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Structure and magnetic properties of benzyl, anilino, and phenoxyl radicals by density functional computations

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A recently developed quantum mechanical approach devoted to the study of structural and magnetic properties of open-shell species was applied to the isoelectronic series formed by benzyl, anilino, and phenoxyl radicals. Hybrid Hartree–Fock/density functional models (here B3LYP) confirm their reliability, whereas, contrary to other cases, vibrational averaging and solvent effects play only a negligible role. The spin dependent properties are interpreted in terms of a new model including first and second order spin polarization effects. © 1998 American Institute of Physics. [S0021-9606(98)30346-3]

I. INTRODUCTION

Organic free radicals are generally short-lived, high reactive species, and the means of experimentally determining their structure and properties are therefore fairly limited. The most successful approach is based on electronic paramagnetic resonance (EPR) spectroscopy, which provides a direct experimental measure of the distribution of the unpaired spin density.^{1,2} Unfortunately, interpretation of these data are quite indirect since the measured quantities, essentially the hyperfine coupling constants (hcc's), result from the superposition of different contributions which are very difficult, if not impossible, to separate. In such circumstances, quantum mechanical approaches can offer a valuable support to experiment, especially when concurrent interpretations are possible or quantitative structure/observable relationships are sought. Of course, the computational model must provide reliable structural and magnetic properties, in particular for large systems which are of current chemical and biological interest. Furthermore, a successful theoretical method should allow an easy evaluation of the contribution of different terms to the overall result, through the switching of different interactions *on* and *off* in the computations.

In recent years it has been shown^{3–5} that hybrid density functional/Hartree–Fock (DF/HF) methods are quite promising in this connection, especially when coupled to a proper treatment of averaging effects issuing from large amplitude vibrations and of solvent effects.^{5–9} Starting from these results, we decided to perform a systematic study of the EPR features of the isoelectronic benzyl, anilino, and phenoxyl radicals. The interest of this series resides in the following points:

- (1) The dimensions of the three radicals approach the size of

radicals of biological interest. Furthermore, phenoxyl has a structure and spin density distribution similar to those of tirosyl radicals, recently detected in a number of proteins.^{10,11}

- (2) They are among the simplest examples of odd-alternant cyclic π radicals, where the disagreement between observed and semiempirically calculated hcc's led to the important concept of negative spin density.¹² Furthermore, the changes in the spin density distribution along the C_6H_5-X ($X=CH_2$, NH , O) series should be related to the electronegativity of the X substituents.
- (3) The benzyl radical has been observed in the gas phase,¹³ in aqueous solution,¹⁴ and trapped in solid matrices.¹⁵ In that case, it is interesting to verify if vibrational motion at the methylenic carbon and/or environmental effects play a significant role.

The most striking experimental observation is the nearly constant relative value of isotropic hcc's of ortho ($a(H_o)$), meta ($a(H_m)$), and para ($a(H_p)$) aromatic hydrogens along the whole series.¹⁶ In terms of the well-known McConnell relationship¹⁷ between hydrogen hcc's and spin populations of the carbon atoms to which they are bound, the above results suggest a nearly constant spin distribution in the aromatic ring irrespective of the X substituent. Moreover, early works^{12,16,18,19} predicted that spin populations at ortho- and para-carbon atoms should be negative, leading to positive hcc's on the corresponding hydrogen atoms. Just the opposite should occur at meta positions.

One of the goals of this paper is to gain some insights in the physics of these empirical correlations through proper computation of hcc's. From a more general point of view, through the description of these difficult systems we would give a flavor of the potential impact of quantum mechanical techniques in the characterization of large chemically-significant open-shell species.

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II. METHODS

Density functional calculations were carried out within the unrestricted Kohn–Sham (UKS) formalism, as implemented in the GAUSSIAN 94 code.²⁰ In particular, we have chosen the so called B3LYP computational model, a self-consistent hybrid approach²¹ obtained by a combination of HF and Becke exchange²² with the Lee, Yang, and Parr correlation functional.²³ The ratios of the different contributions are those optimized by Becke for a closely related, although not identical, functional.²⁴ This electronic method has been tested and validated in a number of studies on organic radicals.^{25,26}

The 6-31G(*d*) basis set has been our standard for all geometry optimizations, while the extended 6-311+G(2*d*,2*p*) basis set was used to check the convergence of the results.^{27–30} Improved magnetic properties were obtained by either the EPR2 or the EPR3 basis sets, which were specifically optimized for computing hcc's by DF methods.^{6,31}

Isotropic hyperfine coupling constants a_N are related to the spin densities at the corresponding nuclei by³²

$$a_N = \frac{8\pi}{3h} g_e \beta_e g_N \beta_N \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha-\beta} \langle \varphi_\mu | \delta(r_{kN}) | \varphi_\nu \rangle, \quad (1)$$

where β_e , β_N are the electron and nuclear magneton, respectively, g_e , g_N are the corresponding magnetogyric ratios, h is the Planck constant, $\delta(\mathbf{r})$ is a Dirac delta operator, and $P^{\alpha-\beta}$ is the difference between the density matrices for electrons with α and β spin. In the present work, all the values are given in Gauss (1 G=0.1 mT), assuming that the free electron g value is appropriate also for the radicals. To convert data to MHz, one has to multiply them by 2.8025. Vibrational averaging can be sometimes very important for an accurate computation of hcc's, since the spin density at some nuclei can change significantly even for motions of not too large amplitude. In the present work, the results have been averaged on the most important vibrational motions using the DiNa program developed by one of us,^{33,34} following the procedure illustrated in Refs. 25 and 31.

