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Spectral Studies on Charge Transfer Complexes Between (*E*)-Dicyclopropylmethylene (2,5-dimethyl-3-furylethyldiene)succinic Anhydride and π-Acceptors

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Charge transfer (CT) complexes formed through the reaction of (E)-dicyclopropylmethylene(2,5-dimethyl-3-furylethyldiene)succinic anhydride as a donor and some π-acceptors namely, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), p-chloranil (CHL) and chloranilic acid (CNA) were prepared. The structure of the synthesized complexes were characterized by elemental analysis, IR and electronic absorption spectra. Spectral characteristics of the CT complexes were discussed in terms of donor molecular structure and π-acceptor electron affinity. Ionization potential of the donor was estimated from the CT transition energies of its complexes.

Irradiation of the ground state electron donor-acceptor complexes of the titled fulgide with DDQ and CNA, the CT band observed at 482 and 485 nm are shifted to longer wavelengths. This may be due to the structural change of the donor due to the cyclization process.

Keywords: charge transfer; fulgide; photochromic; π-acceptors

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INTRODUCTION

Fulgides display excellent fatigue resistance and thermal stability [1–4]. In 1981 Heller and co-worker synthesized the first heterocyclic fulgide that showed neither the side reactions nor the thermal back-reaction. Furthermore, because of ***C*** had a small molar absorption coefficient at 366 nm where ***E*** had larger value, the photochemical back-reaction from ***C*** to ***E*** upon irradiation by 366 nm light was negligible. Therefore, the conversion of ***E*** to ***C*** was close to 100%, Chart 1.

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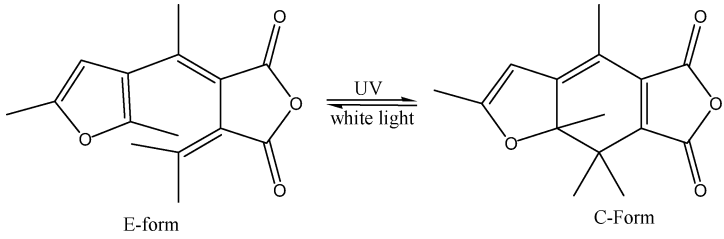


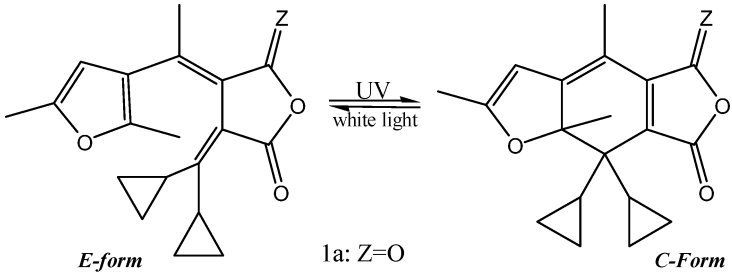
CHART 1

Remarkable efforts have been devoted to increase the wavelength of maximum absorption of the coloured form by tailoring the fulgides molecules [5,6].

Replacement of one of the carbonyl oxygen with dicyanomethylene group (1b) causes a major bathochromic shift >100 nm of the long wavelength absorption band of the coloured form [8], Chart 2.

Replacement one of the cyano group in compound (1c-e) by substituted phenyl moiety causes a bathchoromic shift of about 17 to 42 nm, depending on the substituted group or atoms [9,10].

Charge transfer complexes (CT) play a significant role in many biological processes [11,12]. Literature survey revealed that very few studies were performed on CT complexes of flugides [13]. These facts provided a reasonable inducement for investigation of CT complex formation of the titled flugide (1a). This study investigates the effect of the irradiation on the spectral characteristic of compound (1a) and its CT complexes. The acceptors used are 2,3-dicyano-5,6-dichloro-p-benzoquinone (DDQ), *p*-Chloranil (*p*-CHL) and chloranilic acid



1a: Z=O
1b: Z=$C(CN)_2$
1c: Z=C(CN)*p*-F-C_6H_4
1d: Z=C(CN)*p*-NO_2-C_6H_4
1e: Z=C(CN)*p*-Cl-C_6H_4

CHART 2

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(CNA). The solid complexes are prepared and investigated by spectral methods.

EXPERIMENTAL

The chemicals used in the present study were pure laboratory grade chemicals from BDH.

