NEW COMPOUND SECTION

Charge-Transfer π Complexes Formed from the Pyrylium Ion

James A. Van Allan, Jack C. Chang, Lorenzo F. Costa, and George A. Reynolds*
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

New organic charge-transfer compounds were prepared from an organic cation (pyrylium or thiapyrylium) and a neutral organic molecule (triphenylamine or *N*-amino-4-(dicyanomethylene)-2,6-dimethyl-1,4-dihydropyridine). The absorption spectra of these CT complexes were determined in solution and in the solid state. These salts have the charge-transfer band in the visible region as a result of electron transfer from the organic moiety to the cation. The extinction coefficient, association constant, conductivity, photoconductivity, and emission have been examined for a few members of this series.

The charge-transfer interaction (CT) between heterocyclic onium salts (i.e., pyrylium, pyridinium, and thiapyrylium ion) and organic anions (*13, 22*) and inorganic anions (*2, 3, 7, 9, 15, 18*) has been studied. In general, these CT interactions are strong, and the CT salts can be isolated easily. The CT interaction between these onium salts and neutral organic donors has not been studied extensively, except in the case of the nitrogen heterocycles. Verhoeven and his co-workers (*18*) reported charge-transfer interaction between pyridinium ions and several methoxy-substituted benzenes. Beaumont and Davis (*4*) studied the CT interaction between aromatic amines and quinolinium and acridinium ions. Charge transfer resulting from the interaction between paraquat and a range of neutral organic donors has also been reported (*20*). In all these cases no attempt was made to isolate the crystalline π complexes. To our knowledge, the only reported crystalline π complexes of neutral nature are the phenolic complexes of *N,N'*-dimethyl-4,4'-bipyridylium ion (*12*), phenothiazine and bibenzotropylium ion (*6*), and the complex between 2,4-diphenylpyrrole and a dithiolium salt (*19*). We are reporting the CT interaction between the 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiapyrylium ions with various neutral organic donors. In some cases, the crystalline π complexes have been isolated and studied.

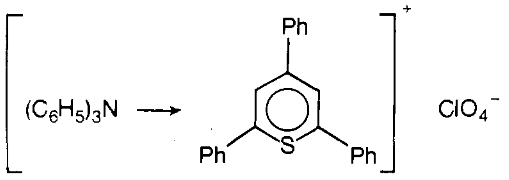
Results and Discussion

During the course of our investigation of the reaction of pyrylium salts with amines, we noted the formation of a green, crystalline 1:1 complex between triphenylamine (I) and 2,4,6-triphenylthiapyrylium perchlorate (II). In a KBr pressing or in a polyethylene terephthalate film a new, broad absorption band appears between 500 and 600 nm which cannot be accounted for by either of these components. At low concentration in acetonitrile this complex dissociates into its components as evidenced by its electronic spectrum: λ (nm) ($\epsilon \times 10^{-3}$), 225 (25.0), 245 (23.5), 285 (32.0), 365 (35.0), a composite of I and II (see Experimental Section). Increasing the concentration of I relative to II shifts the equilibrium in favor of the complex and the new, broad band appears at 590 nm (see Figure 1). The same equilibrium can be approached by increasing the concentration of II relative to I. This may be understood from previous studies of the absorption spectra resulting from charge-transfer interaction between dibenzotropylium ion or tropylium ion with aromatic donors (*6, 8*).

Using Benesi–Hildebrand's treatment (*9*), the formation constant, *K*, between I and II in dichloromethane and the extinction coefficient of the CT complex at 590 nm has been calculated to be $K = 1.1$ l. mol^{-1} and $\epsilon_{590} = 100$, respectively. The small value of *K* in dichloromethane is in accord with the dissociation observed spectrally at low concentration in acetonitrile solution.

It was noted during the equilibrium study that with the addition of I to II the characteristic 475-nm fluorescence emission of II disappears. A decrease in fluorescence of II is noted with increasing concentration of I. When the complex III is excited in the solid state, the emission of the thiapyrylium moiety at 475 nm was not observed. Instead, a new emission appears at 850 nm with an excitation maximum at 640 nm. This new emission band is not associated with any of the known luminescence processes of either I or II, and is assigned to the charge-transfer emission. The excitation spectrum associated with this emission is not distinct; however, new optical absorption in the region between 500 and 650 nm is apparent.

