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Electronic Spectra of Phenanthrene Derivatives. Effect of Substitution

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During the course of studies on the spectral regularities of linear conjugated systems bearing aromatic terminal groups (*cf. Tetrahedron Lett.*, **1964**, 719; *ibid.*, **1968**, 1121; This Bulletin, **39**, 2320 (1966); *ibid.*, **40**, 340 (1967)), we found that the free electron model (FEM) cannot explain the effect of substitution on the electronic spectrum of phenanthrene. In order to get further information the electronic spectra of forty-eight phenanthrene derivatives each bearing a substituent at 2-, 3-, or 9-positions have been examined, and it was found that the electronic spectra of these derivatives also cannot be explained on the basis of FEM. SCF-MO-CI calculation has been carried out on phenanthrylpoly-ynes and hydroxyphenanthrenes revealing that the discrepancy between the observation and the expectation from FEM in the behavior of L_a and L_b of phenanthrene derivative is attributable to a complex configuration interaction.

It is well-known that the free electron model (FEM) proposed by Platt[1] gave a satisfactory explanation for the electronic spectra of polycyclic aromatic compounds. In the case of linear polyacenes, it was concluded on the basis of FEM treatment that the polarizations along the short axis (y-axis) were responsible for the B_a and L_a bands, and the transitions associated with L_b and B_b bands were considered to be polarized in the direction of the long axis (x-axis) (Fig. 1).

Empirical assignment of polarization on the basis of the substituent effect,[2] the result of the measurement of polarized spectrum of crystal[3] and the conclusion of MO calculation were found to be consistent with the FEM assignment.

For the electronic spectrum of phenanthrene, the first member of phene series, Platt assigned[1] long

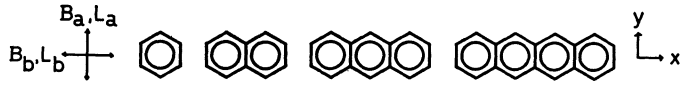

Fig. 1. Polarization diagram of linear-polyacenes on the basis of FEM.

1) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949); J. R. Platt, *ibid.*, **17**, 489 (1949).

2) *E.g.*, for anthracene derivatives, see, R. N. Jones, *Chem. Rev.*, **32**, 1 (1943).

3) D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, **1955**, 539.

axis polarized transitions to L_a and B_b species, and short axis polarized transitions to L_b and C_b species. However, the strong transition, called B_b by Platt[1] was relabeled B_a by Ham and Ruedenberg.[4]

Since SCFMO calculation[5] was consistent with that of Ham and Ruedenberg, the state assignment indicated in Fig. 2 was employed in this paper. Little experimental verification of the assignment has been done, probably owing to the lack of spectral data on phenanthrene derivatives.

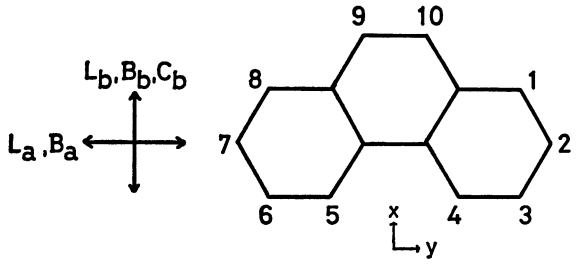

Fig. 2. Polarization diagram of phenanthrene.

During the course of studies on the regularities of the electronic spectra of diarylpoly-ynes,[6] we noticed that the behavior of L_a and L_b bands in the spectra of substituted phenanthrenes could not be explained simply on the basis of FEM. It was desirable to get further spectral data on monosubstituted phenanthrene derivatives to solve the interesting problem. Several monosubstituted derivatives bearing a substituent at 2-, 3-, or 9-positions have been prepared.[7] It was anticipated that the substituent may exert a distinctly different effect on the electronic spectrum at these three positions. The electronic spectra of the 37 phenanthrene derivatives we prepared, together with those of the reported ones (11 compounds), were examined with respect to the nature and position of the substituent, and were compared with the expected effect from FEM consideration. The 48 compounds are given in Fig. 11.

Electronic Spectra[8]

The absorption bands of phenanthrene have been assigned to be L_b, L_a, B_a, and C_b in the sequence of diminishing wavelength.[4,5] From the standpoint of FEM, it was anticipated that a substitution at 2-position of phenanthrene may exert a more marked effect on the B_a and L_a bands than does a substitution at the 3- or 9-position, and C_b and L_b bands should be affected more strongly by a substitution at 3- or 9-position than that at 2-position.

A brief summary of the substituent effect observed in some of the substituted phenanthrenes is given in the following.

Methyl and Hydroxymethylphenanthrenes [R-CH_3 *and* R-CH_2OH] *(R=phenanthryl).* An essestial difference between the electronic spectra of phenanthrene and of methylphenanthrenes could not be observed.[9] As illustrated in Fig. 3, similar spectra have been obtained in hydroxymethylphenanthrenes. The difference of position of substitution gave no appreciable change in the electronic spectra, indicating the lack of electronic interaction between these substituents and the nucleus.