Solvent effects were evaluated by a modified version of GAUSSIAN 94 package, including a new effective implementation of the polarizable continuum model (PCM).^{35–38} In particular, optimized structures and solvation energies have been computed by a cavity model that has been recently introduced and validated,³⁷ namely the United Atoms model for Hartree–Fock (UAHF) computations coupled to the new Conductorlike Polarizable Continuum Model (C-PCM).³⁸ This approach provides results very close to those obtained by the original dielectric model^{35,36} for high dielectric constant solvents, but it is significantly more effective in geometry optimizations, and is less prone to numerical errors arising from the small part of the solute electron cloud lying outside the cavity (escaped charge effects).³⁸

III. RESULTS AND DISCUSSION

A. The phenoxyl radical

Among the radicals belonging to the isoelectronic series considered in the present paper, phenoxyl has been the object

of several vibrational spectroscopic and EPR investigations.^{16,39–47} At the same time a great theoretical effort has been done, using either post-HF (Refs. 48–54) or DF (Refs. 55–58) approaches, in order to describe the electronic structure and the harmonic frequencies of this radical. Less attention has been devoted to the spin-dependent properties (*vide infra*), which are more difficult to reproduce, because the phenoxyl radical is quite large, highly correlated and extensively delocalized.

An unconstrained geometrical optimization of the radical, carried out at the B3LYP/6-31G(*d*) level, leads to a C_{2v} structure, whose geometrical parameters are collected in Table I, whereas the atom labeling is reported in Fig. 1. Since our results are very close to those reported by Qin and Wheeler,⁵⁵ we refer the reader to that paper for a detailed discussion of the results. Here we simply underline the good agreement between the B3LYP/6-31G(*d*) geometry and that obtained at the CAS-SCF/6-311G(2*d*,*p*) level.⁵³ The only significant discrepancy concerns the CO bond length, whose DF value (1.258 Å) is 0.030 Å longer than the CAS result (1.228 Å).⁵³ However, this difference might be due to the choice of the active space in the CAS computations.⁵⁴

From another point of view, it is noteworthy that extension of the basis set up to the 6-311+G(2*d*,2*p*) level, does not introduce any significant variation in the geometries (see Table I), except for a slight shortening of all the bond lengths. The largest contraction involves the C_oC_m bond (−0.006 Å). Since our previous experience⁵⁹ indicates that this basis set gives converged geometrical parameters, we can conclude that the small 6-31G(*d*) basis set already provides reliable geometries for the phenoxyl as well as for the other radicals of the isoelectronic series. As a consequence, all the other geometrical optimizations will be carried out at this computational level.

Table II collects harmonic wave numbers, together with approximate assignments of the corresponding normal modes. A detailed analysis of the phenoxyl force field has already been reported,⁵⁵ so we only point out the good agreement between computed and observed experimental frequencies, the absolute mean error being 28 cm^{−1}. In particular, the largest deviation is found for all the modes involving the CC stretching, such as the $4a_1$ mode (1604 vs 1552 cm^{−1}, from our computations and experiment, respectively), or the $7b_2$ mode (1176 vs 1106 cm^{−1}). Moreover, the good agreement between experimental and quantum mechanical frequencies for the CO stretching (1498 vs 1505 cm^{−1}), strongly supports the reliability of the computed CO bond length. An even better accord is found between the scaled CAS-SCF/6-311G(2*d*,*p*) frequencies⁵³ and our unscaled results.

The hcc's for the 2B_1 electronic state of the phenoxyl radical are reported in Table III. Even if the interpretation of $\langle S^2 \rangle$ is not straightforward in the framework of the DF methods,⁶⁰ its value grossly indicate the extent of contamination by higher spin states. So the computed B3LYP/EPR2 value, $\langle S^2 \rangle = 0.787$, suggests that we are dealing with an essentially pure doublet state, pointing out to the reliability of the computed spin properties.

The EPR spectrum of phenoxyl has been studied in con-

TABLE I. Bond lengths (Å) and bond angles (deg) of X-C₆H₅ radicals. All the values are computed at the UB3LYP level.

	X=O (C_{2v})			X=NH ^a (C_s) vacuum	X=CH ₂ (C_{2v}) vacuum
	6-31G(<i>d</i>)	vacuum 6-311+G(2 <i>d</i> ,2 <i>p</i>)	Solution/ C-PCM 6-31G(<i>d</i>)	6-31G(<i>d</i>)	6-31G(<i>d</i>)
Ring-parameter					
C ^α X	1.258	1.253	1.262	1.341	1.407
C ^α C _{<i>o</i>}	1.452	1.449	1.453	1.435/1.434	1.427
C _{<i>o</i>} C _{<i>m</i>}	1.378	1.372	1.376	1.384/1.383	1.386
C _{<i>m</i>} C _{<i>p</i>}	1.410	1.406	1.411	1.405/1.405	1.403
C _{<i>b</i>} H	1.086	1.082	1.085	1.088/1.086	1.087
C _{<i>m</i>} H	1.087	1.082	1.084	1.087/1.087	1.087
C _{<i>p</i>} H	1.086	1.081	1.083	1.086	1.086
XC ^α C _{<i>o</i>}	121.43	121.40	121.33	124.79/117.80	121.39
C ^α C _{<i>o</i>} C _{<i>m</i>}	120.85	120.77	120.74	120.93/120.98	121.14
C _{<i>o</i>} C _{<i>m</i>} C _{<i>p</i>}	120.22	120.11	120.03	120.30/120.30	120.48
C _{<i>m</i>} C _{<i>p</i>} C _{<i>m</i>}	120.71	120.58	120.52	120.09	120.10
C ^α C _{<i>o</i>} H	117.03	117.15	117.51	118.59/117.21	118.70
C _{<i>o</i>} C _{<i>m</i>} H	120.29	120.26	120.28	119.95/120.00	119.71
C _{<i>m</i>} C _{<i>p</i>} H	119.65	119.76	119.69	119.91/120.01	120.21
substituent-parameter					
NH				1.029	
C ^α NH				108.95	
C [*] H					1.085
C ^α C [*] H					121.21

^aPairs of ortho and meta positions are no longer equivalent in the reduced C_s symmetry.

siderable detail and three different data sets are available for hydrogen hcc's.^{14,46,47} In this connection, a remarkable agreement between computed and experimental values is found, and the theoretical computations reproduce the alternation pattern characteristic of this kind of systems. In particular, the best agreement concerns $a(\text{H}_o)$, whose value is -7.3 G at the B3LYP/EPR2 level, whereas experimental

values range between -6.9 and -6.6 G.^{14,46,47} Slightly higher errors are found for $a(\text{H}_m)$ and $a(\text{H}_p)$. There is a significant difference between our results and those obtained by more conventional DF methods, whose values are underestimated by about 2 G (Ref. 57) as previously found for a number of other organic radicals.^{25,59} Although the oxygen hcc is not experimentally known for phenoxyl, our computed value is in remarkable agreement with that experimentally found for the closely related neutral tyrosyl radical in frozen solution (-9.6 G).⁶¹ Also in this case other functionals provide poor results.

