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Unrestricted Hartree-Fock Spin Density Distributions in Nitro Aromatic Radical Anions

D. N. NANDA, J. SUBRAMANIAN, and P. T. NARASIMHAN
Department of Chemistry, Indian Institute of Technology, Kanpur, India

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The spin density distributions in the radical anions of nitrobenzene and some para substituted nitrobenzenes are calculated using the unrestricted Hatree-Fock formalism of Amos and Snyder. A parameter scheme which gives satisfactory account of the electronic transitions and molecular ionisation potentials of substituted benzenes (nitrobenzene, toluene, aniline, benzaldehyde and benzonitrile) is used for spin density calculations of the nitro radical anions. The importance of spin densities on neighbouring atoms on the hyperfine splitting of nitrogen atom is discussed. It is seen that although Karplus-Fraenkel theory gives a better estimate of ^{14}N splitting constant, the simple McConnell-type of relation is approximately valid for the nitro group-nitrogen. The $\sigma - \pi$-parameters for use with unrestricted Hartree-Fock spin densities for the prediction of nitrogen hyperfine couplings in nitro, amino and cyano groups are summarised.

Die Spindichteverteilungen in den Radikalanionen des Nitrobenzols und einiger parasubstituierter Nitrobenzole werden mit Hilfe des UHF-Formalismus von Amos und Snyder berechnet. Zur Ermittlung der Spindichte der nitroaromatischen Radikalanionen wird ein Parameterschema benutzt, das zufriedenstellende Darstellung der Elektronenübergänge und der molekularen Ionisationspotentiale von substituierten Benzolen (Nitrobenzol, Toluol, Anilin, Benzaldehyd, Benzonitril) gestattet. Der Einfluß der Spins von benachbarten Atomen auf die Hyperfeinaufspaltung des Stickstoffatoms wird diskutiert. Es zeigt sich, daß zur näherungsweisen Beschreibung des Stickstoffs der Nitrogruppe eine einfache Gleichung des McCornell-Typs ausreicht, wenn auch die Karplus-Fraenkel-Theorie eine bessere Abschätzung der ^{14}N-Aufspaltungskonstanten ermöglicht. Die $\sigma - \pi$-Parameter, die zur Voraussage der Stickstoff-Hyperfeinkopplung in Nitro-, Amino- und Cyanogruppen mit Hilfe der UHF-Spindichten erforderlich sind, werden zusammengestellt.

1. Introduction

Although the hyperfine splitting constants for protons bonded to carbon in aromatic radicals are adequately derived by the simple McConnell relation [1], one would expect on the basis of Karplus-Fraenkel theory [2] that such a linear relation may not be sufficient while dealing with ^{13}C or ^{14}N splittings and that the contributions from the spin densities on adjacent atoms may be important. The applicability of Karplus-Fraenkel theory for ^{14}N splittings in aza-aromatic radical ions has been studied in detail by several workers [3]. Similar study has also been made for a series of nitro aromatic radical anions by Rieger and Fraenkel [4] using McLachlan type of calculation. Karplus-Fraenkel relation for ^{14}N hyperfine splitting in case of nitro compounds can be written as:

$$a_N = Q_N^N \varrho_N + Q_{CN}^N \varrho_C + Q_{ON}^N (\varrho_O + \varrho_{O'}) \tag{1}$$

where $Q_N^N = (S_N + Q_{NC}^N + 2Q_{NO}^N)$. The notations have their usual meanings [2, 3]. Rieger and Fraenkel estimated the constants Q_N^N, Q_{CN}^N and Q_{ON}^N from the experimental ^{14}N splitting constants and the spin densities calculated by McLachlan method for a series of nitro substituted aromatic radicals. Geske *et al.* [5] have studied the radical anion of nitrobenzene employing the unrestricted Hartree-Fock procedure, but without annihilation of the quartet spin function.