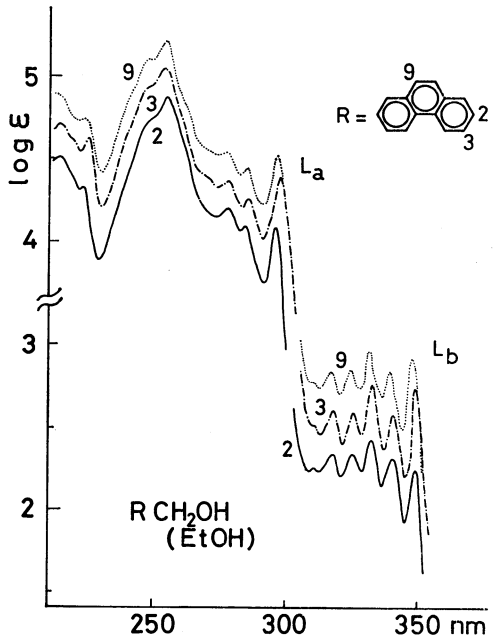

Fig. 3. The absorption curves of hydroxymethylphenanthrenes. The curves, with the exception of 2-substituted compound at the bottom, have been displaced upward on the ordinate axis by 0.1 log ε unit increments from the curve immediately below.

Acetylphenanthrenes [$RCOCH_3$] *and Formylphenanthrenes* [RCHO]. The absorption curves of the methylketones and the aldehydes are given in Figs. 4 and 5. The spectra of 2-isomers show close resemblance to that of phenanthrene itself, while the 3- and 9-isomers exhibit similar absorption curves which differ from that of the 2-isomer. The large red-shift of B_a band of 2-isomers as compared with 3- and 9-isomers is in line with the expectation from FEM. In the case of 3- and 9-isomers, the C_b bands seem to submerge under the B_a bands resulting in broad absorption bands around 250 nm. The large red shift of C_b band of 3- or 9-isomer is also in line with FEM anticipation. On the other hand, contrary to expectation from FEM consideration, the largest blue-shift of L_a band of the

4) N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, **25**, 13 (1956).

5) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965).

6) S. Akiyama and M. Nakagawa, *Tetrahedron Lett.*, **1964**, 719; K. Nishimoto, R. Fujishiro, S. Akiyama, and M. Nakagawa, This Bulletin, **39**, 2320 (1966); S. Akiyama and M. Nakagawa, *ibid.*, **40**, 340 (1967); S. Akiyama, K. Nakasuji, K. Akashi, and M. Nakagawa, *Tetrahedron Lett.*, **1968**, 1121.

7) The synthesis of these substituted phenanthrenes will be reported in the near future as Part V of "Linear Conjugated Systems bearing Aromatic Terminal Groups."

8) The electronic spectra were obtained on a Hitachi EPS-3T spectrophotometer at room temperature using a well-matched pair of 1 cm quartz cell.

9) Reliable spectra of 3- and 9-methyl derivatives were reported in "UV Atlas of Organic Compounds," Vol. III, Butterworths, London and Verlag Chemie, Weinheim (1967). The 2-isomer has been prepared by us.

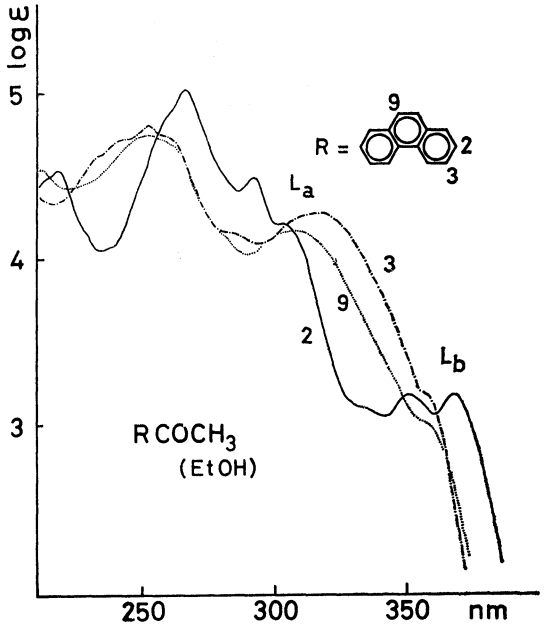

Fig. 4. The absorption curves of acetylphenanthrenes.

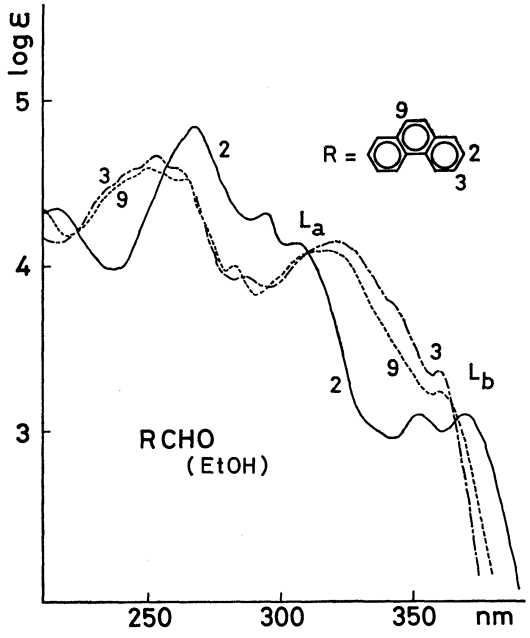

Fig. 5. The absorption curves of formylphenanthrenes.

