The Electrical Conductivity of the Condensed Polynuclear Aza-aromatic Compounds

By Hiroo INOKUCHI

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Introduction

The molecules of the condensed polynuclear aza-aromatic compounds are composed of the net-work plane of the conjugated double bonds of carbon and nitrogen. These substances have some interesting properties as the dyestuff material, and also as the biochemical substance. These vat dyestuffs, for example, have no "light catalytic reaction character" and can be synthesized more easily than the corresponding condensed aromatic compounds.

Little has been known about the physical properties of these compounds. Fox example, when the resonance energy of simple aza-aromatic compounds are compared with the corresponding hydrocarbons, the difference is negligible as shown in Table 1.(1) And it is also known that the replacement of a conjugated carbon atom by a nitrogen atom does not greatly influence the ultraviolet absorption spectrum of the compound.

Table 1

The Resonance Energy of the Condensed Aza-aromatic and Aromatic Compounds

Substance	Benzene	Pyridine	Naphthalene	Quinoline
Resonance energy, kcal./mol	41	43	77	75

(1) G. W. Wheland, "The Theory of Resonance," p. 69-70 (1944).

In the previous report,[2] we have found that violanthrone, pyranthrone etc. have the character of an intrinsic semi-conductor concerning the electrical conductivity in powdered state of these crystals. From these results, the difference in the electrical conductivity is expected to be not so large between aza-aromatic compounds and condensed aromatic hydrocarbons or quinones.

Experimental Procedure

The electrical conductivity of cyananthrone (dark violet), indanthrone black (brownish black), flavanthrone (yellownish orange), indanthrone (violet), indanthrazine (brown), 5,6-(N)-pyridino-1,9-benzanthrone (yellow) and 1,9,4,10-anthradipyrimidine (brown) was measured. The molecular structures of these compounds are illustrated in Table 3.

Indanthrone black, flavanthrone and indanthrone were purified chemically from the commercial vat dyestuffs respectively,[3] and then they were sublimed repeatedly in a vacuum until the conductivity became constant. In the case of indanthrone black (Indanthrene Black B. I. G.), as it contained a large volume of by-products, repeated chemical purifications were needed.

Indanthrazine was made by the reduction of indanthrone with E. Clar method[4] by Mr. T. Handa. And recrystallization and sublimation were repeated alternately until indanthrone was perfectly removed. In the course of this experiment, it was found that the specimen of indanthrone, for the preparation of indanthrazine, could be reduced by zinc powder more easily when it was used as a precipitated form from the concentrated sulphuric acid solution, than the ordinary product or, for example, when it was purified by the sublimation. The cause of this difference can be understood by the following explanation.

Indanthrone (Indanthrene RSN) was purified chemically and was sublimated in vacuum 10^{-4} mm.Hg at 350°. This specimen has violet colour, and is here called specimen (A). Specimen (A) was dissolved in concentrated sulphuric acid, and then this solution was poured into a large amount of water under 10° with strong stirring. This precipitated specimen was then filtered, washed to be made free from acid and dried at 70°. It is believed that no sulphate salt of indanthrone is formed in this case. This specimen has blue colour, and is called specimen (B).

When we compare x-ray Debye-Scherrer patterns of thess (A) and (B), it was found that patterns of the specimen (B) were more diffuse than the specimen (A). And in the case of the specimen (B), some of the patterns which appeared on the photograph of specimen (A), disappeared. (see Table 2.) This fact indicates that the specimen (B) is more irregular in the arrangement of molecules in crystal than (A).[5] Therefore the reactive area of the specimen (B) will be larger than specimen (A). It coinsides with the fact that the specimen (B) is reduced by zinc powder more easily than (A).

Cyananthrone was synthesized from 5,6-(N)-pyridino-1,9-benzanthrone by Mr. Handa[6] and purified in the same manner as described above.

