

**Electronic Spectral Studies
of Some Charge-Transfer Complexes of a Purine Analogue
"Of Biological Interest" with Iodine**

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ABSTRACT. The reaction between 3,7-disubstituted-2,5-diamino-pyrazolo [1,5-a] pyrimidine-6-carbonitriles (DPC) with iodine is studied photometrically in various chlorinated solvents. The results obtained from spectroscopic measurements revealed that in each solvent the (DPC): I₂ ratio is 1:2 and the charge transfer (CT) iodine complex is assigned the formula (DPC) I₂. Values of the formation constant (k), molar absorptivity (ε) and oscillator strength (f) for the I₂(CT) complex were obtained. It was shown that the values of these constants depend entirely on the polarity of the solvent. Where it was indicated that there is a linear correlation between either the oscillator strength or the molar absorptivity and the dielectric constant of the solvent, suggesting a type of interaction between the ionic (CT) complex with the solvent.

The important role that charge transfer (CT) complexes play in biological systems; leads some investigators (Gyorgy 1960) to suggest that the activity of biologically active compounds may depend on their tendencies to form such CT complexes with biological receptors. In connection with the CT complexes of I₂, although a great deal of work has been done (Yarwood 1974, Trotter 1978, Harada 1979, Mulazzi *et al.* 1981, Laane *et al.* 1986) on the interaction of I₂ with different donor compounds, also the conversion of iodine molecules into polyiodide units are known in the literature (Mulazzi *et al.*, Laane *et al.* 1986), much work needs to be done for obtaining compounds of expected biological activity. Pyrazolo [1,5-a] pyrimidines are purine analogues and as such they have useful properties as antimetabolites in purine

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biochemical reactions (Earl *et al.* 1975). Moreover, these compounds have marked antitumor and antileukemic activity (Hildick 1971, Novinson *et al.* 1974).

Continuing our interest for the synthesis of pyrazolopyrimidines as potential CNS regulants and antimetabolites in purine biochemical reactions (Elegemeie 1987, 1988, 1991), we investigated in the present work the tendency to form CT complexes with I₂. The CT complexes were studied photometrically in solutions, where the solvent effect has been investigated. Also, values of some physical parameters, such as the formation constant, the molar absorptivity and the oscillator strength, of such CT complexes were calculated.

Experimental

Absorption spectra were measured using a Perkin-Elmer spectrometer Model 522, with a fused silica cell of 1.0 cm optical pathlength. Spectrograde solvents were used in all measurements. R.G. quality I₂ (Hyashi Pure Chemical Industry Ltd.) was used and its concentration in solution was checked spectrophotometrically.

The DPC compound (Fig. 4) was prepared essentially by the method previously reported (Elgemeie 1988) and were purified by recrystallization from ethanol. The obtained yellow crystalline solid of DPC showed a melting point higher than 573 K. Its infrared spectrum showed absorption bands at 3450 and 3300 cm⁻¹ characteristic of associated NH₂ stretching modes and at 2210 cm⁻¹ of C ≡ N stretching vibration. On the other hand, ¹H nmr spectrum of DPC showed the signals 7.18 ppm (s, br., 2H, NH₂), 7.52-8.02 ppm (m, 8H, 2C₆H₄) and 8.62 ppm (s, br., 2H, NH₂). Also, the mass spectrum of the compound showed that its molecular weight is 423.

Photometric titrations were performed as described (Skoog 1985) in all solvents at 293 K, using a fixed concentration of DPC (10×10⁻⁶M), whilst the concentration of I₂ was varying over the range 5-80 × 10⁻⁶M in order to cover the DPC:I₂ ratios from 1:0.5 to 1:8. The absorbancies of the brown I₂ CT complex formed were measured in each case and were plotted as a function of the I₂ molar ratio as will be seen in the section "Results and Discussion." Photometric titration was also performed in 1,2-dichloroethane but with fixed I₂ concentration and varying DPC concentration.

