

## DERIVATIVES OF PHTHALONES AS SENSITIZERS IN LIGHT-SENSITIVE POLYMERS\*

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A series of N-methyl derivatives of phthalones was prepared. Their electronic spectra were measured and their sensitization efficiency determined in light-sensitive films of polymeric esters of cinnamic and *p*-azidobenzoic acids. The relationship between the photochemical properties and the nature of the N-heterocyclic ring was studied by means of the experimental and quantum chemical data. The sensitization efficiency decreases in the series benzoselenazole, benzothiazole, pyridine, benzimidazole, quinoline.

In the process of photomechanical reproduction, the sensitivity of light-sensitive polymers is enhanced by doping with sensitizers of various types<sup>1</sup>. Previously we reported<sup>2,3</sup> on the photochemical properties of a new group of such compounds — dibenzoylmethylene derivatives of N-heterocyclic bases. The N-substituted phthalones *I*, that are of similar structure with two carbonyl groups, have not yet been used as sensitizers in light-sensitive polymers. The preparation of phthalones has been known for a long time<sup>4-9</sup>. The spectral properties of some their derivatives are also known, especially those with quinoline and pyridine rings that have been used for dyeing synthetic plastics and fibers<sup>10</sup>.

In this paper we report on the spectral and photochemical properties of N-alkylated phthalones *I* with different heterocyclic rings that were prepared by treatment of the respective unsubstituted derivatives with dimethyl sulphate. The sensitization efficiency of these compounds was measured in a light-sensitive film of polyvinyl cinnamates (*II*) and *p*-azidobenzoates (*III*). The experimental results are discussed on the basis of LCI-SCF quantum chemical considerations.

### EXPERIMENTAL

Before analysis the samples were dried 8 hours at 1 Torr at 80°C over phosphorus pentoxide. The electronic spectra were measured in ethanol on a recording spectrophotometer (Optica Milano) in the cell with 1 cm optical path.

\* Part VI in the series Organic Light-Sensitive Compounds. Part V: This Journal 38, 3616 (1973).

*Compounds I—III.* The N-substituted phthalones were prepared according to Huber<sup>7,8</sup> by melting the corresponding 2-methyl substituted bases with phthalic anhydride and zinc chloride at 180–200°. Compounds *Ia—e* were prepared according to Kuhn and Bär<sup>9</sup> by methylation of the sodium salts of the phthalones mentioned above by dimethyl sulphate in xylene. Crude products were purified chromatographically on an alumina column (Brockmann II, neutral) with chloroform and by a twofold recrystallization from acetone. The melting point of known compounds agreed with the literature<sup>8</sup>. Data on the newly synthesized compounds are given in Table I. The light-sensitive polymers *II* and *III* were prepared by reaction of polyvinyl alcohol (1 mol, Mowiol 50/98) with cinnamoyl chloride (1.2 mol) and *p*-azidobenzoyl chloride (1.2 mol), respectively, in pyridine.

*Sensitization efficiency.* This was tested by measuring the sensitivity of light-sensitive films according to Minsk and collaborators<sup>11,12</sup>. For concentrations of solutions used, conditions of exposure and other details see ref.<sup>2</sup>

TABLE I  
New Compounds *Ib—d*

Compound	<i>Ib</i>	<i>Ic</i>	<i>Id</i>
M.p., °C	229–231	254–255	293–294
Yield, %	(39.6)	(21.2)	(24.6)
Formula	C <sub>17</sub> H <sub>11</sub> NO <sub>2</sub> S	C <sub>17</sub> H <sub>11</sub> NO <sub>2</sub> Se	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>
Mol. weight	(293.3)	(340.2)	(290.3)
% C (calc./found)	69.62/69.06	60.02/60.27	74.48/74.62
% H (calc./found)	3.78/3.74	3.26/3.89	4.82/4.88
% N (calc./found)	4.74/4.37	4.12/3.91	9.65/9.99
% S, % Se (calc./found)	10.93/11.15	23.21/22.90	—

TABLE II  
Semiempirical Parameters Used in the LCI-SCF Calculations

Group	—	C—N—C <sup>a</sup>	C—S—C	C—Se—C	C=O
Atom	C	N	S	Se	O
<i>I</i> , eV	11.42	27.30	20.00	20.00	13.60
<i>A</i> , eV	0.58	9.3	9.16	9.16	2.3
$\beta_{C-X}^e$ , eV	-2.318	-1.854	-1.854	-1.159	-2.318
<i>Z</i>	1	2	2	2	1

<sup>a</sup> Methyl groups on nitrogen were disregarded.

