Electronic Spectra of Substituted Aromatic Hydrocarbons. III. Anthrols[*]

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Analysis of the electronic spectra of the polyacene series has been successfully made from both experimental[1-3] and theoretical[4-6] viewpoints. The correlation diagram of Klevens and Platt[1] for the energy levels of the polyacenes predicted that in anthracene a weak $^1A_g \rightarrow {}^1B_{3u}{}^-$ ($^1A \rightarrow {}^1L_b$ in Platt's notation[4]) transition is hidden under the stronger $^1A_g \rightarrow {}^1B_{2u}$ ($^1A \rightarrow {}^1L_a$) transition. (Here the group theoretical notation is the same as that used in the preceding paper[7] of this series.) The above prediction was supported by Pariser's calculations[6]. On the other hand, experimental attempts[3,8] to obtain direct evidence for the existence of the hidden transition have failed. It seems impossible at the present time to detect the hidden transition in the spectrum of anthracene itself.

The situation may be different in the case of substitution products of anthracene. When a substituent group is introduced into anthracene, the two transitions in question, $^1A \rightarrow {}^1L_b$ and $^1A \rightarrow {}^1L_a$, undergo changes different both in location and in intensity, on account of differences in their symmetry types. As a result, it is possible that the $^1A \rightarrow {}^1L_b$ transition may emerge from the $^1A \rightarrow {}^1L_a$ transition. With this in mind, the electronic spectra of α- and β-anthrol have been investigated in the present study. It has been proved that the $^1A \rightarrow {}^1L_b$ transition does appear in the spectrum of β-anthrol.

Experimental

Materials.—α-Anthrol was prepared by fusing potassium anthracene-α-sulfonate with potassium hydroxide[9]; it was recrystallized several times from aqueous ethyl alcohol; m. p. 151°C (literature, 152~152.5°C[10]). β-Anthrol was prepared by fusion of sodium anthracene-β-sulfonate with potassium hydroxide[11], and it was repeatedly recrystallized from benzene; m. p. 264~266°C under reduced pressure in a sealed tube (literature, 254~256°C[10]). Isooctane (2,2,4-trimethylpentane; Enjay Co., Inc., U. S. A.) was purified by distillation over phosphorus pentoxide.

Apparatus and Procedure.—Absorption spectra were obtained at 20°C in the same manner as in the preceding paper[7], with a Hitachi photo-electric spectrophotometer of the EPU-2A type.

Fluorescence spectra were measured at room temperature by attaching a Hitachi fluorescence accessory of the L-3 type to the spectrophotometer. The 365 mμ line of a mercury lamp was used as an exciting light; the slit width was fixed at 0.2 mm. It was found that while a solution of α- or β-anthrol was being illuminated by the exciting light, the intensity of the fluorescence was considerably reduced. This difficulty was overcome by using a light of an extremely low intensity and by measuring the fluorescence quickly.

For the calibration of the spectral energy of the fluorescence, a standard tungsten filament lamp was used. The brightness temperature of the filament was measured with an optical pyrometer, and the true temperature was determined to be 2350°K in the usual way. From the spectral energy distribution (based on Planck's law) of a black body at this temperature and the spectral emissivity of tungsten, the spectral energy distribution of the

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1) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
2) D. S. McClure, ibid., **22**, 1668 (1954).
3) J. W. Sidman, ibid., **25**, 115 (1956).
4) J. R. Platt, ibid., **17**, 484 (1949).
5) W. Moffitt, ibid., **22**, 320 (1954).
6) R. Pariser, ibid., **24**, 250 (1956).
7) H. Baba and S. Suzuki, This Bulletin, **34**, 82 (1961).
8) E. Clar, *Spectrochim. Acta*, **4**, 116 (1950).
9) R. E. Schmidt, *Ber.*, **37**, 66 (1904).
10) K. Lauer, ibid., **70**, 1127 (1937).
11) K. Lagodzinski, *Ann.*, **342**, 59 (1905).

standard lamp was obtained. The transmittance of the envelope of the lamp was assumed to be constant over the range from 380 to 600 mμ. The observed fluorescence spectra were thus corrected to quantum fluorescence spectra by following the procedure of Melhuish[12]. Allowance was made for the reabsorption of fluorescence in the region where fluorescence and absorption overlap.

Results and Discussion

The absorption spectra of α- and β-anthrol in an isooctane solution are shown in Fig. 1, where the spectrum of the parent hydrocarbon, anthracene, is also given for the sake of comparison. Each of the spectra can be divided into two distinguishable parts, with the boundary at about 35000 cm^{-1}. In this paper, particular attention will be devoted to the electronic transitions situated in the low frequency region ($<$35000 cm^{-1}).

