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UV and Visible Absorption Spectra of Monohalogenated Anthracenes.
I. The First Absorption Bands

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UV and visible absorption spectra of monohalogenated anthracenes are measured, and the first absorption band are reported. When anthracene is monohalogenated, the first absorption band slightly shifts toward red or does not shift in accordance with the change in the position and the species of the substituting halogen atom, but the vibrational structure remains unchanged. The sequence of magnitude of red shift due to the position is 9-halo>1-halo>2-halo-anthracene, while that due to the species is different depending on the substituted position: in the 9-position, it is monobromo>monochloro>monofluoro>monoiodo anthracene, and, in the 1 or 2-position, it is monochloro>monofluoro>monobromo≃monoiodo anthracene. For the sequence of red shift due to the species of the substituting halogen atom, there are similarities between the first absorption band of monohalogenated anthracenes and the K or B-band of monohalogenated benzenes. These results are discussed in terms of the simple LCAO MO perturbation treatment.

The effect of monohalogenation and other substitution of aromatic hydrocarbons on UV and visible absorption spectra has been studied by many authors,$^{1-5)}$ where the shift and the intensity-variation of the absorption peaks have been examined. In polyacene, this effect of monohalogenation is so weak that the theoretical consideration may be treated with a perturbation theory containing some parameter determinations. The perturbation consists of two factors; the variation of 1) the steric configuration and 2) the electronic structure.

In UV and visible absorption spectra of anthracene, the first absorption band appears at near 380 mμ, and the second band at near 250 mμ. The first band has a prominent vibrational structure which is characteristic of polyacene, and the calculated energy$^{6)}$ and the assignment of the transition, A_{1g}–B_{2u}, are well supported by many experimental data.$^{7)}$ Since early, UV and visible absorption spectra of some of monochloro and monobromo anthracenes have been reported together with other simple substituted anthracenes.$^{8)}$ Recently, the charge transfer band,$^{9)}$ the excimer fluorescence and dimer absorption spectra$^{10)}$ of these have been studied, but the complete systematic examination has never been reported.

For the extensive study of monohalogenated anthracenes, we have synthesized and purified all isomers of monofluoro, monochloro, monobromo and monoiodo anthracene. In this paper, we will report UV and visible absorption spectra corresponding to the first absorption band; wavelengths for O–O transition, the vibrational assignment and molar extinction coefficients of the first band. Also, these results are discussed systematically in terms of the simple LCAO MO perturbation treatment.

Experimental and Results

Samples were synthesized in the process as shown in Table 1, and purified by recrystallization from a suitable solvent, sublimation and column chromatography. The detail of sample preparation will be reported in another paper, (together with some of their properties and results of their elementary analyses). In this paper, the existence of halogen atoms except fluorine was confirmed qualitatively by Beilstein Method.

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1) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

2) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950); W. W. Robertson and F. A. Matsen, *ibid.*, **72**, 5252 (1950).

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5) K. Iguchi, T. Nozaki, A. Imamura and S. Takahashi, This Bulletin, **36**, 697 (1963).

6) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

7) J. W. Sidman, *ibid.*, **25**, 115 (1956).

8) J. A. Christiansen, *Z. Physik. Chem., (B)*, **33**, 133 (1936).

9) A. Kuboyama, *Rep. Gov. Chem. Ind. Res., Tokyo*, **59**, 1 (1964).

10) E. A. Chandrass and J. Ferguson, *J. Chem. Phys.*, **45**, 3554 (1966).

