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Spin Densities in Some Simple Parasemiquinones

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Received September 19, 1967

The recent observation of oxygen-17 hyperfine splittings (*hfs*) in the ESR spectra of semiquinones [1, 2, 3], in conjunction with the mass of data on proton and carbon-13 *hfs*, prompts us to attempt the calculation of spin densities in these radicals by less empirical procedures than those previously employed. Hückel molecular orbital (HMO) calculations have been made by many investigators but require an arbitrary adjustment of the oxygen coulomb integral and the carbon-oxygen bond integral to obtain a best fit of observed *hfs* with calculated spin densities (assuming certain simple relationships between these quantities). A step further is the use of McLachlan's self-consistent field method (MSCF) [4]. This is however based on HMO quantities and was moreover originally developed for alternant hydrocarbons. The simplifications upon which it is based are not so justifiable for other types of molecule. We have therefore, as a test case, calculated the spin densities in three simple para-semiquinones by the open shell unrestricted Hartree-Fock (UHF) method [5] and by a closed shell selfconsistent field method (SCF). In the SCF calculations we have used the Pariser-Parr-Pople approach [6, 7], and then taken the squares of the atomic coefficients of the lowest vacant molecular orbital as a measure of the spin densities. In addition we have also used the variable electronegativity approach (VESCF) of BROWN and HEFFERNAN [8] to obtain closed shell molecular orbitals. The UHF method gives wavefunctions that are not eigenfunctions of S^2 [9] and we have attempted to correct for this, as is often done, by a single annihilation [10] to remove the quartet contamination.

The SCF eigenfunctions were found by the usual iterative procedure. The matrix elements for the α and β electrons in the UHF method are:

$$F_{ii}^{\alpha(\beta)} = I_i + \sum_{i \neq j} (R_{jj}^{\alpha} + R_{jj}^{\beta} - 1) \gamma_{ij} + R_{ii}^{\beta(\alpha)} \gamma_{ii}$$

$$F_{ik}^{\alpha(\beta)} = \beta_{ik} - R_{ik}^{\alpha(\beta)} \gamma_{ik} \quad (i \neq k)$$

where the symbols are defined in Ref. [5]. The density matrices for the α and β electrons in the UHF method were determined by the steepest descent procedure [11]. The values of the parameters used in the SCF and UHF calculations were chosen as follows. Atom ionization potentials, I_i , were estimated from HARADA's [12] quadratic expression in the effective nuclear charge Z_i , which in turn was estimated [13] from the charge density on atom i . The oxygen atom was assumed

to be in sp^2 hybridization but sample calculations using sp hybridization gave almost the same results. One centre integrals were estimated from PAOLONI's [14] expression, $\gamma_{ii} = 3.294 Z_i$, and two centre integrals by PARISER and PARR's approximations [6]. The value of the carbon-oxygen bond integral, β_{CO} , -2.692 eV, was taken from a VESCF calculation on formaldehyde [13], and the values of β_{CC} estimated from the expression given by ALLINGER [15]. The results of the calculations and of previous HMO and MSCF calculations [3] are given in the Table. It may be seen that the UHF method gives much higher spin densities on the oxygen atoms than the other methods. Comparison of the figures in the table with experimentally observed hyperfine splittings due to protons and to oxygen-17 requires the acceptance of relationships such as the McConnell equation for protons:

$$a_H = Q_H \rho_C \quad (1)$$

and the equation for oxygen-17 hfs [3]:

$$a_O = Q_{OC}^O \rho_O + Q_{CO}^O \rho_C \quad (2)$$

Eq. (1) has been modified by several workers [16, 17] but it provides a satisfactory basis to account for a great amount of experimental data (see e.g. Ref. 18) and is sufficient to bring out the point we wish to make here. Eq. (2) rests on rather a small number of experimental results but the values of the σ - π parameters are not likely to be drastically altered by further measurements on para-semiquinones, the class of substances to which the equation is limited*. Hyperfine constants and by implication spin densities, are solvent dependant. Taking this fact into account we require to know what range of calculated spin densities can be reasonably accepted, assuming the validity of Eq. (1) and (2). Solvent effects on the larger proton hfs of the three semiquinones considered here are small. For example, in water and in the aprotic solvent dimethylsulphoxide the following data have been given [19]:

Semiquinone	Pos.	DMSO	Water
1,4-benzo-		2.419	2.368
1,4-naphtho-	2	3.31	3.23
	5	0.633	0.655
	6	0.300	0.513
9,10-anthra-	1	0.303	0.550
	2	0.986	0.962

If we allow $|Q_H|$ to vary from 23 to 28 gauss (a generous latitude if the literature is examined) and take the splitting constants listed above as extreme values then we deduce a range of acceptable spin densities as listed in column VII of the table. It is seen that the figures, on the whole, are in reasonable accord with the results of all the calculations excepts the UHF results.

