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Acidity Constants of Phenanthrylamines in the Ground, Excited Singlet, and Triplet States

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Measurements of the acidity constants in the ground ($pK_a(S_0)$), the lowest excited singlet ($pK_a(S_1)$), and triplet states ($pK_a(T_1)$) for 2-, 3-, 4-, and 9-phenanthrylamines have been carried out by spectrophotometry. The pK_a values obtained were in the order of $pK_a(S_0) > pK_a(T_1) > pK_a(S_1)$. The absorption and emission spectra of the phenanthrylamines were compared with the results of the calculations by means of the semi-empirical SCF-MO-CI method. A linear relationship between the pK_a values and the net charge (or charge densities) in the ground and excited states was obtained both experimentally and theoretically.

The basic properties of aromatic compounds have been extensively studied especially for the ground states (S_0). The pK_a values determined experimentally have been satisfactorily explained in terms of the π-electronic energy change accompanied by protonation, and also in terms of the charge density on the atom which attacked by the proton. On the basis of the simple Hückel molecular orbital theory,[1] Coulson and Longuet-Higgins[2] pointed out a linear relation between the pK_a values and the charge densities for the ground states. Does the same thing hold when the self-consistent field molecular orbital theory is used?

Experimental studies on the acid-base properties in the excited states were carried out originally by Förster[3] and developed by Weller,[4] who extended the kinetic method to obtain the acidity constants and who succeeded, with substituted aromatic hydrocarbons, in obtaining the same values as those determined by the Förster cycle. Several workers[3-11] have studied the subject of the acidity constants in the

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ground and excited states. Summarize those results, the pK_a values in the lowest excited singlet states (S_1) are very much lower than those in S_0, while the pK_a (T_1) values are a little smaller or similar to those in S_1.

In order to explain these results, several discussions have appeared. Jackson and Porter[5] have explained this tendency of pK_a values as resulting from the differences among the electronic structures: the S_0, S_1, and T_1 states have normal, ionic, and radical structures respectively. The pK_a value in the S_1 state was elucidated by the resonance theory.[6-7] An explanation was also made considering the solvation effect on the pK_a values.[8] On the other hand, some theoretical calculations have been reported: they have suggested that the pK_a values in the excited states correlate with the electron-density distribution in the excited states.[9]

These explanations give us interesting suggestions concerning the basic properties in the excited states. No pK_a values of phenanthrylamines, except for those in S_0,[12] have been reported. Little attention has yet been paid to the theoretical consideration concerning these compounds. The purpose of the present paper is to measure these pK_a values for phenanthrylamines and to see if there exists a quantitative correlation between the charge distributions calculated theoretically by the SCF–MO–CI method and the experimental pK_a values in the ground and excited states.

Experimental

Materials. The 2-, 3-, 4-, and 9-phenanthrylamines used were given by Dr. Etsuro Ohta (Gunma University); these compounds were recrystallized twice from benzene. The cyclohexane was purified by passing it through a silica-gel column and by distillation. The methanol and ethanol were Kanto Chemical Co., Ltd., G. R.-grade products and were used without further purification. The buffer solutions used were adjusted using hydrochloric acid and sodium acetate.[13]

Apparatus. The UV absorption spectra were measured by means of a Hitachi 139 spectrophotometer. The fluorescence and phosphorescence spectra were taken with a Hitachi MPF 2A fluorescence spectrophotometer.

The Determination of pK$_a$ Values. The pK_a values in the ground states (S_0) were measured by spectrophotometry at 20°C. The pK_a (S_1) and pK_a (T_1) values were estimated by means of the Förster cycle[3] as in the following relation:

$$\mathrm{p}K_a(S_0) - \mathrm{p}K_a{}^* = (\Delta E_{\mathrm{HA}} - \Delta E_{\mathrm{A}})/(2.303\boldsymbol{R}T)$$

where ΔE_{HA} and ΔE_{A} are the energy differences between the ground and excited states of the protonated and unprotonated molecules respectively. The pK_a(S_0) and pK_a* (pK_a(S_1) or pK_a(T_1)) denote the pK_a values in S_0 and the excited state (S_1 or T_1) respectively. $\boldsymbol{R}$ and T are the gas constant and the absolute temperature respectively. In the present work, the energy difference between the S_0 and S_1 states was evaluated by means of the absorption and fluorescence spectra; the difference corresponds to the O–O transition energy. The energy difference between S_0 and T_1 was estimated by means of the phosphorescence spectra. If the pK_a(S_0) is known, the pK_a* can then be obtained.

