

Spectroscopic and thermal studies of perylene charge-transfer complexes

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Charge-transfer (CT) complexes formed between perylene (Pery) as donor with iodine (I_2), picric acid (PA) and chloranilic acid (CLA) as acceptors were studied spectrophotometrically. The synthesis and characterization of perylene CT complexes of iodine, $[(\text{Pery})_2\text{I}^+\text{I}_3^-]$, picric acid, $[(\text{Pery})(\text{PA})]$ and chloranilic acid, $[(\text{Pery})(\text{CLA})]$ were described. These complexes were readily prepared by the reaction of Pery with I_2 , PA and CLA using CHCl_3 as a solvent. The IR, UV-Vis and ^1H NMR spectral techniques, as well as elemental analysis (carbon, hydrogen and nitrogen contents) and thermal analysis were used to characterize the three perylene charge-transfer complexes. Benesi-Hildebrand method and its modification were applied to the determination of association constant (K) and molar absorption coefficient (ϵ).

Keywords: Perylene, charge-transfer complexes, picric acid, chloranilic acid, iodine, thermal studies.

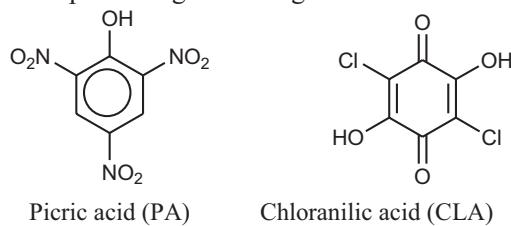
1. INTRODUCTION

Charge-transfer materials have attracted broad interest in the recent years due to their efficiency in the field of magnetic, electrical conductivity and optical properties [1, 2]. Generally, charge-transfer complexes play an important role in biological systems as well as in the field of drug receptor binding mechanisms [3, 4]. The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amines, mixed oxygen/nitrogen cyclic bases, aromatic/aliphatic amines have been studied and categorized [5–13]. The tri-iodide ion I_3^- , penta-iodide ion I_5^- , and ennea-iodide ion I_9^- were formed through the reaction of iodine with various donors like metal acetylacetones [14–16], polyazacyclic [17–19], and crown ethers [20–23]. Some charge-transfer complexes show very interesting applications in the analysis of drugs in pure form or in pharmaceutical preparations [24, 25]. The charge-transfer (CT) in fullerene-based [26, 27] compounds is currently of great interest since these materials can be utilized as superconductors [28] and to produce non-linear optical activity [29]. In this paper the charge-transfer complexes obtained by the interactions of perylene (Pery) as a donor with σ -acceptors, like iodine and π -acceptors such as picric acid (PA) and chloranilic acid (CLA) were studied

spectrophotometrically. The obtained data point to the formation of new and interesting CT complexes of the general formula $[(\text{Pery})_2\text{I}^+\text{I}_3^-]$ and $[(\text{Pery})(\pi\text{-acceptor})]$.

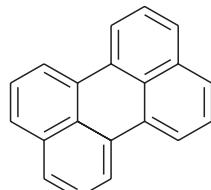
2. MATERIALS AND METHODS

The general chemical structures of donor and acceptors are given in Fig. 1.



Picric acid (PA)

Chloranilic acid (CLA)



Perylene (Pery)

Fig. 1. General chemical structure of donors and acceptors

2.1. Perylene charge-transfer complexes

The solid CT complexes of Pery with π -acceptors like CLA and PA and σ -acceptors like I_2 were prepared by mixing 1 mmol of the donor in chloroform (10 ml) with 1 mmol of each acceptor

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in the same solvent with constant stirring for about 15 min. The solutions were allowed to evaporate slowly at room temperature; the resulting solid complexes were filtered and washed several times with little amount of solvent and dried under vacuum over anhydrous calcium chloride. The CT complexes: [(Pery)/(CLA)] (orange) with empirical formula $C_{26}H_{14}O_4Cl_2$; [(Pery)/(PA)] (yellow-green) with empirical formula $C_{26}H_{15}O_7N_3$ and [(Pery)/(I₂)] (yellow) were formed.

2.2. Electronic Spectra

The electronic spectra of the donors, acceptors and the resulting CT complexes were recorded in the region of (200–800 nm) using a Jenway 6405 spectrophotometer with quartz cells of 1.0 cm pathlength. The electronic (UV/vis) absorption spectrum of the iodine complex was measured in chloroform. The complex was formed by adding X ml of 5.0×10^{-4} M I₂ (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 ml) to 1.00 ml of 5.0×10^{-4} M Pery. The volume of the mixture in each case was completed to 10 ml with the used solvent. The concentration of Pery in the reaction mixture was kept fixed at 0.5×10^{-4} M while the concentration of iodine was varied over the range from 0.125×10^{-4} M to 1.50×10^{-4} M. These concentrations produced donor:I₂ ratios in the range from 1:0.25 to 1:3.00.