2-isomer was observed, and the L_b band showed the largest red-shift in the case of 2-isomer.

Ethynylphenanthrenes [R–C≡CH]. The electronic spectrum of 2-ethynylphenanthrenes was found to be closely related with that of phenanthrene (Fig. 6). 3- and 9-Isomers exhibited C_b bands (230—240 nm) at longer wavelength than 2-isomer (200 nm), and the B_a band of 2-isomer showed a bathochromic shift accompanied with appreciable hyperchromism as compared with B_a bands of 3- and 9-isomers. The spectral change caused by the change of position of substitution is consistent with FEM anticipation. However, though the L_a bands of 3- and 9-isomers showed an appreciable red-shift as compared with that of phenanthrens, no shift of the L_a band was observed in 2-isomer. With regard to the L_b band, the 2-isomer

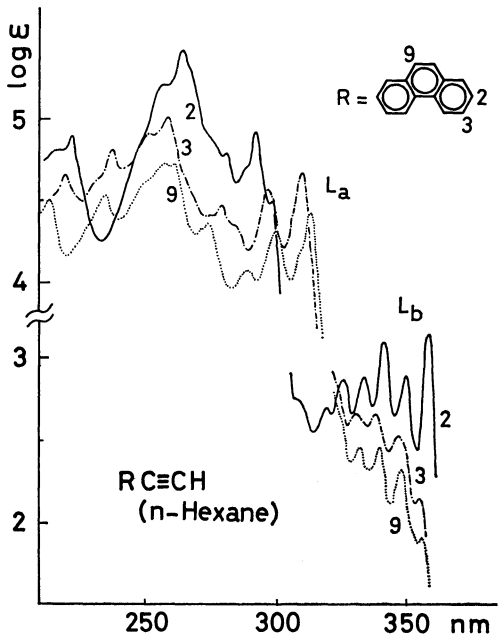

Fig. 6. The absorption curves of ethynylphenanthrenes. The curves, with the exception of 9-substituted compound at the bottom, have been displaced upward on the ordinate axis by 0.2 log ε unit increments from the curve immediately below.

absorbed at the longest wavelength. Thus behavior of L_a and L_b bands are inconsistent with FEM argument.

Diphenanthrylpoly-ynes [R(C≡C)$_n$R]. As illustrated in Fig. 7, 2,2′-diphenanthrylacetylene (n=1) exhibited a characteristic absorption curve owing to the marked red-shift of the B_a band. The broad band observed at around 250 nm in the spectra of the 3- and 9-isomers seem to be the composite of B_a and submerged C_b bands. The increasing red-shift of L_a band in the sequence of 2-, 3-, and 9-isomers is in contrast with the expectation from FEM. The trend observed in the spectra of diphenanthrylacetylenes was also observed in the spectra of di- (n=2), tri- (n=3) and pentaacetylenes (n=5) (Figs. 8, 9, and 10). The regular bathochromic shift of L_a band in line with the increasing number of n is impressive (*cf.*, Fig. 11).

From the results, it is evident that the behavior of C_b and B_a bands is in line with FEM anticipation. However, the spectral shifts of L_a and L_b bands were found to be inconsistent. The effect of substitution

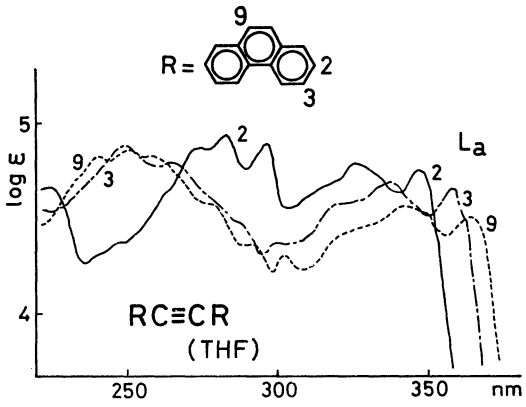

Fig. 7. The absorption curves of diphenanthrylacetylenes.

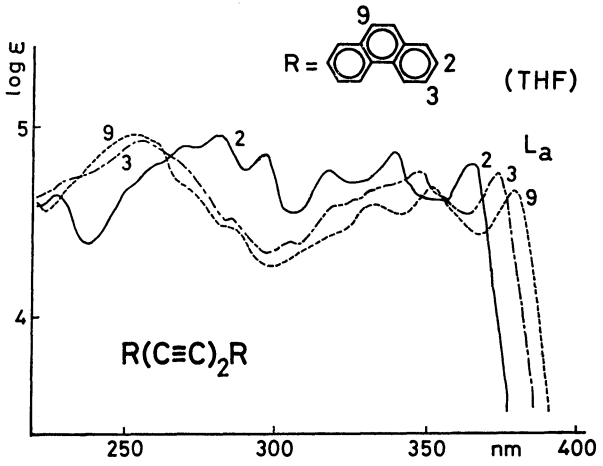

Fig. 8. The absorption curves of diphenanthryldiynes.

