The Electronic Spectra and Electronic Structures of Amino-substituted Benzenes

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Theoretical studies of the electronic structures and spectra of complex aromatic molecules seem to be of increasing importance from various viewpoints. The electronic spectra and electronic structures of substituted aromatic hydrocarbons for instance, have been the subject of a number of theoretical investigations.[1-12]

Baba and Suzuki[12] have made a comparative study of the electronic spectra of phenol and aniline and also of those of naphthols and naphthylamines. These calculations, as well as those by some of the other investigators,[5,9] employed molecular orbitals delocalized over all the cores of the molecules, in contrast to the method of the composite system, where a molecule is regarded as being made up of several fragments and where the interactions among the wave functions of these fragments are calculated to give the wave functions for the whole molecule.[7,8] The latter method is quite suitable for determining the correlation between the spectrum of a molecule and the spectra of fragments of which the molecule is composed and also for ascertaining the extent of charge transfer (CT) interaction among these fragments in the molecule.

Of course, these two methods are not essentially independent of each other. Recently, Fischer-Hjalmars[13] has developed an elegant method for transforming the wave functions calculated by the former method into those obtained by the latter method using natural spin orbital of Löwdin;[14] she has applied that method to toluene and aniline. In the case of aniline, the result of this transformation was rather close to the wave functions calculated by Murrell[7] with the method of the composite system.

As has been said above, the electronic spectrum and the electronic structure of aniline, among other amino-substituted benzenes, have been studied in detail. However, the electronic structures and spectra of poly-substituted amino-benzenes have not been studied in detail.

Because of the strong conjugation of the amino group with the π-electron system of the aromatic ring, perturbation methods* seem to be poor approximations for systematically interpreting the electronic spectra of amino-substituted aromatics; therefore, a variational method should be employed for this study.

Because of this strong conjugation power of the amino group, the electronic structure of the aromatic hydrocarbon will be considerably affected by this substitution. Actually, Köhler and Scheibe[15] have demonstrated that *s*-triaminobenzene is easily protonated on the ring carbon in an almost neutral aqueous solution, whereas aniline, as well as *m*-phenylenediamine, is protonated on the amino-nitrogen. This is a remarkable example of substitution effecting a large change in the physico-chemical property of a molecule.

We have studied this very interesting phenomenon by means of molecular orbital calculations and have shown that the calculated electronic spectrum of the protonated *s*-triaminobenzene agrees satisfactorily with the observed spectrum, and also that the quite large proton affinity of this molecule is in accordance with the results of the calculations.[16]

In view of the circumstances described above, it seems to be desirable to study the electronic spectra and electronic structures of amino-substituted aromatics in a more systematic way.

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1) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).
2) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1949).
3) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
4) S. Nagakura and H. Baba, ibid., **74**, 5693 (1952).
5) I. Fischer, *Ark. Fys.*, **5**, 377 (1952).
6) L. Goodman, I. G. Ross and H. Shull, *J. Chem. Phys.*, **26**, 474 (1957); L. Goodman and H. Shull, ibid., **27**, 1388 (1957).
7) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).
8) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).
9) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958); K. Nishimoto, to be published.
10) Y. I'Haya, *J. Am. Chem. Soc.*, **81**, 6120, 6127 (1959).
11) N. Mataga and S. Mataga, This Bulletin, **32**, 600 (1959).
12) H. Baba, ibid., **34**, 76 (1961); H. Baba and S. Suzuki, ibid., **34**, 82 (1961).
13) I. Fischer-Hjalmars, *Ark. för Fys.*, **21**, 123 (1962); Preprint for the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September, 1962.
14) P.-O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955).

* In the sense of the expansion of the secular determinant in a series.

15) H. Köhler and G. Scheibe, *Z. anorg. u. allgem. Chem.*, **285**, 221 (1956).
16) N. Mataga, This Bulletin, **36**, 1109 (1963).

Accordingly, we have taken up several aminobenzenes, such as aniline, isomeric phenylenediamines (PDA) and *s*-triaminobenzene (TAB), and also several amino-substituted nitrogen heterocycles, such as 4-amino-pyridine, 1, 4-diaminotetrazine and melamine.

In the present report, mainly the results for amino-substituted benzenes will be described.

Method of Calculation

Although our method of calculation in this report is based on the semiempirical ASMO method[12,17,18] with a zero differential overlap, we have tried various approaches including the VESCF[19,20] calculation on *p*-PDA, because the electronic structures of amino-derivatives appear to be much more complicated than those of parent hydrocarbons and simple *n*-heterocycles, where the -CH= groups of the parent hydrocarbon are replaced by -N=.

One of the difficulties with calculation using the MO's delocalized over all the cores of the molecule is the assessment of the core potential at amino nitrogen, which can contribute two electrons to the π-system, in contrast to the case of aromatic hydrocarbons or *n*-heterocycles, where the core potentials for π-electrons are fairly uniform. A similar difficulty arises in the case of pyrrole, for which Brown and Heffernan used the VESCF method.[20]

The outline of our procedure of calculation is as follows:

i) The calculation of Hückel MO's, assuming appropriate values of Coulomb and resonance parameters ($\alpha_N=\alpha+1.2\beta$, $\beta_{CN}=\beta$[12]).

ii) The antisymmetrization of Hückel MO's.

iii) The calculation of electronic spectra invoking configuration interaction (CI) or SCF calculation using Hückel MO's as the starting wave functions, and then the calculation of the electronic spectra by the CI method.

Although the necessary formulas for the ASMO CI calculation have been given elsewhere,[17,18] they will now be described briefly.

The Hückel MO's (ψ_i's) are expressed by linear combinations of $2p\pi$ AO's ($\phi_1 \cdots\cdots \phi_{2n}$) of carbon and nitrogen:

$$\psi_1=\sum_{\mu}^{2n} c_{i\mu}\phi_\mu \tag{1}$$

The Hamiltonian for $2m$ π-electrons can be written as:

$$\mathscr{H}=\sum_{i}^{2m}\mathscr{H}_i{}^{\text{core}}+\sum_{i<j}^{2m}e^2/r_{ij} \tag{2}$$

where $\mathscr{H}_i{}^{\text{core}}$ is the core Hamiltonian for the ith electron and r_{ij} is the interelectronic distance.

By means of the Fock Hamiltonian, $F=\mathscr{H}^{\text{core}}+G$, the apparent orbital energies are expressed by:

$$\varepsilon_i=\langle\psi_i|F|\psi_i\rangle=\sum_{\mu,\nu}c_{i\mu}c_{i\nu}\cdot\langle\phi_\mu|F|\phi_\nu\rangle=\sum_{\mu,\nu}c_{i\mu}c_{i\nu}F_{\mu\nu} \tag{3}$$

Putting $\langle\phi_\mu(i)|\mathscr{H}_i{}^{\text{core}}|\phi_\nu(i)\rangle=\beta_{\mu\nu}$, the matrix elements of Fock Hamiltonian in terms of AO's are written as:

$$\left.\begin{aligned}F_{\mu\mu}&=-I_\mu+(1/2)P_{\mu\mu}\gamma_{\mu\mu}+\sum_{\kappa\neq\mu}(P_{\kappa\kappa}-Z_\kappa)\gamma_{\kappa\mu}\\F_{\mu\nu}&=\beta_{\mu\nu}-(1/2)P_{\mu\nu}\gamma_{\mu\nu}\end{aligned}\right\} \tag{4}$$

The excitation energies for the $i \rightarrow k$ transition, $E({}^{1,3}\chi_{ik})=\langle{}^{1,3}\chi_{ik}|\mathscr{H}|{}^{1,3}\chi_{ik}\rangle-\langle\psi_0|\mathscr{H}|\chi_0\rangle$, where χ_0 is the ground electronic configuration, and the interconfigurational matrix elements, $\langle{}^{1,3}\chi_{ik}|\mathscr{H}|\cdot{}^{1,3}\chi_{jl}\rangle$, are calculated by the following equations:

$$E({}^{1,3}\chi_{ik})=(\varepsilon_k-\varepsilon_i)-(\langle ik|G|ik\rangle-\langle ik|G|ki\rangle)\pm\langle ik|G|ik\rangle \tag{5}$$

$$\langle{}^{1,3}\chi_{ik}|\mathscr{H}|{}^{1,3}\chi_{il}\rangle=\varepsilon_{kl}-(\langle ik|G|il\rangle-\langle ik|G|li\rangle)\pm\langle ik|G|li\rangle,\qquad k\neq l \tag{6}$$

$$\langle{}^{1,3}\chi_{ik}|\mathscr{H}|{}^{1,3}\chi_{jk}\rangle=-\varepsilon_{ji}-(\langle kj|G|ki\rangle-\langle kj|G|ik\rangle)\pm\langle kj|G|ik\rangle,\qquad j\neq i \tag{7}$$

$$\langle{}^{1,3}\chi_{ik}|\mathscr{H}|{}^{1,3}\chi_{jl}\rangle=-(\langle jk|G|il\rangle-\langle jk|G|li\rangle)\pm\langle jk|G|li\rangle,\qquad i\neq j,\ k\neq l \tag{8}$$

$$\langle{}^{1}\chi_{ik}|\mathscr{H}|\chi_0\rangle=\sqrt{2}\,\varepsilon_{ki} \tag{9}$$

In these equations, $\varepsilon_{ki}=\langle\psi_k|F|\psi_i\rangle$, $\langle jk|G|li\rangle=\langle\psi_j(i)\psi_k(j)|e^2/r_{ij}|\psi_l(i)\psi_i(j)\rangle$, the + signs before the last terms in the right hand side are for singlets, and the − signs are for triplets. Thus, only the singly-excited configurations and the ground configuration are taken into account.

