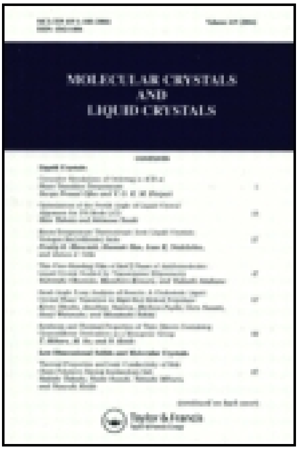

Molecular Crystals and Liquid Crystals

Radical Pairs in Irradiated Anthracene Single Crystals

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Radical Pairs in Irradiated Anthracene Single Crystals

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Angular dependent EPR spectra of anthracene single crystals irradiated with γ rays at 77°K have been measured and two kinds of septet side lines with 7.5 G splitting and maximum separations by 237.5 and 206.3 G were found. From the spectra the presence of two kinds of radical pairs were concluded, whose pair axes lie within ac-plane and directed in 90° and 45° from the a-axis. Similar septet side lines were also found in the crystals which were annealed at room temperature for one hour. Radicals forming a pair were considered to be 9-dibenzo-cyclohexadienyl radical judging from the septet line of 7.5 G splitting and the stability of radicals. The directions of pair axes were discussed on the base of the migration of hydrogen atom within the ab-plane.

1 INTRODUCTION

The EPR investigation on radicals produced upon irradiation of ionizing radiation on aromatic crystals, such as benzene, naphthalene and anthracene have been made by many workers.[1] Radicals in anthracene crystals have been studied from the early days and it has been shown that the stable radical at room temperature is 9-dibenzo-cyclo-hexadienyl radical.[2] However in most cases these studies have been carried out at room temperature and the precise spectrum at low temperature has not been reported.

Recently the existence of radical pairs in irradiated anthracene crystals at low temperature has been reported detecting the EPR signals of $\Delta M_s = 2$ transition of pairs.[3] However the spectrum of $\Delta M_s = 1$ transition of pairs has not been reported. It is difficult to obtain reliable informations about the structure and behavior of radical pairs from the $\Delta M_s = 2$ spectrum only.

In this paper we will report angular dependence of the spectrum of $\Delta M_s = 1$ transition of radical pairs in anthracene single crystals both as irradiated at low temperature and upon annealing at room temperature.

