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Synthesis, Spectroscopy and Photoconductivity of Dimeric Perylene Bisimide Pigments

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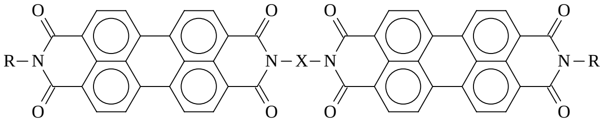
Abstract

Perylene bisimide dimers of the type shown in the structure below could be synthesized in high yield and purity by condensation of the corresponding monoimide-mono-anhydride with diamines. Dimers in which R and X were alkyl, aryl aralkyl and substituted groups were prepared and characterized by absorption and emission spectroscopy. Like the corresponding monomeric bisimides the extent of Π-overlap (manifested in the pigment color) in the solid dimers is dependent on the structure of the terminal R-groups but is even more sensitive to the nature of the X-bridging group. Most notably, xerographic electrical evaluation of model devices showed that dimers in which X was 1,3-propylene generally showed broader visible spectral response and higher photosensitivity than dimers with other bridging groups.



Introduction

Perylene bisimides pigments of the general formula shown in Figure 1are well-known photoconductors that occur in remarkable range of colors including orange, red, maroon, brown, black and olive green. The origin of this color diversity was explained in a series of papers by Graser and coworkers.[1-4] It was shown by single crystal X-ray that the intermolecular spacing between the perylene rings was close to 3.5 A° in all bisimides examined. This allows Π-orbital interaction between adjacent molecules. However the area of overlap between adjacent molecules was found to depend strongly on the nitrogen substituents. For example, pigment with substituents such as neopentyl, which induced a small area of overlap, were orange-red in color. Linear alkyl substituents like n-butyl, n-hexyl, and n-octyl exhibited somewhat more overlap and the corresponding pigments were brown. Increased overlap, which occurred with substituents such as n-propyl, was manifested in a black color. Maximum overlap, which was observed with substituents such as 3-chlorobenzyl,[5] 3-methoxybenzyl,[6] 3-methoxypropyl,[7] or phenethyl[8] resulted in olive green pigments.

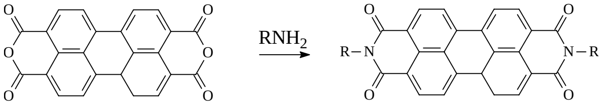


Figure 1. Synthesis of Perylene Bisimides

The latter type, because of their broad spectral absorption from 400-700 nm, were ideal candidates for charge generation pigments in light-lens photocopiers and red laser-addressed digital printers and copiers. However, relatively few such pigments have been reported and other important xerographic electrical criteria, such as dark decay, photosensitivity, and environmental and cycling stability of most of these were less than optimal. In this presentation we will describe the preparation and characterization of a series of dimeric perylene bisimides which includes a variety of novel photogenerator pigments with broad spectral response and desirable xerographic electrical properties.

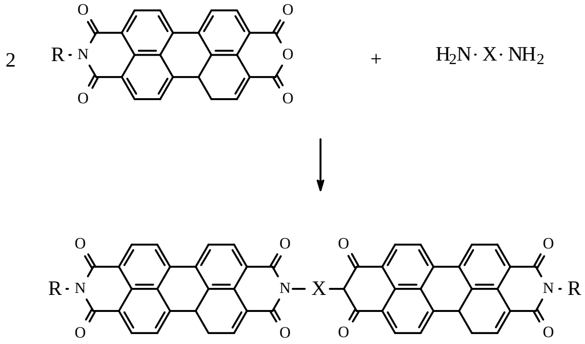


Figure 2. Synthesis of Symmetric Perylene Bisimide Dimers

Perylene Bisimide Dimers

The bisimide dimers ***(Figure 2)*** can be prepared by heating a mixture of a monoimide-monoanhydride intermediate and a diamine, H_2N-X-NH_2, in a high boiling solvent such as N,N-dimethylformamide or N-methylpyrrolidinone. In most cases yields were nearly quantitative. Purification was effected by washing the product with boiling dimethyl-formamide, which removed residual starting monoan-hydride Full details of the synthesis of the pigments described here have been reported elsewhere.[9,10]

The structures were confirmed by proton nmr spectroscopy in solvent mixtures containing trifluoroacetic acid and deuterochloroform. The solution absorption spectra exhibited sharp absorption peaks at about 540 and 504 nm, very similar in shape and relative intensity to the spectra of the corresponding monomeric perylene bisimide pigments. The products were microcrystalline mostly with submicron particles (Figure 3) and highly insoluble in common solvents. The R-terminal groups and X-spacer group that can be used in the above syntheses are restricted only by their availability and by limitations on the successful preparation and purification of the required monoimide-monoanhydride intermediates. A conservative estimate, based on current commercially available amines and diamines indicates that more than 10,000 dimeric pigments could be easily prepared if one had the time and inclination to do so. We have focussed our synthetic work on understanding the effect of substituent and bridging groups on the pigment color and evaluating the efficacy of the groups in influencing xerographic electrical properties.

