Electronic Spectra of Substituted Aromatic Hydrocarbons.
*IV. Anthramines**

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In this series of papers,[1-3] the effect of substitution on the electronic transitions of aromatic hydrocarbons, benzene, naphthalene and anthracene has been discussed in terms of the perturbation by the substituent group concerned. Along the same lines, the absorption and fluorescence spectra of α- and β-anthramines have been examined in the present study.

Theoretical calculations[4-6] predicted that the $^1A_g \rightarrow ^1B_{3u}{}^-$ ($^1A \rightarrow ^1L_b$ in Platt's notation[6]) transition of anthracene is hidden under the stronger $^1A_g \rightarrow ^1B_{2u}$ ($^1A \rightarrow ^1L_a$) transition. The present authors reported in a preceding paper[3] that the ^1L_b band emerged in the absorption spectrum of β-anthrol on the lower frequency side of the ^1L_a band. This shows that the ^1L_b band increases in intensity and undergoes a characteristic frequency shift as a result of the introduction of an electron-donating group at the β-position. As is well known, an amino group is of a more electron-donating nature than a hydroxyl group, so that one may naturally expect that the separation of the ^1L_b band from the ^1L_a band should be pronounced in the spectrum of β-anthramine. In this paper, special attention will be paid to this point. Furthermore, it will be shown that in the low-frequency region α-anthramine has two absorption bands which seem to correspond to the ^1L_a and ^1L_b transitions.

Experimental

Materials.—α-Anthramine was prepared from α-aminoanthraquinone by refluxing it with zinc dust in an aqueous solution of sodium hydroxide.[7] The product was purified by column chromatography, and finally it was subjected to vacuum sublimation; m. p. 117∼119°C in a sealed tube (lit.,[7] 121.5∼122.5°C). β-Anthramine was prepared from β-aminoanthraquinone by the same procedure.[8] The product was sublimed in vacuo after crystallization from benzene; m. p. 237∼238.5°C (lit.,[8] 238°C). Dioxane was purified by the method described in a previous paper.[9] Triethylamine was fractionally distilled, dried with alumina, and then distilled in vacuo.

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[1] H. Baba, This Bulletin, **34**, 76 (1961).

[2] H. Baba and S. Suzuki, ibid., **34**, 82 (1961).

[3] H. Baba and S. Suzuki, ibid., **35**, 683 (1962).

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

[5] R. Pariser, ibid., **24**, 250 (1956).

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

[7] H. E. Fierz-David, L. Blangey and H. Streiff, *Helv. Chim. Acta*, **29**, 1718 (1946).

[8] P. Ruggli and E. Henri, ibid., **13**, 409 (1930).

[9] H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).

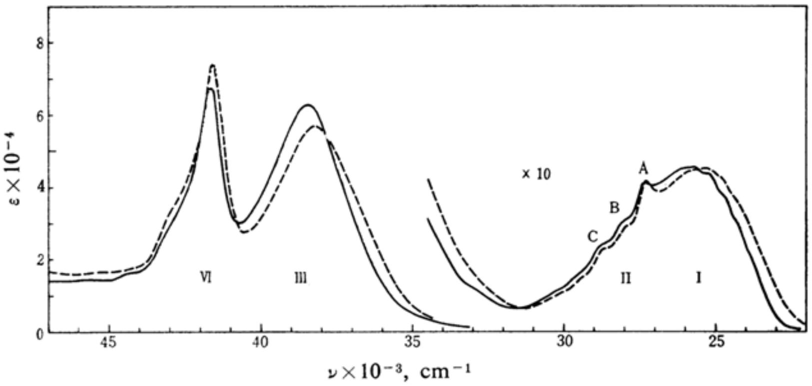

Fig. 1. Absorption spectrum of α-anthramine in isooctane at 20°C and the effect of hydrogen bonding. Solid curve, free molecule; dashed curve, spectrum in the presence of dioxane the concentration of which is 1.0 mol./l.