In the case of the SCF calculation, the secular equation:[21]

$$\sum_{\nu}F_{\mu\nu}c_{i\nu}=\varepsilon_i c_{i\mu} \tag{10}$$

must be solved by an iterative procedure.

In the VESCF method of Brown and Heffernan,[19,20] the SCF procedure involves the dependence of all the integrals except $\beta_{\mu\nu}$ on the charge distribution, $P_{\mu\mu}$.

The wave function, Ψ, for an electronic state is given by a linear combination of χ's. The oscillator strength, f, is calculated by the following equation:

$$f=0.08754\times\nu_{oa}\sum_{r=x,y,z}[m_{oa}^r]^2 \tag{11}$$

where ν_{oa} is the excitation energy in units of eV. of the transition from the ground state, Ψ_0, to an excited state, Ψ_a. The necessary formulas for the calculation of the transition moment, $m^r{}_{oa}$, have been given elsewhere.[17b]

Let us now consider the evaluation of integrals. They have been evaluated by semiempirical procedures. $Z_\kappa=1$ for the carbon core and $Z_\kappa=2$ for the core of amino nitrogen, which contributes two electrons to the π-system. The I_μ values for carbon were taken to be 11.42 eV., and that for the amino nitrogen, 28.85 eV.[22]

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[17] a) R. Pariser and R. G. Parr, *J. Chem. Phys*, **21**, 466, 767 (1953); ibid., **23**, 711 (1955); b) R. Pariser, ibid., 24, 250 (1956).

[18] N. Mataga, This Bulletin, **31**, 453, 459, 463 (1958); *Z. Phys. Chem. N. F.*, **18**, 19 (1958).

[19] R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, 54, 757 (1958); *Australian J. Chem.*, **12**, 543, 554 (1959).

[20] R. D. Brown and M. L. Heffernan, ibid., **12**, 319, 330 (1959).

[21] J. A. Pople, *Trans. Faradaday Soc.*, **49**, 1375 (1953); *Proc. Phys. Soc.*, **A68**, 81 (1955).

$\gamma_{\mu\nu}$'s were evaluated by the same procedure as before.[18,23,24] For the evaluation of m^r and $\gamma_{\mu\nu}$, all nearest neighbor C-C bond distances are assumed to be 1.39Å, and those of C-N bonds, 1.36Å.[5] The core resonance integral, $\beta_{\mu\nu}$, was taken into account only for the nearest neighbors and was neglected for more distant neighbors; the same value as before[18,23,24] was used for β_{CC}, namely, $\beta_{CC}=-2.388$ eV. However, the most suitable value for β_{CN} in the present approximation is not yet known. We have calculated the electronic spectrum of *p*-PDA assuming various values for β_{CN} in order to find out the β_{CN} value which fits the observed excitation energy. In this way, the best value of β_{CN} for reproducing the excitation energies to the first and the second excited singlet states has been found to be -3.6 eV.

We have calculated the electronic spectra of some amino-substituted benzenes and nitrogen heterocycles, such as aniline, *p*-PDA, TAB, 4-aminopyridine, 4,4'-diaminotetrazine and melamine, with this β_{CN} value. However, the agreement between the calculated and observed spectra is not very satisfactory with this β_{CN} value.

One of the main causes for this unsatisfactory agreement seems to be as follows. The value of I_μ for the amino-nitrogen (28.85 eV.) used in the above calculation (Approximation A) is the ionization potential of the $2p\pi$ electron of N^+ in the trigonal hybrid state. This value appears to be too large; the real value is probably smaller than this value and a little larger than that for neutral nitrogen because the actual core for a π-electron at amino-nitrogen is not N^{2+} but is partially shielded because of the existence of another π-electron. Moreover, this value of β_{CN} seems to be too large because the overlap between the $2p\pi$ AO's on the amino-nitrogen and the substituted carbon respectively may not be larger than the corresponding overlap between the nearest neighbor carbons.

In view of these circumstances, we should examine other semiempirical procedures more appropriate to the present case. One of the possible procedures is to regard I_μ or $F_{\mu\mu}$ for amino nitrogen as an adjustable parameter and to select the most suitable value for reproducing the observed spectra satisfactorily. For this purpose, we have used a simplified procedure which gives appropriate values for the $F_{\mu\mu}$'s of amino-nitrogen, That is,

$$\langle F_{NN}\rangle=\langle F_{CC}\rangle_{AV}+\delta_N\cdot\langle F_{12}\rangle_{AV} \qquad (12)$$

where $\langle F_{CC}\rangle_{AV}$ is the simple arithmetic mean of $F_{\mu\mu}$'s for carbon, $\langle F_{12}\rangle_{AV}$ is the same quantity of $F_{\mu\nu}$'s for the nearest neighbor carbon-carbon bonds, and δ_N is the Hückel MO parameter for the Coulomb integral of nitrogen, 1.2.

When $\langle F_{\mu\mu}\rangle$ of Eq. 12 instead of $F_{\mu\mu}$ of Eq. 4 is used for amino-nitrogen, the most suitable value of the core resonance integral β_{CN} appears to be -2.399 eV., the β_{CC} value being the same as before. Therefore, in this approximation, $\beta_{CN}\approx\beta_{CC}$; this result seems to be physically reasonable.

For a more refined calculation, the VESCF method of Brown and Heffernan[19,20] may be used. An analogous idea of "differential ionization" has been proposed by I'Haya.[25]

In the VESCF method, it is assumed that Slater's rule for the effective charges of atoms is applicable to a continuous variation in electron density. Accordingly, the effective charge, Z_μ, of the μ atom is expressed as a function of $P_{\mu\mu}$:

$$Z_\mu=N_\mu-\lambda_\mu-0.35(\sigma_\mu+P_{\mu\mu}) \qquad (13)$$

where N_μ is the atomic number and σ_μ is the number of σ-electrons associated with the μ atom in the molecular framework, e.g., 3 for carbon and the amino-nitrogen. λ_μ is the contribution from the inner shell electrons, and $\lambda_\mu=1.35$ for carbon and nitrogen in the present case.

If the I_μ's are plotted against the Z_μ's for the (sp^3, V_4) valence state of the iso-electronic series, C, N^+ and O^{2+}, and for the (sp^4, V_3) valence state of the iso-electronic series, C^-, N and O^+ respectively, the curves are accurately parabolic. In this way, the form of the relationship between the valence state ionization potential, I_μ, and Z_μ has been established.[26] Therefore, $\gamma_{\mu\nu}$'s can be calculated easily from the relations:

$$\gamma_{\mu\mu}(sp^3, V_4)=I_\mu(sp^3, V_4)-A_\mu(sp^3, V_4)$$
$$=I_\mu(sp^3, V_4)-I_\mu(sp^4, V_3)$$
$$a_{\mu\mu}=14.3949/\gamma_{\mu\mu}$$

and

$$a_{\mu\nu}=2a_{\mu\mu}a_{\nu\nu}/(a_{\mu\mu}+a_{\nu\nu})$$

Thus, in this SCF procedure, the I_μ's and $\gamma_{\mu\nu}$'s become functions of $P_{\mu\mu}$'s from their dependence on Z_μ's. We have applied this method to *p*-PDA.

Results and Discussion

The Hückel MO's and MO energies of aniline and isomeric PDA's are given in Appendix I. The numberings of the atoms in these molecules are given in Fig. 1. The MO's and MO energies of TAB are given elsewhere.[16] C_{2v} symmetry is assumed for aniline, *o*- and *m*-PDA, while D_{2h} symmetry is assumed for *p*-PDA.

Using these Hückel MO's, the electronic spectrum of *p*-PDA was calculated, assuming various β_{CN} values as described in the Method-of-Calculation section. The results are indicated in Fig. 2. The observed excitation energy to the lowest excited singlet state of *p*-PDA is nearly 4 eV. This value can be repoduced by taking either $\beta_{CN}=-1.2$ eV. or $\beta_{CN}=-3.6$ eV. However, with $\beta_{CN}=-1.2$ eV. the disagreement between the calculated and observed values of the excitation energy to the second excited singlet state is considerable (observed value

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[22] S. Mataga and N. Mataga, *Z. Phys. Chem. N. F.*, **19**, 231 (1959).

[23] K. Nishimoto and N. Mataga, ibid., **12**, 335 (1957); N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).

[24] N. Mataga and K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).

[25] Y. I'Haya, *Mol. Phys.*, **3**, 513, 521 (1960).

[26] S. Mataga and N. Mataga, This Bulletin, **32**, 521 (1959).

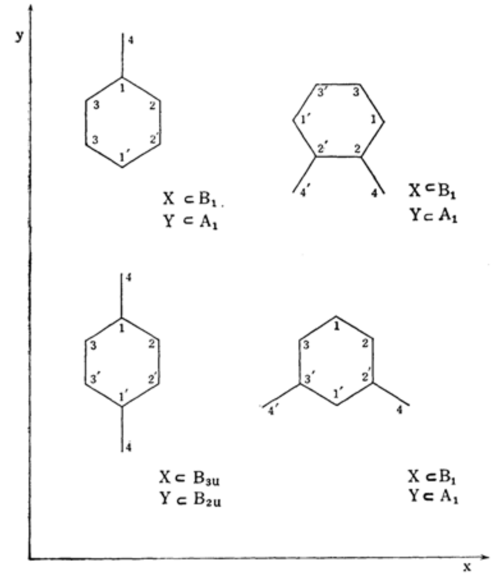

Fig. 1. The numbering of atoms in aminobenzenes.

