

Interactions of Aza Cyanine Dyes with Adenine: UV-Visible Spectrophotometric Study

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UV-Visible absorption studies on the interaction of 2(4) pyrid- and 2(4) quinazamethine cyanine dyes with adenine in aqueous solutions demonstrate the formation of weakly bonded charge transfer complexes. The absorption spectra in the visible region of the complexes formed are located at longer wavelengths and outside the region of those of the pure reacting individuals. The amount of the red shift induced depends mainly on the type of the reacted dye and is independent of the dye concentration on using a fixed large excess of adenine. Equilibrium constants were calculated by assuming 1:1 complexes. Various thermodynamic parameters and molar absorptivities are calculated for the different interactions. The structure-activity relationships of the interacting molecular species are discussed.

INTRODUCTION

Cyanine dyes have found various important applications¹ and have many biological and biochemical effects. Some of these dyes are growth inhibitors to bacteria² and to the mitosis of fertilized sea urchin eggs.³ They possess hormonal effects on plant growth.⁴ They affect the ATP level in the cell and respiration activity,⁵ increase the rate of enzymatic production of glucose from starch,⁶ and are used as anticancer agents.⁷ The biochemical effect may be due to their ability to penetrate the cell, entering all subcellular compartments and getting bound to numerous macromolecules.⁸

The mutagenic and developmental effects of styryl and aza analogues of cyanine dyes were investigated in *Vicia faba* seeds.⁹ Also, the effect of both analogues on the breaking period of dormancy were studied in cloves of *garlic cvs.*¹⁰ These compounds are potent mitodepressive and mutagenic agents and the aza analogue is more effective than the styryl one.^{9,10} These cyanine dyes were found to display a structure-activity relationship with regard to the cytological effects.

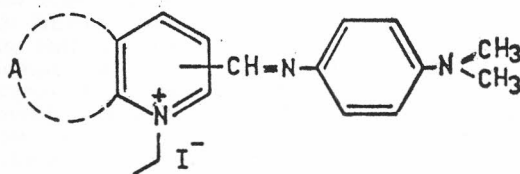
Nucleic acids carry the genetic information required for the synthesis of different types of proteins and enzymes.¹¹ These acids in the living systems seemed to be possible targets for the action of cyanine dyes, either directly or indirectly. Indirect actions are attributed to their interference with protein synthesis; either induction or inhibition. The interactions between nucleic acid bases and cyanine dyes were not mentioned before.

To shed some light upon the structure-activity relationship in the interaction of aza cyanine dyes with one of the nucleic acid bases (adenine), the nature of the complexes formed was investigated in aqueous solution at different temperatures, using a UV-Visible spectroscopic method. The dyes used in the investigation were α , γ , Q, and L-aza cyanine dyes with the scope of comparing the effect of the linkage position and the effect of fused benzene ring within the heterocyclic quaternary nucleus. The compounds used were:

- α = 2(*p*-Dimethylaminophenyl)azamethine-1-ethylpyridinium iodide;
 γ = 4(*p*-Dimethylaminophenyl)azamethine-1-ethylpyridinium iodide;
 Q = 2(*p*-Dimethylaminophenyl)azamethine-1-ethylquinolinium iodide;
 L = 4(*p*-Dimethylaminophenyl)azamethine-1-ethylquinolinium iodide.

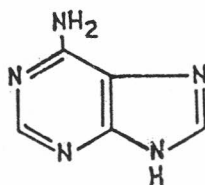
EXPERIMENTAL

Adenine was obtained commercially (Hopkin and Williams Chemical Co., Chadwell Heath, Essex, England) and used without further purification. Aza cyanine dyes were prepared as mentioned in the literature.¹² The solid products obtained were recrystallized from ethanol. The results are shown in Table I and Figure 1. The structures of the compounds prepared are as follows:



- α = 2-pyrid-azamethine cyanine, A = H;
 γ = 4-pyrid-azamethine cyanine, A = H;
 Q = 2-quin-azamethine cyanine, A = C₆H₄;
 L = 4-quin-azamethine cyanine, A = C₆H₄.

whereas adenine has the structure:



The calculated volumes of adenine (0.022 M) and dye (0.001 M) were transferred to a 10 ml dark flask and the volume was completed to the mark with secondary distilled water. The initial concentration of adenine was varied in the range (0—0.02) M while the dye concentration was varied in the range (1.6—10.0) $\times 10^{-5}$ M. All solutions were freshly prepared each day, and their absorbances were measured in rectangular 1 cm path length cells within 5 hours. Most operations were performed in an air-conditioned room ($\sim 22^\circ\text{C}$) with subdued light to avoid photo chemical transformations.

