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Studies on the Electronic Spectra of the Semiquinones of Anthracene and Its Related Heterocycles. II

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The electronic structures of semiquinones of anthracene and its related heterocycles were calculated, using the open shell SCF procedure combined with configuration interaction calculations. A general classification and some peculiarities of the observed absorption spectra of these semiquinones can be readily explained by the present theoretical results. The effects of resonance integral and configuration interactions were examined in detail. The results obtained by considering the effect of hyperconjugation were added.

Semiquinones have been considered as reaction intermediates in photochemical reactions of aromatic compounds such as acridine dyes, xanthene dyes and triphenylmethane dyes. The photochemical behaviors and absorption spectra of anthracene semiquinone and its heterocycles have previously been reported.[2]

The absorption spectra of these semiquinones are classified into three groups; 1) the first band at 250 nm (4.9 eV in transition energy), 2) the second band at 350 nm (3.5 eV), and 3) the third band in the visible region (2.3—2.8 eV). However, some semiquinones have special features, *i. e.*, 1) anthracene semiquinone has no visible absorption, 2) acridine-*N* semiquinone has no first band, and 3) acridine-*C* semiquinone has a prominent peak at 281 nm.

Theoretical consideration of the electronic structures of their excited states is necessary for the assignment of each band. However, the electronic structures have not been reported because of the complexity of the treatment required for an open shell system.

Pople and Longuet-Higgins have proposed the method of semi-empirical SCF MO calculation with zero differential overlap approximation for open shell system and have calculated the transition energies of the benzyl radical.[3] The calculated energies are higher than the observed ones. Configuration interaction would be more important for the calculation of transition energies of open shell systems than for those of closed shell systems, as shown for the anion radicals of substituted benzenes.[4]

In this paper transition energies and oscillator strengths of the π-π^* transitions of anthracene semiquinone and its heterocycles will be reported and the assignment of absorption bands of the semiquinones will be decided by comparing those values with observed values.[2] The calculations were carried out with appropriate values of reasonance integrals β's. They were chosen by examining the effect of resonance integrals on the transition energies of anthracene anion radical, xanthene semiquinone, anion and cation radicals of six membered *N*-heterocycles. The effect of hyperconjugation of CH_2 group in the aromatic ring will be also examined for anthracene semiquinone and acridine-*N* semiquinone.

Method of Calculation

The method of calculation can be divided into two parts: 1) determination of LCAO-MO's by means of the semi-empirical open shell SCF method proposed by Pople and Longuet-Higgins,[3] and 2) generation of the spectroscopic states by configuration interaction.

The molecular orbitals obtained are the eigenfunctions of the Schrödinger equation

$$F\varphi_i = E_i\varphi_i \tag{1}$$

where F is the SCF Hamiltonian operator, E_i is the energy of ith molecular orbital. This equation can be derived by neglecting electronic repulsion integrals between the half occupied molecular orbital φ_m and other orbitals φ_i: $(mi\ mm)$. The elements of the energy matrix (F) are given by the formulae

$$\begin{aligned} F_{pp} &= -I_p+0.5\times P_{pp}\times(pp\ pp)+\sum_{q\neq p}(P_{qq}-Z_q)\times(pp\ qq) \\ F_{pq} &= \beta_{pq}-0.5\times P_{pq}\times(pp\ qq) \end{aligned} \tag{2}$$

where I_p and Z_p represent the ionization potential and the number of π electrons released from pth atom, respectively. The values of ionization potential and electron affinity of the π electron in the appropriate valence state are taken from the table of Pilcher and Skinner.[5]

Z_p is 1 for –C=, –N= and =O; is also 2 for –O– and $-\underset{|}{N}-$. Electronic Coulombic repulsion integrals between two atomic orbitals $(pp\ qq)$ and resonance integrals β_{CX} were calculated using the Pariser-Parr approximation.[6]

