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Photoconductive Properties of Bis-halogenated Anthanthrone Pigments

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ABSTRACT

Photoconductivity measurements using an electrostatic paper analyser and an electrophotographic recorder have been carried out on a series of dual-layer photoconductor devices consisting of thin polycarbonate films doped with bis-halogenated anthanthrone pigments as the charge-generation material (CGM). The pigments, all synthesised by the same chemical route, exhibit photodecays that decrease with an increase in the size of the substituted halogen, with the fluoro pigment exhibiting anomalous behaviour. In most cases anthanthrone itself is found to exhibit the fastest photodecay. Vacuum-deposited films of the pigments exhibit much faster photodecay rates with no significant dark decay, indicating that the photoconductivity is an intrinsic property of the pigments. The nature of the charge-transport material (CTM), also using polycarbonate as the polymer binder, has a marked but variable influence on the photodecay rates. Charge acceptance increases with a decrease in the electron-donating power of the CTM and is in the order oxadiazole < leuco-triphenylmethane, although the effect is reversed for the vacuum-deposited systems. The results indicate that the photoconductivity of the pigments is very much dependent on their synthetic route purity and nature of the CTM and that the mechanism of photodecay occurs through the lowest excited singlet state. This is supported by the lack of any ESR signal from the pigments on optical excitation and the observation that halogen substitution decreases photoconductivity.

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INTRODUCTION

The use of organic photoconductors to replace selenium in the xerographic copying industry is growing rapidly. Despite this, our knowledge of conduction mechanisms is lacking in many aspects, particularly in their relationship with dye and pigment structure, the influence of the nature of the charge transport medium and pigment purity. To this end we have examined the photoconductive properties of a series of bis-halogenated anthanthrone pigments with two charge-transport materials. All the pigments were synthesised from halogenated naphthostyrils and the effect of purification via vacuum deposition on the photoconductive properties has been studied.

Electrophotographic materials can be quite complex but many consist of single or dual layers and in both cases the function of charge generation and transport are usually performed by different materials. Typical charge-generation materials (CGMs) are organic pigments such as phthalocyanine or perylene, and the pigmented system used depends on the region of photosensitivity required and the spectral output of the photocopier lamp. The charge-transport material (CTM) can be either an *n*-type semiconductor such as 2,4,7-trinitrofluorenone for transporting electrons, or a p-type semiconductor such as poly(vinylcarbazole) (PVK) or an aromatic hydrazone for transporting holes. A polymeric binder is required for the CGM and CTM (except where PVK is used as the CTM) and a styrene–acrylate resin or polycarbonate is typical.

In dual-layer devices the transparent charge-transport layer (binder plus active material) is coated over a thin charge-generation layer, whereas in single-layer devices the two materials are mixed.

The mechanism of photoconduction is complex and still the subject of much dispute but essentially it relies on the generation of charge carriers in the pigmented polymer film on irradiation. The most favoured mechanism involves the formation of a charge-transfer complex[1] and its Onsager-type dissociation.[2] The charge-transfer complex is thought to involve a singlet excited polymer molecule such as polycarbonate (D*) and a pigment/dye or impurity centre (A).

$$D^* + A \rightarrow (D^+\text{—}A^-)^* \rightarrow D^+ + A^-$$

In the experimental examples described here, double layers are used with polycarbonate as the binder for both the CTM and CGM layers. Two types of CTMs were chosen for study, namely an oxadiazole and a leuco-triphenylmethane. All the pigments and CTMs were used at a concentration of 50% (w/w) except for the vacuum-deposited pigments on aluminised polyester film.

