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INDO Calculation of Spin Densities in Radical Cations of a Series of Substituted Nitro- and *m*-Dinitrobenzenes

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Abstract—The spin densities in radical cations of 22 substituted nitro- and *m*-dinitrobenzenes were calculated by the INDO method. For radical anions of substituted nitrobenzenes, a good linear correlation was obtained between the spin densities $\rho_{s_N s_N}$ and experimental hyperfine coupling constants with the nitrogen atoms of the NO_2 groups (a^N): $a^N = K_N \rho_{s_N s_N}$, where K_N = 428.58 (R^2 = 0.96). For radical anions of substituted *m*-dinitrobenzenes, no satisfactory agreement between the calculated and experimental a^N constants was attained.

Quantum-chemical calculation of spin densities in radical ions is very important for interpretation of experimental results related to the hyperfine structure of the ESR spectra of these radical ions. Among the existing semiempirical calculation methods, many researchers prefer the INDO method in the Pople parametrization. However, the results of INDO calculations for radical anions are not always consistent with the experiment.

Previously we have studied the ESR spectra of radical anions of several tens of substituted nitro- and *m*-dinitrobenzenes [1–8] and then calculated for some of them the spin density distribution using the Hückel MO method with the MacLachlan corrections for π–π polarization [9]. We attained good agreement of the calculation results with the experiment for radical anions of 18 substituted nitrobenzenes. For radical anions of substituted *m*-nitrobenzenes, reasonable agreement was attained for the nitrogen splitting constants $a^N_{NO_2}$ only taking into account the turn of the NO_2 group at the 3-position, i.e., of the sterically hindered group. The angles were chosen for the situation when the ratios of the spin densities on the nitrogen atoms of the NO_2 groups, $\rho^\pi_N(1)/\rho^\pi_N(3)$, were close to the ratio of the experimental splitting constants, $a^N(1)/a^N(3)$. The proton splitting constants, especially for the 2-position, were poorly consistent.

In this work, we calculated the spin densities by the INDO (UHF) method in the Pople parametrization for 22 radical anions of various substituted nitro- and *m*-dinitrobenzenes. For the radical anions of substituted 1,3-dinitrobenzenes, the INDO method allowed estimation of angles by which the NO_2 groups are turned relative to the aromatic ring plane in the equilibrium structure, based on the total energies of various conformations.

Previously Pople and other researchers [10, 11] calculated the hyperfine coupling constants for a series of radical anions derived from various ^{14}N-containing aromatic compounds: benzonitrile, pyrazines, quinoxalines, certain nitro- and dinitrobenzenes, etc. However, the calculation results were compared to the experimental data obtained under different conditions and in different solvents. Therefore, it was not quite clear why the calculation results for certain radical anions were inconsistent with the experiment. In this work, we compared the calculated hyperfine coupling constants to the experimental data obtained by us previously under the same conditions: electrochemical generation of radical anions in an aprotic solvent (DMF) at room temperature [1–8].

Calculations were performed using standard geometric parameters used by Pople in [10, 12]; the parameters were refined on the basis of experimental data on the geometries of neutral nitrobenzene derivatives in the gas phase [13], calculation results, and intuition (Table 1).

An attempt to improve the results using geometry optimization by the MNDO (UHF) method for each radical anion has not given the expected effect. The calculation results are listed in Tables 2 and 3. In these tables, the experimental hyperfine coupling constants *a* are taken from the literature: for radical anions 1, 2, 4, 11, 13, and 15–22, from [1–8]; for 3, from [14]; for 5, 7, and 9, from [15]; for 6 and 14, from [11]. For 8, 10, and 12, the value was recalculated from the data for acetonitrile using data from [16] for 8 and from [17] for 10 and 12.