Table 1. Color of As-synthesized Pigment and Polymer-Dispersed Film for Some Terminal and Bridging Groups

Terminal	Bridging	As-Synthesized	Dispersed
R-Group	**X-group**	**Colour**	**Film Colour**
n-Propyl	N-N	Dark Brown	Purple
n-Butyl	N-N	Dark Brown	Purple
n-Pentyl	N-N	Purple-Brown	Purple
Methyl	Ethylene	Black	Brown
n-Propyl	Ethylene	Brownish Black	Red-Brown
n-Butyl	Ethylene	Brownish Black	Red-Brown
Phenethyl	Ethylene	Black	Red-Black
H	1,3-Propylene	Black	Orange-Brown
Methyl	1,3-Propylene	Black	Red
Ethyl	1,3-Propylene	Black	Olive Green
n-Propyl	1,3-Propylene	Black	Olive Green
Iso-Propyl	1,3-Propylene	Dark Brown	Red
Allyl	1,3-Propylene	Green-Black	Green
3-Methoxypropyl	1,3-Propylene	Black	Dark Green
n-Butyl	1,3-Propylene	Black	Olive Green
Sec-Butyl	1,3-Propylene	Red	Red
Iso-Butyl	1,3-Propylene	Dark Brown	Reddish Brown
n-Pentyl	1,3-Propylene	Black	Olive Green
NeoPentyl	1,3-Propylene	Red-Brown	Red-Orange
Cyclohexyl	1,3-Propylene	Dark Brown	Magenta
n-Heptyl	1,3-Propylene	Black	Brown
n-Octyl	1,3-Propylene	Black	Black
Benzyl	1,3-Propylene	Jet Black	Green
3-Chlorobenzyl	1,3-Propylene	Black	Green
Phenethyl	1,3-Propylene	Black	Green
n-Propyl	2,2-Dimethyl-1,3-propylene	Dark Brown	Violet
n-Propyl	2-Hydroxy-1,3-propylene	Dark Brown	Red
n-Butyl	2-Hydroxy-1,3-propylene	Black	Black
n-Propyl	1,4-Tetramethylene	Dark Brown	Burgundy
Phenethyl	1,4-Tetramethylene	Orange	Orange
n-Propyl	1,5-Pentamethylene	Black	Burgundy
Phenethyl	1,5-Pentamethylene	Black	Red-Brown
n-Propyl	1,6-Hexamethylene	Dark Brown	Burgundy
n-Pentyl	Bis(3-propyl)methylamine	Brownish red	Burgundy
n-Propyl	1,8-Octamethylene	Dark Brown	Burgundy
3-Chlorobenzyl	1,8-Octamethylene	Black	Dark Purple
Phenethyl	1,8-Octamethylene	Black	Purple
n-Pentyl	1,10-Decamethylene	Brown	Red
n-Pentyl	1,12-Dodecamethylene	Brown	Red
n-Propyl	1,3-Xylylene	Brown	Red
Iso-Butyl	1,4-Phenylene	Dull Red	Orange
n-Pentyl	1,4-Phenylene	Red	Orange
n-Propyl	4,4'-Biphenylene	Orange-Brown	Red-Orange
n-Pentyl	1,5-Naphthylene	Red	Red-Orange
n-Butyl	4,4'-Diphenylene Sulfone	Brown	Orange-Red

The Effect of Bridging and Terminal Substituents on Pigment Color

Table 1 shows the relationship between color, both of the as-synthesized pigment and of finely ground dispersions in a poly(vinyl acetate) film, and the R- and X-groups. (The exact procedure for preparation of the thin film pigment dispersions has been described by Loutfy.[11]

From the Table, it is clear that dimeric perylene bisimide pigments exhibit the same crystal-color effects as the monomeric analogs. The degree of Π-orbital interaction in the solid, which is strongly dependent on the terminal and bridging substituent, results in an impressive array of colors: orange, red, burgundy, purple, violet, black, olive green and green. It is also clear that strong Π-orbital interaction, resulting in black, olive green or green dispersed films, only arises when the bridging group is unsubstituted 1,3-propylene. Although several dimers with other bridging groups appeared black in their as-synthesized form, their true color, manifested in the finely dispersed polymer film, was never black or green. Another requirement for strong Π-orbital overlap is that the R group must be attached to the nitrogen atom via an unsubstituted methylene group (i.e. R-CH$_2$-N). Any branching at this α-methylene group (e.g. isopropyl, sec-butyl and cyclohexyl) precludes strong overlap, presumably due to steric constraints. A similar effect occurs with branching at the β-methylene in alkyl substituents (e.g. isobutyl and neopentyl). The methyl substituent, which results in a red pigment, does not follow this trend, however. Benzyl and phenethyl substituents appear to strongly promote Π-interaction. Overall, the effect of the R-group on color appears to parallel the results in the monomeric pigments.[1-4,12-14] At the present time we have no explanation for the efficacy of the propylene bridge in promoting strong overlap. Attempts to grow single crystals suitable for X-ray analysis, which should give some insight into the effect, have been unsuccessful so far with these highly insoluble dimers.