As is seen in the figure, anthracene shows in the low frequency region a single electronic absorption band with a sharp vibrational structure. This band has been conclusively assigned to the $^1A \rightarrow {}^1L_a$ transition[3]. (For brevity this will hereafter be called the ^1L_a transition.)

The transition of α-anthrol in the low frequency region is undoubtedly analogous to the ^1L_a transition of anthracene, though it is shifted as a whole to the red and its vibrational structure is less sharp. It appears at first sight that the spectrum of β-anthrol involves, in the same region, only one electronic band corresponding to the above-mentioned transition of α-anthrol. However, as will be described below, detailed examination of the β-anthrol spectrum reveals that there exist two different transitions in the frequency region under consideration.

Vibrational Analysis.—The ^1L_a transition of anthracene has a prominent progression whose members are the vibrational components P, Q, etc. shown in Fig. 1, where P is the 0–0 transition. The spacings of these components are almost constant (about 1400 cm^{-1}) and are related to a totally symmetric carbon stretching vibration[3,13].

The frequencies of the principal vibrational components for the absorption bands of α- and β-anthrol are given in Table I, together with their differences. The vibrational components P, Q, etc. in α-anthrol are almost equally spaced; they are considered to correspond, respectively, to the components P, Q, etc. in the parent molecule. Thus, the α-anthrol transition, to which the components P, Q, etc. belong, must be of the ^1L_a type.

There are five main vibrational components, A, B, P, Q and R, in the β-anthrol spectrum. Of the intervals of these components, the one between B and P is exceptionally large, so that it is not possible to regard all five components as members of a single progression. One may thus reasonably assume that there are two different overlapping transitions and that the

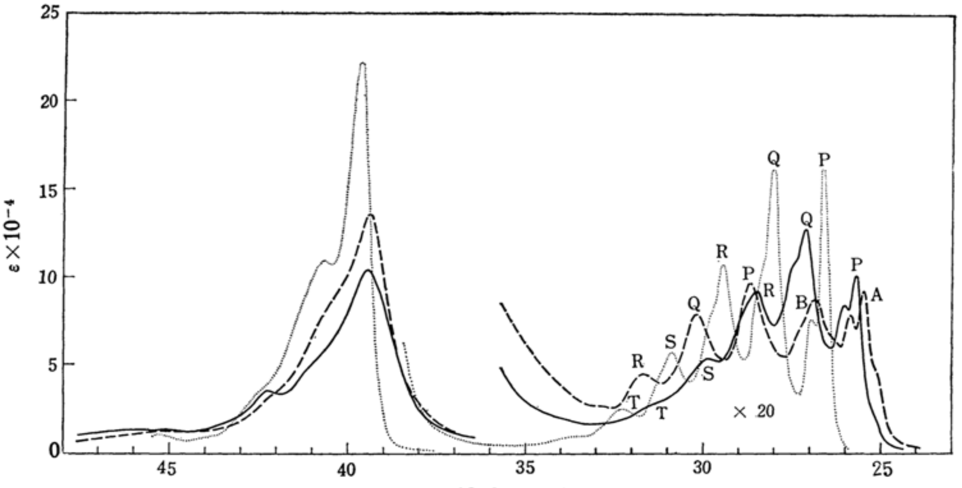

Fig. 1. Absorption spectra of α-anthrol (——), β-anthrol (- - -) and anthracene (······) in isooctane.
The spectrum of anthracene is taken from American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 170.

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[12] W. H. Melhuish, *J. Phys. Chem.*, 64, 762 (1960).

[13] S. Sambursky and G. Wolfsohn, *Trans. Faraday Soc.* 36, 427 (1940).

TABLE I. VIBRATIONAL COMPONENTS OF ABSORPTION BANDS FOR ANTHROLS

	α-Anthrol				β-Anthrol				β-Anthrol negative ion			
			cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}
^1L_b					A	(0-0)	25480	1390	ν_{max}		24210	
					B	(0-1)	26870	(1840)				
^1L_a	P	(0-0)	25730	1410	P	(0-0)	28710	1490	P	(0-0)	28380	1430
	Q	(0-1)	27140	1400	Q	(0-1)	30200	1500	Q	(0-1)	29810	1470
	R	(0-2)	28540	1360	R	(0-2)	31700		R	(0-2)	31280	
	S	(0-3)	29900	1400								
	T	(0-4)	31300									

components A and B belong to one transition and P, Q and R to the other. These two transitions will be referred to as I and II respectively.

Relation between Fluorescence and Absorption. —The fluorescence spectra of α- and β-anthrol in isooctane solution are shown in Figs. 2 and 3, where $F_Q(\nu)$ denotes the relative fluorescence quantum yield per unit frequency interval at frequency ν. In the figures, the absorption spectra are also given for ready comparison.

