The Interpretation of Absorption Spectra of Condensed Polycyclic Aromatic Hydrocarbons by Using a Simple Resonance Theory. I. The Resonance Structure of the Excited State in Correlation with Platt's Theory

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Many theoretical investigations have been made for the purpose of interpreting the absorption spectra of condensed polycyclic aromatic hydrocarbons by such hypotheses as the valence-bond, molecular orbital, and free-electron theories. It is very difficult, however, to understand intuitively the chemical meanings of the upper-state.

With this in mind, the present author has undertaken to learn whether the transition energies of these molecules may be directly related to the differences in empirical resonance energy between the ground and excited states of these molecules. In this case, it is assumed that a chemical resonance structure corresponds to the defined excited state proposed and classified by Platt[1,2].

The estimation of these differences in empirical resonance energy have been carried out by applying Carter's empirical equation to the excited state. We have examined what types of chemical resonance structure correspond to the individual excited states.

The Introduction of the Approximation Formula. — The light-absorption energies of substances can be expressed generally as follows;

$$E_2 - E_1 = \bar{\nu} \qquad (1)$$

where E_2 and E_1 are the total energies of the excited and ground states respectively. These energies, E_2 and E_1, which are caused by the mobile π-electrons in the case of polycyclic aromatic hydrocarbons, can be divided into two pats : bonding-energy (H°) and resonance energy (R), where R means the empirical resonance energy which is the sum of calculated resonance energy and the compression energy. Thus, Eq. 1 can be rewritten into Eq. 2:

$$\bar{\nu} = (H^\circ_{\mathrm{E}} - H^\circ_{\mathrm{G}}) - (R_{\mathrm{E}} - R_{\mathrm{G}}) \qquad (2)$$

where the term $(H^\circ_{\mathrm{E}} - H^\circ_{\mathrm{G}})$ may be understood to correspond to the light-polarization energies between two polarized carbon atoms on the periphery of the molecule without resonance and to be approximately constant for this series of molecules.

It is assumed that, for the estimation of resonance energies in the excited state, Carter's empirical equation, which is consolidated for the estimation of those in the ground state, can be applied, except for the constant term:

$$R = -20 + 12\,D + 69\log N \quad \text{(kcal./mol.)} \qquad (3)$$

where D is the number of double bonds and N is that of the canonical Kekulé resonance structures in this state. Therefore, Eq. 2 can be rewritten into Eq. 4:

$$\bar{\nu} = A - 69\log(N^*/N) \quad \text{(kcal./mol.)} \qquad (4)$$

where A is constant and N^* is the number of canonical Kekulé resonance structures of the residual parts of the structure of the molecule defined as an excited state and N is that of a ground state.

An excited state of a molecule in this series may be chemically represented by the resonance among a specified group of an N^* number of elementary polarized-resonance, structures with the same weights, and their symmetrical character probably can not be reduced to a particular, designative symmetry-group. Therefore, it is considered that they include imaginary unit polarizations which cancel each other out finally, in contrast to the irreducible representation which characterizes the discriminative state in other representations. Hence, we must correlate, in some way, the above method of the representation of an excited state with the theoretical method, which pictures a characteristic excited state with a universal designation over all the molecules of this series, irrespective of the different symmetry-characters of their configuration of π-orbitals or electrons, with a few exceptions.

Platt has already classified and assigned the absorption spectra of acenes and phenes into the L_a-, L_b-, B_a-, B_b-, C_a- and C_b-types of polarization by using his free-electron orbital method.

The chemical resonance structures of polycyclic acenes and phenes corresponding to a

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[1] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

[2] J. R. Platt, ibid., **17**, 484 (1949).

given type of polarization, such as ^1L_a, ^3L_a, ^1L_b, ^3L_b, ^1B_a, ^1B_b, ^1C_a and ^1C_b, are expressed and their numbers of resonance structures (N^*) are estimated in the following section.

As a conclusion, the correctness of the preceding expression of an excited state by resonance structures corresponding to a given type of polarization according to Platt's idea, is judged by plotting $\log(N^*/N)$ versus $\bar{\nu}$ assigned as corresponding to that state, thus determining whether the linear relation prescribed in Eq. 4 is held, and by examining the direction of the resulting electric moment, which is the sum of the elementary moments of each contributing resonance structures, or by examining the oscillator strength due to these structures, as compared to the empirical ones.

Classification of Resonance Structures in Correlation with Platt's Model. — Platt has postulated a convenient diagram for determining the polarizations of transitions from the ground state. The distinctive feature in his theory exists in that he replaces the sign of a free-electron standing-wave to that of a point-charge to picture the transition from the ground state. The polarization of the transition from the ground state will be the same as if we locate + and − point charges at alternate anti-nodes, shrink the perimeter back to its normal shape, and determine the direction of the resulting electric moment. Although it should be emphasized that such a polarization diagram is a device for visualization and not a classical model, it is a very convenient modeling for our purpose in that it pictures an excited state by the resonance of a given type of polarized chemical structures.

For example, the polarization diagrams of each level are illustrated in Fig. 1* for anthracene. The orbital ring quantum number (q) is equal to the ring number (n) in the cata-condensed series, where the number of π-electrons is $2(2n+1)$. Therefore, the total momentum number, Q, is equal to 1 for the B-state and $(2n+1)$ for the L-state.

On the basis of the above considerations, we set resonance structures of a given type of polarization corresponding in our sense to the above polarization diagram of a respective excited state in Platt's sense, as we locate + and − charges along the periphery of the molecule according to the law of alternating polarity. However, the respective transitions from the ground state have been assigned to a simple designation based on the molecular orbital method in the simple and lower molecules. Therefore, it is considered that the above representation of an excited state includes imaginary unit polarizations which cancel each other out finally, in addition to the real representation of an excited state by unit polarizations.

If we separate charges at the cross-linking atoms into $(1-ai)$ and ai in order to eliminate the effect of the cross-linking as we estimate the energy of the ^1L_a and ^3L_a transitions in the following section, and if we select the specified group of polarized structures corresponding to an adequate group designation, the sum of the number of polarized resonance structures of an excited state in this method of computation might be suggested as satisfying Carter's equation in plotting $\log(N^*/N)$ versus the $\bar{\nu}$ value assigned to that excited state.

A Modification of Platt's Idea.—In order to eliminate the effect of cross-linking carbon atoms for the computation of the weights of the resonance structures for the L-state, we will make a little modification of Platt's idea. We will introduce an imaginary point charge vector i to the cross-linking carbon atoms in the ground state in order to divide the corresponding charge-density 1 to $(1-\alpha i)$ and αi; thereby we can divide one cross-linking carbon atom into two imaginary ones with charge-densities of $(1-\alpha i)$ and αi.

It is assumed that that electric current resulting from the motion of the π-electron is not circular on one plane, moving in one direction along the periphery of the molecule, but that it passes through a twisted path imagined to consist of each constituent benzene nuclei as a loop via an imaginary ethylene-linkage formed by cross-linking carbon atoms with the imaginary charges $(1-\alpha i)$ and αi in one direction. In this model, the angular momenta of the π-electrons of each benzene nucleus are not perpendicular to the imaginary twisted orbital plane, but they become parallel as we draw the imaginary atom A with the imaginary charge of αi near to another imaginary atom, A′, with the imaginary charge of $(1-\alpha i)$. The imaginary distance between them may be considered to determine the degree of condensation of the two nuclei. The quantity of the angular momenta is defined as qh where q is the orbital quantum number and the energy is given by q and 1, as in Eq. 5. It is considered that the sum of the orbital ring quantum numbers, q_1 and q_2 of each imaginary twisted path is invariant to the original q, while the sum of each bond-length of the perimeter is increased by an i in an imaginary unit. It is considered in this case that the imaginary bond-length in carbon-atoms is defined as the mean distance multiplied by

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* This polarization diagram is just the same as that shown in the paer of Platt. However, for convenience of explanation it is re-illustrated in this paper.

two charge densities at both ends.

