Theoretical Calculations and Assignments of Electronic Absorption Spectra of Cation Radicals of *o*-, *m*-, and *p*-Disubstituted Benzenes Having Amino and Hydroxyl Groups

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Calculations have been carried out on the electronic spectra and electronic structures of the cation radicals of *o*-, *m*-, and *p*-disubstituted benzenes having the amino and hydroxyl groups, by an open shell SCF MO CI method involving some doubly excited electron configurations. Assignments of the electronic absorption spectra of these cation radicals have been made on the basis of resulting transition energies and oscillator strengths. The results are in good agreement with experimental data. Effects of methyl-substitution on the cation spectra are discussed. Spin densities of these cation radicals have also been calculated and compared with experimental data.

Kimura *et al.*[1-3] observed the electronic absorption spectra of cation radicals of various disubstituted benzenes, *i.e.*, *p*-aminophenol$^+$, *m*-aminophenol$^+$, and their *N*- and *O*-methyl derivatives, by ultraviolet irradiation in rigid glasses at 77K. The electronic absorption spectra of hydroquinone$^+$ and several of its *O*-methyl derivatives have also been measured in concentrated sulfuric acid by Kimura and Yamada.[4] For EPA glasses containing *m*-aminophenol$^+$, *m*-anisidine$^+$, and *m*-phenylenediamine$^+$, appreciable blue shifts of the electronic absorption bands due to trapped electrons have been observed.[5] It has been pointed out that the mangitudes of such spectral shifts depend largely on electronic structures of the cations.

The open shell SCF MO method involving configuration interaction (CI) is now generally known to be advantageous for calculating electronic spectra and structures of organic free radicals having an odd electron. Using a method which combines the open shell SCF procedure of Longuet-Higgins and Pople[6] with CI, Ishitani and Nagakura[7,8] have extensively studied the electronic structures and spectra of the anion radicals of substituted benzenes having nitro, nitroso, and cyano groups and the anion radical of paracyclophane. Zahradnik and Carsky[9] have employed a similar theoretical method for studying the electronic spectra of the free radicals of various alternant hydrocarbons in more detail. Shida and Iwata[10] have recently carried out CI calculations of nitro-substituted aromatic anion radicals in order to explain experimental absorption spectra, by including some doubly excited electronic configurations.

However, as regards the cation radicals of disubstituted benzenes with electron donating groups such as amino and hydroxyl groups, only a few fragmentary reports have been given on their theoretical assignments; by Monkhorst and Kommandeur[11] for the electronic absorption spectrum of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine$^+$ and by Kimura and Mataga[12] for that of *p*-phenylenediamine$^+$, with the open shell MO CI calculation.

In connection with our previous works,[1-5] the present authors used the open shell SCF MO CI method to carry out theoretical studies on the cation radicals of a series of substituted benzenes having amino and hydroxyl groups, in order to clarify the electronic absorption bands already known for these cations and to predict those still unknown in experiment. It is especially interesting to compare the electronic transition of isomers of the disubstituted benzenes.

Method of Calculation

The SCF MO CI method was used in the calculation of cation radicals of *o*-, *m*-, and *p*-disubstituted benzenes having OH and NH_2 groups, and also that of monosubstituted benzenes such as phenol$^+$ and aniline$^+$. Numberings of carbon atoms in the cations are illustrated in Fig. 1.

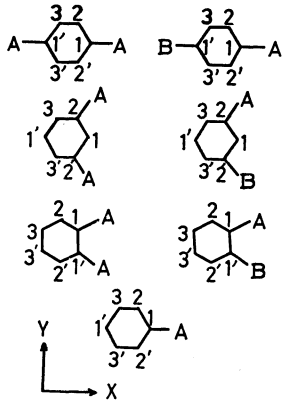

Fig. 1. Numbering of the carbon atoms in the cations of substituted benzenes, A and B indicating substituents.

1) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.* **48**, 440 (1968).
2) K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).
3) A. Egawa, K. Kimura, and H. Tsubomura, This Bulletin, **43**, 944 (1970).
4) K. Kimura and H. Yamada, *ibid.*, **42**, 3032 (1969).
5) K. Kimura, S. Katsumata, and K. Sawada, *J. Phys. Chem.*, **76**, 639 (1972).
6) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. Ser. A*, **68**, 591 (1955).
7) A. Ishitani and S. Nagakura, *Theoret. Chim. Acta*, **4**, 236 (1966).
8) A. Ishitani and S. Nagakura, *Mol. Phys.*, **12**, 1 (1967).
9) R. Zahradnik and P. Carsky, *J. Phys. Chem.*, **74**, 1235, 1240, 1249 (1970).
10) T. Shida and S. Iwata, *ibid.*, **75**, 2591 (1971).
11) H. J. Monkhorst and J. Kommandeur, *J. Chem. Phys.*, **47**, 391 (1967).
12) K. Kimura and N. Mataga, *ibid.*, **51**, 4167 (1969).

TABLE 1. THEORETICAL RESULTS OF ANILINE$^+$ AND *o*-, *m*-, AND *p*-PD$^+$

Symmetry	Energy (eV)	Configurations mainly contributing (%)
		Aniline$^+$
$^2B_1$	−0.584	ground (95)
$^2A_2$	0.640	3→4 (93)
$^2B_1$	2.298	2→4 (73), 4→6 (15), 3→5 (4)′
$^2B_1$	3.747	4→6 (50), 3→5 (23)′, 3→5 (10), 1→4 (6)
$^2A_2$	3.898	4→5 (67), 3→6 (18)′
		o-PD$^+$
$^2B_1$	−0.572	ground (94)
$^2A_2$	0.700	4→5 (91)
$^2B_1$	2.518	3→5 (66), 5→6 (16), 4→7 (4)
$^2A_2$	3.283	5→7 (60), 4→6 (13), 4→6 (11), 2→5 (9)
$^2B_1$	3.892	5→6 (50), 4→7 (29), 3→5 (8)
		m-PD$^+$
$^2A_2$	−0.581	ground (95)
$^2B_1$	0.143	4→5 (92)
$^2B_1$	1.869	3→5 (77), 5→6 (11), 4→7 (5)′
$^2A_2$	3.414	5→7 (54), 4→6 (14), 4→6 (12)′, 2→5 (8)
$^2B_1$	3.707	5→6 (46), 4→7 (32), 4→5, 4→6 (5)
		p-PD$^+$
$^2B_{2g}$	−0.608	ground (95)
$^2B_{3u}$	1.923	3→5 (72), 5→7 (18)
^2A_u	3.206	5→6 (83), 3→5, 3→6 (5), 4→7 (4)′
$^2B_{3u}$	3.418	5→7 (58), 4→6 (21)′, 3→5 (6), 4→6 (6)
$^2B_{3u}$	5.021	4→6 (53), 1→5 (17), 5→7 (9), 3→5 (6)

We used a computer program in which a total of 40 configurations was chosen for each symmetry from the first 100 low-energy configurations of one- and two-electron excitations.[13]

The Coulomb repulsion integrals of the type $(pp|qq)$ were calculated by using the Pariser-Parr approximation. The valence state ionization potentials and electron affinities were taken from literature[14] as follows: I_C=11.22 eV, A_C=0.62 eV, I_N^+=28.88 eV, A_N^+=12.28 eV, I_O^+=34.43 eV, A_O^+=14.97 eV. Nuclear charge values Z_C=1, Z_N=2, and Z_O=2 were used for carbon, nitrogen, and oxygen atoms, respectively. The penetration integrals were neglected, and core resonance integrals parametrized as $\beta_{\mu\nu}$. Bond lengths r(C–C)= 1.39 Å and r(C–N)=r(C–O)=1.36 Å were used throughout this work. The calculations were carried out with a FACOM 230-60 electronic computer in Hokkaido University using a computer program prepared by Iwata and Katsumata.[13]

Results and Discussion

Calculated results for energies of the ground and lower electronic excited states of aniline$^+$ and *o*-, *m*-, and *p*-phenylenediamine$^+$ are given in Table 1, together with electron configurations contributing to the various states by more than 4% (those of doubly excited configurations are underlined). Electronic configurations having doublet states are distinguished from each other with a prime, configurations $(i\to k)$ and $(i\to k)'$ designating $\sqrt{1/2}(|im\bar{k}|-|i\bar{m}k|)$ and $6^{-1/2}(-2|\bar{i}mk|+|i\bar{m}k|+|im\bar{k}|)$, respectively. The resulting transition energies, oscillator strengths and directions of transition moments are summarized in Table 2 together with experimental data available for comparison.

