

Structural , and Photochromic Properties of Thermally Evaporated E-3-(Adamantan -2-Ylidene)-4-[1 - (2,5-Dimethy-3furyl) Ethylidene] Dihydro-2,5-Furandione Thin Films

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Abstract

Thin Films of E-3-(Adamantan -2-Ylidene)-4-[1 - (2,5-dimethy-3furyl) ethylidene] dihydro-2,5-Furandione compound were prepared by conventional thermal evaporation technique. X-ray diffraction patterns indicated that the compound in the powder form has a polycrystalline nature with momoclinic structure . The Miller indices for the powder were calculated for the first time using Check-s cell program . SEM indicated the short range order of the films. FTIR indicated the consist of both the powder and the as-deposited thin films. The films were irradiated with UV light (360 nm) for different times from 1 to 11 min. The color of the films converted to saturated rose color after an exposure time \cong 6 min . The photobleaching time was found to be 13.5 min under the effect of Vis light, using a white light. This behaviour deduced the photochromic effect of the compound which has been explained according to the presence of the open cycle E-isomer which converted to the closed C-isomer under the effect of the UV-light. The refractive index, n , and the absorption index, k , and the parameters of molar extinction coefficient (ϵ_{molar}) were evaluated for both as deposited and the colored films. The concentration of the coloring centers through the thin films were found to be $\sim 1.18 \times 10^{10} / \text{cm}^3$. The studying of the dispersion spectra indicated abnormal behaviour companied with plasma frequency. Finally; The analysis of the absorption coefficient revealed the present of direct optical gap with 3.17 ± 0.006 eV for the deposited films ,which decreased to 2.48 ± 0.003 eV for the colored films .

Keywords: Thin film; Adamantan Fulgide ; Structural properties; optical properties and Photochromic phenomenon.

1. Introduction

Photochromism is a part of photochemistry dealing with reversible photochemical reactions [1], where it was first reported by Fritsche [2].

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In the early period, photochromism was observed as a color formed under sunlight irradiation during the day, fading away into the night. Scientifically spoken, the phenomenon must be extended to all electromagnetic radiation leading to a general definition; photochromism is a reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having distinguishable absorption spectra [3-4]. The radiation changes may be induced by UV, Visible, and IR radiation. Reversibility is an important criterion for the photochromic effect. There are various classes of photochromic in inorganic and organic compounds. Inorganic photochromic glasses can be classified into four groups[5]:rare earth activated silicate glasses [6],silver halide doped borosilicate and aluminophosphate glasses[7-8],silver molybdate or silver doped borosilicate glasses [9] and Copper or Cadmium halide doped borosilicate glasses [10].Oxazines , Pyrans [11] ,Fulgides [12] and dihydro indolizines belong to the group of organic photochromic dyes .Six general categories may be used to classify the mechanisms responsible for the effect : heterocyclic/hemolytic bond cleavage [13],Cis-trans isomerization [14],valence tautomerism,electron transfer systems ,pericyclic reactions and triplet-triplet absorption [15] .

The development of reversible optical storage medium based, on photochromic organic compounds ,had become an optical commercial reality [16,17]. Heller found that the adamantylidene group instead of the isopropylidene group increased the ring opening quantum yield of visible light irradiation [16].Heller and co-works have shown that fulgides containing a heterocyclic structure such as furyl,thienyl, and pyrrolyl , were excellent compounds for data storage medium because of their efficient thermal stability [18,19]. Indoylfulgides were mainly studied by Yokoyama and co-worker and shown to have interesting photochromic properties that meet many of the requirements for use as optical memory media and optical switches [20, 21]. A.M.Asiri showed that for DCPF the photochromism occurred between one of the colorless open form (E-isomer), because the geometry of the double bond connecting the aromatic ring and the succinic anhydride and the photo cyclized colored form (C-isomer).Also, he supporting that; there is an additional E-Z isomerization pathway .The Z-form is the geometrical isomer of the E-form . E-isomer could be transformed to C-isomer by irradiation with UV light and return to E-isomer again by removal of the UV light and the effect of white light [22] El-Nahass et al [23] deduced that the thermal investigation of powder crystalline DCPF material resulted in amorphous yellow-orange films which related to E-isomers. Upon irradiation with UV light (366 nm) for 15 min, the yellow-orange color turned to violent red indicating C-isomer formation .

The photochromic properties of the films were lost as a result of annealing, indicating Z-isomers formation. Annealing temperatures did not influence the amorphous structure of as-deposited films.

