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Study on the synthesis and photoconductivity of bisazo compounds having 1,3,4-oxadiazole

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Abstract

The bisazo compounds were prepared by coupling diazotized 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole with 3-hydroxy-*N*-phenyl-2-naphthalenecarboxamide (Naphthol AS) and its derivants. These compounds were analysed by IR spectra and element analysis. The X-ray diffraction patterns were used to determine their crystal structure. The relationships between treatment methods and crystal structures of the compounds, and the effects of crystal structure on photoconductivity were also studied.

Keywords: Bisazo compound; 1,3,4-Oxadiazole; Photoconductivity; Naphthol AS; Synthesis

1. Introduction

In recent years, organic photoconductive materials have been rapidly developed because of their non-toxicity, low cost, magnitude and variability of development, mechanical and architectural flexibility [1]. Being used as the organic photogenerating pigments, azos have been more extensively studied than phthalocyanines and perylenes. The photoconductive properties of azo compounds were reported as early as 1968 by Rau who observed photocurrents from thin layers of 1-(phenylazo)naphthol [2]. Several years later, Champ and Shattuck reported the use of bisazo pigment derived from 3,3′-dichlorobenzidine as a photogenerating pigment in xerographic devices [3]. Then azo pigments were widely studied as charge generation materials because of their technological advantages such as high sensitivity, wide spectral range (450–800 nm) and excellent stability [4].

In addition, 1,3,4-oxadiazole compound has outstanding capability of transporting electrons, especially its good thermostability and antioxygenation given by its special structure [5]. In the paper, a series of bisazo compounds having 1,3,4-oxadiazole were synthesized. The route of synthesis of bisazo compounds is shown in Scheme 1. And the sample number of compounds synthesized using different naphthols are listed in Table 1.

2. Experimental

2.1. Preparation of the bisazo compound [5–7]

2,5-Bis(4-aminophenyl)-1,3,4-oxadiazole (4.9 g) was added to dilute hydrochloric acid which was prepared by mixing 37 mL of hydrochloric acid into 37 mL of water. The mixture was thoroughly stirred at 60 °C for 30 min and then cooled down to about 0 °C. Then the solution prepared by dissolving 3.0 g of sodium nitrite in 10 mL of water was added dropwise at 0–5 °C in about 30 min. Thereafter, the mixture was stirred for about 30 min at the same temperature as above, and then filtered. The filtrate was poured in 80 mL of 40% borofluoric acid, and the crystals were separated by filtering, then washed in methanol and dried. Tetrazonium fluoroborate (7.4 g) was obtained in 84.7% yield as orange-colored crystals, the decomposition point of which was about 75 °C.

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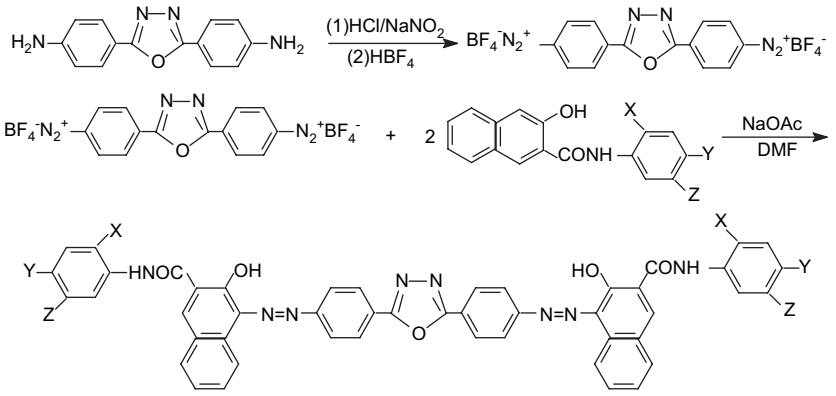

Scheme 1. The route of synthesis of bisazo compounds.

