

# Spectroscopic and Physicochemical Studies of Charge-Transfer Complexes of Some Benzanthrone Derivatives “Luminophore Dyes” with Iodine as $\sigma$ - Acceptor

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## Résumé

*Les complexes de transfert de charge (complexes CT) sont formés durant la réaction des donneurs -  $\pi$ , tels que les colorants benzanthrone substitués par des dérivés azométhines en position 3 avec l'iode comme accepteur -  $\sigma$ . Nous avons étudié les réactions de l'accepteur iode avec les donneurs dérivés benzanthrone par photométrie dans le chloroforme et à température ambiante. Les données obtenues indiquent la formation de complexes de transfert de charge 1:1 de formulation  $[BA].I_2$ , où (BA = dérivés benzanthrone). Nous avons déterminé les valeurs de la constante d'équilibre (K), du coefficient d'extinction ( $\epsilon$ ) et de la force de l'oscillateur (f) pour tous les complexes obtenus dans cette étude.*

## Abstract

*Charge-transfer complexes (CT-complexes) are formed during the reaction of  $\pi$ -donors, such as substituted benzanthrone dyes substituted with azomethine derivative groups at position 3, with iodine as the  $\sigma$ -acceptor. The reactions of iodine (acceptor) with benzanthrone derivatives (donor) were studied photometrically in chloroform at room temperature. The data obtained indicate the formation of 1:1 charge-transfer complexes, and the obtained complexes are formulated as  $[BA].I_2$ , (BA = benzanthrone derivatives). The values of the equilibrium constant (K), extinction coefficient ( $\epsilon$ )*

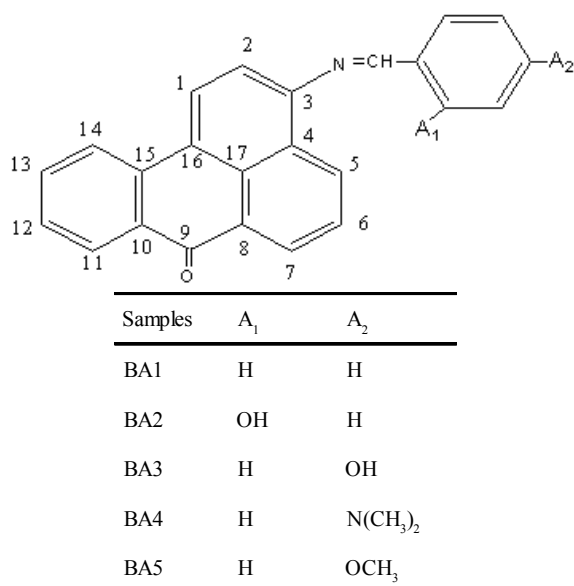
*and oscillator strength (f) were determined for all the complexes obtained throughout this study.*

**Keywords:** benzanthrone, charge-transfer, iodine, photometric titration, infrared spectroscopy.

## Introduction

Benzanthrone dyes are well known as luminophore dyes that emit in the spectral region from yellow-green to red-purple, depending on the structure (1). Benzanthrone dyes exhibit, both in solution and in the solid state, bright fluorescence and high photostability, and thus they find use as daylight fluorescent pigments for synthetic textile materials (2). The introduction of an azomethine group extends the system of conjugated double bonds of the benzanthrone nucleus, thus increasing the chromophore length. In earlier studies (3-5), we have reported the formation of the related charge-transfer complexes formed in the reaction of iodine ( $\sigma$ -acceptor) with various metalacetylacetonate (like Ferric (III) and Nickel (II) acetylacetonate) and polyamidoamines. The results reported in this paper are concerned with the preparation, characterization and structural studies of the new charge-transfer complexes formed during the reaction of benzanthrone derivatives as electron donors with an electron acceptor like iodine ( $\sigma$  - acceptor). The principal techniques used in these studies are based on ultraviolet-visible, mid infrared spectroscopy and photometric titrations, as well as elemental analysis.