A series of nitro aromatic radicals has also been studied by Hinchliffe [6] using both configuration interaction method and the unrestricted Hartree-Fock (UHF) procedure of Amos and Snyder [7]. The proton hyperfine splitting constants calculated by Rieger and Fraenkel using McLachlan method are in better agreement with the experimental values compared to the results of the more sophisticated methods employed by Hinchliffe. This is difficult to rationalise in view of the known superiority of SCF results over the results of Hückel type of calculations for hetero aromatic compounds. The present investigation was undertaken to see whether this discrepancy is due to the SCF parameters involved in the computation of spin densities. An attempt was therefore made to choose a consistent set of SCF parameters which satisfactorily reproduce the closed-shell properties like ionisation potential and electronic spectra of substituted benzenes and use these parameters for computing the spin densities in aromatic nitro radical anions by the UHF method of Amos and Snyder. The substituted benzenes chosen for SCF parametrization are nitrobenzene, toluene, aniline, benzaldehyde and benzonitrile. Since the applicability of Karplus-Fraenkel relation for ^{14}N splitting in nitro group-nitrogen has not been tested by UHF calculations it was considered worthwhile to obtain an estimate of $\sigma-\pi$ parameters occurring in relation (1) employing the results of UHF calculations.

2. Method and Parameter Evaluation

The PPP adaptation of the Hartree-Fock (HF) SCF LCAO method is well known [8, 9]. Neglecting atom penetration integrals, the HF matrix elements are given by:

$$F_{\mu\mu} = U_{(\mu)} + \tfrac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\mu \neq \nu} (P_{\nu\nu} - n_\nu) \gamma_{\mu\nu} , \tag{2}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} (\mu \neq \nu) . \tag{3}$$

$U_{(\mu)}$ is the energy of an electron in the μ-th orbital in the field of the nucleus and inner shell of electrons of the atom to which the orbital belongs. This is generally approximated to the appropriate atomic valence state ionisation potential (VSIP). For satisfactory prediction of molecular ionisation potentials using Koopmans theorem it has been pointed out by a number of authors that lower values of $U_{(\mu)}$ should be used [10]. The molecular ionisation potentials depend on the absolute values of U's while spin density distribution is sensitive to their relative values. A semiempirical adjustment of U's to reproduce the molecular ionisation potentials estimated by using Koopmans' theorem is therefore useful in obtaining the proper spin density distribution. We assumed planarity of the molecules dealt with here and all the C–C bond lengths of the six-membered ring to be 1.397 Å.

The geometry of the substituent in the para substituted nitrobenzene was assumed to be the same as that in the corresponding monosubstituted benzene [11].

We used a calibration procedure for determining electron repulsion integrals using benzene as the reference molecule. The values of β_{cc} and γ_{ij} suggested by Pariser [9], chosen to fit the energies of the two lowest excited singlets and the lowest triplet state of benzene, are (in eV)

$$\beta_{cc} = -2.371 \quad \gamma_{11} = 10.96 \quad \gamma_{12} = 6.895$$
$$\gamma_{13} = 5.682 \quad \text{and} \quad \gamma_{14} = 4.978 .$$

Repulsion integrals between bonded atoms were approximated by an expression of the form proposed by Ohno [12]:

$$\gamma_{ij} = C/\{R_{ij}^2 + [2C/(\gamma_{ii} + \gamma_{jj})]^2\}^{1/2} \tag{4}$$

where R_{ij} is the distance between the atomic centres. The function obeys boundary condition at $R_{ij} = 0$. Using semiempirical values of γ_{12} ($R_{12} = 1.397$) constant C was determined. For non-bonded atoms we assumed an expression of the type:

$$\gamma_{ij} = 13.397/\left\{R_{ij}^2 + C_1\left[\frac{2 \times 13.397}{\gamma_{ii} + \gamma_{jj}}\right]^2\right\}^{1/2} \tag{5}$$

which approximates to e^2/R_{ij} at large internuclear separation. A single value of $C_1 = 0.325$ reproduces both γ_{13} and γ_{14} of benzene. These two expressions were used for estimating two-electron repulsion integrals in all the molecules studied here.

One-centre electron repulsion integrals were estimated by the usual '$I - A$' approximation using the appropriate valence state data of Hinze and Jaffe [13]. For carbon, the spectroscopic value (10.96 eV) of Pariser was used. This is, however, quite close to the value (11.13 eV) obtained from Hinze and Jaffe's table.

