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Semi Empirical Calculations of the Spin Density Distributions in Some Nitro Substituted, Conjugated Anions

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Introduction

Many nitrosubstituted radical ions have been prepared by electrolytic reduction [1], and their E.S.R. spectra have been partly analysed theoretically by Rieger and Fraenkel [1], who used both the Hückel and the McLachlan treatments to calculate the spin density distributions. These methods of calculation are, however, rather approximate, and so we have calculated the spin density distributions using more sophisticated treatments, viz:

(1) the SCF-CI method described in previous work [2]

(2) the Unrestricted Hartree-Fock (UHF) method [3]

(3) the UHF method incorporating annihilation of the quartet spin function from the ground state (UHF AA) [3].

Methods

Method (1) has been described by the present author in previous work, and applied successfully to calculations of the spin density distributions in a large range of radical ions [2]. Methods (2) and (3) have been documented for π-electronic systems, by Amos et al. [3]. Our calculation followed the method of Ref. [3] exactly, fifteen cycles being performed in every case. The molecules were all assumed to be planar, and to have regular geometries. The bond lengths were: r(CN) was 1.4 Å everywhere except in the nitrile group, where it was 1.15 Å; r(CO) was 1.20 Å, and r(NO) 1.25 Å. The integrals of Ref. [4] were followed where appropriate, whilst the value of the one center core integral $\delta\omega_{(0)}$ for an oxygen atom which contributes two electrons to the π system was -16.91 eV, from the SCF results on furan [5].

Results

In Tab. 1, we present the results obtained for the spin density calculations using all three methods. We have also calculated the mean values of S^2, $\langle S^2 \rangle$, for calculations (2) and (3) and these results are presented in Tab. 2. In the figure, we have indicated the nodal properties of the singly occupied orbital [calc (1)], which is identical to the highest occupied orbital for the α-spin electrons [calc (2)] in every case except 1,3 dinitrobenzene. Apart from a few exceptions, the spin densities calculated by methods (1) and (3) agree closely. This was also found to be true for the nitrile anions [6]: differences probably arising due to differences in

Table 1. *Spin densities and coupling constants*

Molecule	Pos.	Spin Density			Coupling Constants			
		ϱ (1)	ϱ (2)	ϱ (3)	a (1)	a (2)	a (3)	$a_{\text{obs.}}$
Nitro Benzene	2	.1346	.2020	.1418	− 3.43	− 2.87	− 3.97	3.37
(N. B.)	3	−.0343	−.1251	−.0300	+ 0.87	+ 1.78	+ 0.84	1.08
	4	.2014	.2974	.2112	− 5.13	− 4.22	− 5.92	4.00
	7	.1150	.0961	.1185	−10.01	−10.01	−10.01	10.01
1,2 DNB	3	−.0236	−.0602	−.0109	+ 0.60	+ 0.85	+ 0.31	0.27
	4	.0973	.1201	.0969	− 2.42	− 1.70	− 2.72	1.68
	7	.0206	−.0176	.0222	− 1.79	+ 1.83	− 1.88	2.94
1,3 DNB	2	.5271	−.0759	−.0242	−13.42	+ 1.08	+ 0.68	3.94
	4	−.0136	.3838	.3157	+ 0.35	− 5.45	− 8.85	4.35
	5	.1730	−.1811	−.0571	− 4.41	+ 2.57	+ 1.60	1.08
	7	.0360	.0123	.0291	− 3.21	− 1.28	− 2.46	4.33
1,4 DNB	2	.0449	.0297	.0475	− 1.14	− 0.42	− 1.33	1.12
	7	.0316	.0073	.0382	− 2.75	− 0.76	− 3.23	1.61
4 Nitro Aniline	2	.1980	−.1577	−.0457	− 5.04	+ 2.24	+ 1.28	1.12
(4 N-A)	3	.3523	.2277	.1539	− 8.97	− 3.23	− 4.31	3.36
	7	.0146	.1201	.1370	− 1.27	−14.27	−11.57	12.18
	10	−.0084	.0369	.0254	+ 0.73	− 3.84	− 2.16	1.12
4 N-Phenol	2	.1961	−.1641	−.0482	− 4.99	+ 2.33	+ 1.35	0.68
	3	.3546	.2320	.1560	− 9.03	− 3.29	− 4.37	3.03
	7	.0151	.1222	.1384	− 1.31	−12.73	−11.69	13.79
4-N	2	−.0122	−.0776	−.0050	+ 0.31	+ 1.10	+ 0.14	0.76
Cyanobenzene	3	.1053	.1477	.1128	− 2.68	− 2.10	− 3.16	3.12
	7	.0779	.0545	.0807	− 6.78	− 5.68	− 6.82	7.15
	11	.0657	.1178	.0717	− 5.72	−12.27	− 6.06	0.76
3-N	2	.1723	.2687	.1975	− 4.39	− 3.81	− 5.53	3.18
Cyanobenzene	4	.0775	.1168	.0837	− 1.97	− 1.66	− 2.35	4.54
	5	−.0121	−.0774	−.0074	+ 0.31	+ 1.10	+ 0.21	0.99
	6	.2470	.3380	.0837	− 6.29	− 4.80	− 2.35	3.58
	7	.0945	.1612	.0979	− 8.23	−16.79	− 8.27	8.17
	11	.0031	−.0134	.0001	− 0.27	+ 1.40	− 0.01	0.01
4-N Biphenyl	2	.0086	−.0461	.0105	− 0.22	+ 0.65	− 0.29	
(4NB)	3	.0759	.1099	.0896	− 1.93	− 1.56	− 2.51	3.60
	8	.0579	.1191	.0666	− 1.47	− 1.69	− 1.87	
	9	−.0120	−.0749	−.0225	+ 0.31	+ 1.06	+ 0.63	
	10	.0609	.1318	.0718	− 1.55	− 1.87	− 2.01	
	13	.0544	.0328	.0591	− 4.74	− 3.42	− 4.99	
4,4′ DNB	2	.0545	.0753	.0615	− 1.39	− 1.07	− 1.72	1.23
	3	.0178	−.0206	.0160	− 0.45	+ 0.29	− 0.45	0.20
	16	.0154	−.0097	.0109	− 1.34	+ 1.01	− 0.93	2.69