The ground state and four types of excited states of the semiquinones are constructed as follows:

$$\begin{aligned} {}^2\Psi_G &= |\varphi_1\bar{\varphi}_1\cdots\varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| && \mathrm{G} \\ {}^2\Psi_A &= |\varphi_1\bar{\varphi}_1\cdots\varphi_i\bar{\varphi}_m\varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| && \mathrm{A}(i\text{–}m) \\ {}^2\Psi_B &= |\varphi_1\bar{\varphi}_1\cdots\varphi_{m-1}\bar{\varphi}_{m-1}\varphi_k| && \mathrm{B}(m\text{–}k) \\ {}^2\Psi_{CA} &= (|\varphi_1\bar{\varphi}_1\cdots\varphi_i\bar{\varphi}_k\cdots\varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| \\ &\quad +|\varphi_1\bar{\varphi}_1\cdots\varphi_k\bar{\varphi}_i\cdots\varphi_m|)/\sqrt{2} && \mathrm{CA}(i\text{–}k) \\ {}^2\Psi_{CB} &= (2|\varphi_1\bar{\varphi}_1\cdots\varphi_i\varphi_k\cdots\varphi_m|-|\varphi_1\bar{\varphi}_1\cdots\varphi_i\bar{\varphi}_k\cdots\varphi_m| \\ &\quad -|\varphi_1\bar{\varphi}_1\cdots\varphi_k\bar{\varphi}_i\cdots\varphi_m|)/\sqrt{6} && \mathrm{CB}(i\text{–}k) \end{aligned} \tag{3}$$

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[1] Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

[2] H. Masuhara, M. Okuda, and M. Koizumi, This Bulletin, **41**, 2319 (1968) (Series I).

[3] H. C. Longuet-Higgins and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **68**, 591 (1955).

[4] A. Ishitani and S. Nagakura, *Theor. Chim. Acta*, **4**, 236 (1966).

[5] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

[6] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

where simple notations in the right column represent configurations in the left column, and i and k denote occupied and vacant orbitals, respectively.

Formulas of the transition energies and transition dipole moments are given in Ref. 3.

In the second step, configuration interaction calculations were carried out for 12 or 13 configurations of A and B types of singly excited states, and for 44 or 45 configurations of A, B, CA and CB types of singly excited states. The oscillator strength of each transition was evaluted by the equation

$$f = 1.085 \times 10^{-5} \times E \times M^2 \qquad (4)$$

where E represents the transition energy in cm^{-1} and M a transition dipole in Å.

Most calculations were carried out on the electronic computer HITAC 5020 in the electronic computer center of the University of Tokyo. The solution of CI determinant and other supplemental calculations were performed on the electronic computer NEAC 2230 in Tohoku University.

Parameterization: Effect of Resonance Integral

Calculated values of transition energies do not agree with observed ones in an open shell system as well as in a closed shell system. This discrepancy may be adjusted to some extent by the choice of the best experimental value of resonance integral, and by consideration of many configurations in the configuration interaction. The effects of both resonance integral and configuration interaction were examined carefully for some of the semiquinones and hydrocarbon anion radicals.

The Effect of Resonance Integral β_{CC}. The transition energies of the anthracene anion radical were calculated using the ordinary value of resonance integrals and by consideration of 13 excited configurations. The C–C bond distance and bond angles were taken as 1.39 Å and 120°, respectively. The value of β_{CC} used is −2.39 eV which corresponds to that of the neutral molecule. Using this value we obtained better agreement with the observed values. The results are shown in Table 1. Consequently, the value of β_{CC} for the neutral molecule was used in the following calculations.

Table 1. Transition energies of anthracene anion radical

E_{cal} (eV)	f_{cal}	E_{obs}[7] (eV)	f_{obs}[7]
1.830	— out of plane		
2.027	— x	1.686	0.95 x
2.538	— y	1.327	— y
3.382	— out of plane		
3.863	— y	3.161	— y
4.660	— x	3.781	1.50 x
4.834	— out of plane		
5.430	— out of plane		

The Effect of β_{CX}. The transition energies of xanthene semiquinone were calculated using different β_{CO}'s (Fig. 1). Lower energy levels decrease and higher energy levels increase with the increase in the absolute value of resonance integral β_{CO}. The magnitude of the shift is about 0.2 eV for lower levels, which is within the accuracy of approximation in the calculations.

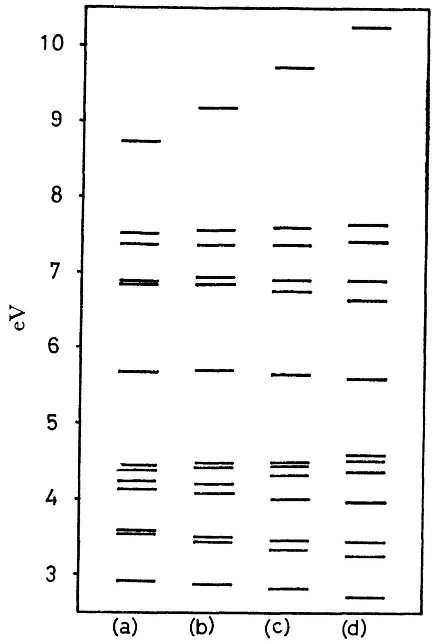

Fig. 1. The transition energies of xanthene semiquinone.
(a) $\beta_{CO} = -1.667$ eV (b) $\beta_{CO} = -1.945$ eV
(c) $\beta_{CO} = -2.223$ eV (d) $\beta_{CO} = -2.501$ eV

