

to be amenable to a continuum treatment but must be approached on a microscopic level.

More specifically, the data on MnSO_4 and MnBDS in dioxane-water mixtures are explained most simply by assuming that the ions are hydrated over the whole solvent composition range studied—dioxane molecules are excluded from the first coordination shells of the ions. In the case of the acetone-water and methanol-water systems, there is a competition between the water and the polar organic molecules for positions in the first coordination sphere of the ions. This competition is modified by the over-all composition of the solvent. On the water-rich side of the inflection point, the competition takes place in a water structure containing the organic polar solvent; but on the organic-rich side, it seems to occur in a quite different solvent. This is not surprising since the very strong and specific interactions between polar solvents have been known for a long time. These strong interactions must be reflected in the electrolyte properties. It must also be true that there are far more solvent systems of the methanol-water type than of the dioxane-water type. The sec-

ond type seems really to be a special case of polar solvent mixtures.

Unfortunately, conductance data alone are not sufficient to clarify this problem since we are examining second- and third-order effects. More direct evidence on such specific solvent interactions is needed. This can be provided both by conventional spectroscopic techniques and by the newer relaxation methods. In this Laboratory we are extending the conductance experiments to different solvent mixtures and examining the same systems by ultraviolet-visible and e.s.r. spectroscopy. At the same time we are using ultrasonic absorption and Wien effect dispersion measurements to probe further into the mechanism of ion association in such systems.

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[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Molecular Complexes and Their Spectra. XVI. Complexes of Anthracene and Phenanthrene with Iodine¹

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Formation constants and molar absorptivities for complexes of iodine with anthracene and phenanthrene have been remeasured by studying the charge-transfer absorption. These complexes are extremely difficult to study quantitatively; they represent a classic example of the problems in studying weak complexes. The data were analyzed following procedures recommended by Briegleb. The value of K at 23° is 3.0 ± 0.2 for the anthracene complex and 0.45 ± 0.06 for the phenanthrene complex. The molar absorptivity for the anthracene complex at 430 $m\mu$ is about 550 ± 300 . These values of K and ϵ for the anthracene complex may still be in considerable error. It is believed that the peak of the charge-transfer band is less than 430 $m\mu$. The molar absorptivity for the phenanthrene complex at the peak of the charge-transfer band ($\lambda_{CT} = 364 m\mu$) is 7100 ± 1200 . A comparison of data for complexes of I_2 with a series of polynuclear aromatic donors indicates that the change in properties with an increasing number of rings is more gradual than reported earlier. No evidence is found for 2:1 complexes of iodine with anthracene in excess I_2 .

Introduction

Some time ago Bhattacharya and Basu reported on the charge transfer spectra of complexes between iodine and several polynuclear aromatic hydrocarbons.⁴ Since then, these measurements have achieved a special significance for several reasons. For one thing, the frequencies of the charge transfer band have been used, together with the theory, to deduce the ionization potentials of these interesting hydrocarbons. Secondly, these complexes are important as examples of complexes with a very large donor molecule and a relatively small acceptor. Murrell,⁵ for example, has used the values of intensities and formation constants to support his argument that the intensities will decrease and the formation constants will increase as the size of the donor increases. Finally we note that the base strength of these hydrocarbons has been linked with their carcinogenic activity.⁶

The values reported by Bhattacharya and Basu⁴ for the formation constant and molar absorptivity of the

phenanthrene- I_2 complex ($K = 1.06$ in units of l./mole; $\epsilon_a = 1420$ at 394 $m\mu$) differ by about a power of ten from those reported earlier by Andrews and Keefer⁷ for the same complexes ($K = 0.15$ l./mole; $\epsilon_a = 13,000$ at 396 $m\mu$). Although the value for K found by Bhattacharya and Basu agreed in order of magnitude with that found by Kortüm and Vogel in a series of solubility studies,⁸ it was thought that the importance of this complex justified reinvestigation of these measurements.

Furthermore, the unusual values of the formation constant, of the wave length of the charge transfer band, and of the molar absorptivity reported by Bhattacharya and Basu for the anthracene- I_2 complex ($K = 52$ l./mole; $\lambda_m = 430 m\mu$, and $\epsilon = 112$) suggested that the latter system should also be reinvestigated.