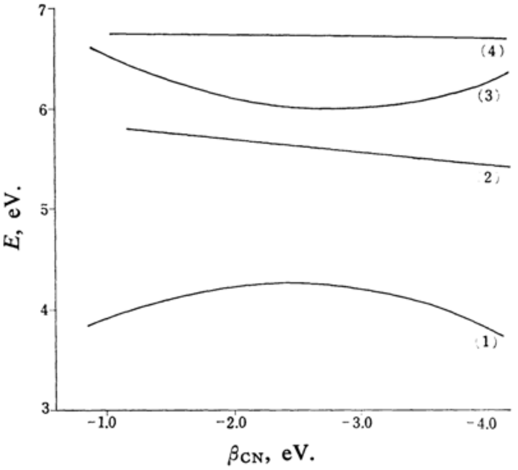

Fig. 2. The change of the excited singlet state energies of *p*-PDA as a function of the β_{CN} values.

(1) $\Psi(^1B_{3u})=a\,{}^1\chi_{56}-b\,{}^1\chi_{47}$
(2) $\Psi(^1B_{2u})=c\,{}^1\chi_{57}+d\,{}^1\chi_{46}$
(3) $\Psi(^1B_{3u})=b\,{}^1\chi_{56}+a\,{}^1\chi_{47}$
(4) $\Psi(^1B_{2u})=d\,{}^1\chi_{57}-c\,{}^1\chi_{46}$

Table I. Calculated electronic spectra of aniline and *p*-PDA (approximation A) in comparison with the observed values

Aniline

$-E$, eV.		State function	f_{calcd}	$h\nu_{\text{obs}}$, eV.	f_{obs}
−0.0038	$(^1A_1)_0$	$0.9997\,\chi_0+0.0062\,{}^1\chi_{46}+0.0174\,{}^1\chi_{35}+0.0133\,{}^1\chi_{26}$			
4.7315	$(^1B_1)_{\text{I}}$	$0.8906\,{}^1\chi_{45}-0.4457\,{}^1\chi_{36}+0.0898\,{}^1\chi_{25}$	0.048	4.33[a)]	0.026[a)]
5.8192	$(^1A_1)_{\text{I}}$	$0.0140\,\chi_0-0.8867\,{}^1\chi_{46}-0.4609\,{}^1\chi_{35}-0.0339\,{}^1\chi_{26}$	0.19	5.29[a)]	0.17[a)]
6.5055	$(^1B_1)_{\text{II}}$	$0.3964\,{}^1\chi_{45}+0.8577\,{}^1\chi_{36}+0.3273\,{}^1\chi_{25}$	0.53	6.29[a)]	—
6.7601	$(^1A_1)_{\text{II}}$	$0.0115\,\chi_0+0.4564\,{}^1\chi_{46}-0.8849\,{}^1\chi_{35}+0.0924\,{}^1\chi_{26}$	1.18	—	—
8.8382	$(^1B_1)_{\text{III}}$	$0.2229\,{}^1\chi_{45}+0.2560\,{}^1\chi_{36}-0.9406\,{}^1\chi_{25}$	0.60	—	—
9.2173	$(^1A_1)_{\text{III}}$	$0.0139\,\chi_0+0.0727\,{}^1\chi_{46}-0.0661\,{}^1\chi_{35}-0.9951\,{}^1\chi_{26}$	0.039	—	—
3.3026	$^3A_1$	$0.7419\,{}^3\chi_{35}+0.6537\,{}^3\chi_{46}-0.1490\,{}^3\chi_{26}$	0	3.32[b)]	—
3.7528	$^3B_1$	$0.9639\,{}^3\chi_{45}+0.2435\,{}^3\chi_{36}-0.1073\,{}^3\chi_{25}$	0	—	—
3.9669	$^3A_1$	$0.6658\,{}^3\chi_{35}-0.7445\,{}^3\chi_{46}+0.0486\,{}^3\chi_{26}$	0	—	—
5.0724	$^3B_1$	$0.2543\,{}^3\chi_{45}-0.9617\,{}^3\chi_{36}+0.1018\,{}^3\chi_{25}$	0	—	—
7.4190	$^3A_1$	$0.0791\,{}^3\chi_{35}+0.1352\,{}^3\chi_{46}+0.9876\,{}^3\chi_{26}$	0	—	—
7.5601	$^3B_1$	$0.0784\,{}^3\chi_{45}+0.1255\,{}^3\chi_{36}+0.9890\,{}^3\chi_{25}$	0	—	—

p-PDA

E, eV.		State function	f_{calcd}	$h\nu_{\text{obs}}$, eV.	$\log\varepsilon_{\text{obs}}^{\text{max}}$
−0.0077	$^1A_g{}^+$	$0.9995\,\chi_0+0.0300\,{}^1\chi_{37}$			
3.9958	$^1B_{3u}{}^-$	$0.8816\,{}^1\chi_{56}-0.4720\,{}^1\chi_{47}$	0.07	3.93[c)]	3.3[c)]
5.4923	$^1B_{2u}{}^+$	$0.9410\,{}^1\chi_{57}+0.3385\,{}^1\chi_{46}$	0.47	5.04[c)]	3.9[c)]
6.0996	$^1B_{3u}{}^+$	$0.4720\,{}^1\chi_{56}+0.8816\,{}^1\chi_{47}$	0.75	—	—
6.7012	$^1B_{2u}{}^-$	$0.3385\,{}^1\chi_{57}-0.9410\,{}^1\chi_{46}$	1.15	—	—
7.6985	$^1B_{1g}$	$^1\chi_{36}$	0	—	—
8.5038	$^1A_g{}^-$	$0.0300\,\chi_0-0.9995\,{}^1\chi_{37}$	0	—	—
2.9611	$^3B_{3u}{}^+$	$0.9739\,{}^3\chi_{56}+0.2268\,{}^3\chi_{47}$	0	—	—
3.1059	$^3B_{2u}{}^+$	$0.8114\,{}^3\chi_{57}+0.5843\,{}^3\chi_{46}$	0	—	—
3.8815	$^3B_{2u}{}^-$	$0.5843\,{}^3\chi_{57}-0.8114\,{}^3\chi_{46}$	0	—	—
4.6262	$^3B_{3u}{}^-$	$0.2268\,{}^3\chi_{56}-0.9739\,{}^3\chi_{47}$	0	—	—
6.7462	$^3B_{1g}$	$^3\chi_{36}$	0	—	—
7.3274	^3A_g	$^3\chi_{37}$	0	—	—

a) See Ref. 12.
b) M. Kasha, *Chem. Revs.*, **41**, 401 (1947).
c) W. F. Forbs and I. R. Leckie, *Can. J. Chem.*, **36**, 1371 (1958).

~5 eV.). Accordingly, $\beta_{\mathrm{CN}} = -3.6$ eV. has been chosen in this approximation.

A Comparison of the Calculated with the Observed Spectra. — Using this β_{CN} value, the electronic spectrum of aniline has been calculated and a more extensive CI calculation of *p*-PDA than that given in Fig. 2 has been carried out. The calculated results are shown in Table I, together with the observed values.

The calculated excitation energies are a little larger than the observed values. The calculated relative spacing among ${}^1A_g{}^+$, ${}^1B_{3u}{}^-$ and ${}^1B_{2u}{}^+$ states of *p*-PDA is especially unsatisfactory. That is, the calculated energy difference, $E({}^1B_{2u}{}^+) - E({}^1B_{3u}{}^-)$, is ca. 0.5 eV. larger than the observed value. Even if we use other values for β_{CN} between -2 eV.~-3.6 eV., this unsatisfactory result is not very much improved, and with β_{CN} values other than -3.6 eV., the agreement between the observed and calculated excitation energies to the ${}^1B_{3u}{}^-$ state become worse, as can be seen from Fig. 2. Thus, the present approximation seems to give rather unsatisfactory results. The reason for this may be the use of too large a value for I_n or F_{NN}, as has already been discussed in the Method-of-Calculation Section. Accordingly, we have tried the next approximation, i. e., the use of Eq. 18. The electronic spectra of aniline and *p*-PDA as

TABLE II. CALCULATED ELECTRONIC SPECTRA OF ANILINE AND ISOMERIC PDA'S (APPROXIMATION B) IN COMPARISON WITH THE OBSERVED VALUES*