TABLE 1. PREPARATIONS OF MONOHALOGENATED ANTHRACENES

Halide	Starting material	Reaction	
9-Fluoro anthracene	Anthracene	$\xrightarrow{p\text{-Tolyliododifluoride}}$	
9-Chloro anthracene		$\xrightarrow{Cl_2}$	
9-Bromo anthracene		$\xrightarrow{Br_2}$	
9-Iodo anthracene	9-Bromo anthracene	$\xrightarrow{Mg+I}$	
1-Fluoro anthracene	1-Amino anthraquinone	The Schieman reaction	Reduction
1-Chloro anthracene		The Sandmeyer reaction	
1-Bromo anthracene			
1-Iodo anthracene			
2-Fluoro anthracene	2-Amino anthraquinone	Same as the above reaction	
2-Chloro anthracene			
2-Bromo anthracene			
2-Iodo anthracene			

The sample (*ca.* 1 mg) was dissolved in purified *n*-hexane (10 m*l*); then a definite volume (*ca.* 1 m*l*) of the solution was withdrawn and added to the same solvent (10 m*l*) in absorption cell. The absorption spectra were measured at room temperature with a Hitachi EPS-3 spectrophotometer in the range 290—410 mμ. They correspond to the first excitation band and are illustrated in Figs. 1—4. Wavelengths of absorption peaks, molar extinction coefficients*[1] and the vibrational assignment are given in Table 2.

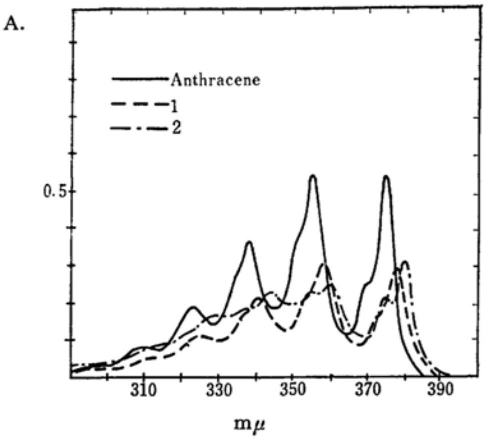

Fig. 1. The first absorption bands of anthracene and monofluoro anthracenes.
Concentration (10^{-5} mol/*l*)
$C_a=5.72$
$C_1=4.60$
$C_2=5.68$

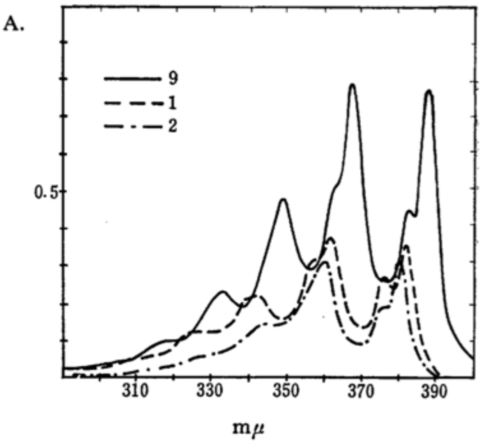

Fig. 2. The first absorption bands of monochloro anthracenes.
Concentration (10^{-5} mol/*l*)
$C_9=8.68$
$C_1=4.90$
$C_2=5.40$

The vibrational structure of the first absorption band of monohalogenated anthracene, two prominent vibrational progressions, appear clearly as those of anthracene. The wavelength of the absorption peak slightly shifts toward red or does not in accordance with the position and the species of the substituting halogen atom. The magnitude of shift is so small that the effect of monohalogenation on the electronic state of anthracene may be regarded as a perturbation, and so we will make a perturbation treatment in later section.

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*[1] We calculated the molar extinction coefficients by k=[absorbance]/[mole concentration]·[light path (cm)].

Though the monofluorination and the monochlorination have an influence on the first absorption band, the monobromination has an influence only when it is made at the 9-position, while the monoiodination has no influence. The sequence of red shift due to the atomic species is varied in accordance with the substituted position. In 9-position, it is monobromo > monochloro > (monofluoro)*2 > monoiodo anthracene, and in the 1 or 2-position, it is monochloro > monofluoro > monobromo > monoiodo anthracene. It is notable that the sequence of red shift due to the species of the substituting halogen atom in the 1 or 2-halo-anthracene is similar to that in the first absorption band, *i. e.*, B-band (A_{1g}–B_{2u}), of monohalogenated benzene, and the sequence in 9-halo-anthracene is almost similar to that in the second absorption band, *i. e.*, K-band (A_{1g}–B_{1u}).