* In Ref. [3] Q_{OC}^O is estimated at about -40 gauss and Q_{CO}^O is much smaller and of indeterminate sign. A value of -40 ± 4 gauss for Q_{OC}^O has been estimated from the oxygen-17 hfs of phenoxyl radicals: DIMROTH, K., A. BERNDT, F. BAR, A. SCHWIEG, and R. VOLLAND: *Angew. Chem.* (English edition) **6**, 34 (1967).

Table

Semiquinone	Pos. ^a	I SCF closed shell.	II VESCF closed shell.	III MSCF	IV HMO	V UHF	VI UHF single annihilation.	VII Proton ^b spin densities.	VIII Oxygen ^b spin densities.
1,4-benzo-	1	.0952	.1069	.0937	.0552	.0356	.0117	—	—
	2	.1009	.0872	.0978	.0985	.0536	.0572	.085	.105
	7	.2030	.2191	.2108	.2477	.3622	.3739	—	.191 — .272
1,4-naphtho-	1	.0824	.0932	.1075	.0615	.0311	.0437	—	—
	2	.1432	.1398	.1350	.1353	.0956	.1019	.115	.144
	5	.0859	.0674	.0364	.0408	.0318	.0410	.011	.022
	6	.0138	.0159	.0147	.0125	.0226	.0207	.023	.029
	11	.1756	.1837	.1800	.2224	.3187	.3238	—	.173 — .245
9,10-anthra-	1	.0126	.0088	.0119	.0137	.0038	.0079	.011	.024
	2	.0344	.0184	.0384	.0407	.0049	.0039	.034	.043
	9	.1006	.1214	.1233	.0691	.0817	.0923	—	—
	11	.0581	.0652	.0598	.0629	.0531	.0413	—	—
	15	.1894	.1938	.1560	.1964	.2947	.3014	—	.167 — .215

^a Labelling of positions as in Ref. [3].^b Calculated from observed *h/s* as explained in the text.

Observed oxygen-17 hfs are also solvent dependent, typical figures [3] being listed:

Semiquinone	DMF	Water	Aq.ethanol
1.4-benzo-	9.53	8.58	—
1.4-naphtho-	8.58	—	7.80
Chloranil	8.89	8.16	—

Again we allow a generous range of acceptable calculated spin densities by putting $|Q_{OC}^O|$ equal to zero but letting $|Q_{OC}^O|$ vary from 35 to 45 gauss. The range of calculated spin densities is then given by the figures in column VIII of the table. Again the agreement between calculated and "observed" spin densities is poor for the UHF method and quite good for the other methods.

The UHF results are disappointing considering the satisfactory results obtained by the same methods for many hydrocarbons [11] and some nitrogen heterocycles [20]. The calculated spin densities are more sensitive to the variation of atom and bond parameters than many other properties, e.g. UV transition energies, and the choice of parameters for heteroatoms and for the atoms in highly polar groups is not as clear as for homocyclics. It is possible to adjust these parameters for a series of parasemiquinones to give a best fit to the observed hfs , but this is a return to arbitrary parameters and in any case the problem lies deeper than this as is shown by the case of orthobenzosemiquinone. For this molecule it is necessary to use entirely different HMO parameters from those for parasemiquinones to obtain acceptable spin densities [21]. VINCOW [22] obtained satisfactory results for the spin densities in a number of orthosemiquinones using the MSCF method, adjusting the basic HMO parameters to get a best fit. However the values of the parameters were very different from those needed to account for the splitting in parabenzosemiquinone. From the observed spectrum of orthobenzosemiquinone [23], and using Eq. (1), the spin densities at positions 3 and 4 are such that the ratio of spin densities ρ_3/ρ_4 is 0.25. In a closed shell SCF calculation we find $\rho_3/\rho_4 = 0.55$ for $I_{\text{oxygen}} = -20.66$ eV and $\rho_3/\rho_4 = 0.87$ for $I_{\text{oxygen}} = -17.103$ eV, ratios which are not acceptable. The fact that the same set of HMO or SCF parameters are not applicable to both types of semiquinones is perhaps a reflection of the neglect of core polarization in these highly polar molecules, but more theoretical work is certainly required. It would be desirable to have a theoretically sound method for choosing the parameters for UHF spin density calculations on heteroatomic molecules.

I wish to acknowledge the help of D. WALLY in programming the Ferranti Pegasus Computer. This work was carried out during the tenure of a grant from the Agricultural Research Council of Great Britain.

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