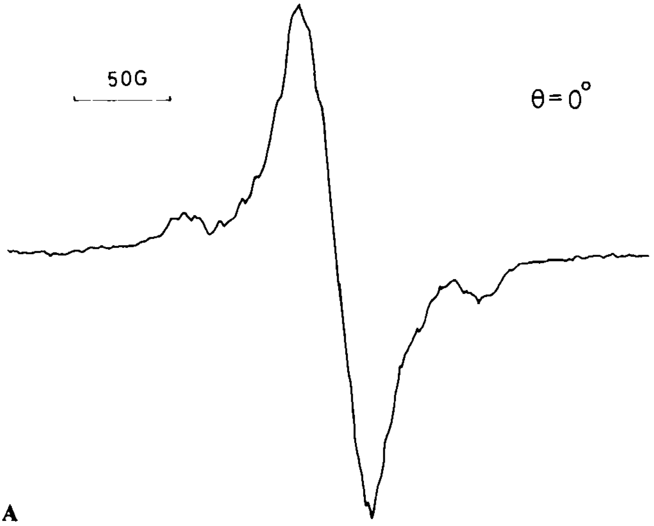
2 EXPERIMENTAL

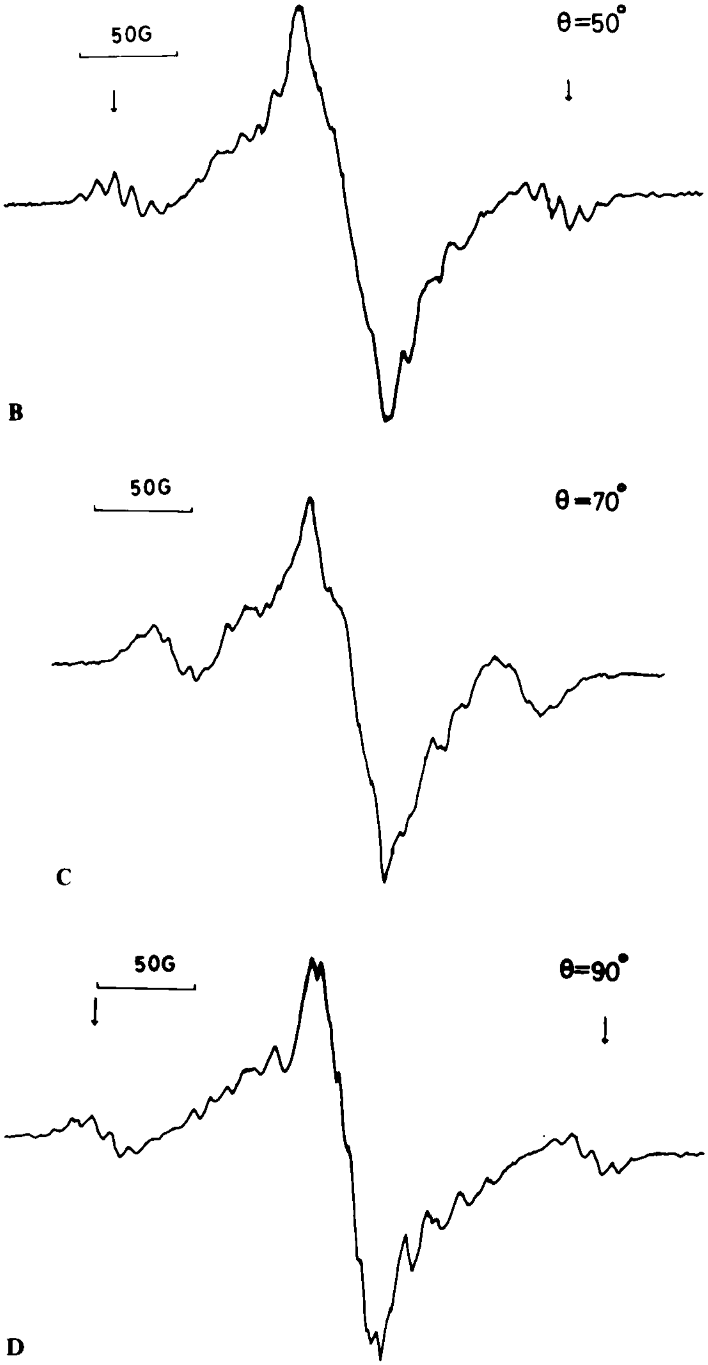
Anthracene powder of the scintillation grade was obtained from Pilot Chemical Inc. and it was further purified with zone refining by 80 passes. Single crystals were grown by the Bridgman technique in an evacuated cell. Crystals of $6 \times 10 \times 2$ mm^3 cut parallel to the ab-plane were irradiated at liquid nitrogen temperature with γ rays up to a dose of 6×10^7 rad. EPR measurements were made at liquid nitrogen temperature using a microwave frequency of approximately 9.5 GHz and a power of 0.2 mW. Crystals were set in the magnetic field with the *b*-axis perpendicular to the field and were rotated around the *b*-axis.

3 RESULTS

Figure 1 shows typical angular dependent EPR spectra at 77° K of anthracene single crystals irradiated at 77° K, where θ denotes the angle between the direction of the magnetic field and the *a*-axis. In the spectra of $\theta = 50°$ and 90°, small multiplets (indicated by arrows) are obviously observed in the both sides of the main center line. When the crystal is rotated from $\theta = 0°$, the side lines which appear to be broad peaks move to the center with increase of θ and we find the other side lines move from the center to the outsides. At $\theta = 50°$

FIGURE 1 EPR spectra of anthracene single crystal which was irradiated and measured at 77° K. The magnetic field is perpendicular to the *b*-axis and θ denotes the angle between the magnetic field and the *a*-axis.




