ELECTRON SPIN RESONANCE STUDIES OF A FREE RADICAL VIOLANTHRONE

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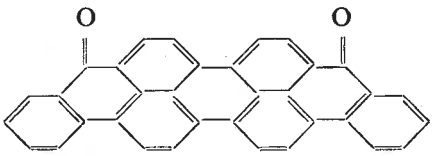
Electron Spin Resonance (ESR) of a stable free radical violanthrone in polycrystalline form and in a magnetically dilute solid solution of about 0.001 M strength in Araldite has been studied by using a varian 4502 EPR spectrometer. The line shape, linewidth and g value of this radical have been determined. It is seen that line shape is Lorentzian in both the cases showing that there is a strong exchange interaction which persists for the excessively diluted solution of the free radical. It is noticed that linewidth becomes almost double in solid solution due to reduction in exchange narrowing. g value for solid solution is found to be more than that of polycrystalline substance which may be due to the anisotropy in g tensor.

1. Introduction

The microwave paramagnetic resonance absorption of a stable organic free radical violanthrone was first observed by Yokozawa and Tatsuzaki [1]. They primarily studied its diamagnetic and paramagnetic susceptibilities. Violanthrone which is also known as dibenzanthrone, has the following structural formula



It exists as violet, blue or black needless when crystallised from nitrobenzene or quinoline. It is insoluble in water, acetic acid and benzene and soluble in xylene, pyridine and nitrobenzene. With a view to study this substance in more details, its EPR spectrum has been recorded by taking the substance in polycrystalline form and also in very dilute solid solution in araldite. From the EPR spectrum, the lineshape, linewidth and g value have been determined.

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2. Experimental details

A varian 4502 EPR spectrometer as described earlier by Das at al. [2] and Khakhar et al. [3], has been used to record the electron spin resonance spectra of violanthrone at room temperature 20°C. The linewidth measurements have been made from the recorder chart, which is calibrated in magnetic field. g value is determined at 9.5 GHz by comparing the resonant magnetic field for the substance with resonant magnetic field for polycrystalline DPPH whose g value is equal to 2.0036.

For preparing the solid solution of violanthrone in araldite of about 0.001 M strength about 0.46 mg of violanthrone was dissolved in anal. r. grade pyridine and it was mixed with about 1 g of araldite and was kept for two to three days so that whole of pyridine was evaporated, leaving behind a very hard dark brown solid solution of violanthrone.

Two types of line shapes for electron spin resonance lines have been proposed viz. (1) Lorentzian, (2) Gaussian.

The expressions for normalized first derivative of χ'' are given by Poole [4].

For Lorentzian

$$\frac{Y'(H)}{Y'_m} = \frac{16\left(\frac{H-H_0}{\frac{1}{2}\Delta H}\right)}{\left[3+\left(\frac{H-H_0}{\frac{1}{2}\Delta H_{pp}}\right)^2\right]^2} \tag{1}$$

For Gaussian

$$\frac{Y'(H)}{Y'_m} = \left(\frac{H-H_0}{\frac{1}{2}\Delta H_{pp}}\right)\exp\left\{-\tfrac{1}{2}\left[\left(\frac{H-H_0}{\frac{1}{2}\Delta H_{pp}}\right)^2-1\right]\right\} \tag{2}$$

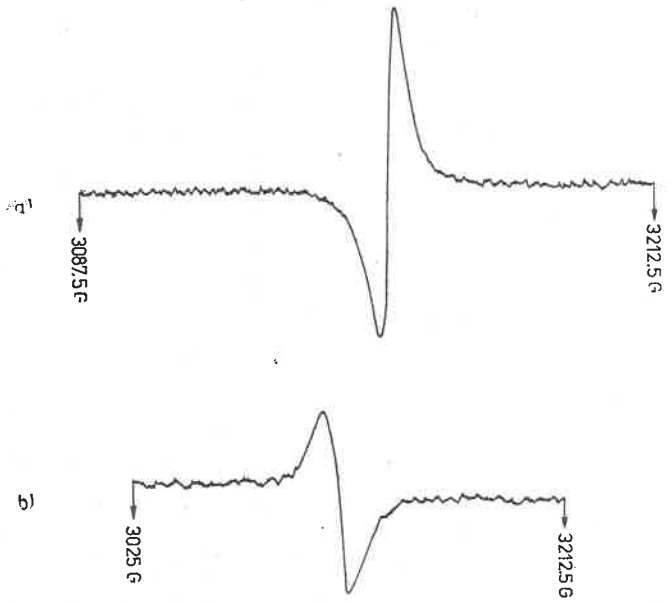

Fig. 1(a). First derivative of electron spin Resonance absorption line of Polycrystalline violanthrone. (b) First derivative of electron spin resonance absorption line of solid solution of violanthrons in Araldite