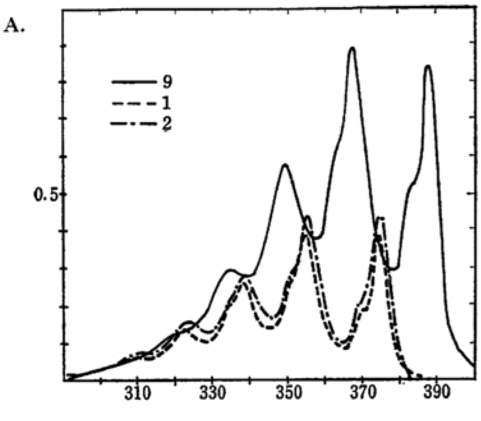

Fig. 3. The first absorption bands of monobromo anthracenes.
Concentration (10^{-5} mol/l)
$C_9=9.03$
$C_1=4.93$
$C_2=4.49$

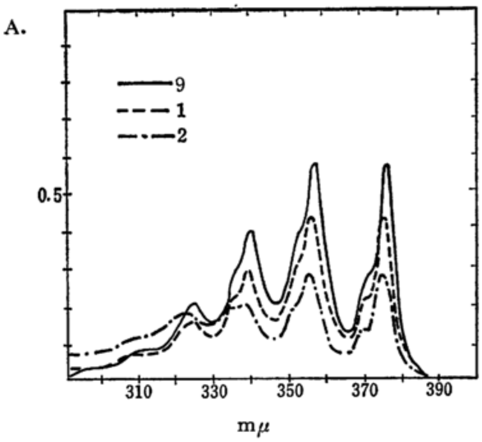

Fig. 4. The first absorption bands of monoiodo anthracenes.
Concentration (10^{-5} mol/l)
$C_9=6.26$
$C_1=3.83$
$C_2=4.20$

Prominent vibrational frequencies are the same as those of anthracene; they are about 1400 cm^{-1} and about 400 cm^{-1}, which slightly depend on states of aggregation (gas, liquid, crystal phase or solvent used). The vibration of 1400 cm^{-1} is assigned to the stretching of carbon skeleton (Gamma Carbon Stretching) and another vibration is assigned to the skeletal bending.7)

Discussion

Since early, experimental and theoretical studies of monosubstituted benzenes have accumulated a lot of information on electronic spectra of aromatic molecules.1-4) These benzene derivatives are divided into two groups4): one has the substituents such as NO_2, NH_2 which interact strongly with the π-electron system of benzene, another has the substituents which interact weakly with it. Fluorine, chlorine and bromine atoms have a weak interaction with benzene, or more generally, with aromatic molecules. Iodine atom shows special effects, in which the Rydberg transition of iodine atom is mixed in the absorption spectra of benzene derivatives4) and the steric effect appears in *p*-terphenyl derivatives,5) but such special effects were not observed by us in the first absorption band of anthracene derivatives.

In spite of the simplicity, LCAO MO perturbation treatment gives many useful and intuitional informations. So this treatment has been used by many authors2,3,5) since early to elucidate the effect of substitution on electronic spectra of aromatic molecules. Iguchi and his co-workers5) applied the perturbation theory11) to *p*-terphenyl derivatives, and obtained a good qualitative agreement between theory and experiment. Now, we intend to explain our experimental data with the same treatment.

It is known that a forbidden transition exists in the neighobrhood of this allowed transition (the first absorption band). In the Hückel approximation, however, both the highest occupied (No. 7) and lowest unoccupied (No. 7′) MO's, are well separated from other MO's. The first absorption corresponds principally to the transition No. 7—No. 7′ of MO's, and the forbidden transition to No. 7—No. 6′ (see Pariser6)). Thus the effect

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*2 Separation of 9-fluoro anthracene from unchanged anthracene was very difficult. We obtained the absorption peak at 386 mμ which is sure to be O-O transition of the first absorption band of 9-fluoro anthracene, but the other vibrational components could not be separated from those of the unchanged anthracene.