The complex of I and II does not yield an ESR signal at room temperature. The absence of an unpaired electron excludes the existence of an ion radical, which might be responsible for the deep coloration. The ir spectrum of III shows only small differences in intensity compared with the sum of the spectra of I and II, indicating only weak interaction between I and II. On the basis of these results, it seems appropriate to formulate this compound as the CT complex III.



III

These results prompted us to examine the CT interaction between this onium salt and the neutral electron donors, durene, penta- and hexamethylbenzene, naphthalene, acenaphthene, 2,6-dimethylphenol, 1-naphthol, acridine, and phenoxazine. In all these cases, the addition of donor to a methylene chloride solution of II immediately quenches the fluorescence of II. The color of the complexes with II is a function of the donor molecule. The light-yellow solution of II changes to various degrees of orange depending on the donor used. There is a corresponding change in the absorption spectrum of II in the vicinity of 470–500 nm indicating the presence of a new band partly obscured by the strong absorption of II in this region. In the case of more efficient donors (see Table I), distinctive new bands are recorded. Experimental evidence for the validity of the donor–acceptor treatment is provided by the linear relationship between the ionization potential of the donor and the energy of the charge-transfer transition (E_{CT}), for complexes of a given acceptor, as required by eq 1:

Table I. Position of the Charge-Transfer Band from 2,4,6-Triphenylpyrylium and 2,4,6-Triphenylthiapyrylium Salts and Various Donors

		λ_{CT} acceptor		
Donors	$(E_{1/2}^{ox})$,[a] V	Pyrylium (nm)	Thiapyrylium nm	eV
a. Diethylaniline	+0.68	670	650	(1.907)
b. *N*-Phenylaniline	+0.83	605	650	(1.907)
c. Triphenylamine	+0.88	555	590	(2.101)
d. Trianisylamine	+0.52	—	730	(1.698)
e. Anthracene	+1.09	570	580	(2.137)
f. 9-Methylanthracene	+0.96	610	620	(1.999)
g. Phenothiazine	+0.57	725	740	(1.675)

[a] Data taken from Mann, C. K., Barnes, K. K., "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N. Y., 1970.

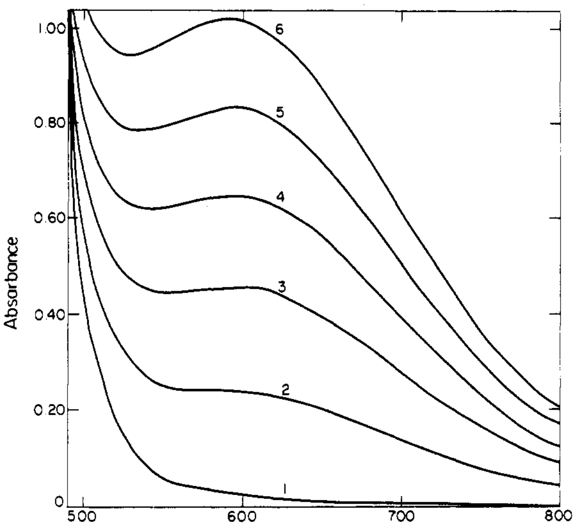


Figure 1. Change of absorbance of CT band with increasing concentration of triphenylamine. Concentration of II = 2.98 × 10^{-3} M; concentration of I for (1) 0.00 M, (2) 0.075 M, (3) 0.150 M, (4) 0.226 M, (5) 0.301 M, (6) 0.377 M.

