The Electrical Conductivity of Heterocyclic Compounds. Fluoridine and Triphenodioxazine

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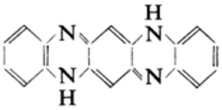
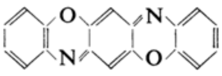
The electrical conductivity of aza-aromatic hydrocarbons has been studied by Akamatu and Inokuchi[1] and by others.[2] The photoconductivity of phenazine has also been reported on recently by Rosenberg,[3] MacGlynn[4] and others.[5] In this paper, for the purpose of investigating the effect of a hetero-atom on the electrical conductivity of a heterocyclic compound, the dark- and photo-conductivities of fluoridine (1) and triphenodioxazine (2) will be compared with those of their parent aromatic compound, pentacene (3), the conductivity of which has been reported by Northrop and Simpson.[6]



(1)



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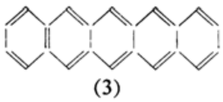

(3)

Experimental

Materials.—Fluoridine and triphenodioxazine were prepared according to the methods reported by Badger[7] and by Fierz-David[8] and were purified three times by sublimation at 200∼250°C under a reduced pressure of 0.1 mmHg. Fluoridine purified is violet-green crystals, does not melt until 360°C, and is slightly soluble in organic solvents, but it is easily soluble in concentrated sulfuric acid, where it gives a pink-colored fluorescence, though no fluorescence is found in ethanol. The spectrum shows two absorption maxima, at about 517 and 552 mμ in dimethylformamide, and at about 541 and 579 mμ in ethanol, with red shifts of about 24∼27 mμ from the bands in dimethylformamide, as is shown in Fig. 8. Triphenodioxazine is red crystals, does not melt until 360°C, and is a little soluble in xylene, giving a green fluorescence. The spectrum shows two absorption maxima, at about 474 and 508 mμ in dimethylformamide, and at about 479 and 510 mμ in ethanol, with red shifts of about 2∼5 mμ from the bands in dimethylformamide, as Fig. 9 shows. That is, the effect of a solvent on the spectrum of triphenodioxazine is less remarkable than that of fluoridine.

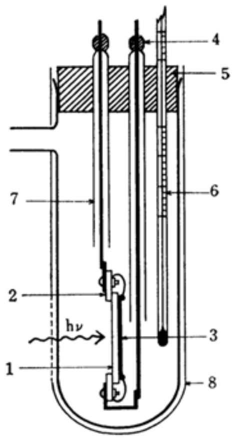

Fig. 1. The chamber used in the measurement of the dark- and photo-conductivity.
1 Glass substrate, 2 terminal electrode, 3 organic thin layer, 4 epoxy-resin seal, 5 rubber stopper, 6 thermometer, 7 quartz tube, 8 copper-film

Apparatus.—The chamber used for the measurement of the electric conductivity is shown in Fig. 1. The resistance of materials, kept in a vacuum of 10^{-2} mmHg or less, was measured with the ultra-megohm meter.

The measurement of the electrical conductivity was performed by using conductivity cells of the following three types.

Surface-type Cell.—This cell was prepared by the sublimation of the sample in a thickness of a few microns on a transparent quartz plate $(3\times 3\ \text{cm}^2)$ which has aluminum or silver electrodes of a comb form that are separated from each other by a gap of 0.2 mm. or 0.5 mm., as in Fig. 2.

Sandwich-type Cell.—The sample was deposited by vacuum sublimation in a thickness of from three to eight microns on a quartz plate, which had previously been provided with an aluminum film as one electrode. Another film-electrode was formed by the sublimation of aluminum onto the surface of the specimen film. When Nessa glass was used

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[1] H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

[2] G. C. Martin and A. R. Ubbelohde, *J. Chem. Soc.*, **1961**, 4948.

[3] B. Rosenberg, *J. Chem. Phys.*, **37**, 1371 (1962).

[4] M. Kleinerman, L. Azarraga and S. P. McGlynn, ibid., **37**, 1825 (1962).

[5] G. Aftergut and G. P. Brown, *Nature*, **189**, 827 (1961).

[6] D. C. Northrop and O. Simpson, *Proc. Roy. Soc.*, **A234**, 124 (1956).