Using β_{cc} and γ's of Pariser's set, $U_{(C^+)}$ was adjusted so that the molecular ionisation potential for benzene calculated using Koopmans' theorem reproduced the experimental value for the molecule [14]. For doubly-charged core atoms $U_{(\mu)}$'s were obtained from the relation

$$U_{(\mu^{++})} = -I(CH_3X) - \gamma_{\mu\mu}(X = OH \text{ or } NH_2) \tag{6}$$

where $I(CH_3X)$ is the observed ionisation potential of the appropriate molecule [15]. β_{CN} and β_{NO} for nitrobenzene were taken from the work of Peacock [16] and $U_{(O+)}$ was adjusted to fit the experimental ionisation potential of nitrobenzene [14]. We adopted β_{C-NH_2} equal to β_{C-NO_2}.

Parameters for CN group were taken from the work of Subramanian and Narasimhan [17]. In their treatment of substituted benzonitriles they estimated β_{C-CN} using Mulliken's relation [18] and adjusted β_{C-N} and $U_{(N+)}$ so as to reproduce the experimental electronic transitions and molecular ionisation potential of benzonitrile and proton hyperfine splittings in the radical anion of benzonitrile. For methyl group, heteroatom model was adopted and necessary parameters for the same were taken from literature [19]. β_{C-O} for carbonyl group was taken from the work of Sidman [20]. Since the distance for the C–CO bond in benzaldehyde is close to the C–CN distance in benzonitrile, we adopted β_{C-CO} equal to β_{C-CN}

for consistency. Table 1 lists the values of different parameters used in the present calculations. In calculating the electronic transitions full configuration interaction is included between all singly excited states.

Table 1. *Parameter values*

Core	U_i (eV)	γ_{ii} (eV)	$i-j$	β_{ij} (eV)
C^+	-9.6	10.96	C–C (benzene)	-2.371
N^+	-12.3	12.34	C–NO_2	-2.576
O^+	-15	15.24	C–NH_2	-2.576
N^{++}	-25.44	16.47	N–O	-2.73
			C≡N	-4.2

Table 2. *Electronic transitions and ionisation potentials* (eV)

Molecule	$s-s$ transitions		$s-t$ transitions			
	Calcd. ΔE	Obsd. ΔE	Calcd. ΔE	Obsd. ΔE[d]	Calcd. I. P.	Obsd. I. P.[e]
Nitrobenzene	4.48	4.38[a]	2.94		10.23	10.18 (10.23)
	5.08	5.11	3.89			
	5.19					
	6.18					
	6.25	6.42				
	7.01					
	7.06					
	7.39	7.56				
	7.76					
Toluene	4.66	4.65[b]	3.16	3.57	9.31	9.18 (8.90)
	5.87	5.86	4.10			
	6.49	6.57—6.79				
	6.50					
Aniline	4.30	4.40[c]	2.91	3.32	8.06	8.32 (8.04)
	5.32	5.39	3.47			
	6.26					
	6.44	6.40				
	7.31	6.88				
	7.45	7.87				
	7.95					
Benzaldehyde	4.51	4.52	2.83		9.95	— (9.80)
	5.41	5.35	3.65			
	6.12	6.35				
	6.35	6.88				
	7.24	6.97				
	7.51					
	7.67	7.50				

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[e] See Ref. [14]. Values in parentheses from Ref. [24].

3. Results and Discussion

The calculated $\pi-\pi^*$ transitions for nitrobenzene, aniline, toluene and benzaldehyde, along with the observed transitions for these molecules are given in Table 2. Computed singlet transitions are in reasonably good agreement with experiment. However, the lowest triplet transitions for toluene and aniline are estimated to be lower than the experimental values by about 0.4 eV. Similarly, when Mataga-Nishimoto relation [21] is employed for calculating the electronic transitions in hydrocarbons and heterocycles, although the singlet-singlet transitions are well reproduced, the singlet-triplet splittings are poorly estimated [22]. It has been shown [23] that $2p_\pi$ atomic orbitals for singlet and triplet states are significantly different. Thus, a single set of parameters is not expected to be adequate for calculating singlet-singlet and singlet-triplet transitions.