Spectrophotometric measurements were recorded on a Shimadzu UV-200 S double beam spectrophotometer using the technique recommended by Al-Ani *et al.*¹³ The baselines were recorded before running the spectra of a given set of solutions, using secondary distilled water in the cells of the sample and reference compartments. At the beginning of the measurements of a set of solutions, the spectra of

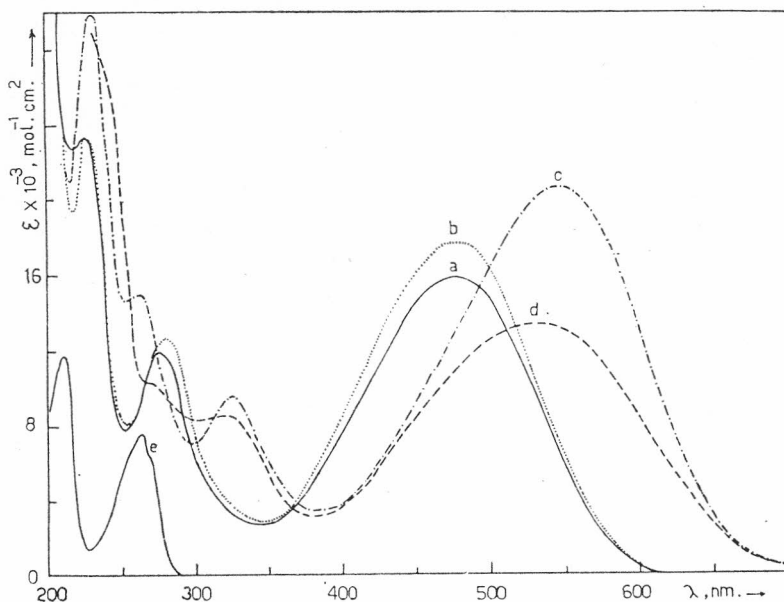


Figure 1. Electronic absorption spectra of the compounds in water at 25 °C: a) α ; b) γ ; c) Q; d) L-aza cyanine dye; and e) adenine.

TABLE I

The Elemental Analysis Data and Melting Points of the Aza Cyanine Dyes

Compound	Formula	m. p. °C	C	% Calc. (Found)		N
				H		
α	$C_{16}H_{20}N_3I$	191	50.40 (50.31)	5.29 (5.17)	11.02 (10.90)	
γ	$C_{16}H_{20}N_3I$	194	50.40 (50.36)	5.29 (5.19)	11.02 (10.93)	
Q	$C_{20}H_{22}N_3I$	185	55.69 (55.58)	5.14 (5.11)	9.74 (9.65)	
L	$C_{20}H_{22}N_3I$	163	55.69 (55.59)	5.14 (5.15)	9.74 (9.70)	

pure compounds were taken at the working temperature to detect any change. The absorbance was measured at fixed wavelengths to minimize errors arising from the steepness of absorption spectra. The spectrum of the complex formed was detected at wavelengths longer than those of the individual pure substances having identical concentrations to those in the mixture. The mixture was measured within approximately 10 min. after mixing the solutions and placing the cell in a thermostated cell holder for equilibrium.