[7] G. M. Badger and R. Pettit, *J. Chem. Soc.*, **1951**, 3211.

[8] H. E. Fierz-David, *Helv. Chim. Acta*, **22**, 1348 (1938).

instead of the quartz plate, the initial sublimation of aluminum was omitted.

Bulk Specimen.—The d-c resistivity was measured under a pressure of 100 kg./cm^2 at an applied electric field of 1000 V./cm. according to the method described in previous papers.[9]

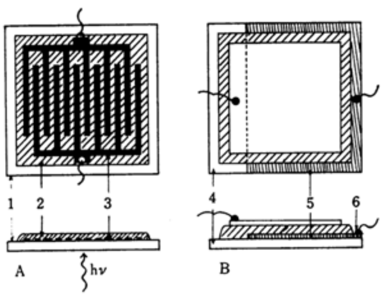

Fig. 2. Conductivity cell.
A Surface type, B sandwich type:
1 Quartz glass, 2 organic film, 3 aluminum film, 4 Pylex glass, 5 Nessa glass, 6 terminal electrode

Results

Dark-conductivities.—*Current/Voltage Relationship.*—The dark-currents of fluoridine and triphenodioxazine measured with sandwich- and surface-type cells were ohmic up to 10^4~10^5 V./cm. The relation between current and voltage is shown in Fig. 3. Even when the electrodes are reversed, identical results were obtained.

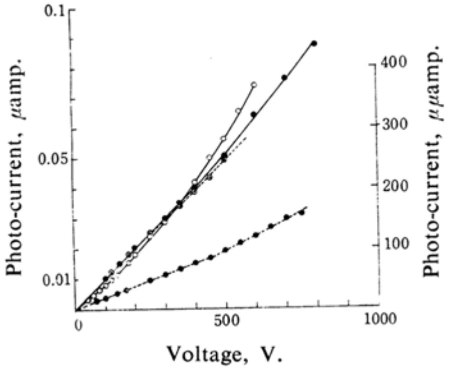

Fig. 3. Current/voltage relationship in the absence of oxygen.
—●— Surface type for fluoridine (μamp.)
---●--- Sandwich type for fluoridine (μμamp.)
—○— Surface type for triphenodioxazine (μμamp.)
---⊙--- Sandwich type for triphenodioxazine (μamp.)

Resistivity/Temperature Relationships.—The resistance of the surface- and sandwich-type cells and of the bulk specimens was measured at a range of 20~140°C under a reduced pressure of 0.1~0.01 mmHg, after the temperature had been kept for about 1/2~1 hr. at 115~120°C for triphenodioxazine and at 130~140°C for fluoridine. The range of the temperature of the measurement was limited because of the high resistances of the samples at temperatures lower than 20°C and because of the easy sublimation at temperatures higher than 140°C. The resistance of triphenodioxazine was too high to measure in bulk.

The electrical resistivity (ρ) at an ascending temperature was identical with that at a descending temperature, and a linear relationship between log ρ and $1/T$ (reciprocal absolute temperature) was observed, as Fig. 4 shows. Thus, the resistivity of the substances as typical organic semiconductors obeyed the following equation:

$$\rho = \rho_0 \exp(\varDelta\varepsilon/2\boldsymbol{k}T)$$

where $\varDelta\varepsilon$ is the energy gap and $\boldsymbol{k}$, the Boltzmann constant. The values of ρ_{20} and $\varDelta\varepsilon$ are shown in Table I, in which the values of pentacene are those given by Northrop and Simpson.[6]

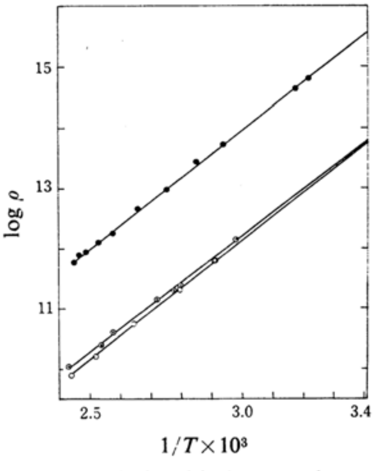

Fig. 4. The relationship between log ρ and $1/T$ for fluoridine.
● Sandwich type cell
⊙, ○ Surface type cell (descending and ascending temperature)