		Aniline			
E, eV.		State function	f_{calcd}		
−0.0100	$({}^1A_1)_0$	$0.9992\,\chi_0 - 0.0379\,{}^1\chi_{46} + 0.0150\,{}^1\chi_{35}$	—		
4.5224	$({}^1B_1)_{\mathrm{I}}$	$0.8851\,{}^1\chi_{45} - 0.4653\,{}^1\chi_{36}$	0.05		
5.4552	$({}^1A_1)_{\mathrm{I}}$	$0.0305\,\chi_0 + 0.9405\,{}^1\chi_{46} + 0.3384\,{}^1\chi_{35}$	0.31		
6.5556	$({}^1B_1)_{\mathrm{II}}$	$0.4653\,{}^1\chi_{45} + 0.8851\,{}^1\chi_{36}$	0.84		
6.7148	$({}^1A_1)_{\mathrm{II}}$	$0.0269\,\chi_0 + 0.3378\,{}^1\chi_{46} - 0.9408\,{}^1\chi_{35}$	1.04		
		p-PDA			
E, eV.		State function	f_{calcd}		
−0.0081	${}^1A_g{}^-$	$0.9998\,\chi_0 - 0.0159\,{}^1\chi_{37}$	—		
3.8957	${}^1B_{3u}{}^-$	$0.8342\,{}^1\chi_{56} - 0.5514\,{}^1\chi_{47}$	0.04		
5.1268	${}^1B_{2u}{}^+$	$0.9659\,{}^1\chi_{57} + 0.2589\,{}^1\chi_{46}$	0.52		
5.7989	${}^1B_{3u}{}^+$	$0.5514\,{}^1\chi_{56} + 0.8342\,{}^1\chi_{47}$	0.77		
6.6660	${}^1B_{2u}{}^-$	$0.2589\,{}^1\chi_{57} - 0.9659\,{}^1\chi_{46}$	0.99		
6.9036	${}^1A_g{}^+$	$0.0159\,\chi_0 + 0.9998\,{}^1\chi_{37}$	0		
		o-PDA			
E, eV.		State function	f_{calcd}	$h\nu_{\mathrm{obs}}$, eV.	$\log \varepsilon_{\mathrm{obs}}^{\mathrm{max}}$
−0.0784	${}^1A_1$	$0.9931\,\chi_0 - 0.1045\,{}^1\chi_{56} + 0.0525\,{}^1\chi_{47}$	—	—	—
4.3423	${}^1A_1$	$0.0661\,\chi_0 + 0.8719\,{}^1\chi_{56} + 0.4852\,{}^1\chi_{47}$	0.09	4.29	3.5
5.0209	${}^1B_1$	$0.9344\,{}^1\chi_{57} - 0.3561\,{}^1\chi_{46}$	0.22	5.26	3.8
6.0700	${}^1B_1$	$0.3561\,{}^1\chi_{57} + 0.9344\,{}^1\chi_{46}$	0.62	—	—
6.2653	${}^1A_1$	$0.1228\,\chi_0 - 0.5576\,{}^1\chi_{56} + 0.8210\,{}^1\chi_{47}$	1.34	—	—
3.0737	${}^3B_1$	$0.8723\,{}^3\chi_{57} - 0.4889\,{}^3\chi_{46}$	0	—	—
3.0843	${}^3A_1$	$0.9808\,{}^3\chi_{56} - 0.1947\,{}^3\chi_{47}$	0	—	—
3.7112	${}^3B_1$	$0.4889\,{}^3\chi_{57} + 0.8723\,{}^3\chi_{57}$	0	—	—
4.5082	${}^3A_1$	$0.1947\,{}^3\chi_{56} + 0.9808\,{}^3\chi_{47}$	0	—	—
		m-PDA			
E, eV.		State function	f_{calcd}	$h\nu_{\mathrm{obs}}$, eV.	$\log \varepsilon_{\mathrm{obs}}^{\mathrm{max}}$
−0.0131	${}^1A_1$	$0.9988\,\chi_0 - 0.0489\,{}^1\chi_{57} - 0.0065\,{}^1\chi_{46}$	—	—	—
4.4527	${}^1B_1$	$0.8279\,{}^1\chi_{56} - 0.5608\,{}^1\chi_{47}$	0.03	4.23	3.4
5.2759	${}^1A_1$	$0.0467\,\chi_0 + 0.8891\,{}^1\chi_{57} + 0.4552\,{}^1\chi_{46}$	0.19	5.16	3.8
5.9196	${}^1A_1$	$0.0231\,\chi_0 + 0.5911\,{}^1\chi_{57} - 0.8062\,{}^1\chi_{46}$	0.65	—	—
5.9793	${}^1B_1$	$0.5608\,{}^1\chi_{56} + 0.8279\,{}^1\chi_{47}$	1.31	—	—
3.0501	${}^3A_1$	$0.9205\,{}^3\chi_{57} + 0.3907\,{}^3\chi_{46}$	0	—	—
3.3867	${}^3B_1$	$0.9306\,{}^3\chi_{56} + 0.3659\,{}^3\chi_{47}$	0	—	—
4.0046	${}^3A_1$	$0.3907\,{}^3\chi_{57} - 0.9205\,{}^3\chi_{46}$	0	—	—
4.3946	${}^3B_1$	$0.3659\,{}^3\chi_{56} - 0.9306\,{}^3\chi_{47}$	0	—	—

* The observed values are taken from Ref. c of Table I.

well as those of *o*- and *m*-PDA have been calculated with this approximation.

The calculated results are shown in Table II, where the observed results for *o*- and *m*-PDA are given for purposes of comparison.

One can see from Tables I and II that the agreement between the calculated and the observed excitation energies is more satisfactory in Approximation B than in Approximation A, although less extensive configuration interactions are invoked to obtain the results given in Table II.

The calculation predicts that the excitation energies to the lowest excited singlet states of *o*- and *m*-PDA will be larger than that of *p*-PDA ; this is in accordance with the observed results. Furthermore, the values of the excitation energies themselves, as well as the relative spacings among the excited states, are given correctly.* These results appear to support the agreements described in Sec. II against Approximation A. However, the procedure of Approximation B seems to be rather arbitrary. Therefore, we have examined a more " theoretical " procedure, i. e., the VESCF method, in the case of *p*-PDA.

The calculated spectrum and the VESCF MO's are given in Table III and Appendix II respectively. The β_{CN} value used in this calculation was the same as that in Approximation B.

As one can see from Table III, the calculated excitation energies are a little smaller than the observed values, although the energy difference between the ${}^1B_{2u}{}^+$ and ${}^1B_{3u}{}^-$ states is correctly given. It seems to be possible that one can fit the observed spectrum if one selects a somewhat different β_{CN} value and repeats the SCF calculation. However, we shall not attempt such a calculation here, for this is quite a laborious procedure.

TABLE III. THE CALCULATED ELECTRONIC SPECTRUM OF *p*-PDA (VESCF METHOD)

	State function	$h\nu$, eV.	f
${}^1A_g$	χ_0		—
${}^1B_{3u}{}^-$	$0.9624\,{}^1\chi_{56}-0.2715\,{}^1\chi_{37}$	3.5693	0.12
${}^1B_{2u}{}^+$	$0.9819\,{}^1\chi_{57}+0.1892\,{}^1\chi_{36}$	4.7091	0.69
${}^1B_{3u}{}^+$	$0.2715\,{}^1\chi_{56}+0.9624\,{}^1\chi_{37}$	6.6306	0.64
${}^1B_{2u}{}^-$	$0.1892\,{}^1\chi_{57}-0.9819\,{}^1\chi_{36}$	6.6332	0.98
${}^1B_{1g}$	${}^1\chi_{46}$	5.5513	0
${}^1A_g$	${}^1\chi_{47}$	6.3188	0
${}^3B_{2u}{}^+$	$0.9624\,{}^3\chi_{57}+0.2714\,{}^3\chi_{36}$	2.4436	0
${}^3B_{3u}{}^+$	$0.9930\,{}^3\chi_{56}+0.1182\,{}^3\chi_{37}$	2.5324	0
${}^3B_{2u}{}^-$	$0.2714\,{}^3\chi_{57}-0.9624\,{}^3\chi_{36}$	3.7282	0
${}^3B_{3u}{}^-$	$0.1182\,{}^3\chi_{56}-0.9930\,{}^3\chi_{37}$	5.3898	0
${}^3B_{1g}$	${}^3\chi_{46}$	4.8127	0
${}^3A_g$	${}^3\chi_{47}$	4.8400	0

The Relation between the Simple Hückel MO Calculation and the Present One. — In the present method, the electronic repulsions are explicity taken into consideration in the calculation of the electronic spectra. However, because of the zero differential overlap approximation, the present method appears to be essentially similar to the simple Hückel MO method. Among the matrix elements of the Fock Hamiltonian, the diagonal element, $F_{\mu\mu}$, and the non-diagonal element, $F_{\mu\nu}$, between the nearest neighbor AO's have appreciable values, whereas the $F_{\mu\nu}$ between the more distant neighbors has a very small value. This circumstance corresponds quite well to the fact that, in the simple Hückel MO method, only the Coulomb integral, α, and the resonance integral, β, between the nearest neighbor AO's are taken into account. Furthermore, the $F_{\mu\mu}$ values for the ring carbons are not very different from each other throughout the mono-, di- and tri-substituted aminobenzenes. The $F_{\mu\mu}$ values for the ring carbons of these compounds are in the range -5.5 eV.~-6 eV. ; the average value is ~-5.8 eV. This value is rather close to that of the alternant hydrocarbon, -6 eV.

$F_{\mu\mu}$ in Eq. 4 can be rewritten as:

$$F_{\mu\mu}=-(I_\mu+A_\mu)/2+(P_{\mu\mu}-1)\cdot\gamma_{\mu\mu}/2 + \sum_{\kappa\neq\mu}(\delta Q_\kappa)\gamma_{\mu\kappa} \tag{14}$$

where $\delta Q_\kappa=(P_{\kappa\kappa}-Z_\kappa)$. When the μth atom is one of the ring carbons, this equation can be further rewritten as:

$$F_{\mu\mu}(\mathrm{C})=-(I_\mu+A_\mu)/2-(\delta Q_\mu)\cdot\gamma_{\mu\mu}/2 + \sum_{\kappa}^{\text{all}}(\delta Q_\kappa)\cdot\gamma_{\mu\kappa} \tag{15}$$

If the electron distribution of the parent hydrocarbon is not very much disturbed by the substitution, the $F_{\mu\mu}(\mathrm{C})$ value may be close to $-(I_\mu+A_\mu)/2$, the $F_{\mu\mu}(\mathrm{C})$ value of the parent hydrocarbon, because the δQ values are small in this case.

As has been described above, this circumstance seems to hold approximately, even in the case of amino-substituted benzenes, in spite of the great conjugation power of the amino group. We can expect that $F_{\mu\mu}(\mathrm{C})$ will become smaller when the Hückel MO parameter, δ_N, becomes smaller. Actually, if we assume $\delta_N\sim0.8$ in the case of TAB, $F_{\mu\mu}(\mathrm{C})$ becomes ca. -5.0 eV.

