Theor Chem Acc (2000) 104:207–209
DOI 10.1007/s002140000132

Theoretical
Chemistry Accounts

Regular article

The mechanism of spin polarization in aromatic free radicals

Carlo Adamo[1], **Vincenzo Barone**[2], **Robert Subra**[3]

[1]Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, 85100 Potenza, Italy
[2]Dipartimento di Chimica, Università "Federico II", via Mezzocannone 4, 80134 Naples, Italy
[3]Laboratoire d'Etudes Dynamiques et Structurales de la Selectivite (LEDSS), Université J. Fourier, 301 avenue de la Chimie, BP 53X, 38041 Grenoble Cedex 9, France

Received: 17 September 1999 / Accepted: 3 February 2000 / Published online: 29 June 2000

Abstract. The spin-polarization mechanism in aromatic systems is analyzed with reference to the prototypical phenoxyl, cyclohexadienyl and benzyl radicals. In particular, a decomposition into "first-order" and "second-order" contributions is proposed, which helps to rationalize the different nature of the spin density for atoms in α or in β positions with respect to the radical center. The different weights of the two contributions are discussed on the basis of Hartree–Fock and density functional computations.

Key words: Spin polarization – Density functional theory – Hyperfine coupling constants

Aromatic free radicals fulfill an essential role in several biological processes [1, 2]. For instance, the tyrosyl radical has been detected in a number of enzymes, such as ribonucleotide reductase [1, 3], whereas radiation damage of DNA bases produces, inter alia, radicals arising from the addition or elimination of hydrogen [2, 4]. The most direct experimental tool for the investigation of these unstable species is provided by electron spin resonance (ESR) spectroscopy, whose direct outcomes are, in most cases, the isotropic hyperfine coupling constants (hcc) of protons, either in model compounds or in true biologically active systems. Well-known empirical relationships [5, 6] are used to relate hydrogen hccs to the spin populations of adjacent carbon atoms, which are, in turn, powerful structural probes. This procedure is still widely applied in the interpretation of ESR spectra [7, 8], although it leads in some cases (e.g. meta hydrogens of aromatic radicals) to very disappointing results [9].

The whole model is rooted in the concept of spin polarization, which was proposed in the early publications on ESR in order to explain the hccs in aromatic free radicals [5, 6]. This concept was later extended to aliphatic radicals [10] and has received more attention recently, as well in the field of molecular magnetism [11] as in polarized neutron diffraction (PND) experiments [12]. A general relationship was proposed [6] between the hcc a_{H}, due to an aromatic proton, and the "unpaired electron density" (a gross atomic spin population in the Mulliken sense [13]) $n^{\mathrm{u}}(\mathrm{C})$ of carbon atom, C, directly bonded to the proton

$$a(\mathrm{H}) = Qn^{u}_{\mathrm{C}} \tag{1}$$

The questions we wish to develop are the following. Under what circumstances is it possible to correlate the spin population on a carbon atom and the spin density on the hydrogen directly bonded to it? Is it possible to develop a qualitative model allowing a simple prediction of the spin distribution in a radical, in sign and magnitude? In the case of aromatic radicals, is it possible to explain the different behavior between ortho and para atoms, on the one hand, and meta atoms, on the other?

The spin density, $\rho^{u}(\boldsymbol{r})$, computed at each point, $\boldsymbol{r}$, of the space, can be decomposed into a direct or delocalization contribution due to the nominally singly occupied molecular orbital (SOMO), $\rho^{u}{}_{\mathrm{SOMO}}(\boldsymbol{r})$, and a spin-polarization or indirect contribution, $\rho^{u}_{\mathrm{SP}}(\boldsymbol{r})$, coming from correlation effects [3]. Only the first term is present in restricted open-shell computations, whereas spin polarization (together with other dynamic correlation effects) is simply the difference between the total spin density and the corresponding restricted open-shell value. The integration of $\rho^{u}(\boldsymbol{r})$ over the whole space gives the saturation magnetization, which is equal to $1N\beta$ for an organic radical. The molecular space is usually divided in atomic regions and the integration of the spin density over these regions gives the atomic spin populations, $n^{u}(\mathrm{N})$, around a given nucleus, N. PND studies provide an experimental measurement of these populations [15] and offer an efficient tool for spin density analysis. More precisely, they can be used to measure microscopic distributions of spin densities and, in contrast to ESR techniques, which are restricted to atomic