From another point of view, the spin properties of the phenoxyl radical have been previously rationalized in terms of spin populations on the aromatic C atoms rather than in terms of spin densities at hydrogen nuclei (Fermi contact terms). In this connection, it must be recalled that hcc's are the only EPR observables, while spin populations can be only experimentally detected by neutron diffraction experiments (see for instance Ref. 62), which have, unfortunately, never been carried out for the phenoxyl radical. Although the well known McConnell equation¹⁷ connects the hcc of the hydrogen atom to the spin population of the adjacent C atom through an empirical parameter, its quantitative validity remains to be verified when comparing different positions of aromatic radicals. Very recently, the spin density distribution of the phenoxyl radical has been the subject of a detailed study⁵⁵ by Qin and Wheeler. These authors compared the computed para/ortho and para/meta ratios of the spin popu-

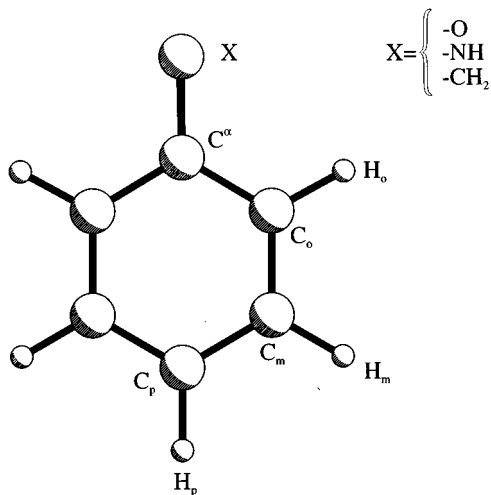
FIG. 1. Structure and atom labeling for the phenoxyl (X=O), anilino (X=NH), and benzyl (X=CH₂) radicals.

TABLE II. Harmonic wave numbers of the X-C₆H₅ radicals computed at the UBLYP/6-31G(d) level.

Approx. description	Sym	X=O Expt ^b	X=NH ^a Expt ^c	X=CH ₂	Expt ^d
<i>in-plane</i>					
(CH str)	<i>a</i> ₁	3223	3221	3215	
CH str	<i>a</i> ₁	3210	3211	3196	
CH str	<i>a</i> ₁	3188	3177	3182	
CC str	<i>a</i> ₁	1604	1552	1607	1560
CX str	<i>a</i> ₁	1498	1505	1326	1324
CH bend+CC str	<i>a</i> ₁	1433	1398	1377	1524
CH bend	<i>a</i> ₁	1175	1157	1179	1167
CH bend+ring def	<i>a</i> ₁	1018	1050	1035	1003
CCC bend	<i>a</i> ₁	986	990	991	996
ring def+CCC bend	<i>a</i> ₁	811	840	835	817
CCC bend	<i>a</i> ₁	531	528	535	533
CH ₂ str	<i>a</i> ₁				3175
CH ₂ bend	<i>a</i> ₁				1515
CH str	<i>b</i> ₂	3221	3197	3201	
CH str	<i>b</i> ₂	3195	3189	3184	
CC str+CH bend	<i>b</i> ₂	1565	1543	1587	1596
CH bend+CC str	<i>b</i> ₂	1458	1437	1489	1452
CC str+CH bend	<i>b</i> ₂	1352	1296	1357	1366
CC str+CC bend	<i>b</i> ₂	1289	1260	1197	1186
CH bend+CC str	<i>b</i> ₂	1176	1106	1182	1127
CH bend+CC str	<i>b</i> ₂	1098	1068	1097	982
CCC bend	<i>b</i> ₂	598	601	619	628
CX bend	<i>b</i> ₂	444	456	418	357
NH str	<i>b</i> ₂		3389		356
NH bend+CN str	<i>b</i> ₂		1507	1505	
CH ₂ str	<i>b</i> ₂			3269	
CC str+CH bend	<i>b</i> ₂			1347	
<i>out-of-plane</i>					
HCCH tor	<i>a</i> ₂	975	967	961	963
CH wag+ring def	<i>a</i> ₂	808	832	836	818
ring def	<i>a</i> ₂	381	390	393	356
CH ₂ tor	<i>a</i> ₂			504	
HCCH tor	<i>b</i> ₁	995	991	985	
CH wag+ring def	<i>b</i> ₁	922	909	897	860
ring def+CX wag	<i>b</i> ₁	796	779	774/703	
+CH wag					
ring def.+CH wag	<i>b</i> ₁	658	675	683	
ring def.+CX wag	<i>b</i> ₁	486	490	482	
ring def.+CX wag	<i>b</i> ₁	196	203	203	
NH wag			686		

^aIn the C_s point group, the in-plane modes belong to the *a'* representation whereas the out-of-plane modes belong to the *a''* representation.

^bReferences 41–43.

^cReference 75.

^dReference 65.

lations (ρ) on C atoms with the experimental derived ratios, evaluated starting from the observed hfs of the hydrogen atoms and applying the McConnell relationship. The experimental hcc ratios (obtained from the data of Ref. 46) are 1.5 for $a(\text{H}_p)/a(\text{H}_o)$ and 5.3 for $a(\text{H}_p)/a(\text{H}_m)$. The B3LYP/EPR2 computations provide a good value (1.3) for the first ratio, while a too low value (3.4) is found for the second ratio. The ratio obtained from the spin populations of carbon atoms (see Table IV) is very close for ortho and para atoms, whereas it is significantly different for the meta position. Thus the McConnell equation seems valid for the ortho and para hydrogens, while different results are found for the meta hydrogens. This discrepancy may be due to the different nature of the mechanism determining the spin distribution; a

first-order spin polarization mechanism for ortho and para atoms and a second-order spin-polarization for the meta atom (see below).⁶³

On the basis of the ratios between the spin population of carbon atoms, the authors of Ref. 55 concluded that the simplest DFT model [the so-called local spin density (LSD)] provides the best results for the phenoxyl radical. However, Table IV shows that this is an artefact, since the true hcc's computed at this level are very poor. This is also the case for UHF and UMP2 approaches, whereas BLYP and, especially, B3LYP functionals provide accurate values for isotropic hcc's.