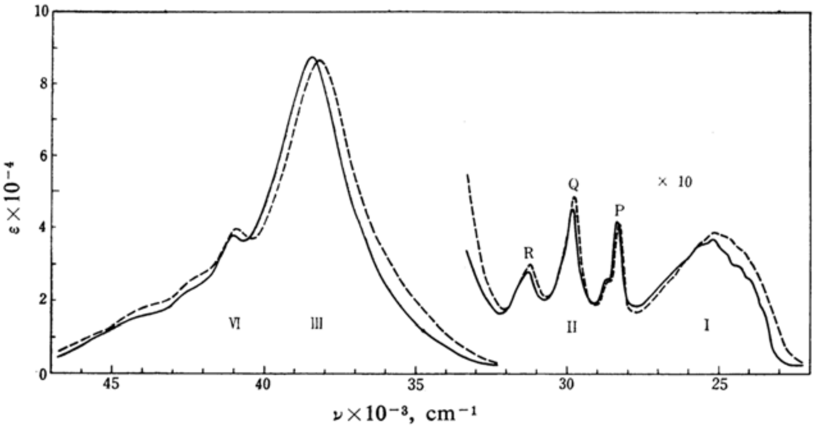

Fig. 2. Absorption spectrum of β-anthramine in isooctane at 20°C and the effect of hydrogen bonding. Solid curve, free molecule; dashed curve, spectrum in the presence of dioxane the concentration of which is 1.0 mol./l.

Apparatus and Procedures.—Absorption spectra at an ordinary temperature were measured with a Hitachi model EPU-2A photoelectric spectrophotometer at the controlled temperature of 20°C. Fluorescence spectra were observed at room temperature by attaching a fluorescence accessory of the L-3 type to the spectrophotometer. Samples were excited with the 365 mμ line of mercury. The slit was kept 0.2 mm. wide for all the fluorescence measurements. The observed spectra were corrected to quantum fluorescence spectra by the procedure described in a preceding paper.(3) All the absorption and fluorescence spectra at ordinary temperature were observed in an isooctane solution.

Absorption spectra at the liquid-nitrogen temperature were obtained using as a solvent the 6 : 1 isopentane—methylcyclohexane mixture which was recommended by Potts(10) as a glass-forming solvent. Measurements of the low-temperature spectra were performed by combining a Hitachi model EPS-2 recording spectrophotometer with a specially-designed low-temperature absorption apparatus. The latter is an all-glass Dewar vessel which has four parallel-plane glass windows transparent down to 250 mμ. Datails about the absorption apparatus and the procedures have been published elsewhere.(11)

Results

Figures 1 and 2 illustrate the absorption spectra of α- and β-anthramines in isooctane at 20°C and the changes in them caused by the addition of dioxane as a proton acceptor. The solid curves depict the spectra of anthramines free from hydrogen bonding. The dashed curves represent the spectra of solutions containing dioxane at a concentration of 1.0 mol./l.

The fluorescence spectra of α- and β-anthramines in isooctane at room temperature are shown in Figs. 3 and 4. In the figures, absorption spectra are given with dashed curves for easy reference.

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10) W. J. Potts, ibid., **21**, 191 (1953).

11) H. Baba, S. Suzuki and S. Miura, *Bull. Research Inst. Appl. Electricity*, Hokkaido Univ., **14**, 59 (1962).

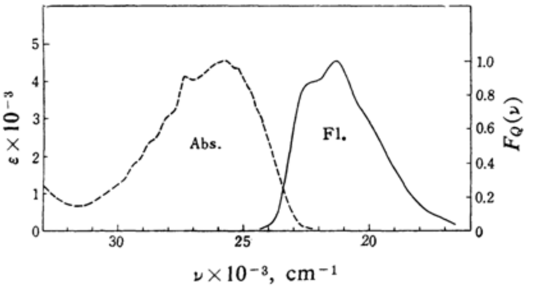

Fig. 3. Fluorescence and absorption spectra of α-anthramine in isooctane. Solute concentration for fluorescence: 8.90×10^{-5} mol./l.