---

Correspondence to: C. Adamo
e-mail: adamo@chemna.dichi.unina.it

Table 1. Isotropic hyperfine coupling constants (a, in gauss) and Mulliken atom spin populations (n^u) for the phenoxyl, benzyl and cyclohexadienyl radicals obtained by different methods. The restricted open shell (ROB3LYP) values are reported in *parentheses*. All calculations were carried out using the UB3LYP/6-31G(d) geometries and the EPR2 basis set (UB3LYP and ROB3LYP) or the D95(d,p) basis set (UHF)

	Phenoxyl			Benzyl			Cyclohexadienyl		
	UHF	UB3LYP	Exp[a]	UHF	UB3LYP	Exp[a]	UHF	UB3LYP	Exp[a]
$a(\mathrm{H}^{\alpha})$							55.5	53.3	47.7
$a(\mathrm{H_p})$	−28.2	−9.4	10.1	−26.2	−6.6	6.3	−32.8	−12.5	13.0
$a(\mathrm{H_o})$	−27.4	−7.3	6.7	−26.1	−5.7	5.1	−30.8	−9.5	9.0
$a(\mathrm{H_m})$	23.6	2.9	1.9	23.0	2.4	1.6	22.9	3.4	2.7
$n^u(\mathrm{C}^{\alpha})$							−0.207	−0.062 (0.013)	
$n^u(\mathrm{C_p})$	0.598	0.333 (0.235)		0.554	0.229 (0.061)		0.682	0.470 (0.401)	
$n^u(\mathrm{C_o})$	0.579	0.263 (0.176)		0.549	0.196 (0.049)		0.635	0.358 (0.244)	
$n^u(\mathrm{C_m})$	−0.504	−0.115 (0.0)		−0.494	−0.093 (0.0)		−0.508	−0.145 (0.0)	

[a] Only absolute values are obtained from electron paramagnetic resonance spectra

sites, they are itinerant probes, giving information on spin density in any given region of the space.

The hcc a_{H} can be obtained through ab initio calculations of the Fermi contact term, $\rho^u(\boldsymbol{r}_{\mathrm{H}})$, which is a spin density, at the hydrogen nucleus by

$$a(\mathrm{H}) = \frac{8\pi}{3h} g_{\mathrm{e}}\beta_{\mathrm{e}} g_{\mathrm{N}}\beta_{\mathrm{N}} \left[\rho^u_{\mathrm{SOMO}}(\boldsymbol{r}_{\mathrm{H}}) + \rho^u_{\mathrm{SP}}(\boldsymbol{r}_{\mathrm{H}})\right] \ , \qquad (2)$$

where β_{e} and β_{N} are the electron and nuclear magneton, respectively, g_{e} and g_{N} are the corresponding magnetogyric ratios and h is the Planck constant[1].

We will consider the following aromatic radicals: phenoxyl (C_6H_5O), cyclohexadienyl (C_6H_7) and benzyl ($C_6H_5CH_2$). The first radical can be considered as the simplest model of the tyrosyl radical, whereas the other two are representative of the products obtained from the elimination and the addiction of a hydrogen atom to DNA bases [4]. Density functional (B3LYP) and Hartree–Fock (HF) computations were carried out by both restricted open-shell and unrestricted (U) formalisms, as implemented in the Gaussian 98 code [16].

The direct contribution, $\rho^u{}_{\mathrm{SOMO}}(\boldsymbol{r})$, is always positive or zero, as can be easily seen from the computed hccs of the H^{α} in the C_6H_7 radical (Table 1). Since this contribution depends only on the SOMO, it is not surprising that very close results are obtained at the UHF and at the UB3LYP level.