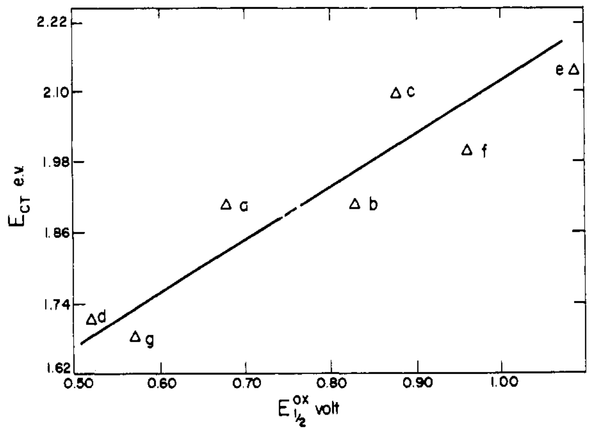


Figure 2. Variation of the energy of the CT band with $E_{1/2}^{ox}$ of donors. (See Table I for the identification compounds.)

Table II. Position of the Charge-Transfer Band from Various Substituted Pyrylium Salts and Some Electron Donors

		λ_{CT} Anthracene donor		
Acceptor	$E_{1/2}^{red}$	nm	eV	Iodide (nm)
IVa-OCH_3[a]	−0.33	545	(2.274)	—
IV-H	−0.26	570	(2.175)	558
IVb-Cl	−0.21	580	(2.137)	560
IVc-CO_2CH_3	−0.19	600	(2.066)	590
IVd-CN	−0.10	610	(2.032)	600
IVe-NO_2	−0.07	610	(2.032)	600

[a] The substituent, in all cases, is in the para position of the 4-phenyl ring in the pyrylium salt.

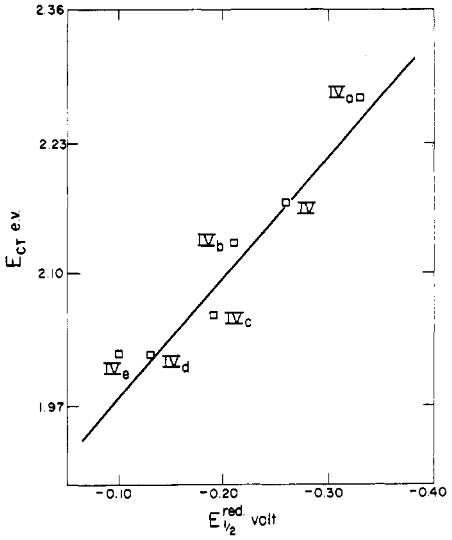


Figure 3. Variation of the energy of the CT band with $E_{1/2}^{red}$ of acceptors. (See Table II for the identification of compounds.)

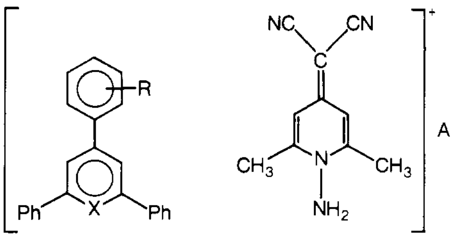
$$E_{CT} = I_D - E_A + C \qquad (1)$$

where I_D is the ionization potential of the donor, E_A is the electron affinity of the acceptor, and C is a sum of interaction terms for ground and excited states of the complex, which may be estimated from an assumption of the geometry of the complex. Owing to the lack of the actual ionization-potential data of the donors used, the oxidation half-wave potentials are employed. For several complexes of the 2,4,6-triphenylpyrylium perchlorate (IV) and 2,4,6-triphenylthiapyrylium perchlorate (II), the variation of the energy of the CT band with $E_{1/2}^{ox}$ of the donor is given in Table I and shown graphically for II in Figure 2. The correlation is not good, but the trend is definitely in the correct direction. The scattering of data is largely the result of uncertainty in the determination of reversible oxidation potential for the donors. A slight shift of the reversible potential is always observed when the overall electrochemical process includes a chemical step. To compensate for this uncertainty, a series of substituted 2,4,6-triphenylpyrylium salts was prepared and examined electrochemically for their reversible reduction potentials. The acceptors (IV, IVa–e, see Table II) were reduced at the platinum electrode in dimethylformamide. The number of electrons associated with this reduction wave is one, and the overall process is reversible as shown by the cyclic voltammetric wave. Table II summarizes the variation of the energy of the CT band with $E_{1/2}^{red}$ of several acceptors using both iodide anion and anthracene as the donor. Figure 3 illustrates graphically the linear relationship obtained between the acceptors and anthracene. In this case, the correlation is much better and the unit slope confirms that the complexes are of donor–acceptor type.