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Scheme 1. Structure of the azomethine derivatives of benzanthrone

## Experimental

The structures of benzanthrone dyes substituted with azomethine derivative groups at position 3 are outlined in scheme 1. All chemicals used throughout this investigation were of analytical grade. 3-Azomethine derivatives of benzanthrone were prepared (6,7) and used without further purification. Iodine was obtained from BDH. The solid charge-transfer complexes were isolated as follows. Excess saturated solution (25 mL) of iodine in chloroform was added to a saturated solution (15 mL) of each of the donors in chloroform. The reaction mixture was in each case stirred for about 15-20 minutes. The solid CT-complexes formed were filtered immediately and washed several times with minimum amounts of CHCl<sub>3</sub> (3-5 mL) and then dried under vacuum over CaCl<sub>2</sub>. The obtained complexes were characterized by their elemental analysis, vibrational spectroscopy and electronic absorption spectroscopy. The elemental analysis data obtained are shown in Table 1.

The electronic spectra of the donors BA1, BA2, BA3, BA4 and BA5, the acceptor (iodine) and the formed CT-complexes in CHCl<sub>3</sub> were recorded in the region of 700-200nm using a 1601 PC Shimadzu UV/VIS spectrophotometer fitted with a quartz cell of 1cm path length. The mid infrared spectra of the reactants and the formed CT-complexes were recorded from KBr discs using a Genesis II FT-IR. Photometric titration was performed (8) at 25 °C for the reactions of BA2, BA3,

Table 1. The obtained and calculated elemental analysis of BA2-iodine, BA3-iodine, BA4-iodine and BA5-iodine complexes

CT-complexes	% C		% H		% N		% I	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[BA2]I <sub>2</sub> (602.8)	47.78	47.65	2.16	2.15	2.32	2.28	42.10	41.97
[BA3]I <sub>2</sub> (602.8)	47.78	47.60	2.16	2.13	2.32	2.30	42.10	42.08
[BA4]I <sub>2</sub> (629.8)	49.54	49.43	2.86	2.79	4.44	4.37	40.30	40.26
[BA5]I <sub>2</sub> (616.8)	48.64	48.55	2.43	2.40	2.27	2.26	41.15	41.09

BA4 and BA5 with iodine in chloroform; this was not done for the BA1-iodine reaction because there is no shift in the electronic spectra (see Figure 1). The concentration of the donors in the reaction mixture was kept fixed at 5.0x10<sup>-6</sup> M, while the concentration of iodine was changed over a wide range from 1.25x10<sup>-6</sup> M to 15.00x10<sup>-6</sup> M. This produced solutions with donor : acceptor molar ratios varying from 1 : 0.25 to 1 : 3, as shown in Table 2.

## Results and Discussion

The ultraviolet-visible absorption spectra of the iodine complexes were measured in CHCl<sub>3</sub> solvent. In chloroform solvent, the complexes are formed by adding X mL of 25x10<sup>-6</sup> M iodine (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 mL) and 1.00 mL of 25x10<sup>-6</sup>M of each azomethine substituted benzanthrone dye (derivatives of 3-amino benzanthrone containing electron donating groups in the ortho or/and para position of the benzene nucleus) [BA2 = o-hydroxy benzaldehyde; BA3 = p-hydroxy benzaldehyde; BA4 = 4-dimethylamino-benzaldehyde and BA5 = p-methoxy benzaldehyde]. The volumes of the BA2-I<sub>2</sub>, BA3-I<sub>2</sub>, BA4-I<sub>2</sub> and BA5-I<sub>2</sub> mixtures were completed to 5 mL with chloroform solvent at 25 °C. The concentrations of BA2, BA3, BA4 and BA5 in their iodine reaction mixtures were kept fixed at 5.00x10<sup>-6</sup> M, while the concentration of iodine was varied over the range of 1.25x10<sup>-6</sup> M to 15.00x10<sup>-6</sup> M. These concentrations produce base:I<sub>2</sub> ratios extending along the range from 1:0.25 to 1:3.00. The electronic absorption spectra of the 1:1 ratio in CHCl<sub>3</sub> with the reactants I<sub>2</sub> and BA1, BA2, BA3, BA4 and BA5 are shown in Figure 1 (A-E) for BA1-I<sub>2</sub>, BA2-I<sub>2</sub>, BA3-I<sub>2</sub>, BA4-I<sub>2</sub> and BA5-I<sub>2</sub> mixtures, respectively. Hypsochromic shifts (from the free base) were observed in the absorption spectra of the iodine complexes of BA3, BA4 and BA5. On the