Briegleb⁹ has also criticized these results of Bhattacharya and Basu,⁴ pointing out that the quantity $[\text{Ar}]\cdot[\text{I}_2]/D$, calculated from their data, does not vary over the concentrations of donor and iodine used in their studies. For weak complexes, at concentrations of donor and iodine such that very little complex is formed in solution, this quantity is constant and equal to $1/K\epsilon$. It is only when the concentration of donor is increased to the point that an appreciable fraction of I_2

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(4) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

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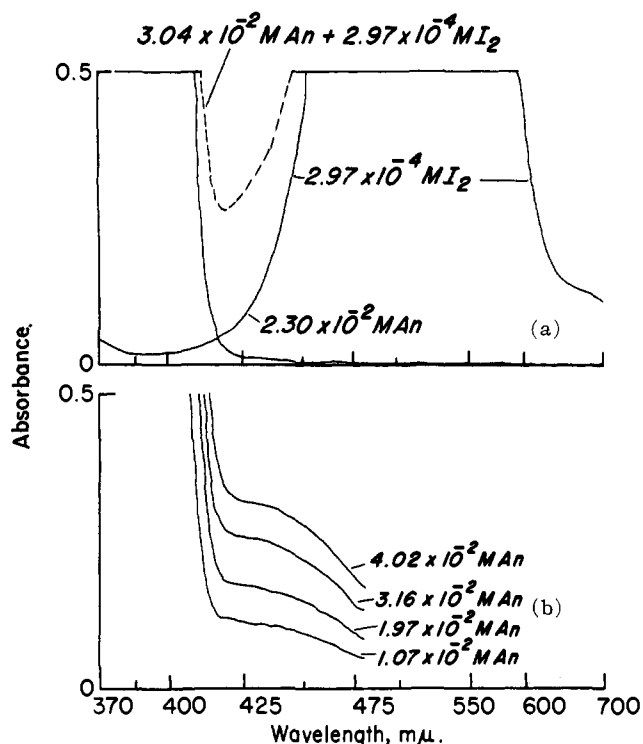


Fig. 1.—Spectrum of anthracene- I_2 in CCl_4 : (a) upper, with CCl_4 in the reference beam; (b) lower, with a solution of I_2 in the reference beam. In the lower graph the anthracene concentration is varying, so the absorption due to uncomplexed anthracene increases also. The cell lengths were 10 cm. In the lower curves, the initial concentration of I_2 was $3.10 \times 10^{-4} M$; concentrations of anthracene are given.

is complexed that a plot of this quantity *vs.* the donor concentration gives a line with slope different from zero so that K and ϵ can be determined separately by the Scott modification¹⁰ of the Benesi-Hildebrand equation.¹¹ Because these complexes form classic examples of this typical experimental problem, and because of the great interest in these complexes, we thought it worthwhile reinvestigating these two systems.

Experimental

Chemicals.—C.P. iodine was sublimed under reduced pressure and stored in a desiccator over Drierite. Carbon tetrachloride (Allied Chemical reagent grade) and methylene chloride (Fisher Spectranalyzed) were dried over calcium chloride and Drierite, respectively, and distilled under conditions which excluded atmospheric moisture.

Eastman anthracene (blue-violet fluorescent) recrystallized from absolute ethanol was used in some of the experiments. A sample of purified anthracene, supplied by Dr. N. C. Yang, was used in others. The ultraviolet spectra of these samples in absolute ethanol were in agreement with the spectrum of anthracene recorded in the literature.¹²

The experiments involving anthracene in CCl_4 were complicated by a slow reaction occurring in dilute solutions and resulting in the disappearance of anthracene. However, concentrated stock solutions could be kept for some time without reaction, and the reaction in dilute solutions was too slow to affect our measurement appreciably since measurements were made within a few hours of preparation of solutions.

Further evidence that CCl_4 is not a good "inert" solvent for anthracene was provided by a marked red shift (by 15–20 $m\mu$) of the first strong absorption band of anthracene in CCl_4 solutions, as compared with solutions in ethanol or *n*-heptane.

No evidence of reaction was noted for any of the other solutions.

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(12) American Petroleum Institute Research Project 44, "Ultraviolet Spectral Data," Carnegie Institute of Technology, Pittsburgh, Pa., and Bureau of Standards, Washington, D. C.