RESULTS

The absorbances of the aza cyanine dyes and adenine at the wavelengths investigated, when measured separately at different concentrations, were temperature independent. The representative spectra, Figure 2, show that the visible absorption spectra of mixed substances were shifted from those of individual pure substances toward longer wavelengths; taking into consideration that adenine has no absorption in the visible region. Similar spectra

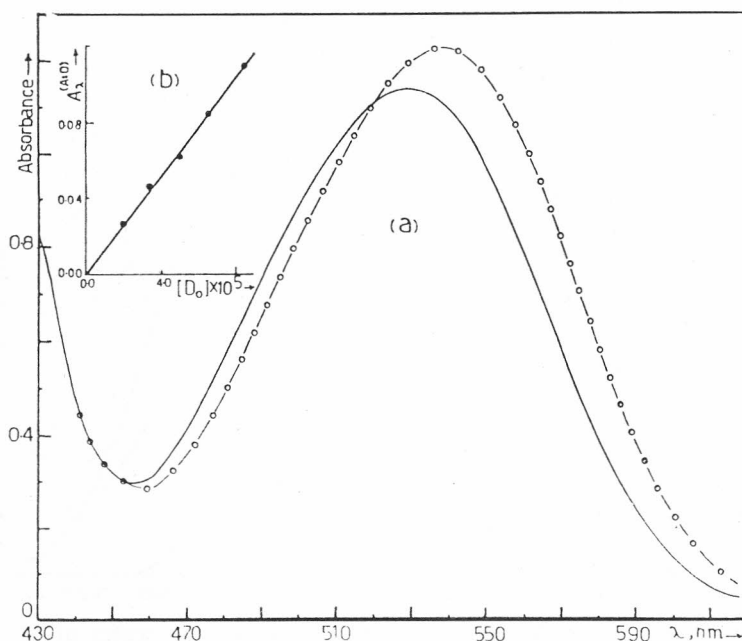


Figure 2. a) Visible absorption spectra of aqueous solutions of 8.4×10^{-5} M L-aza cyanine dye (—), and 8.4×10^{-5} M L-aza cyanine dye plus 2×10^{-2} M adenine (○—○—○), at 28°C .

b) Plot of $A_\lambda^{(A:D)}$ versus $[D_0]$ for aqueous solutions of L-aza cyanine dye containing a fixed concentration of adenine (2×10^{-2} M) at 28°C . $A_\lambda^{(A:D)}$ represents the absorbance of the complex at wavelength λ ($\lambda = 549$ nm).

were obtained for the other dye-adenine combinations. In all cases, the visible absorption spectra of the mixed substances were bathochromically shifted with regard to the pure compounds. The increase in absorption at longer wavelengths was attributed to the weakly bonded charge transfer complex formation.

To calculate the absorbances of the complex formed, the absorptivities of the reacting compounds were calculated at different wavelengths. The absorbance of the complex at a given wavelength was estimated from the difference between the absorbance of a mixture and the sum of the absorbances of pure components at concentrations identical to those used in the mixture. Experimental data which were used to calculate the equilibrium constants (Table II) were measured in regions where the absorption of the complex was appreciable. The accuracy of the measurements was ± 0.01 absorbance unit.

The equilibrium constant of the complex is defined as follows:

$$\text{assuming the interaction } A + D \rightleftharpoons (A : D) \quad (1)$$

where $(A : D)$ is the complex formed

$$K_c^{(A:D)} = \frac{[(A : D)]}{[A_0 - (A : D)][D_0 - (A : D)]} \quad (2)$$

TABLE II

Equilibrium Constants $K_c^{(A:D)}$, Standard Free Energy (ΔG°), Standard Enthalpy (ΔH°), and Standard Entropy (ΔS°) Changes Associated with the Interactions of Aza Cyanine Dyes With Adenine in Aqueous Solutions Together With Molar Absorptivities ($\epsilon_\lambda^{(A:D)}$) at Wavelength (λ)