The donor molecule *N*-amino-4-(dicyanomethylene)-2,6-dimethyl-1,4-dihydropyridine (V) (ADCN) gave easily isolatable complexes in good yield (VI–XIV). It reacts readily with the perchlorate of II and the tetrafluoroborate, perchlorate, or iodide of IV to give the complexes (VI, VII, VIII, and IX). Table III lists the complexes formed. Analytical data are given in Table IV.

Luminescence properties of these charge-transfer complexes in the solid state are summarized in Table V. The emission

Table III. Complexes Formed Using ADCN as Donor



VI,	X = S;	R = H	$A^- = ClO_4$
VII,	X = O;	R = H	$A^- = BF_4$
VIII,	X = O;	R = H	$A^- = ClO_4$
IX,	X = O;	R = H	$A^- = I$
XII,	X = O;	R = 4-CH_3	$A^- = ClO_4$
XIII,	X = O;	R = 3-CH_3	$A^- = BF_4$
XIV,	X = O;	R = 2-CH_3	$A^- = ClO_4$

maxima of these compounds are all in the vicinity of 700–850 nm. The quantum efficiency of luminescence is about 1–5%.

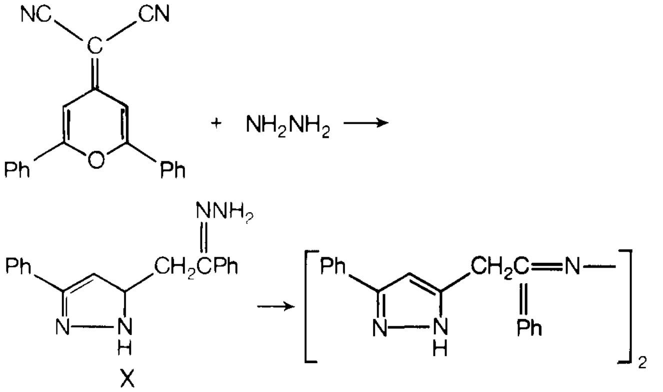
The CT complexes (VI and VIII) were evaluated for electrical conductivity by measuring the resistance of the compressed powder under ambient temperature. In both cases, the observed resistivity was greater than 10^{12} ohm cm. These values fall within the range of most organic material and these complexes could be classified as insulators. This result is consistent with weak interaction of the components. For comparison see the TCNQ complexes of 2,4,6-triphenylthiapyrylium prepared by Klanderman (*11*), which have conductivity at least 12 orders of magnitude greater than that of the ADCN complexes. The experimental details for the preparation of the pyrylium–TCNQ complexes are included in this paper.

Spectrograms of III and VI, coated in poly(vinyl cinnamate) and examined for photoinsolubilization according to the method of Robertson (*14*), show the spectral response of the thiapyrylium moiety (420–500 nm). The CT band occurs in this matrix but is not effective in producing cross-linking. A polyester coating (Vitel 101) of equimolar quantities of I and II shows only the spectral response of the thiapyrylium ion. No sensitization occurs in the region of the CT absorption for either positive or negative coronas (*16*).

Table V. Solid-State Luminescence of Charge-Transfer Complexes

Compound	λ_{abs} (nm)	$\lambda_{emission}$ (nm)	ϕ luminescence
VI	590	850	0.04
XII	555	685	0.02
XIII	560	735	0.01
XIV	560	695	0.05

As a point of chemical interest, attempts to prepare *N*-amino-4-(dicyanomethylene)-2,6-diphenyl-1,4-dihydropyridine, the phenylogue of V from 4-(dicyanomethylene)-2,6-diphenyl-4*H*-pyran (*17*) and hydrazine resulted in the formation of the pyrazole derivative X, which Ainsworth (*1*) obtained from 2,6-diphenylpyrone and hydrazine. On crystallization from acetic acid, X is converted to the azine XI.



