

## ORGANIC LIGHT-SENSITIVE COMPOUNDS. III.\*

## PYRYLIUM SALT SENSITIZERS IN LIGHT-SENSITIVE POLYMERS

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23 pyrylium salts of the types I–III were prepared, their electronic spectra were measured and their sensitization efficiency in light-sensitive layers of polymers IV and V was determined. Relationships found between the structure and photochemical properties are discussed on grounds of the quantum chemical HMO and LCI-SCF calculations.

Pyrylium salts proved useful in photomechanical reproduction as sensitizers of light-sensitive polymers<sup>1,2</sup> or semiconductors in electrophotographical layers<sup>2</sup> and as a component of layers in which a colour image emerges owing to the reaction with mercapto compounds under light irradiation<sup>4</sup>. Photosensitized *cis-trans* isomerization of stilbene<sup>5</sup> represents another example of their application. Synthesis and spectral properties of aryl substituted pyrylium salts have been studied in detail by Wizinger and collaborators<sup>6–8</sup>, discussions of the NMR and electronic spectra on the grounds of the HMO data were reported by other authors<sup>9,10</sup>.

In this paper the spectral properties of 2,6-diphenylpyrylium (I), 2,4,6-triphenylpyrylium (II), and 2,4,6-triphenylthiopyrylium (III) salts are described. Sensitization activity of these compounds was measured in layers where light-sensitivity was due to polymers of vinyl esters of cinnamic (IV) and cinnamylideneacetic (V) acids. Experimental results are discussed by means of HMO and LSI SCF quantum chemical data.

## EXPERIMENTAL

Before the analysis the samples were dried at 0.2 Torr over phosphorus pentoxide at 60°C for 8 hours. Electronic spectra were measured on an Optica Milano CF 4 spectrophotometer using ethanol as solvent.

## Syntheses of Compounds I–V

2,6-Diphenylpyrylium salts (I) were prepared according to Dilthey<sup>11</sup> by a treatment of cinnamylideneacetophenone<sup>12,13</sup> with ferric chloride in acetic acid. 2,4,6-Triphenylpyrylium dyes (II) were prepared by a condensation of aromatic aldehydes with acetophenone in acid media<sup>6,7</sup>.

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2,4,6-Triphenylthiopyrylium salts (*III*) were prepared from the corresponding pyrylium salts *II* and sodium sulfide in aqueous acetone<sup>8</sup>. Details on syntheses are summarized in Table I. Polymers *IV* and *V* were prepared by polymer analogical reaction of poly(vinyl alcohol) (1 mol, Mowiol 50/98) with (a) cinnamoyl chloride (1.2 mol), (b) cinnamylidenacetyl chloride (0.4 mol) and benzoyl chloride (0.8 mol) in pyridine<sup>1,15</sup>.

#### Sensitization Efficiency Tests

Sensitization efficiency of the compounds prepared was tested by measuring the sensitivity of light-sensitive layers<sup>15</sup>. The sensitivity is defined as a reciprocal value of exposure which is necessary for a layer to become insoluble and to remain on a support after development. Solvent used for preparation of films was cyclohexanone, the developer was a mixture of cyclohexanone and ethylene glycol monoethyl ether (1 : 1). Concentrations of solutions, exposures, and the other details were the same as in the paper<sup>16</sup>.