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Table 1. Structural parameters of substituted nitrobenzenes

Fragment	Bond	*d*, Å	Bond (ω) or torsion (φ) angle	ω, φ, deg
Aromatic ring	C–C	1.40	CCC	120
	C–H	1.08		
NO_2 group	C_{arom}–N	1.47	ONO	125
	N–O	1.24		
NH_2 group,	C_{arom}–N	1.40	HNH	113
Ar–NH_2 fragment	N–H	1.01	CNHNH	37.5
CH_3 group,	C_{arom}–C	1.52	$C_{arom}CH$	109.37
Ar–CH_3 fragment	C–H	1.09		
OH group	C_{arom}–O	1.36	$C_{arom}OH$	109.47
	O–H	0.96		
CN group	C_{arom}–C	1.40		
	C–N	1.16		
OCH_3 group,	C_{arom}–O	1.36	$C_{arom}OC$	109.47
C–O–C fragment	O–C	1.43		
CHO group,	C_{arom}–C	1.46	$C_{arom}CO$	120
>C=O fragment	C–O	1.21	$C_{arom}CH$	120
	C–H	1.08		
$CONH_2$ group	C_{arom}–C	1.46		
	C–O	1.22		
	C–N	1.40		

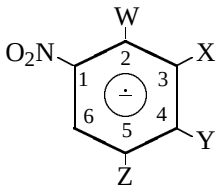
For all the radical anions under consideration, the theoretical hyperfine coupling constants a^X were calculated by Eq. (1):

$$a^X = K_X \rho_{s_X s_X}, \quad (1)$$

where $\rho_{s_X s_X}$ is the calculated *s*-orbital spin density of the X atom, and K_X is the scaling factor. For hyperfine coupling constants with protons, we used the scaling factor K_H 539.86 suggested by Pople [10]. For radical anions of monosubstituted nitrobenzenes, the calculated a^H values reasonably agree with the experiment, and only for the 4-H atoms the difference is as large as 1.1–1.3 Oe, with the calculated constants being underestimated and close to the a^H values for the 2-H and 6-H atoms. The qualitative relationship between the hyperfine coupling constants with protons is well reproduced for radical anions of all the substituted nitrobenzenes.

With radical anions derived from substituted *m*-dinitrobenzenes, there was appreciable disagreement between the calculated and experimental a^H values, especially for unsubstituted *m*-dinitrobenzene for which the relationship between the constants for the 2-H and 5-H atoms was inverse. This situation was already noted by Pople [10]; we obtained a similar

Table 2. Spin densities and hyperfine coupling constants calculated by the INDO (UHF) method in the Pople parametrization for radical anions of substituted nitrobenzenes

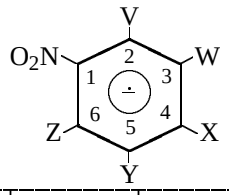


Comp. no.	W	X	Y	Z	Position no.	$\rho_{s_X s_X}$	*a*, Oe	
							calculation	experiment
1	H	H	H	H	N	0.0245	10.5	9.8
					2, 6	–0.0052	2.8	3.4
					3, 5	0.0027	1.5	1.1
					4	–0.0050	2.7	4.0
2	H	H	NH_2	H	N	0.0257	11.0	11.8
					2, 6	–0.0054	2.9	3.3
					3, 5	0.0031	1.7	1.1
3	H	H	CH_3	H	N	0.0240	10.3	10.0
					2, 6	–0.0053	2.9	3.5
					3, 5	0.0028	1.5	1.0
4	H	H	O^-	H	N	0.0313	13.4	13.9
					2, 6	–0.0044	2.4	3.05
					3, 5	0.0020	1.1	0.65

Table 2. (Contd.)