The types of electronic transition responsible for optical absorption were both direct and indirect allowed transitions with energy gaps of 3.08 and 2.76 eV, respectively. The indirectly allowed transition in Z-isomer is of energy gap of 2.52 eV. Also, M.Ibrahim et al [24] showed that the HOMO - LUMO energies of DCPF isomers were 3.8 and 2.7 eV for E and C isomers, respectively. El-Nahass et al also, illustrated that casting DCPF-PMMA films converted to deep pink under the effect of 360 nm UV light and during 38 min and return to E-isomer by Vis light and after 110 min [25]. Yasushi Yokoyama [26] stated that conjugating double bonds in fulgides are lying in an s-cis-cis-s-cis manner so that the carbon atoms that form the C-C single bond upon photoirradiation would come close. Therefore, the conformation of fulgides at their ground state influences the quantum yield of photo-cyclization. One of the factors that govern the conformation is steric bulkiness around the hexatriene moiety. Y.Yokoyama et al [27,28] examined the steric influence of the alkyl group on the methylene carbon next to the furan ring. The ring closing quantum yield upon UV irradiation became larger and the E to C isomerization quantum became smaller when the alkyl group became larger. The present work is concentrated on the preparation of the first thermally evaporated thin films of a new derivative of Fulgide's family to enrich the field of photochromic application and study some structural and optical properties of this derivative in the thin film form, where the new member of Fulgide's family is E-3-(Adamantan -2-Ylidene)-4-[1 - (2,5-dimethyl-3furyl) ethylidene] dihydro-2,5-Furandione, to our knowledge its crystal structure, the lattice parameters, Miller indices, photo chromic effect and the optical properties have not been investigated yet for as thermal evaporated thin films. For only simplification, we will refer to the name of our compound in the initial state as [E-Adamantan -Fulgide] or E-AF and refer to the colored isomer by C-AF

2. Experimental technique

Our fulgide was obtained from Tokyo chemical Ind.Co., LTD[(M.F/M.W= $C_{22}H_{24}O_4$ /352.4 g/mole, CAS No. 94 856-25-4), purity(HPLC); 98%, melting point:179 to 183 °C/min]. E- Adamantan Fulgide (E-AF) thin films were deposited by conventional thermal evaporation technique in a vacuum of 10^{-4} Pa using a coating unit (Edwards, E306A, England). Thin films of different thickness, ranged from (245 to 539) nm, were deposited onto different substrates as; glass, KBr and optically flat quartz. The deposition rate was kept at ~ 4 nm/s, and the thickness was controlled by using a quartz crystal thickness monitor (Model FTM6, Edwards Co.,England). To collect an information about the transformation's temperatures through AF compound (especially the melting point (m_p)) a micro DTA apparatus of a shimadzu DT-30 model was used for the DTA investigation for both the powder and the thin film (with rate = 10 °C/min). X-ray diffraction studies were done using (X'Pert Philips) diffractometer to investigate the crystal structure. The morphology of the surface was detected using SEM (JEOL-JEM-1200EX II electron microscope).

The vibrational structures were indexed by FTIR method using Nicolet 6700 infrared spectroscopy. The investigation was carried for both the obtained powder and thin film in the range (from 400 to 2000 cm^{-1}). For this purpose, 1 mg of (AF) powder was mixed with 50 mg of vacuum dried IR-grade KBr, while the thin film was participated on KBr substrate. After the preparation of the thin films some films were irradiated by UV radiation ($\lambda=360$ nm) for different time (from 1 to 11 min.,) .The photobleaching has been done using Tungsten lamp .The transmittance ,T ,the reflectance ,R, and The absorbance ,A of both as-deposited and saturated colored thin films (which have been participated onto flat quartz substrates) were measured at normal incidence of light in the spectral range from(200 to 2500)nm using (JASCO,V-670 UV-VIS-IR; serial No:B076661154) double -beam spectrophotometer.

3-Results and discussion

3.1. Structural investigation

Fig.1: The Chemical structure of E-3-(Adamantan -2-Ylidene)-4-[1 - (2, 5-dimethyl-3furyl) ethylidene] dihydro-2, 5-Furandione compound.

Fig.1: The Chemical structure of [E-Adamantan - Fulgide]

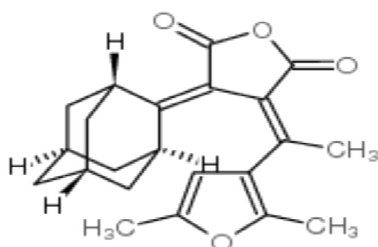


Fig.2:DTA spectra for [E-Adamantan - Fulgide] in the powder form and thin film form with rate ~ 10 $^{\circ}\text{C}/\text{min}$.

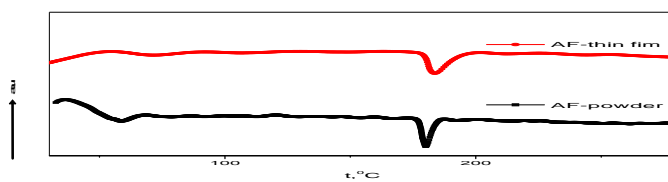


Fig.3: FTIR patterns for [E-Adamantan - Fulgide] in the powder form and thin film form with 539 nm thickness.