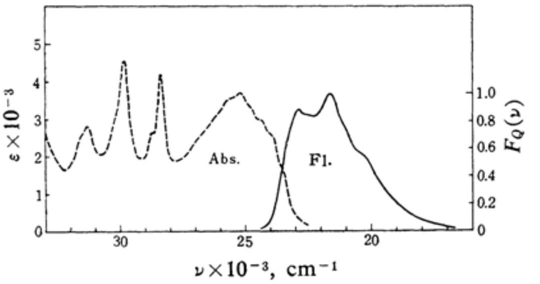

Fig. 4. Fluorescence and absorption spectra of β-anthramine in isooctane. Solute concentration for fluorescence: 3.20×10^{-5} mol./l.

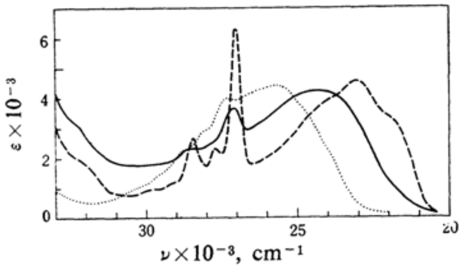

Fig. 5. Absorption spectra of α-anthramine at liquid-nitrogen temperature in 6:1 isopentane—methylcyclohexane mixture. Solid curve, free molecule; dashed curve, spectrum in the presence of triethylamine the concentration of which is 0.2 mol./l.; dotted curve, free molecule at room temperature.

The absorption spectra of α-anthramine at the liquid-nitrogen temperature may be seen in Fig. 5. The solid curve is the spectrum of α-anthramine, while the dashed curve is the spectrum in the presence of triethylamine at a concentration of 0.2 mol./l. In the same figure, the absorption spectrum of α-anthramine at room temperature in the same solvent is cited with a dotted line for the purpose of comparison. The absorption spectra at the liquid-nitrogen temperature have been corrected for the solvent contraction.

Discussion

Jones[12] discussed the effect of substitution on the electronic absorption spectrum of anthracene in terms of the resonance theory. From a consideration along his lines, one may predict whether or not the ^1L_b band will appear in some anthracene derivatives. A substituent group introduced at the β-position lies nearly along the long axis of the molecule. The ^1L_b transition of anthracene has a transition moment along the long axis of the molecule, whereas the ^1L_a has a moment along the short axis. Therefore, the ^1L_b transition is subjected to a greater influence than is the ^1L_a transition by the introduction of the substituent group at the β-position. In fact, the authors have reported that in β-anthrol the ^1L_b band emerged on the lower frequency side of the ^1L_a band.[3,13] In the case of β-anthramine, which has a more electron-donating substituent than does β-anthrol, it is expected that the separation of these two bands will become more distinct. On the other hand, upon substitution in the α-position, the ^1L_a transition is expected to show a large frequency shift as compared with the ^1L_b transition, since the α-substitution seems mainly to perturb transitions along the short axis of the molecule. Consequently, when an amino group is introduced in the α-position of anthracene, the ^1L_a band may probably be displaced to the red, leaving the ^1L_b band in its original position. If this is the case, the ^1L_b band will appear on the higher frequency side of the ^1L_a band. Indeed, the ^1L_b band can be detected in the spectrum of α-anthramine.

When a molecule forms a hydrogen bond, characteristic changes are effected in the positions and intensities of its absorption bands. Thus the authors suggested that the observation of this spectral behavior in hydrogen bonding would be useful for distinguishing and assigning the electronic transitions of a given molecule. The hydrogen-bonding effects on the absorption spectra of the anthramines support the band assignments presented here.