Calculation

The π-electronic structures of some phenanthrylamines were studied by the use of the semi-empirical self-consistent field molecular orbital theory[14,15] combined with the singly excited configuration-interaction calculation. The CI calculation was made by taking 30 configurations of lower energies. The two-center Coulomb repulsion integrals, γ_{ij}, were calculated according to the Mataga-Nishimoto approximation.[16] The one-center Coulomb repulsion integrals, γ_{ii}, were estimated from the corresponding valence-state ionization potentials, (I_i), and electron affinities, (A_i), by the Pariser-Parr method,[14] I_i and A_i being determined from the spectroscopic data using the promotion energies of Hinze and Jaffé.[17] The two-center core resonance integrals, β_{ij}, were evaluated with the Nishimoto-Forster approximation.[18]

Some choices have been made concerning the appropriate I_i value for the nitrogen atom of an amino group. We used three types of parameter values (energies in eV) for the nitrogen atom:

(I) $I_{\mathrm{N}}=28.709$, $\gamma_{\mathrm{NN}}=16.757$, core charge$=2$,[17]

(II) $I_{\mathrm{N}}=27.904$, $\gamma_{\mathrm{NN}}=16.428$, core charge (N)$=$ 1.957, $I_{\mathrm{C'}}=11.5516$, $\gamma_{\mathrm{C'C'}}=11.3236$, core charge (C')$=$ 1.035.

Here, C' denotes the carbon atom next to the nitrogen atom. These parameter values are taken them Dewar and Morita,[19] who took the sigma polarization effect into account.

(III) $I_{\mathrm{N}}=24.71$, $\gamma_{\mathrm{NN}}=13.75$, core charge$=2$.

These parameter values were determined by Hirota and Nagakura[20] based on doubly-excited configuration interaction calculations.

In the SCF calculations, the variable-β,γ procedure developed by Dewar and Schmeising[21] and later by Nishimoto and Forster[18] was employed. The geometry was assumed to be as follows. All the C–C bond lengths and all the bond angles were taken to be equal to 1.39 Å and 120° respectively. The C–N bond length was assumed to be 1.38 Å. The actual calculation was carried out by an electronic computer, HITAC 5020 E, located at the Computer Center, The University of Tokyo.

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Results

Electronic Absorption Spectra. The absorption spectra of the four phenanthrylamines were measured in cyclohexane at room temperature. Figure 1 shows those absorption spectra. By the substitution of an amino group, the π-electronic structure of phenanthrene was perturbed. The experimental and calculated values for the transition energies and oscillator strengths are listed in Table 1. Table 1 shows that the calculated values are in accordances with those obtained experimentally. No significant effect of the variation of parameters on the transition energies was observed.