Photometric titrations were performed [30] at 25°C for the reactions of Pery with σ- or π-acceptor in methanol and/or chloroform as follow:

The concentration of the donor in the reaction mixtures was kept fixed at 1.0×10^{-4} M, while the concentration of acceptors (I₂, PA or CLA) were

Table 1: Elemental analysis CHN and physical parameters of the CT complexes formed in the reaction of Pery with iodine, CLA, and PA.

Complexes (FW)	M.wt	C%	H%		N%		Physical data	
			Found	Calc.	Found	Calc.	Color	Λ_m ($\Omega^{-1}cm^{-1} mol^{-1}$)
[(Pery) ₂]I ₃ ⁻ (C ₄₀ H ₂₄ I ₄)	1012	47.12	47.43	2.29	2.37	-	Violet red	49
[(Pery)(CLA)] (C ₂₆ H ₁₄ Cl ₂ O ₄)	460	67.48	67.83	2.98	3.04	-	Red	10
[(Pery)(PA)] (C ₂₆ H ₁₅ N ₃ O ₇)	481	64.59	64.86	3.08	3.12	7.92	8.73	16

Table 2 Spectrophotometric data for the Pery-iodine CT-complex

Complex	λ_{max} nm	E _{CT}	K 1.mol ⁻¹	ϵ_{max} 1.mol ⁻¹ .cm ⁻¹	f × 10 ²	M (Debyes)	I _p (eV)
(Pery)2I ⁺ .I ₃ ⁻	350	3.55	2.63×104	6.29×104	0.80	77.1	7.65

changed over a wide range from 0.25×10^{-4} to 4.00×10^{-4} M, which produced solutions with donor:acceptor molar ratios varying from 1: 0.25 to 1: 4.00.

2.3. Infrared Spectra

The infrared spectra of the reactants and the resulting CT complexes were recorded in KBr discs on a Bruker IFS 113V FT-IR spectrometer, in the wavenumber range (4000–400 cm⁻¹).

2.4. ¹H-NMR spectra

¹H-NMR spectra were obtained on a Varian spectrometer Gemini 200 MHz using d₆-DMSO as a solvent.

2.5. Thermal analysis

Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA 50H instrument., 2–5 mg samples were heated in standard platinum TGA pans from 25°C to 600°C at a rate of 10°C/min under nitrogen flow rate of 30 ml/min. The amount and weight change of each obtained compound were recorded as a function of temperature to determine thermal stability.

3. RESULTS AND DISCUSSION

Elemental analysis data of all perylene charge-transfer complexes are listed in Table 1. From this table, it can be seen that the data are in a good agreement with the calculated ones, and the composition of the CT complexes matched the molar ratios deduced from the photometric titration of Pery and the acceptors (σ- and π- acceptor).

3.1. Iodine/Pery charge-transfer complex

The conductivity data confirm that this complex has a positive (I^+) and negative (I_3^-) charge resulting from the associated triiodide ion in accordance with the CT transition. The electronic absorption spectra of the 1:1 ratio in $CHCl_3$ together with those of the reactants I_2 and Pery are shown in Fig. 2. The spectra show two absorption bands which are not present in the spectra of the free reactants iodine and Pery. These bands at 350 and 293 nm are assigned to the CT complex formed by the reaction of Pery with I_2 in chloroform solvent. Photometric titration curves based on these two absorption bands are given in Fig. 3.

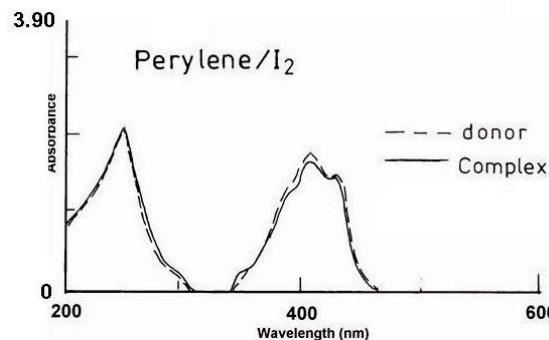


Fig. 2. Electronic absorption spectra of Pery/iodine reaction in $CHCl_3$.