When we switch two of the four imaginary atoms, αi, $(1-\alpha i)$, αi, and $(1-\alpha i)$, the imaginary increase in the perimeter-length by imaginary cross-linking ethylene-linkage is equal to $2\alpha i(1-\alpha i)$ and the imaginary decrease in the bonds among cross-linking carbon atoms and their neighbors is 2 for naphthalene. Therefore, each cross-linking ethylene increases $2\alpha i+2(\alpha^2-1)$ in perimeter-length for acenes. The estimated real length of this imaginary path is determined to be $\sqrt{10^2+2^2}$ by vector-synthesis in the case where α is equal to 1 for the naphthalene molecule. For the phenanthrene molecule, it is proposed that the following operations shall be made as illustrated in Fig. 2. We separate each cross-linking carbon atom in the f-position into two imaginary ones with a charge vector of βi on f and $(1-\beta i)$ on f'; then we rotate the i, h, g, and f' atoms upside down to the molecular plane with the $j-k$ bond as an axis, so as to superpose the f' on the carbon atom in the l-position. The charge-rotation vector $\boldsymbol{r}$ is introduced into this operation, and consequently the charge-density of the rotated atoms in the i, h, g, and f'-positions become $\boldsymbol{r}$, $\boldsymbol{r}$, $\boldsymbol{r}$, and $\boldsymbol{r}+1$ by rotation, where $i\times\boldsymbol{r}=0$ and $\boldsymbol{r}\times\boldsymbol{r}=1$. It is also assumed that the ring quantum number which indicates the angular-momentum is invariant in this operation. Therefore, the same procedure is considered as in the case of the anthracene molecule by separating the charge in the $(l+f')$-position into $\{i(\alpha+\beta)+r\}/2$ and $1-\{(\alpha+\beta)i-r\}/2$. The imaginary length of the perimeter l is estimated as $11.68+3.18i+2\boldsymbol{r}$ when α is equal to 1, and the real number of the imaginary perimeter length becomes $\sqrt{11.68^2+2^2+3.18^2}$, treating i and $\boldsymbol{r}$ as orthogonal vectors.

According to Platt's free-electron orbital method, the energy of light-absorption corresponding to that of the center of gravity (E) is given in Eq. 5;

$$E=\frac{q^2h^2}{2ml^2} \tag{5}$$

where q is the ring quantum number of acenes, m is the mass of the electron, and l is the length of the perimeter in the Ångstrom unit. As is illustrated in Fig. 2, the imaginary perimeter lengths of pseudo-anthracene converted from phenanthrene by rotation may be given as follows:

$$\begin{aligned} l_1&=(8.5+3\alpha^2+\alpha\beta)+(3\alpha+\beta)i+2r\\ l_2&=(7.5+3\alpha^2+2\alpha\beta)+(5\alpha+\beta)i+2r \end{aligned} \tag{6}$$

The real values of l_1 and l_2 should be equal. Therefore, the following relations are deduced from Eq. 1:

$$3\alpha^2\beta^2+(27+6\alpha^2)\alpha\beta+10\alpha^2-16=0 \tag{7}$$

When we put $\alpha=0.775$ as the ^1L_a case in Table II, β is estimated to be about 0.4. As a result, we obtain the imaginary perimeter length l corresponding to the ^1L_a-polarization by substituing α and β into Eq. 6. In the same procedure, we obtain β as nearly equal to 0 when we put α as equal to 1.225, which corresponds to the ^3L_a-polarization. When we put α as equal to 1.0, β is estimated to be 0.18, which corresponds to the case of the center of gravity of L_a-polarization. The estimated values of $\bar{\nu}$ from Eq. 5 corresponding to ^1L_a, ^3L_a and $^{c\cdot g}L_a$ polarization are fairly satisfactory. In the same way, we can estimate β in the case of such simpler phenes as 1,2-benzoanthracene, 1,2-benzotetracene, chrysene, and 1,2-5,6 dibenzoanthracene. The estimated values of $\bar{\nu}$ corresponding to the ^1L_a, ^3L_a and $^{c\cdot g}L_a$ polarizations are considered to be reasonable. The estimated values of the energies of absorptions of the L_a-state of respective compounds are shown in Table I*.

When we switch other two combinations of four imaginary atoms with charges αi and $(1-\alpha i)$, such as αi and αi or $(1-\alpha i)$ and $(1-\alpha i)$, energy-values of the B_a-state are obtained which correspond to the estimated number of resonance structures in the analogous B_a-state, which means that we have imaginarily varied the actual perimeter length or the shape of the potential box of the molecule instead of varying the angular momentum q. The imaginary length of the perimeter of naphthalene with an imaginary increase of $\alpha^2i^2+(1-\alpha i)^2$ in two cross-linking ethylene atoms and a decrease of $2\alpha i+2(1-\alpha i)-4$ in four bonds among cross-linking carbon atoms and their neighbors, is equal to $(9-2\alpha^2)-2\alpha i$. Those of anthracene, naphthacene and phenanthrene are illustrated in Table II. In the case of phenanthrene obtained by being rotated, the residual imaginary charge on the f atom is equal to $(1-\alpha i)$, in contrast to the value of αi in the case of the L_a-state; therefore, the imaginary charge in the $(l+f')$-position is 1, while other elements are equal to those in the above case. The values of $\bar{\nu}\,B_a$ estimated

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* We can empirically obtain satisfactory values of $\bar{\nu}$ in respective polarizations when we put α_1 as equal to 0.775 in the case of the ^1L_a-polarization, α_3 as equal to 1.225 in the case of the ^3L_a-polarization, and $\alpha_{c\cdot g}$ as equal to 1.0 in the case of the $^{c\cdot g}L_a$-polarization in the acene series. The following relations are observed empirically in the case of acenes:

$$\begin{gathered} \bar{\nu}_{^1L_a}+\bar{\nu}_{^3L_a}\fallingdotseq 2\bar{\nu}_{^{c\cdot g}L_a}\\ \alpha_1+\alpha_3\fallingdotseq 2\alpha_{c\cdot g} \end{gathered} \tag{8}$$

where α is considered to determine the degree of the condensation of mutually neighboring benzene nuclei.

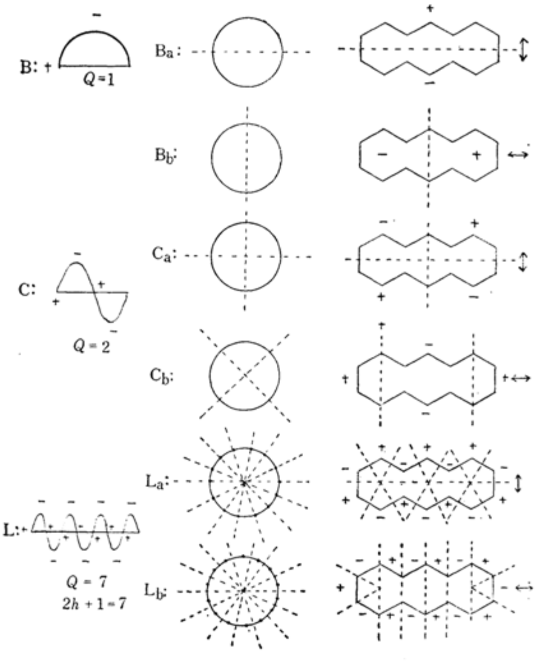


Fig. 1. Polarization diagram of the anthracene molecule according to Platt.