$K_c^{(A:D)} \cdot 10^{-2}$ (M ⁻¹)	Temperature ± 0.5 (°C)	ΔG° k. cal. mole ⁻¹	ΔH° k. cal. mole ⁻¹	ΔS° cal. deg. ⁻¹ mole ⁻¹
<u>α-Aza — Adenine</u>				
10	0.041	-0.800		
20	0.039	-0.798	-0.897	-0.34 \pm 0.02
28	0.038	-0.799		
35	0.036	-0.787		
$\lambda = 484$ nm; $\epsilon_\lambda^{(A:D)} = 9,770$				
<u>γ-Aza — Adenine</u>				
9	0.169	-1.587		
20	0.138	-1.528	-2.966	-4.90 \pm 0.01
28	0.121	-1.491		
35	0.108	-1.460		
$\lambda = 482$ nm; $\epsilon_\lambda^{(A:D)} = 4,328$				
<u>Q-Aza — Adenine</u>				
6	9.483	-3.801		
15	4.139	-3.449		
20	2.774	-3.720	-12.422	-30.85 \pm 0.78
28	1.538	-3.012		
35	0.977	-2.805		
$\lambda = 557$ nm; $\epsilon_\lambda^{(A:D)} = 3,214$				
<u>L-Aza — Adenine</u>				
4	1.357	-2.703		
15	0.930	-2.594		
20	0.693	-2.468	-6.241	-12.78 \pm 0.11
28	0.538	-2.384		
35	0.428	-2.300		
$\lambda = 549$ nm; $\epsilon_\lambda^{(A:D)} = 3,307$				

where $[A_0]$ and $[D_0]$ are the initial concentrations of the interacting adenine and dye, respectively. For two molecules complexing according to the foregoing scheme, the molar absorptivity of the complex at wavelength λ is given by

$$\epsilon_\lambda^{(A:D)} = \frac{A_\lambda^{(A:D)}}{l [(A:D)]} \quad (3)$$

where $A_\lambda^{(A:D)}$ is the absorbance of the complex at the wavelength λ . From Eq.'s (2) and (3):

$$\epsilon_\lambda^{(A:D)} = \frac{A_\lambda^{(A:D)}}{l K_c^{(A:D)} [A_0 - (A:D)] [D_0 - (A:D)]} \quad (4)$$

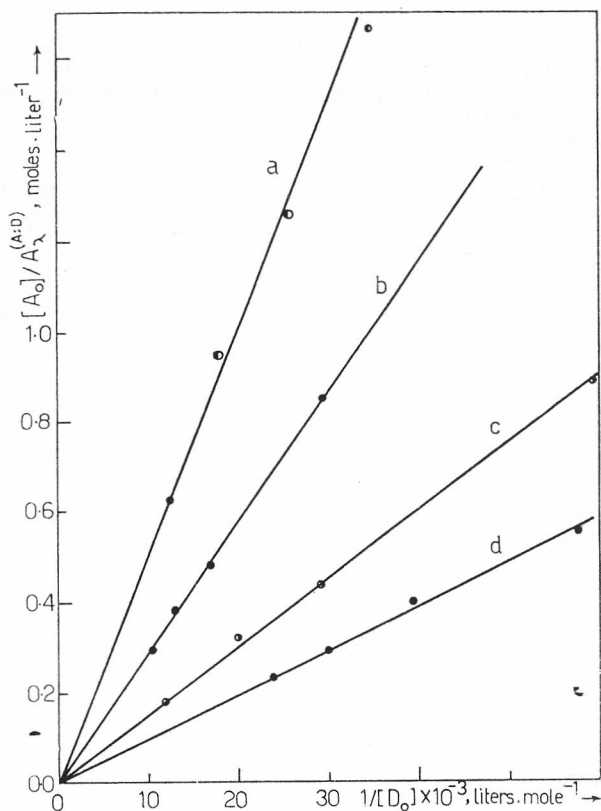


Figure 3. Plots of $[A_o]/A_\lambda^{(A:D)}$ versus $1/[D_o]$ for aqueous solutions of the dyes containing a fixed concentration of adenine at 28°C. The dye-adenine combinations are: a) α -adenine; b) γ -adenine; c) L-adenine; and d) Q-adenine. The adenine total concentration, $[A_o] = 2 \times 10^{-2}$ M, and the dye total concentration, $[D_o] = (1.6 - 10.0) \times 10^{-5}$ M.

or

$$\frac{[A_o - (A:D)] l}{A_\lambda^{(A:D)}} = \frac{1}{\varepsilon_\lambda^{(A:D)} K_c^{(A:D)} [D_o - (A:D)]} \quad (5)$$

For $[A_o] \gg [D_o]$, Eq. (5) becomes,

$$\frac{[A_o] l}{A_\lambda^{(A:D)}} = \frac{1}{[D_o]} \left[\frac{1}{\varepsilon_\lambda^{(A:D)} K_c^{(A:D)}} + \frac{[A_o]}{\varepsilon_\lambda^{(A:D)}} \right] \quad (6)$$

A plot of $\frac{[A_o] l}{A_\lambda^{(A:D)}}$ versus $\frac{1}{[D_o]}$ for constant $[A_o]$ and varying $[D_o]$ will give

a straight line passing through the origin.