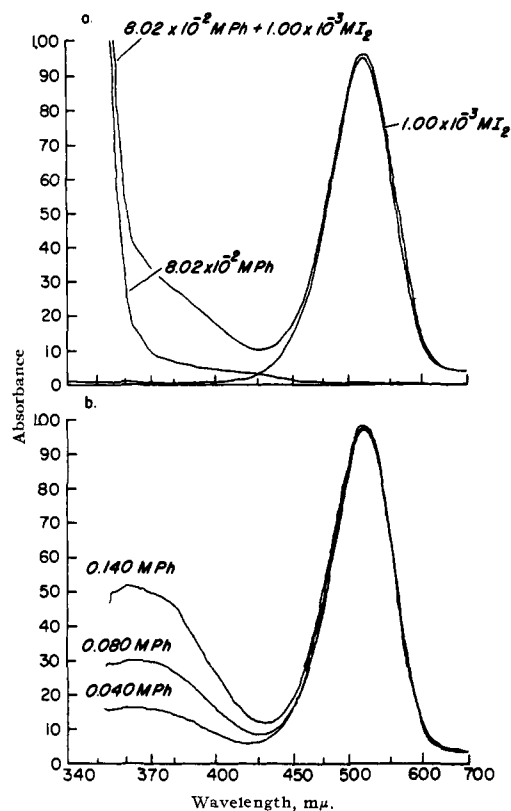


Fig. 2.—Spectrum of phenanthrene- I_2 in CCl_4 solutions: (a), with pure solvent in the reference beam; (b), with solutions of phenanthrene in the reference beam. The concentration of I_2 in (b) was $9.47 \times 10^{-4} M$. The path length was 1.0 cm.

Eastman White Label phenanthrene was used without further purification for most of the studies. In carbon tetrachloride there was a small blue shift of the spectrum from that in *n*-heptane.

Phenanthrene, at the concentrations used in the studies of the phenanthrene-iodine complex, exhibited a peak at 380 $m\mu$, apparently due to about 0.05% anthracene as an impurity. An unsuccessful attempt was made to remove the anthracene by fractional crystallization from absolute ethanol.

The phenanthrene was used without further purification, because the very small amount of anthracene impurity should not affect the measurements of the phenanthrene-iodine complex. To verify this assumption, a few experiments were carried out with a sample of anthracene-free phenanthrene supplied by Dr. R. E. Buckles.¹³ No changes in the results for the complex were observed.

Absorption Spectra.—The spectra were recorded with a Beckman Model DK-2 spectrophotometer. Quartz cells were used.

(i) **The Anthracene-Iodine Complex in CCl_4 .**—The iodine concentration was about $3 \times 10^{-4} M$ and the anthracene concentrations were from 1 to $4 \times 10^{-2} M$. Higher concentrations of anthracene could not be used because of its limited solubility in carbon tetrachloride. Weak absorption by the complex could be detected around 430 $m\mu$ with these solutions in 10-cm. cells.

The spectrum of iodine and anthracene in CCl_4 , with pure CCl_4 as the reference, is shown in Fig. 1a. Interference from the strong absorption bands of free anthracene and free iodine obscures the absorption by the complex. When a solution of iodine in CCl_4 of the same concentration as that in the complex solution was placed in the reference beam, absorption attributable to the complex could be seen as a shoulder at about 430 $m\mu$ on the anthracene peak at 420 $m\mu$ (Fig. 1b). Absorbances of solutions of complex at 430 and 450 $m\mu$, with pure iodine solutions as reference, were corrected for absorption due to the free anthracene.

(ii) **The Anthracene- I_2 Complex in CH_2Cl_2 .**—Iodine concentrations were about $5 \times 10^{-4} M$, and concentrations of anthracene were from 3 to $10 \times 10^{-2} M$. The 10-cm. cells were used. Iodine solutions were again used as the reference and the absorbance of the complex at 430 and 450 $m\mu$ obtained as before.

(iii) **Anthracene in CCl_4 (Excess Iodine).**—Anthracene was about $10^{-3} M$, and iodine concentrations were from 3 to $7 \times 10^{-2} M$. Using 1-cm. cells with an iodine solution in the reference beam, it was possible to obtain absorption attributable to the

(13) Preparation of this sample is described by R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955).