Cations of o-, m-, *and* p-*Phenylenediamines* (o-, m-, *and* p-*PD*$^+$). Electronic transition energies and oscillator strengths of *m*- and *p*-PD$^+$ were calculated for different β_{CN} values from −2.40 to −3.60 eV with an interval of 0.2 eV. The resulting transition energies were plotted against the β_{CN}'s and compared with experimental data available, as shown in Fig. 2. The electronic transition to the excited state to which the (4→5) configuration mainly contributes is forbidden in *p*-PD$^+$ because of molecular symmetry (D_{2h}), whereas

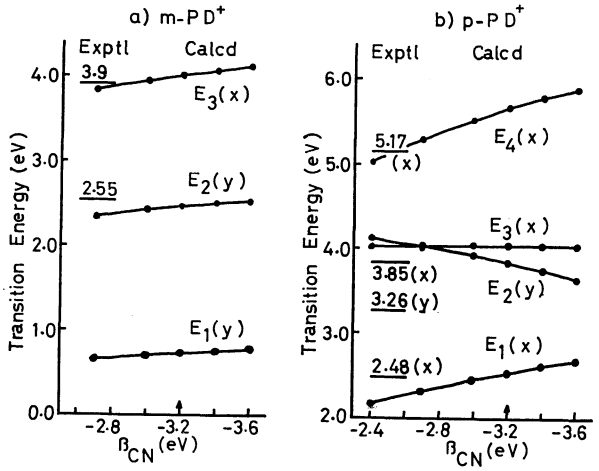

Fig. 2. Transition energies plotted against β_{CN}.

13) The program was prepared by S. Iwata and S. Katsumata, and used in the calculation of Ref. 10.

14) H. Hosoya, *Kagaku No Ryoiki*, **21**, 47 (1967). The values are essentially the same as those given by G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

TABLE 2. THEORETICAL RESULTS OF ELECTRONIC TRANSITION ENERGIES (OSCILLATOR STRENGTHS, AND DIRECTION OF TRANSITION MOMENTS) OF THE CATIONS, COMPARED WITH AVAILABLE EXPERIMENTAL DATA

(E IN eV)

o-PD$^+$		m-PD$^+$		
E_{calcd}	(f_{calcd})	E_{calcd}	(f_{calcd})	E_{exptl}[a]
1.27	(0.01, y)	0.72	(0.01, y)	
3.09	(0.05, x)	2.45	(0.06, y)	2.55
3.86	(0.03, y)	4.00	(0.03, x)	3.90
4.46	(0.10, x)	4.29	(0.00, y)	

p-PD$^+$			
E_{calcd}	(f_{calcd})	E_{exptl}[b]	(f_{exptl})[b]
2.53	(0.10, x)	2.48, 2.67	(0.11)
3.81	(0.04, y)	3.26	(0.06)
4.03	(0.18, x)	3.85	(0.31)
5.63	(0.14, x)	5.17	(0.2)

DMPD$^+$			TMPD$^+$		
E_{calcd}	(f_{calcd})	E_{exptl}	E_{calcd}	(f_{calcd})	E_{exptl}[c] (f_{exptl})[c]
2.36	(0.00, y)		2.16	(0.08, x)	2.19 (0.19, x)
2.42	(0.09, x)	2.37	3.61	(0.04, y)	3.13 (0.05, y)
3.71	(0.04, y)	3.26	3.95	(0.30, x)	3.82 (0.32, x)
4.10	(0.20, x)	3.83	5.52	(0.16, x)	4.80 (0.1)
5.40	(0.11, x)	4.96			

o-AP$^+$		m-AP$^+$			p-AP$^+$		
E_{calcd}	(f_{calcd})	E_{calcd}	(f_{calcd})	E_{exptl}[d]	E_{calcd}	(f_{calcd})	E_{exptl}[e]
1.15	(0.00_5)	0.78	(0.00_4)		1.72	(0.00_0, y)	
3.11	(0.05)	2.67	(0.06)	2.65	2.72	(0.09, x)	2.78
4.06	(0.04)	4.21	(0.04)	4.0	4.00	(0.04, y)	3.50
4.76	(0.00_8)	4.67	(0.00_2)	4.6	4.1	(0.14, x)	4.10

o-DHB$^+$		m-DHB$^+$		p-DHB$^+$		
E_{calcd}	(f_{calcd})	E_{calcd}	(f_{calcd})	E_{calcd}	(f_{calcd})	E_{exptl}[f]
0.88	(0.00_4, y)	0.60	(0.00_2, y)	2.75	(0.09, x)	2.95
2.91	(0.05, x)	2.55	(0.06, y)	4.18	(0.03, y)	
4.08	(0.05, y)	4.21	(0.04, x)	4.22	(0.10, x)	
4.66	(0.00_0, x)	4.57	(0.00_4, y)	5.54	(0.20, y)	