EXPERIMENTAL

Materials

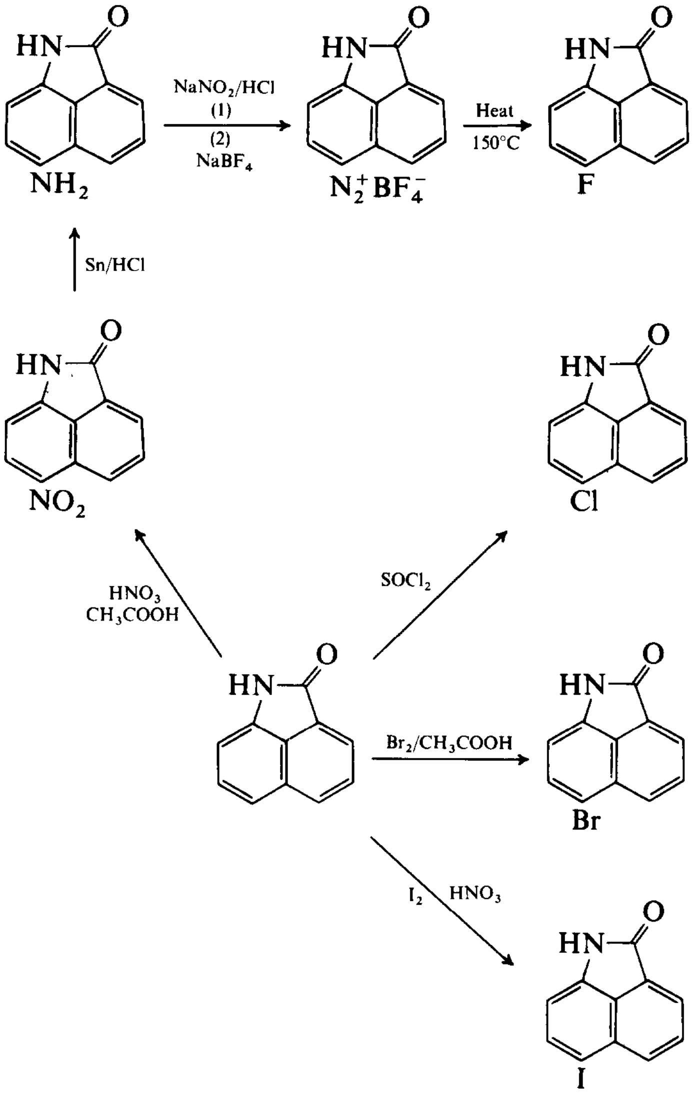
Commercial-grade polycarbonate (Lexan 141, GE Plastics, New York), was used for film preparation. The CTMs were gifts from ICI Organics Division Ltd, Manchester, UK, and were leuco-1,1-bis(4-*N*,*N*-diethylamino-2-methylphenyl)phenylmethane (LTPM) and 2,5-bis(4-diethylaminophenyl)-1,3,4-oxadiazole. Both these compounds are readily commercially available. The CGM layer was prepared by dispersing the pigments ($<1\,\mu$m) in a dichloromethane solution of the polycarbonate to give a 50% (w/w) formulation. This was performed by shaking with glass beads to ensure uniform dispersion. The mixture was then coated onto aluminised polyester using a 50 μm wire-wound drawbar. The aluminised polyester was first coated with an adhesive layer of a vinyl chloride–maleic anhydride copolymer (VMCA, Union Carbide) [2% (w/v) in dichloromethane] using a 6 μm drawbar. After coating with the CGM the films were dried in an oven at 80°C for 1 h and then coated with the CTM layer [50% (w/w) CTM in polycarbonate in dichloromethane] using a 100 μm drawbar. The dual layers were then finally dried for 3 h at 80°C. The CTM layer was measured to be approximately $12(\pm 1)\,\mu$m thick while that of the CGM was $1(\pm 0{\cdot}2)\,\mu$m. The pigments were also vacuum-deposited onto both quartz and aluminised polyester film.

Pigment synthesis

The key to the pigment synthesis was the preparation of the halogenated naphthostyrils. The fluoro- and iodo-naphthostyrils were made as decribed in Ref. 3, the bromo- as in Ref. 4 and the chloro- as in Ref. 5.

The halogenated naphthostyrils were hydrolysed in sodium hydroxide solution (10M) and then coupled via a diazotisation reaction with cuprous chloride. The resulting di-acid was dehydrated using oleum to generate the pigment. The pigments were purified by boiling in nitrobenzene and dried in a vacuum oven at 100°C for 24 h. No melting points were available as all the compounds melt above 300°C. The synthetic pathways are detailed in Schemes 1 and 2 respectively.