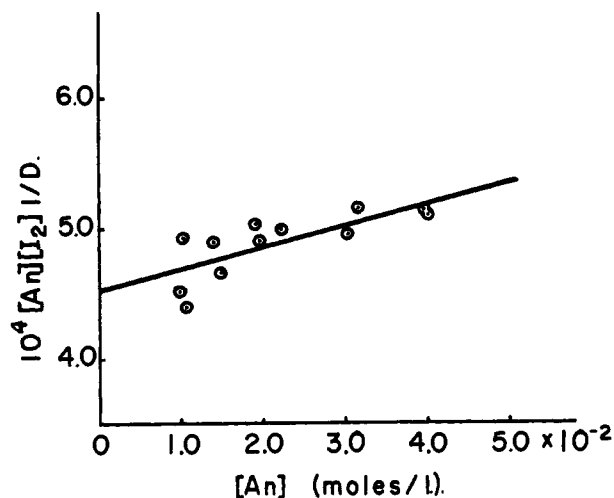


Fig. 3.—Scott equation plotted with the data for the anthracene- I_2 complex in CCl_4 .

complex around $425 \text{ m}\mu$. However, these measurements were not very accurate due to the small absorbances.

(iv) **Phenanthrene-Iodine Complexes in CCl_4 .**—Iodine concentrations were from 0.2 to $1.0 \times 10^{-3} M$; phenanthrene concentrations varied from 0.1 to $8 \times 10^{-1} M$. With pure CCl_4 in the reference beam, absorption attributable to the complex was detected in the region from 360 to $390 \text{ m}\mu$ (Fig. 2a). In order to eliminate interference by the uncomplexed phenanthrene, a solution of phenanthrene was used in the reference beam, yielding a broad band due to the complex with maximum at $364 \text{ m}\mu$ (Fig. 2b). In general, 1-cm. cells were used for these studies. In one experiment 10-cm. cells were used, with an iodine solution in the reference beam. In this experiment interference from uncomplexed donor obscured the region around $364 \text{ m}\mu$, but measurements could be made at $394 \text{ m}\mu$.

In an attempt to estimate ΔH_f for this complex, spectra of the phenanthrene-iodine solutions were recorded at 3° . (All other spectra were recorded at about 22 – 23° .) The temperature regulated cell holder for the Beckman DK-2 was used, and the temperature was adjusted by passing water from an ice bath through the cell holder. Absorbances of the complex were determined at 394 , 370 , and $364 \text{ m}\mu$ in the same way as for the other studies.

Results

Typical spectral results for the anthracene- I_2 complex are presented in Fig. 1, and for phenanthrene- I_2 in Fig. 2. The difficulty due to interference from uncomplexed donor and I_2 is obvious. The low absorbance of the complex in these solutions makes it very difficult to obtain reliable results, owing to the error in the accurate measurement of small absorbances. However, it is not possible to improve these measurements very much because of: (1) the uncertainty about the validity of attempts to correct for interference by use of solutions in the reference beam; (2) the limited solubility of the donor in inert solvents (the anthracene solutions were almost saturated), thus preventing us from raising the concentration of the complex by increasing the donor concentrations; and (3) the uncertainty about stoichiometry and further reactions in solutions with excess I_2 . Hence it was not possible experimentally to increase the concentration of the complex in solution by increasing concentration of either donor or acceptor until accurate absorbances for the complex could be measured.

The data were analyzed following the procedure recommended by Briegleb,⁹ because it seems to make the best use of the experimental data, and because it gives the random error in the results. In this procedure the absorbance D_{ik} of each solution k is recorded at several wave lengths, i , corrected for the absorbance due to free donor or acceptor to give ${}^cD_{ik}$ and then converted to relative absorbances, ζ_{ik} . These values are averaged over all solutions to give a mean value, ζ_i , at each wave length. Dividing the ${}^cD_{ik}$ values by the ζ_i 's, the absorb-

ance ${}^cD_{mk}$ at a particular reference wave length, λ_m , is calculated for each solution. These values, which should all be the same for a given solution, are then averaged over the wave lengths to give a mean absorbance, \bar{D}_k , characteristic of the absorption at λ_m for each solution, k . In this way, full use is made of the data at different wave lengths.