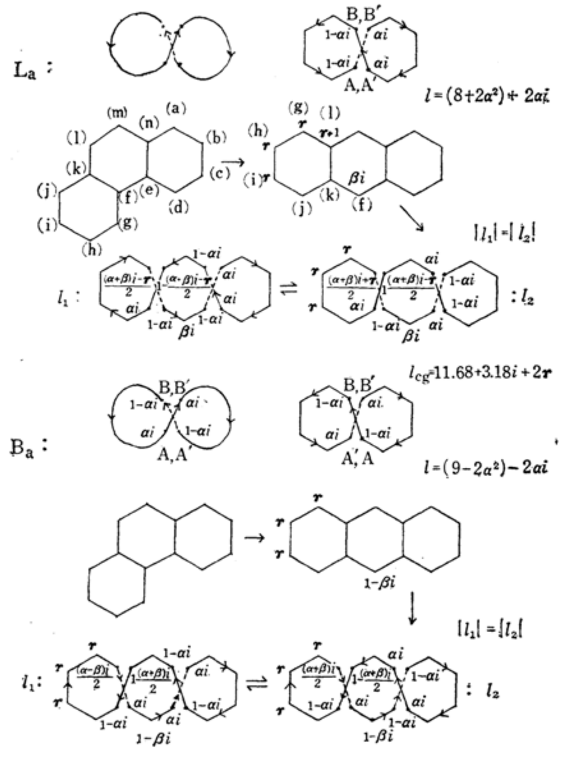
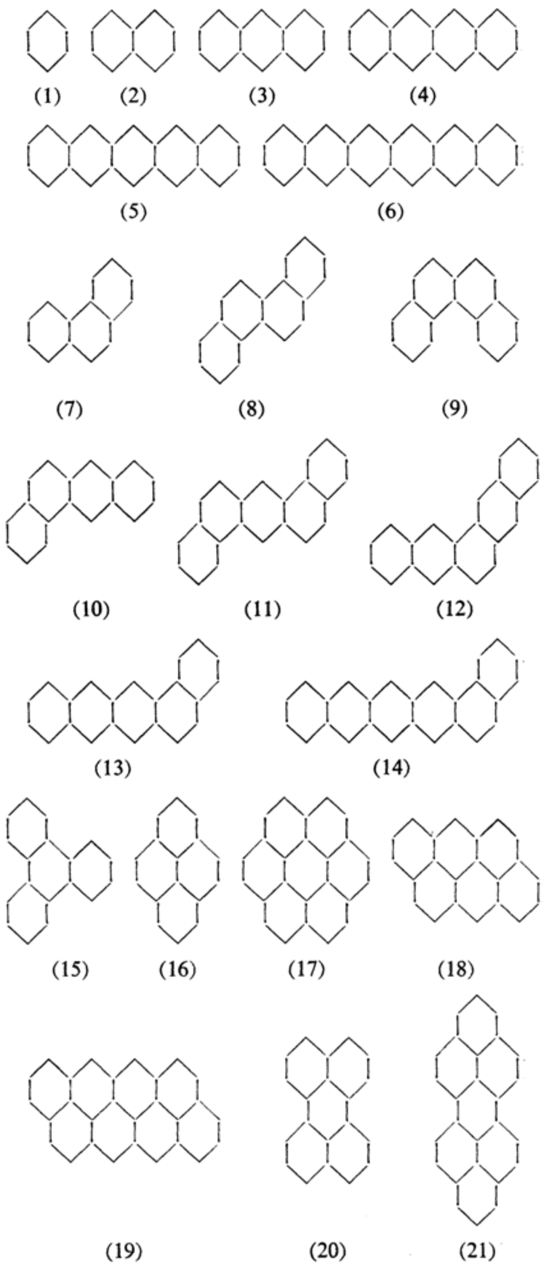


Fig. 2. Imaginary perimeter in the case of L_a- and B_a-polarization.

from the perimeter length are given in Table I. The estimated values corresponding to the ^1L_a- and ^3L_a-excitation illustrated in Table I are considered to be in good agreement, irrespective of their rough estimation.

The above procedure corresponds to the fact that, in the estimation of resonance structures, we put the imaginary charge, *i*, on the cross-linking atom on the perimeter and separate the imaginary ethylene-linkage with charges $(1-i)$ and $-(1+i)$ at both ends in the representation of the L_a-state, while we put $(1-i)$,

Table I



on the perimeter and separate the imaginary ethylene linkage with charges i and i in the case of the B_a-state.

To the problem of the estimation of the number of resonance structures in acenes and phenes, this imaginary point-charge-vector and rotation-vector are also introduced. The correlation with an estimation of their resonance structures will be discussed in the following section. The numbers of Kekulé resonance structures will be given in the analogous form as $a+bi+c\boldsymbol{r}$; their real value is estimated as $\sqrt{a^2+b^2+c^2}$ for phenes and other complex-molecules which are converted into pseudo-acenes, from which we take a given type of resonance structure as corresponding to a given polarization as defined by Platt.

Resonance Structures Corresponding to L_a-type Polarization.—The chemical resonance structures corresponding to the L_a-type polarization of the naphthalene molecule are illustrated in Fig. 3, where + and − point charges are located alternatively on individual elementary carbon atoms on the periphery of the molecule. A combination of one +-labeled atom with all five other −-labeled atoms holding the canonical resonance structures with the residual parts of the molecule produces the 5 or $(2n+1)$ polarized form. The same operation with the four other +-charged atoms produces the 5^2 or $(2n+1)^2$ polarized form, with 32 Kekulé resonance structures.

By superposition of these 5^2 or $(2n+1)^2$ polarized form, Platt's model corresponding to the L-state has been considered to be made. Therefore, the −-charge density on each −-labeled carbon atom in one polarized structure must be $1/4\times1/32$ in estimating the elementary dipole, the 1/4 factor of which will be discussed in a later section. The summation of the elementary dipoles of 32-resonance structures gives only a transversal electric dipole of $11ae'$, where e' is equal to $e/32$. However, it is known intuitively that the weights of the existence of the resonance structures asterisked by $*$ and $**$ may be different from those asterisked by $***$ and $****$, which include polarization on the cross-linking carbon atoms. The effects of cross-linking are eliminated by introducing the imaginary point charge vector i to the cross-linking carbon atoms, which, positively or negatively, separate the independent ethylene-linkage with the imaginary charges $(1-i)$ and $-(1+i)$, in order to supplement the decrease in total electric dipoles with this polarization, which is illustrated in Fig. 4.

The summation of elementary dipoles with the group asterisked by $*$ gives only a transversal dipole with a magnitude of $12\,ae'$, while that with the group asterisked by $**$ gives $2\,ac'$ dipoles, that with the $***$-asterisked group gives a transversal dipole of $-2\,ae'$, and that with the $****$-asterisked group gives $-ae'$ in the same direction. Therefore, the first group asterisked by $*$ possesses a predominant influence for polarization compared with the latter three. The electric dipole of the third group, asterisked by $***$, may be substituted by that of the imaginary ethylene-linkage in the above model with charges of $-(1+i)$ and $(1-i)$ at both ends. Both dipoles possess a $-2\,ae'$ unit of strength. The last group, asterisked by $****$, may be equivalent to the polarized structure among imaginary cross-linking carbon atoms with charges of i and i.