TABLE I. THE VALUE OF RESISTIVITY AT 20°C (ρ_{20}), $\varDelta\varepsilon$ AND ρ_0 OF FLUORIDINE, TRIPHENODIOXAZINE AND PENTACENE

Compound	Cell type	ρ_{20} Ω·cm.	$\varDelta\varepsilon$ eV.	ρ_0 Ω·cm.
Fluoridine	Surface	6×10^{13}	1.6	0.6
	Sandwich	4×10^{15}	1.6	60
	Bulk	2.5×10^{13}	1.95	4×10^{-4}
Triphenodioxazine	Surface	5×10^{14}	1.65	3
	Sandwich	2×10^{16}	1.7	30
Pentacene	Sandwich	6×10^{13}	1.5	10

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[9] H. Inoue, T. Takiuchi and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 1291 (1962).

Photo-conductivities.—A tungsten lamp as the light source, and a band-pass filter which allowed the ray to pass between 350 and 700 mμ, were used for the measurement of photo-conductivities. Light intensity was measured by using a standard cadmium sulfide cell. A surface-type cell was used for the measurement, and the back face of a sample was illuminated (Fig. 2). As Fig. 5 shows, the photo-currents of fluoridine and triphenodioxazine approximately obeyed Ohm's law up to 4×10^3 V./cm. The dependence of the steady-state photo-current on the light intensity in the absence of oxygen gas was investigated at a field strength of 2×10^3 V./cm. The rise and the decay of the photo-current of triphenodioxazine and fluoridine were comparably rapid, 5 sec. or less. The photo-current (i_{ph}) was related to the light intensity (L) by the following equation :

$$i_{ph}\propto L^{0.67}$$

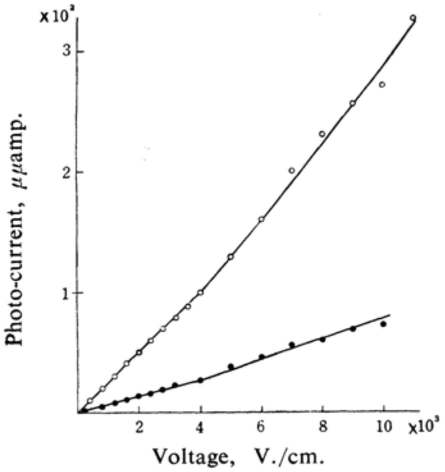

Fig. 5. The variation of the photo-current with the applied voltage : illuminated with tungsten lamp at 6000 lux.
● for fluoridine, ○ for triphenodioxazine

Since the photo-current is nearly proportional to half the order of the light intensity, it seemed probable that the generation of a carrier is bimolecular. The ratio of the photo-current to the dark-current at a light intensity of 10^5 lux was about 39 for fluoridine, and about 8100 for triphenodioxazine. The photo-current of triphonodioxazine was about ten times larger than that of fluoridine.

The Effect of Oxygen.—The effect of oxygen on the dark- and photo-conductivity of fluoridine and triphenodioxazine was examined using a surface-type cell. After a cell of fluoridine had been degassed in vacuo, it was heated on P_2O_5 at 150∼160°C in the presence of air for 2 hr., then the temperature dependence of the dark-conductivity was investigated. As is shown in Fig. 6, the resistivity and the activation energy became smaller after the air treatment, but recovered to some extent when the oxygen absorbed was pumped out in vacuo. The reason why the initial conductivity in vacuo was not recovered entirely, even after prolonged heating at 100°C, may be explained by the retention of a small amount of oxygen in the film. Moreover, the decrease in the activation energy of the dark-conductivity after the air treatment might allow it to assume the energy level of an oxygen-trapped state, similar to the case of phthalocyanine as reported by Vartanian and Karpovitch.[10] Furthermore, the air treatment of fluoridine increased its photo-current, as Fig. 7 shows, and the photo-current was proportional to the intensity (i_{ph}) of light irradiated, as given by the following equation :

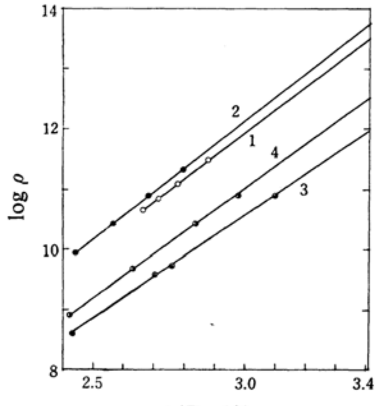

Fig. 6. The effect of oxygen on the surface dark-conductivity of fluoridine : 1, 2 in the absence of oxygen ; 3 heated at 150∼160°C on P_2O_5 in the presence of air for 2 hr. and measured in vacuo ; 4 the oxygen absorbed was pumped out in vacuo.