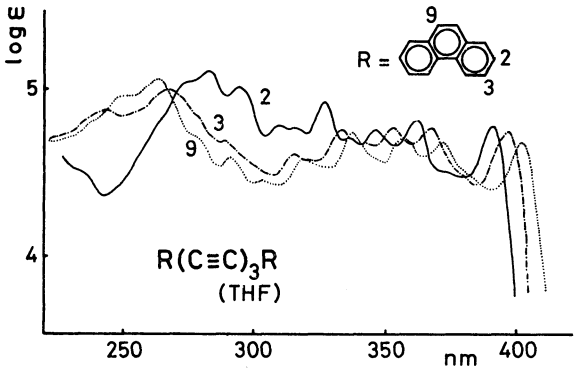

Fig. 9. The absorption curves of diphenanthryltriynes.

on the shifts of L_a and L_b bands is summarized in Fig. 11. When a bulky group such as $NHCOCH_3$, $COCH_3$, or CHO is introduced to the 9-position of phenanthrene nucleus, it should interfere sterically with the hydrogen atom at the 8-position. This seems to be responsible for the observed small red-shift and the hypochromism of the L_a band of phenanthrene bearing a large group at 9-position. The increasing red-shift of L_a band in phenanthryl mono-, di-, and tri-acetylenes [$\mathbf{R(C{\equiv}C)_nH}$, $n=1,2$, and 3] in the sequence of 2-<3-<9-isomers seems to support the above argument, as the linear substituents should suffer minor steric interference from the hydrogen at 8-position.

The Results of Semi-Empirical SCF-MO-Cl Calculation

The apparent contradiction between the observed spectral behavior of substituted phenanthrenes and the expected spectral change from the FEM of substituted phenanthrenes prompted us to elucidate this problem theoretically. In previous papers,[10] it was concluded theoretically that a linear polyacene having a substituent at α-position, such as α-naphthol, should exhibit an electronic spectrum having practically the same band characteristics as those of the parent hydrocarbon. On the other hand, in the electronic spectrum of a β-substituted linear polyacene, such as β-naphthol, a considerable mixing of the L_a and L_b species should occur modifying the band characteristics of the parent hydrocarbon. In the case of β-naphthol, the longest-wavelength absorption band should be the L_b band containing about 30% of L_a component.

Phenanthrene can be regarded as benznaphthalene. Consequently, the 9-position in phenanthrene is either an α- or a β-position of the naphthalene nucleus. Thus a more complicated spectral change by introduction of a substituent in the nucleus of phene-series is expected as compared with that of acene-series.

We have calculated the electronic structures of phenanthrene, 2-, 3-, and 9-phenanthrylpoly-ynes, and 2-, 3-, and 9-hydroxyphenanthrenes by a semi-empirical SCF-MO-CI method based on π-electron approximation and variable β approximation.[3] Two-centre electron repulsion integrals were calculated by the method proposed previously by one of us (K. N.).[11] As shown by Hinze and Jaffé,[12] the valence state ionization potential (I) and the electron affinity (A) associated with carbon atom are almost independent of hybridization. The same values of I and A were used for all carbon atoms in this paper. The parameters are summarized in Table 1. In the vari-

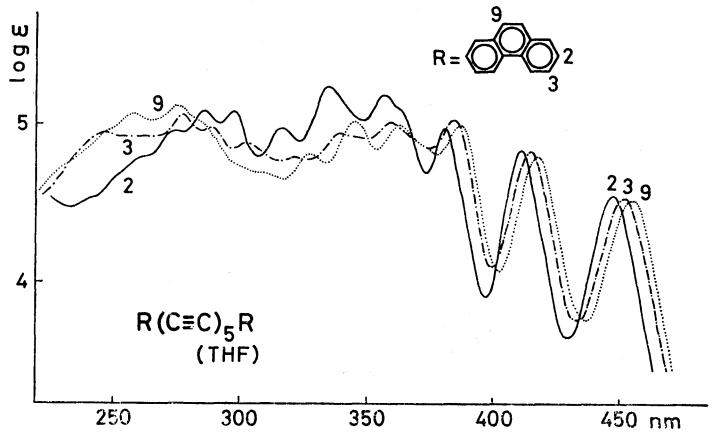

Fig. 10. The absorption curves of diphenanthrylpentaynes.

10) K. Nishimoto, *J. Phys. Chem.*, **67**, 1443 (1963); K. Nishimoto and R. Fujishiro, This Bulletin, **37**, 1660 (1964).

11) K. Nishimoto, *Theor. Chim. Acta*, **5**, 74 (1966).

12) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

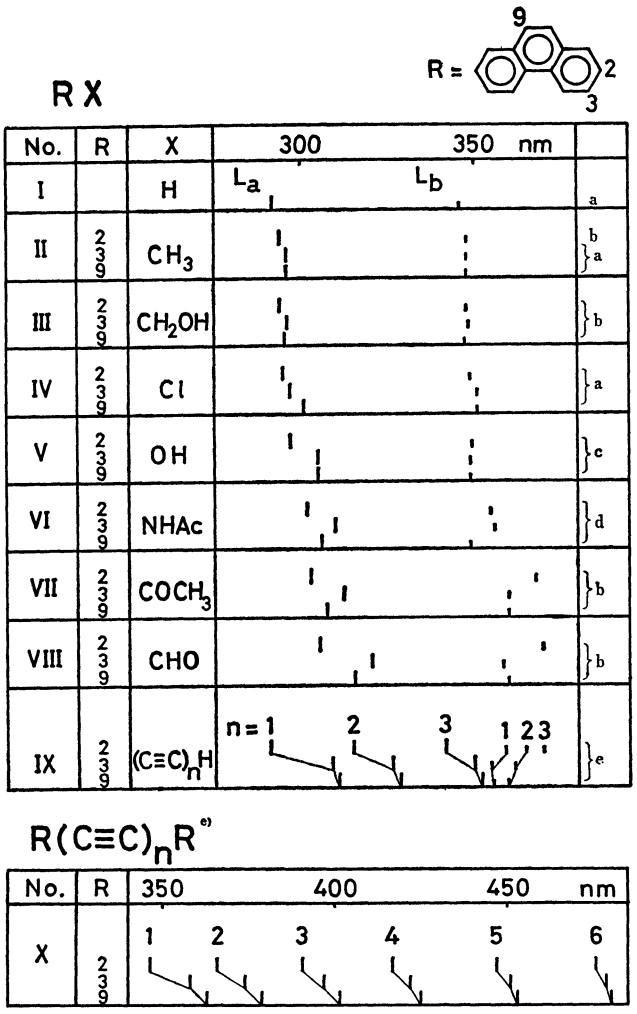

Fig. 11. Solvent: I and IX: hexane; II, III, V, VI, VII, and VIII: ethanol; IV: light petroleum (bp 100—120°C); X: tetrahydrofuran.
a) "UV Atlas of Organic Compounds," Vol. III, Butterworths, London and Verlag Chemie, Weinheim (1967). b) measured by the present authors. c) Table 2, Ref. d. d) "Absorption Spectra in the Ultraviolet and Visible Region," Vol. I, ed. by L. Lang, Publishing House of the Hungarian Academy of Sciences, Budapest (1961), pp. 213, 217, and 221. e) synthesized and measured by the present authors.

Table 1. Parameters

	I (eV)	A (eV)
C^+	6.60	0.00
C^{2+}	30.88	10.85

$\beta_{C-C}=\beta_{C=C}=\beta_{C\equiv C}=-0.51p-1.84$ eV
$\beta_{C-O}=-0.56p-2.20$ eV

able β approximation, a conventional geometry is assumed in which all the bond lengths are set at 1.40 Å.[13] The transition energies have been computed after including approximately the same amount of configuration interaction as involved for phenanthrene.[13] Singly excited configurations up to 3.0 eV from the lowest excited configuration are included in the calculation. The calculated transition energies and intensities are summarized together with experimental data in Table 2. A satisfactory agreement between the calculated results and experimental data was obtained affording theoretical basis to the observed bathochromic shift of L_a band in the 2-, 3-, and 9-substituted phenanthrenes (2-<3-<9-) and that of L_b band (9-<3-<2-).

It is interesting to note that the B_a and B_b species of phenanthrene are approximately degenerated (*i.e.*, $\Delta E(B_a)=4.91$ eV, $\Delta E(B_b)=5.00$ eV). However, B_a should be very intense ($f(B_a)=1.260$; $f(B_b)=0.425$). According to the present calculation, the absorption band at around 250 nm region of phenanthrene is associated with the long-axis (y-axis) polarized transition. The result is in line with the assignment by Ham and Ruedenberg.[4]

For phenanthrene, there are as usual two non-mixing pairs of states. As the calculation indicates, the *b* states arising from the paired excitation $\psi_7\rightarrow\psi_9$ and $\psi_6\rightarrow\psi_8$ are associated with the short-axis polarized transitions, and the *a* states which arise from $\psi_7\rightarrow\psi_8$ and $\psi_6\rightarrow\psi_9$ are related with the long-axis polarized transitions. In the case of phenanthrene derivatives, because of the complete loss of molecular symmetry, all the singly excited configurations usually interact with each other. However, by means of the criteria we obtained,[10] we can assign the state levels as shown in Table 3.

Table 2. Transition energies (eV) and intensities of phenanthrene and its derivatives

Molecule	Transition energy: Singlet Calcd	Singlet Obsd	Triplet Calcd	Triplet Obsd	Oscillator strength Calcd	Oscillator strength Obsd	Polarization[a] Calcd	Polarization[a] Obsd
Phenanthrene	3.58	3.75[b]	2.57	2.68[c]	0	0.003[b]	x	x[b]
	4.27	4.23[b]			0.459	0.18[b]	y	y[b]
	4.91	4.91[b]			1.260	1.09[b]	y	y[b]
	5.00				0.425		x	
	5.32				0.435			
2-Ethynylphenanthrene	3.53	3.45	2.63		0			
	4.24	4.26			0.514		1°	
	4.36	4.70			1.700		175°	
	4.89				0.650		72°	
	5.24				0.225		94°	

13) K. Nishimoto, *Theor. Chim. Acta*, **7**, 207 (1967).