To find the values of $K_c^{(A:D)}$ and $\varepsilon_\lambda^{(A:D)}$, Eq. (6) was applied for two different concentrations of adenine $[A_{o1}]$ and $[A_{o2}]$ at a constant dye concen-

tration $[D_0]$. The values of $[A_{01}]$ and $[A_{02}]$ are chosen in the range where there is no appreciable shift in wavelength λ . (c. f. Discussion and Figure 5 (B-2). At adenine concentration A_{01} Eq. (6) becomes:

$$\frac{[A_{01}] l}{A_{\lambda_1}^{(A:D)}} = \frac{1}{[D_0]} \cdot \frac{1}{\varepsilon_{\lambda}^{(A:D)}} \left[\frac{1}{K_c^{(A:D)}} + [A_{01}] \right] \quad (7)$$

or

$$\varepsilon_{\lambda}^{(A:D)} = \frac{A_{\lambda_1}^{(A:D)}}{[A_{01}] [D_0] l} \left[\frac{1}{K_c^{(A:D)}} + [A_{01}] \right] \quad (8)$$

while at adenine concentration A_{02} it becomes:

$$\varepsilon_{\lambda}^{(A:D)} = \frac{A_{\lambda_2}^{(A:D)}}{[A_{02}] [D_0] l} \left[\frac{1}{K_c^{(A:D)}} + [A_{02}] \right] \quad (9)$$

where $A_{\lambda_1}^{(A:D)}$ and $A_{\lambda_2}^{(A:D)}$ are the absorbances of the complex at adenine concentrations A_{01} and A_{02} , respectively. From Eqs. (8) and (9):

$$\frac{A_{\lambda_1}^{(A:D)}}{[A_{01}]} \left[\frac{1}{K_c^{(A:D)}} + [A_{01}] \right] = \frac{A_{\lambda_2}^{(A:D)}}{[A_{02}]} \left[\frac{1}{K_c^{(A:D)}} + [A_{02}] \right] \quad (10)$$

or

$$K_c^{(A:D)} = \frac{[A_{01}] A_{\lambda_2}^{(A:D)} - [A_{02}] A_{\lambda_1}^{(A:D)}}{[A_{01}] [A_{02}] (A_{\lambda_1}^{(A:D)} - A_{\lambda_2}^{(A:D)})} \quad (11)$$

From Eq. (11), $K_c^{(A:D)}$ can be calculated. Applying the value of $K_c^{(A:D)}$ in Eq. (7), the value of $\varepsilon_{\lambda}^{(A:D)}$ can be evaluated. Plots of Eq. (6) for all dye-adenine combinations at 28°C are represented in Figure 3, while $K_c^{(A:D)}$ and $\varepsilon_{\lambda}^{(A:D)}$ values are given in Table II.

Various thermodynamic parameters for the interaction between adenine and the aza cyanine dyes were calculated from the following well-known equation:

$$\log K_c^{(A:D)} = -\frac{\Delta H^\circ}{2.303 RT} + \text{constant} \quad (12)$$

Therefore, a plot of $\log K_c^{(A:D)}$ versus the reciprocal of the absolute temperature ($1/T$) should give a linear slope of $-\Delta H^\circ/2.303 R$ if the standard enthalpy change of the reaction (ΔH°) does not depend on temperature (R is the gas constant). The Gibbs free energy change of a reaction (ΔG°) is related to the equilibrium constant and the changes in the standard enthalpy and entropy (ΔS°) according to the following relationships:

$$\Delta G^\circ = -RT \ln K_c^{(A:D)} \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (14)$$

Representative plots of Eq. (12) are shown in Figure 4 and the thermodynamic parameters calculated from these equations are given in Table II.