#### Quantum Chemical Calculations

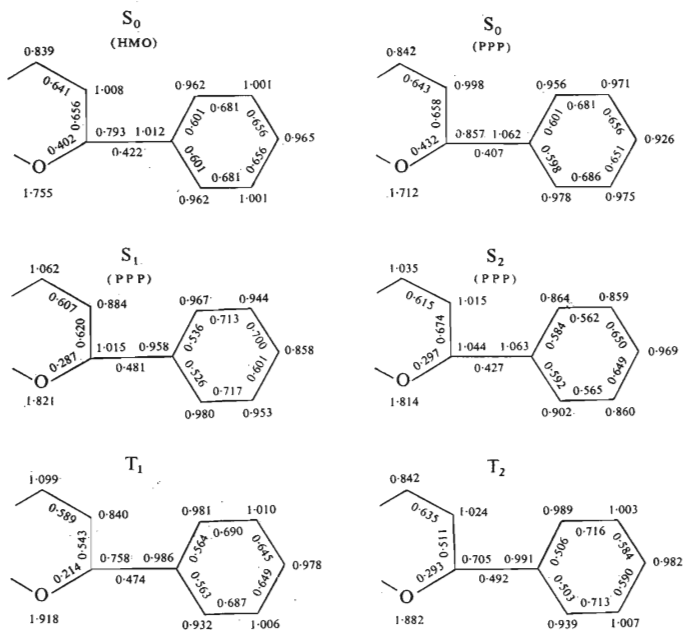
Calculations were performed on a National Elliott 503 computer using the programs written in the Group of Applied Quantum Chemistry, Institute of Physical Chemistry. In HMO calculations the following empirical parameters were employed:  $\alpha_0 = \alpha + 2\beta$ ,  $\beta_{CO} = 0.8\beta$ ,  $\alpha_S = \alpha + \beta$ ,  $\beta_{CS} = 0.7\beta$ . Parameters needful in LCI SCF calculations<sup>17,18</sup> are listed in Table II. For computational details *cf.* ref.<sup>19</sup>. Theoretical quantities not published in this paper are available from the authors on request.

## RESULTS AND DISCUSSION

### *Spectral Properties*

Figs 1a–c present the molecular diagrams for unsubstituted pyrylium salts *I–III*. With pyrylium salts of the types *I* and *II* the HMO and SCF molecular diagrams for ground states are nearly identical while with those of the type *III* a considerably higher electron density on sulphur is predicted by the SCF theory. Owing to a cumulation of electron density on the electronegative O and S atoms a decrease of electron density on C atoms, in 2,4, and 6-positions occurs. The latter are consequently the sites where a reaction with nucleophilic agents can take place. This is in accordance with experimental findings, *e.g.* diphenylpyrylium can be substituted in a 4-position by C-bases<sup>20</sup> like dibenzoylmethane or acetylacetone and triphenyl derivatives of *II* and *III* in 2- and 6-positions react with amines forming pyridines<sup>6,8</sup>.

Absorption spectra of the unsubstituted *I–III* are presented in Fig. 2. The diphenylpyrylium salt exhibits one clean-cut maximum in a long-wave region. Triphenylpyrylium salts possess there two bands; in case of thio derivatives their considerable overlapping occurs. A qualitative interpretation can be given for this by HMO calculations. In 1,3,5-triphenylbenzene the highest occupied molecular orbital is degenerate. If an O or S heteroatom is introduced, the degeneracy is removed and two levels with a narrow energy gap originate. Electron promotions from these levels give rise to two absorption bands located near each to other. In 1,3-diphenylbenzene the



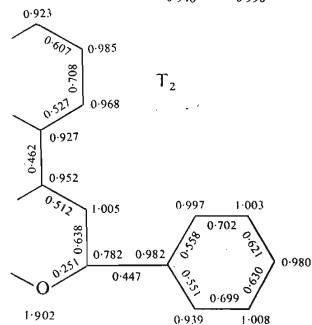
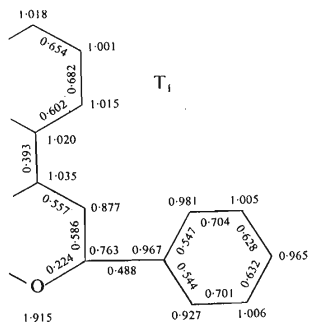
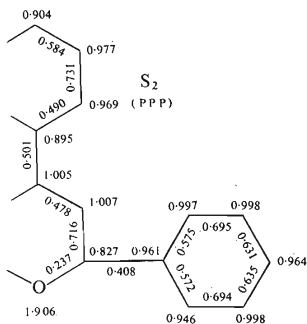
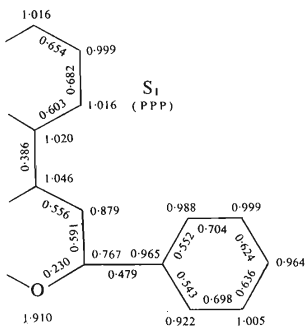
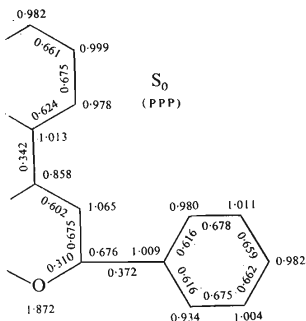
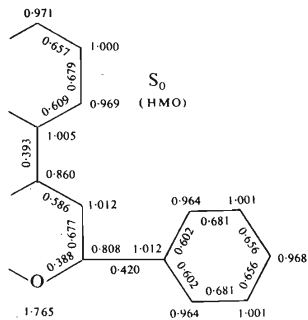
a