Results and Discussion

The electronic absorption spectra of the DPC:I₂ CT complex (1:2), as well as the spectra of I₂ and DPC, at the concentration 10×10⁻⁶M, in 1,2-dichloroethane are shown in Fig.1. The spectra showed that DPC CT complex with I₂ has two strong absorptions at 295 and 365 nm. It should be noted that neither I₂ nor DPC base shows significant absorptions in the UV/Visible region using such low concentrations. Fig.2 shows the photometric titration curves measured at λ_{max} 295 and 365 nm, where the DPC concentration was kept constant. The equivalence points, as shown in the photometric

titration curves, indicate that the CT complex forms in the ratio (1:2). Photometric titration curves carried out in other solvents such as CCl_4 , CHCl_3 and CH_2Cl_2 , showed that DPC and I_2 react in the same 1:2 molar ratio under the conditions of fixed DPC concentration, where the CT complex absorbs in these solvents almost with inconsiderable wavelength shift. It is not out of place to mention that the formation of 1:2 CT complex was further substantiated in 1,2-dichloroethane, but with fixed I_2 in this case.

In the present work, the solvent effect was studied in a quantitative manner. Values of the formation constant (k), the molar absorptivity (ϵ) and the oscillator strength (f) of the complex in each solvent were obtained. Since the concentration of both the donor (DPC) and acceptor (I_2) are remarkably low, the following equation (Balasubramanian 1978, Abu-Eittah 1976) could be used in the calculation:

$$\frac{\text{Ca}^0 \cdot \text{Cd}^0}{A} = \frac{1}{k\epsilon} + \frac{\text{Ca}^0 + \text{Cd}^0}{\epsilon} \dots\dots\dots (1)$$

Where Ca^0 and Cd^0 are the initial concentrations of the acceptor and donor respectively and A is the absorbance of the most intense band at 295 nm. From the plot $\text{Ca}^0 \cdot \text{Cd}^0/A$ vs $\text{Ca}^0 + \text{Cd}^0$, in each solvent using various concentrations of the acceptor, values of both (k) and (ϵ) were obtained. On the other hand, the oscillator strength (f) was calculated from the approximate relation, as has previously been reported (Tsubomura 1961):

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

where $\gamma_{1/2}$ is the half band-width in cm^{-1} .

The calculated values of (k), (ϵ) and (f) for the CT complex in various solvents, together with values of the dielectric constants of the solvents used, are given in Table 1.

Table 1. Spectrophotometric data of DPC- I_2 Charge-Transfer complex and the dielectric constants of the solvents used

Solvent	$k \times 10^{-4}$ (l/mol)	λ_{max} (nm)	$\epsilon_{\text{max}} \times 10^{-4}$	(f)	(D)
CCl_4	12.4	298	2.34	0.635	2.2
CHCl_3	4.6	296	3.44	0.785	4.7
CH_2Cl_2	16.7	298	4.56	1.048	8.9
$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	9.5	295	5.82	1.255	10.4

It is quite evident from the data in Table 1 that the (DPC): I_2 CT complex shows high values of both the formation constant (k) and the molar absorptivity (ϵ) which reflects the high stability of the complex as a direct consequence of the expected high donation ability of the (DPC) molecule (containing eight nitrogens). Whilst the high value of (ϵ) is in good agreement with the existence of the triiodide ion I_3^- which is well known to have

high absorptivity (Kiefer 1972, Andrews 1980, Kaya 1972). It is also clear that by the increase of the solvent polarity the molar absorptivity increases. It is not out of place to mention that this is in accordance with the experimental findings reported by Balasubramanian *et al.* 1978 .

Again it is quite obvious that both (ϵ) and the oscillator strength (f) increase with the increase of the dielectric constant (D) of the solvent, as indicated by the linear relationship obtained by plotting (f) against (D), as shown in Fig.3. It should be noted that the strong solvent hyperchromic effect observed in the electronic spectrum of such CT complex, resulting in a high spectral intensities, could be attributed to a strong solvent interaction with the ionic (DPC) $I + I_3^-$ leading to an alteration of the molecular geometry of the triiodide complex. Such an alteration would be expected to increase of the solvent polarity.