The mean absorbances, \bar{D}_k , are now used in the Scott equation¹⁰ to obtain slope ($1/\epsilon_m$) and intercept ($1/K\epsilon_m$)

$$\frac{[Ar][I_2]l}{\bar{D}_k} = \frac{1}{K\epsilon_m} + \frac{1}{\epsilon_m} [Ar] \quad (1)$$

The fit is made by a least squares analysis which gives not only the values of $1/\epsilon$ and $1/K\epsilon$, but also the uncertainties in each.⁹ In our analysis, no special weighting procedure was used. Since Briegleb⁹ gives two examples of this procedure in detail, we shall give only the results of our analysis in Table I for the anthracene- I_2 complex and in Table II for the phenanthrene- I_2 complex.

TABLE I
RESULTS FOR THE ANTHRACENE- I_2 COMPLEX^a

	$1/K\epsilon (\times 10^4)$	$1/\epsilon (\times 10^3)$	ϵ	K
An- I_2 in CCl_4	4.52 ± 0.11	0.17 ± 0.04	600 ± 200	3.7 ± 1.0
An- I_2 in CH_2Cl_2	7.84 ± 0.48	0.19 ± 0.07	500 ± 300	2.4 ± 1.0
			Av. 550 ± 300	3.0 ± 1.0

^a Data for 2 wave lengths (430 and $450 \text{ m}\mu$) and from 12 solutions were used to obtain the value reported here.

TABLE II
RESULTS FOR THE PHENANTHRENE- I_2 COMPLEX IN CCl_4
SOLUTION^a

$t, ^\circ C.$	$1/K\epsilon (\times 10^4)$	$1/\epsilon (\times 10^4)$ ($\lambda 370$)	ϵ_{370}^b	K
23	3.491 ± 0.004	1.44 ± 0.20	6950 ± 1100	0.45 ± 0.06
3	2.67 ± 0.04	Indeterminate

If ϵ_{370} at $3^\circ = \epsilon_{370}$ at 23° , then $\Delta H = 1.6 \pm 0.5 \text{ kcal./mole}$.

^a Data at 3 wave lengths from 17 solutions were used to obtain these values. However, the value of $1/\epsilon$ is determined primarily by data from only 4 solutions of relatively high phenanthrene concentrations between 0.1 and $0.8 M$. ^b $\epsilon_{364} = \epsilon_{max} = 7100 \pm 1200$.

The relatively small uncertainties in K and ϵ reported in Tables I and II are misleading, especially for the anthracene- I_2 complex. As stated above, it is not possible to adjust concentrations so that an appreciable fraction of the iodine is present in the complex; hence, in eq. 1 the left-hand side does not change very much as the concentration of anthracene is varied. This situation is illustrated in Fig. 3, which shows the graph of the Scott equation for our data for anthracene- I_2 in CCl_4 . As we see there, a line with zero slope and with $1/K\epsilon = 4.88 \times 10^{-4}$ gives almost as good a fit as the line obtained from the least squares analysis. The sum of the squares of the standard deviations of the ordinate from the line with zero slope is only about twice as large as that sum for the least squares line. Thus, $1/K\epsilon$ is determined quite accurately, but the separation into K and ϵ reported in Table I may be in error by a considerable amount.

We believe that the separation into K and ϵ for the phenanthrene- I_2 complex has been done with reasonable certainty in Table II, and that the uncertainties reported there are realistic. The problems of spectral interference and of solubility of the donor were considerably less difficult than for the anthracene- I_2 studies.

The scatter in our experimental values in Fig. 3 is due almost entirely to the random error in measuring the absorbance, just as in the discussion given by Briegleb.⁹ This error is exhibited as a scatter of the values of ${}^cD_{mk}$ about the mean value of \bar{D}_k and amounts to

about ± 0.004 absorbance unit. A propagation of error analysis, assuming this to be the only error, gives predicted deviations in the value of the ordinate in eq. 1 equal within a factor of 2 to the observed deviations of the ordinate from the least squares line.

Because the values computed for the ordinate in eq. 1 from our data at 3° for the phenanthrene- I_2 complex do not vary significantly over the range of donor concentrations studies, it was possible to determine only the product $(1/K\epsilon)$ and not K and ϵ separately. We obtained an estimate for the enthalpy of formation, ΔH , by plotting $\log(1/K\epsilon)$ values at the two temperatures *vs.* $1/T$, determining the slope, and converting it to ΔH in the usual way. This procedure assumes that ϵ does not change with temperature, and so does not affect the slope. We believe this assumption is valid, partly because the temperature change is so small, but mostly because the values of the mean relative absorbances, ζ_i , at 364, 370, and 394 $m\mu$ are the same at the two temperatures, suggesting that the band shape does not change appreciably.