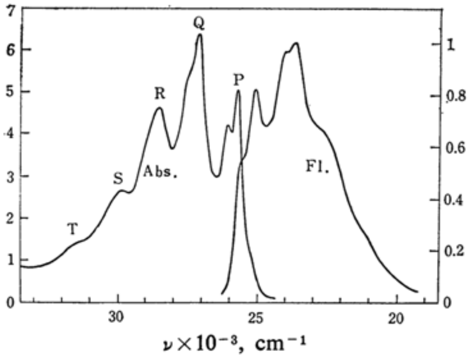

Fig. 2. Fluorescence and absorption spectra of α-anthrol in isooctane. The solute concentration for fluorescence: 5.22×10^{-5} mol./l.

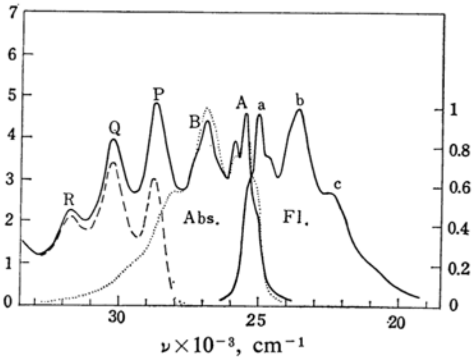

Fig. 3. Fluorescence and absorption spectra of β-anthrol in isooctane. The solute concentration for fluorescence: 4.16×10^{-5} mol./l. See the text for the dotted and broken line curves.

The fluorescence of anthracene is known to be due to the $^1B_{2u}\rightarrow{}^1A_g$ transition[3], which corresponds to the absorption transition of the ^1L_a type. A mirror symmetry has been found between the fluorescence and absorption spectra for anthracene[14]. As is seen in Fig. 2, the fluorescence of α-anthrol has an approximate mirror image relation with the absorption that has been assigned to the ^1L_a transition.

Apparently no such relation exists between the fluorescence and absorption spectra of β-anthrol. In attempting to explain this anomalous fact, let it be assumed, as before, that the low frequency absorption of β-anthrol is due to two overlapping electronic transitions, I and II. It is generally postulated that fluorescence originates in a single electronic transition, which corresponds in most cases to the lowest energy transition. Accordingly, the fluorescence of β-anthrol should be related to that part of the absorption which corresponds to the lower energy transition, I, of the two overlapping transitions.

The above situation can be understood on inspection of the dotted line curve in Fig. 3 which represents the mirror image of the fluorescence spectrum. It is seen that the vibrational peaks a and b of the fluorescence correspond to the absorption peaks A and B respectively. There is another peak, c, in the fluorescence; the corresponding peak cannot be found in the absorption spectrum, probably because it is masked by the absorption due to the higher energy transition, II.

If one is allowed to approximate the absorption due to transition I by the mirror image of the fluorescence, the absorption due to transition II alone may be determined. The latter absorption is depicted in Fig. 3 as a

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[14] G. Kortüm and B. Finckh, *Z. physik. Chem.*, **B52**, 263 (1942).

broken line curve, wihch is obtained by subtracting the absorption of transition I (dotted curve) from the total absorption (solid curve).

Spectral Changes Accompanying Dissociation of Proton.—The foregoing arguments suggest that two absorption bands due to different electronic transitions appear in the low frequency region when a hydroxyl group is introduced into anthracene at the β-position. This phenomenon is presumably caused by the electron-donating character of that group. It is then to be expected that such a phenomenon will be more distinctly observed in the negative ion of β-anthrol, since the $-O^-$ group is of a more electron-releasing nature than the $-OH$ group. Measurements have therefore been made of the absorption and fluorescence spectra of β-anthrol in a 0.4% aqueous solution of sodium hydroxide[15]. The results are shown in Fig. 4; the frequencies of the absorption maxima are recorded in Table I.

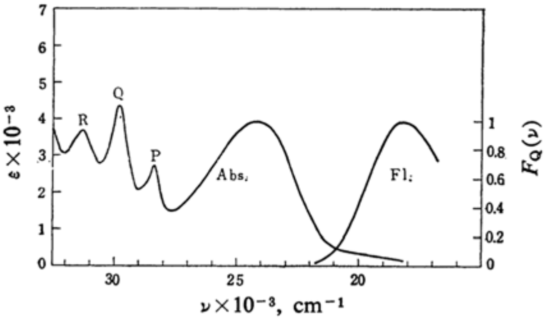

Fig. 4. Fluorescence and absorption spectra of β-anthrol in 0.4% sodium hydroxide solution. The solute concentration for fluorescence: 9.78×10^{-5} mol./l.

