AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. 18, 810 (1950); doi: 10.1063/1.1747780
View online: http://dx.doi.org/10.1063/1.1747780
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v18/i6
Published by the American Institute of Physics.

On the Electrical Conductivity of Violanthrone, Iso-Violanthrone, and Pyranthrone

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(Received February 16, 1950)

Violanthrone, iso-violanthrone, and pyranthrone have electrical conductance to a certain degree. This is due to the molecular structure of these compounds, which are made of the network planes of carbon atoms, and to the assumption that the π-electron contribute to the electrical conduction.

The electrical resistivity of violanthrone, iso-violanthrone, and pyranthrone was measured. The values at 15°C are as follows; 2.3×10^{10} ohm-cm, 5.7×10^{9} ohm-cm, and 3.9×10^{15} ohm-cm respectively. The resistivity decreases with increasing temperature in every case, and a good linear relationships is observed between the logarithm of the resistivity and the reciprocal of the temperature. As the activation energy of the electrical conductance, the following values were observed; 0.39 ev, 0.375 ev, and 0.53 ev respectively. The values for violanthrone and iso-violanthrone suggest that they can be assumed to be intrinsic semiconductors.

THE electrical conductivity of graphite[1] and carbon black has been attributed to their molecular structures which are made of network planes of the conjugated double bonds of carbon atoms with the π-electrons. There are some organic compounds which have similar molecular structures, for example, violanthrone, iso-violanthrone, and pyranthrone (Fig. 1). The analogy between the molecules of carbon black and these compounds has been pointed out by us in a previous paper,[2] although the molecules of these compounds do not form a layer lattice as do the carbon sheets in graphite. In spite of this difference there seems to be a possibility that these substances have electrical conductivity to a certain degree.

As single crystals are not available, we were obliged to deal with powdered specimens. The method was like that used by Brunner and Hammerschmid[3] for measuring the conductivity of powdered graphite. The specimen was packed in a good quality ebonite cylinder, and compressed between the metal ends. The electrical resistance was measured by the current produced for a known applied potential giving not over 800 volts per cm. The small current, less than 10^{-9} amp., was magnified 1500 times by a direct-current amplifier. Pressure was applied by a lever system. The highest value of the pressure was 300 kg/cm^2, and the dimensions of the specimen was between 0.1 and 0.3 cm in height and 0.5025 cm^2 in cross section. To control the temperature, the specimen holder was heated from outside by a small electrical oven. The surface of this oven was covered with copper plate, which was earthed to prevent any electrical disturbance.

Violanthrone, iso-violanthrone, and pyranthrone were obtained by carefully purifying the commercial dyestuffs by the method already described by one of us.[2] The final products give many sharp x-ray diffraction powder pattern lines, and under the electron microscope they are found to be made up of flake-like needle crystals.

The relation between electrical resistivity ρ and pressure p is given in Fig. 2 for iso-violanthrone. The resistivity is approximately constant above 80 kg/cm^2 and values given below are for this range.

The temperature dependency of the electrical resistivity is shown in Figs. 3 and 4. The reproducibility of

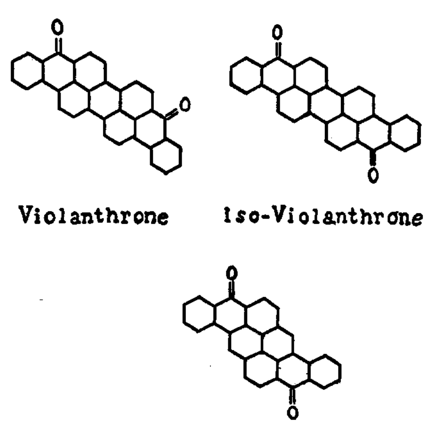

FIG. 1. Violanthrone, iso-violanthrone, and pyranthrone.

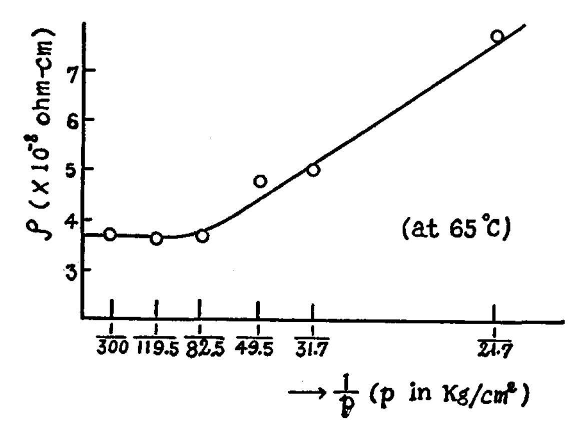

FIG. 2. The relation between resistivity and pressure for iso-violanthrone.

[1] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
[2] H. Akamatu and K. Nagamatsu, J. Colloid Sci. **2**, 593 (1947).
[3] J. Brunner and H. Hammerschmid, Zeits. f. Elektrochemie **40**, 60 (1934).

