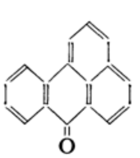
The Paramagnetism of "Violanthrone-B"

By Hideo AKAMATU, Tsuneo MAEKAWA, Yôichi IIDA and Minoru KINOSHITA

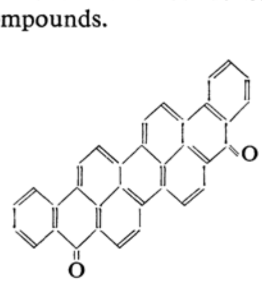
(Received January 18, 1964)

Violanthrone (II), a purplish-blue vat dye, is prepared from benzanthrone (I) by alkali fusion in the presence of phenol or sodium acetate. In this process, a dark violet compound is obtained as a by-product. Maki[1] has found that this compound is barely vattable at 65∼70°C and slightly soluble in chlorobenzene, while violanthrone is insoluble; he has named this compound "violanthrone-B," as distinguished from the violanthrone which he called "violanthrone-A." He assumed formula III for this compound. However, its formula has not been definitely proven, and an alternative formula (IV) has been suggested by Aoki.[2] According to these proposed formulae, violanthrone-B consists of nine condensed rings with one carbonyl group, and one of its peripheral carbon atoms is attached by two hydrogen atoms, so that it possesses a tetrahedral type of bonding.

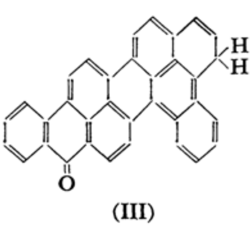
In a preliminary experiment, we have found that violanthrone-B is paramagnetic and shows a strong ESR absorption.[3] However, a question remains concerning its spin concentration, which has not been established. The purpose of the present investigation is to verify the paramagnetic nature of this compound. If it is a paramagnetic compound, the semiconductive properties of this compound will be of interest in comparison with those of other condensed polycyclic aromatic compounds.



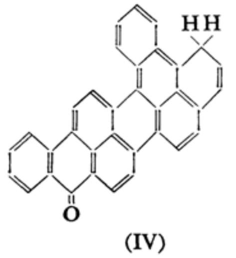
(I)



(II)



(III)



(IV)

---

[1] T. Maki, *J. Soc. Chem. Ind., Japan* (*Kōgyō Kwagaku Zasshi*), 35, 1441 (1932); 38, 1390 (1935).

[2] J. Aoki, This Bulletin, 34, 1817, 1820 (1961).

[3] H. Akamatu, S. Mrozowski and D. C. Wobschall, Proceedings of the 3rd. Conference on Carbon, Pergamon Press, New York (1959), p. 135.

Material

Violanthrone-B was supplied by Mr. J. Aoki, who prepared it from benzanthrone following the procedure described in Maki's paper[1] with a little modification for the condition of alkali fusion.[2] For the purpose of purification, the sublimation method is not applicable to this compound, for it is not stable enough when heated. It was boiled in glacial acetic acid for 2 hr. and then washed with ethanol. Further purification was made by chromatography. The *o*-dichlorobenzene solution of violanthrone-B was passed through the adsorption column of sodium carbonate anhydride. When the adsorbed layer was washed with the same solvent, it developed into two zones. The zone which traveled faster contained impure components and showed a greenish fluorescence under ultraviolet light. All the procedure was carried out in the dark. The separated solution was concentrated by distillation under reduced pressure, after which violanthrone-B was precipitated by adding ethanol. The absorption spectrum of the violanthrone-B is illustrated in Fig. 1.

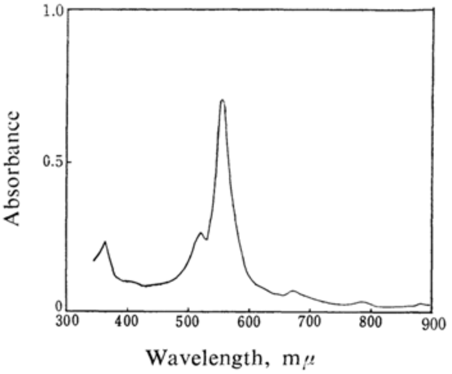


Fig. 1. The absorption spectrum of violanthrone-B in a trichlorobenzene solution.