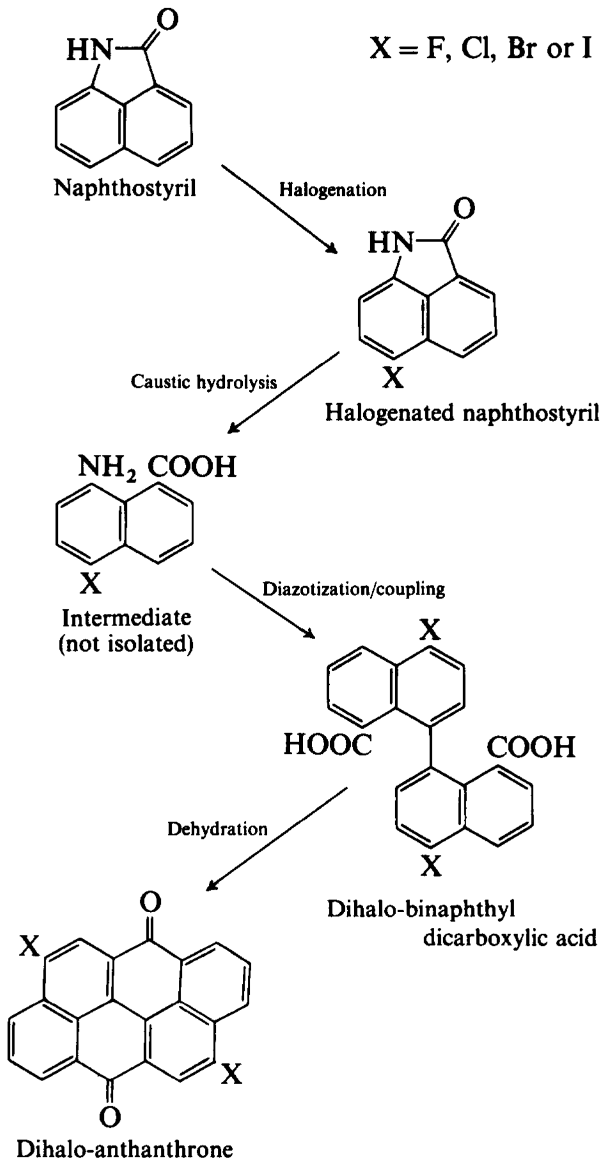
Mass spectral analysis identified the major component of each to be that of the desired material with some traces of mono- and un-substituted anthanthrone materials present, although no sign of anthanthrone was detected by infrared analysis.



Scheme 1. Synthesis of halogenated naphthostyrils.

Instruments

A Kawaguchi Electric Works Electrostatic Paper Analyser, Model SP428, was used for photoconductivity measurements on the impure pigments, whilst all other measurements were obtained on an electrophotographic recorder built at Manchester Polytechnic.[6] In the latter case the films, placed on a revolvable metal drum, are charged using a corotron device and the decay of the surface voltage is then measured under illumination via an



Scheme 2. Synthetic pathway to 2,7-dihalo-anthanthrones.

electrometer coupled to a storage oscilloscope. Absorption spectra were obtained on the vacuum-deposited pigments on quartz plates using a Perkin–Elmer Model 554 spectrophotometer. ESR analysis on irradiated pigments were obtained using a Varian instrument at the University of Manchester, UK.

The photo-responses were adjusted by a multiplication factor to compensate for the different light intensities of the tungsten–halogen lamp at

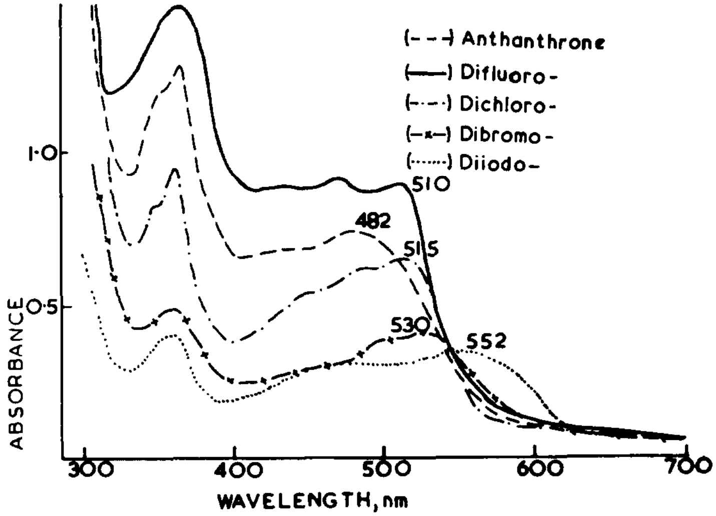


Fig. 1. Absorption spectra of vacuum-deposited pigments on quartz plates.

the various absorption maxima of the pigments. The absorption spectra of the pigments are shown in Fig. 1 for comparison.