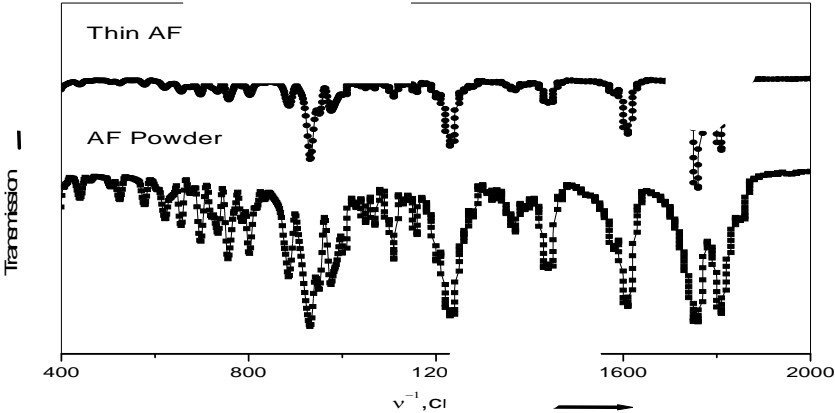
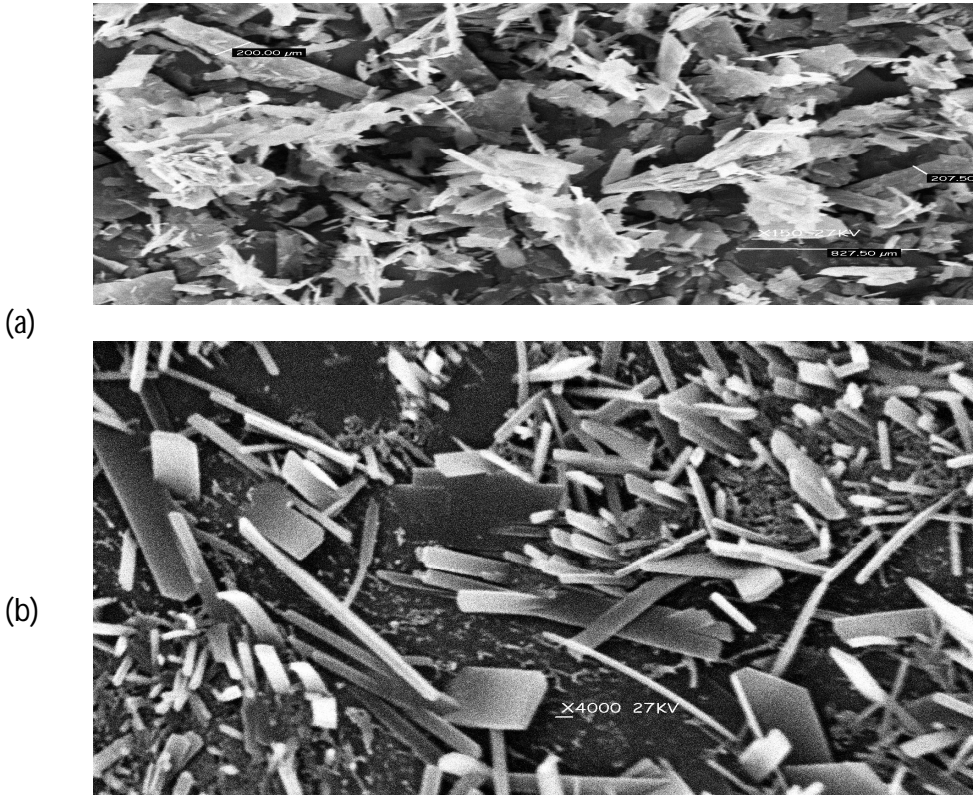


Fig.4: XRD patterns for [E-Adamantan - Fulgide] a) in the powder form and b)thin film form with 539 nm thickness.



Represents the chemical structure of E-isomer of (AF) compound (As obtained from ICT company ,while Fig.2 shows the patterns of DTA of both the powder and a thin film of E-AF compound ,where the m_p was found to be 181 ± 2

°C. Fig.3 shows FTIR spectra of (AF) compound in the powder and thin film form with the wave number range (from 400 to 2000 cm^{-1}).

Table 1: FTIR Spectral data for the powder form and the Thin film form of E-3-(Adamantan -2-Ylidene) -4-[1-(2,5-dimethy-3furyl)ethylidene] dihydro-2,5-Furandione (AF) compound.

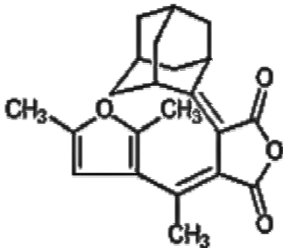
Powder form	Thin film	Assignment
ν^{-1} , cm^{-1} (related to the peaks in the FTIR spectra		
1807.3 1756.5	1807.0 1757.4	Strong =C=O stretching anhydride
1608.1	1609.1	Strong =C=O stretching may be α, β Unsaturated Ketone
1444.2 1434.9 1393.5 1367.5	1443 ----- 1392.7	Medium C-H bending alkane methyl group
1233.7-1201.5 1068.6-1004.1	1232.7,1201.6	Sharp C-O stretching Vinyle ether medium
975.5	976.3	Strong C=C bending alkene
949.9 931.4	950.5 932.1	Strong C=C bending alkene trans distributed
885.7	886.6	Strong C=C bending alken Vinylidene
801.7 756.1 721.4	802.7 757.7 734.0	Medium C-H bending

The assignment of the characteristic bonds are listed in Table 1 and as a comment on the obtained results one can see that; All the peaks in the range of wave number ($2906.4-2850.5 \text{ cm}^{-1}$) appeared at the same position with less than $\pm 2 \text{ cm}^{-1}$ shift in the film. Also, the two peaks at 1757.4 and 1609.1 are sharper than the case of the powder. The peaks at 1444.2 appeared at 1443 with lower intensity. γ 1393.5 appeared at γ 1392.7, γ 1233.7 appeared at γ 1201.2 and γ 1232.7 appeared at γ 1201.6 with lower intensity. All the fingerprint region (1233.7 to 438 cm^{-1}) in the powder of AF compound has no change in position and appeared in AF thin film but with low intensity.