50G
θ=50°
B
50G
θ=70°
C
50G
θ=90°
D

these second side lines are observed clearly separated from the other lines. Thereafter the second side lines move toward the center, and the other side lines, possibly the first side lines, emerge out of the center and move toward outsides. At $\theta = 70°$ these two kinds of side lines overlap together so that the intensities of side lines appear to be large. Thenceforth one side lines go to the center and the other lines move to the outsides and at $\theta = 90°$ the latter side lines becomes to be observed separately.

A fine splitting, d due to radical pair in the $\Delta M_s = 1$ spectrum can be expressed as follows, if the point dipole approximation is valid[4]

$$d = 3g\beta\,(1 - 3\cos^2\Theta)/2\,R^3 \tag{1}$$

where g is the g tensor, β is the Bohr magneton, and Θ is the angle between the magnetic field and the vector IR connecting two radicals of a radical pair. We may draw two curves calculated from Eq.(1), which fit to the experimental values. From Figure 2 we find two directions of pair axis at $\theta = 95°$ and $45°$. The maximum splittings of these side lines are 237.5 G and 206.3 G, respectively. Since in each curve the maximum splitting is just two times of the absolute value of the minimum point in the curve, we can find that the axes of pairs lie within planes perpendicular to the b-axis of the crystal.

Figure 3 shows EPR spectra at 77°K of a crystal which was irradiated at 77°K and kept at room temperature for one hour. In the spectrum at $\theta = 90°$ well desolved large septet lines are observed in the both sides of the center line. When the crystal is rotated from $\theta = 0°$, the side lines move to the center with increase of θ (Figure 3(b)) and at $\theta = \sim 40°$ it overlap upon the center line (Figure 3(c)). Thereafter the side lines go out of the center line and at $\theta = 90°$ the splitting takes a maximum value. The angular dependence of the splittings of the side lines are plotted together with the curve calculated from Eq.(1). The direction of pair axis is parallel to the c'-axis. The maximum splitting is 196.3 G which is a little smaller than that of not annealed crystals. The splittings of each septet lines are 7.5 G which is the same as that of not annealed cystals.

4 DISCUSSION

The signals of radical pairs are found in both crystals as irradiated at low temperature and as annealed at room temperature. The splittings of the $\Delta M_s = 1$ transition are 200 ~ 240 gauss in the both cases and the splitting of each septet lines is 7.5 gauss in all cases. From these similarities it is supposed that radical pairs are formed of the same species in all the cases. The radicals forming a pair are considered to be 9-dibenzo-cyclohexadienyl radical. Because the 7.5 gauss splitting of septet lines in a pair spectrum is just one half of the 15 gauss splitting of quartet lines of an isolated 9-dibenzo-cyclohexadienyl radical. The other possible species in irradiated crystals, three