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* Quite recently, the electronic spectrum of aniline has been examined in detail up to the vacuum ultraviolet region (K. Kimura, H. Tsubomura and S. Nagakura, presented at the 16th Annual Meeting of the Chemical Society of Japan, April, Tokyo, 1963). According to this measurement, the energy difference between $\Psi({}^1B_1)_{II}$ and $\Psi({}^1A_1)_{II}$ amounts to 0.33 eV. In our present study, it is calculated to be 0.26 eV. in Approximation A and 0.16 eV. in Approximation B.

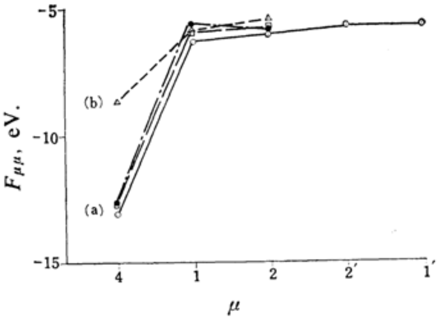

Fig. 3. $F_{\mu\mu}$ values of some aminobenzenes.
(a) Approximation A. —— Aniline
— — p-PDA —·— TAB
(b) VESCF approximation for p-PDA.
$\mu=7$ is for the amino group of TAB.

Some examples of the $F_{\mu\mu}$ values in aminobenzenes are shown in Fig. 3.

As has been described at the beginning of this article, we have calculated the electronic spectra and electronic structures of some aminobenzenes protonated on the ring carbon, employing the localization model.[16] In this case, for example in the benzenium ion, four electrons move in the field of five positive carbon cores. Therefore, the core field is much stronger in this case than in the case of neutral aminobenzene molecules, although, again in this case, we can observe that the $F_{\mu\mu}$(C) values are fairly uniform. Namely, $F_{\mu\mu}(\mathrm{C}) \approx -10\pm0.5$ eV., throughout aniline protonated on para-carbon, m-PDA protonated on the carbon atom at the ortho-position to both amino groups and TABH$^+$. This $F_{\mu\mu}$(C) value is rather close to the average $F_{\mu\mu}$(C) value of the benzenium ion, -10.5 eV.

The non-diagonal matrix element, $F_{\mu\nu}$(C), between the nearest neighbor carbon AO's may be rewritten as:

$$F_{12}(\mathrm{C}) = \beta_{12} - \frac{1}{2}(P^0{}_{12} + \Delta P_{12})\gamma_{12}$$

$$= F^0{}_{12} - \frac{1}{2}(\Delta P_{12})\cdot\gamma_{12} \qquad (16)$$

where $F^0{}_{12}$ is the matrix element of the parent hydrocarbon because, in the present approximations except for the VESCF method, the β_{12} and γ_{12} are the same as those of the parent hydrocarbon.

We can observe that the F_{12}(C) values are not very different from each other throughout the aminobenzene molecules. The average value for these molecules is -4.063 eV.; this is close to the F_{12}(C) value for benzene, -4.1538 eV. However, as Fig. 4 shows, we can observe a definite linear relation between the F_{12}(C) value averaged over all the nearest neighbor pairs of an aminobenzene and the Δq value, the total of the charge which has migrated to the ring from the substituents.

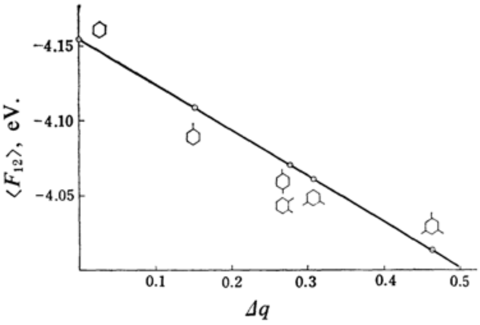

Fig. 4. $\langle F_{12}\rangle_{\mathrm{AV}}$ versus Δq relation for aminobenzenes.

Because the F_{12}(C) value in the present approximation is essentially determined by the P_{12} value, this fact indicates the linear relation between Δq and P_{12} averaged over all the nearest neighbor μ-ν pairs ($\langle P_{12}\rangle$), as is shown in Fig. 5.

Remarks on the Relations among the Charge Migrations, Bond Orders and the Extra Delocalization Energies. — As Fig. 5 shows, the linear relation between $\langle P_{12}\rangle$ and Δq seems to

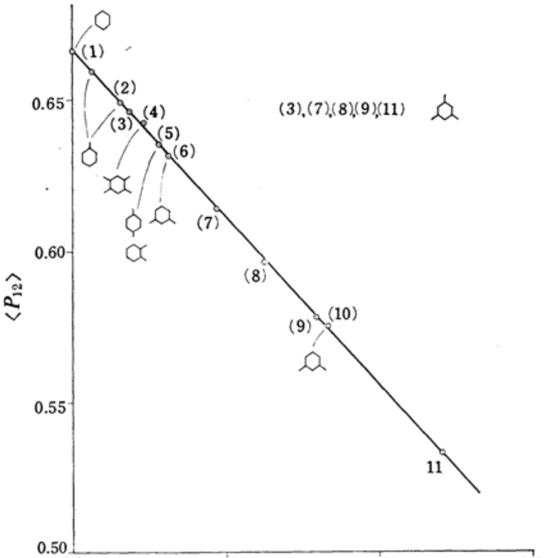

Fig. 5. $\langle P_{12}\rangle$ versus Δq relation for some substituted benzenes.
(1), (3), (4): $\delta_{\mathrm{X}}=1.5$, $\beta_{\mathrm{CX}}=0.7\beta$
(2), (5), (6), (7): $\delta_{\mathrm{X}}=1.2$, $\beta_{\mathrm{CX}}=\beta$
(8): $\delta_{\mathrm{X}}=0.8$, $\beta_{\mathrm{CX}}=\beta$
(9): $\delta_{\mathrm{X}}=0.5$, $\beta_{\mathrm{CX}}=\beta$
(10), (11): $\delta_{\mathrm{X}}=0$, $\beta_{\mathrm{CX}}=\beta$
The values for the case of $\delta_{\mathrm{X}}=1.5$ and $\beta_{\mathrm{CX}}=0.7\beta$ are taken from Ref. 27 and others are calculated by the present author.

hold almost exactly, at least in the case of the benzene derivatives, because the number of the substituents and the Coulomb parameter δ_X are varied from 1 to 4 and from 0 to 1.5 respectively, and the parameters for the resonance integral, β_{CX}, are of two kinds, 0.7 and 1.0.

Thus, the linear relation in this case can be expressed as;

$$\langle P_{12}\rangle=\langle P_{12}\rangle_0-(0.11)\cdot\Delta q \tag{17}$$

where $\langle P_{12}\rangle_0=2/3$, the bond order of benzene.

Furthermore, we can see an almost complete linear relation between the extra-delocalization energy (vertical), $\Delta\varepsilon$ and Δq, as can be seen from Fig. 6. The $\Delta\varepsilon$ versus Δq relation in Fig. 6 involves various amino-substituted nitrogen heterocycles in addition to the amino-substituted benzenes. The Hückel MO parameters for the amino group of the former compounds are the same as those of aminobenzenes, and the parameters for the ring nitrogen are the same as were used before,[18] i.e., $\delta_N=0.5$ and $\beta_{CN}=\beta$. The analogous linear relation between $\Delta\varepsilon$ and Δq has already been demonstrated for hydroxy derivatives of benzene and naphthalene, assuming $\delta_O=1.5$ and $\beta_{CO}=0.7\beta$.[27]

Qualitatively speaking, we can expect a larger Δq value, the greater the $\Delta\varepsilon$ value, in accordance with the concept of the intramolecular charge transfer interaction.[7,8,11,28] Furthermore, we can anticipate a smaller $\langle P_{12}\rangle$ value, the larger the Δq value, because the charge is transferred from the substituents to the antibonding orbitals of benzene or *N*-heterobenzenes.

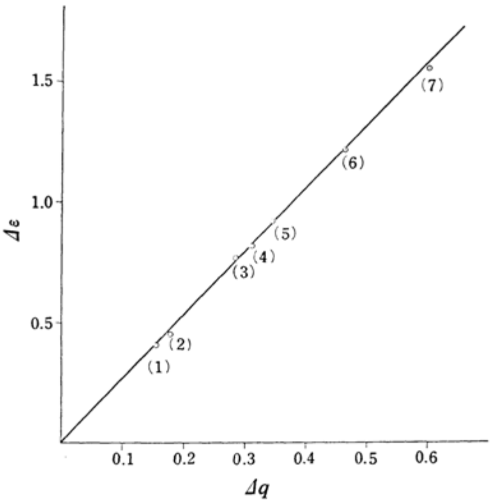

Fig. 6. $\Delta\varepsilon$ versus Δq relation for some amino-substituted benzenes and nitrogen heterocycles.

(1) Aniline (2) 4-Aminopyridine
(3) *p*- and *o*-PDA (4) *m*-PDA
(5) 4,4′-Diaminotetrazine
(6) TAB (7) Melamine
$\Delta\varepsilon$ is in unit of $-\beta$.

As we can see from Appendix I and Figs. 5 and 6, the $\Delta\varepsilon$, Δq and $\langle P_{12}\rangle$ values of substituted benzenes are approximately proportional to the number of the substituents when the same parameter value is used for the substituents. This fact suggests that we may be able to derive such a proportionality relation by the perturbation method. However, this proportionality and the linear relations seem to be rather peculiar, especially in view of the strong conjugation power of the amino group, which probably invalidates perturbation calculation. Nevertheless, we will examine here whether such a perturbation calculation is possible or not in the case of amino-substituted alternant hydrocarbons.