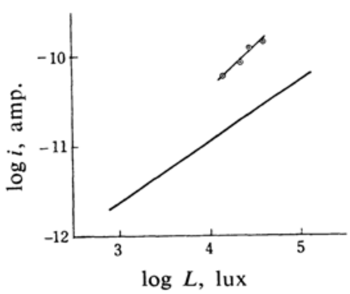

Fig. 7. The effect of oxygen on photo-current of fluoridine : —⊙— kept on P_2O_5 in the presence of oxygen for 1.5 months ; — heated at 130°C in vacuo for 4 hr.

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[10] A. T. Vartanian and I. A. Karpovitch, *Zhur. Fiz. Khim.*, 32, 178, 274, 543 (1958).

$$i_{ph} \propto L$$

On the other hand, the air treatment of triphenodioxazine resulted in a lowering of the dark- and photo-conductivity, but the photocurrent was proportional to the light intensity, similar to the case of fluoridine.

Visible Light Absorption Spectra.—The visible light absorption spectra of fluoridine and triphenodioxazine in dimethylformamide or ethanol, and of their sublimed thin films (0.02～0.03 in thickness), are shown in Figs. 8 and 9 respectively. In these figures, the absorption coefficient was taken for the solution spectra, and the optical density for films. The main absorption bands of fluoridine dissolved in ethanol were in good agreement with those reported by Badger.[7] The main absorption maxima are evident in their visible regions. The absorption curves of sublimed films were broad and seemed to correspond to those in solution, although the absorption densities were altered. Namely, the absorption spectrum of a sublimed film of fluoridine showed two main absorption maxima, at 580 and 640 mμ, which shifted bathochromically from the corresponding band in the solution. On the other hand, the absorption maximum of triphenodioxazine at 479 mμ in solution was shifted to blue, while the one at 510 mμ shifted to red. Also, the spectral shifts of fluoridine were found to be larger than those of triphenodioxazine. The presence of oxygen did not change the spectral curve.

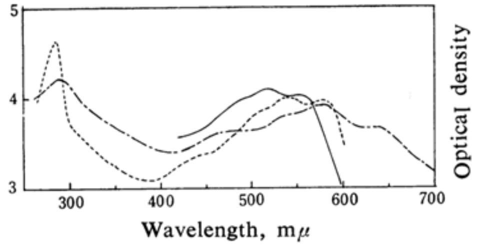

Fig. 8. Absorption spectra of fluoridine: —— in dimethylformamide, ------ in ethanol, —·—·— of sublimed thin film.

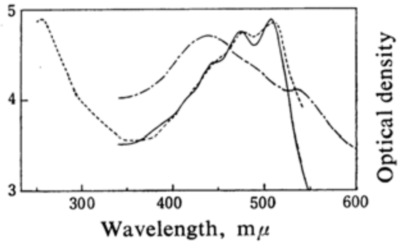

Fig. 9. Absorption spectra of triphenodioxazine: —— in dimethylformamide, ------ in ethanol, —·—·— of sublimed thin film

X-Ray Diffraction.—The X-ray diffraction of the transparent films sublimed on a glass was examined by using a Geiger counter X-ray diffractometer. The number of the diffraction lines in sublimed films decreased in both fluoridine and triphenodioxazine compared with that of the powder, whereas the intensity of the diffraction was very small. No remarkable change of X-ray diffraction pattern in fluoridine upon the thermal or air treatment of a sublimed film was found.