TABLE 2 continued

Molecule	Transition energy				Oscillator strength		Polarization[a]	
	Singlet		Triplet					
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
3-Ethynylphenanthrene	3.57	3.49	2.53		0			
	4.04	4.01			0.856		161°	
	4.75	4.80			0.822		154°	
	4.97				0.544		106°	
	5.07				1.106		52°	
9-Ethynylphenanthrene	3.67	3.49	2.37		0			
	3.99	3.98			0.688		153°	
	4.75	4.77			1.030		78°	
	4.82				0.778		177°	
	4.99				0.348		4°	
2-Butadiynylphenanthrene	3.65	3.40	2.72		0			
	4.03	3.94			2.125		176°	
	4.30				0.097		8°	
	4.82				0.653		81°	
	5.24				0.148		17°	
3-Butadiynylphenanthrene	3.73	3.42	2.43		0			
	3.86	3.80			1.283		147°	
	4.48				0.496		110°	
	4.96				1.041		55°	
	5.12				0.618		9°	
9-Butadiynylphenanthrene	3.67	3.44	2.45		0			
	3.75	3.77			1.148		137°	
	4.47				0.732		85°	
	4.76				0.884		18°	
	5.02				0.417		163°	
2-Hexatriynylphenanthrene	3.64		2.49		0			
	3.73	3.62			2.253		177°	
	4.33				0.204		7°	
	4.75				0.586		91°	
	5.01				0.239		19°	
3-Hexatriynylphenanthrene	3.55	3.54	2.29		1.970		136°	
	3.73				0			
	4.32				0.354		82°	
	4.88				0.881		50°	
	5.09				0.589		172°	
9-Hexatriynylphenanthrene	3.54	3.52	2.41		1.624		132°	
	3.68				0			
	4.34				0.534		75°	
	4.74				0.816		23°	
	5.01				0.601		160°	
2-Hydroxyphenanthrene	3.51	3.37[d]	2.58		0.015		101°	
	4.26	4.25[d]			0.296		1°	
	4.71	4.86[d]			1.445		176°	
	4.95				0.507		68°	
	5.28				0.316		101°	
3-Hydroxyphenanthrene	3.52	3.41[d]	2.54		0.018		21°	
	4.13	4.06[d]			0.536		174°	
	4.91	5.00[d]			1.120		3°	
	4.96				0.330		115°	
	5.20				0.629		84°	
9-Hydroxyphenanthrene	3.56	3.39[d]	2.75		0.026		32°	
	4.09	4.06[d]			0.456		169°	
	4.84	5.00[d]			0.851		23°	
	4.89				0.462		157°	
	5.10				0.389		116°	

a) The numerical value gives the angle between the transition moment vector and y-axis of the molecule.
b) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
c) D. S. McClure, *ibid.*, **17**, 905 (1949).
d) C. Djerassi, H. Bendes, and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955).

TABLE 3. THE COEFFICIENTS OF LOWEST SINGLY EXCITED CONFIGURATIONS IN THE LOWEST EXCITED STATES OF PHENANTHRENE AND ITS DERIVATIVES

State	Coefficients of						Classification
	$\chi_{m\to m+1}$	$\chi_{m-1\to m+2}$	$\chi_{m\to m+2}$	$\chi_{m-1\to m+1}$	$\chi_{m\to m+3}$	$\chi_{m-2\to m+1}$	
				Phenanthrene			
1	0	0	0.6755	0.6755	−0.0768	0.0768	L_b
2	0.9482	−0.2710	0	0	0	0	L_a
3	0.2442	0.9532	0	0	0	0	B_a
4	0	0	−0.6036	0.6036	−0.3151	−0.3151	B_b
5	0	0	−0.3472	0.3472	0.5303	0.5303	C
				2-Hydroxyphenanthrene			
1	0.5303	0.4405	−0.3858	0.5335	−0.1156	−0.0287	L_a+L_b
2	0.6484	0.2483	0.2582	−0.6437	0.0959	0.0325	
3	−0.2038	0.5361	0.6873	0.2777	0.0016	0.1366	B_a+B_b
4	−0.4133	0.6157	−0.2994	−0.3441	0.0491	−0.2661	
5	−0.1835	0.1645	−0.2651	−0.2289	−0.4220	0.5286	C
				3-Hydroxyphenanthrene			
1	0.1757	0.0797	0.7194	−0.6038	0.0512	0.0434	L_b
2	0.9437	0.2138	−0.1368	0.1377	−0.0202	0.0106	L_a
3	−0.1925	0.9197	−0.1215	−0.0879	0.1001	−0.1023	B_a
4	−0.0696	0.2417	0.4796	0.5579	−0.3772	0.3376	B_b
5	0.0108	−0.0251	0.3963	0.4489	0.4295	−0.5394	C
				9-Hydroxyphenanthrene			
1	0.2527	0.1128	0.7051	−0.5876	−0.0949	0.0524	L_b
2	0.9213	0.2123	−0.2397	0.1437	0.0431	−0.0302	L_a
3	−0.1831	0.6469	−0.4172	−0.3725	−0.1712	−0.0854	B_a+B_b
4	−0.1224	0.6358	0.3188	0.4075	0.4696	0.0346	
5	−0.0051	−0.2499	−0.2487	−0.3488	0.7610	−0.111	C
				2-Ethynylphenanthrene			
1	0	0	−0.6679	0.6679	−0.0475	−0.0475	L_b
2	0.9196	0.2402	−0.1209	−0.1209	−0.0620	0.0620	L_a
3	−0.1234	0.8835	0.2692	0.2692	−0.0153	0.0153	B_a
4	0.2494	−0.3357	0.5783	0.5783	0.1568	−0.1568	B_b
5	−0.0808	0.0857	−0.2417	−0.2417	0.3617	−0.3617	—
				3-Ethynylphenanthrene			
1	0	0	−0.6835	0.6835	−0.0446	−0.0446	L_b
2	0.9737	0.1339	0.0062	0.0062	−0.0185	0.0185	L_a
3	−0.0697	0.7975	−0.0113	−0.0113	0.3889	−0.3889	B_a
4	−0.0420	0.2902	0.5583	0.5583	−0.2856	0.2856	B_b
5	0.0575	−0.4224	0.4057	0.4057	0.4329	−0.4329	—
				9-Ethynylphenanthene			
1	0	0	0.6850	0.6850	0.0907	0.0907	L_b
2	0.9710	−0.1813	−0.0237	0.0237	−0.0431	0.0431	L_a
3	0.0160	−0.1779	0.6257	−0.6257	0.1959	−0.1959	B_b
4	0.1180	0.8035	0.2395	−0.2395	−0.2933	0.2933	B_a
5	0.1160	0.4753	−0.1007	0.1007	0.5669	−0.5669	C