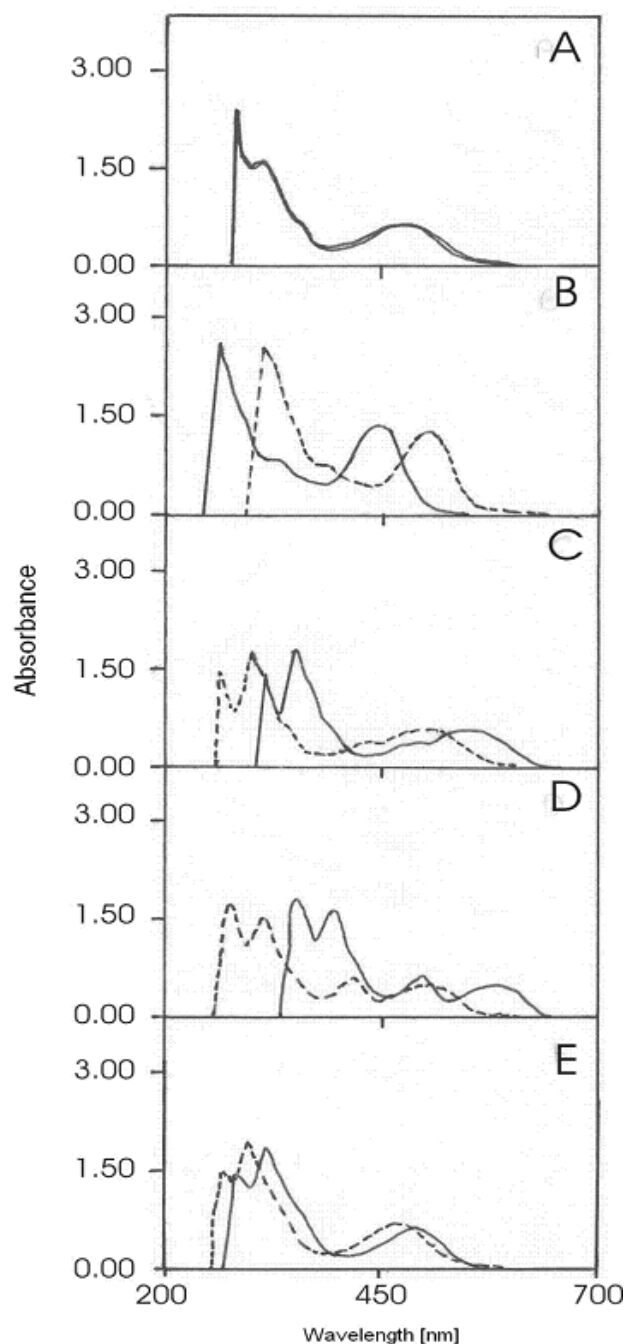


Figure 1. Electronic absorption spectra of (Donor = BA1, BA2, BA3, BA4 and BA5 ( $5 \times 10^{-6}$  M)), iodine ( $5 \times 10^{-6}$  M) and BA1, BA2, BA3, BA4, BA5 - I<sub>2</sub> mixtures (Donor = ( $5 \times 10^{-6}$  M) and iodine ( $5 \times 10^{-6}$  M)). [Key: (—) = donor and (---) = donor-acceptor CT-complexes]

other hand, a bathchromic shift was observed for the BA2-I<sub>2</sub> mixture (the hydroxy electron donating group located in the ortho position of the benzene nucleus which attached to 3-aminobenzanthrone). These bands are attributed to the CT-complexes formed in the reaction of

Table 2. The electronic absorption spectral data for (A): BA2-I<sub>2</sub>, (B): BA3-I<sub>2</sub>, (C): BA4-I<sub>2</sub>, and (D): BA5-I<sub>2</sub> complexes in CHCl<sub>3</sub>. 1mL base ( $25 \times 10^{-6}$  M) + mL iodine ( $25 \times 10^{-6}$  M) + Y mL solvent = 5mL

A			B		
(Base : Iodine) ratio	Absorbance		(Base : Iodine) ratio	Absorbance	
	503nm	316nm		500nm	300nm
1 : 0.25	0.034	0.445	1 : 0.25	0.078	0.357
1 : 0.50	0.051	0.783	1 : 0.50	0.143	0.681
1 : 0.75	0.080	1.054	1 : 0.75	0.201	0.997
1 : 1.00	0.106	1.283	1 : 1.00	0.259	1.301
1 : 1.50	0.115	1.496	1 : 1.50	0.287	1.497
1 : 2.00	0.122	1.680	1 : 2.00	0.350	1.639
1 : 2.50	0.132	1.905	1 : 2.50	0.374	1.820
1 : 3.00	0.137	2.048	1 : 3.00	0.398	2.050