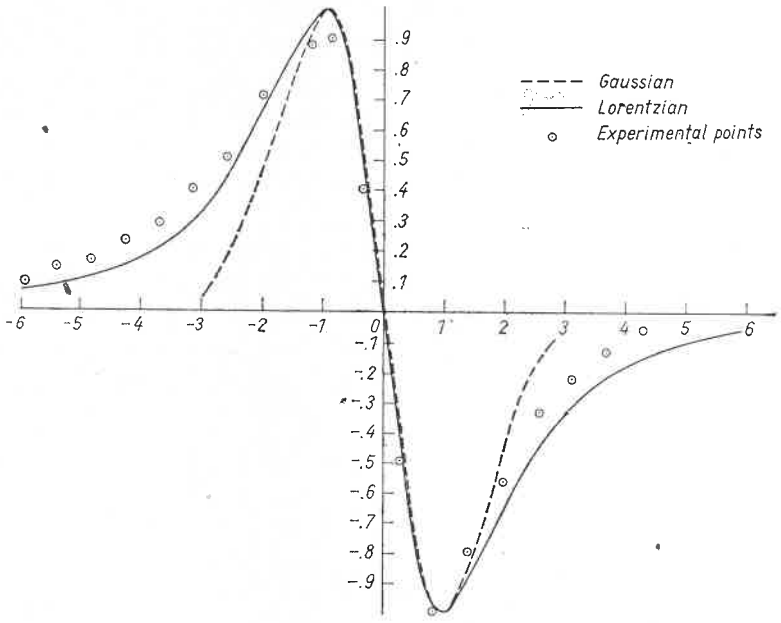

Fig. 2(a). Plot of calculated values of $y'(H)/y'_m$ versus $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ alongwith the observed values in the case of Polycrystalline violanthrone. Theoretical Lorentzian and Gaussian shapes are shown by solid line and dotted line, respectively while observed points are shown by circles

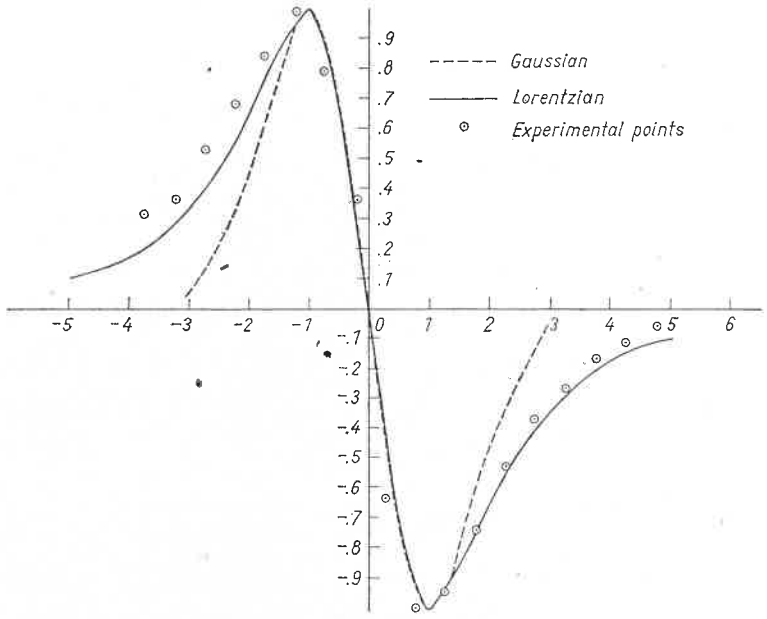

Fig. 2(b). Plot of calculated values of $y'(H)/y'_m$ versus $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ alongwith the observed values in the case of solid solution of violanthrone in Araldite. Theoretical Lorentzian and Gaussian shapes are shown by solid line and dotted line respectively while observed points are shown by circles

Where ΔH_{pp} is peak to peak line width of first derivative of absorption line, H_0 — Resonant Magnetic field, $Y'(H)$ — amplitude of first derivative of absorption line at magnetic field H, Y'_m — max. amplitude of the first derivative of absorption line.

