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ESR Study of the Phosphorescent State of Benzo[*f*]quinoline

Hiroshi Sekiya, Yasuhiko Gondo,* and Yoshiya Kanda

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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Electron spin resonance absorption has been observed in a single-crystal solid solution of benzo[*f*]quinoline in biphenyl under irradiation at 120 K with light from a high-pressure mercury lamp. The fine structure of the resonance spectrum observed at 9.25 GHz can be described by the spin Hamiltonian

$$\mathbf{H} = \beta \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2)$$

in which $S=1$, $D=\pm 0.09926(18)$ cm^{-1}, $E=\mp 0.04781(6)$ cm^{-1}, $g_{xx}=2.0024(6)$, $g_{yy}=2.0018(4)$, and $g_{zz}=2.0018(4)$; the z axis is normal to the molecular plane, the x and y axes being the in-plane fine-structure principal axes. The principal x axis deviates by $\pm 4°$ from the biphenyl long axis and the principal z axis by 7° from the biphenyl out-of-plane axis. The phosphorescence spectra and lifetimes have been measured both at 77 K and at 4.2 K. Marked doublet splittings were observed in the phosphorescence bands at 4.2 K, suggesting a large guest-host interaction.

This work deals with the determination of the principal axes of the zero-field splitting (ZFS) tensor for benzo[*f*]quinoline (BFQ) in its lowest excited triplet state. In order to investigate the nature of the triplet-state wave function, it is important to determine the directions of the principal axes, not to speak of the principal values. However, the number of compounds for which the ZFS principal axes were determined are limited.[1-4] Vincent and Maki[1] showed that the ZFS parameters of quinoxaline, quinoline, and isoquinoline in durene closely resemble those of naphthalene in durene, whereas the principal axes of quinoline and isoquinoline are no longer coincident with the durene axes. Such deviation of the ZFS principal axes has also been found in 1,5-naphthyridine in durene,[2] and 1,6-diazanaphthalene in durene.[3] As for tetramethylpyrazine in durene, de Groot *et al.*[4] showed that the principal axes deviate largely from the durene axes, suggesting that the molecular symmetry does not necessarily specify the principal axes.

The electronic states of BFQ and benzo[*h*]quinoline have been studied extensively in our laboratory, in particular the delayed fluorescence of BFQ in biphenyl host,[5] the concentration depolarization of phosphorescence in ethanol glass,[6] the dipole moments and pK_a values in the ground and first excited singlet states,[7] and the temperature and solvent dependence of the phosphorescence lifetime.[8] The most relevant finding is the fact that no sign of the spin alignment could be detected in these benzoquinolines in their lowest excited triplet states in hexane at 1.3 K, and in biphenyl even at 1.18 K[5,8] According to Antheunis,[9] phenanthrene in its lowest excited triplet state in both biphneyl and fluorene provides intriguing examples; even at 1.2 K the spin-lattice relaxation times are about 1 ms, approximately one thousand times faster than the decay of the lowest excited triplet state to the ground state. The results may justify the claim that the phenanthrene-type compounds are important in the study of the spin-alignment mechanism in the triplet state.

Thus, it seems significant to obtain fundamental information on the lowest excited triplet state of BFQ, in particular, on the ZFS parameters, ZFS principal axes, and ***g***-tensor, from the electron spin resonance (ESR) spectra observed for the single-crystal solid solutions of BFQ in biphenyl. For identification of the triplet state, we have also studied the phosphorescence spectra of BFQ in biphenyl and biphenyl-d_{10} at 77 K and 4.2 K.

Experimental

Materials. BFQ (Tokyo Kasei Kogyo Co., Ltd.) was treated with sulfuric acid and sodium hydroxide as described previously,[10] and then zone-refined extensively. Biphenyl (Wako Pure Chem. Ind., Ltd.) was recrystallized from ethanol or sublimed and then zone-refined. Biphenyl-d_{10} (Merck, Sharp and Dohme Canada, Ltd.) was zone-refined. The sample crystals were grown in Pyrex tubes from the melts in a Bridgman furnace. The initial concentration of BFQ in biphenyl was *ca.* 1.2 mol%, the final concentration in the grown crystals not being known. Samples, sealed in a vacuum into Pyrex tubes, were lowered in the furnace at a rate of 30 mm a day.