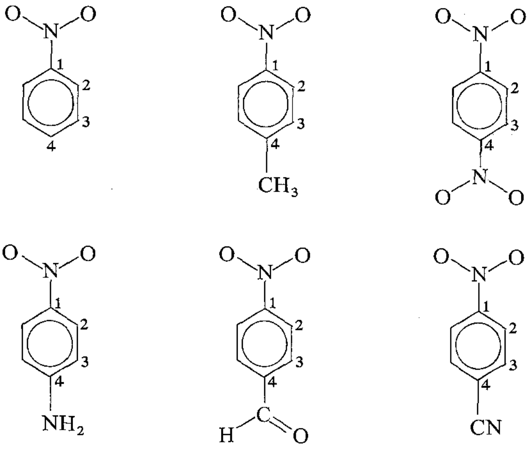

Fig. 1. Topology of the nitro compounds

The values of molecular ionisation potentials estimated using Koopmans' theorem are also presented in Table 2. The value for nitrobenzene used for adjustment of parameter $U_{(O^+)}$ is included for completeness. According to recent measurements of Baker *et al.* [24] the splitting of the two degenerate π-levels of benzene caused by $-CH_3$ and $-NH_2$ substituents are ~0.2 and 1.07 eV respectively. No splitting was observed in the case of nitrobenzene and benzaldehyde. The calculated splittings for toluene, aniline, nitrobenzene and benzaldehyde are respectively 0.26, 1.28, 0.05 and 0.21 eV. Thus, here also fairly resonable agreement between theory and experiment can be noticed.

Tables 3 and 4 contain the results of our UHF calculations. The expectation values of S^2 operator before annihilation, $\langle S^2\rangle_{ba}$, those after annihilation $\langle S^2\rangle_{aa}$ and the spin densities on ring carbon atoms after annihilation are listed in Table 3. The ring proton splittings calculated using the spin densities after annihilation were in much better agreement with observed splittings compared to those obtained from spin densities before annihilation of the quartet function. Similar observa-

Table 3. UHFAA *spin densities and proton hyperfine splitting constants in radical anions of nitro aromatic compounds*

Compound	Position	$\langle S^2\rangle_{ba}$	$\langle S^2\rangle_{aa}$	ϱ_i	a_i (Calcd)[a]	$\lvert a_i\rvert$ (Obsd)[b]
Nitrobenzene	2	0.8000	0.7516	0.1189	−3.21	3.39
	3			−0.0298	0.81	1.09
	4			0.1551	−4.19	3.97
p-Nitrotoluene	2	0.8029	0.7518	0.1208	−3.26	3.39
	3			−0.0326	0.88	1.11
	4			0.1520	3.80[c]	3.98
p-Dinitrobenzene	2	0.7936	0.7503	0.0431	−1.16	1.12
p-Nitroaniline	2	0.8301	0.7541	0.1381	−3.72	3.36
	3			−0.0478	1.29	1.12
p-Nitrobenzonitrile	2	0.7918	0.7510	0.1028	−2.78	3.12
	3			−0.0131	0.35	.76
p-Nitrobenzaldehyde	2	0.8140	0.7519	0.09941	−2.68	3.10
	3			−0.0024	.063	0.44
	5			0.0061	.164	0.44
	6			0.0697	−1.88	2.37

[a] Ring proton splittings calculated employing the relation $a_H = Q^H_{CH}\varrho_C$ where ϱ_c is the spin density on adjacent carbon atom and $Q^H_{CH} = -27.0$ G.

[b] Ref. [4] (acetonitrile solution).

[c] Methyl proton splitting calculated employing the relation $a_{H(CH3)} = Q^H_{CCH3}\varrho_C$, where ϱ_C is the spin density on carbon atom joining the methyl group and $Q^H_{CCH3} = 25.0$ G. (McLachlan, A. D.: Molecular Physics **1**, 233 (1958); Brown, T. H., Karplus, M.: J. chem. Physics **39**, 1115 (1963).)