Apparatus

Melting points were determined on an electrical thermal apparatus and were uncorrected. The C, H and N contents were determined on a Elementar Vario EL elemental analyzer. The electronic absorption spectra were recorded by Shimadzu 1600 PC UV-Vis spectrophotometer. Irradiation of the prepared fulgide as well as its CT complexes were carried out using UV lamp (UV GL-58, 254/366 nm lamp, 50/60 Hz). The IR spectra were recorded on a Shimadzu 8000 FT-IR spectrophotometer as KBr discs. ^{1}H-NMR were measured by JEOL nmr spectrometer using d^6-DMSO as solvent.

Dicyclopropylidene(2,5-dimethyl-3-furyl) Ethylidenesuccinic Anhydride (1a)

A mixture of 3-acetyl-2,5-dimethylfuran (34.5 g, 0.25 moles) and dimethyldicyclopropylmethylene succinate (56.5 g, 0.25 moles) in toluene 50 ml was added dropwise to stirred solution of potassium t-butoxide (28 g, 0.25 moles). Work-up, gave the half ester which hydrolysed by reflux in 10% ethanolic KOH for 3 h. This was followed by cyclization with acetyl chloride, gave the mixture of *(E)* and *(Z)* fulgides which were separated by column chromatography. The *E*-isomer m.p. 133–134°C Lit [14] 129°C. ^{1}HNMR: 5.90 (1H, s, furyl-4-H); 3.01 (1H, m, cyclopropyl); 2.59 (3H, s, methyl cis to carbonyl); 2.22 (3H, s, Me); 2.03 (3H, s, Me); 1.05–0.27 (9H, m, cyclopropyl).

TABLE 1 Elemental Analysis, Colour, m.p of Fulgide (1a) CT Complexes

No.	Acceptor	Colour	m.p°C	Complex	% Analysis Cal (found) C	H	N
1	DDQ	Red brown	210	$(C_{27}H_{20}O_6C_{l2}N_2)H_2O$	58.17 (57.94)	4.95 (4.40)	5.0 (4.66)
2	*p*-CHL	brown	245	$C_{25}H_{20}O_6C_4$	54.70 (55.03)	3.70 (3.84)	–
3	CNA	Yellowish brown	211	$C_{25}H_{22}O_8C_2.2H_2O$	53.86 (53.50)	4.66 (4.67)	–

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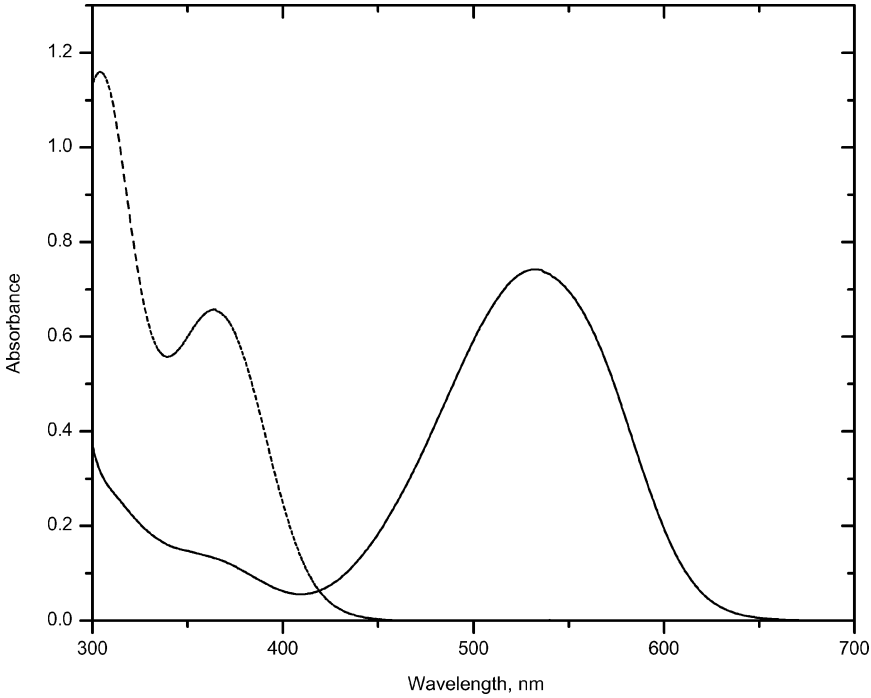

FIGURE 1 Effect of irradiation on fulgide (1a) in dichloromethane.