Measurements. The ESR spectrometer (Echo Electronics Co., Ltd.) essentially consists of a microwave unit (EWG-10), a 100-kHz phase sensitive detector (E-100D), and a klystron power supply (EKS-1PS). Measurements were carried out using a microwave frequency of 9.25 GHz and a magnetic field modulation of 100 kHz. The microwave frequency was determined with a calibrated cavity wavemeter, the external magnetic fields being determined with a proton NMR gaussmeter. Irradiation of the sample crystals was made with a 250-W high-pressure mercury lamp (USH-250D, Ushio Electric Inc.).

Values of direction cosines of the biphenyl molecular axes in the crystal required for mounting the sample crystals properly in the cavity, were obtained from the molecular planes least-squares fitted to the X-ray diffraction data given by Trotter[11a] (Table 1). The unit cell of the biphenyl crystal is shown in Fig. 1. Main features of the biphenyl

Table 1. Biphenyl direction cosines[a]

	L′	M′	N′
a	−0.30311	−0.51754	0.80017
b	0.00662	0.83747	0.54645
c′	−0.95293	0.17550	−0.24723

a) Ref. 11a. Axis c′ is normal to the ab plane. See Fig. 1.

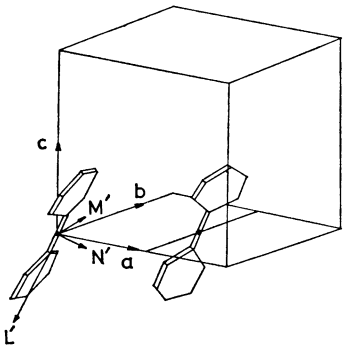

Fig. 1. Biphenyl crystal structure and axis systems.

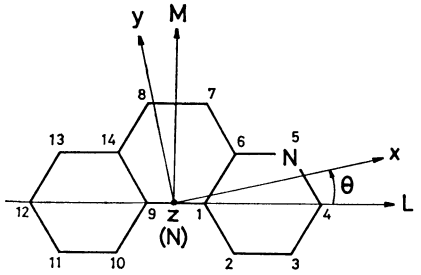

Fig. 2. Molecular axes, L, M, N, ZFS principal axes, x, y, z, and numbering scheme for the benzo[*f*]quinoline molecule.

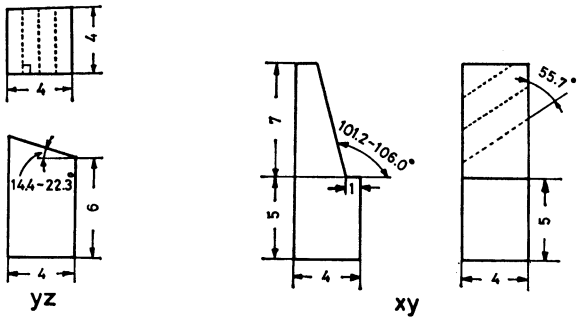

Fig. 3. Quartz wedges used to mount the sample crystals.
The ab plane was attached to the surfaces with the dotted lines which specify the b-axis direction. Lengths are given in mm. With the wedges (a) and (b), the external magnetic field lies in the yz and xy planes, respectively.

crystal are as follows: (1) It is a monoclinic crystal of the space group $P2_1/a$ with two molecules in a unit cell. (2) The crystal cleaves in the ab plane. (3) The long axes of the two molecules in a unit cell are parallel to each other within 3°.[11b,12] Figure 2 shows the molecular axes adopted and designation of the ZFS principal axes, x, y, and z.