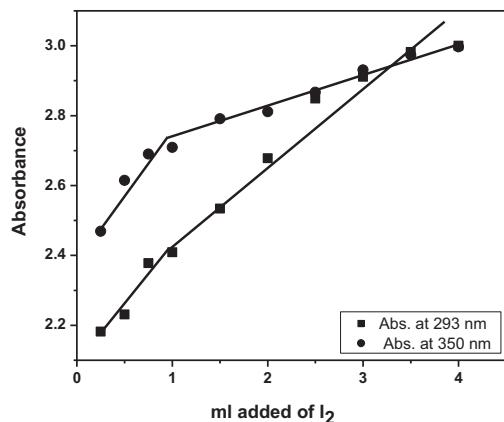


Fig. 3. Photometric titration curves for Pery/iodine system in $CHCl_3$ at 293 and 350 nm.

These photometric titration curves were obtained according to known methods [30] by plotting absorbance against ml added acceptor. The equivalence points shown in these curves clearly indicate that the formed CT complex between Pery and iodine is 1:1. The formation of 1:1 complex was supported by both elemental analysis and

thermal measurements. However, the two absorption bands around 360 and 290 nm are well known [31–33] to be characteristic for the formation of the triiodide ion (I_3^-). Accordingly, the formed complex was formulated as $[(Pery)_2I^+I_3^-]$.

It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the formed $[(Pery)_2I^+I_3^-$ complex. To study the stability of the Pery/iodine complex, it was necessary to calculate the values of the association constant, K, the molar absorption coefficient ϵ , and the oscillator strength, f, of the iodine complex. The 1:1 modified Benesi-Hildebrand equation [34] was used in the calculations.

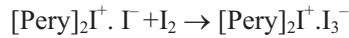
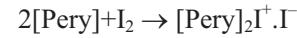
$$\frac{C_a^o C_d^o I}{A} = \frac{1}{K\epsilon} + \frac{C_a^o + C_d^o}{\epsilon} \quad (1)$$

where C_a^o and C_d^o are the initial concentrations of the acceptor (I_2) and the donor (Pery), respectively, and A is the absorbance of the strong bands around 290 and 360 nm. When the $C_a^o C_d^o / A$ values are plotted against the corresponding $C_a^o + C_d^o$ values, straight lines were obtained with a slope of $1/\epsilon$ and intercept of $1/K\epsilon$. The oscillator strength f was obtained from the approximate formula in the equation of Tsubomura and Lang [35]. The oscillator strength values together with the corresponding energy of charge-transfer interaction, E_{CT} , ionization potential, I_p and dipole moment, μ are given in Table 2. The trend of the values in this Table reveals several facts.

The $[(Pery)_2I^+I_3^-$ complex shows high values of both the association constant (K) and the molar absorption coefficient (ϵ). This high value of K reflects the high stability of the iodine complex as a result of the expected high donation ability of Pery (five aromatic rings).

The high value of K agrees quite well with the existence of the tri-iodide ion, I_3^- , which is known to have high absorptivity value [31–33].

Finally, a general mechanism for the formation of the $[(Pery)_2I^+I_3^-$ complex is proposed, as follows:



The mid infrared spectra of Pery and the formed CT-complex, $[Pery]_2I^+I_3^-$ were recorded as KBr discs. The spectral bands, resolved and assigned into their vibrational modes are given in Table 3.

As expected, the bands characteristic for the Pery unit in $[\text{Pery}]_2\text{I}^+\text{I}_3^-$ are shown with small changes in band intensities and frequency values of aromatic ring and phenyl groups. This proves that the charge-transfer transition occurs from the aromatic ring to iodine ($\pi-\sigma^*$).

Table 3. Infrared frequencies^(a) (cm^{-1}) and tentative assignments for the Pery donor and $[(\text{Pery})_2]\text{I}^+\text{I}_3^-$ complex.

Pery	$[(\text{Pery})_2]\text{I}^+\text{I}_3^-$	Assignments ^(b)
3431 s,br	3434 s,br	$\nu_{(\text{OH})}$; H_2O of KBr
3045 s	3046 ms	$\nu_{(\text{CH})}$; □ aromatic
2929 ms	2922 mw	
1653 ms	1647 w	$\nu_{(\text{C}=\text{C})}$; aromatic
1516 ms	1605 mw	
1491 m	1590 w	Phenyl
1374 m	1529 w	
1327 m	1493 s	
1282 m	1379 w	
1210 m	1320 w	
	1213 w	
796 vs	810 vs	Aromatic rings
765 vs	765 vs	

Table 4. Maximum temperature, $T_{\max}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $[(\text{Pery})_2]\text{I}^+\text{I}_3^-$ complex.