Phenol$^+$		Aniline$^+$		
E_{calcd}	(f_{calcd})	E_{calcd}	(f_{calcd})	E_{exptl}[g]
0.78	(0.00_1, y)	1.22	(0.00_3, y)	
2.84	(0.06, x)	2.88	(0.06, x)	2.88
4.43	(0.06, x)	4.33	(0.06, x)	
4.56	(0.00_0, y)	4.48	(0.00_4, y)	

a) Ref. 5. The value 3.90 eV has recently been obtained. b) Ref. 12. c) Ref. 18. d) Ref. 5. The values 4.0 and 4.6 eV have recently been obtained. e) Ref. 2. f) Ref. 4. g) Ref. 15.

it is allowed in o- and m-PD$^+$. We see that E_1, E_2, and E_4 in p-PD$^+$ are considerably sensitive to β_{CN}, while E_3 in p-PD$^+$ and E_1 to E_3 in m-PD$^+$ are insensitive. The E_1 transition energy of p-PD$^+$ corresponding to the first visible absorption band was found to be well reproduced at $\beta_{CN}=-3.20$ eV. This value was therefore employed throughout the present work, and the transition energies and oscillator strengths shown in Table 2 are those calculated with it.

Contributions of nitrogen AO's to SCF MO's (ϕ_3–ϕ_7) of o-, m-, and p-PD$^+$ are as follows. In p-PD$^+$, the contributions of (N_1+N_2) to $\phi_3(b_{3u})$ and $\phi_7(b_{3u})$ are 21 and 7%, respectively, and that of (N_1-N_2) to $\phi_5(b_{2g})$ is 16%. There are no nitrogen contributions to $\phi_4(b_{1g})$ and $\phi_6(a_u)$ corresponding to the e_{1g} and e_{2u} MO's of benzene, respectively. In m-PD$^+$, contributions of (N_1+N_2) to ϕ_3, ϕ_4, and ϕ_6 in symmetry b_1 are 10, 14, and 2%, respectively, and those of (N_1-N_2) to ϕ_5 and ϕ_7 in symmetry a_2 are 11 and 6%, respectively. In o-PD$^+$, contributions of (N_1+N_2) to ϕ_3, ϕ_5, and ϕ_6 in symmetry b_1 are 8, 16, and 2%, respectively, and those of (N_1-N_2) to ϕ_4 and ϕ_7 in symmetry a_2 are 6 and 1%, respectively.

The electronic absorption spectrum of p-PD$^+$ was interpreted by Kimura and Mataga[12] with the open shell MO CI method using Hückel MO's. However, in the present work, much better results were obtained for transition energies and oscillator strengths (see Table 2).

In p-PD$^+$, electron configurations with the largest contributions are (3→5), (5→6), (5→7), and (4—6) in Ψ_1 to Ψ_4, respectively (Table 1).

The calculated results of m-PD$^+$ are also in good agreement with the experimental ones (Table 2). For o-PD$^+$, however, there are no experimental values reported. It is interesting to note that the present calculations of o- and m-PD$^+$ predict that the first transitions $\Psi_0\rightarrow\Psi_1$ (f=0.01) should cause weak absorption bands in near infrared region, although no such absorption bands have so far been reported.

Cations of o-, m-, *and* p-*Aminophenols (*o-, m-, *and* p-*AP$^+$).* Transition energies of p-AP$^+$ were calculated with various β_{CO} values from −2.40 to −3.60 eV with an interval of 0.20 eV. By plotting the resulting transition energies against β_{CO}, it was found that E_2 corresponding to the visible absorption band is fairly sensitive to β_{CO} and the experimental value of this second transition energy is reproduced at $\beta_{CO}=-3.20$ eV. This β_{CO} value and the β_{CN} value (−3.20 eV) previously determined were used in the calculation of all the isomers (Table 2).

