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SCF Calculation of the Spin Density Distributions in Some Nitrile Radical Anions

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The nitriles are an interesting class of organic molecules, in that they have two perpendicular π-electronic systems; one of which lies out of the plane of the molecule, and covers it, whilst the other one is confined to the CN group. Peacock and Wilkinson [4] have used the SCF method to calculate the electronic spectrum of benzonitrile and found, making the assumption that the two π-systems do not interact, that their calculation gave a satisfactory description of the electronic spectrum of the molecule, i.e. the inplane π system could be treated apart from the out-of-plane system.

The E.S.R. spectra of a number of nitrile anions have been reported [5]. Since they were produced by electrolysis, and hence there is no cation present small enough to give any line width alternation effects, it is probable that the measured coupling constants describe accurately the spin density distribution of the unperturbed anions. It is clearly interesting, therefore to see whether our method of calculation will give results in good agreement with experiment.

Methods and Parameters

The molecules were taken to have regular geometries; in particular, all C–C and all C–N bonds, apart from the C–N bond in the nitrile group, were taken to be equal to 1.40 Å; the nitrile C–N bond was given a length of 1.15 Å. All angles were taken as 120° where appropriate, and the C–C–N nitrile fragment was assumed to be linear. The values of the main integrals follow Ref. [4] exactly. β(CN) was taken to have a linear relation with overlap, and the remaining two-center coulomb integrals were calculated using the method of Pariser and Parr [7].

The method of obtaining the Open Shell SCF MO's has been given elsewhere [1]. Lefebvre [8] has pointed out that the introduction of singly excited states $\Psi'_{x \to a}$ produce a spin-polarised wavefunction, and hence changes the spin density distribution from its ground state value. The singly excited states are conveniently mixed into the ground state using First Order Perturbation Theory. Writing the perturbed ground state as

$$\Psi'_{GS} = \Psi_{GS} + \sum_{a,x} \lambda(a, x)\, \Psi'_{a \to x}\,,$$

Table. *Experimental and calculated results for the eight nitriles studied*

Molecule	Posn.	P_i	ϱ_i	Nitrogen	Hydrogen		$a_{(\mathrm{obs})}$[a]
				$a(2)$	$a(1)$	$a(3)$	GAUSS
benzonitrile	2	1.0979	0.1044		−2.63	−2.74	3.63
	3	1.0550	−0.0115		+0.29	+0.31	0.30
	4	1.2560	0.3105		−7.81	−7.53	8.42
	8	1.3118	0.1683	−3.11			2.15
1,2 dicyanobenzene	3	1.0017	−0.0500		+1.26	+1.38	0.42
	4	1.1547	0.1500		−3.77	−3.83	4.13
	8	1.2659	0.1212	−2.24			1.75
1,3 dicyanobenzene	2	0.9668	−0.0563		+1.42	+1.57	1.44
	4	1.1952	0.3131		−7.87	−7.84	8.29
	5	1.0112	−0.0852		+2.14	+2.33	0.08
	8	1.2564	0.0807	−1.49			1.02
1,4 dicyanobenzene	2	1.0618	0.0429		−1.08	−1.15	1.59
	8	1.2708	0.1178	−2.18			1.80
4,4′ dicyanobiphenyl	2	1.0708	0.0757		−1.90	−2.02	1.807
	3	1.0210	0.0005		−0.02	−0.02	0.286
	14	1.2151	0.0564	−1.04			1.047
4, cyanopyridine	2	1.1140	0.1030		−2.59	−2.69	2.62
	3	1.0149	−0.0019		+0.05	+0.06	1.40
	4	1.3149	0.2711	−5.01			5.63
	8	1.3113	0.1746	−3.23			2.33
Tetracyanoethylene (TCNE)	3	0.8803	−0.0066	−1.99			1.574
Tetracyanobenzene (TCNB)	3	0.9718	−0.0652		+1.64	+1.82	1.11
	7	0.8842	0.0049	−0.09			1.15

[a] Ref. [5].

where the "admixture coefficient" $\lambda(a, x)$ is given by

$$\lambda(a, x) = -\sqrt{\tfrac{3}{2}}\,[an \mid nx]\,\{\varepsilon_x - \varepsilon_a - J_{ax} + K_{nx} + K_{ax}\}^{-1}\,, \star$$

it is readily shown that the spin density ϱ_i, at position i is apart from a constant of normalisation

$$\varrho_i = n_i^2 + \frac{4}{\sqrt{6}} \sum_{a,\,x} \lambda(a, x)\, a_i\, x_i - \tfrac{1}{6} \sum_{a,\,x} \lambda^2(a, x)\,[4\, a_i^2 + 4\, x_i^2 - 2\, n_i^2]$$

where, for example, n(i) is the coefficient of the ith atomic orbital in the molecular orbital n. Again, the sum of spin densities was computed as a check on calculation, and was 1.0000 in every case.