The results from this investigation are compared with those from the earlier workers^{4,7,8} in Table III.

TABLE III

COMPARISON OF VALUES OF K_f AND ϵ FOR THE ANTHRACENE AND PHENANTHRENE COMPLEXES OF I_2

	$10^{-3}K\epsilon(\lambda)$	K	$\epsilon(\lambda)$
Anthracene- I_2 in CCl_4			
B. and B. ^a	0.58(430)	52	112(430)
This study	2.22(430)	3.7	600(430)
Anthracene- I_2 in CH_2Cl_2			
This study	1.20(430)	2.4	500(430)
Phenanthrene- I_2 in CCl_4			
B. and B. ^a	1.51(394)	1.06	1520(394)
A. and K. ^b	1.95(396)	0.15	13000(396)
This study	1.98(394)	0.45	{4400(394); 7100(364)}
K. and V. ^c		1.2	

^a Bhattacharya and Basu, ref. 4. ^b Andrews and Keefe, ref. 7. ^c Kortüm and Vogel, ref. 8.

Anthracene with Excess I_2 in CCl_4 .—Recently Chowdhury and Basu have reported a study of the spectra of complexes between polynuclear aromatic hydrocarbons and excess iodine.¹⁴ They interpret their studies as indicating molecular complexes of stoichiometry: $D \cdot (I_2)_2$. We have repeated their measurements on the anthracene- I_2 system using about the same concentrations as they used. Because of the interference from the uncomplexed iodine in these solutions, it was almost impossible to obtain meaningful spectra (see Fig. 4).

Chowdhury and Basu reached their conclusion on the basis of the linearity of a plot of their eq. 5. Their equation should give a straight line when plotted against the inverse of the initial iodine concentration, $1/[I_2]$, if the formation constant for 1:1 complexes is large and that for 2:1 complexes is small. Conversely, if the latter constant is large, the plot against the inverse square of the concentration, $1/[I_2]^2$, should be linear. Both their plots were linear, but the plot against $1/[I_2]$ apparently had zero intercept. They concluded that the 1:1 complex was only a "contact"¹⁵ and the 2:1 complex existed.

On repeating their plots we obtain similar results; *i.e.*, both plots are approximately linear, but both have positive intercepts. The slope and intercept of the plot *vs.* $1/[I_2]$ give about the same values for K and ϵ as obtained for the anthracene-rich experiments described above.

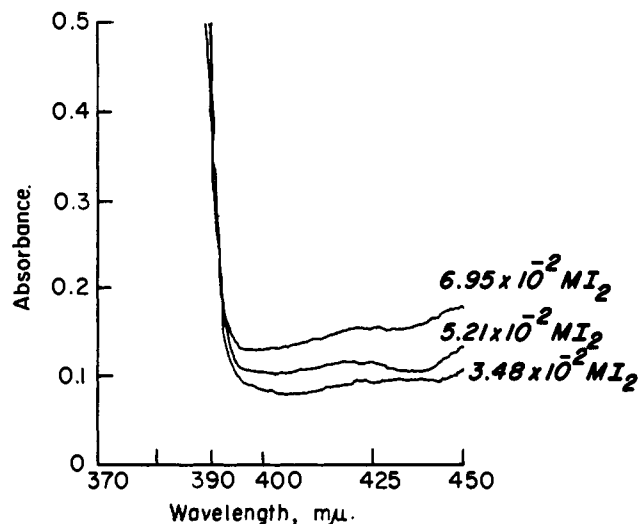


Fig. 4.—Spectrum of anthracene in the excess I_2 in CCl_4 . Iodine solutions in CCl_4 of the same concentration as the initial I_2 concentration in the complex solution were used in the reference beam. The anthracene concentration was $1.18 \times 10^{-3} M$.

The plot of our data against $1/[I_2]^2$ shows some tendency for curvature and suggests that the data do not extend over a wide enough range. Indeed, the curve calculated from eq. 5 of Chowdhury and Basu¹⁴—assuming $K_2 = \epsilon_2 = 0$; $K_1 = 3.0$, $\epsilon = 550$ —fits our data even better than a straight line.

