Zero-field Splitting Tensor and Orientation of the Phosphorescent-state Benzo[*h*]quinoline in Biphenyl Host

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Synopsis. ESR absorption has been observed in a single-crystal solid solution of benzo[*h*]quinoline in biphenyl under UV irradiation at 120 K. The triplet-state zero-field splitting tensor and the guest orientation are reported, in comparison with the previous results on benzo[*f*]-quinoline.

In order to investigate the nature of the triplet-state wave function, it is important to determine the zero-field splitting (ZFS) principal axes, not to speak of the principal values. However, the number of compounds for which the ZFS principal axes were determined are limited.¹⁾ The main object of this work is to determine the ZFS principal axes in the phosphorescent state of benzo[*h*]quinoline (BHQ), to be compared with those of benzo[*f*]quinoline (BFQ) reported previously.¹⁾

Experimental

BHQ (Nakarai GR) was treated with sulfuric acid and sodium hydroxide,²⁾ and then zone-refined extensively. Single-crystal samples were grown from the melts.¹⁾

The ESR measurements were performed as described previously,¹⁾ except for the use of a microwave frequency of 9.15 GHz instead of 9.25 GHz. The sample crystals were cooled at 120±10 K by a flow of cold nitrogen gas, and irradiated with a 250-W high-pressure mercury lamp. Quartz wedges were used in order to rotate the static external magnetic field in the particular magnetic planes associated with one type of BHQ molecule in the crystal. We have also studied the phosphorescence spectra and decays of BHQ in biphenyl at 77 and 4.2 K, and identified the phosphorescent state, as described previously.¹⁾

Results and Discussion

General Remarks. Figure 1 shows the molecular axes adopted, designation of the ZFS principal axes, x, y, z, and the in-plane rotation of the ZFS tensor, θ. For the sake of convenience, the two sites in a unit cell of the biphenyl crystal are designated as sites A and B, respectively, the quartz wedges being assumed to fit site A. The main features of the biphenyl crystal have been summarized previously,¹⁾ and there are two magnetically inequivalent orientations of the BHQ molecule at each site. Since the procedures in this work resemble the previous for BFQ,¹⁾ the presentation will duly be brief.

ESR Spectra in the yz Plane and Tilt of the Guest Plane. Figure 2 shows the resonance fields obtained by rotating the static external magnetic field $\boldsymbol{H}$ nearly in the yz plane with the wedge of an inclination of 17.8° which gave a maximum resonance field; four wedges of inclination in the range 13.8°—19.0° were actually used, while the biphenyl crystal structure specifies the inclination of 17.7° for $\boldsymbol{H}$ to be in the M′N′ plane.

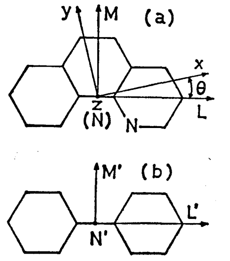

Fig. 1. Axis systems for (a) benzo[*h*]quinoline and (b) biphenyl. ZFS principal axes are denoted by x, y, and z.

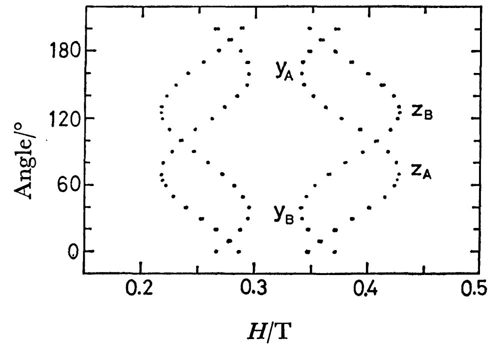

Fig. 2. Magnitude of $\boldsymbol{H}$ for resonance *vs.* rotation of $\boldsymbol{H}$ in a plane close to the yz plane.

The two patterns correspond to sites A and B, and are identical to each other except for the phase. The largest separations correspond to the z axes, while the smallest to the y axes. With very poor resolutions, eight lines could be recognized for some orientations of $\boldsymbol{H}$ between the y and z axes. This indicates the small value of θ to be discussed later on, and that the molecular planes of the two inequivalent guests at each site are parallel to each other within experimental errors. Thus, the angle of 55.0° between the fine-structure z axes may represent the dihedral angle between the planes of the A- and B-site BHQ molecules, in contrast with the corresponding angle of 69.3° for the A- and B-site biphenyl molecules.³⁾ The difference of 14.3° in the two angles amounts to a decrease of 7° in the tilt of the guest plane relative to the host, in coincidence with the case of BFQ in biphenyl,¹⁾ and in a slight deviation from the tilt of 5°—6° found for phenanthrene in biphenyl.⁴,⁵⁾ The nitrogen-atom location essentially does not affect the tilt of the guest plane.

ESR Spectra in the xy Plane. Five wedges were used in order to rotate $\boldsymbol{H}$ in the xy plane, *i.e.*, LM plane, their dihedral angles ranging from 101.0° to 105.9°. Taking account of the yz-plane measurements, the b axis of the crystal was set at 62° on the wedge

TABLE 1. OBSERVED ZERO-FIELD SPLITTING PARAMETERSa)

	Benzo[*h*]quinolineb) in biphenyl	Benzo[*f*]quinolinec) in biphenyl	Benzo[*h*]quinolined) in ethanol	Benzo[*f*]quinolined) in ethanol
D/cm^{-1}	±0.09738(2)	±0.09926(18)	+0.1011	+0.1023
E/cm^{-1}	∓0.04642(2)	∓0.04781(6)	−0.0468	−0.0477
$\|E/D\|$	0.4767	0.4817	0.463	0.466
g_{xx}	2.0016(4)	2.0024(6)		
g_{yy}	2.0023(4)	2.0018(4)		
g_{zz}	2.0018(2)	2.0018(4)		
θ/°	±0.5	±4		

a) Numbers in parentheses are estimated standard deviations in units of the last significant digit. b) This work. c) Ref. 1. d) Ref. 7.

surface as detailed previously.1) The wedge of a dihedral angle of 103.3° gave a maximum resonance field. The y-axis resonance-field separations are the same as those in the yz-plane measurements. In addition, the L axes of sites A and B are practically parallel to each other, since the four lines draw closer together and coalesce into one as ***H*** moves to the x axes, as it is the case for BFQ.1)

*ZFS Tensor, **g**-Tensor, and Hyperfine Structure.* The ZFS parameters were determined with the procedure of Hutchison and Mangum,6) the principal axes of the ***g***-tensor being assumed to coincide with those of the ZFS tensor. The parameters fitting the spin-Hamiltonian are given in Table 1. The D value is somewhat smaller in biphenyl than in ethanol glass,7) while the E value is essentially indifferent to the solvents, as it is the case for BFQ.1,7) The resemblance of the D and E values of BHQ to those of BFQ1) and phenanthrene4) confirms the $\pi\pi^*$ nature of the phosphorescent state in BHQ.

The two pairs of curves in the xy-plane measurements correspond to the two magnetically inequivalent orientations at site A, as exemplified in Fig. 6 of Ref. 1. From the phase difference of 1° between the two curves, we obtain a θ value of ±0.5°, in good agreement with a theoretical value of +0.2°,8) and in contrast with the larger value of ±4° for BFQ,1) as shown in Table 1.

Although the hyperfine structures could be observed for ***H*** nearly on the three ZFS principal axes, they actually are complicated owing to the low molecular symmetry and to overlapping of the signals due to the different sites. Accordingly, the hyperfine coupling constants could not be determined, as it was the case for BFQ.1)

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