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The Paramagnetism of Violanthrone-B

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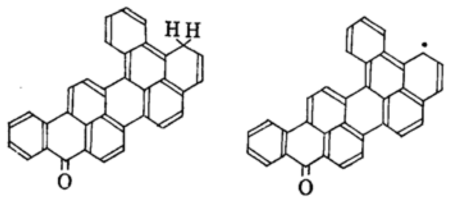
It is well established that the compound named violanthrone-B is a mixture of $C_{34}H_{18}O$ (I) and $C_{34}H_{17}O$ (II). The formula (I) has been suggested by Aoki[1] and the shape of the carbon skeleton of (I) and (II) has been proved to be right by the author with X-ray analysis.[2] In a previous paper[3] the magnetic and some other physicochemical behaviors of violanthrone-B were reported. The present paper deals with the temperature dependence of the paramagnetism of the compound in a lower temperature region.



(I) (II)

Violanthrone-B was recrystallized from a solution in *o*-dichlorobenzene. Washed by ethanol, the precipitate was dried for several hours at 80°C under a pressure of 10^{-5} mmHg. Although this procedure of purification was much shorter than that reported in the previous paper, this method was sufficient to prepare the specimens for the measurement of the magnetic susceptibility.

The magnetic susceptibility was measured by the Faraday method. For the measurement of force on the specimen, the vacuum microbalance of Sartorius was used. The powdered sample was placed in a quartz container, which was suspended with a fine quartz rod from the balance arm and was placed at the point of the maximum field strength. A Faraday type magnet was used. For the temperature measurement the gold-cobalt alloy *vs.* copper thermocouple was used. The measuring-junction was placed under the quartz container as close as possible, since the maximum safe load of the balance was so small that we could not hang the thermocouple wire on the balance arm. In order to make uniform the temperature around the specimen and the thermocouple junction, a cylinder of copper foil was inserted around the specimen. The cryostat used was a simple double Dewar vessel type.

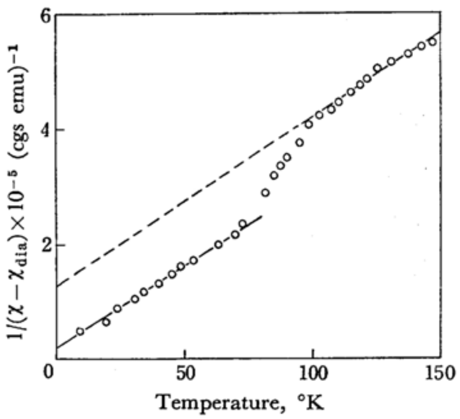


Fig. 1. The temperature dependence of the specific susceptibility of violanthrone-B.

We can summarize the result in Fig. 1, plotting the curve $1/(\chi-\chi_{dia})$ against T, where χ is the specific susceptibility, χ_{dia}, the diamagnetic part, for which the value estimated in the previous paper[3] is used, and T, the absolute temperature. The curve consists of two linear parts and both can be described by the Curie-Weiss law.

$$\chi = \frac{C}{T-\theta} + \chi_{dia} \quad (1)$$

From the higher temperature region the Curie constant and the Curie temperature can be decided

1) J. Aoki, This Bulletin, **34**, 1817, 1820 (1961).
2) T. Maekawa, to be published.
3) H. Akamatu, T. Maekawa, Y. Iida and M. Kinoshita, This Bulletin, **37**, 849 (1964).

as

$$C = 0.343 \times 10^{-3}\ \text{emu°K/g}$$
$$\theta = -41\text{°K}$$

which are nearly equal to the values reported before,[4] while from the lower temperature region we obtain

$$C = 0.344 \times 10^{-3}\ \text{emu°K/g}$$
$$\theta = -5\text{°K}$$

It has been often observed that the magnetic susceptibility of the impure species becomes predominant at low temperature especially for the system of the singlet-triplet equilibrium.[5] In our case, however, the Curie constant observed at low temperature is equal to that of higher temperature, and consequently we obtain the constant density of the magnetic species in all the temperature region. It is accordingly conceivable that the magnetic behavior at low temperature of violanthrone-B is not because of any impurities but due to its own nature. It has been also observed for DPPH[6] that the Curie temperature changes very slightly at low temperature. These phenomena may be due to the phase transition of the crystal.

The author wishes to express his thanks to Professor Hiroo Inokuchi and Dr. Noriko Ohigashi for use of the equipment.

4) In the previous paper, Ref. 3, we decided the values $C=0.306 \times 10^{-3}$ emu°K/g and $\theta=-45$°K, where the magnetic susceptibility was measured also by the Faraday method over the temperature of liquid nitrogen up to the room temperature.

5) D. D. Thomas, H. Keller and H. M. McConnell, *J. Chem. Phys.*, **39**, 2321 (1963).

6) H. Inokuchi and N. Ohigashi, Private communication.