Small and more fundamental radicals such as anion and cation radicals of six-memberd N-heterocycles, allyl derivatives and pentadienyl derivatives were also used for examination of the effect of β_{CN} (Fig. 2). Although in the case of xanthene semiquinone the larger absolute value of β_{CO} gives the lower transition energies in ultraviolet region, the results for these radicals show the reverse effect. Thus, it is difficult to explain theoretically the shift of transition energy with the change of resonance integral. Consequently, the values of β_{CX} used in the calculations for semiquinones are also those for the neutral molecules.

Effect of Configuration Interaction

The results for the naphthalene anion radical with a different number of excited configurations in CI calculations are given in Table 2. This radical was chosen as a model for the examination of the effect of CI because it is intermediate in complexity between the benzyl radical and anthracene semiquinone. Our calculation of CI included 9 configurations of states A and B, and explained the observed absorption spectra rather well. The calculation including 29 configurations of states A, B, CA, and CB by Ishitani and Nagakura was more successful for explaining the transition energies.[4]

The contribution of states CA and CB becomes more

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[7] R. S. Hoijtink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, **3**, 534 (1961).

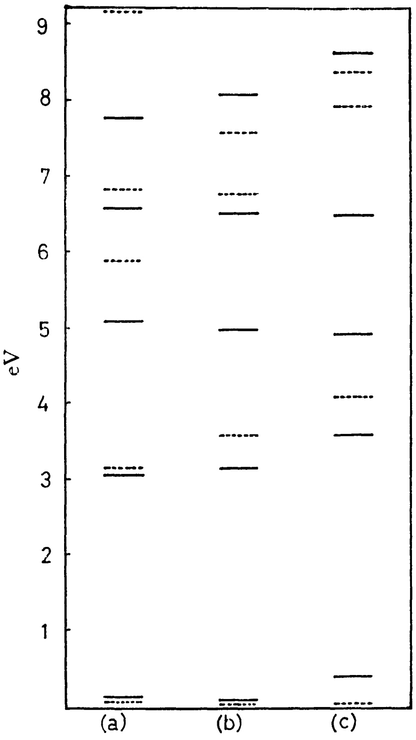

Fig. 2-A. The transition energies of anion radicals of pyridine and *s*-triazine.
——pyridine ……*s*-triazine
(a) $\beta_{CN}=-2.576$ eV (b) $\beta_{CN}=-3.00$ eV
(c) $\beta_{CN}=-3.50$ eV

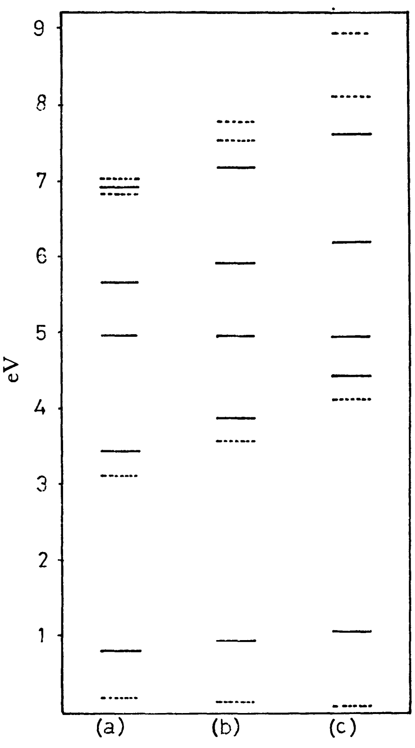

Fig. 2-B. The transition energies of cation radicals of pyridine and *s*-triazine.
——pyridine ------*s*-triazine
(a) $\beta_{CN}=-2.576$ eV (b) $\beta_{CN}=-3.00$ eV
(c) $\beta_{CN}=-3.50$ eV