FIG. 1

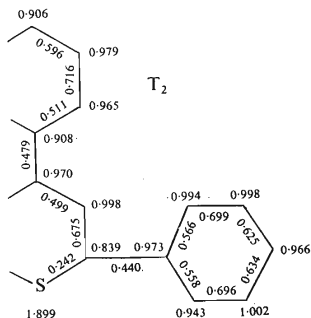
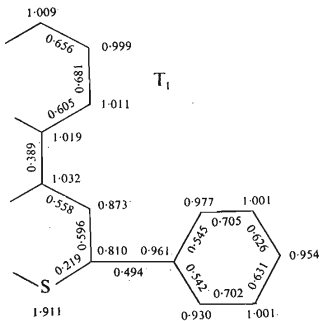
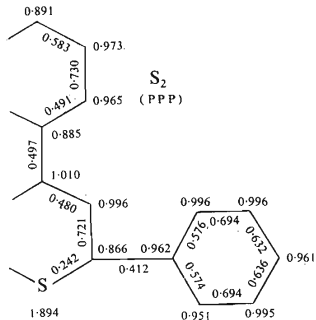
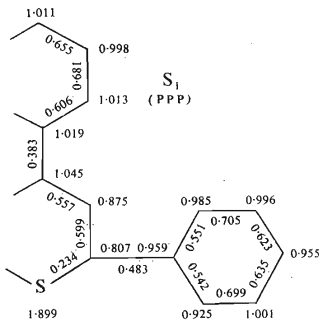
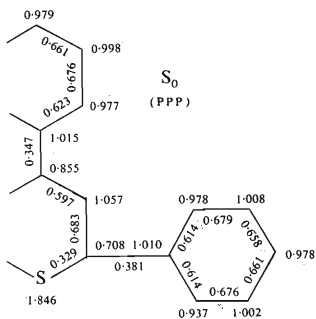
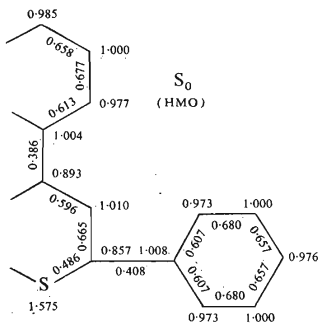
Molecular Diagrams of 1,6-Diphenylpyrylium *Ia* (a), 2,4,6-Triphenylpyrylium *IIa* (b), and 2,4,6-Triphenylthiopyrylium *IIIa* (c)

highest occupied molecular orbital is non-degenerate, therefore only one band of *I* in a long-wave region is observed. Absorption maxima and molar extinction coefficients of the prepared compounds are summarized in Table III.