As a result of the previous investigation, FTIR data revealed that the thermal evaporated (E-AF) films (under our condition of preparation which has been mentioned before) were composed of (E-AF) molecules (see Fig.1) and no chemical change and this indicates that the thermal evaporation technique is a good method for the preparation of E-AF thin films. on the other side ,Fig. 4 exhibited XRD patterns of E-AF compound in both powder and thin film form (with 539 nm thickness).

The pattern of the obtained powder exhibited a polycrystalline nature while the pattern of the as-deposited thin film revealed the short range order which has been supporting by SEM as we will show later. The Miller indices and the lattice parameters were determined for the first time here for E-AF Compound, using Check's cell Program .

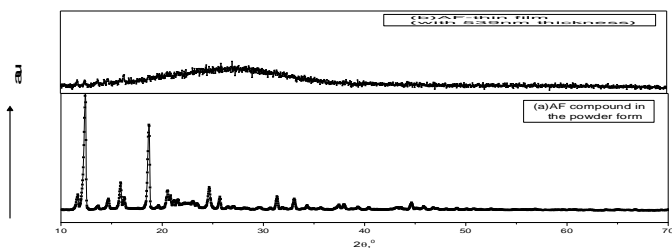
Table 2: The suggested XRD- Card for E-3-(Adamantan -2-Ylidene) -4-[1-(2,5-dimethy-3furyl)ethylidene] dihydro-2,5-Furandione (AF) compound.

E-3-(Adamantan-2-Ylidene)-4-[1-(2,5-dimethy-3furyl)ethylidene]dihydro-2,5-Furandione (AF)M.F/M.W=C ₂₂ H ₂₄ O ₄ /352.4 g/mole, a= 18.646 Å ,b= 2.554Å , c= 4.425Å ,β = 94.53 ⁰ , and V ⁰ = 468 Å ³ . ρ ≅ 1.33gm /cm ³ .							
							
d-space (Å).exp	I _{,exp}	2θ, ⁰ _{exp}	hkl, cal.	d-space (Å).exp	I _{,exp}	2θ, ⁰ _{exp}	hkl, cal.
7.5821	13.09	11.6616	(210)	7.13106	100	12.4021	--
6.4712	3.17	13.6724	----	6.02505	9.62	14.6903	(130)
5.5711	23.37	15.8945	-----	5.44574	10.95	16.2631	(310)
4.7437	72.85	18.6897	(320)	4.51874	3.88	19.6295	(330)
4.3208	16.55	20.5378	----	4.26223	11.39	20.8236	(240)
4.1890	8.36	21.1916	(101)	4.11848	9.05	21.5590	(121)
3.9649	5.53	22.4047	(240)	3.85701	7.02	23.0398	(021)
3.7918	5.61	23.4415	(201)	3.60715	19.51	24.6600	(231)
3.4627	11.26	25.7056	(031)	3.36527	2.62	26.4636	(331)
3.2909	3.22	27.0725	(350)	3.17329	1.71	28.0964	(321)
3.1373	1.51	28.4254	(411)	3.02114	1.88	29.5488	(260)
2.9090	1.99	30.7091	(511)	2.85078	11.72	31.3523	(151)
2.8048	2.42	31.8798	(351)	2.70787	9.63	33.0531	(450)
2.6111	4.12	34.3148	(541)	2.56581	1.16	34.9403	(630)
2.5145	2.10	35.6821	(370)	2.39808	4.66	37.4718	(531)
2.3676	4.33	37.9719	(720)	2.28727	2.73	39.3602	(361)
2.2292	2.1	40.4292	(570)	2.1898	0.75	41.1897	(171)
2.0911	1.91	43.2288	(272)	2.07308	2.5	43.6240	(840)
2.0275	6.22	44.6556	(190)	2.00722	1.65	45.1329	(811)
1.9778	3.11	45.8401	(671)	1.93969	2.29	46.7958	(581)

1.9262	1.53	47.1417	(7 7 0)	1.89086	1.05	48.0794	($\bar{4}$ $\bar{5}$ 2)
1.8520	1.55	49.1532	($\bar{6}$ 6 1)	1.82047	0.83	50.0636	($\bar{8}$ $\bar{6}$ 1)
1.7955	0.89	50.8075	($\bar{1}$ 9 1)	1.77408	0.85	51.4668	(6 9 0)
1.7408	0.89	52.5245	($\bar{7}$ 7 0)	1.71346	0.48	53.4292	(3 $\bar{6}$ 2)
1.6753	0.55	54.7451	($\bar{5}$ $\bar{7}$ 2)	1.61794	0.86	56.8603	($\bar{10}$ $\bar{4}$ 1)
1.5230	0.29	60.7623	($\bar{7}$ 9 0)	1.48924	0.19	62.2932	(3 8 2)
1.4563	0.31	63.8657	(1 $\bar{1}$ 3)	1.4326	0.41	65.0503	($\bar{3}$ $\bar{4}$ 3)
1.4001	0.43	66.7530	(9 1 2)	1.34596	0.16	69.8201	(5 9 2)
1.3459	0.17	69.8201		1.30617	0.32	72.2518	($\bar{10}$ $\bar{8}$ 2)
1.2396	0.32	76.8307	($\bar{13}$ 4 1)	-----	----	----	-----

The obtained data were listed in table 2 , where the system was found to be monoclinic system with $a= 18.646 \text{ \AA}$, $b= 2.554 \text{ \AA}$, $c= 4.425 \text{ \AA}$, $\beta = 94.53^\circ$. The estimated volume of the molecule = 468 \AA^3 and the density $\cong 1.33 \text{ gm /cm}^3$.