DISCUSSION

A charge transfer interaction can occur between two molecules of different electronegativities as a result of inequalities in the sharing of electrons. In the ground state, the two molecules are held together when they are in close proximity by forces such as van der Waals, dispersion, London, and hydrogen bond. Additional forces are contributed by the transfer of a small amount of charge from the donor molecule to the acceptor one.¹⁴ When a complex absorbs light of a suitable energy, it is raised from the ground to the excited state, in which the electron that was slightly shifted toward the acceptor is almost wholly transferred.¹⁵ The transitions involved are called charge transfer transitions.¹⁵

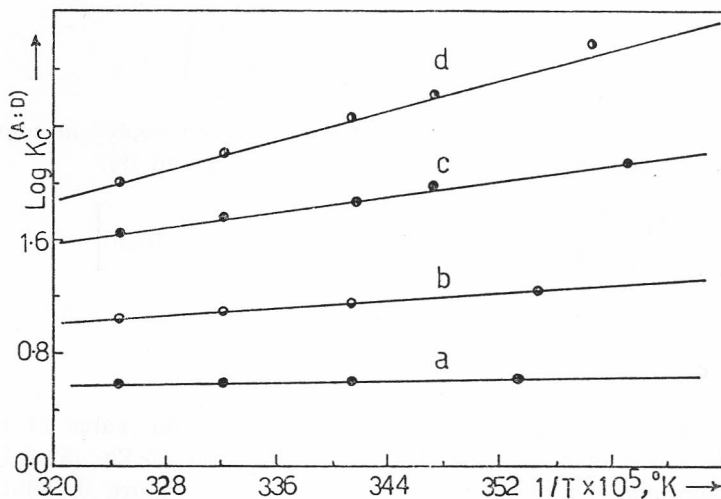


Figure 4. $\text{Log } K_c^{(A:D)}$ versus $1/T$ plots of the interactions: a) α -adenine; b) γ -adenine; c) L-adenine; and d) Q-adenine.

Adenine as one of the nucleic acid bases was found to form charge transfer complexes with many electron donor compounds, e. g., catechol,¹⁶ epinephrine¹⁵ and isoproterenol.¹⁷ The absorption spectra of the complexes formed between DNA or RNA and cationic dyes in the form of thin films showed slight changes in the visible region as compared to the uncomplexed dye. It is assumed that electron transfer takes place from the dye to the nucleic acid.^{18,19}

The type of complexing between adenine and other compounds mainly depends on their molecular structure. In UV-absorption studies on the interaction of adenine with catechol in aqueous solution containing 0.1 M HCl, the equilibrium constant was found to be wavelength independent, assuming a 1:1 charge transfer complex.¹⁶ On the other hand, the interaction of adenine with epinephrine under identical conditions was wavelength dependent, indicating a stoichiometry other than 1:1.¹⁵

Interaction of 2(4) pyrid- and 2(4)quin-azamethine cyanine dyes with adenine was investigated in aqueous solutions and was found to form charge transfer, complexes. This phenomenon was followed up using two routes:

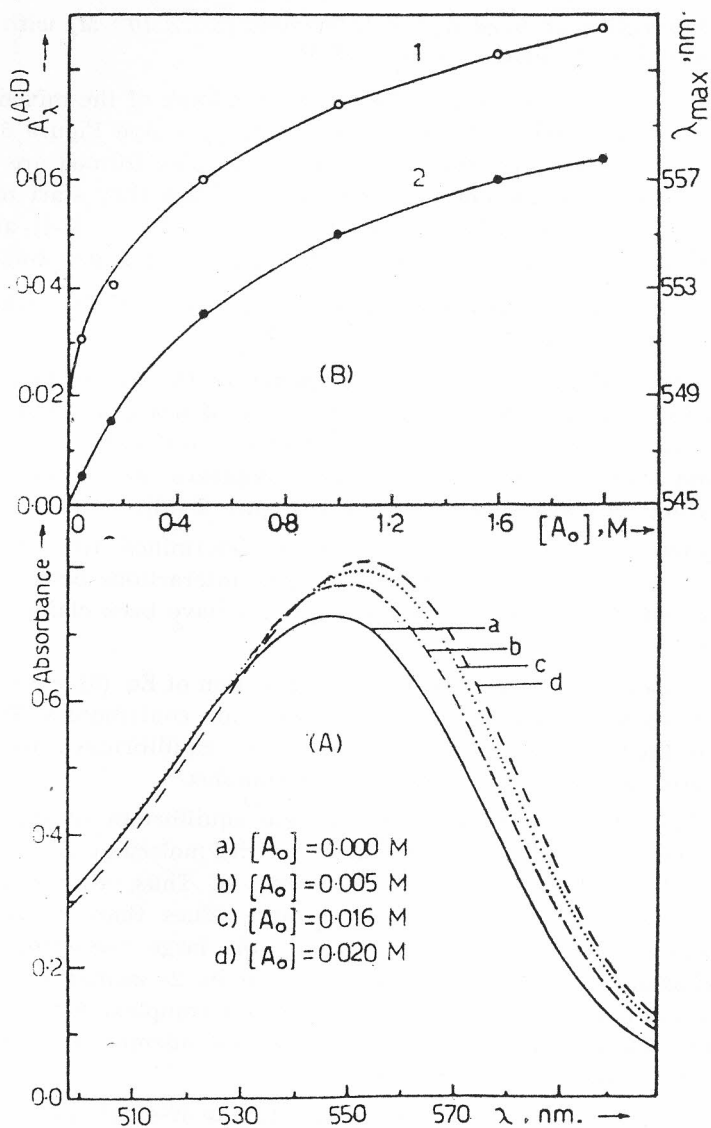


Figure 5. A) Visible absorption spectra of aqueous solutions of 3.5×10^{-5} M Q-aza cyanine dye containing different concentrations of adenine $(0.0 - 2.0) \times 10^{-2}$ M, at 28°C .

B-1) Plot of $A_{\lambda}^{(A \rightarrow D)}$ versus $[A_o]$ for aqueous solutions of 3.5×10^{-5} M Q-aza cyanine dye containing different concentrations of adenine $(0.0 - 2.0) \times 10^{-2}$ M, at 28°C ($\lambda = 557$ nm).

B-2) Plot of the amount of λ_{\max} red shift versus $[A_o]$ for aqueous solutions of 3.5×10^{-5} M Q-aza cyanine dye containing different concentrations of adenine $(0.0 - 2.0) \times 10^{-2}$ M at 28°C .

Route (a): Interaction of fixed dye concentration (3.5×10^{-5} M) with different amounts of adenine (0.00—0.02 M)

It was noticed that the visible absorption maximum of the mixed substances lies at a longer wavelength than that of the pure dye Figure 5 (A). The amount of red shift and the absorbance of the complex formed are increased sharply until a definite adenine concentration at which they start to increase gradually with increasing adenine concentration [Figure 5 (B-1) and (B-2)]. This sigmoid increase was also found in all other dye-adenine combinations.

Route (b): Interaction of fixed large excess of adenine (0.02 M) with different dye concentrations (1.6 — 10.0) $\times 10^{-5}$ M

It was observed that the absorption spectra of the mixed substances are red shifted by 7—21 nm, depending on the type of aza cyanine dye applied, and the amount of the red shift is independent of the dye concentration. Also, it was found that the absorbances of the complexes are increased linearly with increasing the dye concentration [c. f. Figure 2 (b)].

The exact complex geometry cannot be determined from the present absorption measurements, but parallel stacking interactions between adenine and the aza cyanine dyes can be invoked as they have been claimed for similar systems.²⁰⁻²⁴

Linear slopes were obtained from the application of Eq. (6) [c. f. Figure (3)], so that 1:1 complexes are assumed to be the main contributors. The present results show the wavelength independence of the equilibrium constant which could indicate the formation of one type of complex.²⁵

From Table II, it is quite clear that the equilibrium constant and the thermodynamic parameters depend mainly on the molecular structure of the dye used and follow the order: $Q > L > \gamma > \alpha$. Thus, 4-pyrid-azamethine cyanine dye has higher equilibrium constant values than its 2-pyrid-azamethine isomer. This may be interpreted by the large π -electron system of the 4-pyrid-azamethine cyanine as compared to its 2- isomer and, thus, the 4-isomer is a better donor for the charge-transfer complex. Also, the parallel stacking interaction is more pronounced between adenine and 4-pyrid-azamethine cyanine dye.