The indirect term, $\rho^u{}_{\mathrm{SP}}(\boldsymbol{r})$, takes into account the fact that the unpaired electron interacts differently with the two electrons of a σ spin-paired bond or inner shell, since the exchange interaction (which reduces the Coulomb repulsion) is operative only for electrons with parallel spins. This induces a shorter average distance between electrons with parallel spins than between electrons with antiparallel spins, leading to the spin-polarization pattern sketched in Fig. 1. As the molecular plane of a π radical is the nodal plane of the SOMO, the spin density (Fermi contact term) is obviously zero on any atom of the molecular plane. The observed hccs (Table 1) are thus induced by spin polarization of the inner shells or σ bond orbitals [14]. The symmetry of the radicals implies that the unpaired electron is mainly delocalized on ortho and para carbon atoms, leading to large positive π spin densities around these atoms, the largest fraction of unpaired electrons being at the para carbon. This effect is well underlined by the atomic populations obtained by restricted open-shell computations (Table 1).

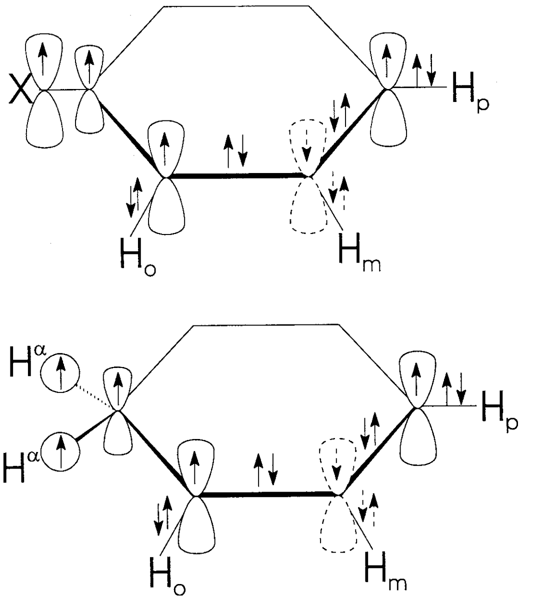

Fig. 1. Schematic drawing of the first-order (*continuous line*) and second-order (*dashed line*) spin-polarization mechanism. The *upper drawing* refers to the phenoxyl (X=O) and benzyl (X=CH_2) radicals, whereas the *lower drawing* illustrates the polarization mechanism in the cyclohexadienyl radical

Here we propose a further decomposition of spin polarization into "first-order" and "second-order" contributions. The first-order contribution can be either the positive spin density induced at each non-hydrogen atom by its own π spin density or the negative spin density induced at atoms in an α position (whatever their chemical nature). The second-order contribution is the positive spin density induced at atoms in a β position

---

[1] In the present work, all the values are given in gauss (1G = 0.1 mT), assuming that the free-electron g_{e} value is also appropriate for the radicals. To convert data to megahertz, one has to multiply them by 2.8025

(Fig. 1). An important point to be stressed is that the spin density due to second-order terms will be generally smaller than the first-order one.

On these grounds, it can be predicted that the spin densities at ortho and para carbon atoms will be positive, inducing large negative first-order spin densities at the ortho and para hydrogens, the latter bearing the largest one. Taking the analysis further, the positive spin density at the ortho carbon induces a weak positive second-order spin density at the meta hydrogen (Fig. 1). The same mechanism is operative for the para carbon atom leading to a weak positive contribution to the meta hydrogen. As a consequence, this explains the occurrence of a small positive hcc at the meta hydrogens and could be predicted by simple inspection of the shape of the SOMO and application of the mechanism presented: the meta hydrogens show a non negligible positive spin density (Table 1) resulting from cumulative second-order effects.