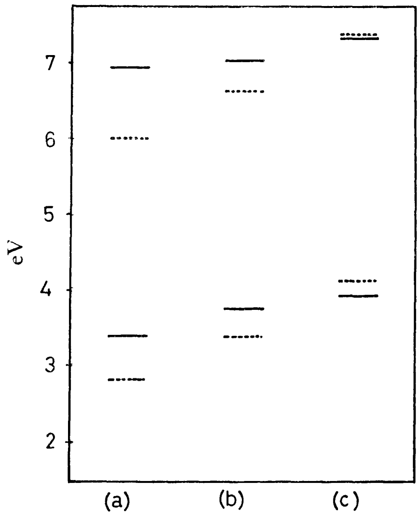

Fig. 2-C. The transition energies of allyl derivatives.
——N=C-C ------C=N-C
(a) $\beta_{CN}=-2.576$ eV (b) $\beta_{CN}=-3.00$ eV
(c) $\beta_{CN}=-3.50$ eV.

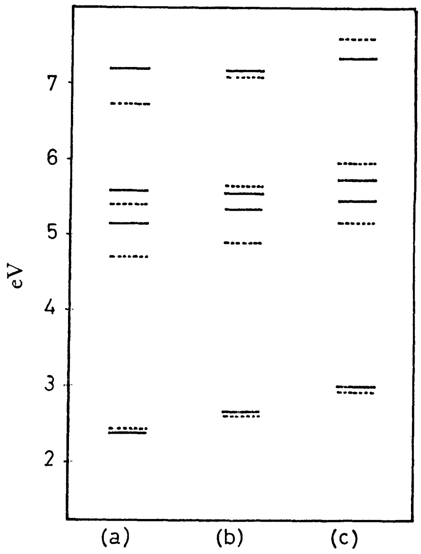

Fig. 2-D. The transition energies of pentadienyl derivatives.
——N=C-C=C-C ------C=N-C=C-C
(a) $\beta_{CN}=-2.576$ eV (b) $\beta_{CN}=-3.00$ eV
(c) $\beta_{CN}=-3.50$ eV

TABLE 2. RESULTS FOR THE NAPHTHALENE ANION RADICAL WITH DIFFERENT NUMBER OF EXCITED CONFIGURATIONS IN CI CALCULATIONS

a) E_{cal} (eV)	f_{cal}	b) E_{cal} (eV)	$f_{cal}{}^{4)}$	$E_{obs}{}^{7)}$ (eV)	$f_{obs}{}^{7)}$
2.088	0.157	1.969	0.413	1.636	0.29(*x*)
2.989	0.015	2.657	0.057	hidded	
4.294	0.570	3.708	0.486	3.657	0.40(*y*)
		4.286	0.014	3.831	0.37(*x*)
5.051	0.734	5.032	0.876	4.228	
		6.374	2.516	5.443	

a) 9 configurations were taken into CI calculation.
b) 29 configurations were taken into CI calculation.

important for anthracene semiquinone and its heterocycles. Calculation of 12 or 13 configurations of states A and B could not explain the observed results. Generation of the spectroscopic states by including a number of configurations is indispensable for the calculations.

Results and Discussion

Transition energies and oscillator strengths of anthracence semiquinone and its heterocycles have been calculated with the same resonance integral as neutral molecules and also using the 44 or 45 configurations of singly excited states A, B, CA, and CB. The results are given in Table 3. The number of π electron in the semiquinones are 13 for anthracene and acridine-*N* semiquinones, and 15 for acridine-*C*, xanthene, and phenazine semiquinones. Molecular structures of these semiquinones assumed from a consideration of the experimental results are shown in Fig. 3 together with the values of bond distances and bond angles. All the molecules are assumed to be planar. Calculated π–π^* transitions of these semiquinones can be divided into three groups. The first consists of strong transition (f=1.0) of about 6 eV transition energy, the second of moderate transitions (f=0.5—1.0) of about 4 eV and third of weak transitions of less than 3 eV. The calculated transitions correspond very well to the three groups of observed absorption bands. Discrepancies between theoretical and experimental results become smaller for lower transition energies. The magnitude of difference is about 1 eV for the 250 nm band (transition energy 4.9 eV), about 0.6 eV for the 350 nm band (3.5 eV) and 0.5 eV for the visible band (2.5 eV). The strong absorption band at 250 nm may be assigned to the π–π^* transition to the excited state, to which the CA configuration contributes predominantly. The other two bands may be assigned to the transition to the excited state which is a mixture of configurations A and B. By elimination of configurations which contribute to a small extent, each excited state can be expressed as follows.