Several quartz wedges were devised in order to rotate the static external magnetic field in the fine-structure xy and yz planes of one of the two molecules in a unit cell. Typical wedges, whose geometries are based on the direction cosines given in Table 1, are shown in Fig. 3. A biphenyl crystal doped with BFQ was mounted with its cleavage plane, *viz.*, ab plane, against the surface of a wedge by use of a varnish (GE-7031, General Electric Co.), the wedge being attached to a quartz rod directly connected to a conventional crystal-rotating device. The sample crystals were cooled by a flow of cold nitrogen gas. The sample temperature was estimated to be 120±10 K by putting a thermocouple in place of the sample crystals in the cavity. The ESR signal decays were observed at 77 K with crystals directly immersed in the liquid nitrogen in a Dewar vessel with a finger.

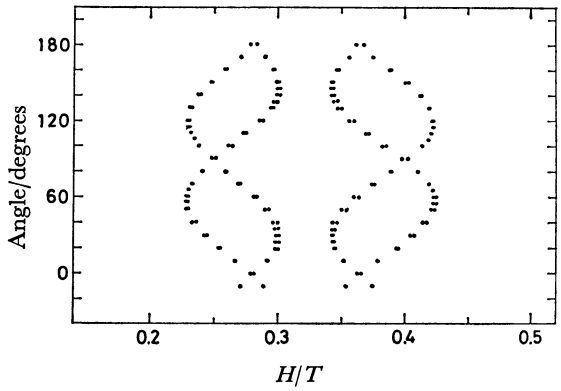

Fig. 4. Angular dependence of the resonance field strength. The magnetic field ***H*** is rotated in the ab plane.

For optical measurements, a 500-W xenon lamp was used for irradiation of the sample crystals directly immersed in the coolant. A saturated aqueous solution of nickel sulfate of 30-mm path length was used to cut the infrared radiation. Emissions from the samples were dispersed with a 750-mm Czerny-Turner-type spectrometer (RM-L21, Nalumi Co., Ltd.). The input signal to a picoammeter (TR-8651, Takeda Riken Industry Co., Ltd.) was obtained with a photomultiplier (R375, Hamamatsu TV Co., Ltd.). The spectra were recorded on a strip chart recorder (model 056, Hitachi, Ltd.), the phosphorescence decay curves being displayed on an oscilloscope (DS-5016, Iwatsu Electric Co., Ltd.) and photographed.

Results and Discussion

ESR Spectra in the ab Plane. Measurements with the external magnetic field ***H*** in the ab plane were carried out in order to confirm the mounting of the sample crystals, without using any particular wedge; the sample crystals were mounted with their cleavage surfaces directly attached to the bottom of the quartz rod. The results are shown in Fig. 4, where the zero degree on the ordinate axis approximately corresponds to the b axis. They closely resemble the corresponding results reported on phenanthrene in biphenyl,[12] except for the fact that eight resonances were found for BFQ, in general, instead of four for phenanthrene. As reported on quinoline, isoquinoline, 1,6-diazanaphthalene, *etc.*,[1-4] the doubling of the number of the resonances can be taken as an evidence for the deviation of fine-structure principal axes from the host molecular axes. It indicates that two magnetically inequivalent orientations are possible for the BFQ molecule at each of the two biphenyl lattice sites. For the sake of convenience, the two sites in a unit cell are designated as site A and site B, respectively, the quartz wedges in Fig. 3 being assumed to fit site A. Arabian numerals, 1 and 2, stand for the two inequivalent

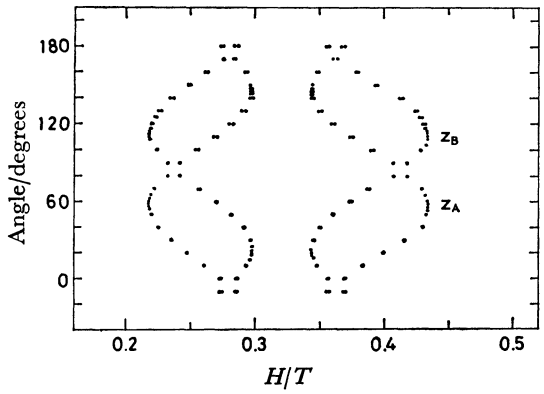

Fig. 5. Angular dependence of the resonance field strength. The magnetic field $\boldsymbol{H}$ is rotated nearly in the yz plane. The inclination of the wedge is 17.6°.