Decomposition	$T_{\max}/^\circ\text{C}$	Lost species	%weight loss	
			Found	Calc.
First stage	92°C	I_2	24.67%	25.10%
Second stage	291°C	$\text{I}_2 + 2\text{Pery}$ moieties	72.44%	74.90%
Total loss			97.11%	100%
Residue		residual carbon	2.89%	0.00%

The far infrared spectrum of $[\text{Pery}]_2\text{I}^+\text{I}_3^-$ was recorded in Nujol mulls dispersed on polyethylene windows in the region 50–400 cm^{-1} . The spectrum associated with the $[\text{Pery}]_2\text{I}^+\text{I}_3^-$ complex shows the characteristic bands for the triiodide ion, I_3^- at 135, 100 and 67 cm^{-1} . These bands can be assigned to the $\nu_s(\text{I}-\text{I})$, A_1 , $\nu_{as}(\text{I}-\text{I})$, B_2 and $\delta(\text{I}_3^-)$, A_1 , respectively. These three absorptions do not exist in the spectrum of the donor, Pery. However, the I_3^- ion may be linear ($D_{\infty h}$) or non-linear (C_{2v}). Group theoretical analysis indicates that the I_3^- with C_{2v} symmetry displays three vibrations $\nu_s(\text{I}-\text{I})$, A_1 , $\nu_{as}(\text{I}-\text{I})$, B_2 and $\delta(\text{I}_3^-)$, A_1 , all infrared active in agreement [31, 36, 37] with the observed three infrared bands for $[\text{Pery}]_2\text{I}^+\text{I}_3^-$. Accordingly, the formed iodine complex is formulated as $[\text{Pery}]_2\text{I}^+\text{I}_3^-$. The conversion of iodine molecules into polyiodide units is well known in the literature [31, 36, 37].

To confirm the proposed formula and structure of the new $[\text{Pery}]_2\text{I}^+\text{I}_3^-$ complex, thermogravimetric analysis (TG/DTG) was carried out for this

complex under N_2 flow. TGA thermograms and DTG curves are shown in Fig. 4. Table 4 gives the maximum temperature values, $T_{\max}/^\circ\text{C}$, together with the corresponding weight loss for each step of the degradation reactions of this complex. The obtained data strongly support the structure proposed for the complex under investigation as follows. The thermal decomposition of the Pery-iodine CT complex in inert atmosphere proceeds approximately with two main degradation steps (Fig. 4).

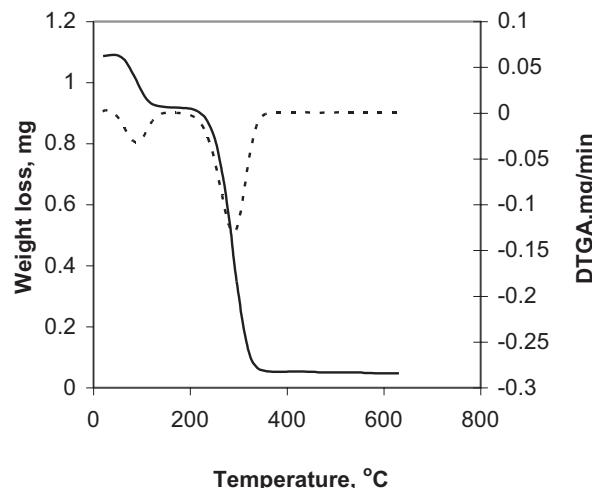
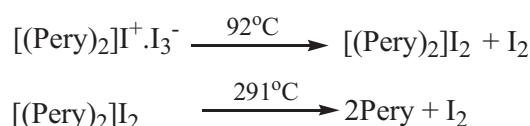


Fig. 4. TGA/DTG thermal diagram of $[(\text{Pery})_2]\text{I}^+\text{I}_3^-$ CT complex; (—) – TGA; (---) – DTGA.

The first stage of degradation at 92°C is accompanied by a weight loss of 24.67% corresponding to the loss of one iodine molecule. Theoretically, the loss of this molecule corresponds to a weight loss of 25.10%. The second decomposition stage occurs at a maximum temperature of 291°C. The weight loss associated with this step (72.44%), can be due to the loss of the second iodine molecule besides the organic moieties of two perylene molecules, in good agreement with the theoretical weight loss values of 74.90%. Accordingly, the mechanism for the thermal decomposition of the complex, $[\text{Pery}]_2\text{I}^+\text{I}_3^-$ is proposed as follows:



In recent years there has been increasing interest in determining the rate dependent parameters of solid-state non-isothermal decomposition reactions by analysis of the TG curves. Several equations [38–45] have been proposed as means of analyzing

a TG curve and obtaining values for kinetic parameters.