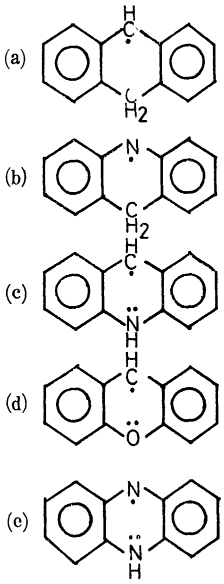

Fig. 3. Molecular structures.
(a) Anthracene semiquinone, 13π. (b) Acridine-*N* semiquinone, 13π. (c) Acridine-C semiquinone, 15π. (d) Xanthene semiquinone, 15π. (e) Phenazine semiquinone, 15π.
C–C, 1.39 Å. C–X, 1.36 Å.
Angles C–X–C, 117.5°. All otherangles, 120°.

$$\Psi(350\,\text{nm}) = a\Psi_\text{A} - b\Psi_\text{B}$$
$$\Psi(\text{visible}) = b\Psi_\text{A} - a\Psi_\text{B}$$

The energy level of a half-occupied molecular orbital in an alternant hydrocarbon radical is located exactly in the center of the highest fully occupied orbital and the lowest vacant orbital, and then energies of configurations A and B are equal. When a carbon atom in this radical is replaced by a nitrogen atom, the half-occupied orbital is stabilized and its energy falls below its original level. The coefficient a for an alternant hydrocarbon radical is equal to $-b$, as proposed by Pople and Longuet-Higgins,[3] and thus f(visible) should be zero. This consideration explains well the experimental fact that anthracene semiquinone has no visible band. The line of argument is correct in the calculation which considers many configurations in CI calculations. The calculated oscillator strength of the visible band for anthracene semiquinone is 0.0000.

For heterocyclic radical, a is not equal to b, and f(visible) does not disappear. This is the reason why acridine-*N* semiquinone radical has a weak band in the visible region. It is possible to assign this weak band to a lone pair of N atom–π^* transition, but we have no evidence to show this.

The 350 nm and visible bands of acridine-*C*, phenazine and xanthene semiqunones are similarly interpreted, noting the difference of the number of molecular orbitals.

A special band at 281 nm of Acridine-*C* semiquinone can be assigned to the transition, whose excited state consists of CB(7—9) configuration predominantly and both CA(7—9) and A(6—8) configurations in a few percent. Although the transition to CB configurations is forbidden, this 281 nm transition has a moderate oscillator strength due to the contribution of CA(7—9) and A(6—8) configurations which have larger transition moments. A similar phenomenon can be expected in phenazine semiquinone, though this spectrum has not yet been observed.

The oscillator strength of the band at 250 nm for acridine-*N* semiquinone is 0.19 and much smaller than for other semiquinones. Thus, the other type of acridine semiquinone which has no band at 250 nm can be identified as acridine-*N* semiquinone.

The observed spectra of semiquinones are well explained by the present theoretical studies.

The Effect of Hyperconjugation

In the above section 13π type semiquinone structures were assumed for anthracene and acridine-*N* semiquinone, excluding the methylene group from the π-electron conjugated systems. The opposite extreme case is the one where electrons in the methylene group flow out to the π-electron conjugated systems. In this case it is appropriate to take the concept of hyper-

TABLE 3. THEORETICAL AND EXPERIMENTAL RESULTS

(a) Acridine-*C* semiquinone

	E_{cal} (eV)	f_{cal}	Direction	E_{obs} (eV)	Relative intensities
I	2.274	0.015	x	2.38	0.02
	2.769	0.071	x	2.52	0.08
	2.858	0.008	y		
	3.387	0.004	y		
II	3.840	0.103	y		
	3.917	0.093	x		
	4.048	0.282	x	3.42	0.16
III	4.852	0.089	x	4.45	0.24
	4.871	0.024	y	4.54	0.18
	5.238	0.003	y		
IV	5.707	0.127	x		
	5.771	0.000	y		
	5.794	2.139	x	4.95	1.00
	5.888	0.006	x		
	6.196	0.003	y		

(b) Xanthene semiquinone

	E_{cal} (eV)	f_{cal}	Direction	E_{obs} (eV)	R. I.
I	2.894	0.015	x	2.13	0.02
	3.050	0.004	y		
	3.171	0.016	x		
	3.234	0.000	y		
II	3.911	0.065	x		
	3.935	0.061	x		
	4.137	0.808	x	3.61	0.67
III	4.789	0.022	x		
	4.869	0.020	y		
	5.203	0.029	y		
IV	6.017	0.372	x	4.95	1.00
	6.100	0.225	y		
	6.301	0.064	y		