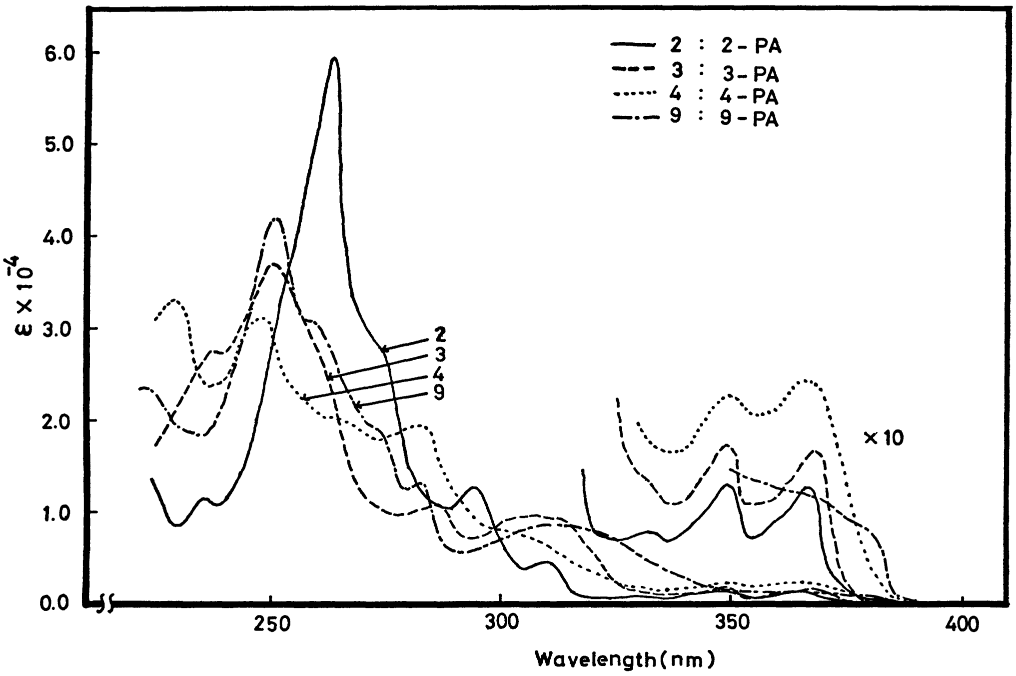

Fig. 1. UV absorption spectra of phenanthrylamines in cyclohexane at 20°C.

Table 1. Transition energies and oscillator strengths

Substance	Obsd.		Calcd(I)		Calcd(II)		Calcd(III)	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f
1-PA	—	—	3.54	0.041	3.53	0.053	3.51	0.068
	—	—	3.99	0.333	3.96	0.325	3.91	0.328
	—	—	4.41	0.042	4.40	0.046	4.38	0.055
	—	—	4.80	0.424	4.77	0.434	4.73	0.402
2-PA	3.55	0.006	3.53	0.013	3.52	0.017	3.50	0.020
	4.00	0.017	4.12	0.119	4.11	0.100	4.10	0.062
	4.21	0.081	4.41	0.041	4.39	0.047	4.37	0.063
	4.52	—	4.70	1.748	4.67	1.775	4.62	1.820
3-PA	3.55	0.007	3.55	0.014	3.55	0.016	3.53	0.022
	4.02	0.111	4.01	0.382	3.98	0.390	3.94	0.417
	4.33	0.087	4.42	0.023	4.41	0.026	4.39	0.030
	4.96	—	4.85	1.244	4.85	1.155	4.84	1.073
4-PA	3.54	0.016	3.51	0.040	3.50	0.047	3.47	0.059
	4.06	0.102	4.05	0.153	4.02	0.133	3.98	0.114
	4.39	0.170	4.38	0.266	4.36	0.323	4.33	0.369
	4.68	—	4.70	0.849	4.69	0.757	4.67	0.606
9-PA	3.36	0.007	3.53	0.025	3.51	0.031	3.49	0.038
	3.91	0.145	3.96	0.334	3.93	0.337	3.88	0.351
	4.38	0.069	4.47	0.039	4.47	0.057	4.46	0.081
	4.52	—	4.78	0.661	4.76	0.412	4.72	0.373

ΔE and f denote the transition energy in units of eV and the oscillator strength respectively. I, II, and III are explained in the text, and PA denotes phenanthrylamine.

Ground-state Acidity Constants, $pK_a(S_0)$. Eliot and Mason[12] have reported the pK_a (S_0) values of phenanthrylamines measured by the potentiometric method. In the present work, the $pK_a(S_0)$ values were determined spectrophotometrically using the buffer solutions. These results are summarized in Table 2.

TABLE 2. GROUND-STATE ACIDITY CONSTANTS

Substance	$pK_a(S_0)$		
	(1)[a]	(2)[b]	ΔH[c]
2-PA	4.06	3.60	4.4
3-PA	3.90	3.59	4.4
4-PA	3.18	—	—
9-PA	3.50	3.19	5.6

a) This work.
b) *Cf.* Reference 12.
c) ΔH denotes the enthalpy change in the dissociation of the conjugate acid of the phenanthrylamine in units of kcal/mol. *Cf.* Ref. 12.

The $pK_a(S_0)$ values obtained in the present work are somewhat high ($pK_a \approx 0.36$) in comparison with those reported by Eliot and Mason[12].

Excited Singlet-state Acidity Constants. The absorptions and fluorescence spectra of the four phenanthrylamines(RNH_2) and of their conjugate acids were measured at 20°C in an aqueous methanol solution (5 vol. percent methanol solution) for the parent molecules and in an aqueous methanol solution with sulfuric acid added for the protonated molecules (RNH_3^+). The absorptions and fluorescence spectra of the parent molecules appeared in various regions perturbed by the substituent amino group. However, the spectra of the protonated molecules are similar to that of phenanthrene. For example, the transition energies of the conjugate acid of 2-phenanthrylamine correspond to those of phenanthrene (Table 3) Similar results were obtained for 3-, 4-, and 9-phenanthrylamines. Therefore, the 345 nm (3.5_9 eV) absorption bands of the conjugate acids were assigned to the $^1L_b \leftarrow {}^1A$ transition of the phenanthrene molecule[22] with a maximum at 344 nm(3.6_0 eV). Little effect of the substituent NH_3^+ group on the phenanthryl group was found.