As has been mentioned above, the number of resonance structures belonging to the second group $(**)$ may be substituted by those belonging to the imaginary ethylene, in estimating which we may count the resonance structures of the residual benzene nuclei or parts. For example, they are 1, 2, 3, 4 and 5 for naphthalene, anthracene, naphthacene and pentacene, in that order. As for the actual number of resonance structures in the estimation, they are multiplied by $(1+i)\times(1-i)$ or 2. The resonance number for the $***$-group is equivalent to that polarized in the i and i position. They are all equal to 1 in one polarized structure. The numbers of polarization among cross-linking atoms mutually with imaginary charges of i are 1 for naphthalene, 4 for anthracene, 6 for naphthacene, etc. This polarization is equivalent to that of the $*$-type elementary structure in unit strength and hence may be included in the first $*$-group instead of the $**$-group, the members of which are mutually canceled. They are also expressed in real number in the above-mentioned imaginary point-charge vector method, while the $***$-groups may be expressed in imaginary number and mutually canceled in symmetric acenes.

The second group, asterisked by $**$, possesses a moment of $2\,ae'$ in naphthalene and hence takes little part in the main polarization. The members of this group are considered to be caused among two neighboring atoms; hence, in that sense they must include some of the polarization asterisked by $***$ and $****$, which polarizations are substituted for by the effect of the introduced imaginary ethylene-linkage with charges $(1-i)$ and $-(1+i)$. For the convenience of the estimation of the number of resonance structures of the ^1L_a- and ^3L_a-states and of the visualization of the excited states in terms of chemical resonance structures, the polarization among mutually neighboring atoms and imaginary ethylene-linkage are considered to be of the ^3L_a-type judging from their small dipole strength. The polarization including the $*$-group and imaginary ethylene-linkage is considered, on the basis of their strong dipoles, to correspond to the ^1L_a-type. The former model of resonance is pictured as if individual dipoles are embedded in combined benzene nuclei independently. The latter model of the ^1L_a-type is pictured as if the electric current flows on the twisted loop along the perimeter of the benzene nuclei and their combining imaginary ethylene-linkage. Their types of polarization are applied to phenes and other higher condensed compounds, where they are developed to be converted into symmetric pseudo-acenes, which process will be referred to in later sections.

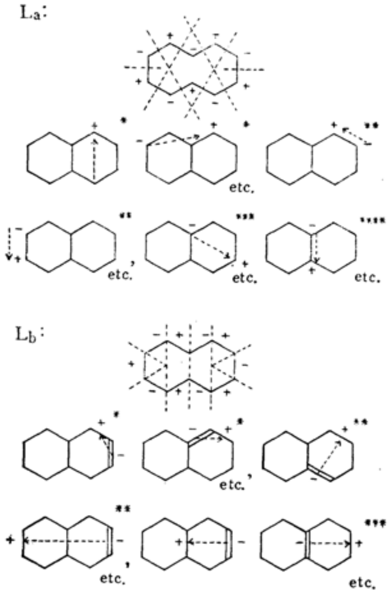


Fig. 3. Resonance structures of naphthalene corresponding to the L_a- and L_b-polarized state.

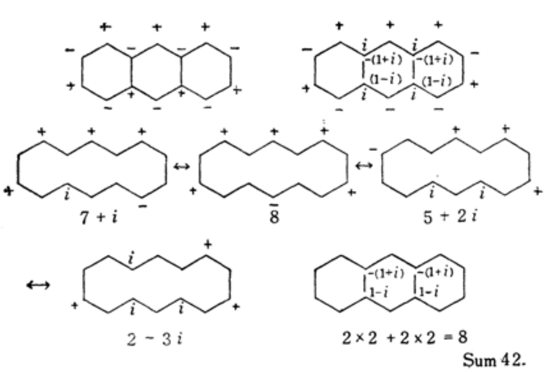


Fig. 4. Resonance structures of anthracene corresponding to the ^1L_a-polarized state, eliminating the effect of cross-linking carbon atoms by introducing the imaginary vector i.

Resonance Structures Corresponding to L_b-Levels.—The L_b-state is considered to be the case where the nodal cuts fall on the atoms or where the nodes are located on the middle point of individual bonds in Platt's model. It is pictured by removing charges on the atoms a half bond length along the perimeter in order to locate them on the middle point of the bonds.

In the usual representation of resonance structures, two ways are considered to remove the charge on the cross-linking atoms among the cross-linking bonds and their neighboring bonds. It seems to be a problem of the conjugation of four imaginary atoms which combine in two benzene nuclei. In order to solve this problem, the modified model will be re-examined. We remove unit charges on the atoms in that model corresponding to the ground state a half bond length along the perimeter of the twisted loop in one direction so as to locate them on the middle point of individual bonds, as is illustrated in Fig. 5. The conjugations of four imaginary atoms are then switched as they are in the case of the b-state. For example, an anthracene molecule is used which possesses a meso-position where the charges are considered to be somewhat localized in the ground state. Then, we remove the unit charges which are on the atom in order to locate them on the middle-point of bonds. It is considered that charges flow along the perimeter of the molecule by polarization and that the excitations are caused in the same locations as in the ground state, thus separating the solutions of the b-state from those of original Platt's model. The imaginary path among meso-positions does not alter the path-length compared to the case in which they are not imagined, as with the a-state.

We switch the four imaginary atoms in the b-state to locate them on bonds in one direction in order that, in the switched two-benzene nuclei and in the half-benzene nuclei in the meso-position, the current will flow in the same direction, giving angular momentum with an opposite vector towards the molecular plane that would be mutually cancelled if they are separated. This gives the features of the L_b-state, which is not such a strongly-polarized state. Using this procedure for other acenes, the perimeter-lengths and the $\bar{\nu}$ values of the L_b-state given on Table I are obtained from Eq. 5. We will represent this L_b-polarized state with the chemical resonance structures shown in Fig. 5 and Fig. 6. In Fig. 5, the location of the $+$ and $-$ charges on the bond is interpreted as meaning that if we fix the bond there, we can hold the residual part of the molecule in the canonical Kekulé structure.