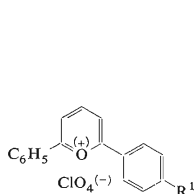
Quantitative results of the LCI-SCF calculations are compared with measured spectra in Figs 3a – c. With diphenylpyrylium *I* the calculation corresponds to a nature of the spectrum. The first two strong bands of triphenylpyrylium salts *II* and *III* are due to nearly pure 12 → 13 and 11 → 13 electronic transitions which are accompanied by an electron density accumulation on O or S heteroatoms; molecular diagrams for corresponding triplet states are very similar. The calculated wavelength of the long-wave band is in agreement with the experimentally found value for *II*



b



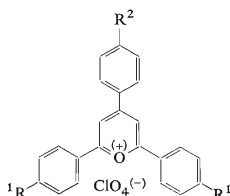
c



Ia,  $R^1 = H$

Ib,  $R^1 = CH_3$

Ic,  $R^1 = OCH_3$



IIa,  $R^1 = R^2 = H^*$

IIb,  $R^1 = H, R^2 = CH_3$

IIc,  $R^1 = CH_3, R^2 = H$

IId,  $R^1 = R^2 = CH_3$

IIe,  $R^1 = H, R^2 = OCH_3$

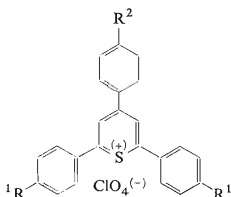
IIf,  $R^1 = OCH_3, R^2 = H^*$

IIg,  $R^1 = R^2 = OCH_3^*$

IIh,  $R^1 = H, R^2 = N(CH_3)_2$

IIi,  $R^1 = CH_3, R^2 = N(CH_3)_2$

IIj,  $R^1 = OCH_3, R^2 = N(CH_3)_2$



IIIa,  $R^1 = R^2 = H$

IIIb,  $R^1 = H, R^2 = CH_3$

IIIc,  $R^1 = CH_3, R^2 = H$

IIId,  $R^1 = R^2 = CH_3$

IIIe,  $R^1 = H, R^2 = OCH_3$

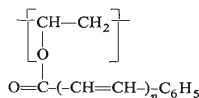
IIIg,  $R^1 = OCH_3, R^2 = H^*$

IIIh,  $R^1 = R^2 = OCH_3$

IIIi,  $R^1 = H, R^2 = N(CH_3)_2^*$

IIIj,  $R^1 = CH_3, R^2 = N(CH_3)_2$

IIIk,  $R^1 = OCH_3, R^2 = N(CH_3)_2$



IV,  $n = 1$

V,  $n = 2$

and III, while with the second band the theory overestimates somewhat the transition energy.

The effect of methyl substitution can be interpreted by means of a first order perturbation treatment using the equation<sup>21</sup>

$$\Delta\tilde{\nu} = (c_{-1}^2 - c_1^2) \delta\alpha_\mu, \quad (1)$$

where  $\Delta\tilde{\nu}$  is frequency shift of the absorption maximum owing to substitution,  $c_{-1}$  and  $c_1$  are HMO coefficients of a  $\mu$ -position in the lowest free and the highest occupied molecular orbital,  $\delta\alpha_\mu$  is a coulomb integral change of the substituted atom;

\* IIa, m.p. 294–296°C, ref.<sup>14</sup> m.p. 289°C; IIg, m.p. 318–320°C, ref.<sup>6</sup> 274–275°C; IIh m.p. 325–327°C, ref.<sup>6</sup> 256°C; IIIg m.p. 290–293°C, ref.<sup>8</sup> m.p. 228–230°C; IIIh m.p. 256–258°C, ref.<sup>8</sup> m.p. 247–249°C.

for methyl substitution  $\delta\alpha_{\mu} = 4290 \text{ cm}^{-1}$ . Results of calculations are summarized in Table IV. For the individual substituted methyl derivatives the following conclusions can be formulated: 1. Owing to methyl substitution in the *para* position of 4-phenyl groups of *II* and *III* the first two absorption bands coalesce forming one band with a higher intensity and with a maximum lying between the former. The interpretation afforded by the calculations is that that substituent causes a small blue