Xerographic Electrical Evaluation

The dimers were evaluated as BGL pigments in layered xerographic devices. The photogenerator layer was prepared as follows: 0.2 g of the perylene dimer pigment was mixed with 0.05 g of poly(vinyl carbazole) and 8.1 mL of methylene chloride in a 30 mL glass jar containing 70 g of 1/8 inch stainless steel balls. The jar was placed on a roll mill for 4 days. Using a film applicator with a 1.5 mil gap, the pigment dispersion was coated on a titanized polyester substrate. After drying, the generator layer was coated with an amine hole transport layer prepared by dissolving 8.3 g of MAKROLON™ polycarbonate and 4.4 g of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine in 82.3 g of methylene chloride. This solution was coated over the above photogenerator layer using a 10 mil applicator. The resultant device was dried for 20 min at 135°C. The dried transport layer was 20 microns thick.

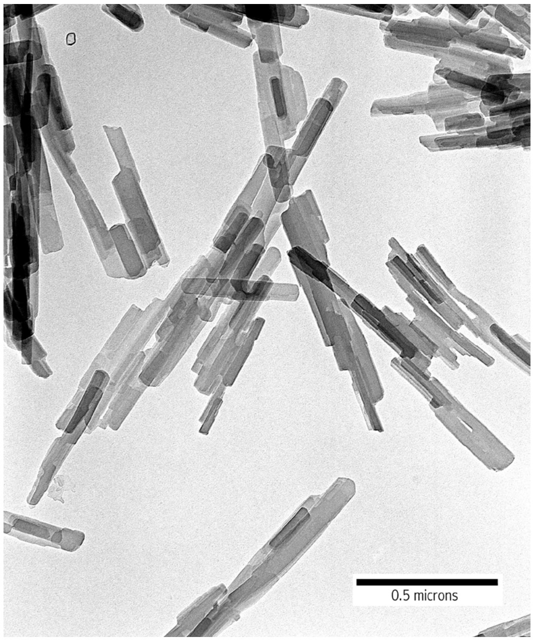


Figure 3. Transmission Electron Micrograph of a dimeric bisimde (Figure 2, with R=3-methylbutyl and X=1,3-propylene)

The imaging members were electrostatically charged with a corona device until the surface potential, measured by a capacitatively-coupled probe attached to an electrometer reached an initial value, V*o.* After 0.5 seconds in the dark, the surface charge potential was remeasured as V*ddp* (dark development potential) and the device was exposed to filtered light from a Xenon lamp. The photodischarge effect reduced the surface potential to V*bg* (background potential). The percent photodischarge was calculated as 100x(V*ddp*-V*bg*)/V*ddp*. The light energy used to discharge the device was measured with a light meter. Key xerographic electrical parameters were: the dark decay, calculated as (V*o*-V*ddp*)/0.5 volts/second, and E*1/2,* the exposure energy (in ergs/cm2) required to achieve 50% discharge from Vddp. Two exposure wavelengths were used: 500 nm for orange, red or brown pigments and 620 nm for the black and green pigments. Results from devices prepared with representative dimers are summarized in Table 2.

All imaging members prepared with the dimeric BGLs exhibited good charge acceptance (V*ddp*=800 volts). Dark decay values varied from excellent (<10 volts/sec) to fair (< 50 volts/sec). Photosensitivities also ranged from good (E*1/2*<10 ergs/cm^2) to moderate (E*1/2*< 25 ergs/cm^2). However, these properties are known to be very sensitive to device fabrication methods and coating materials and they can usually be improved by better BGL design. There does not appear to be any obvious corelation between the electrical properties with the substituent or bridging group; good BGL pigments occur in a wide variety of structures. The best photogenerator pigment candidates for light-lens copying or red laser digital imaging would appear to be the bis(n-butyl)- and bis(n-pentyl)- propylene dimers. The former exhibits very low dark decay and the latter excellent photosensitivity.

Table 2. Xerographic Electrical Properties of Devices Incorporating Perylene Bisimide Dimers.