*Quantum chemical calculations.* The PPP method was used in the form described previously<sup>13</sup>. The empirical parameters used are listed in Table II. The calculations were performed on a National Elliott 503 computer by a program written in the Group of Applied Quantum Chemistry at the J. Heyrovský Institute of Physical Chemistry and Electrochemistry in Prague. Details are available from the authors on request.

## RESULTS AND DISCUSSION

In Fig. 1 we present the molecular diagrams of phthalones *Ia–e* in their ground states. With all compounds under study, the electron density is increased in the indandione part of molecules owing to the two electron withdrawing carbonyl groups. The largest difference in the electron densities of the two subunits of the molecule is in the compound *Id* with the benzimidazole ring, the smallest is in the compound *Ia* with the quinoline ring. Among the carbon atoms, the highest electron density is on the one linking the two carbonyl groups in the indandione ring. This holds for all five derivatives in their ground states. The lowest electron density is found, besides the carbon atoms of the two carbonyl groups, on the carbon atom adjacent to the nitrogen. The positions with the predicted extreme electron densities may be taken as sites sensitive to electrophilic and nucleophilic agents, respectively. On excitation, these differences in electron density are suppressed. With the other heteroatoms, the electron density is lowered on nitrogen and sulphur in the heterocyclic ring,

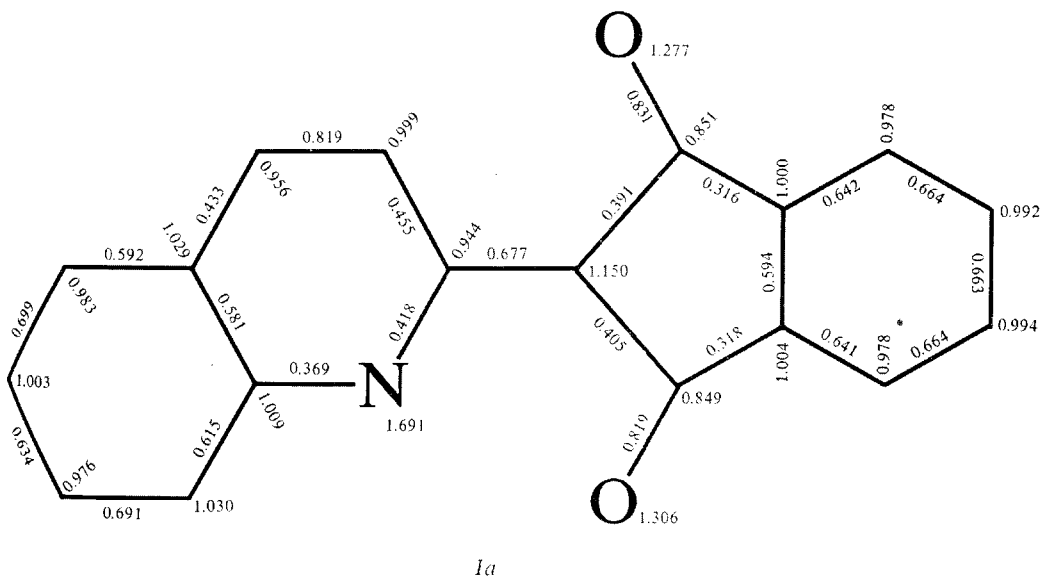
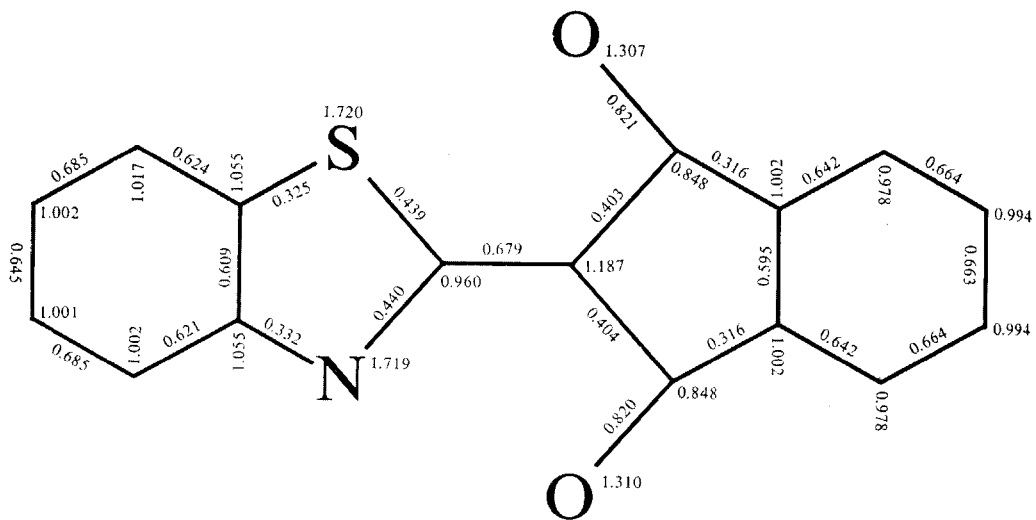
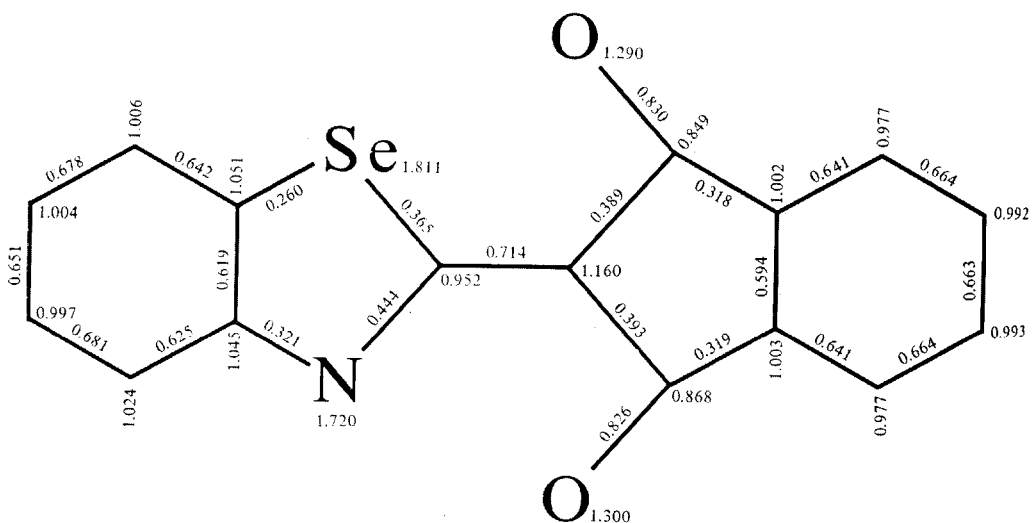
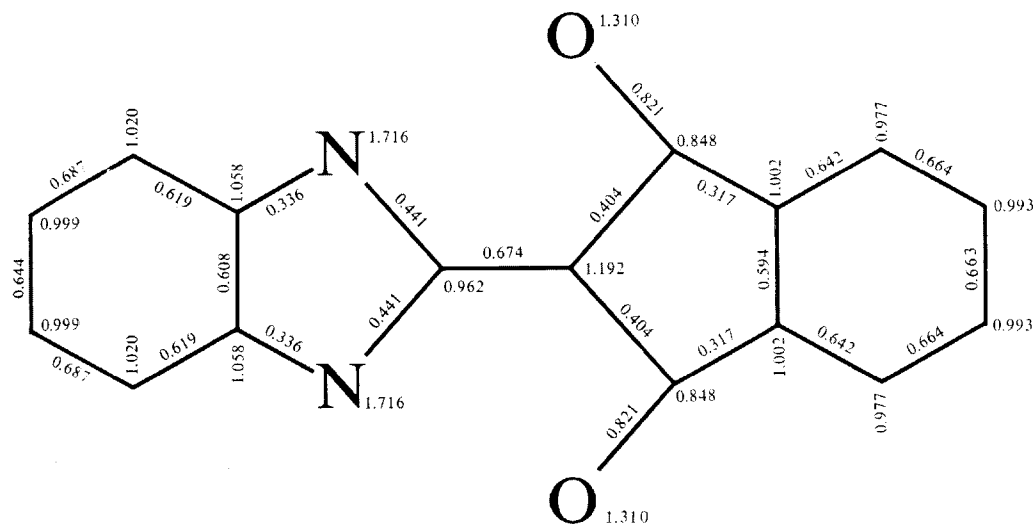
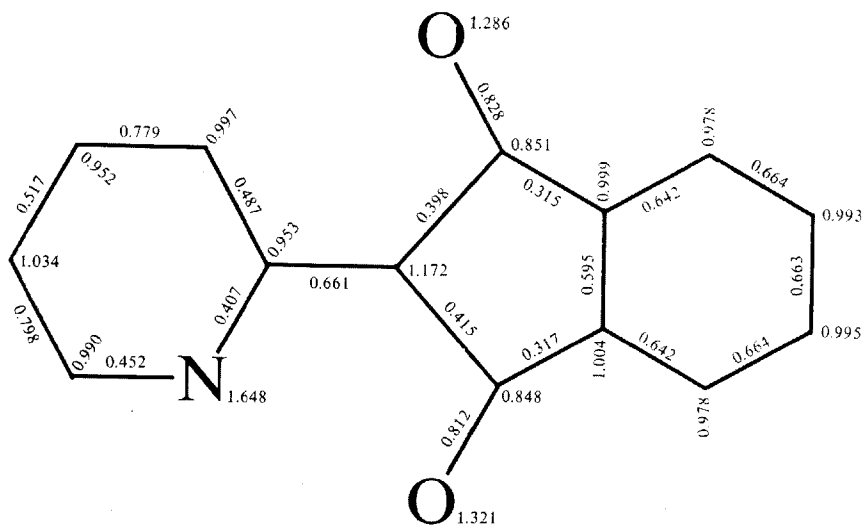