Table 4. ^{14}N *hyperfine splittings in radical anions of some nitro aromatic compounds*

Compound	ϱ_N	ϱ_C	$\varrho_O + \varrho_{O'}$	a_N (Calcd)[a]	a_N (Calcd)[b]	a_N (Obsd)[c]
Nitrobenzene	0.2140	0.1055	0.3471	10.59	10.20	10.32
p-Nitrotoluene	0.2201	0.0993	0.3490	10.97	10.49	10.79
p-Nitroaniline	0.2285	0.0712	0.3408	11.65	10.90	12.18
p-Dinitrobenzene	0.0581	0.1650	0.1907	1.74	2.77	1.75
p-Nitrobenzonitrile	0.1653	0.1384	0.3164	7.70	7.88	7.15
p-Nitrobenzaldehyde	0.1209	0.1494	0.2672	5.24	5.76	5.83

[a] Trilinear relation (see Eq. (7) of text).

[b] Linear relation (see Eq. (8) of text).

[c] Ref. [4] (acetonitrile solution).

tion was made by Hinchliffe. In all further discussion we shall use the spin densities after annihilation only.

Comparison of the proton splittings in Table 3 with the experimental values shows that the presently employed parameters give an adequate description of the spin distribution on ring carbon atoms in the radicals. The spin densities on nitrogen and oxygen atoms of the nitro group and adjacent carbon atom in the radical anions studied were then used to obtain the parameters Q_N^N, Q_{CN}^N and Q_{ON}^N in Eq. (1) by a least-squares fitting procedure and assuming all a_N's to be positive. Thus we obtain $Q_N^N = 55.41\ G$, $Q_{CN}^N = -7.21\ G$ and $Q_{ON}^N = -1.44\ G$. The corresponding expression for a_N then becomes:

$$a_N(\text{nitro}) = Q_N^N \varrho_N + Q_{CN}^N \varrho_C + Q_{ON}^N \varrho_O = 55.41\,\varrho_N - 7.21\,\varrho_C - 1.44(\varrho_O + \varrho_{O'})\,. \quad (7)$$

The ^{14}N splittings estimated using Eq. (7) are given in Table 4. The standard deviation of the fit of calculated to experimental splitting is ±0.59 C. It may be pointed out here that this standard deviation is smaller than that for the bilinear fit obtained by Rieger and Fraenkel (±0.86 G) using McLachlan spin density values [4]. Since the spin densities at the oxygen atoms and the carbon atom attached to the nitro group are not available from Hinchliffe's paper [6] we are unable to compute the $\sigma - \pi$ parameters from Hinchliffe's data and compare with our results. The interesting result that emerges from the present UHF calculations is that both Q_{CN}^N and Q_{ON}^N have small values in comparison to Q_N^N. Thus, Geske *et al.* [5] obtained a value of -5 G for Q_{CN}^N from the ^{14}N splitting constant in hindered poly nitro-anions and Q_{ON}^N has been estimated by Gross and Symons [25] to be -3.7 G from their analysis of NO_3 radical. In spite of the known sensitivity of these quantities to the parameters employed in the calculation of spin densities their closensess to our values is surprising. Assuming that a linear relationship, similar to the McConnell relation, holds for ^{14}N splittings, the proportionality constant, Q_N between the splitting constant and the spin density on nitrogen was found by least squares method to be 47.68 G. Thus we may write:

$$a_N(\text{nitro}) = Q_N \varrho_N = 47.68\,\varrho_N\,. \quad (8)$$

The standard deviation of the fit using Eq. (8) is ±1.05 G. Comparison of the two estimates of nitrogen splittings shows that the linear relationship (Eq. (3)) is at least approximately valid for nitro group-nitrogen splittings. A least squares fit assuming linear relation using Hinchliffe's spin density data [6] yields a value of $+93.14$ G for Q_N and a standard deviation of ±1.17 G. This Q_N value is considerably higher than our estimate in Eq. (6). Earlier, Hinchliffe [6] had used in his calculations a value of $Q_N = -87$ G. This value is at variance with the now generally accepted positive sign for this $\sigma - \pi$-parameter which in turn is based on the positive sign of the nitrogen couplings [26].