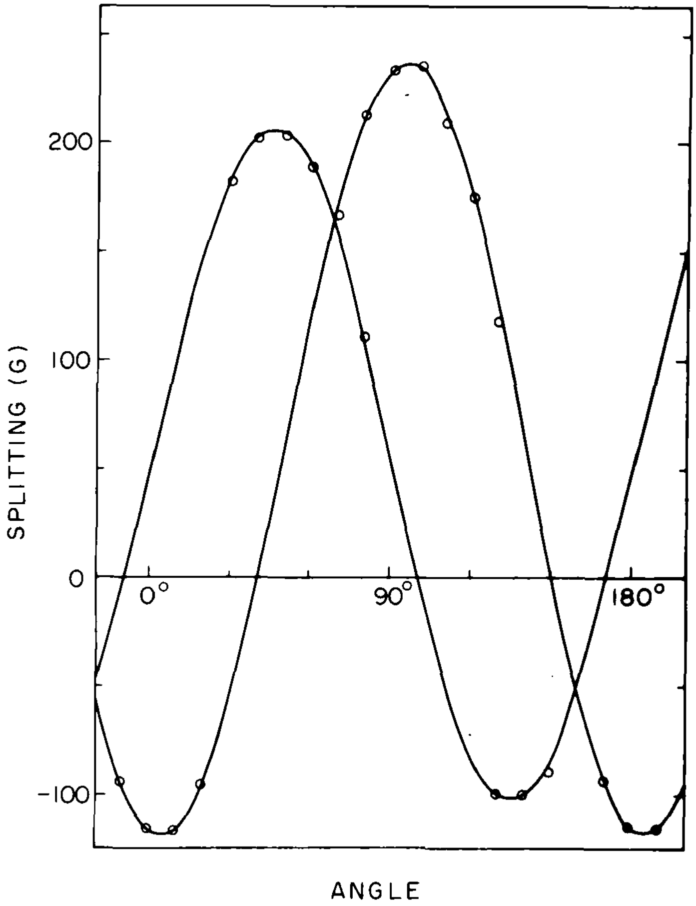
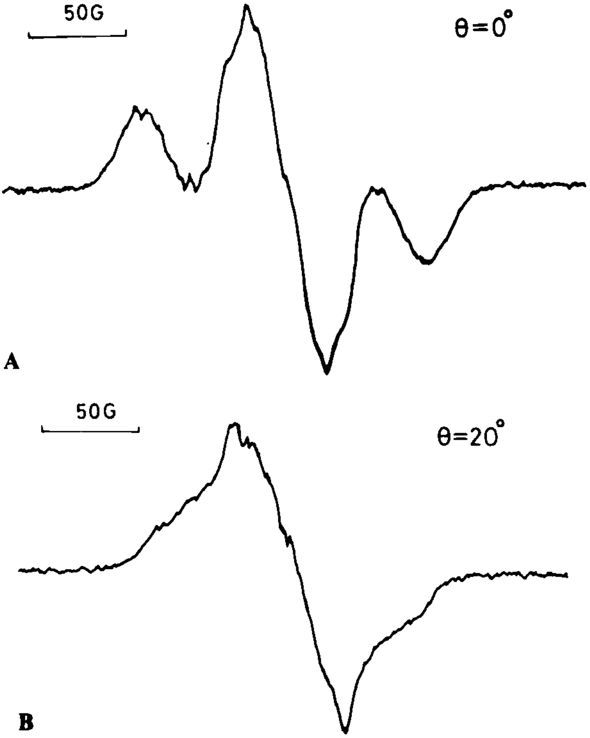


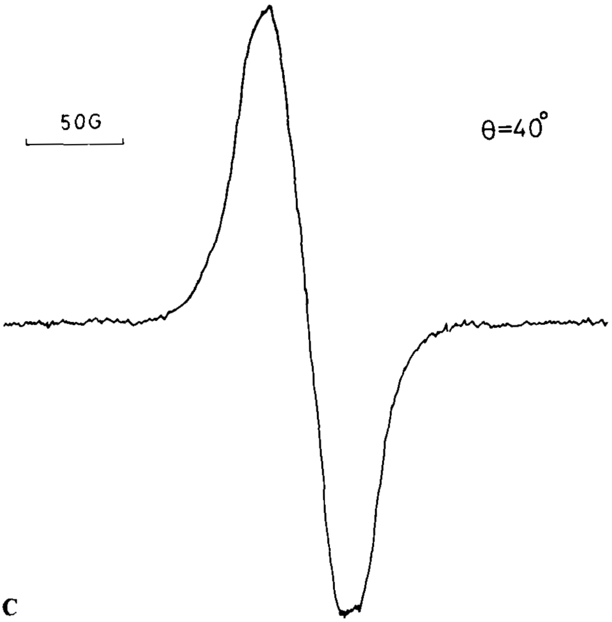
FIGURE 2 The angular dependence of the splitting of the side lines in Figure 1. Curves are *d* values of $\Delta M_s = 1$ spectra due to radical pairs, calculating using Eq.(1). Circles indicate observed values.

kinds of anthracyl radicals[5] and 1- and 2-dibenzo-cyclohexadienyl radicals,[1] do not satisfy the above conditions for the present spectrum of pairs. Moreover the pair spectrum is observed in crystals which were annealed at room temperature for 50 hours. A radical which is stable at room temperature is 9-dibenzo-cyclohexadienyl radical. The maximum splittings of 237.5, 206.3 and 196.3 gauss correspond to 6.16, 6.46 and 6.57 Å of the separations of two radicals calculating using the Eq.(1) in the point dipole approximation.