The above obtained tetrazonium salt (2.8 g) together with 4.3 g of 3-hydroxy-*N*-(2-chlorophenyl)-2-naphthalenecarboxamide was dissolved in 100 mL of cooled DMF. To the resulting solution, a solution consisting of 5.4 g sodium acetate and 45 mL of water was added dropwise in within an hour at 4–8 °C. Then, after stirring for about 3 h at room temperature (about 20 °C), the mixture was filtered.

Other bisazo pigments were obtained in the same method, and the compounds were characterized by IR (KBr) and element analysis. The analysis data are shown in Table 2.

2.2. Treatment of the bisazo compound

The synthesized bisazo pigment was treated by repeating washing with water and DMF, but the number of times of washing, the time and temperature of each washing were different. Four treatment methods were introduced in this paper which are listed in Table 3.

2.3. The fabrication of photoconductor and measurements of photoconductivity

The double-layered photoreceptor device was made by coating an interface layer (IFL, 1 μm) of polyamide, then a charge generation layer (CGL, 0.5 μm) of bisazo pigments, which were dispersed in polyvinylbutyral, and finally a charge transport layer (CTL, 20 μm) of 2-methyl-4-dibenzylaminobenzaldehyde-1,1-diphenydrazone and polycarbonate on an aluminium plate, in that order.

An SP-428 model photoconductivity measuring device was used, the light intensity of exposure was controlled at 4.0 lx. In the measurement, the surface of the photoreceptor device was negatively charged, and the photoinduced discharge curve of the device was recorded, from which the parameters such as V_o, V_r, R_d, and $E_{1/2}$ could be obtained. Here, V_o was the surface charged potential; V_r was the residual potential; R_d was the rate of dark discharge; and $E_{1/2}$ was the photosensitivity, the lower the $E_{1/2}$ value, the higher was the photosensitivity of the material.

Table 1
The couplers and bisazo compounds

Sample no.	X	Y	Z
I	OCH_3	Cl	OCH_3
II	CH_3	H	H
III	OC_2H_5	H	H
IV	OCH_3	H	H
V	Cl	H	H
VI	H	H	H

3. Results and discussion

3.1. The relationship between treatment methods and crystal structure

The photoconductive azo pigments had to have special crystal structure in order to ensure the good photoconductivity of photoreceptor device. At the same time, the synthesis pigments had to be purified prior to be used as charge generation materials. In general, the special crystal was achieved by treated with solvents such as water, DMF or THF. During the sequence of the treatment, the azo compounds could undergo morphological changes. And the treatment number, time and temperature at which they were treated in each solvent were known to be critical to affect crystal structure [8]. In this paper, compound **V** was treated with the methods listed in Table 3, and X-ray diffraction analysis was used to determine the differences of crystal structures.

It was found in Fig. 1 that, all of the samples of **V**-1, **V**-2 and **V**-3 had peaks at $2\theta = 11$ and 27°. Whereas sample **V**-4, which was washed with water for 3 times and DMF for 3 times at room temperature, had no apparant diffraction peaks and was less crystalline.

3.2. The relationship of crystal structure and xerographic performance

In order to discover the relationship between crystal structure and photoconductive performance of the material, photoconductor devices were prepared with samples **V**-1, **V**-2, **V**-3, and **V**-4 as charge generation material. Their

Table 2
The IR spectral and element analysis data of bisazo compounds

Sample no.	Decomposition temperature/°C	$\bar{\nu}$/cm^{-1}	C found (calcd)	H found (calcd)	N found (calcd)
I	340	1212,1012,1148	63.11 (63.10)	3.78 (3.87)	11.36 (11.32)
II	323	754	70.70 (72.45)	4.40 (4.38)	13.50 (13.52)
III	326	1256,1010,737	70.20 (70.26)	4.55 (4.54)	12.66 (12.61)
IV	316	1256,1009,743	69.70 (69.76)	4.28 (4.21)	12.95 (13.02)
V	340	1149,744	64.29 (66.29)	4.10 (3.08)	12.68 (12.88)
VI	312		71.56 (71.99)	4.52 (4.03)	13.63 (13.99)

The following IR data were possessed by all of the compounds: 3440, 1670, 1600, 1590, 1540, 1490, 1450.