Also, the appearance of three raman bands at 147,108 and 85 cm^{-1} which are assigned to γ_{as} (I-I) γ_s (I-I) and δ I_3^- respectively in the raman spectrum of the isolated solid complex adds a substantial evidence supporting the triiodide structure $[DPCI] + I_3^-$. The results of the solid complex may well be published in a separate communication.

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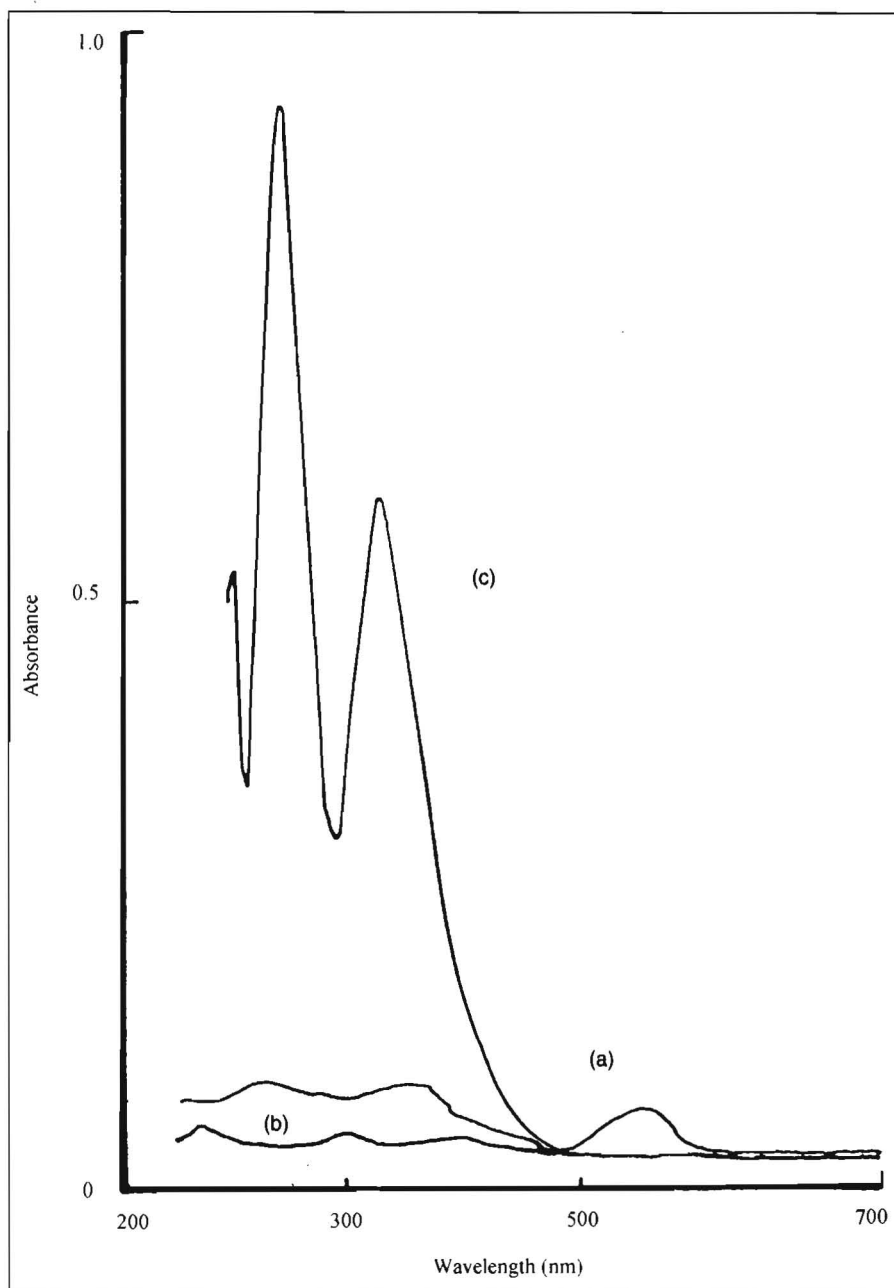


