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Intrinsic Electrical Conductivity of Violanthrene, $C_{34}H_{18}$

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Since 1948, the electrical conductivity of aromatic crystals has been reported on by many workers. However, the conduction mechanism is still ambiguous because the measurement of the intrinsic conductivity is very difficult experimentally. In this study, we measured the electrical resistivity of high-purity violanthrene under a high vacuum.

The material used in the present study was violanthrene A (VEA). The VEA was synthesized from 16,17-dioxyviolanthrene by reduction.[1] The samples were two kinds of VEA. One of them was recrystallized from a 1,2,4-trichlorobenzene solution of the above-synthesized VEA three times and was sublimed once *in vacuo*. This sample will be denoted as VEA (I). In obtaining the second sample, further purification was applied to VEA (I): the sample was recrystallized once from trichlorobenzene and sublimed three times repeatedly. This further-purified sample will be denoted as VEA (II). The concentration of impurities, including that in these samples, was estimated to be 10^{-4} mol/mol for VEA (I) and less than 10^{-5} mol/mol for VEA (II). The single crystal of VEA (II), 5 mm × 8 mm × 70—100 μ in dimensions, was made by means of a sublimation method. Three sorts of specimens, the VEA (I) thin film, the VEA (II) thin film, and the VEA (II) single crystal, were used in the conductivity measurements.

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1) J. Aoki, This Bulletin, **37**, 1356 (1964).

The resistivity of these specimens was measured at 10^{-7} Torr (of air) and 760 Torr in a high-vacuum bell-jar system; the details of the experimental procedure have been reported in a previous paper.2) To make the surface-type cell, evaporated aluminum electrodes were attached on the thin film of VEA prepared by evaporation in a high vacuum. The preliminary X-ray analysis showed that, in the evaporated thin film of VEA (II), the *ab*-plane was parallel with the surface of the quartz substrate. Therefore, we established that the observed resistivity is that along the *ab*-plane.

For the single crystal specimen of VEA(II), silver paste was painted on both sides of that as electrodes. Silver wires, 0.1 mm in diameter, were stuck to the electrodes with the silver paste and connected with the resistivity measurement apparatus. The growth plane of the single crystal of VEA was the *ab*-plane; therefore, for the single crystal specimen, we observed the resistivity perpendicular to the *ab*-plane, this direction being denoted as the c'-axis.

The resistivity was measured in the temperature range from 20°C to 150°C, and a Cary 31-type vibrating-reed electro meter was employed for the high-resistivity measurements.

Table 1. The electrical resistivity and the apparent band gap of various types* of violanthrene A

Type	ρ_{15}** (Ωcm)	$\Delta\varepsilon$** (eV)
Powder	2.1×10^{14}	0.85
Surface-type	$\sim10^{9}$	0.9
Sandwich-type	$\sim10^{14}$	0.9

* H. Inokuchi, H. Kuroda and H. Akamatu, This Bulletin, **34**, 749 (1961).

** $\rho=\rho_0\exp(\Delta\varepsilon/2kT)$, at $T=288°$ K, $\rho=\rho_{15}$.

Some previous results concerning the resistivity of VEA are listed in Table 1. The present results show a large discrepancy from the previous ones; particularly, the effects of ambient oxygen and impurities are extraordinarily great. Table 2 illustrates the present results.

The resistivity of the evaporated VEA (I) thin film, observed at 760 Torr, was of the same order as the previous one. The value of the $\Delta\varepsilon$, derived from the equation in Table 1, of VEA (I), under a pressure of 10^{-7} Torr, was nearly nil; this was very different from the previous value. The resistivity at 10^{-7} Torr was, however, of the same order as that at 760 Torr.

The resistivity of the evaporated VEA (II) thin film could not be observed at a high vacuum because the resistivity was very large ($>10^{15}\,\Omega$ between 20—150°C) compared with that of the VEA (I) thin film and that of the VEA (II) at 760 Torr.

Further, the resistivity of the evaporated VEA (II) thin film at 760 Torr, was three orders higher than the previous ones and that observed for the VEA (I) thin film, and $\Delta\varepsilon$ was probably larger as well.

The results on the VEA (II) single crystal specimen were that the resistivity at 10^{-7} Torr was three orders higher than that at 760 Torr; further, the $\Delta\varepsilon$-value under a high vacuum, 1.95 eV, was the largest one ever observed. The resistivity and $\Delta\varepsilon$ at 760 Torr were larger than those of the evaporated VEA (II) thin film.

We concluded that the $\Delta\varepsilon$-value of the VEA (II) single crystal at 10^{-7} Torr, 1.95 eV, was the intrinsic value of violanthrene A, because the threshold value of the absorption spectrum of the violanthrene evaporated film was 2.0 eV and the threshold value of the spectral response of the photoconductivity was about 1.8 eV[*2]: However, we understand that this $\Delta\varepsilon$-value is not coincident with that of the band-gap energy. We presume that the electrical conduction of violanthrene A is produced through excitonic-carrier generation, because the 500 mμ-peak of the absorption spectrum of evaporated thin film may not be the conduction band absorption and is identified as the exciton level, for a very similar band has been found in a violanthrene A solution.[*2]

The nearly zero of $\Delta\varepsilon$-value of the evaporated VEA (I) thin film was interpreted as indicating that

Table 2. The electrical resistivity of violanthrene A *in vacuo* and in air

	in vacuo		in air	
Specimen	ρ_{15} (Ωcm)	$\Delta\varepsilon$ (eV)	ρ_{15} (Ωcm)	$\Delta\varepsilon$ (eV)
VEA (I) thin film	8.5×10^{8}	0.094	8.5×10^{8}	1.06
VEA (II) thin film	—	—	3.7×10^{12} 1.6×10^{13}	1.10 (<55°C) 1.65 (>55°C)
VEA (II) single crystal	3.8×10^{18}	1.95	6.5×10^{15}	0.99

[*2] The details of these measurements, the photoconduction, and the absorption spectra of violanthrene A will be reported elsewhere by Y. H. and H.I.

2) Y. Maruyama and H. Inokuchi, This Bulletin, **39**, 1418 (1966).

the decrease in resistivity with the increase in temperature compensated for the increase in resistivity by the desorption of oxygen from the VEA (I) thin film with the increase in temperature; therefore, the $\Delta\varepsilon$-value apparently become nearly zero.

The $\Delta\varepsilon$-value of the VEA (II) single crystal, however, was not nearly zero. This may be for two reasons; the purity of VEA (II) was higher than that of VEA (I), so the number of active sites was less and oxygen was adsorbed more easily with the thin film than the single crystal. After all, the VEA (II) single crystal kept in a high vacuum (10^{-7} Torr) adsorbs so little oxygen that the increase in the resistivity by the desorption with an increase in the temperature does not appear. At an atmospheric pressure, the resistivity of the VEA (II) single crystal was three orders larger than that of the VEA (II) evaporated thin film. This was interpreted as indicating that the resistivity of the *c'*-axis was larger than that of the *ab*-plane. These phenomena also appeared in previous works on several kinds of polycyclic aromatic hydrocarbons.

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