Magnetic Susceptibility

The magnetic susceptibility of violanthrone-B and its variation with the temperature were measured by the Faraday method. All the measurements were performed under the reduced pressure of 10^{-2}mmHg.

The specific susceptibility was $+0.470\times10^{-6}$ at 259°K and increased with a lowering of the temperature. When the Curie-Weiss law is applied, the susceptibility, χ, can be described by:

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

where the first term, χ_{dia}, is the diamagnetic part of the susceptibility; the second term, the paramagnetic part; T, the absolute temperature, C, the Curie constant, and θ, the Curie point. The diamagnetic susceptibility of violanthrone-B is not known. A large value may be anticipated for a condensed polycyclic aromatic compound because of the contribution of anisotropic diamagnetism. This is ascribed to the non-localized orbitals of π-electrons and depends on the shape and the size of condensed aromatic molecules.[4] It can be said that the skeleton of the violanthrone-B molecule (III or IV) is not much different from that of the violanthrone molecule (II). Violanthrone is diamagnetic, and its molar susceptibility is -247.4×10^{-6}.[5] From this value, corrected by Pascal's rule for the difference in composition, an approximate value for the diamagnetic susceptibility of violanthrone-B was assumed as:

-252.1×10^{-6} for molar susceptibility,

or

-0.572×10^{-6} for specific susceptibility.

Using this value for χ_{dia}, a good linear relationship was obtained when $1/(\chi-\chi_{dia})$ was plotted against T. This is shown in Fig. 2. Hence, the following values were estimated for C and θ:

$$C=0.306\times10^{-3}\ \text{emu}^\circ\text{K/g.}$$

$$\theta=-45^\circ\text{K}$$

The paramagnetism of violanthrone-B may be associated with the presence of unpaired electrons. As will be discussed in a later section, we assume that some of the violanthrone-B is in the state of a free radical. Therefore, the Curie constant may be given by:

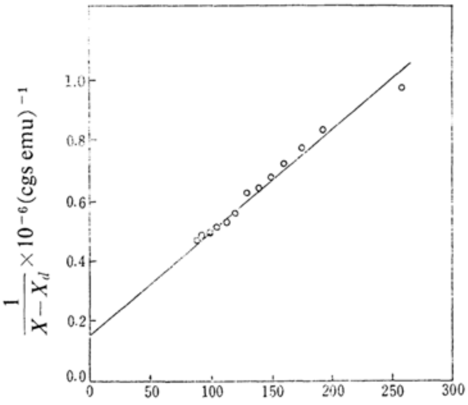


Fig. 2. The temperature dependence for the specific susceptibility of violanthrone-B.

---

[4] H. Akamatu and Y. Matsunaga, This Bulletin, 26, 364 (1953).

[5] This value is more plausible than published.[4]

$$C=\frac{Ng^2S(S+1)\beta^2}{3k} \qquad (2)$$

where k is the Boltzmann constant; β, the Bohr magneton; S, the electron spin; $g=2.00$, and N, the number of molecules, each of them possessing an unpaired electron. This gives $N=2.15\times10^{23}$ per mole. This value indicates that about 36 per cent of the molecules possess unpaired electrons.

ESR Absorption

The experiments of ESR absorption were performed at a frequency of 9400 Mc. $\sec^{-1}$ in association with a Hitachi MPS-1 spectrometer. The violanthrone-B power showed a strong absorption in a vacuum and in air. Its g-value was 2.0041 ± 0.0005, which was determined in comparison with ultramarine ($g=2.0279$). The line width at the half-intensity maximum, $\Delta H_{1/2}$, was 2.32 gauss in a vacuum. It was broadened to 3.88 gauss in air by the oxygen effect.