The following conclusions can be deduced from Table 3.

1) The nature of the excited states of phenanthrene derivatives is considerably dependent on the type of substituent.

2) The effect of substituent on the mixing of configurations at the lower excited states is found to be the largest at 2-position and rather small at 3- and 9-positions.

3) The L_a species of phenanthrene is considerably shifted by the substitution at 3- and 9-positions. Since it was indicated that a rather large interaction between L_a and L_b species should be produced by the substitution at 2-position, very much shifts of the L_a species in 2-substituted derivatives are expected. In fact as indicated in Fig. 11, a small change of L_a band of

phenanthrene by substitution at the 2-position was observed [*e.g.*, phenanthrene: 292 nm (in *n*-hexane); 2-ethynylphenanthrene: 291 nm (in *n*-hexane); 2-hydroxyphenanthrene: 292 nm (in ethyl alcohol)].

This suggests that 3- and 9-positions should resemble the α-position in linear polyacenes, while the 2-position would be similar to the β-position in polyacenes.

The intensities of L_b species of phenanthrylpoly-ynes are calculated to be zero. However, if we use different valence state ionization potentials for different hybridization, we will have non-zero, but very small intensities.

The calculation reveals that the discrepancy between the observation and the expectation from FEM

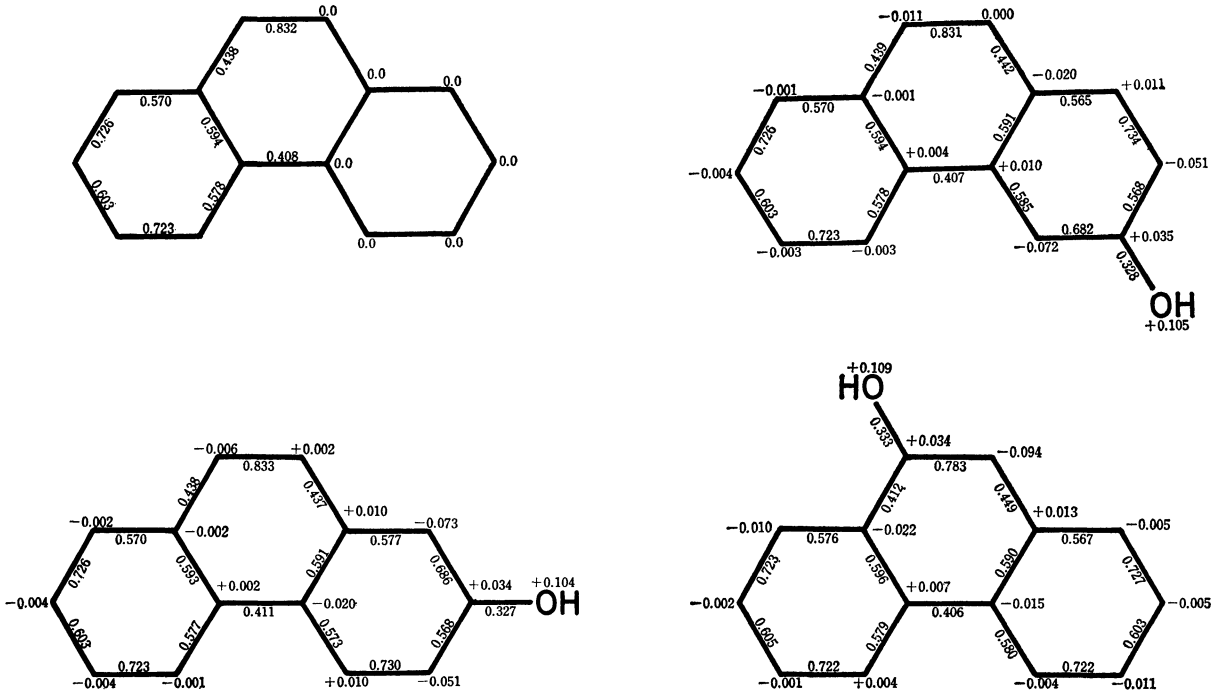

Fig. 12. Molecular diagrams of phenanthrene and its hydroxy derivatives in the ground states.