Bands in the Low-Frequency Region. — The absorption spectrum of β-anthramine in the low-frequency region (below 35000 cm^{-1}) consists of an absorption band, II, which has three sharp vibrational components, P, Q and R, with almost equal spacings (ν_{max}: 28370, 29830, 31300 cm^{-1}), and a broad band, I (see Fig. 2). (I, II, etc. refer to the absorption bands in the order of increasing frequency.) Such a spectral constitution suggests that there are two kinds

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[12] R. N. Jones, *Chem. Revs.*, **41**, 353 (1947).

[13] S. Suzuki and H. Baba, *J. Chem. Phys.*, **38**, 349 (1963).

of electronic transitions in this region. This is supported by the following two facts. First, due to the formation of a hydrogen bond, the two absorption bands behave differently in their frequency shift; the shifts of the components, P, Q and R, are quite small compared with the shift of the I band. Second, the mirror image relation between fluorescence and absorption spectra favors the view that there are two transitions in the low-frequency region; the fluorescence spectrum of β-anthramine can be interpreted as corresponding to the I absorption band alone. It has therefore been concluded that in this region β-anthramine has two different electronic absorption bands, namely, the I and II bands.

By reference to the band assignment for the related compound, β-anthrol,[3,13] the I band at the longer wavelengths can safely be assigned to the $^1A \rightarrow {}^1L_b$ transition and the II band, to the $^1A \rightarrow {}^1L_a$. Döller et al.[14] and Förster and Renner[15] have made the same assignment without any comments. In agreement with the expectation from the foregoing qualitative argument, the separation of these two bands is considerably larger in β-anthramine than in β-anthrol. It may be noted that there is a close resemblance in the spectral shapes of β-anthramine and β-anthrol anion.[3]

The low-frequency spectrum of α-anthramine appears to involve only a single electronic transition, but on closer inspection it is found that there are also weak vibrational components, A, B and C, at the shorter wavelength side. As may be seen in Fig, 1, the components, A, B and C, are little shifted by the formation of a hydrogen bond; on the other hand, the band with a maximum at 25910 cm^{-1}, I, is considerably shifted toward the red. From these facts one may assume that there are two different electronic transitions in this frequency region. One is the I transition, and the other is the transition to which the vibrational components, A, B and C, belong, the latter being referred to hereafter as the II transition. Although the observed fluorescence spectrum gives no reliable evidence in support of the above statement, it does not conflict with the assumption of two transitions.

In order to confirm the existence of two different transitions in the frequency region concerned, absorption spectra at the lipuid-nitrogen temperature have been observed (Fig. 5). In general, a lowering of the temperature will be accompanied by a contraction of the solvent and, hence, by an increase in its refractive index. Accordingly, the solvent effect on absorption spectra will be enhanced by the change from room temperature to the liquid-nitrogen temperature. In Fig. 5 it may be seen that the spectrum of α-anthramine, free from hydrogen bonding, is as a whole displaced to the red by lowering the temperature, but the shift of the I band is much larger than that of the vibrational peaks, A, B and C. This indicates that the solvent has different effects on the I and II transitions. When α-anthramine forms a hydrogen bond with triethylamine at room temperature, the I band exhibits a large red shift, whereas the A, B and C peaks show almost no shift in their frequencies. This tendency becomes more pronounced at a low temperature. Thus, as may be seen in Fig. 5, upon the formation of the hydrogen bond with triethylamine at the liquid-nitrogen temperature, the I band is markedly shifted to the red, and, consequently, a clear minimum appears between the I and II bands. The occurrence of such a large separation of the two transitions, I and II, can be interpreted as due to the co-operative effects of hydrogen bonding and the solvent. The absorption spectra of aryl alkali amides have been observed by Döller et al.[14] and Förster and Renner.[15] By referring to their experimental results, one will find that at the liquid-nitrogen temperature α-anthramine does not seem to dissociate a proton, even in the presence of triethylamine.