Table 2

X-ray Data for Iadanthrone. Values of Spacings (x-ray: Cu Kα Ni-filtered)

Specimen A sublimated in vacuum		Specimen B precipitated from conc. H_2SO_4	
d/n, Å.	intensity	d/n, Å.	intensity
7.80	f	8.10	f diffuse
5.96	mf		
4.60	mf		
3.39	ff	3.46	f diffuse
2.75	mf	2.75	pp very diffuse
2.66	mp		
2.51	mp		
2.36	mf		
2.24	mf	2.24	pp very diffuse
2.12	p		
2.08	mp		
1.99	pp		
1.92	mf		
1.85	mp		
1.79	mf		
1.68	p		
1.58	mp		
1.42	p		
1.32	p		
1.275	p		
1.230	p		
1.190	pp		
1.165	pp		
1.085	pp		

As in the cases of condensed polynuclear aromatic compounds, single crystals could not be obtained. Therefore seven samples were examined in the state of the compressed powdered form. The measuring method of the electrical conductivity has been already described. The specimen was compressed between the metal end and piston in a polished good quality ebonite cylinder, which had 0.8 cm. diameter. The height of the specimen was between 0.3 cm. and 0.5 cm. The electrical resistance was measured by the potential drop

(2) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950); H. Inokuchi, This Bulletin, **24**, 222 (1951).
(3) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1947).
(4) E. Clar, *Ber.*, **72**, 1645 (1939).
(5) It was found frequently that some dyestuffs were crystallized in various ways by which the particle shape and the colour were influenced greatly (*cf.* F. A. Hamm and E. V. Norman, *J. Appl. Phys.*, **19**, 1097 (1948).
(6) T. Maki, *J. Soc. Chem. Ind. Japan*, **37**, 505 (1934).

method with the aid of a direct current amplifier using UX-54 tube. This circuit is illustrated in Fig. 1. The supplied voltage was 400~500 V. per cm. The constancy of the electrical conductivity of these powdered specimens is obtained when the compressed pressure upon them is over 80 kg./cm.^{2} Therefore these specimens were compressed by a lever above 80 kg./cm.^{2}

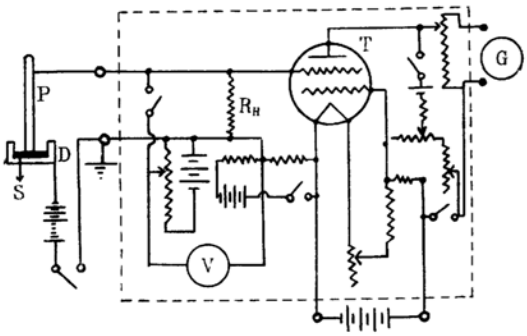


Fig. 1.—The circuit of direct current amplifier: T, electrometer tube UX-54 (This tube has the same character as FP-54); V, voltmeter. (Range is from 0.01 V. to 5 V.); R_H, high resistance ($10^9\Omega$ or $10^{10}\Omega$); G, galvanometer, (Sensitivity is 0.001 μA./mm.); P, piston (0.8 cm. diameter); D, Cyrindrical dish (made of brass coated by chromium); S, specimen. The height of this is between 0.1 cm. and 0.5 cm.

On the other hand, as 5, 6-(N)-pyridino-1, 9-benzanthrone (No. 6) and 1, 9, 4, 10-anthradipyrimidine (No. 7) have high electrical resistivity, these specimens(S)were compressed on a cylindrical dish (D), instead of the ebonite cylinder, by a piston (P) to 80 kg./cm.^{2} with a lever system as shown in Fig. 1 schematically. Because the ebonite cylinder was not used, the surface leakage of the cylinder could be avoided completely and the temperature could be increased to 300°. By this method we could measure the high electrical resistance of these substances.

Results and Discussions

The temperature coefficient of the electrical resistivity was negative in every specimen, and logarithm of electrical resistivity $\log\rho$ and the reciprocal of temperature $1/T$ have the linear relation for a large range of temperature,

$$\rho=\rho_0\exp(\Delta\varepsilon/2kT) \qquad (1)$$

where $\Delta\varepsilon$ is the activation energy, corresponding to the interval of energy band on the model of semi-conductor.

About these behaviours, differences could not be found between this group and condensed polynuclear aromatic compounds.

