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Study of Conformers of 2,2′-, 3,3′-, and 4,4′-Dimethylbiphenyls in the Phosphorescent Triplet States by Electron Spin Resonance and Phosphorescence

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For the phosphorescent triplet (T_1) states of symmetrically-substituted dimethylbiphenyls, the relationship between the twisting angle of the two aromatic rings and the zero-field splitting parameters is discussed in terms of the ESR spectra. Two sets of ESR spectra observed for 2,2′- and 3,3′-dimethylbiphenyls (2DMBP and 3DMBP) are precisely assigned to the corresponding s-cis or s-trans conformer. The results clarify the inadequate assignment of the spectra of these molecular species in the previous literature. The lifetime obtained for the s-cis conformer is different from that of the s-trans one for both 2DMBP and 3DMBP. Examining the T_1–T_1 energy transfer from one conformer to the other, the relative locations for the T_1 states of s-cis and s-trans conformers are obtained, even if phosphorescence measurements do not provide each isolated spectrum: E_T (*s-cis*-3DMBP)<E_T(*s-trans*-3DMBP) and E_T(*s-cis*-2DMBP)>E_T(*s-trans*-2DMBP).

The geometry of biphenyl (BP) has been discussed under different conditions. In the ground (G) state BP is a nonplanar molecule and its twisting angle between the two phenyl rings is 20—40° in the vapor phase and in solutions,[1,2] while it is zero (or nearly zero) in a crystal.[3,4] In the lowest excited triplet (T_1) state, however, BP has been clarified to be planar[5,6] by the phosphorescence and T_n←G absorption measurements[7] as well as photochemical quenching data.[6] Several theoretical calculations[8–10] have supported the coplanar structure between two phenyl rings of BP in its T_1 state.

In the T_1 states, s-cis and s-trans conformers have been detected by ESR for some of biphenyl derivatives and their related molecules. For the ESR spectra of 2,2′-bipyridine (BPY), the s-cis and s-trans conformers are detectable.[11–13] However, their twisting angles (θ's) between the two aromatic rings are nearly zero, and one of the zero-field splitting (ZFS) parameters, D, is almost the same for both conformers.[11–13] As a result, the influence of any deviation from a coplanar structure upon the ZFS parameters could not be experimentally obtained. On the other hand, the dimethylbiphenyls (DMBP's)[††] are actually suitable examples in examining such an influence, since θ is expected to be changed without any large affection of the electronic structures upon the positions of the methyl substituents. Fourteen years ago, Scheve and Wagner[14] studied the ESR of the T_1 states of methyl-substituted biphenyls and found two sets of conformers for some of the DMBP's, although their assignment to the conformation is still uncertain. Their result is distinctly contradictory to the theoretical prediction that the D value decreases with increasing θ. Under these circumstances, we tried to reexamine the ESR of the symmetrically-substituted DMBP's.

In the present paper, we report on the ESR and phosphorescence of symmetrically-substituted DMBP's. For 2DMBP and 3DMBP, two sets of observed ESR spectra have been assigned to the corresponding s-cis and s-trans conformers using a stretched poly(vinyl alcohol) (PVA) film as a host. The spectra obtained for 2DMBP are remarkably different from those reported by Scheve and Wagner.[14] The relationship between the ZFS parameters and θ of the conformers will be discussed.

The ESR spectra observed in the T_1 states of DMBP's are interpreted by the following spin Hamiltonian:

$$\begin{aligned}\mathscr{H} &= g\mu_B \boldsymbol{B}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S}\\ &= g\mu_B \boldsymbol{B}\cdot\boldsymbol{S} - XS_x^2 - YS_y^2 - ZS_z^2 \quad (S=1)\\ &= g\mu_B \boldsymbol{B}\cdot\boldsymbol{S} + D[S_z^2 - (1/3)S^2] + E[S_x^2 - S_y^2]:\end{aligned}$$

where $\boldsymbol{D}(x,y,z)$ is the ZFS tensor with principal values ($-X$, $-Y$, and $-Z$) and principal axes (x,y,z). D and E denote the ZFS parameters and are related to ($-X$,$-Y$,