TABLE I  
Synthesized Compounds of the Types *I*–*III*

Compound	Yield, % m.p., °C	Formula (m. w.)	Calculated/Found			
			% C	% H	% Cl	% S
<i>Ib</i>	14.5 256–257	$\text{C}_{18}\text{H}_{15}\text{ClO}_5$ (346.7)	62.34	4.36	10.22	—
			62.14	4.65	10.50	—
<i>Ic</i>	14.5 261–262	$\text{C}_{18}\text{H}_{15}\text{ClO}_6$ (360.8)	59.60	4.17	9.77	—
			59.80	4.45	10.03	—
<i>IIb</i>	29.0 281–283	$\text{C}_{24}\text{H}_{19}\text{ClO}_5$ (422.9)	68.15	4.53	8.38	—
			68.11	4.52	8.51	—
<i>IIc</i>	15.0 290–292	$\text{C}_{25}\text{H}_{21}\text{ClO}_5$ (436.9)	68.73	4.90	8.11	—
			68.57	5.10	7.82	—
<i>IIId</i>	33.5 305–308	$\text{C}_{26}\text{H}_{23}\text{ClO}_5$ (450.9)	69.26	5.14	7.86	—
			69.15	5.22	7.47	—
<i>IIi</i>	26.0 >360	$\text{C}_{27}\text{H}_{26}\text{ClNO}_5$ (480.0)	66.03	5.34	7.22	—
			66.50	5.52	7.38	—
<i>IIIb</i>	50.0 187–190	$\text{C}_{24}\text{H}_{19}\text{ClO}_4\text{S}$ (438.9)	—	—	8.08	7.30
			—	—	8.48	7.61
<i>IIIc</i>	82.0 211–214	$\text{C}_{25}\text{H}_{21}\text{ClO}_4\text{S}$ (452.9)	—	—	7.83	7.07
			—	—	7.51	6.87
<i>IIId</i>	48.5 254–256	$\text{C}_{26}\text{H}_{23}\text{ClO}_4\text{S}$ (467.0)	—	—	7.59	6.87
			—	—	7.47	7.03
<i>IIIi</i>	70.0 286–288	$\text{C}_{27}\text{H}_{26}\text{ClNO}_4\text{S}$ (496.0)	—	—	7.15	4.47
			—	—	7.28	6.60
<i>IIIj</i>	59.0 295–296	$\text{C}_{27}\text{H}_{26}\text{ClNO}_6\text{S}$ (528.0)	—	—	6.72	6.07
			—	—	6.38	6.09

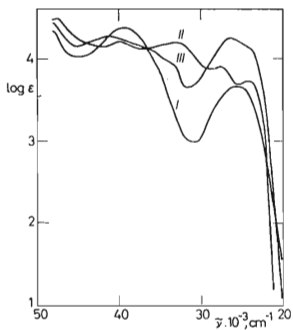


FIG. 2  
Absorption Curves of Pyrylium Salts I-III  
( $R^1 = R^2 = H$ )

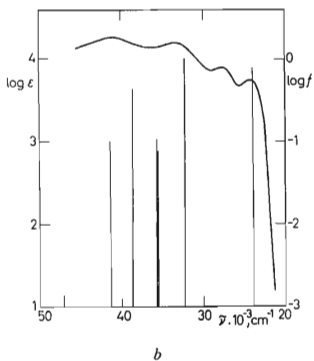
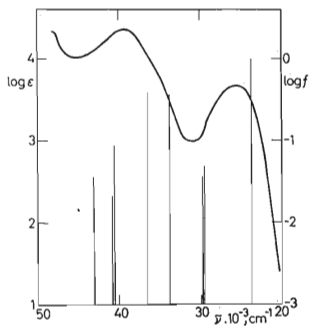
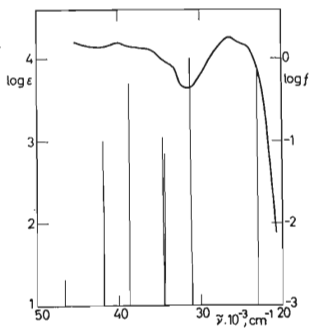


FIG. 3  
Absorption Curves and LCI SCF Transition  
Energies and Intensities

*a* Compound Ia, *b* compound IIa, *c* compound IIIa.