In the present investigation the general thermal behavior of the Pery/iodine CT complex in terms of stability ranges, peak temperatures and values of

Table 5. Kinetic and thermodynamic data of the $[(\text{Pery})_2]\text{I}^+\text{I}_3^-$ CT complex at the essential stage.

Complex	Parameters*	Coats-Redfern equation
	E	67.8
$[(\text{Pery})_2]\text{I}^+\text{I}_3^-$	A	$3.98 \times 10^{+10}$
	ΔS	-23.1
	ΔH	56.8
	ΔG	49.8
	r	0.9954

*Units of parameters: E in KJmole^{-1} , A in s^{-1} , ΔS in $\text{Jmole}^{-1}\text{K}^{-1}$, ΔH and ΔG in KJmole^{-1}

kinetic parameters, is summarized in Table 5. The kinetic parameters E and Z were evaluated using Coats-Redfern equation. The kinetic parameters, ΔH , ΔS and ΔG are tabulated in Table 6. Taking the main decomposition steps as a criterion, the values of the activation entropies, ($-\Delta S$) in this complex indicate that the activated complex has a more ordered structure than the reactants. ΔG is positive for a reaction for which ΔH is positive and ΔS is negative. The reactions for which ΔG is positive and ΔS is negative are considered as unfavorable or non-spontaneous. Reactions are classified as either exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$) on the basis of whether they give off or absorb heat. Reactions can also be classified as exergonic ($\Delta G < 0$) or endergonic ($\Delta G > 0$) on the basis of whether the free energy of the system decreases or increases during the reaction. The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie closer to the value 0.9954, showing a good fit with a linear function. It is clear that the thermal decomposition process of the iodine complex is non-spontaneous, i.e., the complex is thermally stable.

3.2. π -acceptors/Pery charge-transfer complexes

The electronic absorption spectra of the reactants, Pery (1.0×10^{-4} M) and the acceptors CLA and PA (1.0×10^{-4} M) in CHCl_3 along with those of the formed 1:1 CT complexes are shown in Fig. 5 (A and B). The spectra demonstrate that the formed CT complexes have absorption bands at 300 nm for $[(\text{Pery})(\text{CLA})]$ and 348 nm for $[(\text{Pery})(\text{PA})]$ complexes. These bands are located as hypsochromic behavior in the spectra of the CT products rather than reactants. The stoichiometry of the Pery-acceptor reactions was shown in all cases

to be of ratio 1:1. The 1:1 stoichiometry was strongly supported by the photometric titration

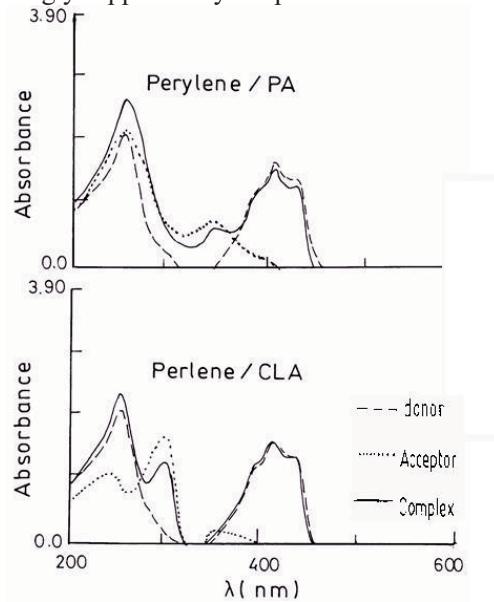


Fig. 5. Electronic absorption spectra of: (A): Pery/CLA and (B): Pery/PA reactions in CHCl_3

measurements as well. In these measurements, the concentration of Pery was kept fixed, while the concentration of the acceptors was varied over the range from 0.25×10^{-4} M to 3.00×10^{-4} M. Photometric titration curves based on these measurements are shown in Fig. 6 (A and B). The Pery-acceptors equivalence points indicate that the Pery: acceptor ratio in all cases is 1:1 and this result agrees quite well with the elemental analysis and infrared spectra of the solid CT complexes. Accordingly, the CT complexes formed upon reaction of Pery as a donor with the π -acceptors under investigation in chloroform have the general formula $[(\text{Pery})(\text{acceptor})]$. The 1:1 modified Benesi-Hildebrand method [34] was used in calculating the values of the association constant, K and the molar absorption coefficient, ϵ . The spectral data of the two Pery CT complexes are given in Table 6. These complexes show high values of both the association constant (K) and the molar absorption coefficients (ϵ). These high values of K confirm the expected high stability of the formed CT complexes as a result of the expected high donation power of Pery as a chromophore system containing a conjugated structure (C=C). The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents, such as nitro and halo groups.