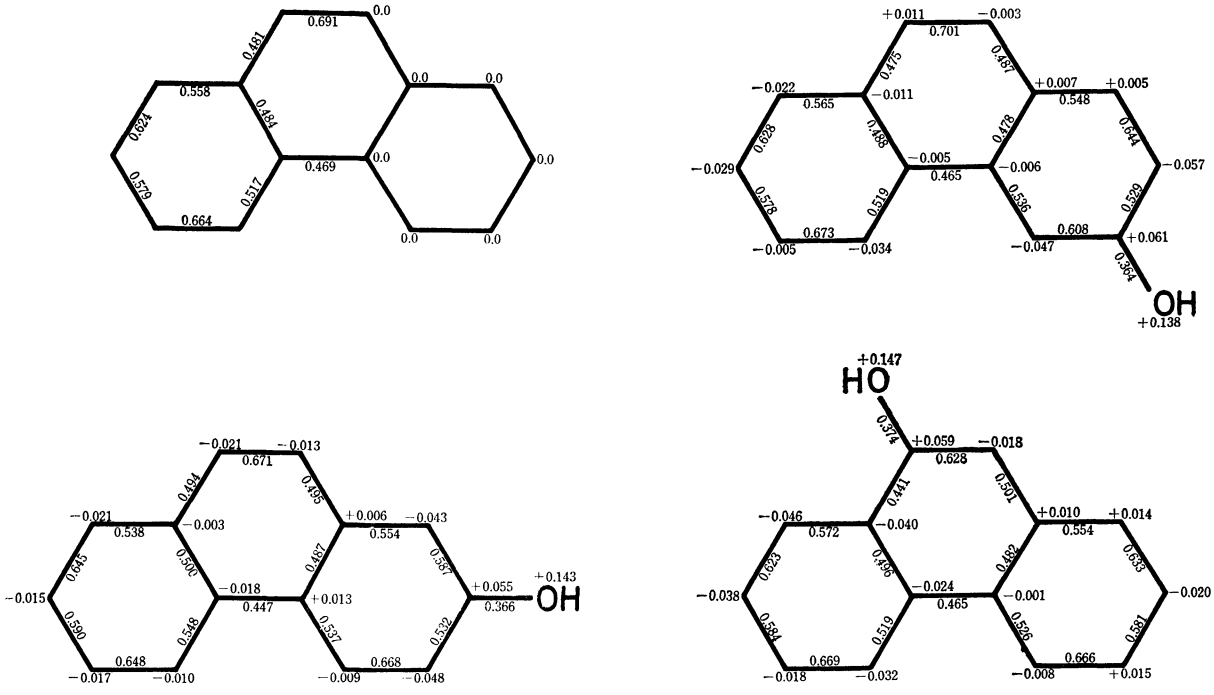

Fig. 13. Molecular diagrams of phenanthrene and its hydroxy derivatives in the lowest exited singlet states.

on the behavior of L_a and L_b species of phenanthrene derivatives should be attributed to a complex configuration interaction. It should be noted that the FEM treatment should be carefully applied to phene-series, especially in the case of qualitative argument of substituent effect on the electronic spectra of phene-series.

Appendix

Appendix 1. Changes of the molecular properties of hydroxyphenanthrenes by excitation.

The molecular diagrams of phenanthrene and its hydroxy derivatives are given in Figs. 12 and 13. The molecular properties, expected by the present SCF-MO calculation are summarized as follows:

Molecular Geometry: As indicated by the molecular diagram (Fig. 12), the molecule will expand and take a round shape in the excited state. The marked change of the bond order at 9—10 position is noteworthy.

Reactivity: In the ground state, the nucleus bearing hydroxy group will be most reactive. However, in the excited state, the 1-, 3-, 8-, and 9-positions in 2-hydroxy derivative, the 2-, 4-, 5- and 7-positions in 3-hydroxy isomer and 5-, 7-, and 8-positions in 9-hydroxy derivative are expected to be reactive.

pK_a: The molecular diagrams indicate that the acidity (pK_a) of the hydroxy derivatives will be as follows:

Ground state: $2 \approx 3 > 9$

Excited state: $3 > 2 > 9$

The change of charge density in hydroxy derivatives on excitation is found to be fairly large. On the other hand, no change of charge density is found in the phenanthryl-poly-ynes on excitation.

Appendix 2. Calculated ionization potentials and electron affinity of phenanthrene and its derivatives (eV).

Molecule	I	A
Phenanthrene	8.14	1.46
2-Hydroxyphenanthrene	8.01	1.35
3-Hydroxyphenanthrene	7.78	1.28
9-Hydroxyphenanthrene	7.71	1.21
2-Ethynylphenanthrene	8.14	1.46
3-Ethynylphenanthrene	7.98	1.63
9-Ethynylphenanthrene	7.91	1.69
2-Butadiynylphenanthrene	7.99	1.61
3-Butadiynylphenanthrene	7.83	1.77
9-Butadiynylphenanthrene	7.74	1.86
2-Hexatriynylphenanthrene	7.80	1.80
3-Hexatriynylphenanthrene	7.70	1.90
9-Hexatriynylphenanthrene	7.62	1.98