All of the results of the low-temperature experiments mentioned above show that in the α-anthramine spectrum the vibrational components, A, B and C, belong to an electronic transition which is entirely different in origin from the I transition. As was stated at the beginning of this section, the I band of α-anthramine can reasonably be assigned to the $^1A \rightarrow {}^1L_a$ transition and the II band, to the $^1A \rightarrow {}^1L_b$.

Bands in the High-Frequency Region.—α-Anthramine has two absorption maxima with comparable intensity in this region (above 35000 cm^{-1}). It is evident from their behavior in the hydrogen bond formation that these two bands originate in different kinds of transitions. The one at the lower frequencies shifts toward the red and decreases in intensity, but the other at the higher frequencies shows only a little shift with a slight increase in intensity.

As may be seen in Fig. 2, β-anthramine possesses one intense band, with a weak one on the higher frequency side. The spectral changes caused by hydrogen bonding indicate that the latter belongs to a transition distinct from the former.

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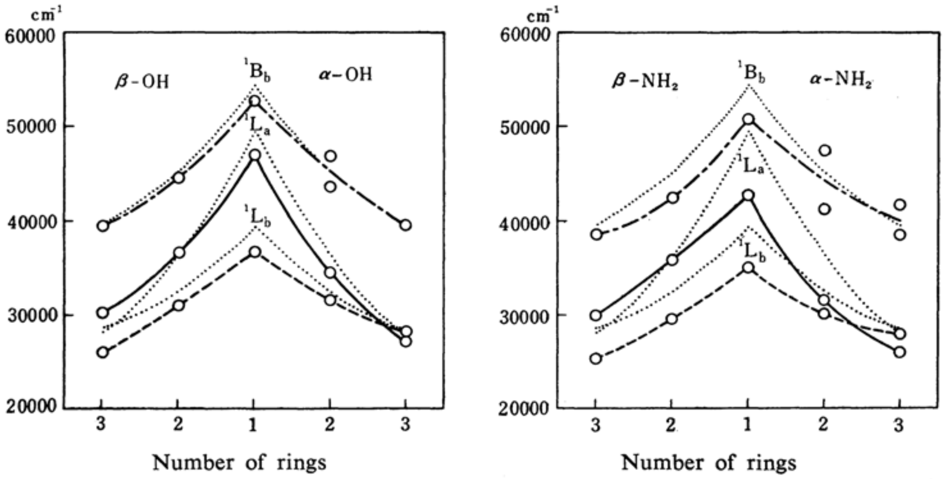
14) E. Döller, Th. Förster and H. Renner, *Z. physik. Chem. Neue Folge*, **15**, 34 (1958).

15) Th. Förster and H. Renner, *Z. Electrochem.*, **61**, 340 (1957).



(a) Hydroxyl derivatives (b) Amino derivatives

Fig. 6. Energy correlation diagrams of substituted aromatic hydrocarbons. Circles represent the experimental electronic energies. (Dotted curve refers to parent hydrocarbons.) --○--: ^1B_b, —○—: ^1L_a, --○--: ^1L_b.

In this region anthracene gives an intense absorption band which is assigned to the $^1A_g \rightarrow {}^1B_{3u}^+$ ($^1A \rightarrow {}^1B_b$) transition.[4-6] The intense band of β-anthramine is considered to correspond to the ^1B_b transition of anthracene. The appearance of two intense bands in α-anthramine is interpreted as follows: In anthracene there are symmetry-forbidden or low-intensity transitions in the vicinity of the ^1B_b transition. The introduction of a substituent into the anthracene molecule leads to the destruction of the symmetry of the molecule; therefore, in α-anthramine the ^1B_b transition may happen to be mixed with a neighboring transition to give two mixed transitions of a high intensity. The situation is similar to the case of high-frequency transition in some α-derivatives of naphthalene.[2]