				Exposure
R-Group	**X-Bridge**	**D. D.**	**E1/2**	**λ**
n-Propyl	N-N	9.5	25.6	500 nm
n-Butyl	N-N	9	21.9	500 nm
n-Pentyl	N-N	10	19.4	500 nm
Methyl	Ethylene	15.4	19.4	500 nm
n-Pentyl	Ethylene	47.5	5.9	500 nm
Methyl	1,3-Propylene	17.8	74	500 nm
Ethyl	1,3-Propylene	22	18.2	620 nm
n-Propyl	1,3-Propylene	13.4	9.9	620 nm
Allyl	1,3-Propylene	28.1	11.2	620 nm
3-Methoxypropyl	1,3-Propylene	13	17.7	620 nm
n-Butyl	1,3-Propylene	7.3	6.7	620 nm
n-Pentyl	1,3-Propylene	33.8	4.4	500 nm
n-Pentyl	1,3-Propylene	52.8	3.4	620 nm
NeoPentyl	1,3-Propylene	25.5	16.5	500 nm
Benzyl	1,3-Propylene	65.4	7.1	620 nm
3-Chlorobenzyl	1,3-Propylene	24.5	27.8	500 nm
Phenethyl	1,3-Propylene	26.5	6	620 nm
n-Propyl	2,2-Dimethyl-1,3-propylene	21.9	13.9	500 nm
n-Butyl	2-Hydroxy-1,3-propylene	8.4	10.3	500 nm
n-Pentyl	1,4-Tetramethylene	49.5	6.8	500 nm
n-Pentyl	1,6-Hexamethylene	24.7	8.9	500 nm
n-Pentyl	1.8-Octamethylene	26.9	6.3	500 nm
n-Propyl	1,3-Xylylene	95.2	10.2	500 nm
Iso-Butyl	1,4-Phenylene	21.5	36.6	500 nm
n-Propyl	4,4'-Biphenylene	27.2	20.3	500 nm
n-Pentyl	9,9-Bis(4-phenylene)fluorene	88.7	20.1	500 nm
n-Butyl	4,4'-Diphenylene Sulfone	70.6	23.2	500 nm
n-Butyl	1,4-bis(4'-phenyleneoxy)benzene	19	7.3	500 nm

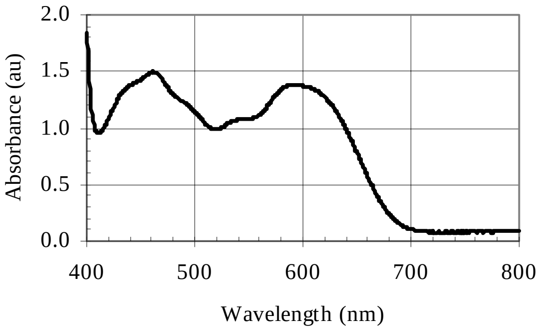


Figure 4. Visible Absorption spectrum of the bis(n-pentyl0-propylene dimer (Figure 2, R=n-pentyl, X= 1,3-propylene)

The absorption spectrum of the n-pentyl dimer, ***Figure 4***, shows excellent panchromatic absorption from 430 to about 640 nm. Almost all of the propylene dimers with linear alkyl, benzyl or phenethyl substituents had similar broad spectra and thus have the potential to be excellent visible light photogenerator pigments.

The photosensitivity of the bis(n-pentyl) dimer (E*1/2*=3.4 ergs/cm^2) is significantly higher than that of the corresponding monomeric n-pentyl- or n-propyl bisimides (E*1/2*=7 and 10 ergs/cm^2, respectively). This is an indication that at least some dimeric pigments are inherently better photoconductors than the corresponding monomers. Further work will be required to validify this, however.

Conclusion

Synthesis and evaluation of a series of novel, dimeric perylene bisimide pigments with different terminal substituents and bridging groups showed that the structure of the bridging group played a dominant role in the solid state organization of the molecule. Specifically, only dimers having an unsubstituted 1,3-propylene bridge exhibited strong Π-interaction between adjacent molecules, resulting in broadened visible absorption. It was possible to prepare a wide range of colors in this class of pigment. Many of the dimers were shown to be good to excellent BGL charge generation pigments for light-lens or red laser xerographic imaging.

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Biography

Jim Duff received his BSc and PhD degrees at the University of Toronto in the field or Organosilicon Chemistry-synthesis, spectroscopy and photochemistry. He then spent two years at the University of Leeds, UK, studying organometallic complexes. Following a two year appointment as Research Associate at the University of Toronto he joined Xerox Research Centre of Canada in 1975. He has held a number of management positions in fields such as polymer synthesis LID and Ink Jet ink development and chemical toner design. He is currently a Principal Scientist. Throughout his career he has been actively involved in the synthesis and characterization of photoconductive organic pigments.