Hyperfine coupling constants are sensitive to a number of different physical effects like vibrational averaging and polarization by the solvent.^{8,25} Concerning vibrational averaging we recall that, among low-frequency vibrations, only those involving out-of-plane distortions have a significant effects for π -radicals.²⁵ The influence of these motions on the hcc's can be efficiently monitored by considering the so-called distinguished coordinate (DC) approach,²⁵ in which all the other geometrical parameters are optimized at selected values of the out-of-plane displacement of the oxygen atom (τ , see Fig. 2). This displacement corresponds to a "soft" mode with harmonic frequency of 316 cm⁻¹ and an anharmonic constant of only 3 cm⁻¹. However, since for all the considered τ angles, the phenoxyl radical retains a C_s structure, characterized by an essentially planar arrangement of the aromatic ring, negligible effects (<0.1 G) are found for the hcc's of all the atoms.

From another point of view, the hcc's, evaluated at the the B3LYP/EPR2 level with solvent effects included by the C-PCM model, show a slight reduction (0.4–0.6 G), which is largest at the ortho position (0.6 G). Although this variation improves the agreement with the experimental data, it is sufficiently small to be neglected in the analysis of general trends and the same remark applies to the effect of geometry reoptimization in the presence of the solvent (see Tables I and III).

In summary, we can conclude that the reliable hcc's can be obtained at the B3LYP level by using the EPR2 basis set at geometries optimized *in vacuo* with the 6-31G(d) basis set since both vibrational averaging and solvent effects are negligible. Therefore this computational level will be used for the other radicals in the series.

B. The anilino and benzyl radicals

Starting from the previous analysis, we have next considered the other two isoelectronic radicals, with the aim of analyzing the effect of the X substituent on the molecular properties. The structure, spectroscopic, and magnetic properties of benzyl radical have been the object of several experimental studies,^{64–69} and some theoretical work has been also carried out.^{70–74} Comparatively less attention has been devoted to the anilino radical. To the best of our knowledge, only one experimental paper deals with the EPR spectrum of this radical,⁴⁶ and another one with its Raman spectrum.⁷⁵ Furthermore, no theoretical investigation has been carried out for the spin distribution of both radicals.

TABLE III. Hyperfine coupling constants (G) of the $X-C_6H_5$ radicals computed at the UB3LYP level, both *in vacuo* and in aqueous solution. The hcc's are evaluated using the EPR2 basis set at the 6-31G(d) geometries, unless otherwise noted.

Geometry	Wave function	$a(H_o)$	$a(H_m)$	$a(H_p)$	$a(H^a)$	$a(X^*)$
<i>phenoxyl</i> (2B_1)						
vacuum	vacuum	-7.3	2.8	-9.4		
vacuum	vacuum ^a	-7.2	2.8	-9.5		
vacuum	solution	-6.6	2.4	-9.9		
solution	solution	-6.6	2.4	-9.8		
expt ^{b,c}		6.9/6.6/6.7	1.9/1.9/1.8	10.1/10.2/10.1		
<i>anilino</i> ($^2A''$)						
vacuum	vacuum	-6.4/-6.6	2.7/2.8	-7.6	-14.3	7.2
vacuum	vacuum ^a	-6.4/-6.5	2.7/2.7	-7.8	-14.2	7.3
vacuum	solution	-6.4/-6.5	2.6/2.7	-7.5	-14.5	7.3
expt ^{b,d}		6.2	2.0	8.2	12.9	8.0
<i>benzyl</i> (2B_1)						
vacuum	vacuum	-5.7	2.4	-6.6	-17.0	21.8
vacuum	vacuum ^a	-5.7	2.4	-6.6	-17.0	21.7
vacuum	solution	-5.6	2.4	-6.6	-17.0	21.8
expt ^{b,d}		5.1/5.2	1.6/1.8	6.3/6.2	16.4/16.4	

^aEPR3 basis set.^bAbsolute values from Refs. 14, 45, 46.^cAqueous solution.^dAbsolute values from Ref. 46.

Let us look at the geometries of the two radicals, depicted in Fig. 1, and whose optimized B3LYP/6-31G(d) values are reported in Table I. As concerns the benzyl radical, the good agreement between our results and those obtained by large MC-SCF computations⁷¹ underlines, once again, the reliability of the B3LYP method in predicting the geometries of open-shell systems.

Starting from the phenoxyl radical, some trends in the geometrical parameters can be found as the electronegativity of X decreases (from O to CH₂). These variations concern the C ^{α} C_o and C_mC_p bonds, whose lengths decrease in going from phenoxyl to benzyl. In particular, the C ^{α} C_o length decreases from 1.452 Å in phenoxyl to 1.427 Å in the benzyl radical. Smaller variations are found for the C_oC_m bond distance (1.378–1.386 Å).

As expected, vibrational frequencies involving the modes characteristic of the six-membered ring reflect the larger aromaticity of benzyl with respect to phenoxyl radical. Since no significant mixing is observed between the vibra-

tional modes of the ring and those characteristic of the substituents (except, of course, for C₆H₅–CH₂), these relationships are quite apparent. Furthermore, the same assignments of phenoxyl can be used for the ring modes of the other two radicals. In particular, the frequencies of all the in plane modes involving a CC stretching (e.g., the 4a₁ or the 3b₂ mode) or CCC bending (e.g., 9a₁) slightly increase along the series (see Table II). Anyway, the largest variations (about -20 cm⁻¹) are found for the CH stretchings. As concerns the out-of-plane modes, a weakening of the HCCH torsional modes is found (about -12 cm⁻¹), together with an increase of the CH wagging frequencies.