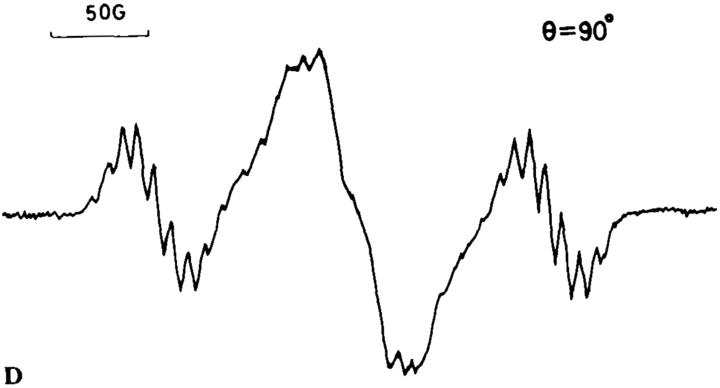
Now we discuss about the directions of the radical pairs. In crystals as both irradiated and annealed the axes of pairs lie within the ac-plane and not within the ab-plane. By the irradiation of γ rays hydrogen atom is released from the parent molecule. The released hydrogen atom is supposed to migrate mainly within the ab-plane in which the overlap of electron is large comparing with that in the direction parpendicular to ab-planes. When the hydrogen atom in the last stage of the migration happens to meet with a 9-dibenzo-cyclohexadienyl radical which locates in the just neighboring ab-planes, the hydrogen atom is trapped in the molecule to form a radical pair whose pair axis is perpendicular to the ab-plane. An encounter of the hydrogen atom with a radical within the ab-plane may give rise to a chemical reaction and therefore may not result in a formation of radical pair. Two 9-dibenzo-cyclohexadienyl radicals may draw close to each other upon a formation of pair, since the distance of $6 \sim 6.5$ Å between the two radicals of a pair is fairly smaller comparing with the distance of 9.18 Å between the neighboring ab-planes.[6] If we suppose that a radical lies at the lattice point Q (Figure 5) and a hydrogen atom which is migrating in the ab-plane involving the lattice point P attaches to the molecule at the lattice point P, a radical pair P'-Q' may be possibly formed. In the case that a radical lies at the lattice point S, a radical pair P''-S''

FIGURE 3 EPR spectra of anthracene single crystal which was irradiated at 77° K and annealed at room temperature for one hour. Measurements were made at 77° K.





C



D

may be considered as one of possible models of the 45°-pair. In the above model of 90°-pair the distance between the centers of radicals of pairs are calculated to be 6.08 Å for not annealed crystals, assuming that the spin distributes over the radical[7] and the orientations of radicals are same as a molecule in a unit cell.

When the crystal is warmed up to room temperature hydrogen subtracted radicals (R) may react with the neighboring molecules (RH) or hydrogen added radicals (RH_2).