The same analysis holds for spin populations. This explains the success of the McConnell relationship [6], which can be strictly applied to first-order spin-polarization effects and predicts $a(H_p)/a(H_o)$ ratios in good agreement with Fermi contact computations and with experiment. By contrast, such a relationship cannot be applied directly to spin densities and populations at hydrogen atoms either in α or in meta positions. In particular, this explains the difference between the experimental or computed hcc ratios, $a(H_p)/a(H_m)$, and the corresponding carbon spin population ratios, namely $n^u(C_p)/n^u(C_m)$.

Strictly speaking, in the unrestricted formalism there is not such a thing as the SOMO. The α electron on the highest occupied orbital does not interact with the α electron of a given "doubly" occupied orbital in the same way as with the β electron of the corresponding "doubly" occupied orbital. Some part of the spin polarization is taken into account in the computation, together with delocalization. As a consequence, both positive and negative atomic spin populations are possible (Table 1). Although unrestricted spin calculations generally overestimate spin polarization, due to contamination by higher spin states, they lead directly to negative spin populations at meta carbon atoms. The unrestricted Kohn–Sham approach is much less prone to spin contamination than UHF, but some residual overestimation of second-order effects could explain why the computed hccs at meta hydrogens are slightly larger than their experimental counterparts.

From a more computational point of view, a detailed analysis of the results reported in Table 1 shows that direct and first-order polarization effects are almost quantitatively reproduced in the framework of the UB3LYP approach. In contrast, second-order effects are modeled only partially. Finally, the proposed spin-polarization mechanism is general and an inspection of Table 1 shows the same trends for the series cyclohexadienyl, benzyl and phenoxyl. The presence and the electronegativity of the substituent atom (C, O) modifies the shape of the SOMO and provides an explanation for the trend of the hccs along the series for atoms in ortho, meta and para positions.

The whole spin-polarization mechanism is depicted in Fig. 1 and illustrates the correlation between spin density (or spin population) at the given carbon atom and spin density at the hydrogen directly bonded to it. The same mechanism applies obviously to spin populations, $n^u(N)$, obtained by a simple integration of spin density over a given region of the space and can be useful in interpreting experimental results in molecular magnetism and/or in PND studies.

References

1. Stubbe J, van der Donk WA (1998) Chem Rev 98: 705
2. Halliwell B, Arnoma OI (eds) (1993) DNA and free radicals. Ellis Norwood, Chichester
3. Barone V, Adamo C, Grand A, Brunel Y, Fontecave M, Subra R (1995) J Am Chem Soc 117: 1083
4. Jolibois F, Cadet J, Grand A, Subra R, Rega N, Barone V (1998) J Am Chem Soc 120: 1864
5. McConnell HM (1956) J Chem Phys 24: 764
6. McConnell HM, Chesnut DB (1958) J Chem Phys 28: 107
7. Qin Y, Wheeler RA (1995) J Chem Phys 102: 1689
8. (a) Hulsebosch RJ, van den Brink JS, Nieuwenhuis SAM, Gast P, Raap J, Lugtenburg J, Hoff AJ (1997) J Am Chem Soc 119: 8685
   (b) Farrar CT, Gerfen GJ, Griffin RG, Force DA, Britt RD (1997) J Phys Chem B 101: 6634
9. Adamo C, Subra R, Barone V (1998) J Chem Phys 109: 10244
10. Luz Z (1968) J Chem Phys 48: 4186
11. Kahn O (1993) Molecular magnetism. VCH, Berlin
12. Gillon B, Schweitzer J (1989) In: Maruani J (ed) Molecules in physics, chemistry and biology, vol II. Kluwer, Dordrecht
13. Mulliken RS. (1955) J Chem Phys 23: 1833
14. Barone V, Subra R (1996) J Chem Phys 104: 2630
15. Zheludev A, Barone V, Bonnet M, Delley B, Grand A, Ressouche E, Rey P, Subra R, Schweitzer J (1994) J Am Chem Soc 116: 2019
16. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterschi J, Cui Q, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson Morokuma K, Malick DK, Rabuck AD, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Liu J, Liashenklo A, Piskorz P, Komaromi I, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, DeFrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1999) Gaussian 98, revision A.7. Gaussian, Pittsburgh, Pa