Fig.5 (a, b) shows the Scanning electron micrographs (SEM) of both powder and a thin film of thickness (539 nm) respectively. The micrographs reveal that the powder has a polycrystalline nature, while the thin film has a short range order.



3.2. Optical characterization

3.2.1. Absorption spectra

The average absorbance spectra of the as-deposited and colored AF thin films are shown in Fig.6.

Fig.6: The absorbance spectra of ([Adamantan -Fulgide] [AF] thin films with different time of coloration (from 0 to 11 min) at room temperature and under the effect of 360 nm UV light .

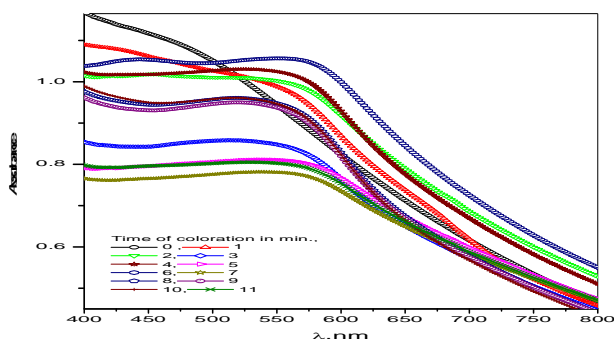
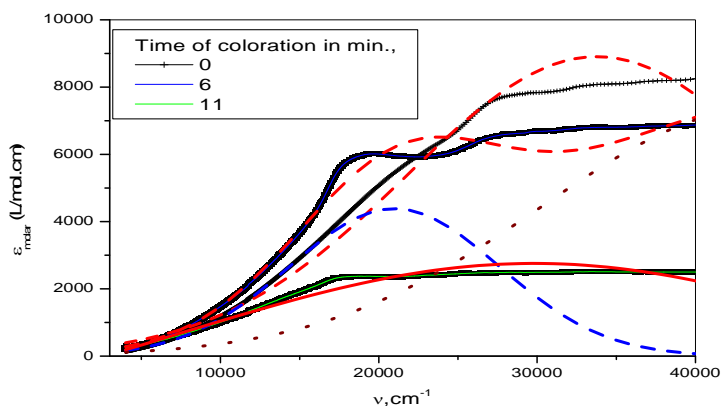


Fig.7 represented the spectral distribution of the molar extinction coefficient (ϵ_{molar}), where the obtained data are listed . **Fig. 7:** The molar extinction coefficient (ϵ_{molar}) vs., the wave number (ν) for [Adamantan -Fulgide] thin film ,with 539 nm thickness, for different time of coloration (0,6 and 11 min);The dash lines represent The Gaussian distribution.



The films started from transparent (E-isomer) till reach to saturated rose color after 6 min., under UV irradiation (C-isomer). The spectra represented an increasing in the absorbance with increasing of the exposure time with photochromic absorption peak in the wavelength range from 400 to 650 nm. The spectra also, illustrated an isosbestic point at 537 ± 15 nm after which the behaviour of the absorbance inverted to decrease with time of illumination.

The isosbestic point revealed the presence of only one product in the photoreaction[23]. The spectral distribution of the average values of the absorption coefficient (α) for the as-deposited (E-isomer) and colored AF(C-isomer) thin films , was calculated using the following equation [29,30];

$$\alpha = \frac{2.303 \text{ Abs}}{d} = \frac{2.303 \text{ OD}}{d} \quad (1)$$

Where Abs is the absorbance, d is the thickness and OD is the optical density, where;

$$\text{Abs} = \text{OD} = \log\left(\frac{I_0}{I_t}\right) = \log\left(\frac{1}{T}\right) \quad (2)$$

, and according to the following expression we could determine the molar extinction coefficient (ϵ_{molar}) and its parameters, especially the oscillator strength (f) and electric dipole strength (q^2 , \AA^2), according to the following simple equations [29, 30];

$$\alpha = 2303\left(\frac{\epsilon}{M}\right) \epsilon_{\text{molar}} \quad (3)$$

$$f = 4.38 \times 10^{-9} \int \epsilon_{\text{molar}} d\nu \quad (4)$$

$$q^2 = \frac{1}{2500} \epsilon_{\text{molar}} \Delta\lambda/\lambda \quad (5)$$

Table 3: Calculated spectral parameters f, q^2 (\AA^2) and E_{os} , eV for both as deposited and saturated colored (6 min ,360 nm UV)[Adamantan -Fulgide] films .

The state of the films	f	q^2 (\AA^2)	E_{os} , eV
As deposited	1.664	0.59	4.1868
Saturated colored with (6 min)	5.039	0.37	3.2898

Table 4 : The plasma frequency (ω_p , sec^{-1}), free carrier concentration (n , m^{-3}) and the ratio (N/m , $\text{g}^{-3} \text{m}^{-3}$) for both as deposited and saturated colored (6 min ,360 nm UV)[Adamantan -Fulgide] films.