The spin concentration at room temperature was determined by a comparison of the integrated ESR absorption with that of a standard sample. A sample of α,α-diphenyl-β-picrylhydrazyl (DPPH) was employed as the standard sample. For this purpose, the spin concentration of the DPPH had to be known. This was determined from the magnetic susceptibility and its variation with the temperature. The Curie point of DPPH has been reported as $\theta=-17^\circ$K.[6] Using this value, when the observed susceptibility was plotted against $1/(T-\theta)$, a good linear relationship was found in the temperature range of 80～260°K. Hence, the Curie constant for the DPPH was estimated as $C=0.857\times10^{-3}$ emu°K/g., and the diamagnetic susceptibility as $\chi_{dia}=-0.533\times10^{-6}$ emu/g. (or -210×10^{-6} emu/mol.). Equation 2 can be applied to its Curie constant. This gives the spin concentration $N=5.42\times10^{23}$ per mole. Thus, our sample of DPPH contained free radicals of 90.3 per cent of all the moles.[7]

In practice, a subsidiary standard sample was used. This was a sample of "crude" violanthrone,[8] the spin concentration of which was determined in comparison with the standard DPPH.

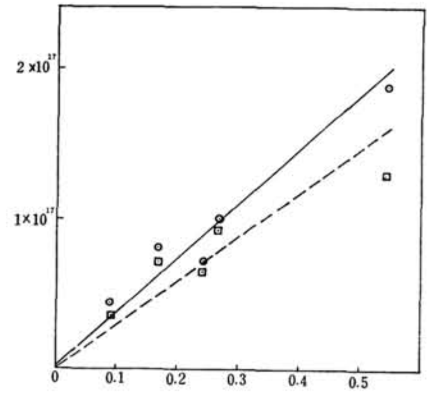


Fig. 3. The number of unpaired electrons in violanthrone-B.

⊙—— in vacuo, ▣- - - in air

The number of spins of violanthrone-B was measured in air and in a vacuum for the same specimen. The results are shown in Fig. 3. The spin concentration was estimated as 4.9×10^{20} per g. in air and 5.9×10^{20} per g. in vacuum. When we assume that a spin center is a molecule which possesses an unpaired electron, the number of such molecules will be 35.7 per cent of the total molecules in air, and 42.7 per cent of those in a vacuum. A slightly larger value was thus observed in a vacuum than in air. However, the difference is so small as to be within the range of experimental error; thus one can say that the air has essentially no effect on the spin concentration. On the average, the molecules of 39 per cent of the total molecules possess unpaired electrons.

In some cases, the spin population of a solid material increases when the material is ground. In such a case, one can assume a spin center which is ascribed to a trapped electron at a crystal defect. This was not the case with violanthrone-B. For violanthrone-B, when it was ground in an agate-mortar to a fine powder, the line width increased to 5.3 gauss in air, but no appreciable change in the spin concentration has been found.

Furthermore, the ESR-absorption of the violanthrone-B was observed in a dilute solution in trichlorobenzene (0.1 mg. per 1.). Although the hyperfine structure could not be resolved, the absorption line spread into a broad one, the over-all width of which was about 30 gauss.

---

6) J. Turkevich and P. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941); W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

7) The purity of the DPPH was determined on the basis of its paramagnetism. Alternatively, spectroscopy can be used for the same purpose. For a chloroform solution of the same sample, the absorbance at absorption maximum (532.5 mμ) gave the extinction coefficient $\epsilon=30.9\,\mathrm{g}^{-1}\mathrm{l.\,cm}^{-1}$ for DPPH, after correction had been made for the free radical content as determined from its magnetic susceptibility. The value of $32.3\,\mathrm{g}^{-1}\mathrm{l.\,cm}^{-1}$ for chemically-pure DPPH has been reported by J. A. Lyons and W. F. Watson [*J. Poly. Sci.*, **18**, 141 (1955).].

8) The ESR absorption of violanthrone was reported by Y. Yokozawa and I. Tatsuzaki [*J. Chem. Phys.*, **22**, 2087 (1954)]. It has been found, however, that the spin concentration of this substance decreased progressively when it was purified repeatedly. Therefore, a large part of the unpaired spins in "crude" violanthrone seem due to the presence of an impurity. The most probable impurity is violanthrone-B.