RESULTS AND DISCUSSION

The electrophotographic properties of all the double-layer films under negative charging using the oxadiazole and leuco-triphenylmethane CTMs are summarised in Tables 1–6. These results will be referred to throughout the discussion.

TABLE 1

Electrophotographic Properties of Anthanthrone Pigments in the Charge-Generation Medium when using an Oxadiazole in the Charge-Transport Medium (83·3 lux Illumination) under Negative Charging

Pigment	*Charge acceptance (V)*	*Corona current (A)*	*Dark decay loss in 5 s (%)*	*Adjusted photodecay (Vs^{-1})*	*Adjusted half-life (s)*
Anthanthrone	1 210	1·9	14·9	277·0	2·1
Fluoroanthanthrone	1 210	1·9	19·4	99·7	5·5
Chloroanthanthrone	1 042	2·2	21·9	259·5	2·1
Bromoanthanthrone	956	2·4	20·9	81·9	7·0
Iodoanthanthrone	1 121	2·0	21·2	59·1	11·3

TABLE 2

Electrophotographic Properties of Anthanthrone Pigments in the Charge-Generation Medium when using a Leuco-triphenylmethane in the Charge-Transport Medium (83·3 lux Illumination) under Negative Charging

Pigment	*Charge acceptance (V)*	*Corona current (A)*	*Dark decay loss in 5 s (%)*	*Adjusted photodecay (Vs^{-1})*	*Adjusted half-life (s)*
Anthanthrone	1 312	1·4	15·7	273·6	2·1
Fluoroanthanthrone	1 278	1·3	14·9	73·0	10·1
Chloroanthanthrone	1 257	1·1	18·1	234·1	2·8
Bromoanthanthrone	1 167	1·4	17·0	30·1	29·1
Iodoanthanthrone	1 089	1·4	21·0	33·8	17·7

TABLE 3

Electrophotographic Properties of Anthanthrone Pigments in the Charge-Generation Medium when using a Leuco-triphenylmethane in the Charge-Transport Medium (280 lux Illumination) under Negative Charging using an Electrophotographic Recorder

Pigment	*Charge acceptance (V)*	*Dark decay loss in 5 s (%)*	*Adjusted photodecay (lux s)*
Anthanthrone	422	5·8	616
Fluoroanthanthrone	367	2·7	6 664
Chloroanthanthrone	426	4·6	655
Bromoanthanthrone	422	3·5	3 556
Iodoanthanthrone	426	5·7	3 388

TABLE 4

Electrophotographic Properties of Anthanthrone Pigments in the Charge-Generation Medium when using an Oxadiazole in the Charge Transport Medium (280 lux Illumination) under Negative Charging using an Electrophotographic Recorder

Pigment	*Charge acceptance (V)*	*Dark decay loss in 5 s (%)*	*Adjusted photodecay (lux s)*
Anthanthrone	358	2·7	706
Fluoroanthanthrone	260	6·6	2 755
Chloroanthanthrone	373	8·6	454
Bromoanthanthrone	275	4·5	1 266
Iodoanthanthrone	296	9·1	1 747

TABLE 5
Electrophotographic Properties of Vacuum-Deposited Anthanthrone Pigments in the Charge-Generation Medium when using a Leuco-triphenylmethane in the Charge-Transport Medium (100 lux Illumination) under Negative Charging using an Electrophotographic Recorder

Pigment	*Charge acceptance (V)*	*Dark decay loss in 5 s (%)*	*Adjusted photodecay (lux s)*
Anthanthrone	281	0·6	92
Fluoroanthanthrone	385	0·0	96
Chloroanthanthrone	380	1·3	120
Bromoanthanthrone	468	0·0	358
Iodoanthanthrone	427	1·0	136

TABLE 6
Electrophotographic Properties of Vacuum-Deposited Anthanthrone Pigments in the Charge-Generation Medium when using an Oxadiazole in the Charge-Transport Medium (10 lux Illumination) under Negative Charging using an Electrophotographic Recorder

Pigment	*Charge acceptance (V)*	*Dark decay loss in 30 s (%)*	*Adjusted photodecay (lux s)*
Anthanthrone	600	3·2	21·0
Fluoroanthanthrone	600	5·6	43·7
Chloroanthanthrone	628	5·7	17·9
Bromoanthanthrone	578	6·9	10·0
Iodoanthanthrone	612	5·0	22·6

Absorption spectra

The absorption spectra of the vacuum-deposited pigments on quartz plates are shown in Fig. 1. There is a typical hyperchromic effect from fluoro-, chloro-, bromo- to iodo- substitution from 510, 515, 530 to 552 nm respectively.