C			D		
(Base : Iodine) ratio	Absorbance		(Base : Iodine) ratio	Absorbance	
	500nm	313nm		457nm	300nm
1 : 0.25	0.037	0.153	1 : 0.25	0.103	0.222
1 : 0.50	0.070	0.282	1 : 0.50	0.164	0.395
1 : 0.75	0.102	0.397	1 : 0.75	0.235	0.557
1 : 1.00	0.125	0.526	1 : 1.00	0.309	0.754
1 : 1.50	0.153	0.640	1 : 1.50	0.340	0.934
1 : 2.00	0.177	0.822	1 : 2.00	0.385	1.033
1 : 2.50	0.193	0.925	1 : 2.50	0.450	1.225
1 : 3.00	0.215	1.051	1 : 3.00	0.497	1.291

azomethine substituted benzanthrene dyes with iodine, and they can be assigned as follows: for BA2-I<sub>2</sub> CT-complex, these bands are observed at 503 and 316 nm; for BA3-I<sub>2</sub> at 500 and 300 nm; for BA4-I<sub>2</sub> at 500 and 313 nm; and for BA5-I<sub>2</sub> at 457 and 300 nm in CHCl<sub>3</sub>, respectively (see Figure 1, A–D). Table 2 (A–D) gives the values of the absorbances obtained from photometric titrations based on the absorption bands around 503 and 316 nm for BA2-iodine; 500 and 300 nm for BA3-iodine; 500 and 313 nm for BA4-iodine; 457 and 300 nm for BA5-iodine systems in chloroform, respectively. Photometric titration curves based on these absorption bands are given in Figures 2 (A–D) for BA2-iodine, BA3-iodine, BA4-iodine and BA5-iodine systems in the respective solvent, CHCl<sub>3</sub>. These photometric titration curves were obtained by the plot of the absorbance