The electronic absorption spectra of p-AP$^+$ and its *N*- and *O*-methyl derivatives are known to consist of three bands in a wavelength region greater than about 250 nm.[2] We see that agreement between the calculated and experimental transition energies is excellent for m- and p-AP$^+$.

Cations of o-, m-, *and* p-*Dihydroxybenzenes (*o-, m-, *and* p-*DHB$^+$).* The electronic absorption spectra of cation radicals of several p-dialkoxybenzenes (hydroquinone, p-methoxyphenol, p-dimethoxybenzene, p-ethoxyphenol, p-diethoxybenzene, and 2,3,5-trimethylhydroquinone) were measured in concentrated sulfuric acid by Kimura and Yamada.[4] Our calculation (Table 2) indicates that the first allowed transition of p-DHB$^+$ (hydroquinone$^+$) occurs at E=2.75 eV, in good agreement with the experimental value of 2.95 eV obtained from the 420 nm band.

Phenol$^+$ and Aniline$^+$. Electronic spectra of phenol$^+$ and aniline$^+$ were also calculated with the same parameter values as mentioned above. The visible absorp-

tion bands of aniline$^+$,[15] *N*-methylaniline$^+$,[16,17] and *N,N*-dimethylanilinc$^+$ [15–17] have been reported in the region 400—450 nm. According to the present results, such absorption bands may be interpreted as transition $\Psi_0 \rightarrow \Psi_2$ (f=0.06), which is mainly due to configuration (2→4).

No absorption data concerning phenol$^+$ are available. The present calculation predicts that a visible band should be located around 440 nm (2.84 eV) with f= 0.06.

Cations of N,N-*Dimethyl*-p-*Phenylenediamine and* N,N,N′,N′-*Tetramethyl*-p-*Phenylenediamine (DMPD$^+$ and TMPD$^+$).* The electronic absorption spectrum of TMPD$^+$ (so-called Würster's blue cation) has been studied in solution and crystalline state by many workers, this being the only cation whose experimental polarization has been reported.[18] Thus, it is of particular interest to compare the calculated results of TMPD$^+$ with experiment. In the present calculations of DMPD$^+$ and TMPD$^+$, the effect of methyl substitution was taken into account in such a way that the valence state ionization potential of the methyl-substituted nitrogen atom is reduced by 2.0 eV[19] and β_{CN} is made equal to −3.05 eV proportional to $1/2\,(I_N+I_C)$. Very good agreement was obtained between theory and experiment (Table 2).

The first transition of DMPD$^+$ is not symmetry-forbidden, but its intensity is very low. The first visible absorption band can be assigned to the second transition.

Effect of Methyl Substitutions. It was indicated[2] that the experimental shifts of the absorption bands of

Table 3. Shifts (in eV) of the first visible bands of the cations due to methyl substitutions

Methyl derivatives of *p*-PD$^+$					
Substituent	NH_2 NH_2	NH_2 $N(Me)_2$	NHMe NHMe	NHMe $N(Me)_2$	$N(Me)_2$ $N(Me)_2$
Calcd	−0.15	−0.31	−0.31	−0.46	−0.61
Exptl[a]	−0.16	−0.30	−0.29	−0.40	−0.50
Methyl derivatives of *p*-AP$^+$					
Substituent	NH_2 OMe	NHMe OH	$N(Me)_2$ OH	NHMe OMe	
Calcd	−0.17	−0.12	−0.24	−0.41	
Exptl[b]	−0.04	−0.10	−0.25	−0.37	
Methyl derivatives of *p*-DHB$^+$					
Substituent	OH OMe	OMe OMe			
Calcd	−0.13	−0.26			
Exptl[c]	−0.14	−0.27			

a) Obtained from the data reported by Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2535 (1968).
b) Obtained from the data of Ref. 2.
c) Obtained from the data of Ref. 4.