Fig. 1. Electronic absorption spectra of
(a) DPC [$10 \times 10^{-6} \text{ M}$],
(b) Iodine [$10 \times 10^{-6} \text{ M}$] and
(c) CT complex: DPC [$10 \times 10^{-6} \text{ M}$] and Iodine [$20 \times 10^{-6} \text{ M}$]

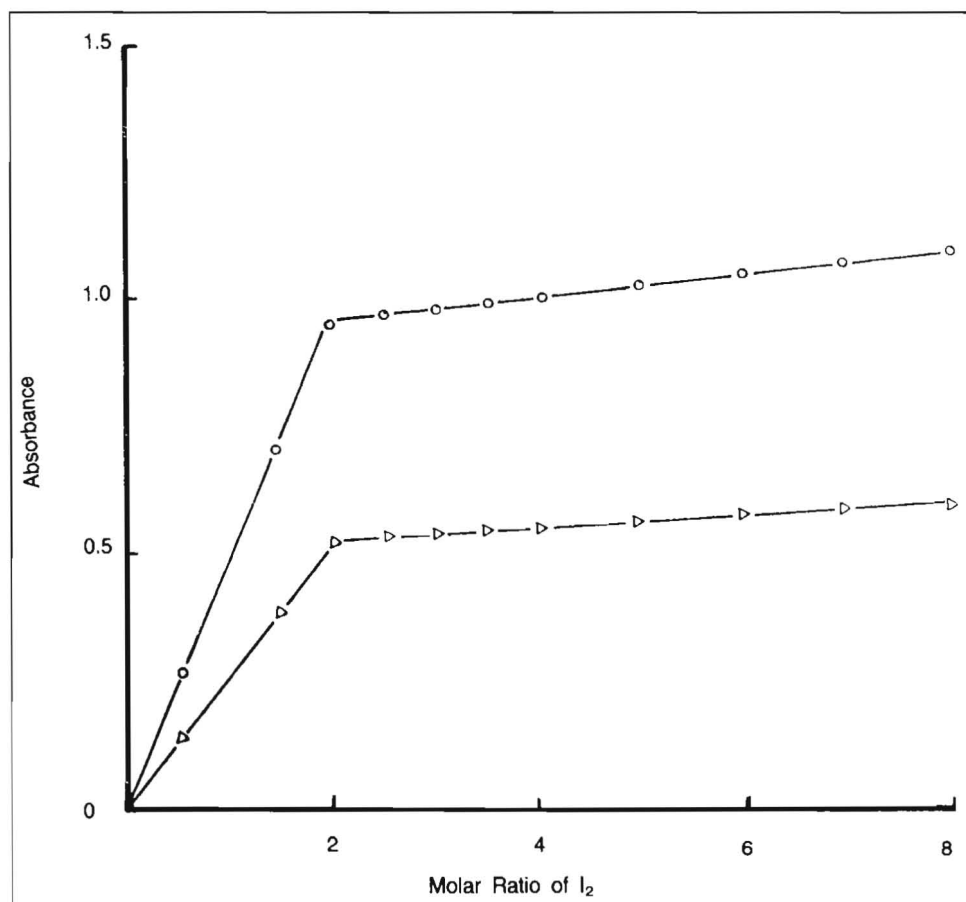


Fig.2. Photometric titration curves of DPC-I₂ system in 1, 2-dichloroethane,
- Upper curve for the absorption at 295 nm and
- Lower curve for the absorption at 365 nm.