TABLE 3. TRANSITION ENERGIES FOR THE CONJUGATE ACID OF 2-PHENANTHRYLAMINE

Excited singlet state	Transition energy (eV)		
	a	b	c
S_1	3.5_9	3.6_0	3.56
S_2	4.2_3	4.2_4	4.09
S_3	4.4_4	4.4_3	4.59
S_4	4.5_4	4.5_2	4.74

a) Experimental data for the conjugate acid of 2-phenanthrylamine.
b) Experimental data of phenanthrene in cyclohexane.
c) Calculated values of phenanthrene in the present work.

The $pK_a(S_1)$ values estimated by the Förster cycle are listed in Table 4.

Triplet-state Acidity Constants. The phosphorescence spectra of the four phenanthrylamines were measured in the rigid methanol-ethanol (1 : 1 mixture in volume) matrices[23] at 77°K. These data are summarized in Table 5. The conjugate acids had the same $T_1 \rightarrow S_0$ transition energies as those of phenanthrene. These results show that the features of the lowest triplet states of the conjugate acids are very similar to those of phenanthrene. The $pK_a(T_1)$ values of protonated PA (RNH_3^+) were also determined by the Förster cycle, as is shown in Table 5. In the present work, the order of the pK_a values of protonated PA is $pK_a(S_0) > pK_a(T_1) > pK_a(S_1)$, as is shown in Tables 2, 4, and 5.

Charge Densities. The charge densities on the nitrogen atom in phenanthrylamines have been estimated by the semi-empirical SCF–MO–CI calculations using the parameters described above. Table 6 shows the calculated charge densities.

Discussion

The lone-pair electron on the amino-nitrogen atom would migrate to the phenanthryl ring much more intensely in the excited singlet state than in the ground state and a little more intensely in the triplet than in the ground state. The calculated results show this is true, as may be seen in Table 6. Accordingly, the basicities would be the largest for the ground state, medium for the lowest triplet state and the least for the lowest excited singlet state. The experimental

TABLE 4. $S_1 \leftarrow S_0$ TRANSITION ENERGIES AND $pK_a(S_1)$ VALUES OF PHENANTHRYLAMINES

Substance	Absorption (eV)		Fluorescence (eV)		O-O Transition energy (eV)[b]		pK_a (S_1)	ΔH (S_1)[a]
	RNH_2	RNH_3^+	RNH_2	RNH_3^+	RNH_2	RNH_3^+		
2-PA	3.4_8	3.6_0	2.9_2	3.5_7	3.2_0	3.5_8	-2.5_7	-2.4_6
3-PA	3.4_5	3.5_9	3.0_5	3.5_4	3.2_5	3.5_7	-1.6_0	-2.9_8
4-PA	3.4_4	3.5_7	2.7_8	3.5_2	3.1_1	3.5_5	-4.4_9	—
9-PA	3.4_4	3.5_9	2.8_2	3.4_4	3.1_3	3.5_2	-3.2_1	-3.1_6

a) Estimated from the relation: $\Delta H(S_1) = \Delta H(S_0) - (\Delta E_{AH}(S_1) - \Delta E_A(S_1))$, ΔH are in units of kcal/mol.
b) The O-O transition energies were evaluated by means of the absorption and fluorescence spectra.

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TABLE 5. PHOSPHORESCENCE SPECTRA, $pK_a(T_1)$, AND ENTHALPY CHANGES

Substance	Phosphorescence spectra (nm)		$pK_a(T_1)$	$\Delta H(T_1)$[a] (kcal/mol)
	RNH_2	RNH_3^+		
2-PA	487	453	0.7_2	-0.0_3
3-PA	475	453	1.7_7	1.5_4
4-PA	495	453	-0.3_7	—
9-PA	500	453	-0.9_2	-0.3_3
Phenanthrene	450			

a) Estimated from the relation: $\Delta H(T_1) = \Delta H(S_0) - (\Delta E_{AH}(T_1) - \Delta E_A(T_1))$.

results indicate this very tendency. Furthermore, as is shown in Table 4, the dissociation of protonated phenanthrylamines in the lowest excited singlet state is an exothermic reaction.