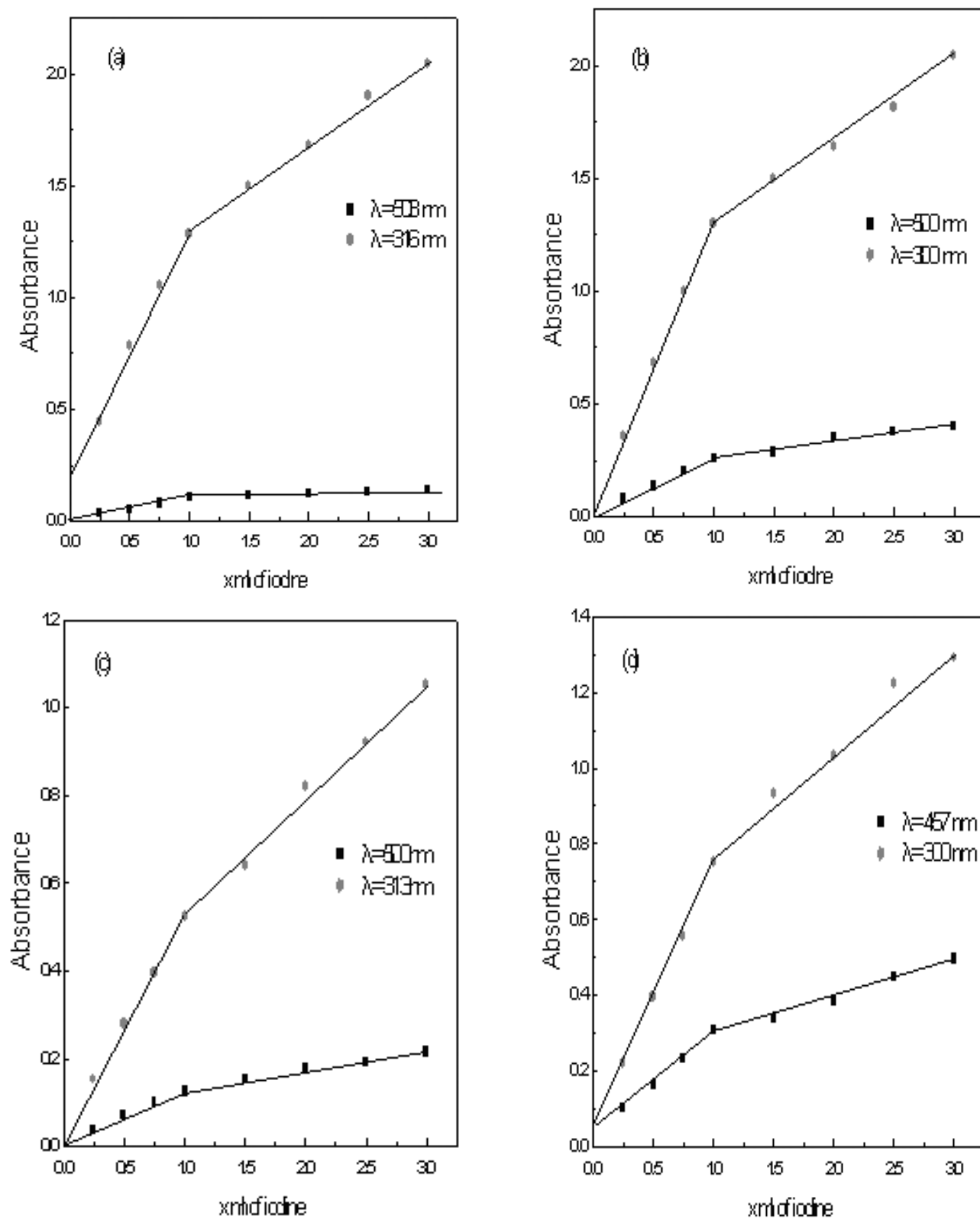


Figure 2. Photometric titration curves for (a): BA2-I<sub>2</sub>, (b): BA3-I<sub>2</sub>, (c): BA4-I<sub>2</sub> and (d) : BA5-I<sub>2</sub> systems in CHCl<sub>3</sub>.

Table 3. The values of  $[D]_0$ ,  $[A]_0$ ,  $[A]_0 + [D]_0$ , and  $[A]_0 [D]_0$  for (A): BA2-I<sub>2</sub>, (B): BA3-I<sub>2</sub>, (C): BA4-I<sub>2</sub>, and (D): BA5-I<sub>2</sub> systems in CHCl<sub>3</sub>

A (Base:Iodine) ratio	$[D]_0 \times 10^{-5}$	$[A]_0 \times 10^{-5}$	Absorbance		$[A]_0 + [D]_0 \times 10^{-7}$	$[A]_0 [D]_0 \times 10^{-10}$	$[A]_0 [D]_0 / A \times 10^{-10}$	
			503nm	316nm			503nm	316nm
1 : 0.25	0.50	0.125	0.034	0.445	62.5	0.0625	1.840	0.140
1 : 0.50	0.50	0.250	0.051	0.783	75	0.1250	2.451	0.160
1 : 0.75	0.50	0.375	0.080	1.054	87.5	0.1875	2.343	0.178
1 : 1.00	0.50	0.500	0.106	1.283	100	0.2500	2.358	0.195
1 : 1.50	0.50	0.750	0.115	1.496	125	0.3750	3.261	0.251
1 : 2.00	0.50	1.000	0.122	1.680	150	0.5000	4.098	0.298
1 : 2.50	0.50	1.250	0.132	1.905	175	0.6250	4.735	0.328
1 : 3.00	0.50	1.500	0.137	2.048	200	0.7500	5.474	0.366

B (Base:Iodine) ratio	$[D]_0 \times 10^{-5}$	$[A]_0 \times 10^{-5}$	Absorbance		$[A]_0 + [D]_0 \times 10^{-7}$	$[A]_0 [D]_0 \times 10^{-10}$	$[A]_0 [D]_0 / A \times 10^{-10}$	
			500nm	300nm			500nm	300nm
1 : 0.25	0.50	0.125	0.078	0.357	62.5	0.0625	0.801	0.175
1 : 0.50	0.50	0.250	0.143	0.681	75	0.1250	0.874	0.183
1 : 0.75	0.50	0.375	0.201	0.997	87.5	0.1875	0.933	0.188
1 : 1.00	0.50	0.500	0.259	1.301	100	0.2500	0.965	0.192
1 : 1.50	0.50	0.750	0.287	1.497	125	0.3750	1.307	0.250
1 : 2.00	0.50	1.000	0.350	1.639	150	0.5000	1.428	0.305
1 : 2.50	0.50	1.250	0.374	1.820	175	0.6250	1.671	0.343
1 : 3.00	0.50	1.500	0.398	2.050	200	0.7500	1.884	0.366