*a*



*c*



TABLE II  
Semiempirical Parameters Used in LCI SCF Calculations

Group	Atom	$I_{\mu}$ , eV	$\gamma_{\mu\mu}$ , eV	$\beta_C$ , eV	$Z_{\mu}$
PPP — ground and singlet states					
—	C	11.42	10.84	-2.318	1
$\overset{+}{\text{C}}=\text{O}-\text{C}$	O	27.17	14.58	-2.318	1
$\overset{+}{\text{C}}=\text{S}-\text{C}$	S	20.0	10.84	-1.623	1
triplet states <sup>25</sup>					
—	C	8.80	8.20	-2.5	1
$\overset{+}{\text{C}}=\text{O}-\text{C}$	O	24.55	11.94	-2.5	1
$\overset{+}{\text{C}}=\text{S}-\text{C}$	S	17.38	8.20	-1.75	1

shift of the longest-wavelength band (12  $\rightarrow$  13) and a large red shift of the shorter-wavelength band (11  $\rightarrow$  13). Thus an overlapping of these bands occurs and only one maximum with a higher intensity is observed. 2. Methyl substitution in the *para* position of 2- or 6-phenyl group leads to a red shift of the first band whereas the second band remains nearly unaffected. This experimental finding is seen, from Table IV, to be confirmed by calculations which predict a red shift for the 12  $\rightarrow$  13 transition and a small blue shift for the 11  $\rightarrow$  13 transition. 3. Introduction of methyl groups into all three phenyl rings shifts both bands bathochromically, in agreement with calculations. The shift of the first band is probably due to substituents in 2- and 6-phenyl rings while the shift of the second band is due to the methyl group in a 4-phenyl ring. 4. Methyl substitution on the phenyl ring of *I* gives rise to a little red shift, which was confirmed by calculations.

The effect of methoxy and dimethylamino substituents on the absorption maxima positions was studied in detail by Wizinger<sup>6-8</sup>. We obtained the same results: both substituents in all positions considered cause a considerable red shift, in particular in these derivatives. This shift is much larger than that estimated by the perturbation calculations, where only the inductive effect of substituents is considered. As the positive mesomeric effect equilibrates the electron density distributions in molecules, the calculations for unsubstituted compounds cannot afford any interpretation of experimental data.

#### Sensitization Efficiency

A sensitization of the compounds synthesized was tested by an enhanced sensitivity of a light-sensitive layer prepared from polymer esters *IV* and *V*. In the condensation