Comp. no.	W	X	Y	Z	Position no.	$\rho_{s_X s_X}$	*a*, Oe	
							calculation	experiment
5	H	H	CN	H	N	0.0205	8.8	6.24
					2, 6	–0.0054	2.9	3.02
					3, 5	0.0029	1.6	0.73
6	H	H	$CONH_2$	H	N	0.0183	7.8	7.85
					2.6	–0.0052	2.8	3.15
					3, 5	0.0026	1.4	0.87
7	H	H	CHO	H	N	0.0116	5.0	5.11
					2	–0.0050	2.7	2.95
					3	0.0023	1.2	0.38
					5	0.0023	1.2	0.23
					6	–0.0049	2.6	2.26
8	H	H	OCH_3	H	N	0.0253	10.8	11.0
					2, 6	–0.0054	2.9	3.43
					3, 5	0.0031	1.7	1.11
9	H	H	NO_2	H	N	0.0006	0.3	1.48
					H	–0.0018	1.0	1.12
10 (10°)	CH_3	H	H	H	N	0.0251	10.8	10.5
					3	0.0028	1.5	1.04
					4	–0.0048	2.6	3.91
					5	0.0028	1.5	1.04
					6	–0.0052	2.8	3.12
11	OH	H	H	H	N	0.0273	11.7	12.5
					3	0.0022	1.2	0.6
					4	–0.0045	2.4	3.7
					5	0.0028	1.5	0.6
					6	–0.0054	2.9	3.7
12	H	CH_3	H	H	N	0.0241	10.3	9.9
					2	–0.0053	2.9	3.30
					4	–0.0052	2.8	3.88
					5	0.0027	1.5	1.07
					6	–0.0053	2.9	3.30
13	H	CN	H	H	N	0.0234	10.0	7.9
					2	–0.0054	2.9	3.1
					4	–0.0058	3.1	4.4
					5	0.0029	1.6	1.0
					6	–0.0057	3.1	3.1
14	H	$CONH_2$	H	H	N	0.0238	10.2	9.24
					2	–0.0054	2.9	3.21
					4	–0.0058	3.1	4.24
					5	0.0030	1.6	1.07
					6	–0.0059	3.2	3.55
15	H	CN	CH_3	H	N	0.0228	9.8	8.6
					2	–0.0055	3.0	4.0
					5	0.0031	1.7	1.1
					6	–0.0058	3.1	4.0
16	H	CN	H	CN	N	0.0219	9.4	6.7
					2.6	–0.0060	3.2	3.4
					4	–0.0069	3.7	5.7

Table 3. Spin densities and hyperfine coupling constants calculated by the INDO (UHF) method in the Pople parametrization for radical anions of substituted *m*-dinitrobenzenes



Comp. no.	V	W	X	Y	Z	Position no.	$\rho_{s_X s_X}$	*a*, Oe	
								calculation	experiment
17	H	NO_2	H	H	H	N	0.0017	0.7	4.0
						2	0.0008	0.4	2.8
						5	0.0057	3.1	1.1
						4, 6	–0.0140	7.6	4.5
18	H	NO_2	H	CN	H	N	0.0010	0.4	3.0
						2	0.0008	0.4	2.0
						4, 6	–0.0146	7.9	5.0
19 (30°)	H	NO_2	CH_3	H	H	N^1	0.0225	9.6	5.2
						N^3	0.0014	0.6	3.6
						2	–0.0054	2.9	2.8
						5	0.0030	1.6	1.5
						6	–0.0057	3.1	5.2
20 (30°)	H	NO_2	CH_3	CN	H	N^1	0.0207	8.9	4.0
						N^3	0.0015	0.6	2.6
						2	–0.0060	3.2	1.1
						6	–0.0060	3.2	2.6
21 (10°)	H	NO_2	CH_3	H	CH_3	N	–0.0026	1.1	6.6
						2	0.0017	0.9	–
						5	0.0055	3.0	5.9
22 (10°)	CH_3	NO_2	H	CN	H	N	–0.0010	0.4	3.1
						4, 6	–0.0146	7.9	4.8

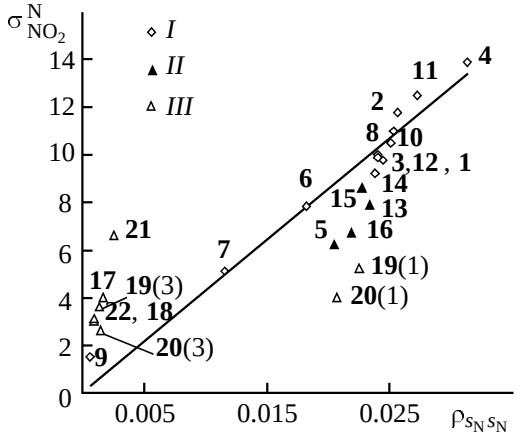
result in our previous Hückel MO calculations with the MacLachlan correction.