Discussion

As Table I shows, the activation energy ($\Delta\varepsilon$) obtained from the dark-conductivity of a sandwich cell was in quite good agreement with that of the surface cell for both fluoridine and triphenodioxazine. However, the resistivity of a surface-type cell was less than that of the sandwich-type cell by a factor of 10～10^2; this indicates an anisotropy of resistivity which may be caused by the mode of the arrangement of crystallites, as has already been mentioned by Akamatu and Inokuchi.[11] The ρ_0 of three compounds decreased in the following order: triphenodioxazine>fluoridine in the surface type, and fluoridine>triphenodioxazine>pentacene in the sandwich type. The ρ_0 of fluoridine along the surface of the film is the smallest in three compounds; particularly, the anisotropy in the surface and sandwich conductivity of fluoridine becomes larger than that in the case of triphenodioxazine. This probably means that the mode of the arrangement of crystallites in fluoridine may become better than that in triphenodioxazine, because of the effects of –NH– groups in fluoridine, for example, the hydrogen bond between adjacent molecules. Thus, the substitution of a hetero-atom for a ring carbon atom has a large effect on ρ_0. On the other hand, the relation between the lowest singlet absorption level ($^1E_1$) in a solution and $\Delta\varepsilon$ for fluoridine and triphenodioxazine coincided with that for various aromatic hydrocarbons, as Fig. 10 shows. Thus, the $\Delta\varepsilon$ of triphenodioxazine and fluoridine depends on the $^1E_1$ of the absorption spectrum.

The property of being a charge carrier was investigated by means of the effect of oxygen on the dark- and photo-conductivity. The effects of oxygen on the electrical conductivity of many dye stuffs have been examined by Meier,[12] who has shown that the electrical conductivity of a p-type compound increases in the presence of oxygen, while that of a n-type compound decreases. If Meier's results are applied to the present case, the charge carrier must be posi-

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[11] H. Inokuchi, H. Kuroda and H. Akamatu, This Bulletin, 34, 749 (1961).

[12] H. Meier, *Z. Wiss. Phot.*, 53, 1 (1958).

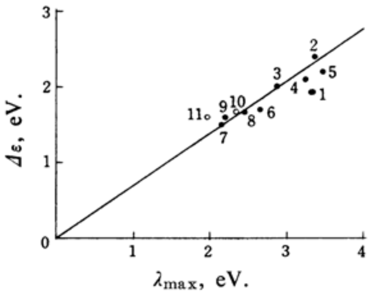

Fig. 10. Relationship between activation energy and the lowest absorption level ($^1E_1$).
1 anthracene, 2 pyrene, 3 perylene, 4 1,2-benzanthracene, 5 chrysene, 6 tetracene, 7 pentacene, 8 triphenodioxazine, 9 fluoridine, 10 triphenodioxazine (film), 11 fluoridine (film)

tive for fluoridine (p-type) and negative for triphenodioxazine (n-type). Moreover, it is found from the report of Vartanian[13] that the photo-current of a p-type compound containing heteroatoms is generally less than that of an n-type compound containing heteroatoms. As has been described above, the characters of the photo-current of fluoridine and triphenodioxazine coincided with Vartanian's results; that is, the photo-current of fluoridine, which is considered to be p-type, is less than that of triphenodioxazine, which is n-type. That is, the mobility of the photo-current is less than that of triphenodioxazine in spite of the large molecular interaction in fluoridine. This implies that the probability of a drift of a hole is small because of the localization of a hole on heteroatoms, as has been shown by Rosenberg[3] in the difference in photo-current in anthracene and phenazine of the p-type.

Summary

The electrical conductivities of fluoridine and triphenodioxazine have been measured, and it has been confirmed that (1) the ρ_0 of three compounds decreased in the following order: triphenodioxazine>fluoridine in the surface-type cell and fluoridine>triphenodioxazine>pentacene in the sandwich-type cell; (2) $\Delta\varepsilon$ depended on the $^1E_1$ of the absorption spectrum; (3) in the presence of oxygen, the dark- and photo-current of fluoridine increased, while those of triphenodioxazine decreased; (4) the photo-current of fluoridine was less than that of triphenodioxazine, and (5) the generation of the charge carrier in both fluoridine and triphenodioxazine was bimolecular in the absence of oxygen.

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[13] A. T. Vartanian and L. D. Rosenstein, *Doklady Akad. Nauk S. S. S. R.*, **124**, 295 (1959).