The state of the films	(ω_p , sec^{-1})	n , m^{-3}	N/m , $\text{Kg}^{-3} \text{m}^{-3}$
As deposited	1.89×10^{15}	1.12×10^{27}	1.23×10^{47}
Saturated colored with (6 min)	2.15×10^{15}	1.45×10^{27}	1.59×10^{47}

All the obtained results are new for both E & C - AF thin films.

3.2.2. The optical constants

The spectral distribution of both T and R at normal incidence in the wavelength range from (200 to 2500) nm for the as deposited and saturated colored films are shown in Fig.8.

Fig. 8 : The spectral distribution of both transmittance and reflectance for both as deposited (E-isomer) and saturated colored [Adamantan -Fulgide] thin film(C-isomer), with 539 nm thickness and 6 min of coloration.

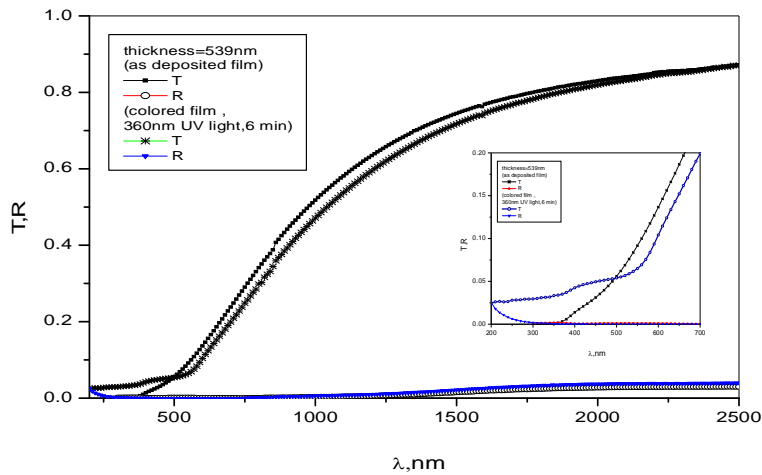


Fig.9 : The spectral distribution of both refractive index(n) and absorption index (k)for both as deposited and colored [Adamantan -Fulgide] thin film (with 539 nm thickness and 6 min., of coloration) .

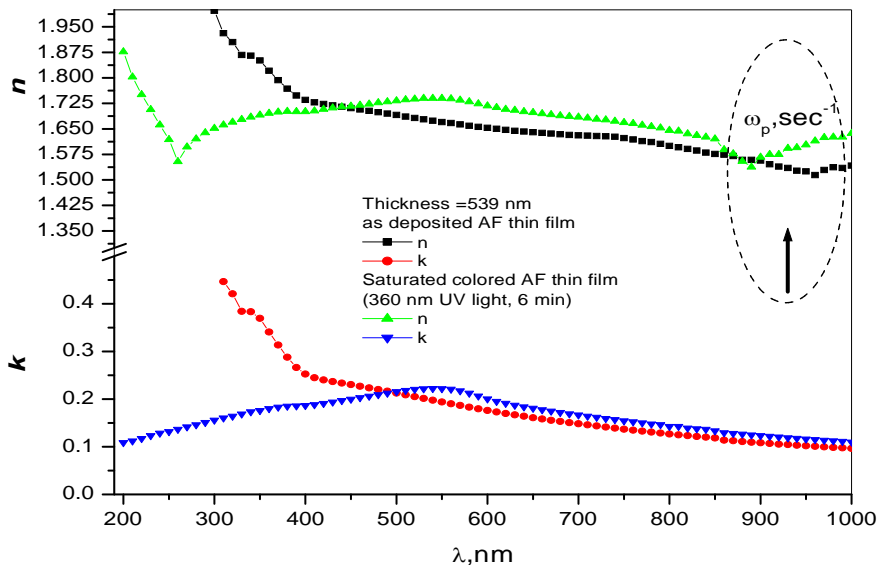
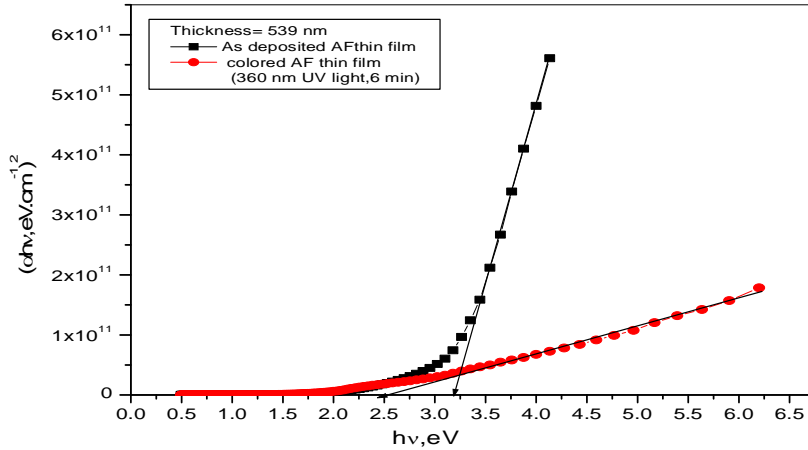


Fig.10 : $(\alpha hv)^2$ vs., (hv) for both as deposited and colored [Adamantan -Fulgide] thin film (with 10 min., of coloration and 539 nm thickness) .