Table 4. Comparison of calculated and experimental spin densities

Cation	Atom	C(1) C(1′)	C(2) C(2′)	C(3) C(3′)	N	O
o-PD$^+$	Calcd	0.185	−0.030	0.114	0.231	
m-PD$^+$	Calcd	−0.049	0.052	0.373	0.142	
p-PD$^+$	Calcd	0.158	0.058	0.058	0.226	
	Exptl[20]		0.076	0.076	0.236	
DMPD$^+$	Calcd	0.088	0.074	0.028	0.390	
					0.177[a]	
TMPD$^+$	Calcd	0.088	0.047	0.047	0.318[a]	
	Exptl[21]		0.070	0.070	0.270[a]	
o-AP$^+$	Calcd	0.223	0.003	0.075	0.248	0.092
		0.230	−0.060	0.190		
m-AP$^+$	Calcd	−0.001	0.139	0.282	0.212	0.025
		−0.061	−0.037	0.367		
p-AP$^+$	Calcd	0.158	0.093	0.026	0.266	0.107
		0.229				
	Exptl[22]		0.143	0.021	0.332	
o-DHB$^+$	Calcd	0.249	−0.047	0.162		0.135
m-DHB$^+$	Calcd	−0.056	0.124	0.359		0.083
		−0.078				
p-DHB$^+$	Calcd	0.243	0.062	0.062		0.133
	Exptl[23]		0.080	0.080		0.158
Phenol$^+$	Calcd	0.243	0.128	−0.004		0.165
		0.343				
Aniline$^+$	Calcd	0.135	0.150	−0.024	0.317	
		0.295				

a) Spin density on the N atom belonging to the $N(CH_3)_2$ group

15) K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, **73**, 1868 (1969).
16) E. J Land and G Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).
17) S. Arimitsu, K. Kimura, and H. Tsubomura, This Bulletin, **43**, 1858 (1969).
18) A. C. Albercht and W. T. Simpson, *J. Amer. Chem. Soc.*, **77**, 4454 (1955).
19) Since the first ionization potentials of NH_3, CH_3NH_2, and, $(CH_3)_2NH$ are 10.16, 9.18, and 8.36 eV, respectively (A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.*, **B 1968**, 22), it is inferred that the change in the valence state ionization potential of the nitrogen atom per one CH_3 group is about −0.9 eV.

p-aminophenols$^+$ from that of *p*-phenylenediamine$^+$ are approximately interpreted in terms of differences in valence-state ionization potentials of the substituents by using the first-order perturbation theory. In the present work, using the SCF MO's for the parent cations as unperturbed systems, we applied this perturbation method in order to explain the experimental band shifts of the various methyl substituted cations. The shifts of the first visible bands for the methyl derivatives of *p*-PD$^+$, *p*-AP$^+$, and *p*-DHB$^+$ (Table 3) may be given by $\{-0.0765(\Delta I_{N_1}+\Delta I_{N_2})\}$, $\{-0.0591\Delta I_N-0.0597\Delta I_o\}$, and $\{-0.0438(\Delta I_{o_1}+\Delta I_{o_2})\}$, where $\Delta I_N=2.0$ eV and $\Delta I_o=3.0$ eV were used. We see that calculated shifts are in good agreement with the experimental shifts of the longest wavelength absorption bands.

Spin Densities. Spin densities in cation radicals are obtainable from an analysis of hyperfine splittings of ESR spectra. Since hyperfine ESR splittings of *p*-PD$^+$,[20] TMPD$^+$,[11,21] *p*-AP$^+$,[22] and *p*-DHB$^+$ [23] have already been measured, we carried out theoretical calculations of the spin densities of these cation radicals and other related cations, obtained from the McLachlan relationship[24] using the experimental hyperfine splittings and appropriate Q values.[25] The calculated results are shown in Table 4. As far as comparison is possible, the calculated spin densities are in agreement with the experimental ones.

Effect of Doubly Excited Configurations. It should be mentioned that all the singly excited electron configurations are included for all the compounds studied except for aminophenols, in which a few of the singly excited configurations with high energies are excluded because of the low molecular symmetries. Contribution of the doubly excited configurations is less than a few percent in the lower states of the cations as underlined in Table 1.

20) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).
21) J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 615 (1962).
22) W. M. Fox and W. A. Wates, *J. Chem. Soc.*, **1964**, 6010.
23) P. D. Sullivan, *J. Amer. Chem. Soc.*, **89**, 4294 (1967).
24) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).
25) $Q_{C-H(ring)}=-28$ Gauss, $Q_{N-H}=Q_{N-CH_3}=25$ Gauss, and $Q_{O-H}=20.8$ Gauss.