C (Base:Iodine) ratio	$[D]_0 \times 10^{-5}$	$[A]_0 \times 10^{-5}$	Absorbance		$[A]_0 + [D]_0 \times 10^{-7}$	$[A]_0 [D]_0 \times 10^{-10}$	$[A]_0 [D]_0 / A \times 10^{-10}$	
			500nm	313nm			500nm	313nm
1 : 0.25	0.50	0.125	0.037	0.153	62.5	0.0625	1.689	0.408
1 : 0.50	0.50	0.250	0.070	0.282	75	0.1250	1.786	0.443
1 : 0.75	0.50	0.375	0.102	0.397	87.5	0.1875	1.838	0.472
1 : 1.00	0.50	0.500	0.125	0.526	100	0.2500	2.000	0.475
1 : 1.50	0.50	0.750	0.153	0.640	125	0.3750	2.451	0.586
1 : 2.00	0.50	1.000	0.177	0.822	150	0.5000	2.824	0.608
1 : 2.50	0.50	1.250	0.193	0.925	175	0.6250	3.238	0.676
1 : 3.00	0.50	1.500	0.215	1.051	200	0.7500	3.488	0.714

D (Base:Iodine) ratio	$[D]_0 \times 10^{-5}$	$[A]_0 \times 10^{-5}$	Absorbance		$[A]_0 + [D]_0 \times 10^{-7}$	$[A]_0 [D]_0 \times 10^{-10}$	$[A]_0 [D]_0 / A \times 10^{-10}$	
			457nm	300nm			457nm	300nm
1 : 0.25	0.50	0.125	0.103	0.222	62.5	0.0625	0.607	0.281
1 : 0.50	0.50	0.250	0.164	0.395	75	0.1250	0.762	0.316
1 : 0.75	0.50	0.375	0.235	0.557	87.5	0.1875	0.798	0.337
1 : 1.00	0.50	0.500	0.309	0.754	100	0.2500	0.809	0.332
1 : 1.50	0.50	0.750	0.340	0.934	125	0.3750	1.103	0.401
1 : 2.00	0.50	1.000	0.385	1.033	150	0.5000	1.299	0.484
1 : 2.50	0.50	1.250	0.450	1.225	175	0.6250	1.389	0.510
1 : 3.00	0.50	1.500	0.497	1.291	200	0.7500	1.509	0.581

