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Studies on Organic Semiconductors. XVIII. Photoconductivity of Heteroaromatic Compounds and Their Substituted Derivatives

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Synopsis. The effects of hetero atoms and substituents on the photocurrents of the parent compounds were investigated by comparison of the photocurrents of 52 specimens of the aza-benzenoid and oxa-benzenoid compounds.

Recently, we have reported the photoconductivity of condensed aromatic or heteroaromatic compounds and their substituted derivatives.[1-4] The photoconductivity of the compounds was found to depend strongly on their chemical structures.

The purpose of this paper is to summarize the effects of the substituents and the hetero atoms on the photoconductivity of the parent compounds.

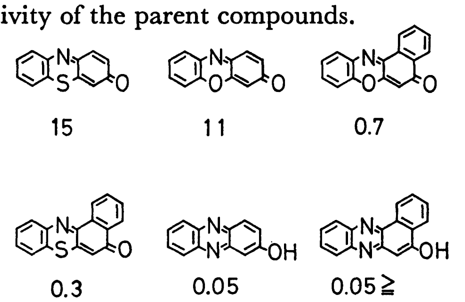
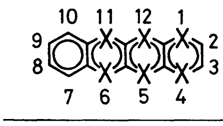
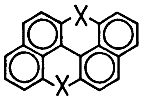
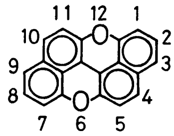
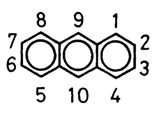


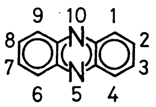
Fig. 1.
The values indicated below the chemical structures are the photocurrents (pico A).

TABLE 1. PHOTOCURRENTS OF OXA- AND AZA-BENZENOIDS, PARENT COMPOUNDS AND THEIR SUBSTITUTED COMPOUNDS

Compound	Hetero atom or substituent	Photocurrent (pico A)[a]
	X=CH	10^3
	X (5,12)=N	0.4
	X (1,4,6,11)=N	0.2
	X (5,6,11,12)=N	0.2
	X=(-O-)	10^3
	X=(=CH-)	10^2—10^3
	X=(=N-)	0.1
	H	10^3
	1,10-$(NO_2)_2$	10^2
	4,10-$(NO_2)_2$	2
	1,4-$(NO_2)_2$	0.2
	1,5-Cl_2	40 (410)
	H	35 (395)
	1,5-$(OCH_3)_2$	5 (410)
	1,5-$(COCH_3)_2$	5 (475)
	1,5-$(C_2H_5)_2$	1 (395)
	9-CN	0.07 (430)
	1-$COCH_3$	0.05 (430)
	9-$COCH_3$	<0.05

a) The values in parentheses are wavelength (nm).

TABLE 2. PHOTOCURRENTS OF SUBSTITUTED PHENAZINES

	Substituent	Photocurrent (pico A)
	2-NO_2	10^3
	1-OCH_3-7-NO_2	10
	2-OCH_3-8-NO_2	10
	2-OCH_3-7-NO_2	1
	1-OCH_3-8-NO_2	1
	1-NO_2	0.1
	1-OCH_3-6-NO_2	0.1
	1-OCH_3-9-NO_2	<0.05
	2-OCH_3-6-NO_2	
	2-OCH_3-9-NO_2	
	1,6-Cl_2	9
	1,6-$(OCH_3)_2$	2
	1,6-$(C(CH_3)_3)_2$	1
	1,6-$(NO_2)_2$	0.6
	1-Cl	0.3
	2-OH	0.05
	2-OCH_3	0.05
	others[a]	<0.05

a) 1-OH, 1-OCH_3, 1-NH_2, 2-Cl, 2,7-$(OCH_3)_2$, 2,7-$(C(CH_3)_3)_2$, 2,7-Cl_2, 1,6-$(CH_3)_2$, 1,6-$(OH)_2$, 1,6-$(NH_2)_2$, 1,4,6-$(OCH_3)_3$, 1,4,6,9-$(OCH_3)_4$

The compounds are of two types; condensed aza-benzenoids containing pyridine-type nitrogen hetero atoms and condensed oxa-benzenoids containing pyran-type oxygen hetero atoms. The former is expressed by Albert[5] as a π-electron deficient system. The compounds belonging to the system are generally oxidized with difficulty by oxygen and apt to behave as an electron acceptor in the formation of a charge-transfer complex. In contrast, oxa-benzenoids are easily oxidized by oxygen and tend to behave as an electron donor in the formation of a charge-transfer complex. Thus, oxa-benzenoids are classified as a π-electron excessive system. The photocurrents of these compounds are summarized in Fig. 1 and Tables 1 and 2.