If the chemical non-crossing rule[2] could be applied for the excited states, the linear relation between the charge densities and the excited state pK_a values might be anticipated. Figure 2(a) shows the plot of the pK_a values against the charge densities: a good linear fit is seen for the excited singlet states. Points corresponding to the ground-state pK_a values also lie on the same straight line. Treatment by the least-squares method gives the following equation:

$$pK_a = 133.46P - 248.34 \quad (1.83 < P < 1.90) \qquad (1)$$

for this linear correlation. The slope of the line and the correlation coefficient, except for the plot for the triplet state, are 133.46 and 0.992 respectively. In this plot, we used charge densities calculated using the (II) parameter set, which is based on the consideration of the sigma polarization effect, because the charge densities computed by the (II) parameter set gave a somewhat better linear correlation than those calculated by the (I) and (III) parameter sets.

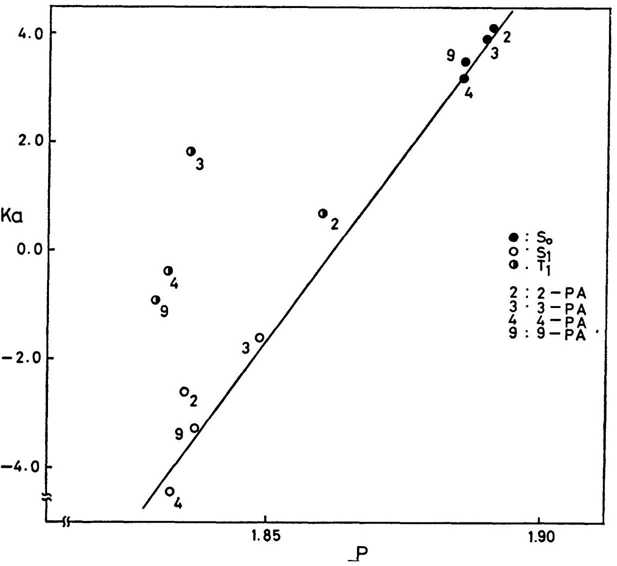

Fig. 2(a). Plot of the pK_a values *vs*. the charge densities. The S_0, S_1, and T_1 denote the ground, the lowest excited singlet, and the triplet states respectively.

The enthalpy change (ΔH) in the dissociation of RNH_3^+ (Eq. 2) can be estimated approximately as follows:

$$RNH_3^+ \overset{K_a}{\rightleftharpoons} RNH_2 + H^+ \qquad (2)$$

where K_a denotes the equilibrium constant. The enthalpy change can be written as:

$$\Delta H = -\boldsymbol{RT} \ln K_a = (2.303\,\boldsymbol{RT})pK_a \qquad (3)$$

The value of ΔH is approximated by the following equation:

$$\Delta H = I_N - A + C \qquad (3')$$

where I_N is the valence-state ionization potential of the nitrogen atom as determined by the method of Dewar and Morita[19] (see Eqs. (5) and (6); A is the electron affinity of a proton, and C is a constant). Equation (4) is derived from Eqs. (3) and (3′):

$$pK_a^{\text{theo}} = \frac{1}{2,303\,\boldsymbol{RT}}(I_N - A + C) \qquad (4)$$

$$= \frac{1}{2.303\,\boldsymbol{RT}} I_N + \text{const.}$$

According to Eq. (4), the theoretical pK_a values should be proportional to the valence-state ionization potential of the nitrogen atom.

The estimations of the I_N values were carried out using the following relation[19]:

$$I_N = a + bq + cq^2 \qquad (5)$$

where q denotes the total valence-shell electron density, and for the trigonal nitrogen, *a*, *b*, and *c* are equal to −89.402, 24.6265 and −1.4515 respectively. Equation (5) can be also given in the form of Eq. (6):

$$I_N = -10.1622\,Q_\pi - 2.1130\,\text{eV} \qquad (6)$$

where Q_π is the net charge on the nitrogen atom; the term of $(Q_\pi)^2$ is disregarded since the $(Q_\pi)^2$ values are very small.