The reliability of our computations is confirmed by comparison with the available experimental data for the benzyl radical,⁶⁵ where a remarkable good agreement (mean absolute error=21 cm⁻¹) is found. In a similar manner, a deviation of 19 cm⁻¹ is obtained for the anilino radical. Here, however, the assignement of the computed harmonic frequencies with respect to the experimental data⁷⁵ can be done

TABLE IV. Isotropic hyperfine coupling constants (a, G) and Mulliken atomic spin populations (ρ) obtained for the phenoxyl radical by different methods. The values in parentheses are the ratios between the value obtained for the para position and that of the actual position.

	LSD ^a	BLYP ^a	B3LYP ^a	UHF ^b	UMP2 ^b	Expt ^c
$a(O)$	-0.19	-5.72	-9.28	-36.53	-10.28	9.6
$a(H_p)$	-5.92	-8.05	-9.40	-28.23	-3.67	10.1
$a(H_m)$	-4.33 (1.4)	-5.94 (1.4)	-7.27 (1.3)	-27.37 (1.0)	-6.95 (0.53)	6.7 (1.5)
$\rho(C_p)$	0.36 (-16.4)	1.44 (-5.6)	2.85 (-3.3)	23.57 (-1.2)	0.08 (-47.1)	1.9 (5.3)
$\rho(C_b)$	0.320	0.341	0.384	0.828	0.335	
$\rho(C_m)$	0.229 (1.4)	0.250 (1.4)	0.295 (1.3)	0.782 (1.1)	0.221 (1.5)	
	-0.055 (-5.8)	-0.083 (-4.1)	-0.141 (-2.7)	-0.709 (1.2)	-0.066 (-5.1)	

^aEPR2 basis set.^bD95(d, p) basis set.^cAbsolute values from Refs. 14, 45, 46, 61.

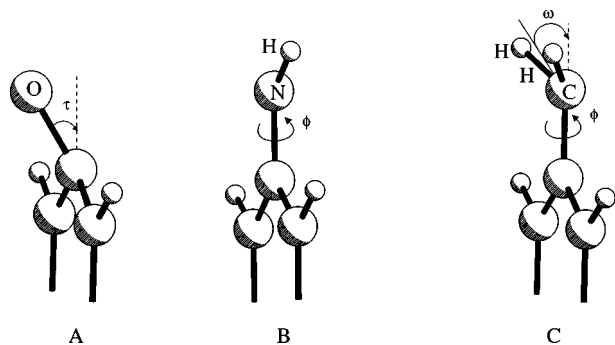


FIG. 2. The distinguished coordinates considered in vibrational averagings. (A) phenoxyl; (B) anilino; and (C) benzyl.

without any particular problem for all normal modes except one. In particular, a detailed analysis of the computed spectrum shows that the mode at 1326 cm^{-1} should correspond to a CN stretching rather than to a CC stretching, as suggested in Ref. 75. Although the lack of further experimental information does not allow to definitely solve the problem, our assignment is consistent with the observed decreasing of the CX stretching frequencies in going from phenoxyl [$\nu(\text{CO})=1498\text{ cm}^{-1}$] to benzyl [$\nu(\text{C}-\text{CH}_2)=1299\text{ cm}^{-1}$] and with the vibrational spectrum of the aniline radical cation.⁷⁶

Table III collects the hcc's of the anilino and benzyl radicals, computed at the UB3LYP level, using the EPR2 basis set and 6-31G(*d*) geometries. As a first general remark, we can observe for both radicals the same good overall agreement with the few available experimental data already found for phenoxyl. In going from phenoxyl to anilino and to benzyl a progressive decreasing of the spin density at H_o and H_p is observed. In contrast, the spin density at the meta hydrogen is roughly constant along the series.

Both geometrical and spin-density trends can be rationalized in terms of the relative weights of the different electronic resonance structures depicted in Fig. 3. In particular, our computations strongly suggest an increased weight of the resonance structure A in going from phenoxyl to benzyl radicals. Structure A is characterized by an aromatic ring with a single C^aCX bond, whereas structures B and C have single C^aC_o and C_mC_p bonds, respectively. The same effects are at work for the spin densities of the H_o and H_p atoms, since the stabilization of structure A induces an increase of the spin density on the X substituent, whereas structures B and C have a larger spin density delocalized over the pseudoaromatic ring. Since no resonance structure allows for a direct spin localization on the meta carbon, more subtle mecha-

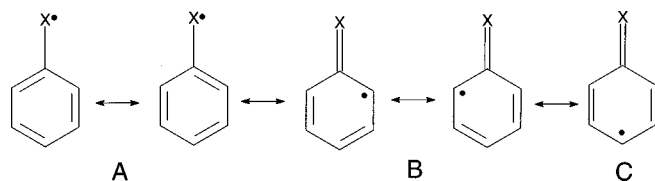


FIG. 3. The three electronic resonance structures governing the molecular properties of the whole isoelectronic radical series.

nisms are responsible for the positive spin density on H_m (see below).

The natural resonance theory (NRT) (Refs. 74,77,78) allows a more quantitative analysis of the contributions of different resonance structures (see Fig. 3) to the molecular geometries and properties. The results show that the weight of structure A increases in going from phenoxyl (32.6%) to benzyl (35.2%), while the weight of the other resonance structures (B and C) decreases. For instance the weight of the structures B is 30.6% in the phenoxyl radical and only 21.4% in benzyl, with an intermediate value (28%) in the anilino radical. Similar conclusions can be drawn in terms of three electron–three orbital interactions (see below).

Even if the hcc's of the phenoxyl radical are not significantly modified by introducing a continuum solvent model (see Table III) and by vibrational averaging effects, previous experience on the related aniline radical cation ($\text{X}=\text{NH}_2$) (Ref. 76) induced us to investigate both effects on the anilino and benzyl radicals. We have explicitly considered the out-of-plane motions involving the hydrogen atoms of the substituent (NH for anilino and CH_2 for benzyl radical). In particular, we have chosen as DC the rotation of the NH group around the C^aN bond (ϕ in Fig. 2) for the anilino radical. Along this path we found a first order saddle point, 15.5 kcal/mol higher than the planar arrangement, characterized by a C_s symmetry with the torsional angle ϕ equal to 90.0° and the HNC angle equal to 71.6° . The high barrier governing the rotation strongly suggests that no averaging effects are at work along this coordinate.