To calculate the hyperfine coupling constants with nitrogen, we analyzed the correlation between the *s*-orbital nitrogen spin densities $\rho_{s_N s_N}$ calculated by us by the INDO (UHF) method and the experimental hyperfine coupling constants a^N; we found that, for 12 radical anions derived from substituted nitrobenzenes, there is a linear correlation (see figure) described by Eq. (2):

$$a^N = K_N \rho_{s_N s_N}, \quad (2)$$

with K_N = 428.58 (R^2 0.9614). The scaling factor K_N obtained by us somewhat differs from that suggested by Pople (K_N 379.340). However, Pople derived this K_N value from the results obtained for radical anions of a wide set of compounds containing ^{14}N. The coupling constants $a^N_{NO_2}$ calculated for the radical anions of substituted nitrobenzenes with the scaling factor suggested by us are much better consistent with the experiment. Only for the CN-substituted radical anions the calculated and experimental values of $a^N_{NO_2}$ appreciably differ. The data for these radical anions fall with a reasonable accuracy on a separate straight line. We obtained previously a similar pattern in Hückel MO calculations of CN-substituted radical anions [9] using the parameters of the Coulombic and resonance integrals suggested in [15]. Calculations with the parameters suggested by us gave for all the CN derivatives the ρ^π_N and $a^N_{NO_2}$ values that well fitted in the general linear correlation for all the 30 radical anions derived from substituted nitro- and *m*-dinitrobenzenes.

Unfortunately, the hyperfine coupling constants $a^N_{NO_2}$ for the radical anions of *m*-dinitrobenzene and its derivatives lie out of the linear correlation between $\rho_{s_N s_N}$ and $a^N_{NO_2}$. In our calculations, we varied only the angle φ by which the NO_2 groups in the corre-



Correlation between the absolute spin densities on the NO_2 nitrogen atoms ($\rho_{s_N s_N}$), calculated by the INDO (UFH) method, and experimental hyperfine coupling constants ($a^{N}_{NO_2}$, Oe): (*I*) substituted nitrobenzenes, (*II*) substituted nitrobenzonitriles, and (*III*) substituted *m*-dinitrobenzenes. Straight line: correlation by Eq. (2). Figures at curves are compound nos. in Tables 2 and 3.

sponding positions are turned relative to the aromatic ring plane. This angle was varied at a 5° step in the range $-40° \le \varphi \le 40°$, with fixed values of the other geometric parameters (Table 1). For the radical anion of 1,3-dinitro-4,6-dimethylbenzene, φ was varied for both NO_2 groups in 1- and 3-positions synchronously, so as to preserve the C_{2v} symmetry of the molecular core in any conformation.

Calculations showed that, for radical anions **19**–**22**, the total energy passes through a minimum in the range 10°–40°. In Table 3, we present the calculated spin densities and hyperfine coupling constants for the conformations with the angle φ providing a minimum in the total energy according to INDO (UHF) calculations (10°–40° range). For radical anions **19** and **20**, φ was 30°, whereas the values of φ estimated by us previously [9] for the same radical anions by the Hückel MO method with MacLachlan corrections were 20° and 19°, respectively.

Table 3 shows that the absolute values of the calculated constants $a^{N}_{NO_2}$ for radical anions of substituted *m*-dinitrobenzenes appreciably differ from the experiment. At the same time, in radical anions **19** and **20** the qualitative relationship between the spin densities on the 1-N and 3-N atoms is reprodeuced correctly, namely, the spin density on the 1-N atom is appreciably larger ($\rho_{s_{N^1}s_{N^1}} > \rho_{s_{N^3}s_{N^3}}$). We also performed the calculations for the angles φ at which the Hückel MO calculations with the MacLachlan correction give the $a^{N}_{NO_2}$ values that reasonably agree with the experiment; however, the calculations did not give the desired result.

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