TABLE II

Name of substance	Index number	Imaginary perimeter length (l) in unit of mean carbon-carbon distance and estimated values of $\bar{\nu}$ in cm^{-1} unit			
		l_{La}	† $\bar{\nu}^1_{\mathrm{La}}$ $\alpha_1=0.775$ cm^{-1}	$\bar{\nu}_{\mathrm{La}}$ $\alpha_{cg}=1.0$ cm^{-1}	$\bar{\nu}^3_{\mathrm{La}}$ $\alpha_3=1.225$ cm^{-1}
Naphthalene	2	$(8+2\alpha^2)+2\alpha i$	35460 35000*	29690 28200*	24300 21300*
Anthracene	3	$(10+4\alpha^2)+4\alpha i$	26450 26700*	20920 20700*	15430 14700*
Naphthacene	4	$(12+6\alpha^2)+6\alpha i$	20970 21000	15450 15500*	11200 (10000)* est
Pentacene	5	$(14+8\alpha^2)+8\alpha i$	17330 17300*	12390 11800*	8800 (6300)* est
Phenanthrene	7	$(8.5+3\alpha^2+\alpha\beta)$ $+(3\alpha+\beta)i+2r$ or $(7.5+3\alpha^2+2\alpha\beta)$ $+(5\alpha+2\beta)i+2r$	33000 $\beta\fallingdotseq0.4$ 33000*	28710 $\beta\fallingdotseq0.18$	23080 $\beta\fallingdotseq0$ 21600**
1,2-Benzo-anthracene	10	$(10.5+5\alpha^2+\alpha\beta)$ $+(5\alpha+\beta)i+2r$ or $(9.5+5\alpha^2+2\alpha\beta)$ $+(7\alpha+2\beta)i+2r$	27530 $\beta\fallingdotseq0.21$ 27300*	20170 $\beta\fallingdotseq0.065$	15520 $\beta\fallingdotseq0.016$ 16500**
Chrysene	8	$(8+4\alpha^2+4\alpha\beta)$ $+3(2\alpha+\beta)i+4r$	31200 $\beta\fallingdotseq0.3$ 30200*		19800**
1,2-5,6-Dibenzo-anthracene	11	$(10+6\alpha^2+4\alpha\beta)$ $+(8\alpha+3\beta)i+4r$ or $(11+6\alpha^2+2\alpha\beta)$ $+(6\alpha+2\beta)i+4r$	26100 $\beta\fallingdotseq0.15$ 28400***	19920 $\beta\fallingdotseq0.03$	15870 $\beta\fallingdotseq-0.03$ 18100****

Name of substance	Index number	Imaginary perimeter length (l) in unit of mean carbon-carbon distance and estimated values of $\bar{\nu}$ in cm^{-1} unit			
		l_{Ba}	$\bar{\nu}^1_{\mathrm{Ba}}$ $\alpha_1=0.995$ cm^{-1}	l_{Lb}	$\bar{\nu}^1_{\mathrm{Lb}}$ $\alpha=1.05$ cm^{-1}
Naphthalene	2	$(9-2\alpha^2)-2\alpha i$	58060 59800*	$(8+2\alpha^2)+2i$	29400 32200*
Anthracene	3	$(12-4\alpha^2)-4\alpha i$	53700 53700*	$(10+2\alpha^2)+2i$	28000 (28000)*est
Naphthacene	4	$(15-6\alpha^2)-6\alpha i$	47180 47400*	$(12+2\alpha^2)+2i$	26870 (25500)*est
Pentacene	5	$(18-8\alpha^2)-8\alpha i$	41280 —*	$(14+2\alpha^2)+2i$	25390 24000*
Phenanthrene	7	$(11-3\alpha^2-\alpha\beta)$ $-(4\alpha+2\beta)\mathrm{i}+\mathrm{r}$ $(10-\alpha^2+\alpha\beta)$ $-(2\alpha+\beta)i+r$	53100 $\beta=0.22$ 53400*		

† α_1, α_3 and $\alpha_{c.g}$ are corresponding to the coefficient of imaginary charge-separation at the cross-linking carbon atoms which hold the following mutual relations:

$$\alpha_1+\alpha_3\fallingdotseq2\,\alpha_{c.g} \qquad \bar{\nu}1_{\mathrm{La}}+\overline{\nu}3_{\mathrm{La}}\fallingdotseq2\,\bar{\nu}_{c.g\mathrm{La}}$$

* H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 481 (1949).

** D. S. McClure, ibid., **17**, 905 (1949).

*** E. Clar, "Aromatische Kohlenwasserstoffe", Zweites Band, Springer Verlag, Berlin (1952).

Because the charge is re-located to the neighboring bond through the twisted path, the polarized structures or the position of the bonds that are negatively charged, for instance, become different from those made from the untwisted path along the perimeter. For that reason, the + and − polarizations which occur in ordinary forms are inhibited in order to hold the residual part in the Kekulé canonical form. The polarizations are allowed mainly in the same benzene nucleus or in the neighboring nuclei, and the long-range polarizations among the separate benzene-nuclei are not allowed for the most part, illustrating that, in the L_b-type, the polarizations occur mainly in the same benzene nucleus, so that each

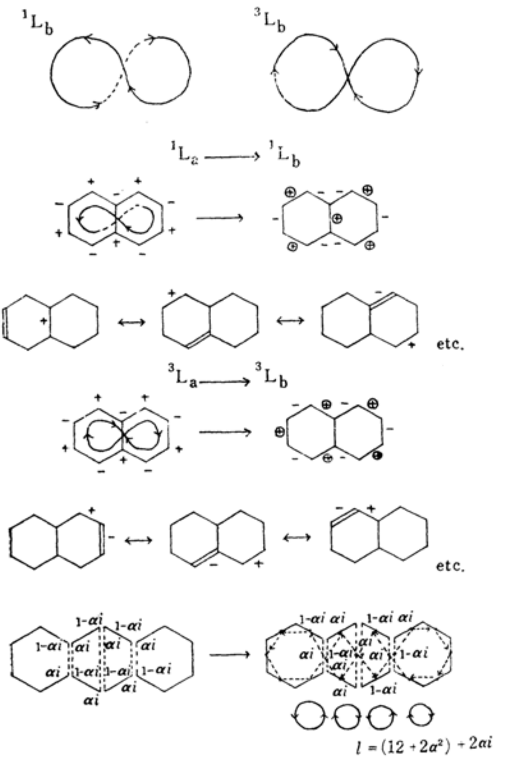


Fig. 5. Resonance structures corresponding to the ^1L_b- and ^3L_b-polarized state of naphthalene.

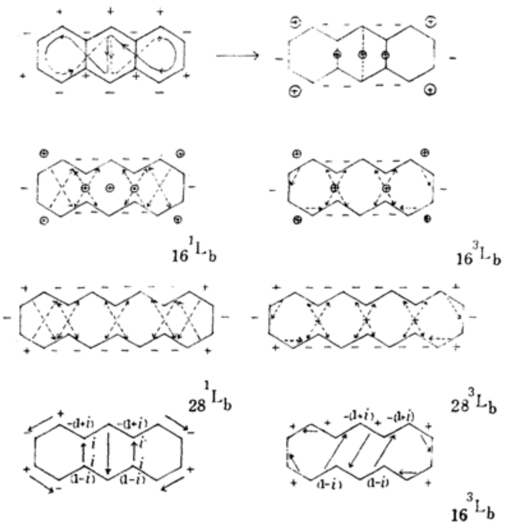


Fig. 6. Resonance structures corresponding to the ^1L_b- and ^3L_b-polarized state of anthracene converted by the half-bond length removal along the perimeter from the polarization diagram corresponding to the ^1L_a-polarization.

elementary dipole is canceled in that nucleus. It is suggested that, therefore, the strength of absorption in the position where polarization occurs is very similar to that where ^3L_a-type polarization occurs. Therefore, it is easily supposed that the numbers of resonance structures corresponding to ^3L_b-type polarizations are nearly equal to those corresponding to the ^1L_b-state. The sum of the elementary dipoles of individual structures described in Fig. 3 possesses only a longitudinal component and is small compared to the case of ^1L_a; similarly, each sum of the *-, **- and ***-asterisked groups possess only a longitudinal component and are small.

The general diagram for determining the number of th resonances of ^1L_b- and ^3L_b-structures is shown in Fig. 6. The same relation has been found for phenes and for other circular molecules when they are converted into pseudo-acenes. We can find the numbers of Kekulé resonance structures of the ^1L_b- or ^3L_b-type for acenes and phenes, the estimations of the position of polarization and the method of the estimation of the resonance numbers being like those in the case of ^3L_a.