Effects of Hetero Atoms: Aza-benzenoid compounds show much smaller photocurrents than those of the parent aromatic hydrocarbons.[6] On the other hand, the photocurrent of the oxa-benzenoid compound becomes slightly larger (Table 1). No significant difference of photocurrent between the oxa- and thia-quinonoid compounds was observed. This indicates that the quinonoid structure is a dominant factor governing the photoconductive process (Fig. 1).

Effects of Substituents: (1) The electron-withdrawing substituent, such as a nitro group, gave rise to a decrease in the photocurrent of an oxa-benzenoid compound such as *peri*-xantheno[2,1,9,8-k,l,m,n,a]xanthene, and an increase in the photocurrent of an aza-benzenoid compound such as phenazine.[2]

(2) The electron-releasing substituent, such as a methoxyl group, has no detectable effect on the photoconductivity of the aza-benzenoid compound. In the case of the oxa-benzenoid compound, the effect of the electron-releasing substituent was uncertain, since the photocurrent could not be measured due to instability in the air.

(3) The substituents at the *peri*-position of the nitrogen atom of phenazine, except for OH or NH_2 group, caused a rise in the photocurrent.[1]

(4) Introduction of the methoxyl, acetyl, ethyl, and cyano groups at 1-, 9-, or 1,5-positions of the anthracene ring resulted in a decrease in the photocurrent of the unsubstituted anthracene (Table 1).[3]

Experimental

Materials. All the samples, except 1,6-dimethyl-, 1,4,6-trimethoxy- and 1,4,6,9-tetramethoxyphenazine, were prepared by the methods described in literature[7] and purified by repeated recrystallization, vacuum sublimation and chromatography.

1,4,6,9-Tetramethoxyphenazine. A mixture of 2,5-dimethoxyaniline (1.5 g, 0.01 mol), 2,5-dimethoxynitrobenzene (5.5 g, 0.03 mol), a powdered KOH (50 g), and benzene (50 ml) was refluxed under stirring for 5 hr, then subjected to steam distillation. After being allowed to stand overnight, a gummy product was filtered off and washed successively with ethanol (100 ml) and benzene (50 ml) until it changed into powder. The powder was subjected to chromatography on alumina with chloroform eluent. From the first reddish fraction, 1,4,6,9-tetramethoxyphenazine was obtained. Recrystallization from benzene gave 300 mg (10%) of reddish vermilion needles: mp >360 °C; NMR (CF_3COOH) δ 7.70 (s, aromatic H, 4H) and 4.34 (s, CH_3, 12H).

Found: C, 63.71; H, 5.30; N, 9.39%. Calcd for $C_{16}H_{16}O_4N_2$: C, 63.99; H, 5.37; N, 9.33%.

1,4,6-Trimethoxyphenazine. This compound was prepared with 6.85 g of *o*-anisidine, 29 g of 2,5-dimethoxynitrobenzene, 80 g of KOH, and 150 ml of benzene according to the method used in the preparation of 1,4,6,9-tetramethoxyphenazine. Recrystallization from benzene gave 1,4,6-trimethoxyphenazine as red crystals (600 mg): mp 254—254.5 °C; NMR (CF_3COOH) δ 8.55—8.12 (m, aromatic H, 2H), 7.81—7.40 (m, aromatic H, 3H), 4.30 (s, CH_3, 6H), and 4.35 (s, CH_3, 3H).

Found: C, 66.42; H, 5.07; N, 10.09%. Calcd for $C_{15}H_{14}O_3N_2$: C, 66.65; H, 5.22; N, 10.37%.

1,6-Dimethylphenazine. A mixture of 3-methyl-2-methoxyaniline (3.5 g), 2-methoxy-3-nitrotoluene (8 g), and KOH (20 g) was added to 150 ml of toluene and refluxed for 5 hr. 1,6-Dimethylphenazine was obtained according to the reported method[8]: mp 218.5—219 °C (lit,[9] 221—222 °C).

Measurements. The surface-type cells of the samples were prepared according to methods given in previous papers and their photocurrents measured under conditions similar to those reported[1—4] (nitrogen atmosphere, 1900 lux, 200 V/cm). The photocurrents of the substituted anthracenes (Table 1) were measured by irradiating the surface-type cell with a monochromatic light, the wavelength of which is shown in parentheses in Table 1. In the case of the other compounds, the cells were irradiated with a white light (320—800 nm).

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