FIG. 1  
Molecular Diagrams of Phthalones in Ground States

*Ib**Ic*

and increased electron density is predicted for carbon atoms of the two carbonyl groups. In the molecules with the pyridine and quinoline rings, the electron density is higher on the oxygen atom adjacent to the nitrogen than on the other oxygen.

*Id**Ie*

This difference is considerably lower in the molecules with benzothiazole and benzoselenazole rings. In the molecule with the benzimidazole ring the two oxygen atoms are equivalent.

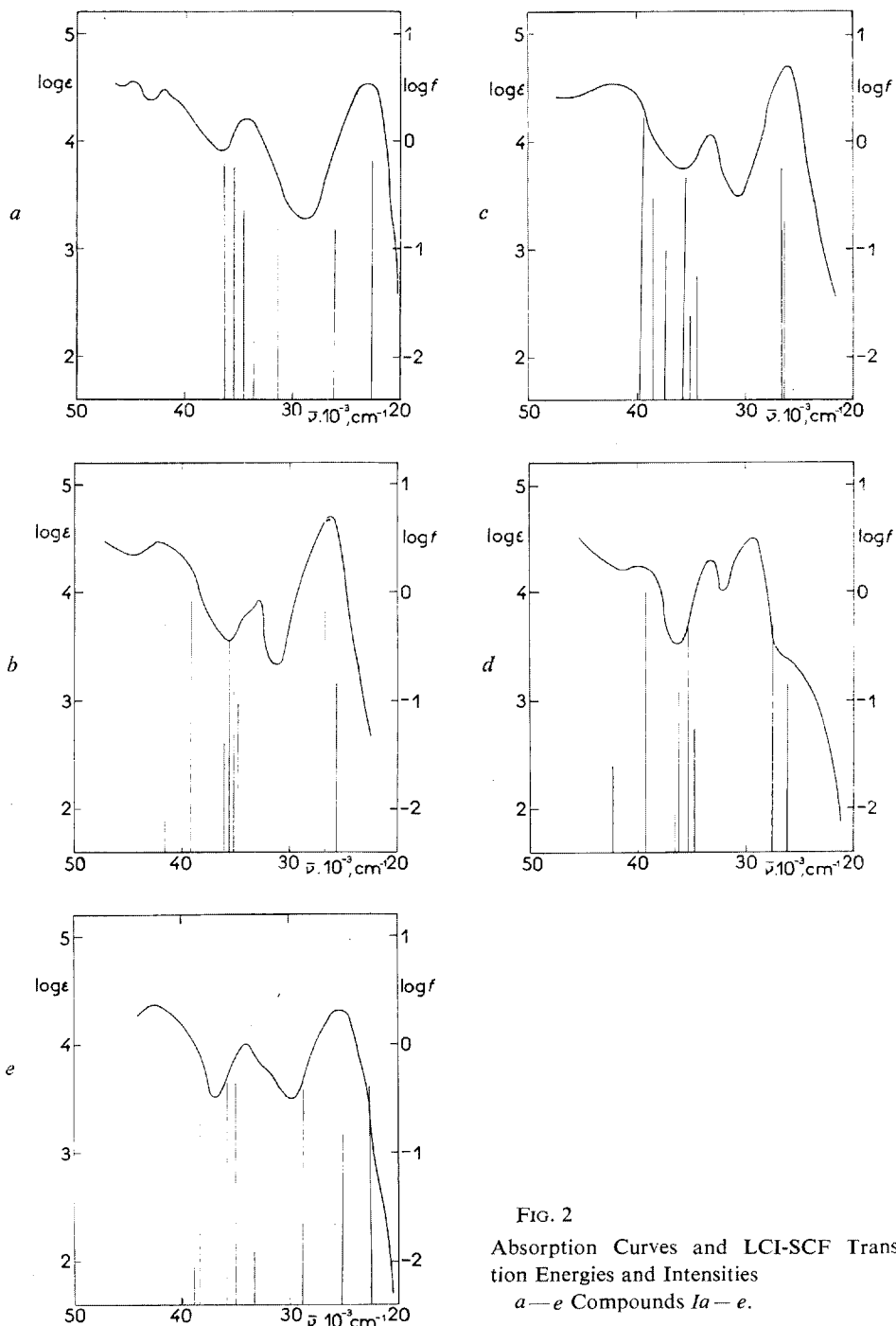
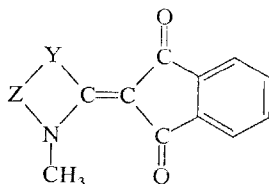


FIG. 2  
Absorption Curves and LCI-SCF Transition  
Energies and Intensities  
a—e Compounds Ia—e.

Fig. 2a–e presents the observed electronic spectra of compounds *Ia–e* and the results of the LCI-SCF calculations. Good agreement between theory and experiment, inclusive of intensities, was obtained. With the dyes *Ia–d* with the fused benzene ring in the heterocyclic part, the main absorption band is due to two allowed transitions  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  that are close in energy and correspond to almost pure  $11 \rightarrow 12$  and  $11 \rightarrow 13$  electron promotions. The smallest energy difference between the two transitions is predicted for the compounds *Ib* and *Ic* ( $X = S, Se$ ) which is in agreement with the observed least half-widths of their bands with the maxima at 380 and 385 nm (see Table III). With the dye *Ic* with the benzimidazole subunit, a weakly allowed transitions  $S_0 \rightarrow S_1$  gives rise to a mere shoulder on the long-wave tail of the absorption curve. The quinoline unit brings about broadening of the band and its red shift by 60 nm. A somewhat different picture was found with the transitions of the phthalone *I* possessing the pyridine ring. There the main absorption band is due to the  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_2$ , and  $S_0 \rightarrow S_3$  transitions that can be assigned to the



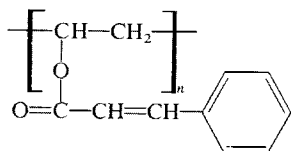
- Ia*, Z = *o*-C<sub>6</sub>H<sub>4</sub>, Y = CH=CH  
*Ib*, Z = *o*-C<sub>6</sub>H<sub>4</sub>, Y = S  
*Ic*, Z = *o*-C<sub>6</sub>H<sub>4</sub>, Y = Se  
*Id*, Z = *o*-C<sub>6</sub>H<sub>4</sub>, Y = N-CH<sub>3</sub>  
*Ie*, Z = CH=CH, Y = CH=CH