Non-hysteresis of electrical resistivity and independency of the current upon the time prove the electronic conductance. Therefore the mechanism of semi-conductive character of those aza-aromatic compounds is assumed to be intrinsic, from their perfect molecular crystals as in the cases of the condensed polynuclear aromatic compounds.

The value of ρ_{15}, extrapolated to 15°, $\Delta\varepsilon$ and ρ_0 were tablulated in Table 3, and the relation of equation (1) were illustrated on Figs. 2 a, b and c.

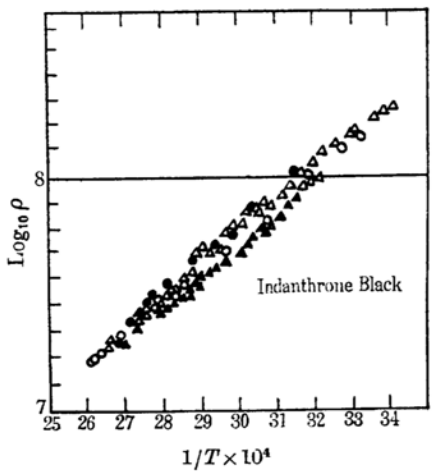


Fig. 2 a.—The relation between resistivity and temperature for indanthrone black: △82.1 kg./cm.^{2}, increasing temperature; ▲82.1 kg./cm.^{2}, decreasing temperature; ○119.5 kg./cm.^{2}, increasing temperature; ●119.5 kg./cm.^{2}, decreasing temperature.

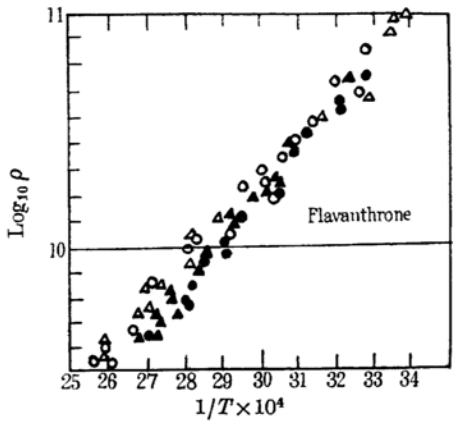
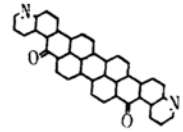
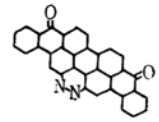
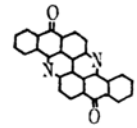
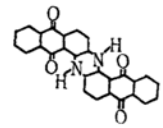
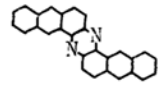
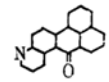


Fig. 2 b.—The relation between resistivity and temperature for flavanthrone. The same symbols as in Fig. 2 a.

Concerning the value of the electrical conductivity, cyananthrone and indanthrone black

Table 3

The Values of ρ_{15}, Δe and ρ_0 of the Condensed Polynuclear Aza-aromatic Compounds

No.	Substance	Structure	ρ_{15}, Ω cm.	Δe, e. V.	ρ_0, Ω cm.
1	Cyananthrone		1.2×10^{7}	0.20	2.24×10^{5}
2	Indanthrone Black		2.5×10^{6}	0.56	3.45×10^{3}
3	Flavanthrone		1.4×10^{11}	0.70	9.5×10^{4}
4	Indanthrone		7.5×10^{14}	0.63	2.5×10^{9}
5	Indanthrazine		1.4×10^{15}	0.66	2.2×10^{9}
6	5, 6-(N)-Pyridino-1, 9-benzanthrone		8.5×10^{22}	3.20	1.4×10^{-5}
7	1, 9, 4, 10-Anthradipyrimidine		8.8×10^{24}	3.21	1.3×10^{-3}