Introducing an extra fused phenyl ring to the *N*-ethyl quaternary pyridinium moiety largely influenced its effect. It caused a dramatic increase in $K_c^{(A:D)}$, ΔG° , ΔH° , and ΔS° values (Table II). This extra fused phenyl ring increases the π -electron cloud and its mobility through the whole molecule which stabilizes the charge transfer complex formed with adenine. The effect of the extra fused phenyl ring is more pronounced in case of 2-aza cyanine dye relative to its 4-aza cyanine isomer. The structure of the 2-quin-azamethine cyanine dye is more linear than that of the 4-quin-azamethine isomer. Thus, parallel stacking interaction is more effective for adenine-2-quin-azamethine cyanine than for adenine-4-quin-azamethine isomer. To illustrate these effects the structures of the cyanine dyes are drawn as follows:

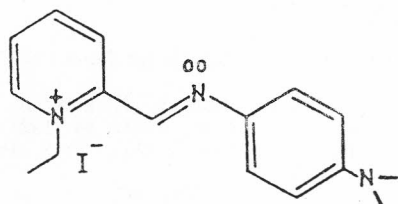
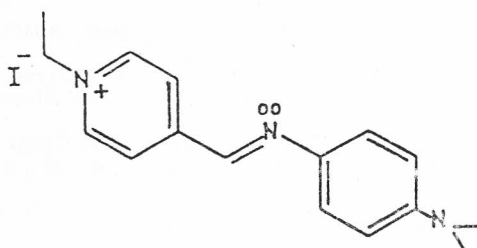
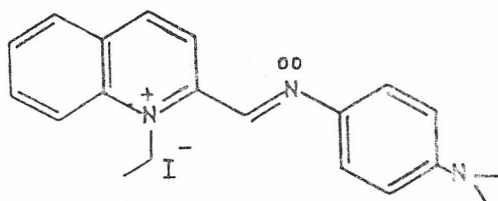
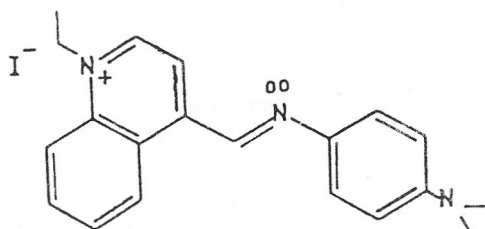
2-pyrid-azamethine cyanine
(α)4-pyrid-azamethine cyanine
(γ)2-quin-azamethine cyanine
(Q)4-quin-azamethine cyanine
(L)

Table II also shows that the order of the standard enthalpy of formation (ΔH°) is parallel to the equilibrium constant ($K_c^{(A:D)}$), the free energy change (ΔG°) and the standard entropy change (ΔS°) associated with such reactions. Higher values are observed for Q-adenine combination. A high ΔS° indicates a high degree of specificity of these reactions, as well as a high degree of change in the structure of the solvent when the complex is formed. Linear relationship between ΔH° and ΔS° was observed for many complexes between a given acceptor and the related donors.²⁶

Finally, it is hoped that the finding of the charge transfer phenomenon between aza cyanine dyes and adenine will help to understand the mechanism of the action of these dyes in living systems at the molecular level.

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SAŽETAK

Interakcija aza cijaninskih boja s adeninom

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Studij interakcije 2(4)-pirido- i 2(4)-kinazametin cijaninskih boja s adeninom pokazuje u ultraljubičastim i vidljivim spektrima stvaranje slabo vezanih kompleksa s prijenosom naboja. Apsorpcijske vrpce nastalih kompleksa u vidljivom području nalaze se izvan područja apsorpcije čistih komponenata na većim valnim duljinama. Iznos induciranog crvenog pomaka uglavnom ovisi o tipu izreagirale boje, te je neovisan o koncentraciji boje pri stalnom velikom suvišku adenina. Ravnotežne konstante izračunane su za komplekse sastava 1:1. Izračunani su razni termodinamički parametri i molarne apsorpcije za različite interakcije. Raspravlja se o odnosu strukture i aktivnosti molekulskih vrsta u interakciji.