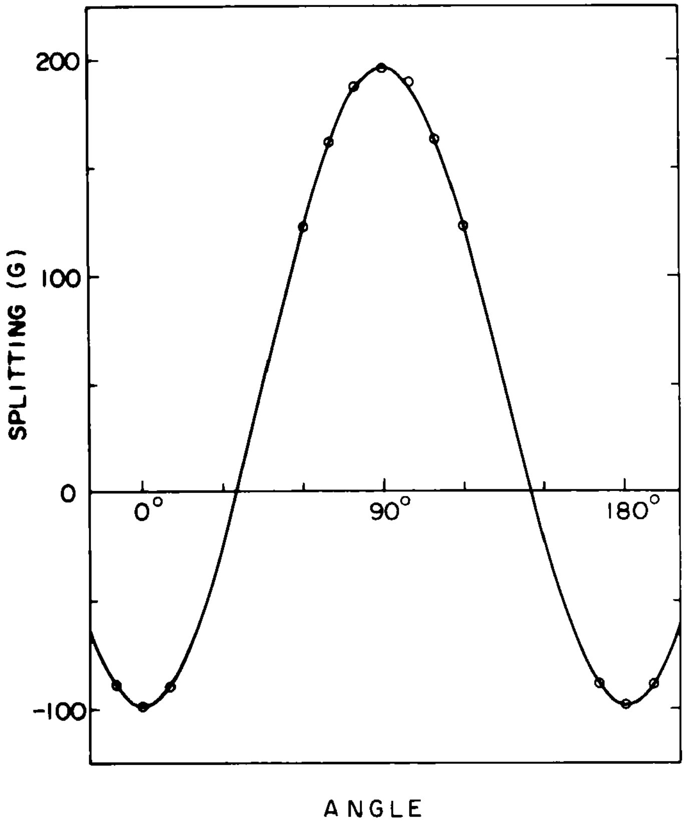


FIGURE 4 Angular dependence of the splitting of the side lines in Figure 3. Curve is calculated *d* values. Observed values are indicated by circles.

$$R + RH \rightarrow R_2 + H \text{ (}R_2\text{: dianthracene)} \qquad (2)$$

$$R + RH \rightarrow R_2H \text{ (}R_2H\text{: hydro-dianthracyl radical)} \qquad (3)$$

$$R + RH_2 \rightarrow 2RH \qquad (4)$$

These reactions (2) ~ (4) are supposed to occur mainly within the ab-plane. The hydrogen atom which is produced in the reaction (2) may migrate also within the ab-plane and attach to anthracene molecule to form a radical pair whose pair axis is perpendicular to the ab-plane. For annealed crystals the distance between the radicals of a pair is calculated to be 6.57 Å adopting the distributed spin model.

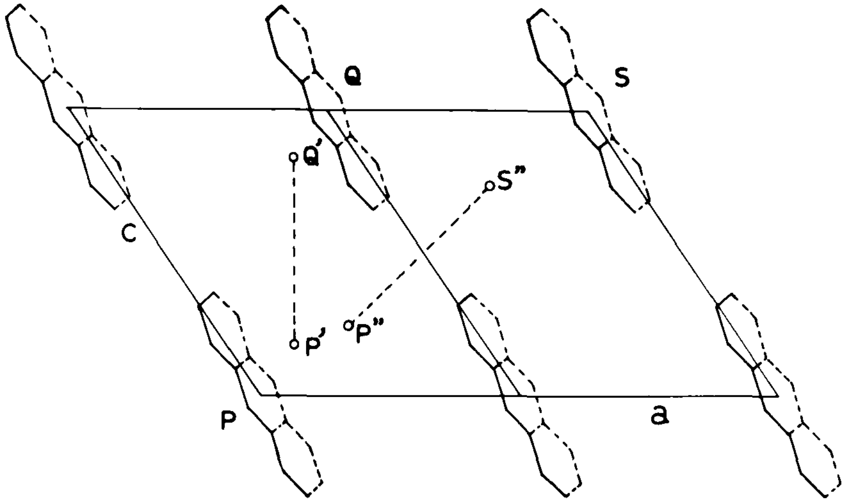


FIGURE 5 Molecules within an ac-plane in anthracene crystals and proposed radical pair models. *P'* and *Q'* indicate the centers of radicals in a radical pair *P'*-*Q'*. *P"*-*Q"* is a 45°-pair.

5 CONCLUSIONS

By the analysis of angular dependent spectra, it has been found that radical pairs are formed in crystals both as irradiated at low temperature and as annealed at room temperature. The pair axes lie within the ac-plane in both crystals and direct in 95° and 45° from the *a*-axis in the former crystals and in 90° in the latter crystals. These directions of pair axes may be explained on the base of the consideration that a migration of a hydrogen atom and chemical reactions occur mainly within the ab-plane and hardly take place between different ab-planes, so that a pair is formed within an ac-plane.

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