Table 6. Spectrophotometric results for the CT complexes of (A): [(Pery)(CLA)] and (B): [(Pery)(PA)].

Solvent	λ_{\max} (nm)	E_{CT} (eV)	K (l.mol ⁻¹)	ϵ_{\max} (l.mol ⁻¹ .cm ⁻¹)	f $\times 10^{+2}$	M (Debyes)	I _p (eV)
A	300	4.14	$117 \times 10^{+2}$	$132 \times 10^{+2}$	0.142	30.10	8.01
B	348	3.57	$117 \times 10^{+2}$	$264 \times 10^{+2}$	0.246	42.40	7.61

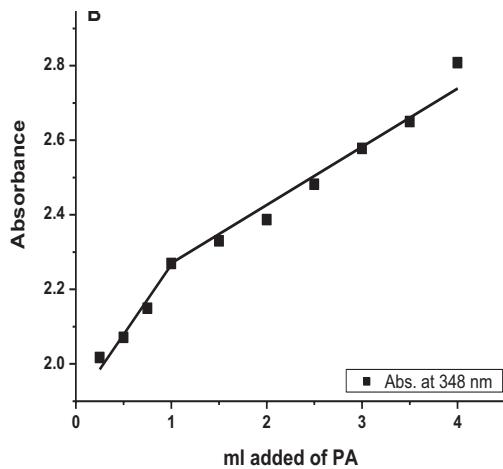
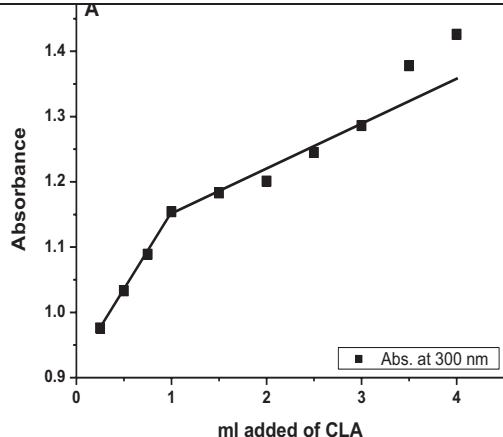


Fig. 6. Photometric titration curves for (A): Pery/CLA and (B): Pery/PA reactions in CHCl_3 at 300 and 348 nm, respectively.

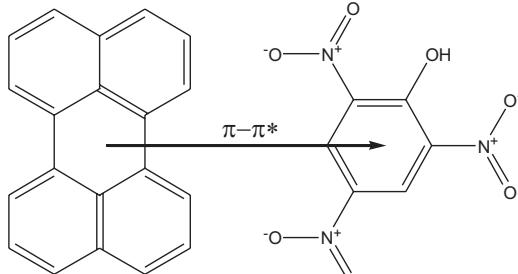


Fig. 7: Structure of the [(Pery)(PA)] CT complex

Full assignments for the infrared bands of [(Pery) $(\pi\text{-acceptor})$] CT complexes are given in Table 7. A comparison of the relevant IR spectral bands of the free donor, Pery and acceptors (CLA and PA) with the corresponding ones appearing in

the IR spectra of the isolated CT complexes clearly indicated that the characteristic bands of Pery show some shift in the frequencies, as well as some change in their band intensities. This could be

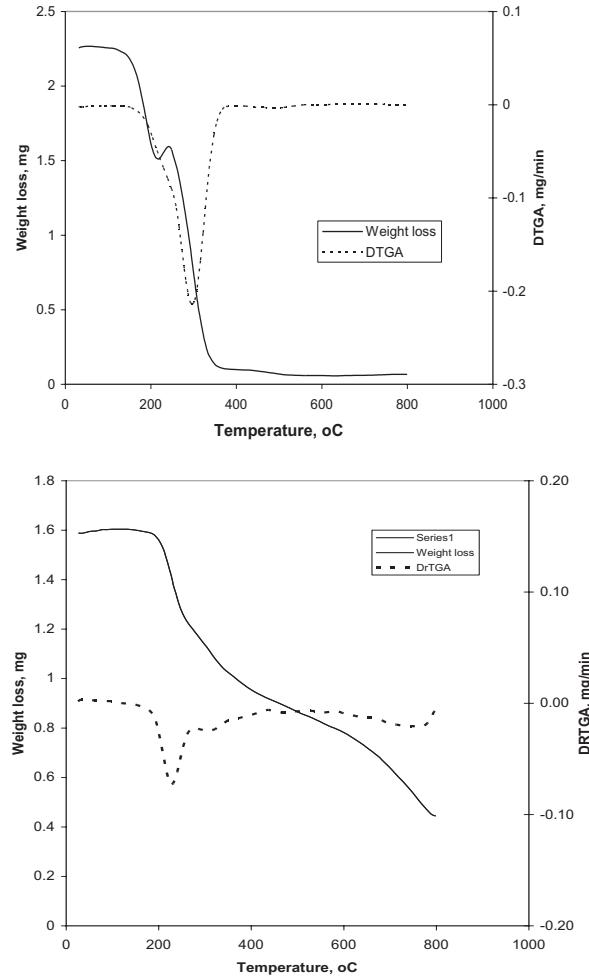


Fig. 8. TGA/DTG thermal diagrams of: (A): [(Pery)(CLA)] and (B): [(Pery)(PA)] CT complexes.