The Estimation of Resonance Structures Corresponding to the L-State.—In the case of ^1L_a-polarization, those among neighboring atoms are principally inhibited, except those in the case of imaginary ethylene, as has been stated in a preceding section. The estimated numbers of resonance structures (N_{L_a}) of polyacenes are illustrated in Table III. The correlation of $\log(N_{L_a}/N)$ with $\bar{\nu}_{L_a}$ is illustrated in Fig. 7. They retain the straight-linear relation in Eq. 4 with gradients of 69 kcal./mol. Phenes are transformed into pseudo-polyacene by introducing the charge rotation vector which is illustrated in Fig. 8.

After this procedure, the charges on the (g), (h), and (i) atoms become $-\boldsymbol{r}$, $\boldsymbol{r}$ and $-\boldsymbol{r}$. That on the ($l+f'$) atom becomes $1+\boldsymbol{r}$ where it is assumed that $i\times\boldsymbol{r}$ is equal to zero. Therefore, the separation of the imaginary ethylene-linkage with the charges $(1-i)$ and $-(1+i)$ charges the charge on the superposed cross-linking atoms $(l+f')$ to $(i+\boldsymbol{r})$ and that on atom (k) to i. The number of resonance structures is estimated to be (N), which is enumerated without a vector and multiplied by $\boldsymbol{r}$ or $N\times\boldsymbol{r}$ where one of the two atoms is labeled with vector $\boldsymbol{r}$, and is estimated to be $N\times\boldsymbol{r}^2$ or N where both atoms are labeled with vector $\boldsymbol{r}$. For instance, the numder of resonance structures corresponding to polarization between atoms (g) and (b) is estimated to be $N_{gb}\times\boldsymbol{r}$, while that between ($g$) and ($h$) is estimated to be $N_{gh}\times\boldsymbol{r}^2$ or N_{gh} where N_{gb} is the number of resonance structures corresponding to those between atoms (g) and (b) in the ordinary phenanthrene molecule.

TABLE III

Index No.	Name of substance	Number of resonance structures of respective state				
		^1L_a	^3L_a	^1L_a*	^1L_b	^3L_b
1	Benzene	3	3	3	3	3
2	Naphthalene	15	10	15	8	8
3	Anthracene	42	24	42	16	16
4	Naphthacene	93	48	93	28	28
5	Pentacene	178	85	178	41	41
6	Hexacene	—	—	—	—	—
7	Phenanthrene	$22+10i+7r$	$15-2i+3r$	$27+8r$	$18-4i$	$19+i+3r$*
8	Chrysene	$42-3i+19r$	$26-3i+14r$	$56+12r$	$39-9i$	$34+4i+10r$*
9	3,4-Benzo-phenanthrene	$46+2i+23r$	$26+6i+10r$	···	$34+12i$	$34+12i$*
10	1,2-Benzo-anthracene	$69+9i+12r$	$36-3i+8r$	$53+40r$	$34+5i$	$35+i+3r$*
11	1,2-5,6-Dibenzo-anthracene	$84+16i+47r$	$47+10i+13r$			
12	Naphthoanthracene	$97+20i+36r$	$50+3i+8r$			
13	1,2-Benzotetracene	$110+21i+44r$	$74+4i+5r$			
14	1,2-Benzopentacene	$243+17i+70r$	—	$171+80r$		
15	Triphenylene	$35+34i+38r$	$17+9i+13r$		$24+24r$*	
16	Pyrene	$45+18i+21r$	$25+12r$	48	$10+20r$*	
17	Coronene	$118+18i+48r$	$74-6i+34r$		$122+28r$*	
18	Anthanthrene	—	—			
19	Naphtho anthanthrene	—	—			
20	Perylene	$129+11i+48r$	$12-6i+48r$			
21	Peropyrene	—		$260+48r$		

* Number of resonance structures of ^1L_b or ^3L_b obtained by the conversion following Fig. 12.

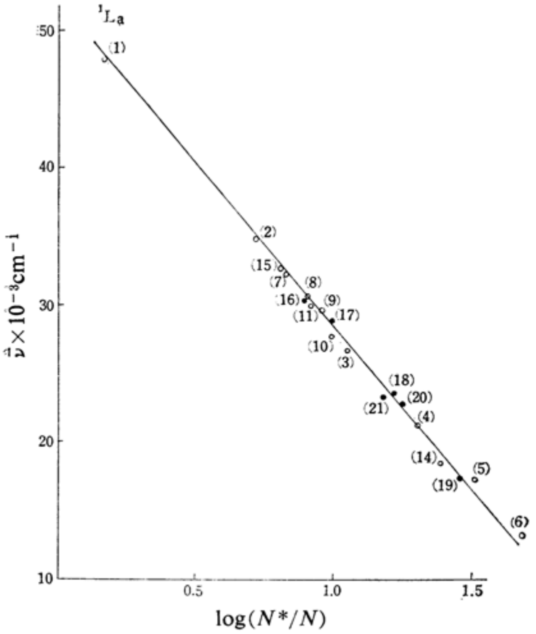


Fig. 7. Correlation of $\bar{\nu}_{^1L_a}$ with log(N_{La}/N), keeping the linear relation with a gradient of about 69 kcal./mol.

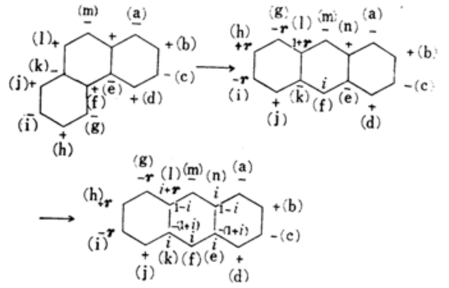


Fig. 8. Estimation of the number of resonance structures of phenanthrene converted by rotation to pseudo-anthracene corresponding to L_a-polarization.

In this way, the numbers of resonance structures corresponding to the ^1L_a-state of phenanthrene, benzoanthracene, benzotetracene, and benzopentacene are estimated in Table III.

As for the chrysene and 1, 2-5, 6-dibenzoanthracene molecules, which are transformed into pseudo-naphthacene and pseudo-pentacene by separating the charge at the joint of the concaved benzene, the imaginary charge densities on the new joint become $i+\boldsymbol{r}$ and $i-\boldsymbol{r}$

respectively. In the cases of pyrene, perylene, and coronene, the transformations are convert them into pseudo-tetracene, pseudo-pentacene, and pseudo-hexacene. Their numbers of resonance structures are illustrated in Table III. When the $\log(N_{\mathrm{L_a}}/N)$ of the above compounds is plotted versus $\bar{\nu}_{\mathrm{L_a}}$, they keep the straight-linear relation set forward in Eq. 4 and illustrated in Fig. 7.

The Estimation of the Number of Resonance Structures Corresponding to the $^1\mathrm{L_a}$-Type Polarization of Acenes and Circular Molecules.— The above procedure for estimating the number of resonance structures corresponding to $^1\mathrm{L_a}$ has been devised for acenes and phenes or for long-shaped hydrocarbons with inner ethylene-linkage. All these molecules have been converted to acenes by imaginary separation and rotation. However, it is very difficult, using the above procedure, to reduce such circular molecules as pyrene, triphenylene, and coronene to pseudo-acenes. They become pseudo-acenes only after complicated trials. Therefore, another approximation method for estimating the number of resonance structures has been devised; it is illustrated in Fig. 9.