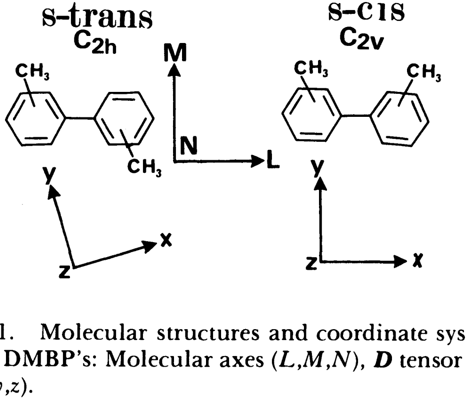

Fig. 1. Molecular structures and coordinate systems for DMBP's: Molecular axes (L,M,N), $\boldsymbol{D}$ tensor axes (x,y,z).

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[††] In the present paper, 2,2′-, 3,3′- and 4,4′-dimethylbiphenyls are abbreviated as 2DMBP, 3DMBP, and 4DMBP, respectively.

$-Z)$ by $D=(-3/2)Z$ and $E=(-1/2)(X-Y)$. The other symbols have their usual meanings. The anisotropy of the g tensor is neglected since the observed ESR spectra could be reasonably analyzed with the isotropic g_e for free electrons.

For the planar conformation of DMBP's in their T_1 states, the principal axes of $\boldsymbol{D}(x,y,z)$ and the molecular axes (L,M,N) are taken to be as shown in Fig. 1. For $\boldsymbol{D}(x,y,z)$, the x-axis is relatively close to the longest direction of the molecule, the y-axis is perpendicular to it in the molecular plane and the z-axis is normal to the molecular plane. For the molecules treated here, L is parallel to the central C–C bond that connects two of the same aromatic rings, M is perpendicular to it in the molecular plane, and N is normal to the molecular plane. For a stretched PVA film, s is the stretched direction, $\boldsymbol{c}$ is perpendicular to it in the film plane, and $\boldsymbol{n}$ is normal to the film plane.

Experimental

4,4′-Dimethylbiphenyl (Tokyo Kasei) was purified two times by recrystallization from its ethanol solution. 3DMBP (Tokyo Kasei) was distilled under reduced pressure (bp=114—115 °C/400 Pa). 2DMBP (Tokyo Kasei) was distilled under reduced pressure (bp=90 °C/153 Pa) and was further purified with a silicagel (Kanto Chemicals C-200) column using hexane as an elutant (more than five times). Three unremovable impurities still remained after only distillation. Two of them could be easily removed by column purification, though the other was very difficult to remove. At least four column purifications were required in order to obtain pure 2DMBP, which is sufficient for ESR and phosphorescence measurements. Hexane was the best elutant among the solvents studied. The solvents suitable for a rigid glass medium, ethanol (Wako S.S.G.) and methylcyclohexane (Dotite Spectrosol), were used without further purification after being carefully checked for the absence of an extraneous ESR and phosphorescence signals prior to use.

The purity of 2DMBP and 3DMBP was checked by gas chromatography (GC) with a Shimadzu GC-4A apparatus using a Shimadzu SE-30 column. They exhibited a single peak after purification (more than 99.95%). No impurities were spectroscopically detected for 4DMBP and BP by phosphorescence and ESR measurements.

The PVA films containing 2DMBP, 3DMBP, or 4DMBP were prepared following the same method as described previously.[15] The PVA sample films were prepared by the diffusion method using methanol solutions.[16] The standard concentrations of the 4DMBP, 3DMBP, and 2DMBP solutions used were 1.0×10^{-3}, 8.9×10^{-4}, and 8.3×10^{-3} mol dm^{-3}, respectively. The concentrations of the sample solutions for 3DMBP and 2DMBP were chosen in order to obtain the nearly equal intensities of spectra between s-cis and s-trans conformers. The PVA films obtained were stretched at 80 °C with Shibayama SS-60 film stretcher. The films, thus obtained, have about 200% of stretch in the stretched direction s.

Sample-cooling was controlled by the penetration rate of a quartz tube (5 mm o.d.) into liquid nitrogen from rapid cooling to 0.042 mm s^{-1}. For the magnetophotoselection experiments, a Glan-Thompson polarizer was placed between the Xe-Hg lamp and the sample cavity.