The situation is more involved for the benzyl radical, since two displacements might have a significant influence on the observed hcc's; the rotation of the methylenic group around the C^aC bond and the out-of-plane displacement of the hydrogens belonging to the X substituent. Although the computed energy barrier governing the internal rotation is significantly smaller than that previously obtained at the HF/3-21G level⁷¹ (16.6 vs 20.0 kcal/mol), it remains sufficiently high to introduce at most negligible averaging effects. On the other hand the out of plane motion of the hydrogen atoms (τ in Fig. 2) is relatively “soft,” the harmonic wave number being 668 cm^{-1} , and the anharmonic correction only 2 cm^{-1} . The vibrational averaging effect of this motion is negligible for the hcc's of the C and H atoms belonging to the ring, but increases the static value of $a(\text{C})$ by 3.5 G (from 21.8 to 25.6 G), i.e., by about 15%. This effect should be detectable by ^{13}C experimental analysis, but, at the best of our knowledge, this aspect has been never investigated. At the same time, the effect on methylenic hydrogens (H^α), although not very large (0.7 G), improves the agreement with the experimental value.

As concerns the influence of the solvent, all the hcc's are not significant modified by introducing a continuum model (see Table III), this behavior being in striking contrast with that of the related aniline cation radical in which significant variations are found for all the hcc's. For instance, the absolute value of $a(\text{H}^\alpha)$ increases by about 2 G (from -9.6 to -11.7 G) in going from vacuo to aqueous solution.⁷⁶

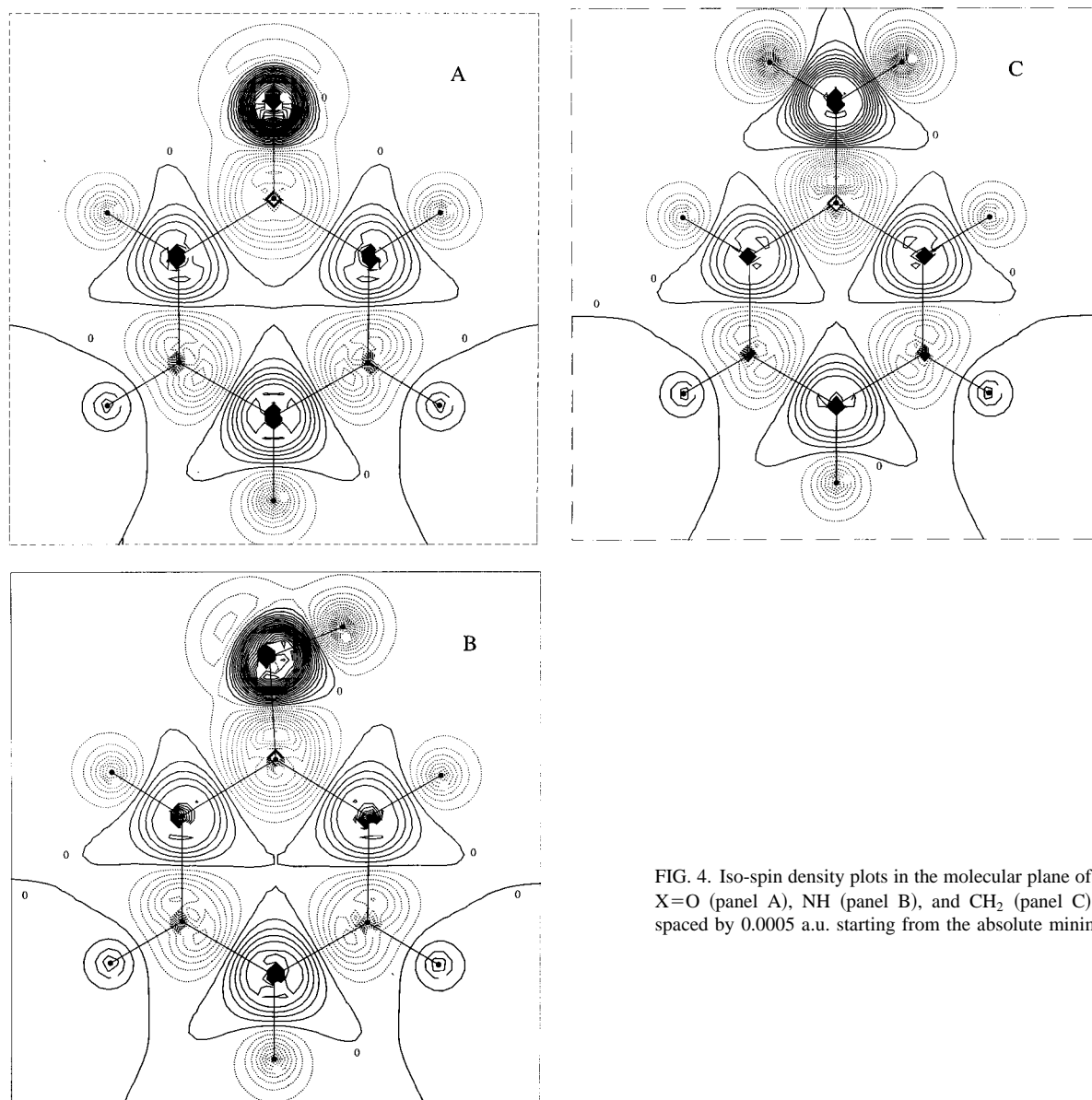


FIG. 4. Iso-spin density plots in the molecular plane of C_6H_5X radicals with $X=O$ (panel A), NH (panel B), and CH_2 (panel C). Contour levels are spaced by 0.0005 a.u. starting from the absolute minimum on the X atom.

C. Trends in the magnetic properties

The good agreement between computed and experimental hcc 's suggests that the B3LYP computational model is able to correctly reproduce the characteristics of the spin distribution in the whole series of the odd-alternant cyclic π -radicals including the occurrence of negative spin densities on H_o and H_p .

As mentioned above, and in agreement with the conclusion given in an early work on benzyl and phenoxy radicals,¹⁴ the ratio $a(H_o)/a(H_p)$ is roughly constant in the whole series. The general trend for the aromatic hydrogen hcc 's is always $|a(H_p)| > |a(H_o)| > |a(H_m)|$, the absolute values of all the spin densities being increased by more electronegative X substituents. This effect is more pronounced at the ortho and para hydrogens than at the meta positions.

