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ESR SPECTRA OF THE TRIPLET STATE OF 2,2'-BIPYRIDYL WITH Z AND E CONFORMATIONS

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Two sets of ESR spectra of the triplet state of 2,2'-bipyridyl in PVA films have been observed and explained to be due to its Z and E conformations from the experimental and theoretical viewpoints.

On the electron spin resonance (ESR) of the lowest excited triplet state of 2,2'-bipyridyl, only one set of spectrum was detected in ethanol glass.1) In polyvinyl alcohol (PVA) films, however, we have succeeded to observe spectra of its Z and E conformations. 2,2'-bipyridyl was purchased from Tokyo Kasei Co. and purified by recrystallization. The non-drawn films are about 2×10^{-2}cm thick, this being obtained by drying 200 ml of aqueous solution containing 20 g of PVA and 0.25 g of 2,2'-bipyridyl on a 29×29 cm^2 glass plate for about ten days. The drawn films are about 7×10^{-3}cm thick, with about 250% of stretch in the stretching direction *s* and about 30% of contraction in direction *c* which is perpendicular to the *s* direction in the film plane. The drawn films were oriented in a quartz sample tube in a quartz dewar with fingertip which was inserted in a cavity. The ESR spectra were observed for rotation of the films around the *s* and *c* directions which were set to be perpendicular to the applied magnetic field. Measurements were carried out at 77°K using a JEOL JES-ME-3X spectrometer. The exciting light was provided by a high-pressure mercury arc lamp.

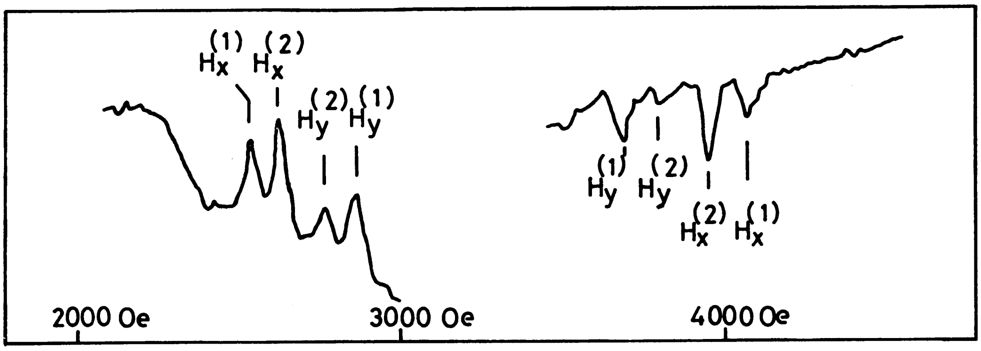

Fig. 1. $\Delta m=1$ transitions in triplet state of 2,2'-bipyridyl in a drawn PVA film.

Figure 1 shows peaks for $\Delta m=1$ transitions when the magnetic field was applied parallel to the stretching direction. They correspond to two kinds of high and low field *x*- and *y*-axis peaks, one of which is in accord with that observed in ethanol glass [denoted by (1)] and another is a quite different spectrum [denoted by (2)] which was not detected until now. The intensity of $H_x^{(2)}$ peak is apparently stronger than that of $H_y^{(2)}$, while both the intensities of $H_x^{(1)}$ and $H_y^{(1)}$ are nearly the same.

When the magnetic field was applied perpendicular to the film plane, one set of strong z-axis peaks at high and low fields were observed at the same positions as in the ethanol glass and the other peaks were obscure. For the other orientations of the films, the resonance fields were almost the same as those in the above cases For $\Delta m=2$ transitions, the observed peaks were nearly the same as those in ethanol glass. In the case of non-drawn films, both the spectra of (1) and (2) were also observed with same intensity. Under the condition of $|D_{zz}|\geqq|D_{yy}|\geqq|D_{xx}|$, one obtains two sets of fine structure parameters from the observed fields as follows:

$$|D^{(1)}|/hc = 0.1095\ \mathrm{cm}^{-1},\ |E^{(1)}|/hc = 0.0117\ \mathrm{cm}^{-1}$$

and

$$|D^{(2)}|/hc = 0.1095\ \mathrm{cm}^{-1},\ |E^{(2)}|/hc = 0.0049\ \mathrm{cm}^{-1}.$$

It should be noted here that, concerning the purity for the samples used, there is no possibility existing an observable triplet state of another species than that of 2,2'-bipyridyl. Only a possible elucidation for the above results is that these two sets of spectra are due to the triplet state of both E- and Z-2,2'-bipyridyls, since the molecular structure in the triplet state is considered to be planar.[1,2]

As the signals (1) are observed in ethanol glass, they should be due to the more stable E conformation. The fact that the intensity of $H_x^{(2)}$ is stronger than that of $H_y^{(2)}$ in the magnetic field parallel to the stretching direction means that the principal x axis of fine structure tensor is closely parallel with the longest axis of imperfectly oriented molecules. Such a condition is satisfied only for the Z conformation, since the directions of these axes for the E conformation are considerably different each other. In consideration of both the geometries, there is no significant difference of the spin distribution concerning the z direction perpendicular to the molecular plane. This is in consistent with the fact that both the D values are nearly the same. As a result, one may reasonably assign that $D^{(1)}$ and $E^{(1)}$ correspond to the triplet state of E-2,2'-bipyridyl, while $D^{(2)}$ and $E^{(2)}$ are those of the Z conformation. This conclusion have also been confirmed by a calculation of D and E in which the wavefunctions were constructed taking all the singly excited configurations in use of Pariser-Parr-Pople type SCF-LCAO-MO's.

Actually, similar phenomena with the present work have recently been observed for 3,3'-dimethylbiphenyl[3] and 3,3'-difluorobiphenyl[4] in rigid glass. In the present communication, however, we would like to emphasize the facts that the existence of a conformation which could not be detected in usual rigid glass with less strong hindrance have been confirmed and that the two sets of fine structure parameters have reasonably been assigned from both the experimental and theoretical viewpoints.

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