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Relationes

Unrestricted Hartree-Fock Calculations of Spin Density Distributions in the Radical Anions of Some Heterocycles Derived from Thiophene, Furan and Pyrrole

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Spin density distributions in the radial anions of some heterocycles derived from thiophene, furan and pyrrole have been obtained using the unrestricted Hartree-Fock method. Good agreement between the calculated results and experimental data has been observed.

Solony *et al.* have successfully studied [1] various physical and chemical properties of thiophene, furan and pyrrole by employing the Pariser, Parr and Pople (PPP) method [2]. Recently ESR data for some of the heterocycles derived from thiophene, furan and pyrrole have become available [3] and it was considered worthwhile to study the spin density distributions in these systems by the UHF and UHFAA methods of Amos and Snyder [4–7] especially with a view to test the transferability of the hetero-atom parameters given by Solony *et. al.* [1]. Results of such a study are reported in this paper.

Valence state ionization potentials and electron affinities needed for various hetero-atoms in the present study in the evaluation of one-centre two-electron repulsion integrals (γ_{kk}) were taken from the work of Solony *et al.* [1]. Valence state ionization potential and electron affinity values for carbon were taken from the work of Hinze and Jaffé [8]. Two-centre two-electron repulsion integrals (γ_{kl}, $k \neq l$) were obtained according to the prescription of Pariser and Parr [9]. Various core resonance integrals (β_{rs}) needed for the present study were also taken from the work of Solony *et al.* [1].

Proton splittings were calculated by employing the McConnell relation with $Q^{\mathrm{H}}_{\mathrm{CH}} = -27\,\mathrm{G}$ [1]. Nitrogen splitting constants (a_{N}) were obtained using the following two relations:

$$a_{\mathrm{N}} = 21\,\varrho_{\mathrm{N}} \qquad [7, 10] \tag{1}$$

and

$$a_{\mathrm{N}} = 30.9\,\varrho_{\mathrm{N}} - 2.0(\varrho_{\mathrm{C}} + \varrho_{\mathrm{C'}}) \qquad [3, 11] \tag{2}$$

where ϱ_{N} is the spin density on nitrogen and ϱ_{C} and $\varrho_{\mathrm{C'}}$ are those on carbon atoms adjacent to nitrogen. Results of UHF and UHFAA calculations are given in the Table while the topologies of the various systems studied here are given in Fig. 1.

It can be seen from the Table that the spin density values obtained by the use of the UHF method are not in good agreement with experiment and this is understandable in the sense that though the UHF wave functions are self-consistent, they are not true eigenfunctions of S^2 (see Table). Amos and Snyder have demonstrated [4] that in aromatic hydrocarbon radicals and radical anions, annihilation of the quartet spin component improves the value of $\langle S^2 \rangle$ and also the values of the spin densities. We have found this to be true in the radical anions of these S-, O- and N-heterocycles also (see Table).

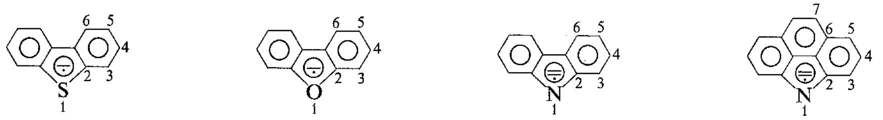
For the prediction of nitrogen splitting constants the use of relation (2) appears to give slightly better results (numbers in parenthesis in column 7 of the Table)

Table. *Calculated and observed splitting constants (in G) in the radial anions of a series of heterocycles derived from thiophene, furan and pyrrole*

System	Position	$\langle S^2 \rangle_{ba}$	$\langle S^2 \rangle_{aa}$	Spin density		Splitting	
				UHF	UHFAA	calculated[a]	Observed[b]
I	3	0.8123	0.7529	−0.0269	0.0193	−0.52	−1.46
	4			0.2520	0.1821	−4.92	−5.16
	5			−0.1016	−0.0287	0.77	0.86
	6			0.1897	0.1351	−3.65	−4.48
II	3	0.8113	0.7528	0.0293	0.0578	−1.55	−1.96
	4			0.2351	0.1736	−4.69	−4.87
	5			−0.1134	−0.0362	0.98	0.98
	6			0.2332	0.1692	−4.57	−4.87
III	1	0.8109	0.7527	0.0105	0.0079	0.17 (0.16)	0.10
	3			0.0262	0.0548	−1.48	−2.48
	4			0.2366	0.1745	−4.71	−4.10
	5			−0.1132	−0.0359	0.97	0.59
	6			0.2293	0.1665	−4.50	−4.10
IV	1	0.8207	0.7539	−0.0225	−0.0072	−0.15 (−0.34)	−0.60
	3			0.1903	0.1253	−3.38	−3.00
	4			−0.1006	−0.0325	0.90	0.51
	5			0.2014	0.1361	−3.67	−3.00
	7			0.1985	0.1930	−5.21	−5.08

[a] Proton splittings were obtained by using UHFAA spin densities and employing McConnell relation with $Q^{H}_{CH} = -27$ G (see Ref. [4]). Use of the Copa-Bolton relation [4] did not give any better agreement. Nitrogen splittings were obtained by using UHFAA spin densities and employing both relations (1) and (2) (see text). $\langle S^2 \rangle_{ba}$ and $\langle S^2 \rangle_{aa}$ are respectively the expectation values of the S^2 operator obtained before and after annihilation.

[b] Obtained from Ref. [3]. Signs are not obtained experimentally; they have been assigned on the basis of our theoretical results.



(I) (II) (III) (IV)

Fig. 1. Topology of heterocycles

than those obtained with the use of relation (1). Use of relation (1) predicts the nitrogen splitting constants in III and IV to be almost equal in magnitude, contrary to experiment. The spin density values on carbon atoms adjacent to the nitrogen atom being positive (0.0224 for III and 0.0229 for IV) use of relation (2) gives a larger nitrogen splitting (absolute value) for IV in good agreement with experiment.

In this study we have not attempted to get the best agreement with experiment by adjusting various hetero-atom parameters. It is clear, however, that it is possible to explain the spin density distributions in the radical anions of these heterocycles using the UHFAA scheme along with the same set of hetero-atom parameters as those employed by Solony *et al.* [1]. We have also made a similar study of the radical anions of several other sulfur containing heterocycles and the results will be presented elsewhere.

Calculations reported here were made using an IBM 7044 computer. We are grateful to the staff of the Computer Centre, Indian Institute of Technology, Kanpur for their valuable co-operation.

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