IT could be observed that at longer wavelengths the AF films became transparent. Also, we observed that through the transmission curve for colored film (see the inset of Fig.8) and in the UV-region there is an inverted peak which nearly compatible with the coloration peak which appeared in the absorbance spectra. The absolute values of the measured T and R and then the optical constants n (the refractive index) and k (the absorption index) were calculated according to the following famous equations [31];

$$T = \left(\frac{I_{ft}}{I_q} \right) (1 - R_q) \quad (6)$$

$$R = \left\{ \left(\frac{I_{ft}}{I_m} \right) R_m \left(1 + (1 - R_q)^2 \right) - (T^2 R_q) \right\} \quad (7)$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (8)$$

$$k = \frac{\alpha \lambda}{4\pi} \quad (9)$$

, where all the symbols which involved in the pervious equations have the usual meaning. Fig.9 represents the dispersion spectrum in addition to the absorption index for our (E&C) AF films .The dispersion curves exhibited abnormal behavior which accompanied with plasma frequency (ω_p) which has been shifted to higher frequency with coloration . For colored films the spectrum of the refractive index can be divided into three regions starting with decreasing till a minimum value then started to increase to reach a maximum value and again decrease to reach minimum value related to plasma frequency (ω_p) and again return to increase with the increasing of the wavelength .

On the other hand ,for as deposited AF thin films the spectrum (n vs. λ) can be divided into two regions before and after the plasma frequency (ω_p) .The behavior was abnormal before (ω_p) and changed to be normal after it ,Where (ω_p) can be represented by the following equation[32];

$$(\omega_p) = \frac{Ne^2}{m\epsilon_0} \quad (10)$$

N is the free carrier concentration, e is the charge of an electron, ϵ_0 is the dielectric constant in vacuum, and m is the free electron mass. Also, the analysis of the peak of coloration and depending on the following approximate Smakula's equation [33, 34]

$$N_f = 0.89 \times 10^{17} \left\{ \left(\frac{n}{n^2 + 2} \right) \alpha \mu \right\} \quad (11)$$

, Where N_f is the density of the coloring centers, n is the refractive index of the films and μ is the width at the half maximum of the absorption peak. The calculated concentration of the coloring centers, N_f , through the colored (AF) thin films was found to be $\sim 1.18 \times 10^{10} / \text{cm}^3$.

3.2.3. Optical energy gap determination

To obtain an information about the type and the values of the interband transition ,the optical gaps were determined from the analysis of the spectral dependence of the absorption near the absorption edges by introducing the framework of one electron theory [35]; $(\alpha h\nu) = A(h\nu - E_g)^r$ (12), where E_g is the value of the optical gap corresponding to the transition, and A is factor depending on the probability of the transition and r is a number depending on the type of transition. This theory can be used to analyze the absorption edge of molecular solids and the value of energy can be explained as an energy gap, which is minimum energy formation of a separated, uncorrelated free electron and hole, and associated with the transport of single particles in the solid [36]. The best fitting of the experimental data was obtained for the allowed direct transition (see Fig.10) with direct optical gap $E_g^d = 3.17 \pm 0.006$ eV for the deposited films ,which decreased to 2.48 ± 0.003 eV for the colored films.

Finally, we can depend on the explanation of photochromic effect which illustrated by Maher Tadros [37]for free Fulgide ,where he illustrated that upon irradiation with UV light at $\lambda_{\text{max}} = 360$ nm, the near colorless compound undergoes electrocyclic ring - closer to form the saturated colored cyclized product which absorbs in the visible region and he attributed the bath chromic shift to the extended resonance conjugation from the lone pair electrons on the furan oxygen atom at the end to the nitrile atoms at the other end.

4. Conclusion

The DTA thermogram of E-3-(Adamantan-2-ylidene)-4-[1-(2,5-dimethylfuryl) ethylidene] dihydro-2,5-Furandione compound confirms a $M_p \approx 181 \pm 2^\circ \text{C}$. The FTIR spectra deduced that the as deposited films are composed of (AF) molecules and no chemical change has been happened during the thermal evaporation. The analyzed of XRD patterns using CHECK Cell's program supporting a polycrystalline nature of the powder with orthorhombic structure. The SEM deduced that the powder has a poly crystalline nature; while the as deposited (AF) thin film (E-isomer) (has a short range order. The UV-VIS absorption spectra of colored (AF) thin films (C-isomer) represented photochromic phenomenon during illumination time (6 min and under the effect of 360nm UV light) with an isosbestic wavelength $\cong 537 \pm 15 \text{ nm}$. The photobleaching has been achieved under the effect of Vis light coming from a Tungsten Lamp and after 13.5 min. The concentration of the coloring centers (N_f, cm^{-3}) through the colored AF thin films (C-isomer) was found to be $\sim 1.18 \times 10^{10} / \text{cm}^3$. On the other hand, the analysis of both the transmittance and the reflectance deduced that the refractive index has abnormal behaviour with plasma frequency, $(\omega_p) = 1.89 \times 10^{15} / \text{sec}$ and $2.15 \times 10^{15} / \text{sec}$ and free carrier concentration (n) = $1.12 \times 10^{27} / \text{m}^3$ and $1.45 \times 10^{27} / \text{m}^3$ for as deposited (E-isomer) and saturated colored (6 min) AF thin films (C-isomer) respectively. Finally the best fitting of the absorption coefficient (α, cm^{-1}) supporting direct energy gap with average value $\approx 3.17 \pm 0.006 \text{ eV}$ for as deposited films (E-isomer) which decreased to $\approx 2.48 \pm 0.003 \text{ eV}$ for the saturated colored AF thin films (6 min, 360 nm UV light) (C-isomer).