Now, the energy matrix for the secular determinant may be written as follows according to the LCMO approximation:

$$\left(\begin{array}{cccccc|ccccc}
\varepsilon_1^b & & & & & & \eta_{11}^b & \cdots & \eta_{1\sigma}^b & \cdots & \eta_{1n}^b \\
& \ddots & & & & & \vdots & & \vdots & & \vdots \\
& & \varepsilon_j^b & & 0 & & \eta_{j1}^b & \cdots & \eta_{j\sigma}^b & \cdots & \eta_{jn}^b \\
& & & \ddots & & & \vdots & & \vdots & & \vdots \\
& & & \varepsilon_m^b & & & \eta_{m1}^b & \cdots & \eta_{m\sigma}^b & \cdots & \eta_{mn}^b \\
& & & & \ddots & & \vdots & & \vdots & & \vdots \\
& & & & \varepsilon_1^a & & \eta_{11}^a & \cdots & \eta_{1\sigma}^a & \cdots & \eta_{1n}^a \\
& & & & & \ddots & \vdots & & \vdots & & \vdots \\
& & & & & \varepsilon_j^a & \eta_{j1}^a & \cdots & \eta_{j\sigma}^a & \cdots & \eta_{jn}^a \\
& & & & & \ddots & \vdots & & \vdots & & \vdots \\
& & & & & \varepsilon_m^a & \eta_{m1}^a & \cdots & \eta_{m\sigma}^a & \cdots & \eta_{mn}^a \\
\hline
& & & & & & \lambda_1 & & 0 & & \\
& & & & & & & \ddots & & & \\
& & & & & & & & \lambda_\sigma & & \\
& & & & & & & & & \ddots & \\
& & & & & & & & & & \lambda_n
\end{array}\right) \tag{18}$$

In Eq. 18, the ε^a's and ε^b's are the orbital energies of the antibonding and bonding orbitals of the hydrocarbon respectively, and the λ_σ's are those of the lone pair orbitals of the substituents. $\eta_{j\sigma}$ is the matrix element between the jth MO ψ_j of the hydrocarbon and the lone pair orbital, θ_σ, of the σth substituent; that is,

$$\eta_{j\sigma}^a=\int\psi_j^a\mathscr{H}_{\text{eff}}\theta_\sigma\mathrm{d}\tau$$

$$\eta_j^b=\int\psi_j^b\mathscr{H}_{\text{eff}}\theta_\sigma\mathrm{d}\tau$$

If $(\varepsilon_1^b)'$, $\cdots$, $(\varepsilon_m^b)'$, $(\varepsilon_1^a)'$, $\cdots$, $(\varepsilon_m^a)'$, $\cdots$, and $(\lambda_1)'\cdots(\lambda_n)'$ are the exact solutions of the secular equation, then, because of the invariance of trace,

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[27] K. Nishimoto, This Bulletin, 32, 445, 699 (1959).

[28] S. Nagakura, *Mol. Phys.*, 3, 105 (1960).

$$\sum_{j}^{m}[(\varepsilon_j^a)'+(\varepsilon_j^b)']+\sum_{\sigma}^{n}(\lambda_\sigma)'$$

$$=\sum_{j}^{m}[\varepsilon_j^a+\varepsilon_j^b]+\sum_{\sigma}^{n}\lambda_\sigma \qquad (19)$$

Accordingly,

$$\Delta\varepsilon=2\sum_{j}^{m}[\varepsilon_j^b-(\varepsilon_j^b)']+\sum_{\sigma}^{n}[\lambda_\sigma-(\lambda_\sigma)']$$

$$=2\sum_{j}^{m}[(\varepsilon_j^a)'-\varepsilon_j^a] \qquad (20)$$

If we approximate $(\varepsilon_j^a)'$ by the second order perturbed energy, then, from Eq. 18,

$$(\varepsilon_j^a)'\cong\varepsilon_j^a+\sum_{\sigma}^{n}(\eta_{j\sigma}^a)^2/(\varepsilon_j^a-\lambda_\sigma) \qquad (21)$$

From 20 and 21,

$$\Delta\varepsilon\cong2\sum_{j}^{m}\sum_{\sigma}^{n}(\eta_{j\sigma}^a)^2/(\varepsilon_j^a-\lambda_\sigma)$$

$$=2\sum_{j}^{m}\sum_{\sigma}^{n}(c_{js}^a\beta_{s\sigma})^2/(\varepsilon_j^a-\lambda_\sigma) \qquad (22)$$

In deriving Eq. 22, we have used the ordinary approximation,

$$\eta_j^a=\int\psi_j^a\mathscr{H}_{\mathrm{eff}}\theta_\sigma\mathrm{d}\tau$$

$$=\sum_{\mu}c_{j\mu}^a\int\phi_\mu\mathscr{H}_{\mathrm{eff}}\theta_\sigma\mathrm{d}\tau\cong c_{js}^a\beta_{s\sigma} \qquad (23)$$

where σth substituent is attached to the sth carbon.

In the case of aminobenzenes, Eq. 22 can be further simplified as follows:

$$\Delta\varepsilon=2\beta^2[\sum_{s}(c_{1s}^a)^2/(\varepsilon_1^a-\lambda)$$

$$+\sum_{s}(c_{2s}^a)^2/(\varepsilon_2^a-\lambda)+\sum_{s}(c_{3s}^a)^2/(e_3^a-\lambda)]$$

$$=(0.407)\cdot n_s\cdot(-\beta) \qquad (24)$$

where n_s is the number of the substituents; this equation holds almost exactly.

The approximate MO corresponding to 21 may be written as:

$$(\psi_j^a)'\cong\psi_j^a+\sum_{\sigma}^{n}(\eta_{j\sigma}^a)\theta_\sigma/(\varepsilon_j^a-\lambda_\sigma)$$

and the normalized form of $(\psi_j^a)'$ is:

$$(\psi_j^a)'\cong[\psi_j^a+\sum_{\sigma}^{n}(\eta_{j\sigma}^a)\theta_\sigma/(\varepsilon_j^a-\lambda_\sigma)]/$$

$$[1+\sum_{\sigma}^{n}\{\eta_{j\sigma}^a/(\varepsilon_j^a-\lambda_\sigma)\}^2]^{1/2} \qquad (25)$$

If $(\psi_j)'$'s are the exact solutions of the secular equation, there exists the following relation for the coefficients, $c_{j\sigma}$'s, of θ_σ:

$$\sum_{j}^{m+n}(c_{j\sigma}^b)^2+\sum_{j}^{m}(c_{j\sigma}^a)^2=1$$

Accordingly,

$$\Delta q=2[n_s-\sum_{j}^{m+n}\sum_{\sigma}^{n}(c_{j\sigma}^b)^2]=2\sum_{j}^{m}\sum_{\sigma}^{n}(c_{j\sigma}^a)^2 \qquad (26)$$

From 23, 25 and 26, the expression for Δq may be written as:

$$\Delta q\cong2\sum_{j}\left[\frac{\sum_{s}(c_{js}^a)^2}{(\varepsilon_j^a-\lambda)^2}\cdot\left\{1+\frac{\sum_{s}(c_{js}^a)^2}{(\varepsilon_j^a-\lambda)^2}\right\}^{-1}\right] \qquad (27)$$

where $\lambda_\sigma=\lambda=1.2$.

If we neglect the second term in the curled bracket compared to 1, then Eq. 27 can be rewritten in the following form:

$$\Delta q\cong(0.170)\cdot n_s \qquad (28)$$

However, because the exact value of Δq for aniline is 0.155, Eq. 34 is not a very good approximation.

If we use Eq. 27, the Δq values are calculated to be 0.160, 0.317 and 0.467 for aniline, *m*-PDA and TAB respectively. These values are fairly close to the exact values and are approximately proportional to the number of substituents.

Thus the linear relation between $\Delta\varepsilon$ and Δq and the proportionality of these quantities to n_s in the case of aminobenzenes can be accounted for approximately by the perturbation method.** However, when smaller δ_{X} values are used, the perturbation method becomes quite a poor approximation.

The calculation of $\langle P_{12}\rangle$ by the perturbation method gives quite poor results. In any way, we cannot explain the linear relation between $\langle P_{12}\rangle$ and Δq for the wide range of parameter values shown in Fig. 5.

The MO of a substituted benzene can be written in the LCMO form as follows:

$$\psi_i=\sum_{j=1}^{6}c_{ij}\psi_j^{\mathrm{B}}+\sum c_{i\sigma}\theta_\sigma \qquad (29)$$

where $\psi_1^{\mathrm{B}}\cdots\psi_6^{\mathrm{B}}$ are the MO's of benzene from the lowest bonding to the highest anti-bonding orbitals.

From Eq. 29, we can derive the following equation;

$$6\cdot\langle P_{12}\rangle=\sum_{i}^{v}(2c_{i6}^2+c_{i4}^2+c_{i5}^2)$$

$$-\sum_{i}^{v}(2c_{i1}^2+c_{i2}^2+c_{i3}^2) \qquad (30)$$

where $\sum_{i}^{v}$ means the summation over the vacant orbitals of the substituted benzene.

** The following points should be noted here. In several parts of this paper, we have insisted that the perturbation method in the sense of the expansion of the secular determinant in a series seems to be a poor approximation for amino-substituted aromatics. The calculation of the orbital energies and MO's themselves for the occupied orbitals of these compounds by the perturbation method is certainly a very poor approximation. Therefore, we cannot use the perturbation method for the calculation of the electronic spectra. However, we can use this method to calculate some ground state quantities, such as $\Delta\varepsilon$ and Δq, expanding only the unoccupied orbitals which are affected only slightly by the substitution.