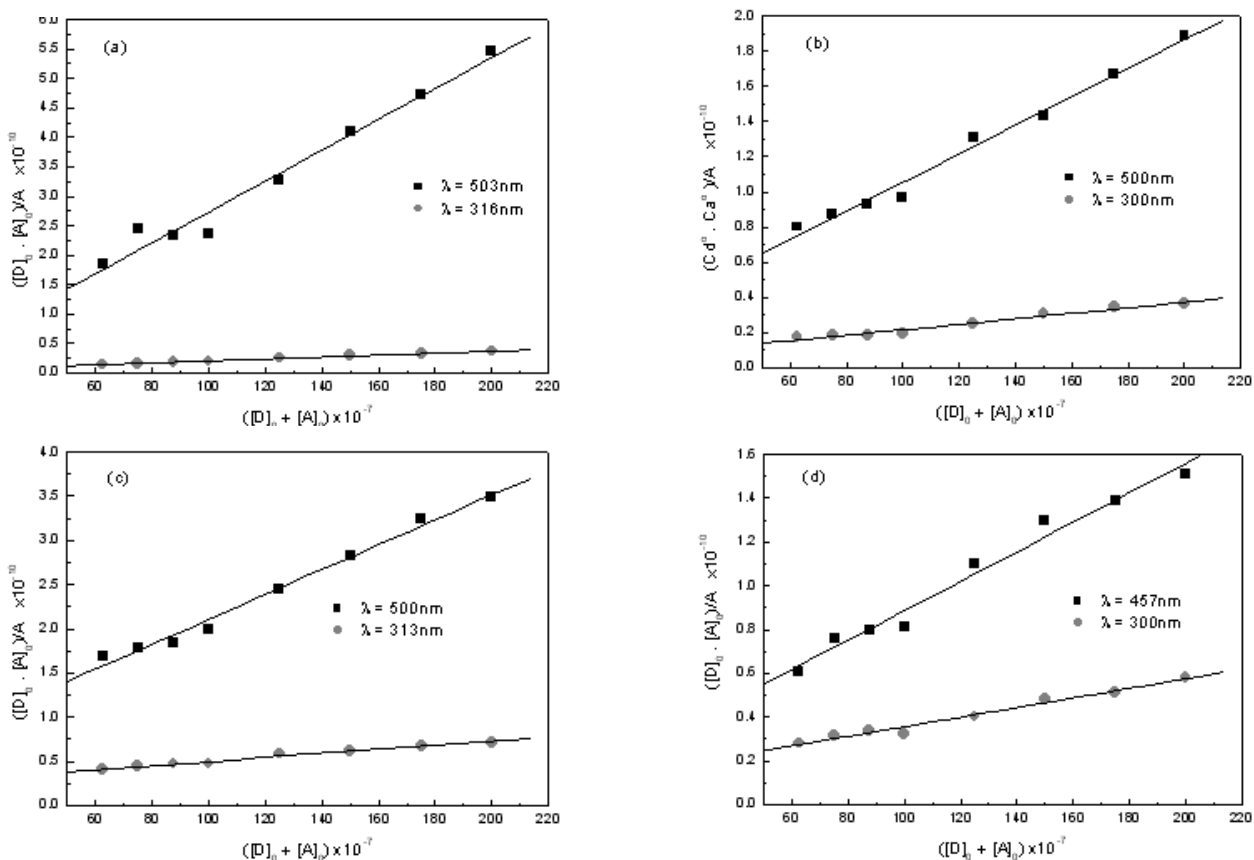


Figure 3 The plot of  $[A]_0 + [D]_0$  values against  $[A]_0[D]_0/A$  for (a): BA2, (b): BA3-I<sub>2</sub>, (c): BA4-I<sub>2</sub> and (d): BA5-I<sub>2</sub> reactions in CHCl<sub>3</sub>.

against the X mL of the added acceptor (8). The equivalence points shown in these curves clearly indicate that the formed CT-complexes between azomethine substituted benzanthrone dyes (BA2, BA3, BA4 and BA5) and iodine are of 1:1 ratio. The spectrophotometric data are employed to calculate the equilibrium constant ( $K_{CT}$ ) and the molar extinction coefficient ( $\epsilon_{CT}$ ) for BA-I<sub>2</sub> complexes in chloroform using the Scott modifications (9) of the Benesi-Hildebrand equation (10). This equation is based on the assumption of 1:1 (Acceptor-Donor) complex formation and can be written as follows:

$$\frac{[A]_0[D]_0}{A} = \frac{[D]_0 + [A]_0}{\epsilon_{CT}} + \frac{1}{K_{CT}\epsilon_{CT}} \quad (1)$$

Where  $[A]_0$  and  $[D]_0$  are the initial molar concentrations of the acceptor and the donor, respectively. A is the absorbance of the CT-complex. The data obtained for  $[D]_0$  of [BA2, BA3, BA4 and BA5],  $[A]_0$  of I<sub>2</sub>,  $[A]_0 + [D]_0$  and  $[A]_0[D]_0/A$  in CHCl<sub>3</sub> are summarized and given in Table 3 (A–D) for when the  $[A]_0[D]_0/A$  values for each

donor are plotted against the corresponding  $[A]_0 + [D]_0$  values. Straight lines are obtained with a slope of  $1/\epsilon$  and intercept of  $1/K\epsilon$  as shown in Figure 3 (A–D) for the reactions in CHCl<sub>3</sub>. The oscillator strength (f) was

Table 4. Spectrophotometric results of BA2–iodine, BA3–iodine, BA4–iodine and BA5–iodine complexes and the dielectric constant of chloroform constant as solvent