References

- M.A.Agerter, M.Mening, K.Fries, C.Fink-Straube, M.Mening, H.Schmidt, Sol-Gel-Technologies for Glass Producers and Users Ch.1 Photochromic coating (2004) 251-259; ISBN:978-1-4419-5455(print) 978-0-387(online).
- M.Fritsche, Comp.Rend., 69 (1867) 69.
- T.L.Phipson, Chem.News, (1881)283; J.B.Orr, Chem.News, 44 (1881)12.
- Y.Hishberg, photochromy in the bianthrone series, comp.Rend., 231(1950)903.
- W. Vogel, Glaschemie, DVG, Leipzig(1979).
- A.J.Cohen, Variable Transmission Silicate Glasses Sensitive to Sunlight, Science, 137(1962)981.
- X.Feng, W.Gao, effect of phase separation on the optical properties of photochromic glasses containing silver halides, J.Non Cryst.Sol., 112(1989)302.
- T.Kawamoto, R.Kikuchi, Y.Kimura, Photochromic glasses containing silver chloride, part 1 effect of glasses composition on photosensitivity, phys.chem.Glss., 17 (1976)23.
- L.G.Sawchuk, S.D.Stookey, Glass article and method of making it, US-pat. 3293052, BRD-Pat.1496082. Baltramiejūnas, Superlattices and Microstructures, 10(1991)307.

- E.Fischer, Y.Hirshberg, Formation of saturated colored forms of spiropyran by low temperature irradiation, *J.Chem.Soc.*, (1952)4522.
- P.J.Darcy, H.G.Heller, P.J.Strydom, J.Whittal, *J.Chem.Soc., Perkin Trans.1* (1981)202.
- K.Maeda, A.Chinone, T.Hayashi, photochromic thermochromism, and piezochromism of dimmers of tetraphenylpyryl, *Bull .Chem.Soc.Jp.*, 43(1970)1431.
- G.H.Brown, photochromism, Wiley interscience, N.Y.(1970).
- K.Fukui, Recognition of stereochemical paths by orbital interaction, *Acc. Chem.Res.*, 4(1971)57.
- H.G.Heller *IEEE.Proc.Part.1*, 130(1983)209.
- J.Whittal, in H.Durr, B.Bouas-Laurent (Eds), photochromism Molecules and systems, Elsevier, New York, (1990) 314.
- H.G.Heller, J.R.Langan. *J.Chem.Soc, Perk in trans.* 11(1981)341.
- A.A.Bahajaj and A.M.Asiri *Optical Materials* 28(2005)1.
- Y.Yokoyama, K.Takahashi, *Chem.Lett* (1996)1037. Yongchaoliang, A.S.Dvornidov, M.Rentze pis, *J.Photochem.Photobiol .A* 146 (2001)83.
- A.M.Asiri. *J.Chem.Res.* (5)(1997)302.
- M.M.EL-Nahass, M.M.Zeyada and A.A.Hendi, *Optical Material* 25(2004) 43.
- M.Ibrahim, A.A.EL-Barbary, M.M.EL-Nahass, M.A.Kamel, M.A.M.EL-Mansy, A.M.Asiri, *Spec tro chimica Acta Part A :Molecular and Biomolecular spectroscopy*, 87 (2012)202.
- M.M. El-Nahass, A.M.A.EL-Barry, and E.Abd EL-Hady, *Int.J.Adv.Res.* 5(1)(2017)838.
- Yasushi yokoyama, *Chem .Rev.* 100(2000)1717. Y.Yokoyama, T.Goto, T.inoue, M.Yokoyama, Y.Kurita, *Chem.Lett*(1988)1049.
- Y.Yokoyama, T.Inoue, M.Yokoyama, T.Goto, T.Iwai, N.Kera, I.Hitomi, Y.Kurita, *bull.Chem.So.Jpn.* 67(1994)3297.
- M.M. El-Nahass, A.A.Atta, H.E.A.EL-Sayed, E.F.M.EL-Zaidia *Appl.Sur.Sci.* 254(2008) 2458.
- G.A.Kumar, J.Thomas, N.George, B.A.Kumar, P.Radhakri, V.P.N.Shaman, C.P.G.Poori, N.V.Vallabhan unnikrishnan, *Phys.Chem.Glass.* 41(2000)89.
- M.M. El-Nahass, M.A.M.Ali, A.S.Gadallah, M.Atta Khedr and H.A.Afify *Eur .Phys.J*(2015) 69.
- Scott h.Brewer, Stefan Franzen *J.alloy & Comp.* 328 (2002)73.
- S.K.Deb. *Philo.Mag.* 27(1973)801.
- M.M. El-Nahass, M.M. Saadeldin, H.A.M. Ali, M .Zaghlol, *Materials Science in Semiconductor Processing*, 28(2015)201. M.M.El-Nahass, H.M.Zayadia, K.F.Abd-EL-Rahman, A.A.M.Farag, A.A.A.Darwish, *Int.J.Modern P hys.B*(2004)421.
- M.M.El-Nahass, Tamer .E.Youssef, *J.Luminescence.* 131 (2011)1419. Mahar Tadros *Tetra chem.Lett* 36 (20)(1995)3453.