We conclude that there is no indication from our experiments that 2:1 complexes exist. Furthermore, the data from the excess iodine experiments are consistent with the more accurate determination of K and ϵ for the 1:1 complex in the anthracene-rich solutions.

Discussion

Perhaps the most important result of this investigation has been to emphasize once more the importance of experimental error and the difficulty of obtaining reliable data, even for systems which are of so much interest to the theorist. The inability to adjust concentrations so the absorbance will be sensitive to the complex and the interference by the absorption of the uncomplexed components are problems which will be difficult to eliminate for all of the extremely interesting complexes between I_2 and the large polynuclear aromatic hydrocarbons.

Our data do not determine the wave lengths of maximum absorption for the charge transfer complex of anthracene and iodine (see Fig. 1). We believe the absorption near 430 $m\mu$ is correctly interpreted as the charge transfer band. The low value of ϵ at 430 $m\mu$ indicated from our studies (Table I) suggests that the absorption maximum is probably at longer wave lengths, masked by strong anthracene absorption. Hence, we believe attempts¹⁶ to estimate the ionization potential for anthracene from the wave length of the charge transfer band may be misleading. For the phenanthrene- I_2 complex in CCl_4 solution, we believe $\lambda_{CT} = 364 m\mu$ (see Fig. 2), or about 10 $m\mu$ lower than that reported by Bhattacharya and Basu.⁴

The value of the maximum absorptivity, ϵ_{max} , for the phenanthrene complex given in Tables II and IV appears to be consistent with values for other substituted benzene compounds (see Briegleb,¹⁷ for example). In the series of aromatic donors, only benzene itself and some of the mono- and disubstituted benzenes have ϵ_{max} greater than 10,000. Note the great similarity in Table IV between the naphthalene and phenanthrene

(14) M. Chowdhury and S. Basu, *J. Chem. Phys.*, **32**, 1450 (1960).

(15) L. S. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

(16) G. Briegleb, ref. 9, p. 80.

(17) G. Briegleb, ref. 9, Table II.

complexes. The transition dipoles, μ_{mn} , and f -values presented in Table IV are estimated from the reported values of ϵ_{\max} and $\Delta\nu_{1/2}$, the half-intensity width ($\Delta\nu_{1/2}$ is usually estimated from figures presenting spectra in the references cited) using the approximation: $\int \epsilon d\nu = \epsilon \Delta\nu_{1/2}$. This estimate is probably low (see Briegleb⁹), but we do not believe the data are good enough to warrant refinements.

TABLE IV
COMPARISON OF THE PROPERTIES OF ANTHRACENE-I₂ AND PHENANTHRENE-I₂ COMPLEXES WITH OTHER RELATED I₂ COMPLEXES

Donor	K_{25}°	$-\Delta H_f$		λ_{CT} m μ	ϵ	$\Delta\nu_{1/2}$ cm. ⁻¹	$\mu_{mn},^a$ Debyes/ Å.
		kcal./mole	m μ				
Benzene ^b	0.15	1.3	292	15,000	5100	4.6	
<i>o</i> -Xylene ^b	.27	2.0	318	11,000	(5000) ^c	(4.0) ^c	
Durene ^b	.63	2.8	332	9,000	(5000) ^c	(3.7) ^c	
Naphthalene ^b	.25	1.8	360	7,400	4700	3.4 ^d	
Phenanthrene	.45	1.6	364	7,100	4900	3.4	
Anthracene	3.0 ^e	...	<430	(550) ^e	(5000) ^c	(>1.0) ^{c,e}	

^a Approximate transition dipole for the charge-transfer absorption, defined by $\mu_{mn}^2 = 0.0092 \int \epsilon d\nu / \nu_{\max}$; the integral is approximated by $\epsilon_{\max} \Delta\nu_{1/2}$. ^b Values from Briegleb, ref. 9, except for μ_{mn} and $\Delta\nu_{1/2}$, which were estimated from figures in the original papers cited by Briegleb, or else guessed. ^c These values are "educated guesses" and should not be used for more than order-of-magnitude estimates. ^d This value is to be compared with a value of $\mu_{mn} = 4.0$ D./Å. computed from the f -values obtained by actual numerical integration of ϵ ; see N. W. Blake, H. Winston, and J. A. Patterson, *J. Am. Chem. Soc.*, **73**, 4437 (1951). ^e The product of K and ϵ is believed to be correct, but each could be in error. *I.e.*, K could be as low as 0.3 and ϵ as high as 5500. Furthermore, the maximum in the charge-transfer absorption may not be at 430 m μ .