The Correlation of Energy Levels for Derivatives of Aromatic Hydrocarbons from Benzene to Anthracene.—The papers of this series have revealed the origins of the electronic bands of hydroxyl- or amino-substituted aromatic hydrocarbons. The results are summarized in Fig. 6. In the figure, observed electronic energies are plotted against the number of rings separately for α- and for β-derivatives. A diagram of this kind was previously presented by Klevens and Platt for the polyacene series.[4] Adopting the assignment or classification of the electronic bands proposed by the present authors for the derivatives, one will see that the plots give smooth curves, as in the case of the parent hydrocarbons. Regarding the ^1B_b states of α-derivatives, the average energies of two transitions with comparable intensities fall on smooth curves. (In order to facilitate comparison, curves for the parent hydrocarbons are depicted with dotted lines in the same figure.) An inspection of these curves will show that the substitution effect can be interpreted in terms of the perturbation by the substituent.

From the figure one may find several similarities in behavior of the transitions which belong to the same class. In α-derivatives, the curve for the ^1L_b state declines more gently than in the parent hydrocarbons with an increasing number of rings, while the curve for the ^1L_a state of the same derivatives runs almost parallel with that of the hydrocarbons. Consequently, the curves for the ^1L_a and ^1L_b states cross at a smaller number of rings in both hydroxyl and amino derivatives than in the unsubstituted hydrocarbons. On the other hand, the ^1L_a state of β-derivatives moves downward more slowly than does the ^1L_a state of the parent hydrocarbons with an increasing number of rings, but the curve for the ^1L_b state is nearly parallel with the curve for the same state of the parent hydrocarbons, the former curve being located at lower energies. Thus the interval between the ^1L_a and ^1L_b state increases so that, in the β-derivatives of anthracene, the ^1L_b band is clearly separated from the ^1L_a band, as has already been stated. The behavior of the ^1B_b state of β-derivatives resembles that of the same state of the parent hydrocarbons. In α-derivatives the correlation of the high-frequency bands is somewhat complicated, but their average energies lie on smooth lines. This, in turn, suggests that the ^1B_b state is split into two states by substitution because of mixing with one of the neighboring states. It should be noted here that the state of aniline at 42700 cm^{-1} falls on the intersecting point of the two curves extrapolated from α- and β-amino-derivatives of naphthalene and anthracene. In view of this fact, there is no reason to believe that the corresponding absorption band of aniline should be assigned to a band characteristic of the substitution product, e. g., to a charge-transfer band.

The ^1L_a bands of β-derivatives have a sharp, fine structure, with equally-spaced vibrational peaks.

There are some resemblances in the band shifts produced by the hydrogen bond formation. Thus, in α-derivatives the magnitudes of the frequency shifts of the ^1L_b bands are smaller than those of the ^1L_a bands. On the contrary, the ^1L_a bands of β-derivatives are little shifted, but the ^1L_b bands are noticeably shifted to the red by the formation of hydrogen bonds.[9,13]

Summary

Absorption and fluorescence spectra of α- and β-anthramines have been observed. The $^1A \rightarrow {}^1L_b$ transition, which is masked by the $^1A \rightarrow {}^1L_a$ in anthracene, emerges in both α- and β-anthramines because of the perturbation by the substituent. In β-anthramine, the ^1L_b band is clearly separated from the ^1L_a band. In α-derivatives, the ^1L_b band exists on the higher frequency side of the ^1L_a band. These results may be confirmed by observing the effects of hydrogen bonding on the spectra. At the liquid-nitrogen temperature remarkable changes in the absorption spectrum of α-anthramine occur in the presence of triethylamine; these changes have been interpreted as due to the co-operative effects of hydrogen bonding and the solvent. By using the band assignments proposed in this series of papers, reasonable correlation diagrams of the electronic energy levels have been presented for substituted aromatic hydrocarbons, from benzene to anthracene.

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