The ESR and phosphorescence spectra were measured at 77 K in the same way as reported previously.[13]

Results

The ESR spectrum of $\Delta M_S=\pm1$ transitions for the T_1 state of 4DMBP was measured in an ethanol glass, as shown in Fig. 2a. For the assignment of the observed signals to the corresponding magnetic principal axes of $\boldsymbol{D}(x,y,z)$, we measured the ESR spectra using a stretched PVA film as a host. According to the general relationships concerning the orientation of planar guest molecules in the stretched PVA films,[15,16] the assignment of the observed signals is straightforward, as shown in Figs. 2b ($\boldsymbol{B}/\!/\boldsymbol{s}$) and 2c ($\boldsymbol{B}/\!/\boldsymbol{n}$). As a result, we can reasonably assign all of the observed signals, as indicated in Fig. 2a.

For 3DMBP, the ESR of $\Delta M_S=\pm1$ transitions was measured in an ethanol glass. As shown in Fig. 2d, we clearly observed two sets of spectra, which are ascribed

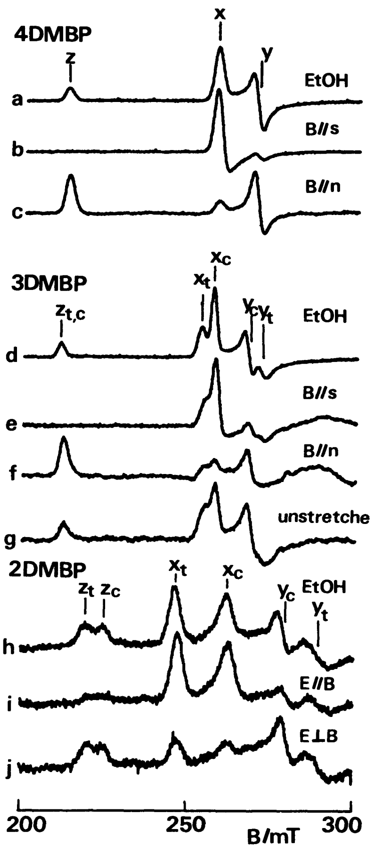

Fig. 2. ESR spectra of the low field $\Delta M_S=\pm1$ transitions for the T_1 state of 4DMBP in ethanol (a) and in PVA films [$\boldsymbol{B}/\!/\boldsymbol{s}$ (b) and $\boldsymbol{B}/\!/\boldsymbol{n}$ (c)], 3DMBP in ethanol (d) and in PVA films [$\boldsymbol{B}/\!/\boldsymbol{s}$ (e), $\boldsymbol{B}/\!/\boldsymbol{n}$ (f) and unstretched (g)], and 2DMBP in ethanol with no polarization (h) and in ethanol with $\boldsymbol{E}/\!/\boldsymbol{B}$ (i) and $\boldsymbol{E}\perp\boldsymbol{B}$ (j).

to the s-cis and s-trans conformers. The spectra resembled those reported by Scheve and Wagner.[14] As in the case of 4DMBP, the observed signals were reasonably assigned to the corresponding magnetic principal axes of $\boldsymbol{D}(x,y,z)$ using a stretched PVA film as a host,[15,16] as shown in Figs. 2e and 2f.

In a randomly oriented rigid glass, the assignment of two sets of spectra to the corresponding s-cis and s-trans conformers is generally impossible. Here, we tried to assign the observed two sets of spectra to the corresponding conformers with the help of the orientation of guest molecules in stretched PVA films.[11] For the s-cis conformer with symmetry C_{2v}, the principal x-axis is parallel to L ($x/\!/L$), while that of the s-trans one with symmetry C_{2h} should deviate from L to some extents. When $\boldsymbol{B}$ is applied parallel to s ($\boldsymbol{B}/\!/s$), the intensity of the x-signal for the s-cis conformer would be more enhanced than that for the s-trans one. For 3DMBP, the relative intensity of the x-signal at 260 mT to that at 256 mT was enhanced in stretched PVA films with $\boldsymbol{B}/\!/s$ [Fig. 2e], compared with that in unstretched PVA films [Fig. 2g]. As a result, a set of signals belonging to the x-signal at 260 mT was assigned to the s-cis conformer, and the other set of signals belonging to the x-signal at 256 mT was assigned to the s-trans one. The assignment carried out in this work disagrees with that by Scheve and Wagner,[14] possibly because of their unreasonable postulation that the larger anisotropic electron distribution in the molecular plane is for the s-cis conformer.