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Preparation of CT Complexes

The solid CT complexes were prepared, as previously reported [14a], by mixing fulgide in 5 ml dichloromethane with the acceptors (DDQ, *p*-CHL, and CNA) in 10 ml of the same solvent (molar ratio 1:1). The resulting solutions were stirred at room temperature for ~4 hrs and then reduced the volume of the solution whereby the solid complexes precipitated out. The separated complexes were filtered off, washed with CH_2Cl_2 and dried.

RESULTS AND DISCUSSION

The analytical data of the CT complexes (C, H and N) along with some of their physical parameters are listed in Table (1). The stoichiometry of the synthesized solid CT complexes was assigned on the basis of their elemental analyses which reveal the formation of 1:1 CT complexes.

The electronic spectra of the freshly prepared fulgide (1a) as well as its CT complexes were measured in acetonitrile and CH_2Cl_2. For the free fulgide, the absorption spectrum immediately prepared shows band at 362 and 363 nm (Fig. 1). After irradiation, the absorption spectrum exhibits a new band at 525 and 532 nm in acetonitrile and CH_2Cl_2, respectively. For Fulgide (1a)-DDQ complex in acetonitrile, the absorption band at 486 nm shows a red shift (524 nm) after irradiation, and then decreases again to 469 nm. For the same complex in CH_2Cl_2, a red shift of the wavelength (from 482 to 527 nm) is observed as the time of irradiation increases, see Figure 2. For Fulgide (1a)–CNA complex, a new band is observed at 524 and 531 nm in acetonitrile and CH_2Cl_2 respectively, as the time of radiation increases, see Figure 3. The above data was confirmed when equal mole of fulgide and DDQ was mixed in acetonitrile and measuring the absorption spectra immediatedly where a band at 363 nm is observed. When the mixture was irradiated, a new band at 532 nm is observed. The

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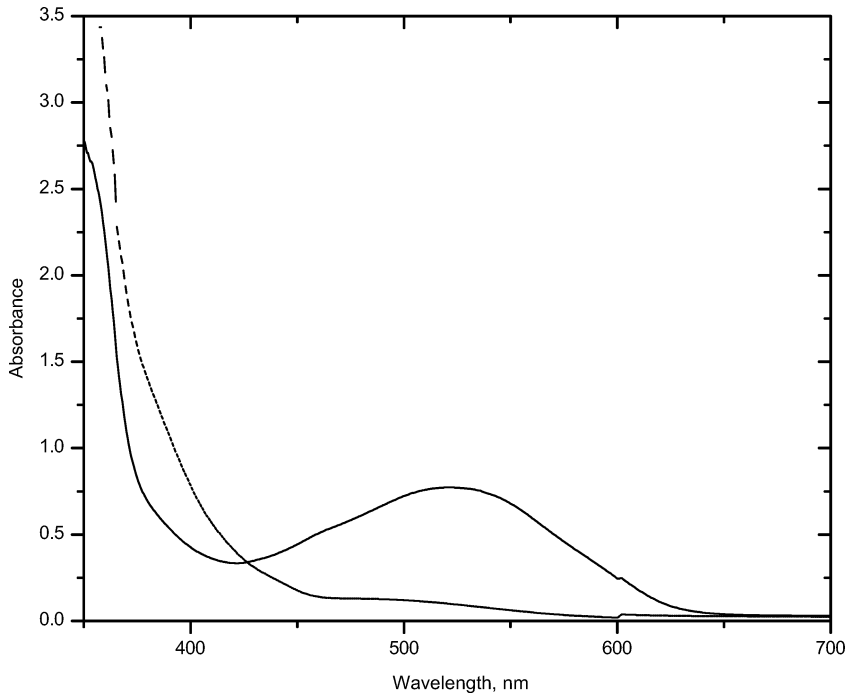

FIGURE 2 Absorption spectral of change of acetonitrile solution (1×10^{-4} M) of CT complex (1) under irradiation at 366 nm.