TABLE III  
 Absorption Maxima of Compounds I—III

Compound	R <sup>1</sup>	R <sup>2</sup>	$\lambda_{\max}$ , nm ( $\epsilon \cdot 10^{-3}$ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$ )			
<i>Ila</i>	H	H	245 (18.4)	300 (15.9)	362 (8.20)	414 (5.5)
<i>IIIa</i>	H	H	248 (15.8)	270 (13.4)	378 (17.8)	415 s (13.6)
<i>Ilb</i>	H	CH <sub>3</sub>	242 (19.5)	317 (15.2)	—	382 (11.2)
<i>IIIb</i>	H	CH <sub>3</sub>	255 (19.1)	290 s (13.7)	—	404 (28.9)
<i>Ilc</i>	CH <sub>3</sub>	H	260 (20.0)	295 (20.5)	368 (4.8)	434 (3.8)
<i>IIIc</i>	CH <sub>3</sub>	H	257 (16.2)	282 s (18.2)	378 (15.5)	436 (14.10)
<i>Ild</i>	CH <sub>3</sub>	CH <sub>3</sub>	257 (18.9)	310 (16.7)	382 (13.5)	430 (8.8)
<i>III d</i>	CH <sub>3</sub>	CH <sub>3</sub>	258 (16.8)	280 (15.9)	403 (23.4)	430 s (19.6)
<i>Ile</i>	H	OCH <sub>3</sub>	241 (20.4)	275 (14.1)	—	422 (24.6)
<i>IIIe</i>	H	OCH <sub>3</sub>	234 (15.7)	263 (21.4)	—	440 (29.1)
<i>Ilf</i>	OCH <sub>3</sub>	H	287 (18.2)	312 (18.2)	426 s (9.3)	472 (10.3)
<i>III f</i>	OCH <sub>3</sub>	H	270 (17.0)	300 (18.4)	410 s (10.4)	481 (16.0)
<i>Ilg</i>	OCH <sub>3</sub>	OCH <sub>3</sub>	274 (20.5)	310 s (16.5)	420 (23.5)	460 s (17.5)
<i>III g</i>	OCH <sub>3</sub>	OCH <sub>3</sub>	233 (19.6)	295 (17.0)	448 (30.4)	475 s (27.8)
<i>Ilh</i>	H	N(CH <sub>3</sub> ) <sub>2</sub>	240 (10.4)	270 (9.9)	384 (9.0)	542 (25.3)
<i>III h</i>	H	N(CH <sub>3</sub> ) <sub>2</sub>	262 (17.3)	290 s (17.3)	388 (18.3)	584 (53.8)
<i>Ili</i>	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	250 (10.6)	295 (10.6)	403 (13.0)	540 (41.3)
<i>III i</i>	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	272 (18.2)	292 s (14.9)	410 (15.4)	580 (52.8)
<i>Ilj</i>	OCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	271 (18.9)	300 (16.9)	438 (17.4)	536 (47.6)
<i>III j</i>	OCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	235 (15.3)	292 (18.5)	456 (18.0)	573 (40.1)
<i>Ia</i>	H	—	255 (23.5)	—	—	398 (4.7)
<i>Ib</i>	CH <sub>3</sub>	—	260 (23.5)	—	—	400 (3.5)
<i>Ic</i>	OCH <sub>3</sub>	—	225 (14.0)	277 (19.1)	—	390 (3.6)

 TABLE IV  
 Effect of Methyl Substitution on the Absorption Maxima Positions of Compounds I—III

Compound	R <sup>1</sup>	R <sup>2</sup>	Transition 12 → 13		Transition 11 → 13	
			$\Delta\tilde{\nu}$ , cm <sup>-1</sup>	$\Delta\lambda$ , nm	$\Delta\tilde{\nu}$ , cm <sup>-1</sup>	$\Delta\lambda$ , nm
<i>Ib</i>	CH <sub>3</sub>	—	-100 <sup>a</sup>	+2	—	—
<i>III b</i>	H	CH <sub>3</sub>	+210	-4	-630	+8
<i>Ilc</i>	CH <sub>3</sub>	H	-300	+5	+160	-2
<i>Ild</i>	CH <sub>3</sub>	CH <sub>3</sub>	-90	+1	-470	+6
<i>III b</i>	H	CH <sub>3</sub>	+210	-4	-670	+10
<i>III c</i>	CH <sub>3</sub>	H	-320	+6	+320	-5
<i>III d</i>	CH <sub>3</sub>	CH <sub>3</sub>	-110	+2	-350	+5

<sup>a</sup>Transition 9 → 10.

of the latter a mixture of cinnamylidenacetyl chloride and benzoyl chloride was used because the sensitivity measurements of the poly(vinyl cinnamylidene acetate) alone did not give reproducible results. (Table V). Owing to a low solubility some compounds could not be measured at higher concentrations. Otherwise the same concentration of all sensitizers in light-sensitive layers was used in order to obtain values, from which one can judge on relative sensitization efficiencies of individual compounds. From the values measured in polyester *IV* the following conclusions can be drawn: 1. Triphenylthiopyrylium salts of the type *III* are more effective than the corresponding pyrylium salts of the type *II*. 2. From the triphenylpyrylium salts of types *II* and *III* the most effective are the unsubstituted parent compounds. 3. The substituents decrease the sensitization efficiency in the series 4-(4-methylphenyl) > 2,6-bis-(4-

TABLE V

Sensitization Efficiency of Compounds *I–III*, Measured on the Layer of Sensitized Polymer *IV* and *V*

*c* Weight concentration of a sensitizer in a dry light-sensitive layer. Sensitivity of unsensitized polymer: *IV* 2, *V* 830.