For 2DMBP, two sets of ESR spectra were also observed in an ethanol glass as shown in Fig. 2h. However, these obtained spectra were markedly different from those reported by Scheve and Wagner.[14] Furthermore, no dependence of cooling rate on the relative intensity between the two sets of spectra was found in our experiments (see, Experimental section), which is also contradictory to their report.[14] ^{1}H NMR and GC measurements supported that 2DMBP used here is extremely pure (more than 99.95%). In their ESR measurements, therefore, some impurities might be incorporated and their assignment on the basis of the cooling rate dependence seems to be meaningless.

We tried to assign the two sets of spectra to the corresponding s-cis or s-trans conformer, and each signal to the principal axes of $\boldsymbol{D}(x,y,z)$ using the stretched PVA film method. However, 2DMBP was tremendously difficult to incorporate into PVA films to obtain an ESR spectrum with sufficient intensity, even if a high concentration of 1.0×10^{-2} mol dm^{-3} was adopted. For the assignment of the principal axes of $\mathbf{D}(x,y,z)$, therefore, we used the magnetophotoselection method.[17] The main excitation path for 2DMBP is associated with the absorption of a strong band centered at around 250 nm, which shows mainly a long-axis polarization.[18] Therefore, the transition moment of 2DMBP at the wavelength of the exciting light used in this experiment is considered to be parallel (or nearly parallel) to L. If the electric vector of the exciting light ($\boldsymbol{E}$) is parallel to $\boldsymbol{B}$ ($\boldsymbol{E}/\!/\boldsymbol{B}$), the x-signals would be more enhanced than the other signals and be easily distinguishable from the others. As shown in Figs. 2i and 2j, the signals at 249 mT and 264 mT were more enhanced than the others with $\boldsymbol{E}/\!/\boldsymbol{B}$, indicating that these two signals are x-signals. The two sets of outer signals are assigned to the z-signals, since the character of the T_1 states of 2DMBP should not be largely different from that of BP because of the D values of ca. 0.1 cm^{-1} and the lifetimes of 2—4 s. The assignment of these two sets of spectra to the s-cis and s-trans conformers will be described in the following paragraph.

The ZFS parameters and the lifetimes obtained in the present work are listed in Table 1, including the D^* values obtained from the $B_{\min}$ signals. The D values are considered to be closely related to the twisting angle between two aromatic rings. From this table, the $|D|$ values for the s-cis and s-trans conformers of 3DMBP are almost identical within the resolution of our experiments and are close to that of 4DMBP. This

Table 1. ZFS Parameters, Lifetimes, τ, and 0–0 Energies of the $T_1 \rightarrow G$ Transitions, $\nu_{0\text{-}0}$ for BP and DMBP's in the T_1 States

Molecule	Host	$\lvert X \rvert$	$\lvert Y \rvert$	$\lvert Z \rvert$	$\lvert D \rvert$	$\lvert E \rvert$	D^*[a]	τ[b]	$\nu_{0\text{-}0}$
		cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	s	cm^{-1}
BP	EtOH	0.0406	0.0331	0.0738	0.1107	0.0037	0.1109	4.4	23010
s-trans-2DMBP	EtOH	0.0472	0.0192	0.0664	0.0996	0.0140	0.1010[c]	4.6	>24390[d]
s-cis-2DMBP	EtOH	0.0374	0.0259	0.0633	0.0950	0.0058	0.1010[c]	2.0	
s-trans-3DMBP	EtOH	0.0415	0.0296	0.0714	0.1070	0.0060	0.1068[c]	4.5	22670[e]
s-cis-3DMBP	EtOH	0.0391	0.0322	0.0714	0.1071	0.0035	0.1068[c]	4.2	
s-trans-3DMBP	PVA	0.0410	0.0304	0.0711	0.1067	0.0055	0.1061[c]	3.6	—
s-cis-3DMBP	PVA	0.0391	0.0319	0.0711	0.1067	0.0036	0.1061[c]	2.7	—
4DMBP	EtOH	0.0391	0.0315	0.0708	0.1061	0.0038	0.1059	4.4	22540
4DMBP	PVA	0.0390	0.0312	0.0707	0.1058	0.0039	0.1056	4.2	—