TABLE 6. CHARGE DENSITIES IN THE S_0, S_1, AND T_1 STATES

	$P(S_0)$[a]			$P(S_1)$[a]			$P(T_1)$[a]		
	(I)[b]	(II)	(III)	(I)	(II)	(III)	(I)	(II)	(III)
2-PA	1.899	1.891	1.873	1.858	1.835	1.790	1.861	1.860	1.837
2-PA	1.898	1.890	1.872	1.865	1.849	1.810	1.852	1.836	1.796
4-PA	1.894	1.886	1.867	1.849	1.833	1.786	1.847	1.832	1.789
9-PA	1.894	1.886	1.867	1.852	1.837	1.796	1.846	1.830	1.784

a) $P(S_0)$, $P(S_1)$, and $P(T_1)$ denote the charge densities in S_0, S_1, and T_1 states.
b) Meanings of (I), (II), and (III) are described in the text.

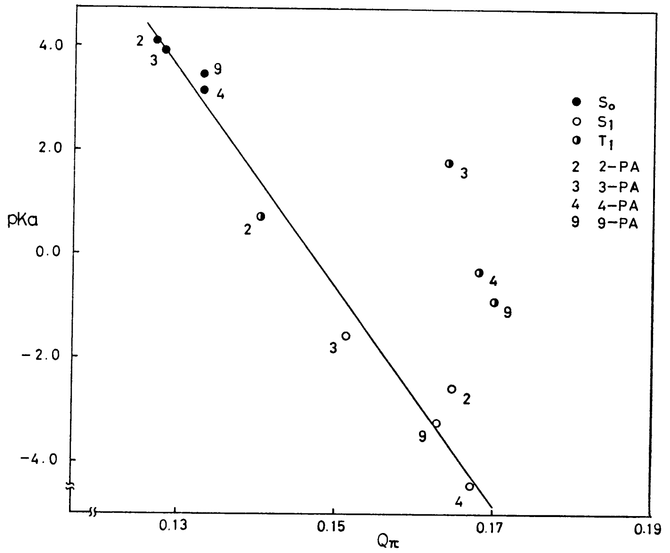

Fig. 2(b). Plot of the pK_a values *vs*. the net charges. The S_0, S_1, and T_1 denote the ground, the lowest excited singlet, and the triplet states respectively.

From the substitution of Eq. (6) into Eq. (4), Eq. (7) is given by:

$$\mathrm{p}K_a{}^{\mathrm{theo}} = -\frac{1}{2.303\,\boldsymbol{RT}}(10.1622\,Q_\pi+2.1130+A-C) \quad (7)$$
$$= -1.748\times10^2\,Q_\pi + \text{const.}$$

where T equals 293°K. Therefore, the linear relationship between the p$K_a{}^{\mathrm{theo}}$ values and the net charge Q_π can be derived; the slope of this relationship equals -1.748×10^2, as is described in Eq. (7). Figure 2(b) shows the plot of the experimental pK_a values *vs*. the net charge, Q_π; a good linear relationship is obtained. The following equation is given by the least-squares method:

$$\mathrm{p}K_a = -2.05\times10^2\,Q_\pi + 30.322 \quad (8)$$

The slope of the line and the correlation coefficient, except for the plot for the triplet state, are -2.05×10^2 and 0.999 respectively. The slope of the line obtained experimentally is almost the same as that derived by the theoretical method, as is shown in Eqs. (7) and (8).

The pK_a values for the 1-phenanthrylamine can be estimated from the linear relationship in Figs. 2(a) and (b), if the charge densities are known. The estimated pK_a values are shown in Table 7.

TABLE 7. ESTIMATED pK_a VALUES FOR THE 1-PHENANTHRYLAMINE

	State	
	S_0	S_1
$p^{a)}$	1.886	1.837
pK_a	3.3_7	-3.1_7

a) P denotes the charge density calculated using the (II) parameter set, as has been described in the text.

The triplet-state pK_a values deviated from linearity. This must be due to some factors such as:

(1) In the present treatment, entropy changes in the dissociation of the conjugate acids are assumed to be constant for the three states of this series of compounds.

(2) The measured pK_a values are for the phosphorescent states. The charge densities to be used in plotting, therefore, should be calculated for the same states. The charge densities in the triplet state calculated by the present method are not precisely equal to those for the phosphorescent state, since the excited molecular orbitals are determined on the basis of the ground-state energy minimization. In order to improve this situation, we tried computations using Roothaan's open-shell procedure based on the minimization of the triplet-state energy.[24] Unfortunately, we were not successful in using it. In the large molecules such as we treated here, the MO energies were very close to each other, and at each stage of iteration an exchange of the MO levels occurred, resulting in no convergence of the charge densities.

Finally, it can be said that a linear relationship between the pK_a values and the net charge (or charge densities) is obtained both experimentally and theoretically in the ground and excited states.

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