11) K. Fukui, C. Nagata, T. Yonezawa, H. Kato and K. Morimura, *J. Chem. Phys.*, **31**, 287 (1959).

TABLE 2. WAVELENGTHS, WAVE NUMBERS AND MOLAR EXTINCTION COEFFICIENTS OF THE ABSORPTION PEAKS OF ANTHRACENE AND MONOHALOGENATED ANTHRACENES

[λ in mμ, ν in 10^4 cm^{-1} and k in 10^3 mol^{-1} l cm^{-1}]

λ	ν	k	λ	ν	k	λ	ν	k	λ	ν	k
i) Anthracene			iv) 9-Cl			vii) 9-Br			x) 9-I		
375*	2.66	9.51	387*	2.58	8.99	388*	2.57	10.46	375*	2.66	9.08
370	2.70	4.47	383	2.62	5.30	383	2.61	5.75	370	2.70	4.35
356	2.80	9.56	367	2.72	9.08	368	2.71	9.99	356	2.80	9.19
351	2.84	6.26	362	2.76	5.87	363	2.75	6.67	351	2.84	6.32
339	2.94	6.35	349	2.86	5.53	350	2.85	6.44	339	2.94	4.42
335	2.98	4.73	344	2.90	4.03	345	2.89	4.99	335	2.98	3.32
324	3.08	3.28	333	3.00	2.74	334	2.99	3.33	324	3.08	2.53
319	3.13	2.29	329	3.04	2.19	330	3.03	2.44	319	3.13	1.26
310	3.22	1.35	318	3.14	0.92	319	3.13	1.39	310	3.22	0.95
297	3.36	0.52	304	3.28	0.46	305	3.27	0.55	297	3.36	0.47
ii) 1-F			v) 1-Cl			viii) 1-Br			xi) 1-I		
377*	2.65	6.37	382*	2.62	7.38	375*	2.66	7.87	375*	2.66	11.22
372	2.69	3.68	376	2.66	5.75	370	2.70	3.86	370	2.70	5.48
358	2.79	6.72	362	2.76	7.85	356	2.81	7.91	356	2.81	11.27
353	2.83	4.77	357	2.80	6.67	351	2.85	5.27	351	2.85	7.30
341	2.93	4.73	344	2.90	5.50	339	2.95	5.35	339	2.95	7.62
336	2.97	3.58	340	2.94	4.89	335	2.99	3.95	335	2.99	5.61
325	3.07	2.60	329	3.04	2.95	324	3.09	2.84	324	3.09	4.04
321	3.11	2.08	324	3.08	2.55	320	3.13	2.03	320	3.13	3.13
311	3.21	1.30	314	3.32	1.34	310	3.23	1.23	310	3.23	1.85
			301	3.32	0.77	296	3.37	0.63	297	3.37	0.86
iii) 2-F			vi) 2-Cl			ix) 2-Br			xii) 2-I		
379*	2.63	5.49	380*	2.63	5.92	375*	2.66	9.76	375*	2.67	6.66
374	2.67	3.80	375	2.67	3.38	370	2.70	4.68	370	2.71	3.49
360	2.77	4.45	360	2.77	6.03	356	2.81	9.81	355	2.81	6.73
354	2.82	4.04	356	2.81	5.18	351	2.85	6.13	351	2.85	4.40
343	2.91	4.04	342	2.92	4.31	339	2.95	6.24	339	2.95	4.48
338	2.95	3.34	339	2.95	4.10	335	2.99	4.91	335	2.99	4.45
329	3.04	2.97	327	3.05	2.51	323	3.09	3.59	323	3.09	4.28
322	3.10	2.16	323	3.09	2.47	320	3.13	2.67	319	3.13	3.76
313	3.19	1.58	313	3.19	1.29	310	3.23	1.69	310	3.23	2.66
301	3.32	0.79	300	3.33	0.74	309	3.31	0.67	297	3.37	1.76

* denotes O-O transition

of forbidden transition is neglected in our treatment.