The spin densities in the molecular planes of the three radicals are shown in Fig. 4. Their analysis depends on the way the wave function is built. In a restricted formalism, the spin densities can be decomposed into three contributions; a

delocalization or direct term, which is always positive (or null), a spin polarization or indirect term,⁷⁹ which arises from a configuration interaction limited to monoexcited states,⁸⁰ and a true correlation term (neglected in the following qualitative analysis), originating from the contribution of higher excited configurations. The spin polarization term takes into account the fact that the unpaired electron interacts differently with the two electrons of a spin-paired bond, since the exchange interaction (which reduces the Coulomb repulsion) is operative only for electrons with parallel spins.⁸¹ This induces a shorter average distance between parallel electrons than between antiparallel ones, leading to the spin polarization pattern sketched in Fig. 5. The sign of spin polarization has been shown to follow a number of general rules, at least for hydrocarbon radicals.⁸⁰ Within such a formalism, the molecular plane is the nodal plane of the singly occupied molecular orbital (SOMO) and the only contribution to spin densities at nuclei comes from the indirect (spin polarization) contribution. As mentioned above, a qualitative

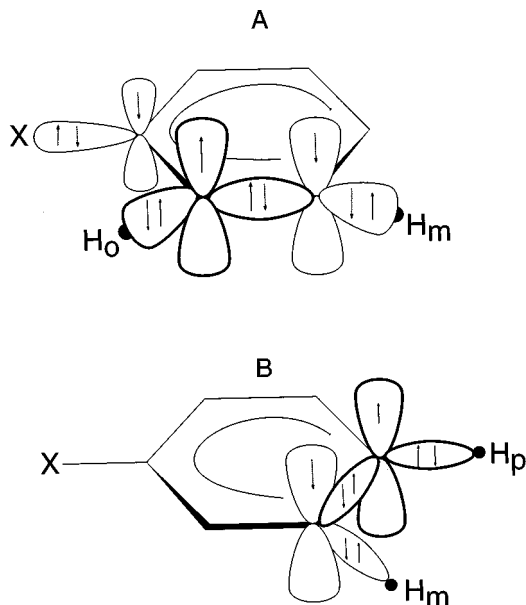


FIG. 5. Schematic drawing of the first- and second-order spin polarization induced by ortho (upper panel) and para (lower panel) carbon atoms.

relationship was proposed^{12,79} between the hcc of aromatic protons and the spin populations (in the Mulliken sense) of carbon atoms to which they are bound. Such a relationship converts the spin population due to delocalization (direct effect) into spin polarization (indirect effect). Furthermore, we propose a further decomposition of spin polarization into “first-order” and “second-order” contributions. The first order contribution is the positive spin density induced at the nucleus bearing the π -spin population and the negative spin density induced at atoms in α -positions (either hydrogen or carbon atoms). The second order contribution is the positive spin density induced at atoms in β -position (see Fig. 5). Of course the spin density due to second-order terms will be smaller than the first-order one.

In order to separate the delocalization contribution we have performed ROB3LYP computations which include only this term. It is quite apparent that the SOMO (shown in Fig. 6) is mainly localized on ortho and para carbon atoms, leading to large π -spin populations on these atoms, which induce large positive spin densities at the corresponding nuclei and negative “short-range” hcc’s at ortho and para hydrogens.

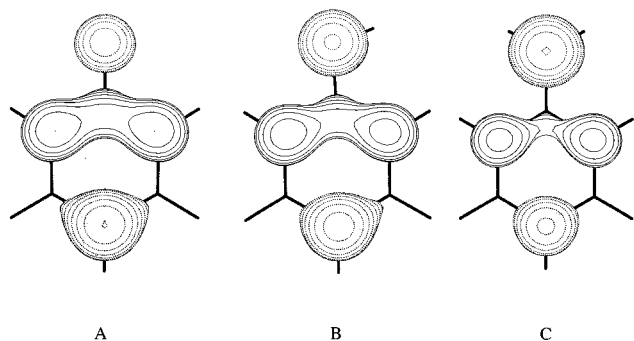


FIG. 6. Schematic drawing of the SOMO of C_6H_5X radicals with $X=O$ (panel A), NH (panel B), and CH_2 (panel C).

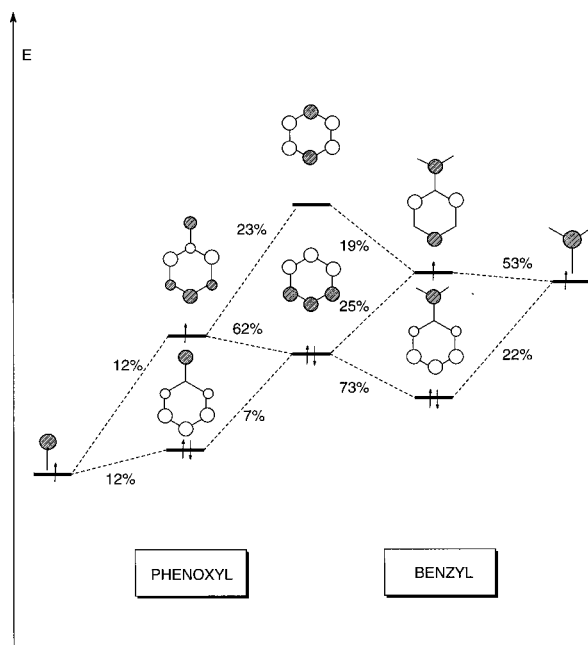


FIG. 7. Schematic interaction diagrams for the three-electron/three orbital interaction in phenoxy and benzyl radicals.

Going further in the analysis, the positive spin population at the ortho carbon atom induces a weak, positive, second order spin density at the meta hydrogens (Fig. 5). The same mechanism is operative for the para carbon atom leading to a further positive contribution to the meta hydrogen. As a consequence the meta hydrogens shows a non-negligible positive spin density resulting from cumulative second-order effects.