TABLE III  
Absorption Maxima of Compounds *Ia–e*

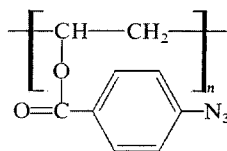
Compound	$\lambda_{\max}$ , nm ( $\epsilon \cdot 10^{-3}$ , l. mol <sup>-1</sup> . cm <sup>-1</sup> )	$\Delta\nu_{1/2}$ <sup>a</sup> , cm <sup>-1</sup>
<i>Ia</i>	238 (31.01) 291 (16.24) 441 (34.03) <sup>b</sup>	3 400
<i>Ib</i>	235 (31.62) 304 (8.13) 380 (49.51)	2 600
<i>Ic</i>	235 (32.82) 305 (11.41) 385 (48.76)	2 500
<i>Id</i>	252 (17.82) 299 (20.10) 340 (31.91) <sup>c</sup>	2 800
<i>Ie</i>	235 (23.92) 293 (9.88) 390 (20.89)	3 800

<sup>a</sup> Half-widths of the longest-wavelength absorption band; <sup>b</sup> 223 (36.17); <sup>c</sup> 390 sh (2.24).

one-electron transitions  $9 \rightarrow 10$ ,  $9 \rightarrow 11$ , and  $9 \rightarrow 13$ . Accordingly, the first band is rather broad. All compounds measured exhibit also a weaker band located in the region at 300 nm. The calculations suggest that it originates in electronic transitions to upper states  $S_3$  to  $S_7$  which are close in energy.



II



III

The sensitization efficiency of the compounds was measured in films prepared from light-sensitive polymers *II* and *III*. Results of the measurements are summarized in Table IV. The sensitization efficiency varies over a wide range. It is affected considerably more by the nature of the heterocyclic ring than by its substituents<sup>2,3</sup>. It decreases in the series benzoselenazole > benzothiazole > pyridine > benzimidazole > quinoline. The highest sensitization efficiency was found with the phthalone with a benzoselenazole subunit; this compound belongs to the most powerful sensitizers, in contrast to its sulphur analog, which is only of medium efficiency. This proves again that the replacement of sulphur by selenium brings about a considerable enhancement of the sensitization efficiency<sup>2,3</sup>. A minor but observable sensitization effect was found with compounds with the pyridine and benzimidazole rings, whereas

TABLE IV

Sensitization Efficiency of Compounds *I* in Light-Sensitive Polyvinyl Cinnamate (*II*) and Polyvinyl *p*-Azidobenzoate (*III*) Films

Compound	<i>II</i> <sup>a</sup>				<i>III</i> <sup>b</sup>			
	1%	3%	6%	10% <sup>c</sup>	1%	3%	6%	10% <sup>c</sup>
<i>Ia</i>	2	2	5	—	210	260	210	—
<i>Ib</i>	410	520	660	660	660	830	1 300	1 300
<i>Ic</i>	470	830	1 040	1 300	830	1 300	1 650	2 100
<i>Id</i>	50	85	105	105	330	410	470	470
<i>Ie</i>	260	330	330	410	470	660	750	750

<sup>a</sup> Sensitivity of the unsensitized polymer *II* is 2; <sup>b</sup> Sensitivity of the unsensitized polymer *III* is 210; <sup>c</sup> Weight concentration of sensitizer in a dry light-sensitive film.



the quinoline analog is completely ineffective. These conclusions about sensitization hold for both *II* and *III* polymers, the difference being only in the extent of the sensitization. In the former the sensitivity is enhanced by a factor of about 600, whereas in the latter it is only enhanced by a factor of 10. As regards the mechanism of sensitization, energy transfer is assumed<sup>14-17</sup> from a triplet state sensitizer molecule (donor) to a molecule of polymer (acceptor). With phthalones *I* the presence of the lone electron pair on the carbonyl oxygen gives rise to the  $^3n - \pi^*$  triplet state, in analogy to benzoylmethylene derivatives described previously<sup>2</sup>.

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