Table 2. *Mean values of* S^2

Molecule	Method (2)	Method (3)
nitrobenzene	0.81222	0.75250
1,2 dinitrobenzene	0.80787	0.75246
1,3 dinitrobenzene	0.81017	0.75200
1,4 dinitrobenzene	0.78612	0.75044
4 nitroaniline	0.83054	0.75426
4 nitrophenol	0.83546	0.75480
4 nitro cyano benzene	0.80061	0.75152
3 nitro cyano benzene	0.81639	0.75270
4 nitrobiphenyl	0.81417	0.75291
4,4′ dinitro biphenyl	0.80789	0.75169

rates of convergence of the two processes, and the fact that the UHF. AA wavefunction is still not accurately an eigenfunction of S^2. However, in every case, $\langle S^2 \rangle$ improves drastically with annihilation, approaching the doublet value of 3/4, whilst a comparison of spin densities calculated by (2) and (3) shows that the effect of other spin states is quite important, and the fact that $\langle S^2 \rangle$ is never accurately 3/4 in calculations (3) can still probably lead to errors, especially at positions of low spin density.

To correlate the results with experiment, we have used the simple relation $a = Q\varrho$, and the values of Q for the hydrogen hyperfine splittings were calculated by averaging a/ϱ for the three positions in nitrobenzene anion. They were -25.46, -14.19 and -28.02 gauss for methods (1) – (3) respectively. The other coupling constants were then calculated, and are presented in Tab. 1. Marshall [7] has suggested that it is a poor approximation to use UHF. AA, and claims that UHF results should give a more accurate description of spin densities: our results are not particularly conclusive, but method (3) does seem to be more accurate, especially at positions of low spin density. Other results [6] support this conclusion.

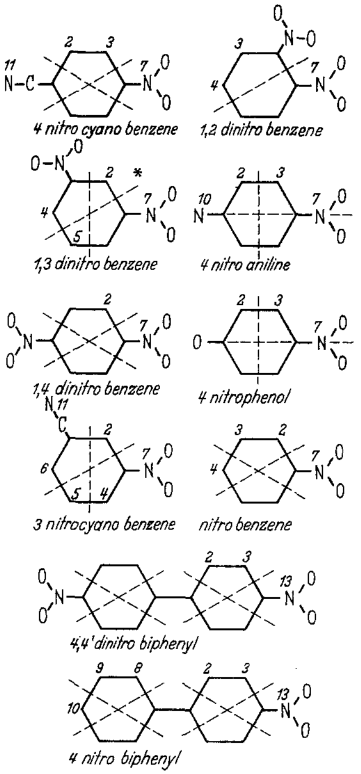

Fig. 1. Conjugated nitro anions studied

All three calculations show that the spin density at position 2 in 4,4′ dinitrobiphenyl is greater than that at position 3, whilst other calculations [1] have suggested that the situation ought to be reversed. This is assumed to mean that, regarding 4,4′ dinitro biphenyl as nitrobenzene with a 4′ nitrobenzene substituted at the 4 position, the nitro group acts as a less strongly electron withdrawing group than the 4′ nitrophenyl group, in common with phenyl and 4′ cyano phenyl, when compared to hydrogen and cyano respectively. However, it should be remembered that these conclusions are valid for the mononegative ions, and not of necessity also for the neutral molecules. The nitrogen coupling constants were fitted to similar relationships, and Q values of -87.04, -104.16 and -84.47 gauss were used to fit the coupling constant in nitrobenzene. These values are unrealistically large, and the error is due to either: a poor value for $\delta\omega_{(N)}$ for the nitro nitrogen, an incorrect assumption of an all-planar geometry, or an incorrect correlation between a and ϱ. That SCF calculations on nitrobenzene and *s*-trinitro benzene [*4*] show good agreement with experiment offers weak evidence that the first is untrue, and it was hoped that a calculation on 4 nitro aniline would answer the third possibility. However, the methods (1) and (3) give widely different answer, i.e. different minima have been reached on the energy surface, and so the question cannot be decided on our data.

The results for 1,3 dinitrobenzene show poor agreement with experiment, although (2) is the best set: work in this laboratory [*8*] has shown that the spin density at position 2 is negative, whilst that at position 4 is positive; in agreement with our results.

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