

Short Communications

Influence of Spin Contamination and Basis Set on Electrostatic Potential and Hfs Coupling Constants of Organic Radicals

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Received November 14, 1975

Ab initio UHF wavefunctions for organic radicals have been obtained with different basis sets, before and after spin annihilation. It has been verified that the shapes of the electrostatic potential surfaces of these radicals are basis and spin contamination independent, at difference from hfs coupling constants.

Key word: Organic radicals

1. Introduction

The anion-cation interaction in ion pairs is generally weak, as shown by the ESR spectra of ion pairs obtained by reaction of organic substrates with alkali metals in solvents of low dielectric constant [1]. Since the electrostatic potential of the free radical anion is only slightly perturbed by the presence of the cation it can give information on the position of the metal around the anion.

In this view an *ab initio* UHF wavefunction, evaluated with a minimal basis set, has been previously [2-4] used to calculate the electrostatic potential surface [5]. It has been also verified [3] that the shape of the potential surface evaluated *in vacuo* is not significantly modified by the inclusion of the effect of solvents of low dielectric constant.

As the UHF wavefunctions are not eigenfunctions of S^2 , in this paper we study the influence of spin contamination on the electrostatic potential to ascertain its dependence on spin annihilation. The dependence of the same observable on the basis set is also investigated.

Experimental information about the structures of the ion pairs [2-4] has been obtained through ESR spectroscopy; then the present study has been extended to the calculation of hyperfine coupling constants of the magnetic nuclei present in the radicals, to verify the reliability of the hfs coupling constant values evaluated with the same wavefunctions.

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For purposes of comparison eight radicals have been treated: three, ethynyl, vinyl and formyl, are σ radicals; allyl is π radical and four, naphthalene, pyrazine, 4-nitropyridine and 4-nitropyridine N-oxide, are π anion radicals.

2. Method

The wavefunctions of the organic radicals have been evaluated by using the *ab initio* UHF method, adopting both a minimal STO-3G [6] and an extended 4-31G [7] basis set. The calculations have been performed by the "GAUSSIAN 70" program [8].

The experimental geometry has been used for formyl radical [9]. The experimental geometries of the parent neutral molecules have been adopted for pyrazine [10] and 4-nitropyridine N-oxide [11] radical anions. The geometries optimized through STO-3G minimal basis set have been assumed for ethynyl [12], vinyl [12] and allyl [13] radicals. Model geometries have been adopted for naphthalene ($\overline{CC} = 1.4 \text{ \AA}$, $\overline{CH} = 1.08 \text{ \AA}$, $\widehat{CCC} = \widehat{CCH} = 120^\circ$) and 4-nitropyridine [14] radical anions.

The quartet component of the UHF wavefunction has been annihilated with the single projection operator according to Amos and Sneyder [15, 16].

The density matrices computed before and after quartet component annihilation have been used to calculate the electrostatic potential surfaces, according to the method of Scrocco and Tomasi [5]. The hfs coupling constants have been evaluated by using the same density matrices.

3. Results and Discussion

The mean values of S^2 , before and after spin annihilation, of the UHF wavefunctions calculated with the minimal basis set are collected in Table 1. Calculations with the extended basis set have been performed only in the case of the four smallest radicals, and the corresponding $\langle S^2 \rangle$ values are collected in the same table.

The results show that the contamination is present at different degrees in all the considered radicals, and the single annihilation procedure does not always reduce

Table 1. Mean values of S^2 before (*sd*) and after (*aa*) quartet component annihilation on the minimal (STO-3G) and extended (4-31G) basis set

Radical	STO-3G		4-31G	
	$\langle S^2 \rangle_{sd}$	$\langle S^2 \rangle_{aa}$	$\langle S^2 \rangle_{sd}$	$\langle S^2 \rangle_{aa}$
Ethynyl	1.359	1.011	1.279	0.942
Vinyl	1.231	0.777	1.117	0.766
Allyl	1.072	0.770	0.984	0.760
Formyl	0.848	0.751	0.764	0.750
Naphthalene ⁻	0.880	0.764		
Pyrazine ⁻	0.824	0.751		
4-Nitropyridine ⁻	1.325	1.021		
4-Nitropyridine N-Oxide	1.276	0.963		

the contamination enough to give an almost pure doublet wavefunction. The use of the extended basis leads to a systematic, but slight improvement of S^2 mean value.

The high spin contamination of UHF wavefunctions might question their use in the calculation of potential surfaces. To this purpose the potential surfaces evaluated before and after quartet spin annihilation, have been compared. In the case of the four smallest radicals the comparison has been extended to the use of the different bases.

The data relative to ethynyl are shown in Figs. 1 and 2. In Fig. 1a the potential surface has been obtained by using a STO-3G wavefunction. The quartet component annihilation ($\langle S^2 \rangle_{sd} = 1.359$, $\langle S^2 \rangle_{aa} = 1.011$) changes the energy of the minimum by 1.5 kcal/mole, but it does not modify the shape of the surface: indeed the drawings of Figs. 1a and 1b are practically overlapping. When the extended basis set is used the same trend is found (see Fig. 2). It is noteworthy that the shape of the potential surface does not change on going from the minimal to the extended basis.