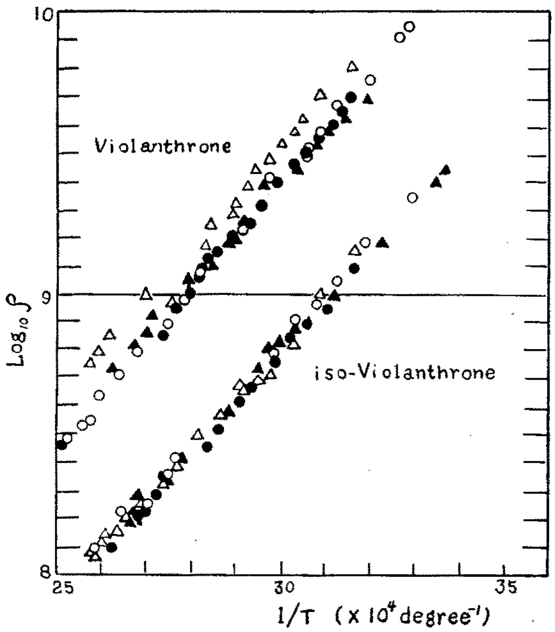

FIG. 3. The relation between resistivity and temperature for violanthrone and iso-violanthrone. △ 82.1 kg/cm², rising temp. ▲ 82.1 kg/cm², falling temp. ○ 119.5 kg/cm², rising temp. ● 119.5 kg/cm², falling temp.

the values observed was good, and hysteresis was not observed when the temperature was raised or dropped.

The temperature coefficient of the electrical resistivity was negative in every case, with a linear relation between $\log\rho$ and $1/T$ corresponding to $\rho=\rho_0\exp(E/kT)$, where E is the activation energy. Values of E, and of ρ at 15°C are given in Table I.

The purity of the specimen was proved by measurements of the resistivity after repeated sublimations, the value being highest after the first sublimation but thereafter constant. Thus initial impurities reduced the electrical conduction. The effect of moisture was also checked, but no important effect was observed. In the case of ionic conduction, it is known[4] that a relaxation time is frequently observed before the stationary current is established. No dependency of the current upon the time could be observed in our experiments. All of the observations seem to prove that the conduction is electronic.

The equation expressing resistivity can be rewritten

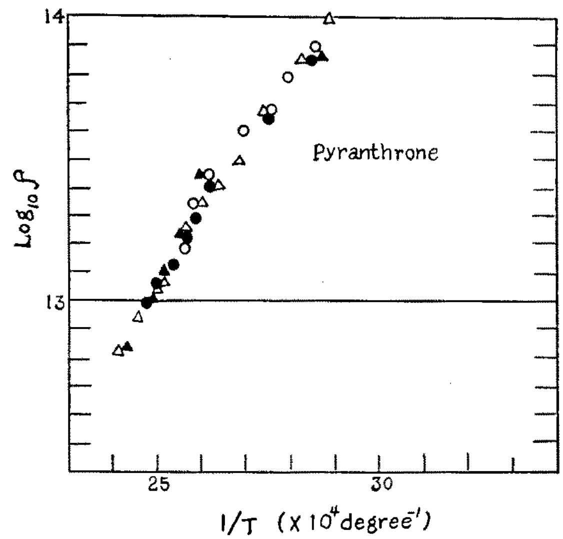

FIG. 4. The relation between resistivity and temperature for pyranthrone. The same symbols as in Fig. 3.

TABLE I. The values of ρ at 15°C, σ_0, E, and $\Delta\epsilon$ of violanthrone, iso-violanthrone, and pyranthrone.

	Violanthrone	Iso-violanthrone	Pyranthrone
ρ15°	2.3×10^{10} ohm-cm	5.7×10^{9} ohm-cm	3.9×10^{15} ohm-cm
E	0.39 ev	0.375 ev	0.53 ev
σ_0	3.4×10^{-4} ohm^{-1}-cm^{-1}	6.8×10^{-4} ohm^{-1}-cm^{-1}	4.1×10^{-7} ohm^{-1}-cm^{-1}
$\Delta\epsilon$	0.78 ev	0.75 ev	1.06 ev

as

$$\sigma=\sigma_0\exp(-\Delta\epsilon/2kT), \qquad (1)$$

where σ is the electrical conductivity and the formula is written intentionally analogous to that for semiconductors. Values of σ_0 and $\Delta\epsilon$ are given in Table I. By the theory of semiconductors, $\Delta\epsilon$ is the energy difference between the empty level and the occupied level of the crystal, and the observed values of $\Delta\epsilon$ are comparable to those of usual semiconductors, of the order of $10^{-1}\sim10^{-2}$ ev generally. Hence the electrical conductivity of these three compounds is similar to that of the usual semiconductors. If we assume that the observed resistivities are attributed largely to contact resistances at the boundaries of the crystallites, the crystals themselves must have considerably higher conductivities than the values observed. If these compounds can be assumed to be semiconductors, they must be so-called intrinsic semiconductor, because the presence of impurities is not necessary.

[4] M. F. Manning and M. E. Bell, Rev. Mod. Phys. 12, 215 (1940).