For ^{14}N splitting in the nitrile group Rieger and Fraenkel [27] obtained the constants $Q_N^N = 23.1$ G, $Q_{CN}^N = -6.8$ G in the Karplus-Fraenkel formalism from the results of their McLachlan type of calculations on a series of nitrile radical anions. Thus here,

$$a_N(\text{nitrile}) = Q_N^N \varrho_N + Q_{CN}^N \varrho_C = 23.1\,\varrho_N - 6.3\,\varrho_C\,. \quad (9)$$

The nitrile nitrogen splitting in the radical anion of *p*-nitrobenzonitrile using these constants along with our UHF spin density results is 0.82 G which may be compared with the experimental value of ±0.76 G. The spin density on nitrile carbon being very small, has negligible contribution to the estimated ^{14}N splitting in this case.

Barton and Fraenkel [28] found that in the case of dihydropyrazine cation radical Q_{NH}^H is uniquely determined from the value of Q_{CH}^H. Using their approach we find that with $Q^{\mathrm{H}}_{\mathrm{CH}} = -27$ G the value of $Q^{\mathrm{H}}_{\mathrm{NH}}$ is -29.6 G. Our calculated UHF spin desnities on amino-nitrogen and adjacent carbon in the radical anion of *p*-nitroaniline are, respectively, 0.0326 and 0.1462. With the above estimate of $Q^{\mathrm{H}}_{\mathrm{NH}}$, the amino proton splitting is calculated to be -0.96 G as compared to the experimental value of ± 1.12 G. Following the analysis of Barton and Fraenkel and using the present estimate of $Q^{\mathrm{H}}_{\mathrm{NH}}$ we obtain the expression for ^{14}N splitting constant of amino nitrogen:

$$a_{\mathrm{N}}(\text{amino}) = Q^{\mathrm{N}}_{\mathrm{N}}\varrho_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{CN}}\varrho_{\mathrm{C}} = 25.32\,\varrho_{\mathrm{N}} + 2.61\,\varrho_{\mathrm{C}}\,. \tag{10}$$

It should be noted that the above estimate of $Q^{\mathrm{N}}_{\mathrm{CN}} = 2.61$ G by Barton and Fraenkel was obtained without using any theoretically calculated spin density values and is free from any assumption regarding the magnitude of other $\sigma-\pi$-parameters. With the spin density values for amino nitrogen and the adjacent carbon noted above, Eq. (10) yields $a_{\mathrm{N}} = 1.21$ G for the amino nitrogen in *p*-nitroaniline. This value may be compared with the experimental value of ± 1.21 G. A small and positive value for $Q^{\mathrm{N}}_{\mathrm{CN}}$ seems to be necessary to fit the experimental splitting for amino nitrogen in the case of *p*-nitroaniline while a negative value for $Q^{\mathrm{N}}_{\mathrm{CN}}$ is clearly indicated from our calculations for the nitro group. It is to be noted that in case of aromatic azine radicals both positive and negative values for $Q^{\mathrm{N}}_{\mathrm{CN}}$ have been suggested by different authors [3]. Barton and Fraenkel, in their detailed discussion on this point, argued that since the absolute value of this parameter is small, variations in molecular geometry and charge in the neighbourhood of nitrogen atom have larger effect on this parameter than expected.

4. Conclusion

From the present study we suggest the following relationships to calculate ^{14}N splitting constants from UHF spin densities for nitrogen in three different environments.

Nitro group:

Trilinear relation: $a_{\mathrm{N}} = 55.41\,\varrho_{\mathrm{N}} - 7.21\,\varrho_{\mathrm{C}} - 1.44(\varrho_{\mathrm{O}} + \varrho_{\mathrm{O'}})$

Linear relation: $a_{\mathrm{N}} = 47.68\,\varrho_{\mathrm{N}}$

Amino group:

$$a_{\mathrm{N}} = 25.32\,\varrho_{\mathrm{N}} + 2.61\,\varrho_{\mathrm{C}}$$

Cyano group [27]:

$$a_{\mathrm{N}} = 23.1\,\varrho_{\mathrm{N}} - 6.3\,\varrho_{\mathrm{C}}\,.$$

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Professor P. T. Narasimhan
Department of Chemistry
Indian Institute of Technology
Kanpur, India