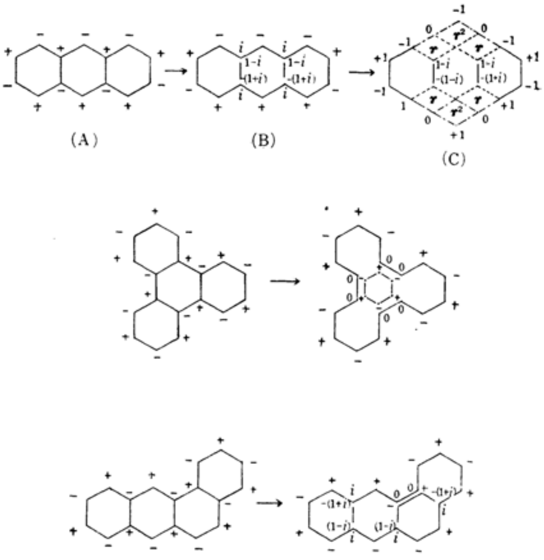


Fig. 9. Estimation of the number of resonance structures of those acenes and phenes corresponding to $^1\mathrm{L_a}$-polarization by rotation and by imaginary charge separation.

The cross-linking carbon atoms of acenes and other molecules are separated into two imaginary atoms with charges of i and $(1-i)$, leaving the inner ethylene-linkage with a charge of $(1-i)$, etc. Then, it is converted into hexagon by rotation. For instance, in the anthracene molecule (A), the imaginary carbon atoms with a charge of i in the cross-linking positions on the perimeter are converted into the structure (B) in Fig. 9 by rotation perpendicular to the molecular plane; after this procedure, the atoms in the meso-position are converted into structure (C) by rotation in the second step. In the first-step rotation, the charges i on the cross-linking position are converted to $i\times \boldsymbol{r}$, which is equal to zero owing to the orthogonality of both vectors defined. In the second-step rotation, the meso-carbon atoms which are rotated in the first-step procedure are afflicated by the second-step rotation. Therefore, the charges of meso-atoms in the converted positions are equal to $\boldsymbol{r}^2$ or 1. Therefore, we select two atoms with alternative + and − signs on the new perimeter to form the polarized resonance structures except for those between neighboring atoms. The number of resonance structures corresponding to the $^1\mathrm{L_a}$-state is estimated to be the sum of all those mentioned above and of those of two ethylene-linkages.

In the case of phenanthrene as an example of a convex molecule, the charge separations in the concaved positions are different from those in acenes, and the four linked carbon atoms are separated as in butadiene, as is illustrated in Fig. 9. The same example is an instance of a triphenylene molecule. The charge-separation in the concaved positions leaves six carbon atoms linked as a benzene nucleus, with charges alternately signed by $(1-i)$ and $-(1+i)$. The numbers of resonance structures in the case of phenanthrene are the sum of the 26 structures with atoms on the perimeter and of the 8 separated structures with inner butadiene. The number of resonance structures in the case of the triphenylene molecule is the sum of the 51 structures concerning atoms on the perimeter and of the 6 structures concerning atoms on the inner benzene nucleus.

1, 2-Benzoanthracene is converted into pseudo-anthanthrene, which is further converted into a hexagon, leaving one imaginary butadiene and one imaginary ethylene inside the molecule. The number of resonance structures concerning the perimeter is equal to $45+18\,\boldsymbol{r}$, while those concerning the inside dienes and ethylene are equal to 20. The pyrene molecule is converted into outer and inner structure. The number of resonance structures concerning atoms on the perimeter is equal to 43 and those concerning the inner conjugation are 5, as has been mentioned above. The total number of resonance structures is equal to 48 in the pyrene molecule. The correlation of $\log(N^*_{\mathrm{La}}/N)$ versus $\bar{\nu}_{\mathrm{La}}$ is illustrated in Fig. 7 by the black spot. The values of the absorption

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3) P. G. Carter, *Trans. Faraday Soc.*, **45**, 597 (1947).

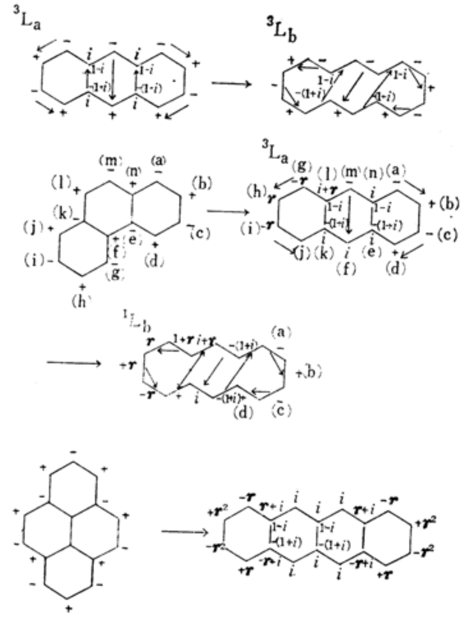

Fig. 10. Estimation of the number of the resonance structures crresponding to ^1L_b- and ^2L_b-polarization from those corresponding to ^3L_a-polarization.

energies $\bar{\nu}_{L_a}$ are mostly based on the data of Klevens and Platt[1]. Those of coronene, pyrene, peropyrene, etc. are based on the data on p-bands reported by Clar and on those of Matsen[4].

The Estimation of the Number of Resonance Structures Corresponding to the ^3L_a-Polarized State.—The preceding section has discussed how the resonance structures of the naphthalene molecule are classified into groups which possess different sums of elementary dipoles. One of those groups, that whose polarizations are among neighboring atoms and an imaginary ethylene-linkage, possesses too small an electric dipole to be classified as the ^3L_a-state. The ^3L_a-type of polarization is pictured in Fig. 10, where, in the case of anthracene, polarization among meso-positions (9 and 10) is included as the ^3L_a-type.

When the log $(N_{^3L_a}/N)$ of acenes is plotted versus the $\bar{\nu}_{L_a}$ value assigned in the report of Klevens and Platt, they keep the linear correlation with gradients of 69 kcal./ml. set forth in Eq. 4, which suggests that the above classification of resonance structures corresponding to the ^3L_a-state and the estimation of their number of resonance structures are adequate, as well as the results of oscillator-strength which will be mentioned later.

With a series of phenes, they are transformed into corresponding pseudo-aceness, as in the case of the ^1L_a-state discussed in the preceding section.

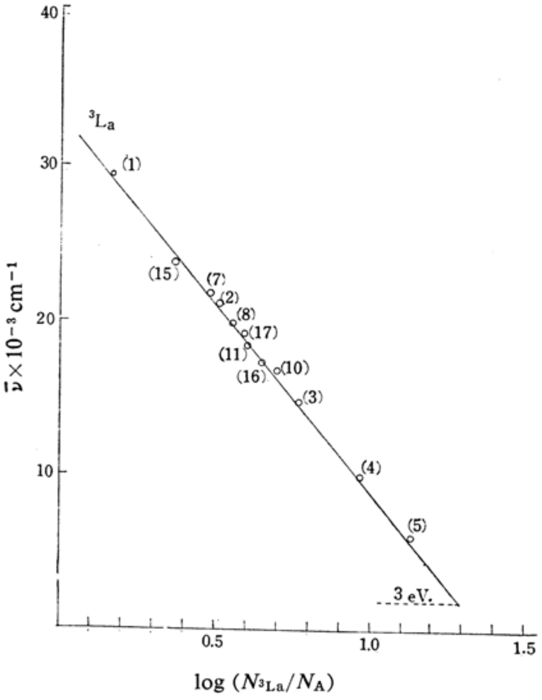

Fig. 11. Correlation of the $\bar{\nu}_{^3L_a}$ value of the polycyclic aromatic hydrocarbons with their log $(N_{^3L_a}/N)$.