attributed to the expected symmetry and electronic structure changes upon formation of the CT complex. Moreover, the IR spectra of the molecular complexes of CLA and PA with Pery indicate that the $\nu(\text{C-Cl})$ and $\nu(\text{NO}_2)$ of the free acceptors (CLA and PA) are generally shifted to lower wavenumber values upon complexation. Thus we can conclude that the molecular complexes are formed through $\pi-\pi^*$ charge migration from HOMO of the donor to the LUMO of the acceptor (Fig. 7).

The ^1H NMR spectrum of the [(Pery)(PA)] CT complex in d_6 -DMSO displayed distinct signals with appropriate singlet and multiplets. The singlet accounting for the proton centered at δ 3.40 (1H; OH) is assigned to the proton of the phenolic group of picric acid; the other multiplet peaks at δ 7.30–8.40 ppm are due to protons of the aromatic groups of Pery and PA. The decrease in the intensities of hydrogen protons of Pery and PA proved that the CT interaction occurred.

Thermogravimetric analysis (TGA) and DTG was carried out in dynamic nitrogen atmosphere (30

Table 7. Infrared frequencies^(a) (cm^{-1}) and tentative assignments for CLA, PA, [(Pery)(CLA)] and [(Pery)(PA)] compounds.

CLA	PA	Pery/CL Pery/PA	Assignments
3235 s,	3416 br	3234 vs	3435 s,br v(O-H); H-bonded br
		3103 ms	3046 m
		3104 s	v(C-H); aromatic
		3056 vw	
---	2980 sh	2924 vw	2920 vw
	2872 w		$\nu_s(\text{C-H})$
			$\nu_{as}(\text{C-H})$
1664 ms	1861 ms	1866 vw	1613 s
1630 vs	1632 vs	1782 w	$\nu(\text{C=O}); \text{NO}_2$ of PA
		1605 vs	$\nu(\text{C=C})$
	1608 vs	1663 s	1590 w
			Ring breathing bands
1529 vs	1630 vs	1516 s	
		1542 vw	
---	1432 s	1491 s	1492 ms
1368 s	1343 ms	1369 vs	$\nu(\text{C-C})$
1263 vs	1312 w	1265 vs	$\nu(\text{C-N})$
1207 w	1263 w	1210 s	$\nu(\text{C-O})$
1168 w	1150 ms	1184 w	Phenyl
		1339 vs	
	1086 s		1305 s
			1277 s
			1216 s
			1184 w
			1149 s
			1078 s
981 vs	917 vs	982 vs	938 ms
851 vs	829 w	851 s	(C-H) bend
		809 vs	Aromatic rings
752 vs	781 s	763 vs	817 vs
690 vs	732 s	692 s	Skeletal vibrations
	703 s	570 s	
	652 sh		
569 vs	522 ms	541 w	$\delta(\text{ONO}); \text{PA}$
		544 ms	
		419 w	CNC deformation

ml/min) with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzer. CLA and PA complexes of Pery were studied by thermogravimetric analysis from ambient temperature to 800°C in nitrogen atmosphere. The TG curves were redrawn as % mass loss vs. temperature curves. Typical TG curves are presented in Fig. 8 (A and B), and the temperature ranges and percentage mass losses of the

decomposition reaction are given in Table 8 together with evolved moiety and the theoretical percentage mass losses. The overall mass loss from the TG curves is 97.16% for Pery/CLA and 72.75% for Pery/PA complexes. All complexes show two peaks of mass loss. The first and the second peak are due to the decomposition of the acceptors and the Pery moieties. The final products were polluted with carbon.

Thermal analysis curves of the Pery complexes show that decomposition takes place in two stages in the temperature range between 100–400 °C for the Pery/CLA complex and between 150–800°C for

Table 8. Maximum temperature, $T_{\max}/^\circ\text{C}$, and weight loss values of the decomposition stages for the [(Pery)(CLA)] and [(Pery)(PA)] compounds.

