out at their optimum UHF geometry, computed using the same basis set employed for the spin calculations. The results

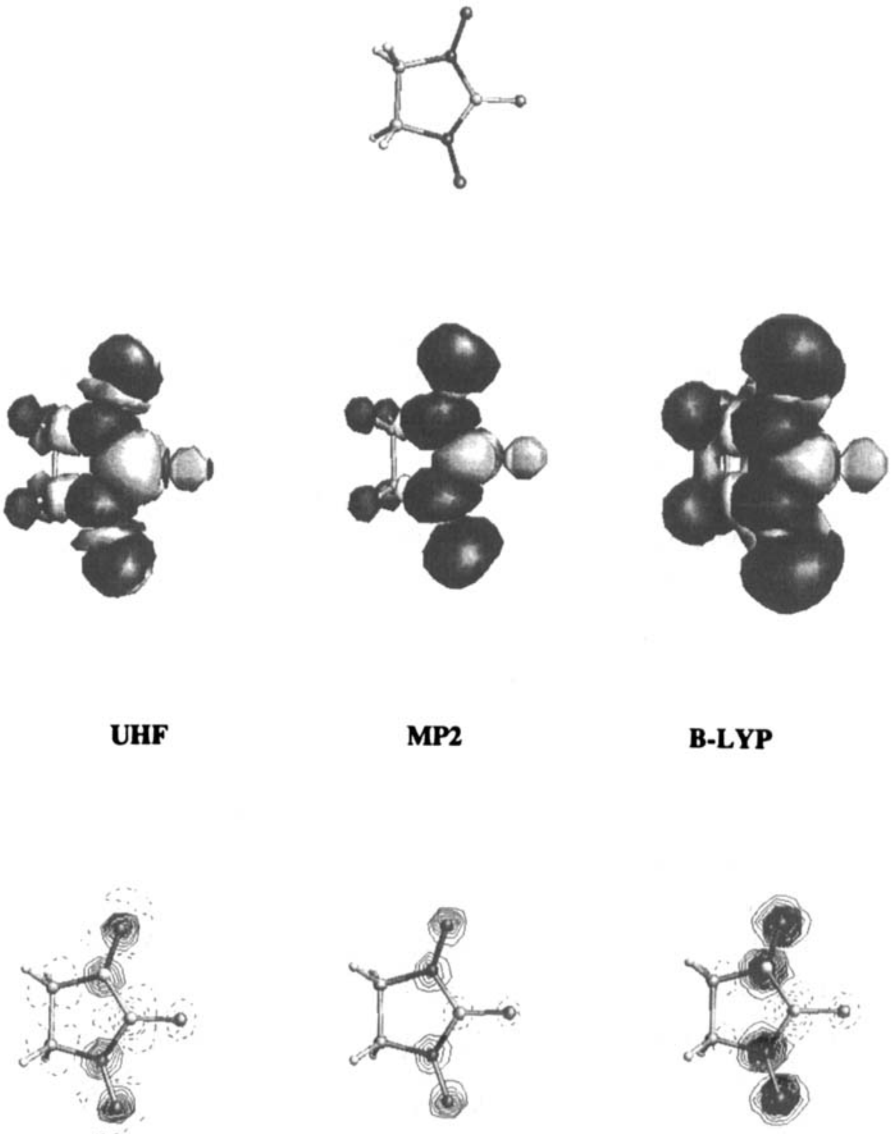

FIGURE 4 Distribution of the spin density for the F substituted form of compound 1. Its chemical structure is shown in the first row, the spatial distribution of the 0.001 (dark) and -0.001 (light) e/Å^3 contours is shown in the second row, and the counter map with the variation of the spin distribution in the O-N-C-N-O molecular plane (continuous dark lines = positive, broken dark lines = negative, lighter lines = zero; increment = 0.01 e/Å^3) is shown in the third row.

obtained using the Mulliken method are collected in Table IV. These results show that at the UHF level the C(sp^2) atom is strongly negative (all the values are close to -0.8) and the R atom slightly positive. However, when the electronic correlation is included the C(sp^2) atom strongly decreases its atomic spin population (it gets close to -0.3), while that on the R atom (R = F, Cl, Br, I) becomes, surprisingly, slightly negative, that is, of the same sign of the C(sp^2) atom to which it is linked. The negative spin density of the F atom is also clear after looking at the distribution of the spin density on the F-substituted molecule in Figure 4. Preliminary results on the phenyl, p-nitrophenyl, and p-hydroxyphenyl substituted α-nitronyl nitroxide radicals shown the same effect on the C atom of the six-member ring attached to the C(sp^2) atom of the five-member ring, so it seems to be a constant of the MP2 computations. Such behavior, however, is not reproduced by the B-LYP results. Further investigations are under progress at the moment.

TABLE IV Mulliken atomic spin populations for the substituted forms of compound 1 computed using the UHF and MP2 methods (first, and second row, respectively). R indicates the substituyent attached to the C(sp^2) atom.

R	Atom					
	R	C_2	N	O	C_3	H_3
H	0.08	-0.84	0.45	0.45	-0.06	0.02
	0.01	-0.34	0.33	0.33	-0.03	0.02
F	0.00	-0.70	0.43	0.43	-0.06	0.02
	-0.03	-0.21	0.29	0.32	-0.02	0.01
Cl	0.01	-0.78	0.42	0.47	-0.06	0.02
	-0.05	-0.28	0.33	0.31	-0.02	0.02
Br	0.07	-0.88	0.46	0.47	-0.06	0.02
	-0.06	-0.28	0.42	0.26	-0.04	0.02
I	0.07	-0.88	0.47	0.47	-0.07	0.02
	-0.06	-0.29	0.41	0.27	-0.04	0.02

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