Pyrene, coronene, and triphenylene are transformed into pseudo-naphthacene, pseudo-hexacene, and pseudo-naphthacene, as they are in the case of the ^1L_a-state. Their number of resonance structures are given on Table III. The correlation with their log (N_{L_a}/N) and E_{ST} values given by McClure illustrates the linear relation illustrated in Fig. 11, which is consistent with the same relation in the case of acenes.

The Estimation of the Number of Resonance Structure Corresponding to the ^1L_b-Type Polarization.—The features of chemical resonance structures corresponding to the ^1L_b-level have been mentioned in the preceding section. In these ^1L_b-type resonance structures, + and − polarizations in the separate benzene nuclei do not hold the residual part of molecule in the Kekulé form. Therefore, it seems that there is little difference between ^1L_b- and ^3L_b-type polarizations. The resonance structures corresponding to the L_b-type polarizations of naphthalene and anthracene molecules are illustrated in Figs. 5 and 13. Generally, resonance structures corresponding to ^1L_b-type polarization can be obtained by a half bond-length removal of the charge from atoms to

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[4] F. A. Matsen, *J. Chem. Phys.*, 24, 602 (1956).

bonds along the perimeter, irrespective of inner ethylene-linkage, from ^3B_a structures.

The number of resonance structures of ^1L_b-type and ^3L_b-type polarizations are approximately equal in acenes, as is illustrated in Table II.

The ^1L_b-type polarization of phenes and other circular-type molecules considered to be in the form of converted pseudo-acenes should be enumerated in such a way as is equal to the number of resonance structures of this polarization in the original molecule multiplied by the charges on polarized atoms in the converted form.

The estimated numbers of resonance structures corresponding to phenanthrene, chrysene, pyrene, etc. are given in Table II. The relation of their $\log(N_{^1L_b}/N)$ and $\log(N_{^3L_b}/N)$ to the absorption energies of these levels, $\bar{\nu}_{^1L_b}$ and $\bar{\nu}_{^3L_b}$, is illustrated in Fig. 13. They are satisfied by the linear correlations described in Eq. 4. These $\bar{\nu}$ values are mostly based on data of Klevens and Platt[1]. Those of pyrene and coronene are based on the data concerning the energies of α-bands obtained by Clar[5]. The ^1L_b-absorptions of these compounds correspond to those assigned as α-bands by Clar[5], while the p-bands assigned by him correspond to the ^1L_a-absorption.

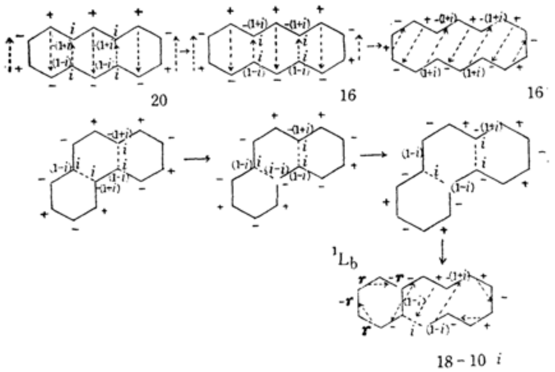

Fig. 12. Relations and estimation of the number of the resonance structures corresponding to ^1L_b, ^1B_b, and other types of resonance structures.

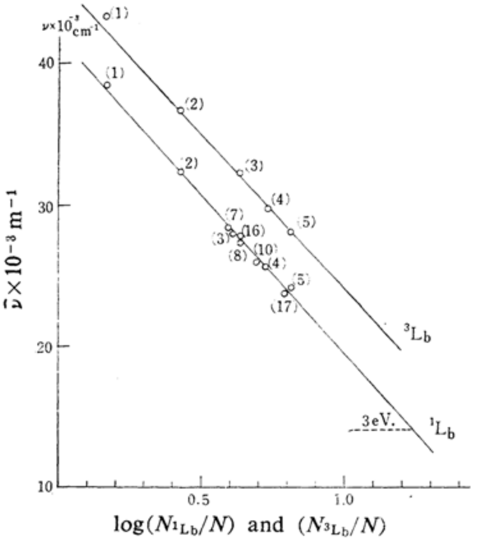

Fig. 13. Correlation of $\bar{\nu}_{^1L_b}$ and $\bar{\nu}_{^3L_b}$ values with their $\log(N_{^1L_b}/N)$ and $\log(N_{^3L_b}/N)$ values respectively.

These results suggest that the assumptions concerning resonance structures of the ^1L_b and ^3L_b states are reasonable.

Results and Discussion

The foregoing results support our assumptions concerning the chemical features of individual excited states, which are represented in terms of hybrid resonance structures corresponding to the characteristic polarization of standing waves of individual excited states, as well as the validity of Carter's empirical equation for the estimation of the empirical resonance energies. There is no mixing or confusion of properties in representing L-excited states in terms of chemical resonance structures.

They are considered to be fairly visualized as corresponding to the motion of mobile π-electrons as currents in interpreting Platt's theory.

The complicated absorption peaks of higher condensed aromatic hydrocarbons can be explained and assigned to their respective levels by this approximation method. In general, the α-bands and p-bands assigned by Clar are considered to correspond to ^1L_b-bands and ^1L_a-bands in this case.

Imaginary charges are introduced in order to eliminate the effect of cross-linking and also in order to visualize easily the hybrid resonance structures corresponding to Platt's theory. We have replaced the sign of the standing wave in his theory to that of the real charge in the above discussion. The differences between the L and B types of polarization may be considered to be reduced to the difference in the method of the conjugation of the switch of four imaginary cross-linking carbon atoms with the charge-densities $(1-i)$, i, $(1-i)$ and i. It is assumed that the angular momenta and other characteristic states, shells and configurations are invariant in this operation. In the above procedure, the perimeter length, which may be interpreted as defining the depth and shape of the constant potential box is given in imaginary units,

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[5] E. Clar, " Aromatische Kohlenwasserstoffe ", Zweites Band, Springer Verlag, Berlin (1952).

which may be expected to include the length to the free end-point of the standing wave.

The difference between a and b types of polarization may be interpreted as having been reduced in this model to the difference in the method of the conjugation of individual benzene nuclei considered as independent closed circuits, in either the parallel (twisted loop) or anti-parallel (perimeter loop) direction, which may be considered as producing the difference in synthesized electric dipole-vector or oscillator strength relating to absorption-intensities in their estimation from corresponding resonance structures.

The estimated number of resonance structures corresponding to L_a, L_b, B_a and B_b states are considered as a result of the above discussions to be fairly consistent with Carter's empirical equation in representing the excitation-energies corresponding to the respective polarization as the difference in empirical resonance energies as well as the absorption intensities estimated from the unit-dipoles in the resonance structures which are described above.

Summary

The chemical resonance structures of the excited states are assumed to correspond to the type of polarization in each state. This theory can explain the absorption energies as the difference in the empirical resonance energies between the ground and excited states by an application of Carter's empirical equations. Imaginary charges are introduced to estimate the number of resonance structures, thus eliminating the influence of cross-linking atoms; the meaning of the resonance hybride corresponding to each levels is easily interpreted in correlation with Platt's theory. As a result, the individual excited state can be represented as a chemical resonance hybride consisting of a group of simple polarized structures; this theory may be said to be adequate from the view-point of absorption energies and of absorption intensities in relation to the direction of electric dipoles.

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