After the solution had been kept in a cool, dark place for a month, no appreciable change in the signal intensity was found. This indicates that the absorption is due to a fairly stable free radical.

Physico-Chemical Properties

Violanthrone-B is not stable in solution when it is kept in the light. Its *o*-dichlorobenzene solution gradually lost its deep violet color when it was illuminated with ultraviolet light from a mercury lamp. It was also found that the spectroscopic concentration of violanthrone-B decreased rapidly. In this process, a black substance precipitated, and a benzene-soluble product was obtained. Neither part of the products showed any appreciable ESR absorption.

It is well known that, in a polymerization reaction, a stable free radical, for instance DPPH, can terminate the chain propagation. The effect of violanthrone-B on the thermal polymerization of stylene at 80∼100°C was examined in comparison with that of DPPH. The rate of polymerization was measured qualitatively by the increase of viscosity. It was remarkably supressed when stylene contained violanthrone-B or DPPH in a concentration of one milligram per 100 cc. The color of both solutions was deep violet at the beginning, but it changed to orange for the violanthrone-B solution and to colorless for the DPPH solution as the polymerization reaction proceeded. It was concluded that violanthrone-B inhibited the thermal polymerization of stylene even more strongly than did DPPH.

Semiconductivity

The electrical resistivity of violanthrone-B and its variation when temperature ranges from 10 to 160°C were examined with the DC method. The measurements were performed with the sample powder under a compression of 80 kg. per cm^2 between brass electrodes in a quartz cylinder. A good linear relationship was obtained when the logarithm of the resistivity was plotted against the reciprocal of the absolute temperature. Hence, the resistivity (ρ) was described by:

$$\rho = \rho_0 \exp(E/kT) \qquad (3)$$

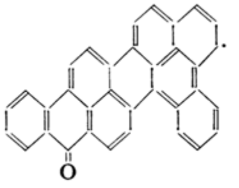
where E, the activation energy for conduction, was 0.34±0.01 eV. and ρ_0 was 8.5 ohm. cm; the resistivity at room temperature was $\rho_{15°} = 6.9\times10^6$ ohm. cm. These data should be compared with those for violanthrone: $E = 0.39_5$ eV., $\rho_0 = 1.6\times10^4$ ohm. cm. and $\rho_{15°} = 1.1\times10^{11}$ ohm. cm.

Discussion

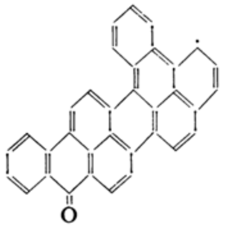
Polycyclic aromatics give often a signal of ESR absorption. The origin of spin centers is not known. Usually these signals are weak and are considered to be due to impurities which could be produced incidentally in synthetic processes. In such cases, the signal decreases as the sample is purified repeatedly. However, this was not the case with violanthrone-B. The crude sample of violanthrone-B gave an absorption with a broad line width. When it was purified by chromatography, the line width became narrower and the integrated intensity increased.

There are many reasons to believe that the observed paramagnetism for violanthrone-B is of a free radical. The *g*-value observed, 2.0041, is similar to those of many organic free radicals. The absorption line width is as narrow as 2.32 gauss, as is characteristic of crystalline-stable free radicals. The same can be said for the relatively high negative Curie point of −45°K.$^{6)}$ The ESR absorption is observable in a dilute solution; this implies that a spin center exists on a molecule. Furthermore, the physico-chemical behavior also suggests the free radical nature of violanthrone-B.

If the observed paramagnetism is a property of violanthrone-B, instead of the structure III or IV, $C_{34}H_{18}O$, the structure V or VI, $C_{34}H_{17}O$, can be assumed as the most plausible one to explain its free radical nature. The tetrahedral bonding in the former structures is replaced by a trigonal bonding in the latter structures, in which the unpaired electron will be delocalized and in which it will be stabilized by some delocalization energy.