The comparison in Table IV suggests that the intensities of the charge transfer bands for I₂ complexes with polynuclear aromatic compounds may decrease somewhat as the strength of the complex increases. However, the magnitude of the change is much smaller than reported earlier⁴ and discussed by Murrell.⁵ Especially for anthracene-I₂, it seems very likely that

the charge transfer maximum is at longer wave lengths and more intense than reported here.

Finally, we note that the strength of the complexes between aromatic donors and I₂ does increase in the order: benzene < naphthalene < phenanthrene < anthracene (see Table IV). However, instead of an increase in K by a factor of 50 from phenanthrene to anthracene,⁴ we now find a change by only a factor of 7. This increase in base strength is still sizable, and, *if real*, is apparently due to the increase in resonance stabilization (X_0) of the ground state of the complex. Some increase should be expected because the lower ionization potential of anthracene causes the energy of the dative state (W_1) to be less, so that the resonance interaction with the ground state is greater.

It has been suggested elsewhere^{9,18} that the resonance energy of these weak complexes of I₂ with aromatic donors can be calculated from the perturbation equation

$$X_0 = -\beta_0^2 / (W_1 - W_0) = -0.36 / (I_D - 5.2) \text{ e.v.}$$

For phenanthrene-I₂, $X_0 = -0.12$ e.v. = -2.8 kcal./mole; for anthracene-I₂, $X_0 = -0.14$ e.v. = -3.2 kcal./mole.¹⁹ As shown earlier,¹⁸ the energy of formation of these complexes should approximately equal X_0 , in agreement with these results. However, this estimate of ΔH_f suggests that the difference between the K 's for phenanthrene and anthracene complexes in Table IV is still too large, and that our value for the anthracene complex may still be too high.

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(18) W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963); R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

(19) These values are obtained using calculated ionization potentials of 8.1 and 7.7 for phenanthrene and anthracene, respectively.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILL., THE UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY, CALCUTTA, INDIA, AND AEROSPACE RESEARCH LABORATORIES, WRIGHT-PATTERSON AIR FORCE BASE, OHIO]

The Stereochemistry of Metal Chelates with Multidentate Ligands. II

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Complexes of bis-salicylaldehyde-triethylenetetramine with manganese(III), cobalt(II), nickel(II), indium(III), and gallium(III) have been prepared. Their structures, as indicated by their spectra in the infrared, are discussed.

In view of the stereochemical properties of the chelating agent, bis-salicylaldehyde-triethylenetetramine $\text{HOC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ (I), described in part I,¹ it was considered worthwhile to prepare and study compounds with a series of metals. Two different methods have been used to synthesize these compounds. In one method, tris-(salicylidene-amino)-triethylenetetramine is formed by mixing salicylaldehyde and triethylenetetramine. When a metal ion is introduced, 1 mole of salicylaldehyde is cleaved and a metal complex of I is formed. In the second method, a metal complex of salicylaldehyde is allowed to react with triethylenetetramine to form the complex of I.

Crystalline complexes of I with manganese(III), cobalt(II), nickel(II), indium(III), and gallium(III) have been isolated and purified. Attempts to isolate pure compounds of iron(II), palladium(II), platinum(II), cadmium(II), zinc(II), and rhodium(III) were unsuccessful.

It was reported previously¹ that the complexes of iron(III), copper(II), aluminum(III), and cobalt(III) possess sufficient solvolytic stability to be resolved into their optical isomers. Magnetic measurements showed the iron(III) complex to be a spin-paired d^2sp^3 compound. In the present work, however, the manganese(III), nickel(II), and cobalt(II) complexes were found to be spin-free, with magnetic moments of 5.05, 2.88, and 4.12 B.M., respectively.²

(2) The moment for the cobalt(II) complex is a little lower and for manganese(III) is slightly higher than ordinarily expected. The reason for this

(1) B. Das Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476 (1955).