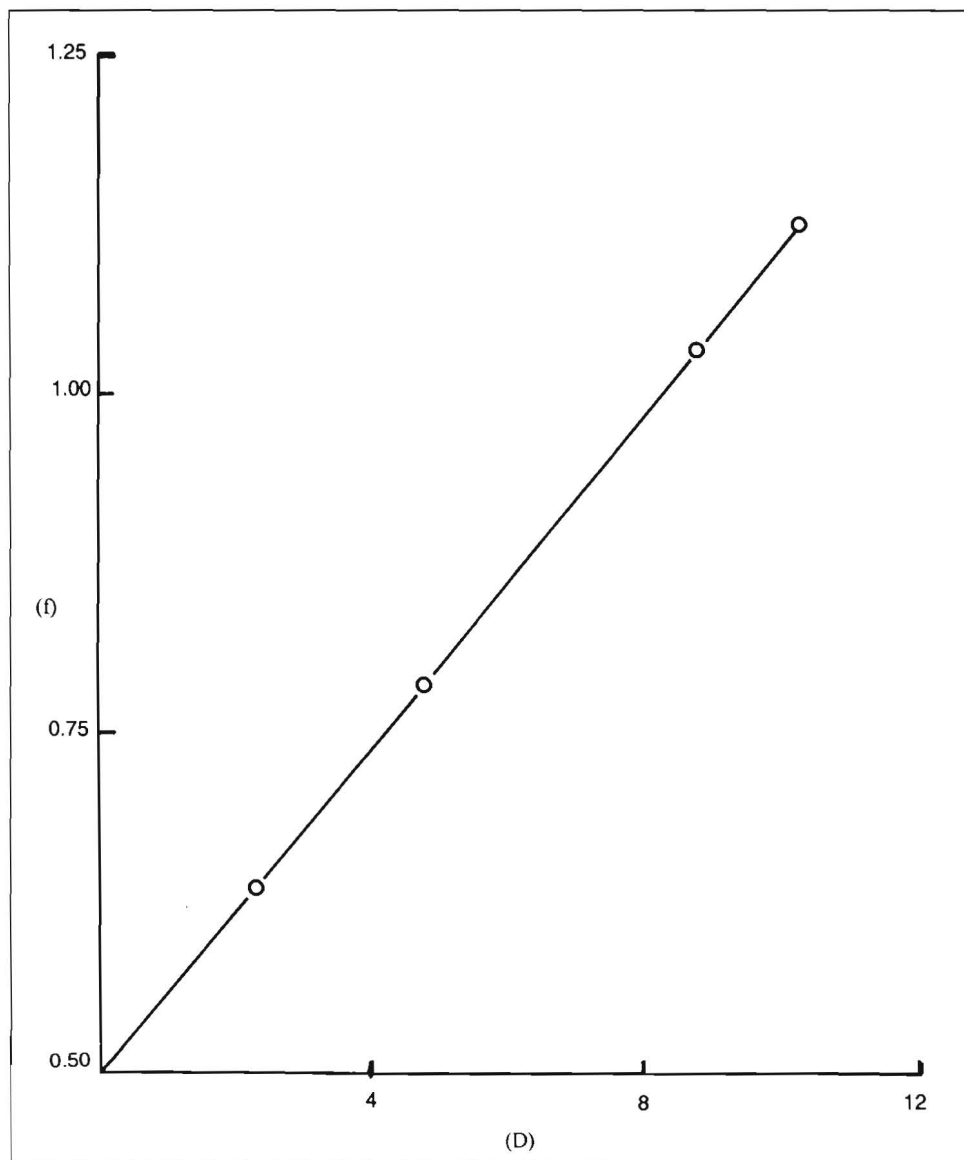


Fig.3. Dependence of the oscillator strength (f) of the CT complex on the dielectric constant of the solvent.

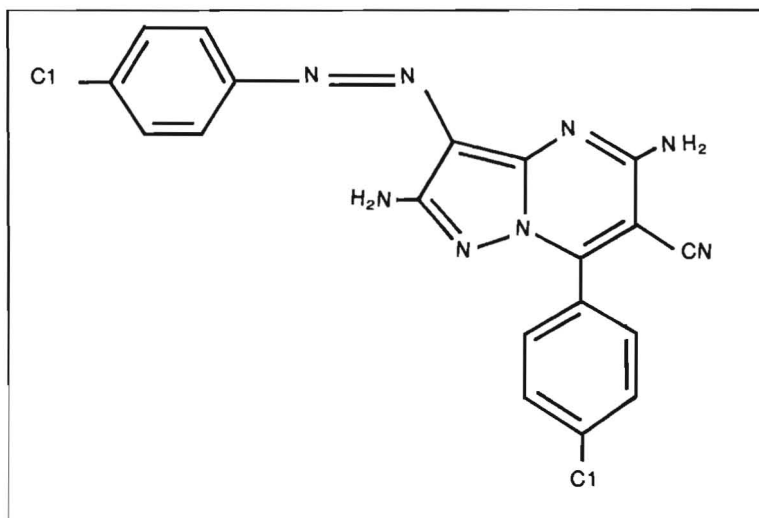


Fig.4. The DPC compound.