X

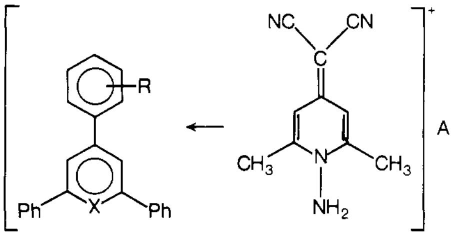
Experimental Section

Either a Cary 14 or a Cary 15 spectrophotometer was used for the absorption measurements. The transmission spectra in solid state were obtained using the KBr technique. The solution samples were prepared by mixing appropriate amounts of donor and acceptor in methylene chloride solution. The luminescence spectra and yields were measured using an absolute spectrofluorimeter (*5*). In this case, the microcrystalline charge-transfer complexes were used directly in a quartz cell.

The electrochemical measurements were performed in dimethylformamide solvent using 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. A platinum button electrode and a platinum gauze were used as the indicating and counter electrode. The reference electrode was aqueous saturated calomel. The cyclic voltammetry curves were obtained using a solid-state potentiostat coupled to a Moseley 2D-2A x-y recorder.

The following compounds have been described previously: 2,4,6-triphenylthiapyrylium perchlorate (*21*) (II) (λ nm, ($\epsilon \times 10^{-3}$) 226 (14.6), 246 (17.3), 269 (15.2), 366 (25.2), 400 (13.0) in CH_3CN); 1-amino-4-dicyanomethylene-2,6-dimethyl-1,4-dihydropyridine (*1, 10*) (V) 240 (7.5), 358 (40.0) in acetonitrile; oxidation potential 0.97 V, reduction potential −1.94 and −2.15;

Table IV. Analytical Data[c]



			A	Mp, °C	Empirical formula	Method	% yield
VI[a]	X = S	R = H	ClO_4	270	$C_{33}H_{27}N_4ClO_4S$	A	85
VII	X = O	R = H	BF_4	296	$C_{33}H_{27}N_4BF_4O$	A	66
VIII	X = O	R = H	ClO_4	293	$C_{33}H_{27}N_4OClO_4$	A	74
IX[b]	X = O	R = H	I	257	$C_{33}H_{27}IN_4O$	A	81
XII	X = O	R = 4-CH_3	ClO_4	280	$C_{34}H_{29}N_4ClO_5$	A	72
XIII	X = O	R = 3-CH_3	BF_4	260	$C_{34}H_{29}N_4OBF_4$	A	62
XIV	X = O	R = 2-CH_3	BF_4	245	$C_{34}H_{29}N_4OBF_4$	A	81

[a] Electronic spectrum in acetonitrile, λ_{max} ($\epsilon \times 10^{-3}$): 232 (36.0), 275 (22.5), 358 (61.0), 405 (21.0). [b] 240 (37.0), 274 (23.0), 345 (73.0), 405 (24.8). [c] Elemental analyses in agreement with theoretical values were obtained and submitted for review.

NMR (Varian A60 spectrometer) 144 Hz (S, 6 H), 355 Hz (S, 2 H), 395 Hz (S, 2 H), in Me_2SO-d_6; the 355-Hz band disappears on the addition of D_2O. Triphenylamine was used as obtained from Eastman Chemicals (λ_{max} 298 nm, ϵ 22.3 × 10^3 in CH_3CN). Elemental analyses for the compounds in the experimental section were submitted for review and are in agreement with theoretical values.

Preparation of the π Complexes. Method A. A hot solution of 2.5 × 10^{-3} mol of the pyrylium salt in 20 ml of acetonitrile was added to a hot solution of 2.5 × 10^{-3} mol of V in 30 ml of acetonitrile. On cooling, the complex separates in pure form. It may be crystallized from acetonitrile.

Method B. A solid mixture of 2.5 × 10^{-3} M quantities of the pyrylium salt and V was placed in the extraction thimble of a Soxhlet extractor and extracted overnight with ethanol. On cooling, the ethanolic extract deposited the complex in good crystalline form. This method was used if method A was not successful.