a) Obtained from the observed resonance field of the $\Delta M_S = \pm 2$ transition with Kottis–Lefebvre's correction.[23] b) Obtained from the x-signals of $\Delta M_S = \pm 1$ transitions. c) Could not be isolated for each conformer. d) Phosphorescence was broad with no vibronic structures. e) Phosphorescence could not be isolated for each conformer.

implies that the twisting angle of the T_1 state of 3DMBP is nearly the same and possibly zero for both s-cis and s-trans conformers. On the other hand, one of the $|D|$ values observed for 2DMBP was especially small among those for the other DMBP's and BP, while the $|D|$value of the other species is slightly smaller than those for the other DMBP's and BP. The twisting angle of the *s-cis*-2DMBP is considered to deviate substantially from zero due to the large repulsion between the two methyl substituents, though its deviation of *s-trans*-2DMBP would be small. From this consideration, the different features of one ESR spectrum from that of the others lead us to its assignment to the s-cis conformer.

The $|E|$ values for the s-cis conformers were smaller than those for the s-trans ones for both 3DMBP and 2DMBP. For a planar conformation, if the coordinate system is chosen to be in the same direction of the molecular axes (L,M,N), the nonzero off-diagonal elements of the $\boldsymbol{D}$ tensor appear only for the s-trans conformers with C_{2h}, while all of the off-diagonal elements are zero for the s-cis ones with C_{2v} from the viewpoint of their symmetries.[11] From this consideration, the $|E|$ value for the s-cis conformers should be smaller than that for the s-trans ones if the electron spin distribution is not much different from each other. The tendency of the $|E|$ values observed for 3DMBP would be simply explained by this analysis. For a discussion concerning 2DMBP with a nonplanar conformation in the T_1 state, a similar relationship is also valid, although further studies of other 2,2′-disubstituted biphenyls are required.

The lifetimes in the T_1 states of DMBP's were obtained from the decay of the low-field x-signals of the ESR spectra. All decay's were exponential over at least three times the lifetimes (within experimental error). For 3DMBP, the lifetime of the s-cis conformer (4.2 s) was different from that of the s-trans one (4.5 s). Although the difference was very small, it was beyond the experimental error. For 2DMBP, the lifetime of the s-cis conformer (2.2 s) was almost half of that of the s-trans one (4.6 s). The difference was quite large. Considering that the T_1 lifetimes of DMBP's except *s-cis*-2DMBP are very close to that of BP, the twisting angle of only *s-cis*-2DMBP would deviate to a great extent from zero, due to a steric hindrance between the two methyl groups.

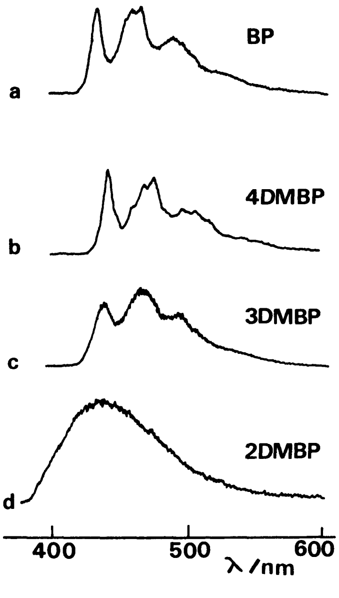

Fig. 3. Phosphorescence spectra of BP (a), 4DMBP (b), 3DMBP (c), and 2DMBP (e) in ethanol at 77 K.