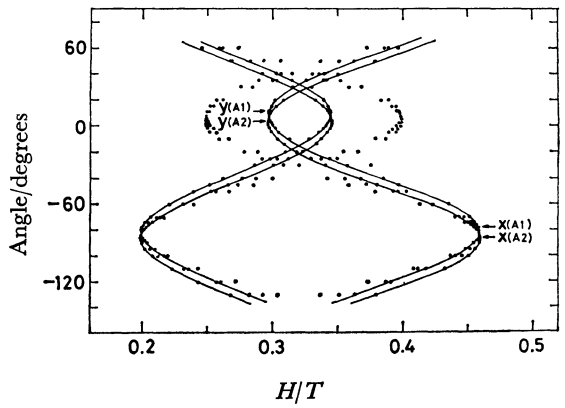

Fig. 6. Angular dependence of the resonance field strength. The mangetic field $\boldsymbol{H}$ is rotated nearly in the xy plane. The dihedral angle of the wedge is 104.8°. Points are experimentally obtained, while solid curves are drawn using the experimental D, E, and g values.

orientations at each site, respectively. Thus, magnetically the orientations of the BFQ molecules are distinguished from each other by the notations, A1, A2, B1, and B2. One of the two patterns (Fig. 4) corresponds to the lattice site for A1 and A2, and the other to that for B1 and B2. The two patterns are essentially the same except for the phase difference, as expected from the crystal structure of biphenyl. This shows that the ab plane has been identified properly in the mounting of sample crystals.

ESR Spectra in the yz Plane. On the basis of results from X-ray diffraction of the biphenyl crystal,[11a] the inclination of the surface of an appropriate wedge should be 17.7° (Fig. 3(a)), for rotation of the external magnetic field $\boldsymbol{H}$ in the M'N' plane of any one of the two biphenyl molecules in a unit cell. Four wedges of inclination in the range 14.4°—22.3° were used. The resonance fields obtained by rotating $\boldsymbol{H}$ nearly in the yz plane are shown in Fig. 5. The apparent principal value of the fine-structure tensor reaches a maximum for the inclination of 17.6° of the wedge surface, *viz.*, the largest separations correspond to the resonances with $\boldsymbol{H}$ on the z axes, the smallest those nearly on the y axes. The low-field transitions with $\boldsymbol{H}$ nearly parallel to the z axes shift to the higher fields for wedge inclinations differing from 17.6°. The spectra corresponding to orientations 1 and 2 are seen to draw closer togerher, coalescing into one spectrum as the directions of $\boldsymbol{H}$ rotates to coincide with the z axis, showing that the molecular planes of the two inequivalent guests at each of the two lattice sites, A and B, are parallel to each other within experimantal errors. Consequently, the angle between the two fine-structure z axes may lead to the dihedral angle between the planes of the A-site and B-site BFQ molecules. From the phase difference in the two distinct patterns (Fig. 5), the dihedral angle can immediately be estimated to be 55.0°, in contrast to 69.3° found for the corresponding dihedral angle between the two biphenyl molecules in a unit cell.[11] Thus, the molecular plane of BFQ is not parallel to that of biphenyl. In particular, the difference of 14.3° in the two angles indicates a decrease of 7° in the relative tilt of the guest plane as compared with the host. Similar observations have been reported by Vincent and Maki[1] for isoquinoline in durene, and by Brandon *et al.*[12] for phenanthrene in biphenyl. Hutchison and McCann studied in detail the system of phenanthrene-d_{10} in biphenyl with the aid of ENDOR at 2 K, reporting that a site of biphenyl is replaced by four differently oriented phenanthrene molecules, and that a maximum difference of 5° is found in the angles defined for the guest and host molecular planes.[13]