The shape of the SOMO (Fig. 6) can be qualitatively interpreted in terms of orbital interactions^{82,83} between the matching π orbitals of the phenyl fragment and the singly occupied p -AO of the exocyclic substituent (Fig. 7). In the case of benzyl ($X=CH_2$), which is the reference radical in the following analysis, the methylene group interacts almost equally with the π and the π^* orbitals of the phenyl fragment. This three-electron three-orbital interaction results in a single occupied π MO bearing important coefficients on ortho and para carbons on the benzene ring and on the exocyclic carbon atom. When the electronegativity of X increases, the interaction of the X fragment with the π doubly occupied MO (DOMO) of the phenyl fragment increases, thus the main orbital character in the SOMO is contributed by the benzene ring DOMO, while the coefficient of X in the SOMO decreases. These results are easily verified, on inspection of the interaction scheme shown in Fig. 7 and confirmed by the results of B3LYP calculations. This leads to an increased direct contribution to spin populations, not only on ortho and para carbon atoms, but also at meta positions. As a result one obtains at the same time enhanced second-order positive and first-order negative spin densities at meta hydrogens. In conclusion the hcc’s of ortho and para hydrogens increase with the electronegativity of the exocyclic substituent, whereas the hcc’s of meta hydrogens remain roughly

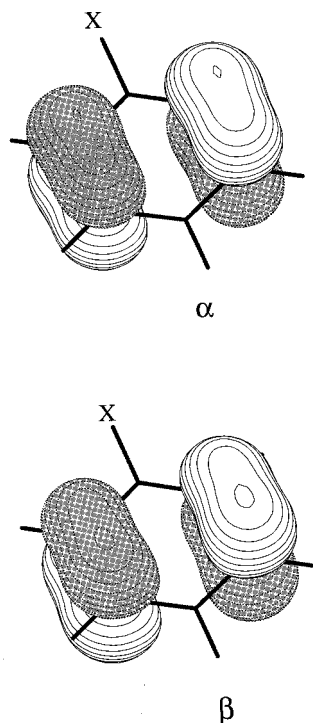


FIG. 8. Higher occupied α (upper panel) and β (lower panel) spin orbitals of B1 symmetry.

constant due to the compensation of positive and negative variations along the series.

The McConnell relationship can be strictly applied only to first-order spin polarization effects and this explains (Table IV) the success of that relationship when predicting $a(H_p)/a(H_o)$ ratios in good agreement with complete computations and with experiment. By contrast, the McConnell relationship cannot be applied directly for the spin density at meta hydrogens which originates from a more subtle mechanism; this explains the large difference between the ratios of carbon spin populations and those of hydrogen hcc's.

Let us now examine the unrestricted wave function. The results given in Table IV reveal negative spin populations at meta carbon atoms. This results from the fact that spin polarization is directly taken into account in the computation, together with delocalization. However, unrestricted spin orbitals generally overestimate this term, due to contamination by higher spin states. Although the unrestricted Kohn–Sham (UKS) approach is much less prone to spin contamination than UHF, some residual overestimation of second-order effects could explain why the computed hcc's at meta hydrogens are slightly larger than their experimental counterparts.

The polarization effects are well evidenced by the different shapes of the higher occupied α and β spin orbitals (Figs. 8 and 9). In particular, the spin orbitals of Fig. 8 show the accumulation of negative (β) spin population on meta carbon atoms, which increases in going from benzyl to anilino and phenoxyl radicals. This accumulation (a first order effect) increases the spin population on the meta hydrogen, through a second order mechanism. The spin orbitals of Fig. 9 illustrate, instead, the accumulation of negative (β) spin density

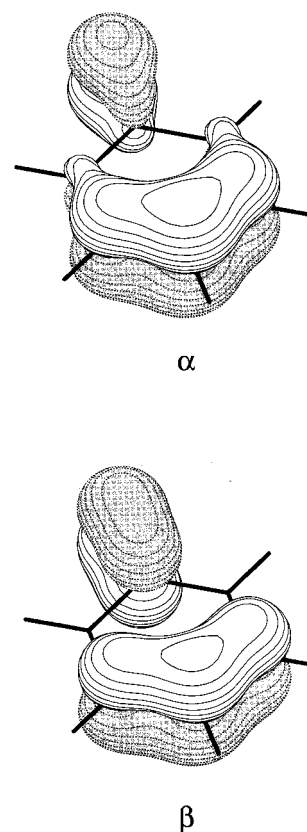


FIG. 9. Higher occupied α (upper panel) and β (lower panel) spin orbitals of A2 symmetry.

on C_α , which follows the opposite trend in going from benzyl to anilino radical.

IV. CONCLUDING REMARKS

The results presented in this paper call for the following general remarks:

- (1) The isoelectronic series of the simplest odd-alternant cyclic π -radicals presents a general feature, predicted by the earliest papers,^{12–17} i.e., the occurrence of negative spin densities on free radicals, confirmed experimentally by neutron diffraction investigation⁷² and whose importance has increased in the interpretation of molecular magnetism.^{84,85} There is an alternation in sign of the hcc's around the aromatic cycle, whatever the nature of the substituent.
- (2) When the electronegativity of X increases, the spin density at the exocyclic group decreases and the delocalization on the aromatic ring increases. This can be simply interpreted in terms of fragment orbitals.
- (3) The hcc's of the ortho and para hydrogens are well predicted by theoretical computations, the difficulty encountered for meta hydrogens being probably related to an “excess” of spin polarization.
- (4) Neither solvent effects nor vibrational averaging influence the EPR features of this class of radicals in a significant way.

From a more general point of view spin populations (in the Mulliken sense) are very useful in the analysis of the mechanism of spin propagation along the molecular backbone, but cannot be used without caution for the analysis of hyperfine coupling constants. On the other hand, direct computation of spin densities at nuclei (Fermi contact terms) leads to hyperfine coupling constants in excellent agreement with experiment, but the results can be analyzed in chemical terms only with care.^{80,84} Thus, thanks to the reliability and favourable scaling of hybrid HF/DF methods, completely *a priori* studies of aromatic π radicals appear now feasible for quite large systems. They offer a powerful additional tool for interpretation of magnetic properties especially when only partial experimental data are available or concurrent interpretations are possible.

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