Table 3
The four treatment methods of bisazo pigment

Sample no.	Washing with water, times/time	Washing with DMF, times/time	Temperature/°C
V-1	3 times/2 h	8 times/2 h	70
V-2	3 times/2 h	3 times/2 h	70
V-3	1 time/6 h	1 time/6 h	Room temperature
V-4	3 times/2 h	3 times/2 h	Room temperature

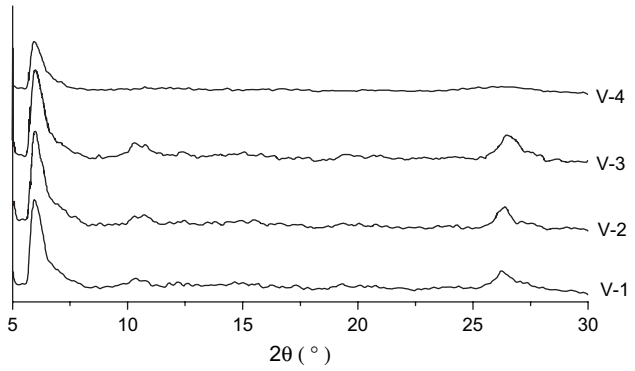

Fig. 1. The X-ray diffraction curves of compound **V** treated with different methods (the diffraction peak at $2\theta = 7^\circ$ was the peak of instrument).

Table 4
The photoconductivities of compound **V** treated with different methods

Sample no.	X-ray diffraction curve	V_o/V	V_r/V	R_d/V s^{-1}	$E_{1/2}$/lx s
V-1	a	660	40	18	12.0
V-2	b	640	15	12.5	19.2
V-3	c	640	90	7.5	14.8
V-4	d	630	20	10	7.6

Table 5
The structures of compounds and xerographic data

Sample no.	Substituent			V_o/V	V_r/V	R_d/V s^{-1}	$E_{1/2}$/lx s
	X	Y	Z				
I	OCH_3	Cl	OCH_3	650	500	15	20.4
II	CH_3	H	H	660	520	10	9.2
III	OC_2H_5	H	H	536	440	10	9.2
IV	OCH_3	H	H	480	370	14	6.8
V-4	Cl	H	H	630	20	10	7.6
VI	H	H	H	810	640	17.5	1.8

photoconductivities were measured and are listed in Table 4.

An excellent photoconductive material should have high surface charged potential (V_o), small dark decay (R_d), low residual voltage (V_r), and small photosensitivity value ($E_{1/2}$). From Table 4, it could be observed that $E_{1/2}$ value of sample **V**-4 was the lowest, at the same time, it also had higher V_o (630 V), lower V_r (20 V) and the R_d was 10 V s^{-1}. The results indicated that photoconductivity of sample **V**-4 was better than that of other samples. On the other hand, sample **V**-4 had no apparent X-ray diffraction peak (see Fig. 1). Then it could be drawn a conclusion that the compound having less crystalline had good xerographic property.

3.3. The effects of substituting group on photoconductivity

The other five compounds synthesized were treated with the same method as that of sample **V**-4. The influence of the substituting group on photoconductive performance was shown in Table 5.

The analysis data showed that, when the phenyl in naphthol was substituted by groups such as $-CH_3$, Cl etc, the surface charged potential (V_o), residual voltage (V_r) and the data of dark discharge (R_d) decreased, whereas the photosensitivity value ($E_{1/2}$) increased. In addition, the V_r was very high when the phenyl had electron-donating substituents, such as $-CH_3$, $-OC_2H_5$ etc; the *ortho*-position of phenyl was substituted by Cl, the organic photoconductive device with the compound as charge generation material had the best photoelectric data.

4. Conclusion

The bisazo pigment, which was treated with water for 3 times and then with DMF for 3 times at room temperature had less crystalline and good photoconductivity when being used as charge generation material.

The photoconductor device had good xerographic property with bisazo compound of the phenyl in naphthol was substituted by Cl as charge generation material, but the residual voltage of the device was very high when the phenyl being substituted by electron-donating groups.

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