ESR Spectra in the xy Plane. Five wedges were used for measurements with $\boldsymbol{H}$ in the xy plane, *viz.*, LM plane, their dihedral angles being in the range 101.2°—106.0° (Fig. 3(b)); a maximum resonance field was realized with a wedge of the dihedral angle 104.8°, and with the b-axis orientation of 55.7° on the wedge surface. In these initial measurements in the xy plane, no account was taken of the fact that the molecular plane of BFQ deviates from that of biphenyl, the external magnetic field not being rotated exactly in the xy plane. In order to bring the external magnetic field exactly in the xy plane, we assumed that the host and guest molecular planes at each site make an angle in the range 6°—7°, on the basis of the finding on the yz-plane experiments. The angle determines the b-axis orientation on the wedge surface; for the angle 6°, the b-axis orientation should be 61.2° instead of 55.7° shown in Fig. 3(b), and for the angle 7°, it should be 62.2°. Measurements were carried out with the wedge of dihedral angle 104.8° and with the two b-axis orientations of 62.0° and 62.8°. Figure 6 shows the results obtained with the orientation of 62.0°. The separations for the resonance fields with $\boldsymbol{H}$ on the y axes are larger than the minimum separations in the yz-plane experiments (Fig. 5), reflecting the fact that the experiments did not sweep the y axes exactly. The L axes of the two sites A and B are parallel to each other, since the four resonances draw closer together and coalesce into one as $\boldsymbol{H}$ moves to the x axes. The coalescence makes it impossible to determine the angle between the principal x axes of A1 and A2 exactly. As for $\boldsymbol{H}$ parallel to the y

Table 2. Observed zero-field splitting parameters[a)]

	Benzo[*f*]quinoline[b)] in biphenyl	Phenanthrene[c)] in biphenyl	Benzo[*f*]quinoline[d)] in ethanol
D/cm^{-1}	±0.09926 (18)	±0.100430 (10)	+0.1023
E/cm^{-1}	∓0.04781 (6)	∓0.046576 (9)	−0.0477
$\|E/D\|$	0.4817	0.46377	0.466
g_{xx}	2.0024 (6)	2.0041	
g_{yy}	2.0018 (4)	2.00279 (5)	
g_{zz}	2.0018 (4)	2.00209 (5)	
θ/degrees	±4	0	

a) Numbers in parentheses are estimated standard deviations in units of the last signfiicant digit. b) This work. c) Ref. 12. d) Ref. 15.

axes, the relative deviation of the principal y axis of A1 from that of A2 was found to be 8° in the xy plane, so that the corresponding deviation of the x axes should also be 8°. In view of the observations on other aromatic nitrogen heterocyclic compounds,[1-4)] we assume that the deviation of the x axis from the L axis in A1 is as large in magnitude as and opposite in sign to that in A2. We thus obtain an in-plane rotation of 4° in the ZFS tensor, due to the introduction of a nitrogen atom in the phenanthrene skeleton.

ZFS Parameters. The ZFS parameters were determined by means of the procedure developed by Hutchison and Mangum.[14)] The canonical resonance fields H_{1x}, H_{2x}, H_{1y}, and H_{2y}, were determined from the measurements in the xy plane, whereas H_{1z} and H_{2z} were determined from those in the yz plane, where subscripts 1 and 2 refer to the low- and high-field resonances, respectively. The principal axes of the $\boldsymbol{g}$-tensor have been assumed to coincide with those of the fine-structure tensor, *viz.*, the ZFS tensor. The parameters fitting the spin Hamiltonian

$$\mathbf{H} = \beta \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2)$$

are given in Table 2.

The ZFS parameters of BFQ resemble those of phenanthrene in biphenyl,[12)] which confirms that the lowest excited triplet state of BFQ is of the $\pi\pi^*$ type. A remarkeble feature of the ZFS parameters in the phenanthrene-type compounds is the large E value. The E value of BFQ is slightly larger than that of phenanthrene, and the ratio $|E/D|$ of BFQ increases as compared with that of phenanthrerne by *ca.* 4%, suggesting that the spin distribution in BFQ would be more assymmetric than that in phenanthrene. In the ESR study of BFQ in ethanol glass performed by Gondo and Maki,[15)] the signs of D and E were determined to be plus and minus, respectively, by means of magnetophotoselection. The E value in the crystal is almost identical to that in the ethanol glass, whereas the D value is smaller than that in the ethanol glass by *ca.* 2%. Such variations were reported on quinoxaline[1a)] and on phenoxazine by Löhste *et al.*[16)] who suggested that the variations of the ZFS energies in phenoxazine might be due to the solvent polarities and the hydrogen bonding which may induce some change in the molecular geometry. It is not clear, however, what interaction is operative in the case of BFQ.