This kind of result has been found for all the considered radicals; the largest variation of the minimum energies obtained with the two bases, is about 20% (9 kcal/mole) in the case of the formyl radical. However the shape of the potential surfaces does not change; this behaviour is in line with the conclusion of other

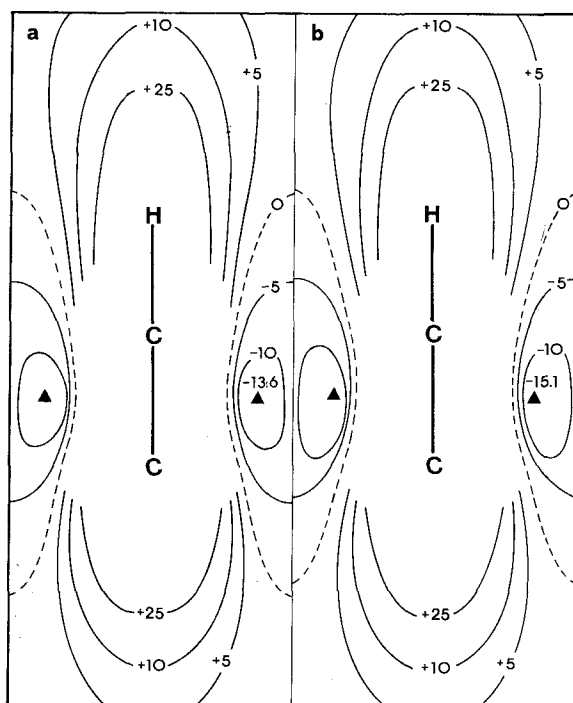


Fig. 1. Contour lines of the electrostatic potential of the ethynyl radical before (a) and after (b) quartet component annihilation: STO-3G basis set. \blacktriangle : minimum energy position

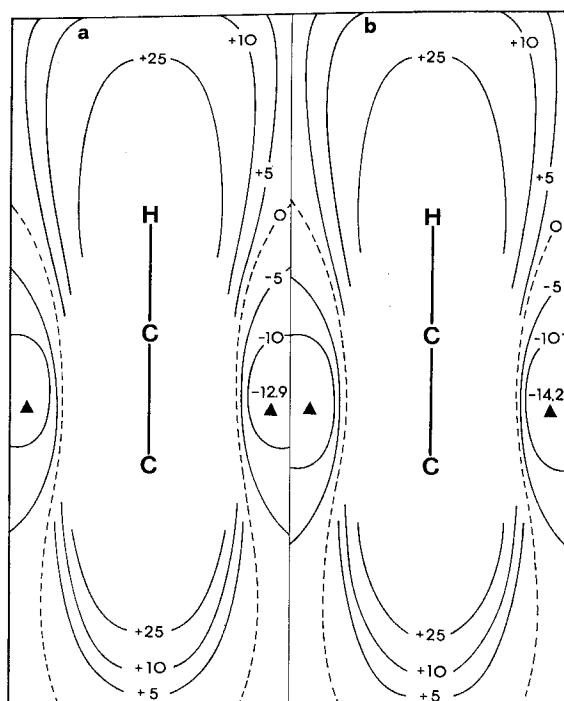


Fig. 2. Contour lines of the electrostatic potential of the ethynyl radical before (a) and after (b) quartet component annihilation: 4-31G basis set. ▲: energy minimum position

authors [5]. The shapes and the energy values are stable also on quartet component annihilation. In particular it is gratifying that when more minima are present, their relative order of stability is preserved, as in the case of 4-nitropyridine and 4-nitropyridine N-oxide radical anions [3, 4], where the stability inversion would not be consistent with the evidence given by their ESR spectra.

Calculated hfs coupling constants are collected in Table 2. Those relative to pyridine derivatives are not reported as in disagreement even qualitative with experimental ones. In the other cases the calculated values reproduce qualitatively the experimental values, even if their absolute values are strongly basis and spin contamination dependent. This fact is not surprising, because it reflects the present situation [26–35] in the calculation of this observable.

In conclusion it emerges clearly that the potential surfaces evaluated by using wavefunctions of this type, can be safely used to study the structure of complexes, in which these radicals are present. On the contrary the evaluation of spin distribution through the same wavefunctions is highly inadvisable.

Table 2. Hfs coupling constants (*gauss*) before (*sd*) and after (*aa*) quartet component annihilation on the minimal (STO-3G) and extended (4-31G) basis set

Radical	STO-3G		4-31G		Exp. <i>a</i>	Ref.
	<i>a_{sd}</i>	<i>a_{aa}</i>	<i>a_{sd}</i>	<i>a_{aa}</i>		
Ethyne						
H	71.41	29.37	73.43	29.30	15.7	[17]
C ^a	- 67.43	- 60.29	- 47.87	7.71	55.7	[17]
C	402.12	320.54	426.92	346.80	321.9	[17]
Vinyl						
H	- 33.51	10.00	- 22.73	8.61	16.0	[18]
H _{cis}	77.46	38.01	79.34	30.30	68.0	[18]
H _{trans}	54.12	23.98	58.01	26.65	34.0	[18]
C	235.97	166.60	223.14	158.19	107.5	[19]
C ^b	- 83.13	- 22.64	- 75.28	- 18.91	8.5	[19]
Allyl						
H	32.84	11.24	29.43	9.99	+ 4.06	[20]
H _{cis}	- 45.16	- 14.78	- 43.41	- 14.21	- 13.93	[20]
H _{trans}	- 45.40	- 14.86	- 43.77	- 14.33	- 14.83	[20]
Formyl						
H	106.77	93.34	139.70	111.46	137	[21]
C	172.24	169.15	145.24	150.98	137.4	[21]
Naphthalene ⁻						
H ₁	- 19.94	- 6.29			- 4.90	[22]
H ₂	- 0.35	- 0.11			- 1.89	[22]
C ₁	33.13	11.23			7.10	[23]
C ₂	- 5.95	- 1.98			1.20	[24]
Pyrazine ⁻						
H	- 1.71	- 0.56			2.64	[25]
C	- 6.85	- 2.25			2.88	[25]
N	13.56	4.58			7.18	[25]

^a C atom bonded to the H atom.^b CH₂ group carbon.

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