As was expected, the negative ion gives two electronic absorption bands at about 24000 cm^{-1} and 30000 cm^{-1}, with a clear minimum between them. Comparison of the absorption spectra for the neutral molecule and the negative ion of β-anthrol shows that, upon dissociation of the proton, transition I is markedly displaced to the red and its vibrational structure is smoothed out, while transition II is shifted only slightly to the red. As a result, the two transitions are separated from each other in the negative ion. The fluorescence of the ion is seen to correspond to the absorption at 24000 cm^{-1}.

Assignment.—It has already been stated that the low frequency absorption of α-anthrol is to be assigned to the ^1L_a transition.

As to the absorption spectrum of β-anthrol in the low frequency region, the results of the present experiments indicate that, in all probability, it consists of two different electronic transitions. It is then natural to consider that the ^1L_b transition, which is believed to be hidden under the ^1L_a transition in the parent molecule, emerges owing to the perturbation of the hydroxyl group at the β-position. If this is the case, the next problem is to decide which of the two transitions, I or II, is of the ^1L_b type.

In order to get a clue to this problem, reference will be made to the absorption spectra of α- and β-naphthol. According to the experimental results reported in the preceding paper[7], substitution of a hydroxyl group into naphthalene at the α-position gives rise to a red shift in both the ^1L_a and ^1L_b transitions. On the other hand, when the substitution is made at the β-position, the ^1L_b transition is noticeably shifted to the red and intensified, whereas the ^1L_a transition is slightly displaced to the blue with a reduction in intensity.

Now, let it be assumed that similar spectral changes take place in the ^1L_a and ^1L_b transitions in going from anthracene to the anthrols. Then the ^1L_b transition is to be expected to appear in β-anthrol on the lower frequency side of the ^1L_a transition, while it remains under the ^1L_a transition in the case of the α-isomer. Transitions I and II of β-anthrol may thus be assigned to the ^1L_b and ^1L_a transitions respectively. The same assignment applies to the transitions of the negative ion of β-anthrol.

It is seen from the observed spectral data that the above assignment in turn leads to the following conclusion: The ^1L_b transition is situated at lower frequencies and is of a higher intensity in β-anthrol (or its negative ion) than in anthracene, while the reverse is true of the ^1L_a transition. The assignment and the interpretation of the individual vibrational peaks are given in Table I for α-anthrol and for the neutral molecule and the ion of β-anthrol.

The effect of substitution on electronic transitions was discussed for anthracene by Jones[16] in terms of the resonance theory. It was suggested that the shift of a transition due to substitution should depend both upon the direction of the electric moment associated with the transition and upon the position of the substitution. Since the ^1L_b and ^1L_a transitions are polarized along the long and short molecular axes respectively, it may be said that the present assignment of the transitions for α- and β-anthrol is compatible with the view of Jones.

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[15] The absorption spectrum of α-anthrol in the same solution was found to be subject to change during the measurement, so that it is not reported on here.

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

Mention should also be made of the high frequency transitions. The strong absorption of anthracene at 40000 cm^{-1} has been assigned to a $^1A_g \rightarrow ^1B_{3u}{}^+$ ($^1A \rightarrow ^1B_b$) transition[4,6]. It is seen in Fig. 1 that this absorption does not undergo a substantial change when passing from the parent molecule to the anthrols, although a red shift and a change of intensity are seen to occur. Apparently the anthrols have one or two other transitions in the higher frequency region. Discussion of these transitions will be undertaken in a later paper[17].

Summary and Conclusion

The present study of the absorption and fluorescence spectra of α- and β-anthrol has made it possible to explain in a satisfactory manner the origins of their lower electronic transitions. The absorption of α-anthrol in the low frequency region is due to a single electronic transition, which can be assigned to the ^1L_a transition. It is concluded on the basis of vibrational analysis, relation between fluorescence and absorption, and spectral changes accompanying dissociation of the proton that the corresponding absorption in β-anthrol consists of two overlapping electronic bands; this conclusion is further supported by an investigation of spectral changes accompanying the formation of a hydrogen bond between β-anthrol and dioxane[17]. Of the two overlapping bands, the one at the lower frequencies is reasonably assigned to the ^1L_b transition, which has not been found in the spectrum of anthracene, and the other to the ^1L_a transition.

It is of interest to apply to other anthracene derivatives the idea that substitution at the β-position causes the hidden ^1L_b transition of anthracene to appear at lower frequencies. In this connection it is worthy of note that the absorption spectra of β-aminoanthracene and β-acetylanthracene exhibit abnormal features in the lowest frequency region[16]. This fact may perhaps be best explained in the light of the present interpretation of the spectrum of β-anthrol.

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[17] S. Suzuki and H. Baba, to be published in *J. Chem. Phys.*