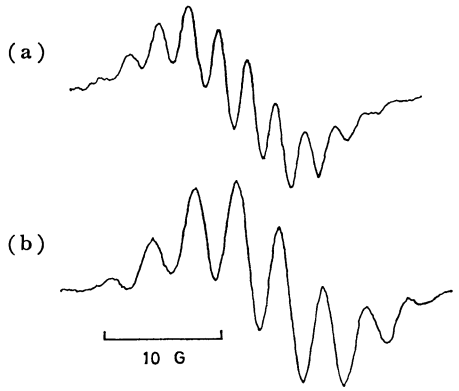

Fig. 7. Observed hyperfine structure of the triplet benzo[*f*]quinoline.
(a): High-field transition with $\boldsymbol{H}$//y, (b): low-field transition with $\boldsymbol{H}$//y.

Gondo and Kanda calculated the principal values and axes of the ZFS tensors for the $\pi\pi^*$ excited triplet states of some aromatic compounds, by employing the Pariser-Parr-type two-center Coulomb repulsion integrals and the core integrals of $\beta_{CC}=-2.39$ eV and $\beta_{CN}=-2.576$ eV.[17)] The results obtained for BFQ are $+0.1105\ cm^{-1}$, $-0.0582\ cm^{-1}$, and $+0.6°$, for D, E, and θ, respectively, where θ is the angle defined in Fig. 2(a). The calculated principal values confirm that the observed triplet state is of the $\pi\pi^*$ type. On the other hand, the calculated θ value would not determine the sign of the observed θ of ±4°, since the value is absolutely small.

Hyperfine Structure. The hyperfine structure of the triplet BFQ was observed for the magnetic field nearly parallel to the fine-structure x axis as well as y axis. The observed spectra are shown in Fig. 7. Although the hyperfine structure is apparently well resolved for the x axis, it is in fact complicated owing to overlapping of the signals due to the different sites. In order to aid the computer simulation of the hyperfine structure, the triplet spin densities given in Table 3 were calculated by an LCAO-SCF-MO-CI approach in which all the singly excited configurations were taken into account, and the Pariser-Parr and Nishimoto-Mataga approximations were adopted for the two-center Coulomb repulsion integrals. It should be noted that these two approximations give essentially the same spin densities for the nitrogen atom, although the Nishimoto-Mataga approximation gives much more

Table 3. Theoretical normalized spin densities ρ based on the Pariser-Parr (PP) and Nishimoto-Mataga (NM) approximations for Coulomb repulsion integrals

Atomic position[a)]	ρ(PP)	ρ(NM)
1	0.0411	0.0429
2	0.0433	0.0524
3	0.0621	0.0615
4	0.0148	0.0260
5	0.0614	0.0690
6	0.0248	0.0261
7	0.2104	0.1869
8	0.2064	0.1826
9	0.0418	0.0436
10	0.0668	0.0718
11	0.0716	0.0705
12	0.0225	0.0354
13	0.1024	0.1016
14	0.0277	0.0296

a) See Fig. 2(a).