Sensitizer	R <sup>1</sup>	R <sup>2</sup>	<i>IV, c</i>			<i>V, c</i>		
			1%	3%	6%	1%	3%	6%
<i>Ila</i>	H	H	160	520	660	1 040	1 300	1 875
<i>IIIa</i>	H	H	335	830	1 300	1 210	1 650	2 100
<i>Ilb</i>	H	CH <sub>3</sub>	260	415	520	935	1 300	1 875
<i>IIIb</i>	H	CH <sub>3</sub>	330	520	830	1 040	1 650	2 100
<i>Ilc</i>	CH <sub>3</sub>	H	55	105	210	1 040	1 300	1 450
<i>IIIc</i>	CH <sub>3</sub>	H	260	520	660	1 300	1 875	—
<i>Ild</i>	CH <sub>3</sub>	CH <sub>3</sub>	27	105	210	935	1 300	—
<i>III d</i>	CH <sub>3</sub>	CH <sub>3</sub>	165	520	660	1 040	1 875	2 350
<i>Ile</i>	H	OCH <sub>3</sub>	165	210	—	1 450	—	—
<i>IIIe</i>	H	OCH <sub>3</sub>	165	210	235	1 650	2 100	2 840
<i>IIf</i>	OCH <sub>3</sub>	H	27	35	55	1 040	—	—
<i>III f</i>	OCH <sub>3</sub>	H	35	70	—	1 475	1 875	2 600
<i>Ilg</i>	OCH <sub>3</sub>	OCH <sub>3</sub>	10	14	—	660	935	—
<i>IIIg</i>	OCH <sub>3</sub>	OCH <sub>3</sub>	45	—	—	1 300	1 875	—
<i>Ilh</i>	H	N(CH <sub>3</sub> ) <sub>2</sub>	10	14	17	830	520	—
<i>IIIh</i>	H	N(CH <sub>3</sub> ) <sub>2</sub>	10	14	—	660	—	—
<i>Ili</i>	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	10	12	—	830	660	—
<i>IIIi</i>	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	10	10	14	660	—	—
<i>IIf</i>	OCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	10	12	—	830	660	—
<i>IIIj</i>	OCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	10	12	—	1 170	830	—
<i>Ia</i>	H	—	10	35	55	1 040	1 650	—
<i>Ib</i>	CH <sub>3</sub>	—	10	35	65	1 040	1 650	—
<i>Ic</i>	OCH <sub>3</sub>	—	10	22	27	935	—	—

methylphenyl) > 4-(4-methoxyphenyl) > 2,6-bis-(4-methoxyphenyl) > 4-(4-dimethylaminophenyl). 4. Diphenylpyrylium salts appear to be low effective sensitizers. In polyesters *V* layers the following conclusions hold: 1. Triphenylthiopyrylium salts of the type *III* are more effective than the corresponding pyrylium salts of the type *II*. 2. From the triphenylpyrylium salts of types *II* and *III* the most powerful sensitizers are those bearing a methoxy group in a 4-phenyl ring; with other substituents the efficiency decreases in the series 2,6-bis-(4-methoxyphenyl) > 2,6-bis-(4-methylphenyl) > 4-(4-methylphenyl) = 2,4,6-triphenyl. 3. Dyes substituted by a dimethylamino group do not work as sensitizers, at higher concentration a light-sensitivity of the layer is even lowered. 4. Diphenylpyrylium salts appear to be little effective and tending to form a fog.

In both *IV* and *V* polyesters the thio derivatives are superior sensitizers. On the contrary the methoxy group has a quite opposite effect in *IV* and *V*. In the former the methoxy substitution decreases the efficiency while in the latter the methoxy derivatives are the most powerful sensitizers. This difference is probably due to different energy levels of triplet states, which appear to be responsible for energy transfer from a sensitizer to a polymer molecule<sup>22-24</sup>. This will be studied in some detail in a next paper.

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