The effect of monohalogenation on electronic spectra of aromatic molecules may be divided into three types: 1) steric effect, 2) inductive effect and 3) resonance effect. Other types may not be considered for the first approximation. Type 1) may be neglected in polyacene because of the rigidity of the framework. while it is essential in polyphenyl such as *p*-terphenyl.5) It is assumed that the inductive and resonance effects by the halogen atom are restricted to the AO of carbon atom to which the halogen is attached. So, when the anthracene molecule is monohalogenated, the change of energy of the *i*th MO is given by12):

$$\Delta e_i = e_i - e_i{}^0 = (C_t{}^i)^2\alpha^{(1)} + (C_t{}^i)^2/[e_i{}^0 + (C_t{}^i)^2\alpha^{(1)} - \alpha_x]\cdot\gamma^2 \qquad (1)$$

Where $e_i{}^0$ and $C_t{}^i$ are the energy and coefficient of the *t*th AO in the *i* th MO, respectively; *t* denotes the position of monohalogenation. Also, α_x designates the energy of the highest occupied orbital (p-orbital) of halogen atom, while γ is the resonance integral of the bond between halogen atom and anthracene, $\alpha^{(1)}$ is the change of core integral of carbon atom by the inductive effect of halogen atom. Here we may neglect the change of α_x (H_{77} in Matsen's notation) by the inductive effect of anthracene molecule.2) In the estimation

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12) K. Iguchi, *ibid.*, **30**, 319 (1959).

of the order of magnitude $(-\boldsymbol{e}_i^0)$ and $(-\alpha_x)$ may be regarded almost equal to ionization potentials of anthracene and methyl halides, respectively.[13] So, we have $(-\boldsymbol{e}_i^0)\simeq 7$ eV, $(-\alpha_x)\simeq 10$ eV, $(\boldsymbol{C}_t^i)^2 \lesssim 0.2$ and $\alpha^{(1)} \lesssim 3.3$ eV (see Table 3 and Fig. 5), then $(-\boldsymbol{e}_i^0)$ and $(-\alpha_x) \gg (\boldsymbol{C}_t^i)^2\alpha$.[1] Thus we may neglect the term $(\boldsymbol{C}_t^i)^2\alpha^{(1)}$ in denominator in Eq. (1). In alternant hydrocarbons the square of each AO coefficient is the same for both the highest occupied MO and the lowest unoccupied MO. Thus, the shift, δ, of the first absorption peak is expressed simply as

$$\varDelta \boldsymbol{e}_{i'} - \varDelta \boldsymbol{e}_i = \delta$$

$$= (\boldsymbol{C}_t^i)^2[1/(\alpha - k_i) - 1/(\alpha + k_i)]\cdot\gamma^2$$

and $$\alpha = \alpha_c^0 - \alpha_x,\ \boldsymbol{e}_i^0 = \alpha_c^0 + k_i \qquad (2)$$

Here α_c^0 is the core integral of carbon atom and k_i is the root of Hückel seqular equation.

Since $(\alpha - k_i)$ is larger than $(\alpha + k_i)$, δ is always negative. Thus, so far as the resonance effect is dominant, the red shift of absorption peak occures in anthracene derivatives, or more generally in alternant hydrocarbon derivatives. The magnitude of the red shift is determined by three factors: 1) $(\boldsymbol{C}_t^i)^2$, *i. e.*, the square of the coefficient of the *t*th AO in the *i*th MO, 2) the energy of the highest occupied orbital (p-orbital) of halogen atom and 3) the resonance integral between anthracene and halogen atom.