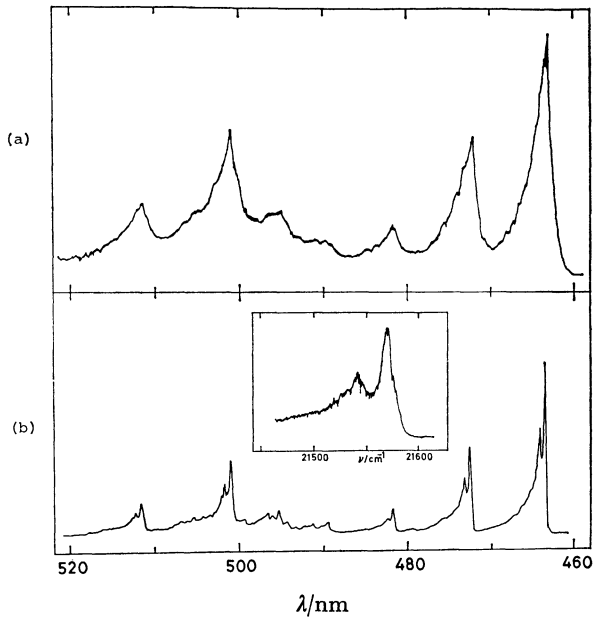

Fig. 8. Phosphorescence spectra of benzo[*f*]quinoline in biphenyl host; (a) at 77 K and (b) at 4.2 K. The insert in (b) shows the details around the 0,0-bands.

uniformly distributed spin densities for the carbon atoms than the Pariser-Parr.[18)]

Simulation of the hyperfine structure was performed by combining the calculated spin densities with the experimentally determined principal values of the hyperfine coupling tensor.[1,19)] The simulated spectra disagree definitely with those observed. The hyperfine structure of BFQ is expected to be complicated owing to its low molecular symmetry; even a small change in the spin distribution tends to provide quite a different hyperfine spectrum. Thus, for further clarification of the hyperfine structure and spin distribution, study on deuterated BFQ's is important.

Table 4. Phosphorescence lifetimes τ of benzo[*f*]-quinoline in biphenyl single crystals

Host	At 4.2 K		At 77 K	
	$\nu_{0,0}$/cm^{-1}	τ/s	$\nu_{0,0}$/cm^{-1}	τ/s
Biphenyl	21573	2.90	21575	2.08(2.2)[a)]
	21544	2.61		
Biphenyl-d_{10}	21570	2.83	21576	2.29(2.2)[a)]
	21540	2.57		

a) The values in parentheses were obtained from ESR signal decays.

Phosphorescence Spectra and Lifetimes. Figure 8 shows the phosphorescence spectra of BFQ in biphenyl observed at 77 K and 4.2 K. The obvious difference between the spectra is the multiplet splitting in the spectrum at 4.2 K, each vibronic band apparently consisting of a doublet. Hochstrasser and Noe reported similar multiplet splittings in the fluorescence and phosphorescence spectra of phenanthrene–biphenyl mixed crystals at 1.8 K.[20)] Enlarged features (Fig. 8(b)) are shown around the 0,0-band observed at 4.2 K, the splitting amounting to 29 cm^{-1} in biphenyl and to 30 cm^{-1} in biphenyl-d_{10}. These are considerably larger than the corresponding value of 11 cm^{-1} found for phenanthrene in biphenyl.[20)] The paramagnetic species observed as the triplet BFQ can be identified in part by the phosphorescence lifetimes (Table 4). The phosphorescence lifetime has been found to depend markedly on the solvents as well as temperature.[8)]

Orientation of the Guest Molecule in the Crystal. The angle of rotation of the z axis, *viz.*, N axis, of BFQ in biphenyl is slightly larger than that of phenanthrene in biphenyl.[12)] Such deviation of the principal axes of the guest molecules in the host crystal was studied by Hochstrasser and Small[21)] in connection with the site splittings in the electronic spectra. Their calculations suggest that we should not in general expect exact alignment of the principal axes of a guest and a host molecule. Since the volume occupied by a BFQ molecule is larger than that occupied by a biphenyl molecule, there would naturally be intermolecular interactions which would tilt the z axis of the guest molecule. Incidentally, the z axis of isoquinoline is tilted by 13° in durene,[1)] while that of 1,5-naphthyridine is tilted by 2° also in durene. These results indicate that the z-axis tilting in the aromatic nitrogen heterocyclic compounds would depend on the location of the nitrogen atoms in a complicated manner.

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