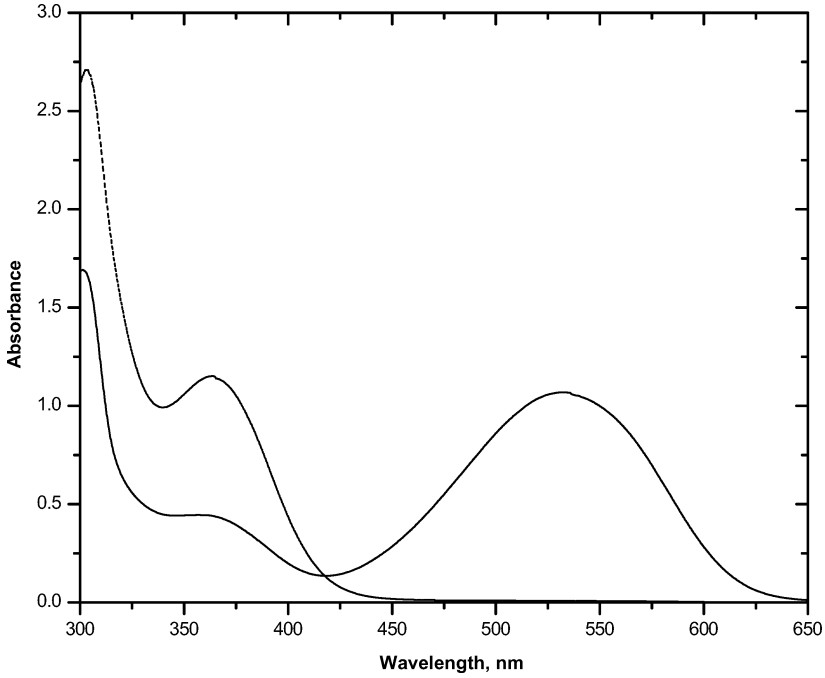

FIGURE 3 Effect of irradiation at 366 nm on CT complex (3) in dichloromethane.

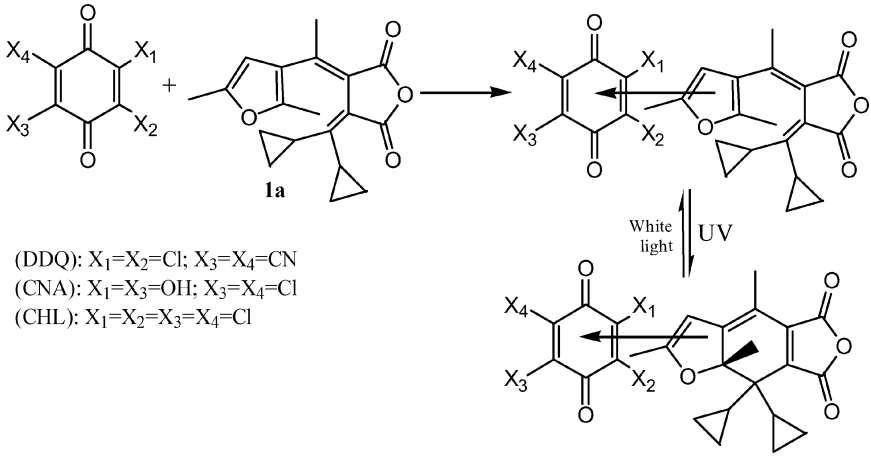

CHART 3

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TABLE 2 The Electronic Absorption Spectra of Fulgide (1a) CT Complexes

No.	Solvent	Form	λ_{CT}	E_{CT}	Ip_{ev}		
					Ref. [17]	Ref. [16]	Mean
1	CH_2Cl_2	E	482	2.58	9.23	8.91	9.07
		C	527	2.36	8.92	8.64	8.78
	Ac		486	2.56	9.12	8.89	9.00
			524	2.37	9.02	8.66	8.84
2	CH_2Cl_2	E	363	3.43	9.50	–	–
		C	532	2.34	8.41	–	–
3	CH_2Cl_2	E	485	2.56	8.36	–	–
		C	531	2.34	8.14	–	–
	Ac	E	359	3.46	9.26	–	–
		C	524	2.37	8.17	–	–

appearance of the latter band confirms the cyclization process of fulgide (1a) in the free state as well as its CT complexes. Chart 3.

The experimental values of the transition energy of the CT complexes (E_{CT}) have been calculated from the electronic spectra of the CT complexes using the following equation [15]:

$$E_{CT} = 1243.667/\lambda_{CT} \text{ nm}$$

The E_{CT} values are listed in Table (2).

The values of transition energies of the CT complexes were used to calculate the ionization potential of fulgide (1a). The ionization potential (Ip) of the fulgide (1a) can be estimated from the equation [16]:

$$Ip = 5.76 + 1.52 \times 10^{-4}\upsilon_{CT} \qquad \text{(DDQ)}$$

Where υ_{CT} is the wave number corresponding to CT band.

Also, the value of the Ip can be calculated from Briegleb equation [17]:

$$E_{CT} = Ip - (E_A + C)$$

Where E_A is the electron affinity of the acceptor, C is the coulombic factor between the electron transferred and positive hole left behind ($C = 4.7$ eV) [15].

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