Now, let us consider the sequence of red shift. First, we consider the sequence due to the monohalogenated position. In this case, factor 2) and 3) are common for all position, so that the shift is determined by factor 1). From Fig. 5, giving the value of $(\boldsymbol{C}_t^i)^2$ calculated by Hückel approximation, the theoretical prediction of the sequence of red shift due to the position may be 9-halo > 1-halo > 2-halo-anthracene. This prediction is almost in harmony with our experimental data. Next, we consider the sequence of red shift due to the atomic species. In this case, factor 1) is common for all species, so that the sequence is determined by factor 2) and factor 3). Ionization potentials of halogenated methyls and the pure anthracene are listed in Table 3, and the sequence of its value is F > Cl > Br > I-methyls > anthracene. The evaluation of the resonance integral between halogen atom and anthracene is one of the most important problem in discussion of the effect of substitution and will be discussed elsewhere. Here we will use semi-empirical values determined by Nagakura[4] in electronic spectra of monohalogenated benzene. The sequence of magnitude is Br > Cl > I > F, as shown in Table 3. So, the theoretical prediction for the sequence of red shift of the absorption peak is monobromo > monochloro > monoiodo > monofluoro anthracene. The agreement between this prediction and our experimental data is not satisfactory; this prediction is only in harmony with the sequence of 9-bromo and 9-chloro anthracene, but does not the other monohalogenated anthracenes. And further the difference of the sequence due to the species in accordance with the substituted position cannot be explained by this treatment.

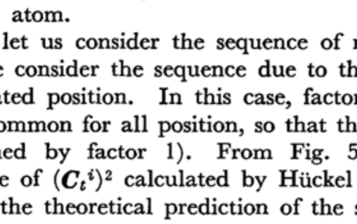

Fig. 5. The square of MO coefficients in the highest occupied orbital (same as the lowest unoccupied orbital).

TABLE 3. IONIZATION POTENTIALS OF METHYL HALIDES[a] AND THE PURE ANTHRACENE[b], RESONANCE INTEGRAL OF C-X BOND[c], AND CHANGES OF CORE INTEGRAL OF CARBON ATOM BY THE INDUCTIVE EFFECT OF HALOGEN ATOM ($\alpha^{(1)}$ IN OUR NOTATION)[d]

i) Ionization potentials (eV)	
CH_3F	12.61
CH_3Cl	11.34
CH_3Br	10.50
CH_3I	9.55
Anthracene	7.4
ii) Resonance integral, γ (eV)	
C-F	1.28
C-Cl	1.58
C-Br	1.93
C-I	1.20
iii) Changes of core integral, $\alpha^{(1)}$ (eV)	
F	3.3
Cl	2.4
Br	1.8
I	

a, c) See Ref. 4.

b) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley and Sons, Inc., New York, N. Y. (1967).

d) See Ref. 2. These values were roughly estimated from the oscillator strengths of phenyl halides.

Some reasons for this disagreement will be thought as following. Essentially, the magnitude of the shift is too small to predict exactly with the simple LCAO MO perturbation treatment. Scince the density of π-electron in the highest occupied orbital and that in the lowest unoccupied orbital are largest at the 9-position, it may be allowed to neglect the resonance between halogen atom and carbon atoms to which the halogen atom is not attached, in the case of 9-halo-anthracenes. But in the cases of the other halogenated anthracenes,

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[13] R. S. Mulliken, *Phys. Rev.*, **74**, 736 (1948).

it may not be allowed. We neglected the steric effect. If the substitution of the heavy atom such as bromine and iodine causes the distortion of the skeletal framework, it may affect the electronic structure. Our experimental fact is well explained if we assume that this distortion effect causes the blue shift and cancels out the red shift by the resonance effect in monohalogenated anthracene. However, there is no decisive evidence to support this assumption. On the contrary, it is reported that the distortion of skeletal framework causes red shift in substituted benzene.[14)]

In this experiment it is found that the wavelengths of absorption peaks of monoiodo anthracenes and 1 or 2-bromo anthracene are not different from those of anthracene. This point will require a more detail examination. We are planning the elementary analysis and the measurement of infrared spectra to make sure the structure of monohalogenated anthracenes, and the results will be published in another paper.

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14) J. Dale, *Chem. Ber.*, **94**, 2821 (1961).