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دراسات عن الطيف الالكتروني لبعض متراكبات انتقال الشحنة لمشتقات البيورين (ذات النشاط البيولوجي) مع اليود

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تلعب متراكبات انتقال الشحنة دوراً هاماً في الأنظمة البيولوجية، مما دعا بعض الباحثين إلى الاقتراح بأن نشاطية أي مركب بيولوجياً تكمن في قدرة هذا المركب على تكوين مثل هذا النوع من متراكبات انتقال الشحنة مع بعض المستقبلات البيولوجية. يتلخص هذا البحث في محاولة الحصول على متراكبات انتقال الشحنة (CT) بين بعض البيورينات واليود. فقد وجد أن البيورين DPC (شكل ٤) يتفاعل مع اليود بنسبة ١:٢ معطياً متراكباً من متراكبات انتقال الشحنة. وحيث أن مركبات بيرازولو (١،٥ - أ) بيريميدينز تُعتبر من البيورينات والتي عُرِفَت بأن لها خواص نافعة كمضادات لعمليات الأيض في تفاعلات البيورين البيوكيميائية، ومن ثم فإن هذه المركبات يكون لها تأثير فعال كمضادات للأورام السرطانية وكمضادات لمرض اللوكيميا. وقد تلخص هذا البحث في دراسة هذه المتراكبات عن طريق دراسة الطيف الالكتروني لهذه المتراكبات في المحاليل المختلفة، ومن ثم فقد تمّ دراسة تأثير المذيب على الامتصاص في الأطياف الالكترونية لهذه المتراكبات في المحاليل المختلفة.

وبدراسة طيف الامتصاص الالكتروني للمتراكب CT I₂: DPC وجد أن المتراكب يظهر اثنين من قمم الامتصاص مقاسة عند λ_{max} تساوي ٣٦٥، ٢٩٥ nm لا تظهر في طيف الامتصاص للمادتين المتفاعلتين DPC واليود.

وبرسم منحني المعايرة الطيفية وجد أن المترابك يتكوّن من DPC واليود بنسبة ١:٢. وقد تمّت دراسة تأثير المذيبات المختلفة على طيف الامتصاص بطريقة كمية حيث تمّ تعيين قيم ثابت التكوين (K) والامتصاص الجزيئي (ε) وقوة التذبذب (f) للمترابك في كل من المذيبات التي استُخدمت وهي رابع كلوريد الكربون وثنائي كلوروإيثان وثنائي كلوروميثان والكلوروفورم.

أيضاً وجد أن قيم (ε), (f) تزداد بزيادة ثابت العزل الكهربائي للمذيبات المختلفة، كما تبين من العلاقة الخطية التي تمّ الحصول عليها برسم قيم (f) مع قيم (D) كما هو مبين في شكل (٣). وقد لوحظ أن طيف الامتصاص الالكتروني للمترابك يعتمد على قطبيه المذيب الأمر الذي لا يحدث إلا إذا كان المترابك أيوني مثل $(DPC)I^+I_3^-$ مؤدياً إلى حدوث تغيير في الشكل الهندسي للمترابك مثل هذا التغيير من المتوقع أن يزداد بزيادة قطبية المذيب. ومن الجدير بالذكر أن ظهور ثلاث حزم في طيف رامان لهذا المترابك عند ١٤٧، ١٠٨، ٨٥ سم^{-١} وهي الحزم الخاصة بالترددات التالية $\delta(I_3^-)$, $\gamma_s(I-I)$, $\gamma_{as}(I-I)$ على التوالي. وبذا فإن المترابك يكون له التركيب الأيوني $(DPC)I^+I_3^-$