(V)



(VI)

Assuming the free radical $C_{34}H_{17}O$, its concentration was estimated from the spin concentration which was observed to be 39 per cent of all the moles. This value coincides with the result of magnetic susceptibility measurements. Hence, although not all the molecules are free radicals, two out of five molecules are. Thus, violanthrone-B might be a mixture of $C_{34}H_{18}O$ and $C_{34}H_{17}O$.

It is uncertain that these two species are in a chemical equilibrium:

$$C_{34}H_{18}O = C_{34}H_{17}O + \frac{1}{2}H_2$$

However, the free radical may be produced by such a dissociation process. Thus, violanthrone-B behaves as if it were a free radical.

There remain a few points to be discussed. There is no direct proof for the proposed structure, V or VI. Hoping to derive information from the infrared absorption spectrum, we examined it by the KBr-disk technique. The stretching vibration of $C=O$ of violanthrone-B is of particular interest in comparison with that of violanthrone. For violanthrone the absorption peak due to the $C=O$ stretching was observed at $1642\,cm^{-1}$, while for the violanthrone-B two peaks were observed, at 1619 cm^{-1} and $1643\,cm^{-1}$, in the same region of frequency. The latter peak coincides with that of violanthrone and may be ascribed to the $C=O$ stretching of $C_{34}H_{18}O$. The peak at 1619 cm^{-1}, which fairly shifts to the low-wave number side, might be due to the $C=O$ stretching of $C_{34}H_{17}O$; this implies somewhat of a reduction of the bond order, which can result from the contribution of the structure of $\geqslant C-\dot{O}$ because of the delocalization of the unpaired electron.

Usually the sharp line width of ESR absorption is ascribed to the narrowing that occurs when electrons are exchanged between the orbitals of different molecules. The line width of violanthrone-B was as narrow as 2.32 gauss, which is comparable with that of DPPH, 2.4 gauss.⁹⁾ In this case, however, not all the molecules are free radicals; only two out of five molecules have unpaired spins, and they still showed the effect of exchange interaction.

The semiconductive property of violanthrone-B may be interestingly compared with that of violanthrone, as the molecules of these two compounds have nearly the same shape and size, even though the former has a free radical character. Eley¹⁰⁾ has proposed a potential box model to describe the semiconductive properties of organic solids. This model, assuming the tunnel effect for electron transfer between molecules, indicated that a solid free radical would behave as a semiconductor, with a very small or zero energy gap ($\varepsilon = 2E$). The small value of the activation energy of DPPH (0.13 eV.) was interpreted by means of this model. This theory can not be strictly applied to violanthrone-B, as it contains free radicals only partially. Nevertheless, it is noteworthy that no apprecible difference in the activation energy between violanthrone-B and violanthrone could be found. On the other hand, the electrical conductivity of violanthrone-B is improved more than 10^4 times at room temperature as compared with that of violanthrone. The higher conductivity of violanthrone-B may be ascribed to its free radical character. However, the mechanism for the contribution of unpaired electrons to the conduction still remains in question.

Summary

The paramagnetic nature of "violanthrone-B" has been studied. The spin concentration in this substance has been determined by the ESR absorption, which is consistent with the value estimated from the magnetic susceptibility and its variation with the temperature. It has been concluded that the molecules of violanthrone-B, in the amount of about 40 per cent of all the molecules, are in a free radical state. It has been suggested, according to the proposed structure of violanthrone-B, that the free radical might result from detaching a hydrogen atom from a peripheral carbon of the tetrahedral type of bonding, which changes thereafter to the trigonal type of bonding.

The authors wish to express their thanks to Mr. Junji Aoki, who prepared the sample of violanthrone-B, and to Dr. Chizuko Tanaka, who examined the infrared absorption spectra of violanthrone and violanthrone-B.

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

---

9) H. Inokuchi and M. Kinoshita, This Bulletin, 33, 1627 (1960).

10) D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, 51, 1529 (1955); D. D. Eley and M. R. Willis, Symposium on Electrical Conductivity in Organic Solids, Wiley, New York (1960).