(c) Phenazine semiquinone

	E_{cal} (eV)	f_{cal}	Direction	E_{obs} (eV)	R. I.
I	2.669	0.000	x		
	2.758	0.021	y	2.06	0.05
	2.961	0.002	x		
II	3.619	0.005	y		
	3.724	0.045	x		
	3.870	0.068	y		
	3.947	0.515	x	3.35	0.36
III	4.844	0.016	y		
	5.032	0.220	x		
	5.230	0.002	y		
IV	5.739	0.661	x	5.27	1.00
	5.797	0.753	x	5.46	
	6.058	0.000	y		
	6.115	0.262	x	(ethylphenazil[8])	

(d) Anthracene semiquinone

	13π model			15π model[a)]				
	E_{cal} (eV)	f_{cal}		E_{cal} (eV)	f_{cal}		E_{obs} (eV)	R. I.
I	2.723	0.00002	x	2.916	0.000	x		
	3.251	0.000	y	3.131	0.004	y		
	3.274	0.000	x	3.650	0.001	x		
II	3.643	0.000	y	4.221	0.006	y		
	3.869	0.016	x	3.870	0.241	x		
	3.930	0.087	y	3.973	0.349	y	3.26	0.01
	4.129	0.985	x	4.220	0.721	x	3.54	0.72
III	4.753	0.000	x					
	4.824	0.000	y					
	5.244	0.023	y					
IV	5.640	0.000	y					
	5.691	0.000	x					
	6.207	0.922	x				4.95	1.00
	6.251	0.004	x					
	6.337	0.019	y					

a) Including the effect of hyperconjugation.

(e) Acridine-*N* semiquinone

	13π model			15π model[b)]				
	E_{cal} (eV)	f_{cal}		E_{cal} (eV)	f_{cal}		E_{obs} (eV)	R. I.
I	2.538	0.126	x	2.654	0.136	x	2.19	0.17
	3.127	0.008	y	2.926	0.061	y		
	3.135	0.003	x	3.371	0.010	x		
II	3.731	0.005	y	4.127	0.081	y		
	4.068	0.026	x	4.124	0.244	x		
	4.126	0.086	y	4.366	0.292	y		
	4.286	0.870	x	4.504	0.629	x	3.52	1.00
III	4.776	0.021	x					
	4.940	0.009	y					
	5.471	0.010	y					
IV	5.770	0.001	y					
	5.782	0.001	x					
	6.161	0.190	x					
	6.225	0.070	y					

b) Including the effect of hyperconjugation.

NOTES.

1) The notations I, II, III, and IV in the tables, represent the groups of theoretical transition energies and differ from those appearing in the text.
2) In each group the observed bands are tentatively assigned to the theoretical bands whose f_{cal}'s are large.
3) R. I. denotes the relative intensity of observed band, the highest energy band being taken as a standard. It is easily estimated without precise molecular extinction coefficients.
4) As no data on phenazine semiquinone have been obtained for precise comparison, those on ethylphenazil are compared with theoretical results.
5) The transition with direction x is polarized along the long axis direction.

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[8] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

conjugation of methylene group into consideration. Here the 15π electron model was adopted for these semiquinones and the semi-empirical parameters used are the same as those reported by Morita.[9] This model treats the methylene group as a methylene cation. The real state of semiquinone molecule should be somewhere between these two models, which define the limits of delocalization of methylene electrons.

First the calculated orbital energies are compared with those of 13π electron models. The effect of hyperconjugation on transition energies appears on the orbitals, which have nothing to do with the observed electronic transitions. The difference of the orbital energies of the half-occupied orbitals in the 13π and 15π models is small (about 0.1 eV).

Calculated transition evergies and oscillator strengths are given in Table 3. The configurations included are 15 (cofigurations A and B) and the assignment of the 250 nm peak is omitted. The calculated intensity of the absorption polarized along the short axis direction is stronger in the 15π model. In the configurations of types A and B, calculated results are in better agreement with experimental ones in the 15π model than in the 13π model for both semiquinones. From the consideration of wave functions, it is concluded that the charge density of unpaired electron is lowered and more delocalized than that predicted by the 13π model. Although the larger conjugated systems, *i. e.* 15π model, have lower absorptions in general, it may be said that the unpaired electron and the electrons of methylene group are delocalized to some degree in anthracene and acridine-*N* semiquinones.

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[9] T. Morita, This Bulletin, **33**, 1486 (1960).