On the other hand, the expression for Δq can be written as:

$$\Delta q = 2\sum_i^v \sum_\sigma c_{i\sigma}^2 = 2\sum_i^v \left(1-\sum_{j=1}^{6} c_{ij}^2\right)$$
$$= 6 - 2\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2)$$
$$-2\sum_i^v (2c_{i6}^2 + c_{i4}^2 + c_{i5}^2) + 2\sum_i^v (c_{i1}^2 + c_{i6}^2) \tag{31}$$

From 30 and 31 we can derive the following relation between $\langle P_{12}\rangle$ and Δq:

$$\langle P_{12}\rangle = 0.5 + \sum_i^v (c_{i1}^2 + c_{i6}^2)/6$$
$$-\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2)/3 - \Delta q/12 \tag{32}$$

When the ionization potential of the lone pair orbital of the substituent becomes infinitely large, Δq, $\sum_i^v c_{i1}^2$ and $\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2)$ approach zero, and $\sum_i^v c_{i6}^2$ approaches 1. Thus $\langle P_{12}\rangle$ becomes the bond order of benzene, 2/3.

Even in the case of amino-substituted benzene, $\sum_i^v (c_{i1}^2 + c_{i6}^2)$ may perhaps be close to unity and $\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2)$, to zero. For example, in the case of aniline, $\sum_i^v (c_{i1}^2 + c_{i6}^2) = 0.986$, $\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2) = 0.007$, and $\sum_i^v (c_{i1}^2 + c_{i6}^2) = 0.971$, while $\sum_i^v (2c_{i1}^2 + c_{i2}^2 + c_{i3}^2) = 0.014$ for *m*-PDA. Thus, the sum of the first two terms in the right-hand side of Eq. 32 is approximately equal to the bond order of benzene, and the sum of the 3rd and the fourth terms may be close to $(0.1)\cdot\Delta q$.

In this way, we can "*understand*" to some extent the linear relation between $\langle P_{12}\rangle$ and Δq, although this is not a "*proof*" of the relation in Eq. 17, which holds for a wide range of Hückel MO parameters.

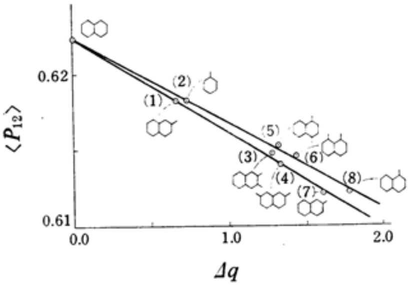

Fig. 7. $\langle P_{12}\rangle$ versus Δq relation for some substituted naphthalenes.

(1)—(6): $\delta_X = 1.5$, $\beta_{CX} = 0.7\beta$ (Taken from K. Nishimoto and R. Fujishiro, This Bulletin, **35**, 390 (1962) and Ref. 27)

(7), (8): $\delta_X = 1.2$, $\beta_{CX} = \beta$ (Taken from Ref. 9)

This sort of approximate linear relation between $\langle P_{12}\rangle$ and Δq holds not only for the benzene derivatives but also for the naphthalene derivatives, as Fig. 7 shows, although there is a slight difference between the α- and β-derivatives in this case.

A Comparison of the Calculated Dipole Moments of Aniline in the Ground State, as Well as in the Excited State, with the Experimental Values. — Using the wave functions given in Tables I and II, we have calculated the π-moment of aniline and compared it with the observed values.

The theoretical expression for the dipole moment in terms of the state function, Ψ, is given by:

$$\vec{\mu} = \langle \Psi | \boldsymbol{M} | \Psi \rangle \tag{33}$$

where $\boldsymbol{M} = \sum_\tau e_\tau \boldsymbol{r}_\tau$

e_τ and $\boldsymbol{r}_\tau$ are the charge and the position vector of τth particle respectively. In the π-electron approximation, $\boldsymbol{M}$ can be separated into two parts:

$$\boldsymbol{M} = e\sum \boldsymbol{r}_\lambda + \sum e_\kappa \boldsymbol{r}_\kappa$$

The first summation is over π-electrons, and the second, over the cores.

The necessary formulas for the expansion of 33 have been given elsewhere.[17a,29]

The ground state dipole moment of aniline has been calculated to be:

2.20 D. (Approximation A)
and 1.72 D. (Approximation B)

On the other hand, from the experimental value Smith[30] has estimated the π-moment of aniline to be ~1.67 D., which is very close to the value calculated with Approximation B.

In addition to this study of the ground state dipole moment, we have calculated the π-moment in the lowest-excited singlet state.

On the other hand, we can use the difference between the solvent shifts of the absorption and fluorescence spectra in order to get experimental information on the electronic structure of the excited molecule.[29,31,33]

We have measured the absorption and fluorescence spectra of aniline in several solvents. The light source for the fluorescence measurement was a 300 W. Xenon discharge

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[29] N. Mataga, This Bulletin, **36**, 654 (1963).

[30] J. W. Smith, *J. Chem. Soc.*, **1961**, 81.

[31] N. Mataga et al., This Bulletin, **28**, 690 (1955); **29**, 465 (1956).

[32] E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); *Z. Elektrochem.*, **61**, 962 (1957).

[33] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

tube with a stabilizer. The fluorescence was excited at 285 mμ, the monochromatic exciting light from the Xenon discharge tube being taken out by a quartz prism monochromator. Aniline, which had been purified[34] by the standard method and stored in a vacuum and in a dark place, was distilled in a vacuum before use. The other details of the experimental procedures have been described elsewhere.[29,35]

Using the experimental results given in Table IV and by means of the following equation,[31,32] we can estimate the difference between the dipole moment in the excited state ($\overrightarrow{\mu_e}$) and that in the ground state ($\overrightarrow{\mu_g}$); i. e., $\overrightarrow{\Delta\mu}=(\overrightarrow{\mu_e}-\overrightarrow{\mu_g})$, where the excited state is the fluorescence state.

$$hc(\sigma_a^m-\sigma_f^m)\simeq\text{Const.}+2\left[\frac{D-1}{2D+1}-\frac{n^2-1}{2n^2+1}\right]\frac{(\overrightarrow{\Delta\mu})^2}{a^3} \qquad (34)$$

In Eq. 34, σ_a^m and σ_f^m are the wave numbers of a peak of the fluorescence band and that of the corresponding absorption band respectively. D and n are the dielectric constant and the refractive index of the solvent respectively, and a is the cavity radius in Onsager's theory of the reaction field.

TABLE IV. THE WAVE NUMBERS OF THE BAND MAXIMA OF ANILINE IN SEVERAL SOLVENTS (in unit of $10^4\,\text{cm}^{-1}$)

Solvent	σ_a^m	σ_f^m	$\sigma_a^m-\sigma_f^m$
Cyclohexane	3.48	3.14	0.34
Dichloroethane	3.47	3.07	0.40
n-Butylacetate	3.44	3.00	0.44
Acetonitrile	3.46	2.99	0.47

There are some ambiguities concerning the magnitude of a, although perhaps $a\simeq 2\sim 2.5$ Å. For these a values, $\overrightarrow{\Delta\mu}$ values are estimated to be $2\sim 2.5$ D. because $(\overrightarrow{\Delta\mu})^2/a^3\sim 2000\,\text{cm}^{-1}$.

It should be noted here that, if the change in the π-electronic structure induced by the electronic excitation is small, the observed $\overrightarrow{\Delta\mu}$ value represents approximately the difference between the π-moment in the excited state and that in the ground state. The theoretical $\overrightarrow{\Delta\mu}$ values are calculated as follows:

$$\overrightarrow{\Delta\mu}=4.82\text{ D. (Approximation A)}$$

and $$\overrightarrow{\Delta\mu}=4.12\text{ D. (Approximation B)}$$

Although the theoretical values are a little larger than the experimental values, their order of magnitudes is the same.

In our previous work[29] on the experimental and theoretical estimation of the $\overrightarrow{\Delta\mu}$ values of naphthylamines, it has been argued that the MO calculation may overestimate the $\overrightarrow{\Delta\mu}$ values.

If the calculated $\overrightarrow{\Delta\mu}$ value in the present case is reduced by multiplying by the same factor as before, i. e., 1/4, then the theoretical value becomes smaller than the experimental value, as was the case in the previous work.

In the case of naphthylamines, it has been suggested that the structure of the amino group changes a little during the life time of the excited state and that this is the cause of the observed value of $\overrightarrow{\Delta\mu}$ being larger than the theoretical value.

However, it is not quite certain whether or not the same factor to reduce the calculated $\overrightarrow{\Delta\mu}$ value as for naphthylamines is appropriate in the present case. Therefore, we cannot discuss in detail the structural change of the amino group during the life time of the excited state.

Summary

The electronic spectra and electronic structures of amino substituted benzenes have been studied by the semiempirical MO method, with the explicit inclusion of the electron repulsion.

According to the calculated results, we can interpret the difference between the spectra of various poly-substituted aminobenzenes; also, the calculated excitation energies and oscillator strengths are in satisfactory agreement with the observed values.

The relation between the present calculation and the simple Hückel MO calculation has been analyzed. Moreover, several interesting relations between the Hückel MO quantities of substituted benzenes and naphthalenes have been demonstrated and discussed.

The calculated π-moment of aniline in the ground state is in satisfactory agreement with the experimental value. Furthermore, the π-moment of aniline in the lowest excited singlet state has been calculated and compared with the experimental value obtained from the measurement of the solvent shifts of the absorption and fluorescence spectra.

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[34] N. Mataga and S. Tsuno, This Bulletin, 30, 711 (1957).

[35] N. Mataga, Y. Torihashi and Y. Kaifu, *Z. Phys. Chem. N. F.*, 34, 379 (1962).