4-(2-Methylphenyl)-2,6-diphenylpyrylium Perchlorate. A mixture of 12 g of *o*-tolylaldehyde and 18 g of acetophenone in 50 ml of BF_3 etherate was heated for 2 h on the steam bath, cooled, diluted with ether, and chilled and the solid was collected. Crystallization of the crude product from acetic acid gave 8 g, mp 230–231 °C, of the fluoroborate. Four grams of the fluoroborate was dissolved in acetonitrile and 3 ml of 70% perchloric acid was added to give 3.5 g of the perchlorate salt, mp 264–265 °C. Also prepared in a similar manner are:

4-(3-Methylphenyl)-2,6-diphenylpyrylium Fluoroborate: mp 253–254 °C from acetonitrile; λ, nm (ϵ × 10^{-3}), 253 (18.3), 273 (17.5), 362 (22.2), 397 (18.1) in CH_3CN.

4-(4-Methylphenyl)-2,6-diphenylpyrylium Perchlorate: mp 291–292 °C; λ, nm (ϵ × 10^{-3}), 235 (17.2) 274 (19.0) 378 (30.4) 390 (29.8) 440 (12.0) in CH_3CN.

2,4,6-Triphenylpyrylium TCNQ–TCNQ Complex. A. A solution of 0.44 g of 2,4,6-triphenylpyrylium iodide in 20 ml of acetonitrile was added to a solution of 0.41 g (2 equiv) of TCNQ in 30 ml of acetonitrile. The complex separated immediately in pure condition, mp 297 °C, yield, 0.6 g (83%). Crystallization from acetonitrile did not change the melting point.

B. A solution of 1.0 g of 1,3,5-triphenylpentene-1,5-dione in 30 ml of acetonitrile and 1.26 g of TCNQ (2 equiv) was heated at reflux for 1 h. After cooling, 1.2 g (58%) of product was collected. Resistivity 4.2 ohm/cm (*11*).

5-Phenacyl-3-phenylpyrazoleazine. A mixture of 3 g of 2,6-diphenylpyrone, 1 ml of hydrazine, and 50 ml of ethanol was heated to reflux for 4 h. After standing overnight, the white solid that had separated was collected and recrystallized from ethanol and then from benzene: mp 168 °C; yield, 72%.

5-Phenacyl-3-phenylpyrazole Hydrazone. A mixture of 2.0 g of 4-(4-dicyanomethylene)-2,6-diphenyl-4*H*-pyran, 10 ml of ethanol, and 5 ml of 64% hydrazine was refluxed for 2 h. Water was added and the mixture was acidified with acetic acid. The product was collected and crystallized from acetic acid to give 1.5 g of the azine: mp 233 °C.

A 5–10% solution of III in a solution of hydroxypropylcellulose (high molecular weight) in dimethylformamide was whirl coated on a polyethylene terephthalate support. After drying, an electronic spectrum was obtained showing peaks at 362 and 430 nm and a broad band centered at 580 nm.

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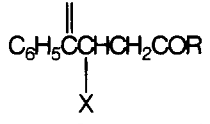
Structure of the Diazonium Coupling Products of γ-Phenyl-$\Delta^{\beta,\gamma}$-butenolide

Samir A. Khattab,* Sami A. Shawali, and Ahmed M. Farag
Department of Chemistry, Faculty of Science, University of Cairo, Giza, A. R. Egypt

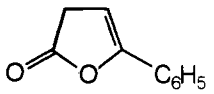
On spectral evidence, the diazonium coupling products of γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide are shown to exist essentially as α-arylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolides. This conclusion is supported by the synthesis of their *N*-methyl derivatives and also by their rearrangement in acid and alkaline media into 1,5-diarylpyrazole-3-carboxylic acids.

Whereas much research has been directed to the study of the structurally similar 4-arylazoisoxazoline-5-ones (*5, 6, 20*), 4-arylazooxazoline-5-ones (*2, 18*), and 4-arylazopyrazolin-5-ones (*11, 13, 16, 19, 22*), only a very little attention has been paid to α-arylazo-γ-phenyl-$\Delta^{\beta,\gamma}$-butanolides. Only four diazonium coupling products (III i, ii, xii, xiii) of γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (II), the lactone of β-benzoylpropionic acid (I), were



$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle X}{|}}{C}HCH_2COR$$

I, R = OH; X = H
a, R = OCH_3; X = H
b, R = OC_2H_5; X = H
c, R = OH; X = Br
d, R = OH; X = Cl



II