Complexes	K [Lmol <sup>-1</sup> ]	$\lambda_{max}$ [nm]	$\epsilon_{max}$ [Lmol <sup>-1</sup> cm <sup>-1</sup> ]	f
BA2-iodine	0.557 x10 <sup>5</sup>	503	128 x10 <sup>3</sup>	80
	1.000 x10 <sup>5</sup>	316	667 x10 <sup>3</sup>	628
BA3-iodine	3.750 x10 <sup>5</sup>	500	40 x10 <sup>3</sup>	19
	1.428 x10 <sup>5</sup>	300	526 x10 <sup>3</sup>	494
BA4-iodine	0.971 x10 <sup>5</sup>	500	73 x10 <sup>3</sup>	37
	0.525 x10 <sup>5</sup>	313	476 x10 <sup>3</sup>	447
BA5-iodine	10.688 x10 <sup>5</sup>	457	17 x10 <sup>3</sup>	9
	8.861 x10 <sup>5</sup>	300	50 x10 <sup>3</sup>	47

Table 5. Main bands ( $\text{cm}^{-1}$ ) in infrared spectra of BA2–iodine, BA3–iodine, BA4–iodine and BA5–iodine CT-complexes.

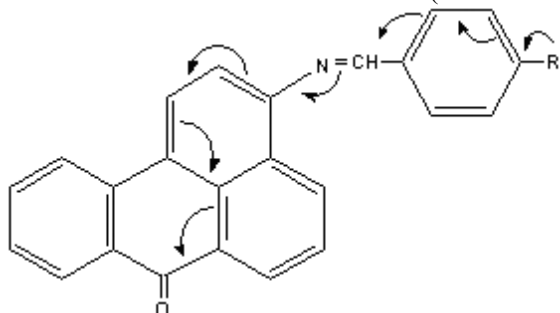
Complex	Frequencies [ $\text{cm}^{-1}$ ]							
	$\nu_{\text{OH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{N=CH}}$	$\nu_{(\text{C-C})}$	$\nu_{(\text{CH}_3)}$	$\nu_{(\text{C-OH})}$	$\nu_{(\text{C-O-C})}$	$\delta_{\text{CH(ar)}}$
BA2-I <sub>2</sub>	3423 ms	1635 s	1585 ms	1575 s 1460 s	----	1139 mw	----	785 s 718 s
BA3-I <sub>2</sub>	3429 s,br	1642 s	1594 ms	1558 ms 1457 s	----	1147 mw	----	794 ms 709 ms
BA4-I <sub>2</sub>	----	1639 s	1582 s	1562 s 1453 s	1447 ms 1372 ms	----	----	770 ms 692 ms
BA5-I <sub>2</sub>	----	1645 s	1587 s	1567 ms 1458 s	1439 ms 1377 s	----	1262 ms 1164 ms 1033 ms	774 mw 748 mw 701 mw

s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.  $\nu$  = stretching;  $\delta$  = bending.

obtained from the approximate formula (11).

$$f = (4.319 \times 10^{-9}) \epsilon_{\text{max}} \nu_{1/2} \quad (2)$$

Where  $\nu_{1/2}$  is the band width for half-intensity in  $\text{cm}^{-1}$ . The oscillator strength values, together with both the equilibrium constant (K) and extinction coefficient ( $\epsilon$ ), for all CT-complexes are given in Table 4. The trend of the values in this table reveals high values of both the equilibrium constant (K) and extinction coefficient ( $\epsilon$ ). This high value of (K) reflects the high stability of the iodine complexes as a result of the expected high donation of the hydroxy group for BA2 and BA3, dimethylamine for BA4, and methoxy for BA5 besides the azomethine group. By comparison between the interaction of BA1 and other azomethine derivatives (BA2, BA3, BA4 and BA5) with a  $\sigma$ -acceptor (iodine), we can conclude that the reaction between BA2, BA3, BA4 and BA5 with iodine is accompanied by a bathochromic or/and hypsochromic shift according to the electron donating groups OH,  $\text{N}(\text{CH}_3)_2$  and  $\text{OCH}_3$  of the benzene nucleus attached to the benzanthrone molecule (see Scheme 2).



Scheme 2. R = OH,  $\text{N}(\text{CH}_3)_2$ , and  $\text{OCH}_3$

However, the interaction between BA1 and iodine has not given any shift in wavelength or absorbance (R = H). This observation led to the conclusion that the shift in azomethine group occurs in the presence of electron donating groups (e.g. OH,  $\text{N}(\text{CH}_3)_2$ , and  $\text{OCH}_3$ ).

The infrared spectra of the azomethine derivatives (BA2, BA3, BA4 and BA5) and the formed CT-complexes and their band assignments are reported in Table 5. As expected, the bands characteristic of the azomethine derivative unit in the CT-complexes are shown with small changes in band intensities and frequency values.

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