Charge acceptance

The charge acceptance value is important in providing information on the electron-accepting/donating ability of the CTM layer. The results in Tables 1 and 2 for the synthetic pigments with the oxadiazole and LTPM as respective CTMs using the electrostatic paper analyser show that charge acceptance is higher for all pigments except the iodo-, and increases in the order LTPM > oxadiazole. A similar effect is seen for all the synthetic pigments in Tables 3 and 4 where LTPM and oxadiazole are used as respective CTMs using the electrophotographic recorder, whereas the reverse effect is seen for the pure vacuum-deposited pigment systems in Tables 5 and 6 with the same respective CTMs.

Electrostatic charging is a complex phenomenon and depends to a great extent on the charge injection from the ground electrode and free carriers in the photogenerator. Both the CTMs used here are electron-donating in character with the LTPM being less so than the oxadiazole. During the charging operation, charge will be lost due to the dark current and it is also possible that re-exchange of an electron may take place with the atmosphere.

Dark decay

It is important in electrostatic recording that the film retains the applied charge until optically excited. The results for dark decay of the surface voltage are shown in Tables 1–4 for the synthetic pigments and Tables 5 and 6 for the vacuum-deposited systems. These results show that for all the synthetic pigment films the dark decays are more rapid than for the pure vacuum-deposited systems. In fact, in the latter case no significant dark decays were observed. This could be explained by the fact that there is some intermixing of the CTM with the CGM layer and that the enhanced dark decay for the synthetic pigment films is due therefore to charge injection from the ground electrode. Thus, the rate-determining step for the dark decay is the process of electron transfer across the CGM–CTM boundary. However, the absence of any significant dark decay in the case of the vacuum-deposited pigments indicates that impurities in the CGM may be more important.

Photodecay

Two values are used to measure the photodecay rates in Tables 1 and 2. They are the initial photodecays of the surface charge in volts per second and the time in seconds for the surface charge to decay to one-half of its original value. For measurements obtained using the electrophotographic recorder, the adjusted photodecays are obtained by multiplying the half-life decays of the surface charges by the illumination intensities in lux. These results show a number of interesting features, some of which are consistent with the above discussion.

The first result is that, from Tables 1 and 2, the photodecay rates decrease with an increase in the size of the substituted halogen. The exception is chloro- > bromo- in the case of the oxadiazole CTM and also iodo- > bromo- for the LTPM CTM. In both cases however, it is to be noted that the unsubstituted anthanthrone pigment is the most effective system and that this is reflected in the results in Tables 3–5. In the case of Table 6 for the oxadiazole CTM, the chloro-pigment system exhibits the most rapid photodecay.

The second interesting feature is that the photodecay rates follow the order in the electron-donating power of the CTMs oxadiazole > LTPM and this is also consistent with the electron-accepting ability of the CGM layer. The substitution effects of the halogens on the photodecay rates implicate the involvement of the lowest excited singlet state in the charge-transfer mechanism. This is attributed to the heavy-atom spin–orbit coupling effect enhancing the rate of intersystem-crossing to the triplet state, which is a well-known phenomenon.[7] Analysis of the pigments by luminescence spectroscopy has so far proved negative. Furthermore, all the pigments were irradiated in an ESR spectrometer and no signal could be detected, which supports the absence of a triplet state.

The third interesting feature is that the photodecay rates for the vacuum-deposited pigments are all significantly faster than those for the corresponding synthetic pigments. This indicates that the photoconductive properties of this series of pigments are intrinsic to the pigments themselves and that impurities are operating as electron traps.

Finally, there is a notable difference in the relative order of photodecay efficiencies for the pigments between the two measurement techniques and this may well be associated with their different methodologies. It also highlights another important phenomenon in the field of photoconductivity.

CONCLUSION

For an effective electrophotographic system the CTM layer should be strongly electron-donating and coupled with a CGM layer containing an appropriate effective electron-accepting photoresponsive pigment with a high yield in the lowest excited singlet state. Also, the photoconductive properties of anthanthrone itself are impaired by halogenation and for the series of pigments studied very dependent on their synthetic route and presence of impurities.

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