APPENDIX I. HÜCKEL MO'S AND MO ENERGIES OF ANILINE AND ISOMERIC PDA'S (MO ENERGIES ARE IN UNITS OF β)

MO energy	MO
Aniline	
2.2565	$\psi_1(\mathrm{b_2})=0.3556(\phi_2+\phi_3)+0.2596(\phi_{2'}+\phi_{3'})+0.2301\phi_{1'}+0.5429\phi_1+0.5140\phi_4$
1.5712	$\psi_2(\mathrm{b_2})=0.1203(\phi_2+\phi_3)+0.4037(\phi_{2'}+\phi_{3'})+0.5139\phi_{1'}-0.2145\phi_1-0.5782\phi_4$
1.0000	$\psi_3(\mathrm{a_2})=0.5000(\phi_2-\phi_3)+0.5000(\phi_{2'}-\phi_{3'})$
0.5750	$\psi_4(\mathrm{b_2})=0.3866(\phi_2+\phi_3)-0.1332(\phi_{2'}+\phi_{3'})-0.4634\phi_{1'}+0.3556\phi_1-0.5692\phi_4$
−1.0000	$\psi_5(\mathrm{a_2})=0.5000(\phi_2-\phi_3)-0.5000(\phi_{2'}-\phi_{3'})$
−1.1431	$\psi_6(\mathrm{b_2})=0.2001(\phi_2+\phi_3)+0.3297(\phi_{2'}+\phi_{3'})-0.5771\phi_{1'}-0.5585\phi_1+0.2384\phi_4$
−2.0596	$\psi_7(\mathrm{b_2})=0.4113(\phi_2+\phi_3)-0.3779(\phi_{2'}+\phi_{3'})+0.3669\phi_{1'}-0.4691\phi_1+0.1439\phi_4$
	$P_{11}=0.934,\ P_{22}=1.081,\ P_{2'2'}=0.996,\ P_{1'1'}=1.064,\ P_{44}=1.845$
p-PDA	
2.3503	$\psi_1(\mathrm{b_{1u}})=0.3100(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})+0.4186(\phi_1+\phi_{1'})+0.3639(\phi_4+\phi_{4'})$
1.9708	$\psi_2(\mathrm{b_{3g}})=0.1395(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})+0.4144(\phi_1-\phi_{1'})+0.5376(\phi_4-\phi_{4'})$
1.1299	$\psi_3(\mathrm{b_{1u}})=0.3028(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})+0.0393(\phi_1+\phi_{1'})-0.5612(\phi_4+\phi_{4'})$
1.0000	$\psi_4(\mathrm{b}^2{}_\mathrm{g})=0.5000(\phi_2+\phi_{2'}-\phi_3-\phi_{3'})$
0.3370	$\psi_5(\mathrm{b_{3g}})=0.2842(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})+0.3799(\phi_1-\phi_{1'})-0.4403(\phi_4-\phi_{4'})$
−1.0000	$\psi_6(\mathrm{a_u})=0.5000(\phi_2-\phi_{2'}-\phi_3+\phi_{3'})$
−1.2802	$\psi_7(\mathrm{b_{1u}})=0.2493(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})-0.5684(\phi_1+\phi_{1'})+0.2292(\phi_4+\phi_{4'})$
−2.1077	$\psi_8(\mathrm{b_{3g}})=0.3869(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})-0.4285(\phi_1-\phi_{1'})+0.1295(\phi_4-\phi_{4'})$
	$P_{11}=0.986,\ P_{22}=1.076,\ P_{44}=1.860$
o-PDA	
2.4120	$\psi_1(\mathrm{b_2})=0.2799(\phi_1+\phi_{1'})+0.4769(\phi_2+\phi_{2'})+0.1982(\phi_3+\phi_{3'})+0.3935(\phi_4+\phi_{4'})$
1.7094	$\psi_2(\mathrm{a_2})=0.2252(\phi_1-\phi_{1'})+0.3018(\phi_2-\phi_{2'})+0.0830(\phi_3-\phi_{3'})+0.5926(\phi_4-\phi_{4'})$
1.5231	$\psi_3(\mathrm{b_2})=0.2827(\phi_1+\phi_{1'})-0.1098(\phi_2+\phi_{2'})+0.5406(\phi_3+\phi_{3'})-0.3403(\phi_4+\phi_{4'})$
0.7930	$\psi_4(\mathrm{a_2})=0.5421(\phi_1-\phi_{1'})+0.1275(\phi_2-\phi_{2'})+0.3023(\phi_3-\phi_{3'})-0.3135(\phi_4-\phi_{4'})$
0.3509	$\psi_5(\mathrm{b_2})=0.2049(\phi_1+\phi_{1'})+0.3876(\phi_2+\phi_{2'})-0.3156(\phi_3+\phi_{3'})-0.4564(\phi_4+\phi_{4'})$
−1.0859	$\psi_6(\mathrm{b_2})=0.5475(\phi_1+\phi_{1'})-0.3320(\phi_2+\phi_{2'})-0.2624(\phi_3+\phi_{3'})+0.1452(\phi_4+\phi_{4'})$
−1.1841	$\psi_7(\mathrm{a_2})=0.0983(\phi_1-\phi_{1'})+0.4177(\phi_2-\phi_{2'})-0.5341(\phi_3-\phi_{3'})-0.1752(\phi_4-\phi_{4'})$
−2.1183	$\psi_8(\mathrm{a_2})=0.3815(\phi_1-\phi_{1'})-0.4671(\phi_2-\phi_{2'})-0.3411(\phi_3-\phi_{3'})+0.1408(\phi_4-\phi_{4'})$
	$P_{11}=1.090,\ P_{22}=0.994,\ P_{33}=1.059, P_{44}=1.860$
m-PDA	
2.3640	$\psi_1(\mathrm{b_2})=0.2841(\phi_2+\phi_3)+0.4313(\phi_{2'}+\phi_{3'})+0.2404\phi_1+0.3650\phi_{1'}+0.3707(\phi_4+\phi_{4'})$
1.9168	$\psi_2(\mathrm{a_2})=0.2057(\phi_2-\phi_3)+0.3941(\phi_{2'}-\phi_{3'})+0.5498(\phi_4-\phi_{4'})$
1.3450	$\psi_3(\mathrm{b_2})=0.4008(\phi_2+\phi_3)-0.0568(\phi_{2'}+\phi_{3'})+0.5962\phi_1-0.0848\phi_{1'}-0.3931(\phi_4+\phi_{4'})$
0.6696	$\psi_4(\mathrm{b_2})=0.0962(\phi_2+\phi_3)-0.2232(\phi_{2'}+\phi_{3'})+0.2876\phi_1-0.6666\phi_{1'}+0.4210(\phi_4+\phi_{4'})$
0.5102	$\psi_5(\mathrm{a_2})=0.5259(\phi_2-\phi_3)+0.2683(\phi_{2'}-\phi_{3'})-0.3890(\phi_4-\phi_{4'})$
−1.0684	$\psi_6(\mathrm{b_2})=0.3275(\phi_2+\phi_3)+0.2633(\phi_{2'}+\phi_{3'})-0.6134\phi_1-0.4930\phi_{1'}-0.1162(\phi_4+\phi_{4'})$
−1.2271	$\psi_7(\mathrm{a_2})=0.4255(\phi_2-\phi_3)-0.5221(\phi_{2'}-\phi_{3'})+0.2152(\phi_4-\phi_{4'})$
−2.1101	$\psi_8(\mathrm{b_2})=0.3763(\phi_2+\phi_3)-0.4373(\phi_{2'}+\phi_{3'})-0.3567\phi_1+0.4145\phi_{1'}+0.1321(\phi_4+\phi_{4'})$
	$P_{11}=0.992,\ P_{22}=1.139,\ P_{2'2'}=0.933,\ P_{1'1'}=1.170,\ P_{44}=1.846$

APPENDIX II. VESCF MO'S AND MO ENERGIES OF *p*-PDA (MO ENERGIES ARE IN UNITS OF eV.)

MO energy	MO
−13.6929	$\psi_1(\mathrm{b_{1u}})=0.3435(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})+0.4406(\phi_1+\phi_{1'})+0.2642(\phi_4+\phi_{4'})$
−12.2245	$\psi_2(\mathrm{b_{3g}})=0.1711(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})+0.4903(\phi_1-\phi_{1'})+0.4484(\phi_4-\phi_{4'})$
− 9.9838	$\psi_3(\mathrm{b_{2g}})=0.5000(\phi_2+\phi_{2'}-\phi_3-\phi_{3'})$
− 9.5396	$\psi_4(\mathrm{b_{1u}})=0.2674(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})-0.0605(\phi_1+\phi_{1'})-0.5943(\phi_4+\phi_{4'})$
− 7.4495	$\psi_5(\mathrm{b_{3g}})=0.2645(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})+0.2938(\phi_1-\phi_{1'})-0.5232(\phi_4-\phi_{4'})$
− 0.4914	$\psi_6(\mathrm{a_u})=0.5000(\phi_2-\phi_{2'}-\phi_3+\phi_{3'})$
0.0951	$\psi_7(\mathrm{b_{1u}})=0.2457(\phi_2+\phi_{2'}+\phi_3+\phi_{3'})-0.5498(\phi_1+\phi_{1'})+0.2775(\phi_4+\phi_{4'})$
2.6572	$\psi_8(\mathrm{b_{3g}})=0.3882(\phi_2-\phi_{2'}+\phi_3-\phi_{3'})-0.4162(\phi_1-\phi_{1'})+0.1589(\phi_4-\phi_{4'})$
	$P_{11}=1.049,\ P_{22}=1.077,\ P_{44}=1.796$