Results and Discussion

The orbitals of any substituted benzene can clearly be thought of as being a perturbation on the corresponding two lowest antibonding orbitals of benzene,

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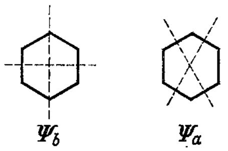
⋆ The notation is as follows: $[an \mid nx] = \int a\,(1)\, n\,(2)\, \frac{1}{r_{12}}\, n\,(1)\, x\,(2)\, d\tau_1\, d\tau_2$
$J_{a,x} = [aa \mid xx]$, $K_{a,n} = [an \mid an] \cdot \varepsilon_i$ is the ith root of the Hartree-Fock Hamiltonian.

which we may take in real form as shown in (1), where the dotted lines are the nodal planes. A small perturbation on these orbitals by a substituent will split the degeneracy, and which of the two becomes the lower in energy will depend on the properties of the substituent. Thus, if the perturbation is mainly of the Inductive type, and the substituent is electron attracting, the orbital Ψ_a should be the lower one, as this permits a larger charge density near to the substituent. Thus CARRINGTON [9] has discussed the spectra of the nitrile anions from this viewpoint, and indeed an examination of the experimental results indicates that this argument can be used with success.



(1)

However, our calculation is more sophisticated than this simple argument, and allows for delocalisation onto the nitrile group also. In order to correlate our results with the observed coupling constants, we have fitted the results to three straight lines, using least squares methods;

1. $a_H^{(i)} = -25.14\,\varrho_c^{(i)}$ 2. $a_N^{(i)} = -18.47\,\varrho_N^{(i)}$ 3. $a_H^{(i)} = -[27.53 + 12.82\,\varepsilon_i]\,\varrho_c^{(i)}$

where $\varepsilon(i) = I\text{-}P(i)$ is the "excess charge" as introduced by COLPA and BOLTON [10].

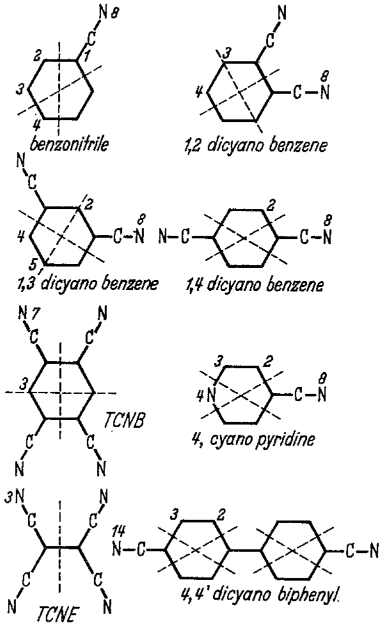


Fig. 1. Nitrile Anions studied

The fit between experiment and calculation is quite satisfactory, in nearly all cases, and the relative orders of coupling constants, in a particular molecule, are generally correctly calculated, as before [10]. However, the results for 1,3 dicyanobenzene do indicate that one assignment has been made incorrectly, namely the proton splittings at positions 2 and 5 of 1,3 dicyanobenzene ought to be reversed. This new assignment was made for the purpose of calculating the three relations given previously, whilst further experimental work seems necessary to resolve this point.

Conclusions

It is seen from a comparison of our results, assuming that the new assignments we have made are correct, that the parameter set chosen, namely the one which gives a reasonable description of the electronic spectrum of benzonitrile, also gives a good description of the spin density distributions in a number of nitrile anions; of course, it is necessary to assume one of the relatively simple correlations between experimental and calculated results, and this is the real problem at present. It is also seen that the other assumption, namely the neglect of the in-plane system is a perfectly valid approximation, in this case: in any case, any interactions between the two planes would be of the exchange type, and so would presumably be an order of magnitude less than the other interactions considered.

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References

[1] Hinchliffe, A.: Theoret. chim. Acta **5**, 208 (1966).
[2] —, M. A. Ali, and R. E. Stainbank: Theoret. chim. Acta **5**, 95 (1966).
[3] —, J. N. Murrell, and N. Trinajstic: Trans. Faraday Soc. (In press).
[4] Peacock, T. E., and P. T. Wilkinson: Proc. Phys. Soc. **79**, 105 (1962).
[5] Rieger, P. H., I. Bernal, W. H. Reinmuth, and G. K. Fraenkel: J. Amer. Chem. Soc. **85**, 683 (1963).
[6] Mulliken, R. S.: J. Chim. physique **46**, 497 (1949).
[7] Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1956).
[8] Lefebvre, R.: Lecture presented at the International Summer School of Quantum Chemistry. 1964.
[9] Carrington, A.: Quarterly reviews **67** (1963).
[10] Colpa, J. P., and J. R. Bolton: Mol. Phys. **6**, 273 (1963).

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