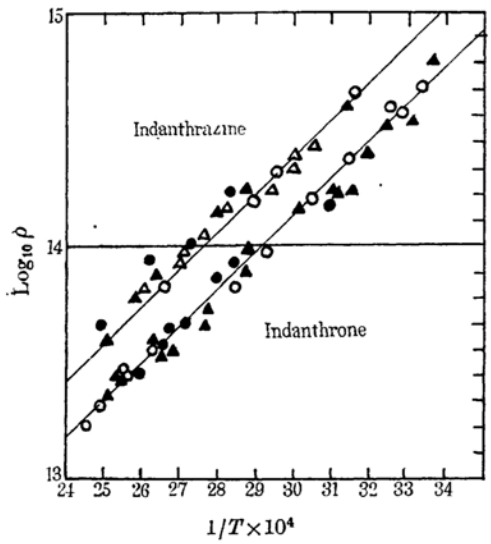


Fig. 2c.—The relation between resistivity and temperature for indanthrone and indanrthazine. The same symbols as in Fig. 2a.

have the typical values of semi-conductor, $10^{-7}\Omega^{-1}\text{cm.}^{-1}\sim10^{-8}\Omega\text{cm.}^{-1}$[7]

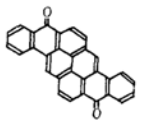
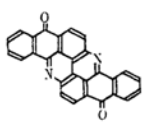
When the number of rings is increased, the illustration shows that the value of electrical conductivity and activation energy approach those of carbon. The electrical conductivity and the activation energy of commercial graphite is the order of $10^{2}\,\Omega^{-1}\,\text{cm.}^{-1}$ and 10^{-2} e. V. respectively[8].

It is found that the values of the electrical resistivity of aza-aromatic compounds are much smaller than those of related aromatic compounds. A typical one is shown in Table 4. It is interesting to compare this result to the fact that intensities of flourescence spectra of aza-aromatic compounds (6-azachrysene and 1-azapyrene) are about ten times as great as those of the related hydrocarbons (chrysene and pyrene)[9].

(7) M. F. Manning and M. E. Bell, *Rev. Mod. Phys.*, **12**, 215 (1940).
(8) S. Mrozowski, *Phys. Rev.*, **77**, 838 (1950).
(9) R. Schoental and E. J. Y. Scott, *J. Chem. Soc.*, 1683 (1949).

Table 4

The Values of $\Delta\varepsilon$ and ρ_{15} of Pyranthrone and Flavanthrone

Substance	Pyranthrone	Fravanthrone
		
$\Delta\varepsilon$	1.06 e.V.	0.70 e.V.
ρ_{15}	$3.9\times10^{15}\Omega$ cm.	$1.4\times10^{11}\Omega$ cm.

The electrical conductivity of indanthrone is very poor as compared with the value of flavanthrone. We think that the cause of this irregularity is a spatial structure. The spatial structure of indanthrone has not yet been researched, but a magnetic susceptibility of this suggests non-coplaner structure.[10]

Summary

The electrical conductivity of the condensed polynuclear aza-aromatic compounds; (1) cyananthrone, (2) indanthrone black, (3) flavanthrone, (4) indanthrone, (5) indanthrazine, (6) 5, 6-(N)-pyridino-1, 9-benzanthrone and (7) 1, 9, 4, 10-anthradipyrimidine,—has the character of a semi-conductor. The electrical resistivity of these compounds can be expressed as $\rho=\rho_0\exp(\Delta\varepsilon/2kT)$ and the mechanism of the conduction is assumed to be that of the intrinsic semi-conductor as in the cases of the condensed polynuclear aromatic compounds. The value of $\Delta\varepsilon$ and ρ at 15° were found as; (1) 0.20 e.V., $1.2\times10^{7}\Omega$ cm., (2) 0.56 e.V., $2.5\times10^{8}\Omega$ cm., (3) 0.70 e.V., $1.4\times10^{11}\Omega$ cm., (4) 0.63 e.V., $7.5\times10^{14}\Omega$ cm., (5) 0.66 e.V., $1.4\times10^{15}\Omega$ cm., (6) 3.2 e.V., $8.5\times10^{22}\Omega$ cm. and (7) 3.21 e.V., $8.8\times10^{24}\Omega$ cm. The values of the electrical resistivity of this group are smaller than that of related condensed polynuclear aromatic compounds.

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Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

(10) H. Akamatu, suggestion.