Values of $Y'(H)/Y'_m$ for different values of $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ are determined for polycrystalline violanthrone and violanthrone in Araldite from first derivative of their ESR absorption line shown in Fig. 1(a) and 1(b), respectively. Theoretical graphs have been plotted between $Y'(H)/Y'_m$ and $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ for Lorentzian and Gaussian lines using Equations (1) and (2), respectively. These graphs along with the observed values of $Y'(H)/Y'_m$ for different values of $(H_0-H)/\frac{1}{2}\Delta H_{pp}$ for polycrystlline violanthrone and violanthrone in araldite are shown in Fig. 2(a) and 2(b), respectively.

One can easily calculate linewidth of the ESR absorption line using following Eqs. [4] For Lorentzian line

$$\Delta H_{1/2} = \sqrt{3}\,\Delta H_{pp} \tag{3}$$

For Gaussian line

$$\Delta H_{1/2} = (2 \ln 2)^{1/2} \Delta H_{pp}. \tag{4}$$

3. Results and discussions

Line shape: — Normalized line shape graphs of polycrystalline violanthrone and solid solution of violanthrone in Araldite as shown in Fig. 2(a) and 2(b), respectively show that line shape in both the cases is Lorentzian since most of the points are close to theoretically drawn Lorentzian curve. The Lorentzian nature of the lines is due to exchange interaction. Since exchange interaction is very strong when distance between the molecules is very small (few Å only). But the line shape of violanthrons in Araldite (A solid solution of about 0.001 M strength) is also Lorentzian which shows that exchange interaction also persists for the diluted solution.

Line width: — Paramagnetic properties of violanthrone have been studied by Yokozawa and Tatsuzaki [1]. They found out g and $\Delta H_{\frac{1}{2}}$ for polycrystalline violanthrone as 2.00 and 15.0 respectively. In the present case linewidth for polycrystalline violanthrone and solid solution of violanthrone in araldite is calculated from Fig. 1(a) and 1(b), respectively using equation (3) because from Fig. 2(a) and 2(b) it is clear that line shape is Lorentzian in both the cases. Linewidth and g values for polycrystalline violanthrone and violanthrone in araldite are given in Table I.

TABLE I

Comparision of $\Delta H_{\frac{1}{2}}$ and g values for polcrystalline violanthrone and violanthrone in araldite

Sample	$\Delta H_{\frac{1}{2}}$ [Gauss]	g
Polycrystalline violanthrone	9.0	2.0458
Violanthrone in Araldite	18.0	2.074

From Table I one can see that linewidth for polycrystalline violanthrone is less than that given by Yokozawa and Tatsuzaki [1]. One reason for this may be that they found out linewidth from photograph of the absorption line of polycrystalline violanthrone and not from the first derivative of absorption line as has been done in the present investigations. Determination of linewidth from first derivative is more suitable than from absorption line because from first derivative one can very accurately find out peak to peak width and then from equations (3) and (4) can find out linewidth for Lorentzian and Gaussian lines, respectively. From absorption line one cannot find out $\Delta H_{\frac{1}{2}}$ very accurately because it is not sure that the intensity at resonance is the exact value because it depends upon scanning rate of the magnetic field. Linewidth in Araldite is more because exchange interaction is reduced which is due to freezing of the molecular motion of Violanthrone molecules in Araldite. Though in diluted solution spin-spin interaction is less because the average distance between the molecules increased and since the interaction falls as $1/r^6$, where r is the average distance between the violanthrone molecules, and the broadening due to spin-spin interaction is not there, but due to reduction in exchange interaction, linewidth is broadened. A broader line of polycrystalline violanthrone than DPPH can be explained from spin lattice interaction which is weaker than that of transition elements but is stronger than that of DPPH.

g — factor: — g is very close to free spin value of 2.0023. This is because the electrons are delocalized and there is very little coupling between their spin and any orbital motion and so, unlike most paramagnetic atoms, there is not much contribution from the orbital momentum to the g-value. Difference in g-value of the polycrystalline violanthrone and violanthrone in araldite is due to anisotropy in g-factor which arises due to spin-orbit interaction.

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