Decomposition of $T_{\max}/^\circ\text{C}$		Lst species	%weight losses	
First stage	219°C		Found	Calc.
Second stage	299°C	$\text{C}_{24}\text{H}_{14}\text{O}_4\text{Cl}_2$	97.16%	97.39%
Total loss			97.16%	97.39%
Residue		Carbon residual	2.84%	2.61%
Decomposition of $T_{\max}/^\circ\text{C}$		Lst species	%weight losses	
First stage	230°C		Found	Calc.
Second stage	325°C	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_7$	72.75%	72.65%
Total loss			72.75%	72.65%
Residue		Carbon residual	27.25%	27.35%

the Pery/PA complex (Fig. 8 A and B). The two endothermic decomposition stages correspond to decomposition of the donor and acceptors. The TG curves of the two complexes show weight losses (Found 97.16, Calcd. 97.39%) for the Pery/CLA complex and (Found 72.75%, Calcd. 72.65%) for the Pery/PA complex corresponding to the loss of $\text{C}_{24}\text{H}_{14}\text{O}_4\text{Cl}_2$ organic moiety and $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_7$ organic moiety for Pery/CLA and Pery/PA complexes, respectively. The final product formed at 800°C is residual carbon. Reported data on thermal analysis studies in nitrogen atmosphere indicate that the two Pery complexes decompose to give a number of remaining carbons according to the acceptor.

The kinetic and thermodynamic parameters of the decomposition of the Pery complexes, namely, activation energy (E), enthalpy (ΔH), entropy (ΔS) and free energy of decomposition (ΔG) as well as the pre-exponential factors (A) were evaluated graphically using the Coats-Redfern relationship. A plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ gives a slope

from which E was calculated and Z (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS), enthalpy of activation (ΔH^*) and the free energy changes of activation (ΔG) were calculated using the following equations:

$$\Delta H = E - RT_m ; \Delta G = \Delta H - T_m \Delta S$$

The calculated values of E, Z, ΔS , ΔH and ΔG for the decomposition steps are given in Table 9. On comparing the activation energy of the first stage of decomposition for the two CT complexes, the order of the activation energy values of the

Table 9. Kinetic and thermodynamic parameters data of (I): [(Pery)(CLA)] and (II): [(Pery)(PA)] compounds.

Compounds	Paramet er	E / kJmol ⁻¹	Z / s ⁻¹	$\Delta S /$ Jmol ⁻¹ K ⁻¹	$\Delta H /$ kJmol ⁻¹	$\Delta G /$ kJmol ⁻¹
I	101	4.53×10^8	-83.5	97.1	139	0.9940
II	48	2.89×10^4	-161	45.5	106	0.9887

different acceptors was PA>CLA. This difference may be due to the reactivity of the complexes and the electronic configuration of the acceptors attached to Pery. These results agree well with those of the TG analysis detailed above. The ΔS values of the main stage for all complexes were found to be negative, indicating that the activated complex was more ordered than the reactants.

CONCLUSION

Perylene, as a powerful laser dye, formed stable intermolecular CT complexes with the electron acceptors iodine (I₂), picric acid (PA) and chloranilic acid (CLA) in CHCl₃. The stoichiometry of the present CT complexation determined by the molar ratio method showed that association was in 1:1 molecular ratio. The equilibrium constants, K, and molar absorption coefficients, ε, of the complexes were determined by the Benesi-Hildebrand method. The increase in the K values reflected the high stability of the Pery charge-transfer complexes as a result of the expected high donation power of Pery (five aromatic rings). The activation of enthalpies and entropies of Pery complexes were calculated utilizing Coats-Redfern equation. The entropies were more negative, suggesting that the formation of Pery charge-transfer complexes is favored at low temperatures and the complexes are more ordered than the reactants.

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СПЕКТРОСКОПСКИ И ТЕРМИЧНИ ИЗСЛЕДВАНИЯ НА ПЕРИЛЕНОВИ КОМПЛЕКСИ С ПРЕНОС НА ЗАРЯД

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Изследвани са спектроскопски комплексите с пренос на заряд, образувани между перилен като донор с йод, никринова киселина и хлоранилова киселина. Описани са синтезите и охарактеризирането на тези комплекси. Те се приготвят лесно, като за разтворител се използва хлороформ. Използвани са инфра-червена, UV-Vis and ¹H-ядрено-магнитно-резонансна спектроскопия, елементен анализ (за въглерод, водород и азот) както и термогравиметричен анализ за охарактеризиране на трите комплекса. Приложен е методът на Benesi-Hildebrand и негова модификация за определянето на асоциационната константа (K) и моларния абсорбционен коефициент (ϵ).