The phosphorescence spectra for DMBP's were measured in ethanol at 77 K, as shown in Fig. 3. Especially for 2DMBP, the phosphorescence spectrum was very broad and did not show any vibronic structure. We could not isolate the phosphorescene of s-cis and s-trans conformers for both 2DMBP and 3DMBP. From the edge of the high-energy region, as well as the 0–0 bands of the phosphorescence, we estimated the locations of the T_1 states (E_T) for DMBP's and BP in the order of $E_T(\text{2DMBP}) > E_T(\text{BP}) > E_T(\text{3DMBP}) \sim E_T(\text{4DMBP})$.

The lifetimes for DMBP's in the T_1 states were also measured from the decay of phosphorescence. BP and 4DMBP showed the same lifetimes as those obtained by ESR (within experimental error). The decay of 3DMBP was almost single exponential at any wavelength monitored; however, it could not be discussed in detail because of the overlapping of the two types of phosphorescence with very close lifetimes of s-cis and s-trans conformers. On the other hand, 2DMBP showed a nonexponential decay because of the coexistence of the conformers with appreciably different lifetimes.

Discussion

An important question to be argued concerns the state, from which the s-cis and s-trans conformers detected in the T_1 states are formed. There are two possibilities: one is that these conformers are formed from the two species in the G states trapped in a rigid medium prior to excitation; the other is that they are formed in the excited states, S_1 and/or T_1, through the conformational change after excitation, even if a species with only one conformation is trapped in a rigid medium. Information related to this problem is provided by the dependence of the excitation wavelength and the kind of rigid media upon the ESR signal intensity ratio between the s-cis and s-trans conformers.

For 3DMBP the ESR spectra were measured in ethanol with various filter combinations. The results are shown in Figs. 4a—4c. The intensity of the ESR signal for the s-trans conformer relative to that for the s-cis one decreased under lower energy excitation. This indicates that two kinds of species with different

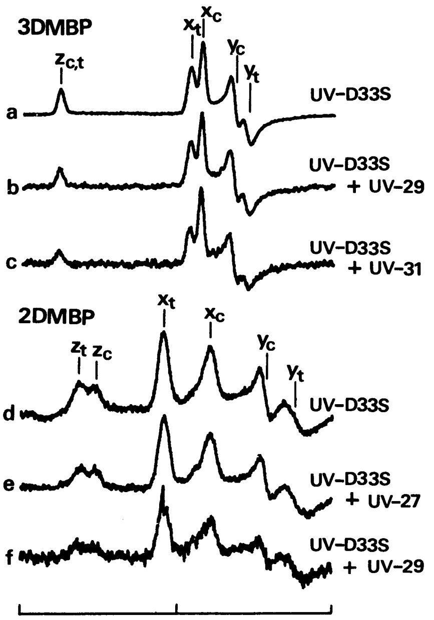

Fig. 4. ESR spectra of the low field $\Delta M_S=\pm1$ transitions for the T_1 state of 3DMBP in ethanol with UV-D33S (a), UV-D33S+UV-29 (b) and UV-D33S+UV-31 (c) excitation, and for 2DMBP in ethanol with UV-D33S (d), UV-D33S+UV-27 (e) and UV-D33S+UV-29 (f) excitation. The filters used, UV-D33S, UV-27, UV-29, and UV-31, cut off the shorter wavelength region and have transmittances of 50% at $\lambda\approx255$, 270, 290, and 310 nm, respectively. The UV-D33S filter also cuts off the longer wavelength region and has a transmittance of 50% at $\lambda=$ 385 nm.

absorption characteristics exist in the frozen media prior to excitation. The s-cis conformer arises from a species with longer wavelength absorption than the other, from which the s-trans conformer arises. The ESR spectra observed for 3DMBP were independent of the kind of frozen media, ethanol or methylcyclohexane, as shown in Figs. 5a and 5b, although two kinds of species with different conformations exist.

For 2DMBP, the dependence of the ESR spectra on the kind of frozen media was also studied using ethanol and methylcyclohexane, as shown in Figs. 5c and 5d. The intensity ratio of the ESR signal of the s-cis conformer to that of the s-trans one was distinctly influenced by the rigid media. This phenomenon shows the existence of two kinds of species trapped in the frozen media: that is, the s-cis and s-trans conformers are independently formed from the two kinds of species in their G states. No excitation wavelength dependence on the signal intensity ratio between the s-cis and s-trans conformers was observed, as shown in Figs. 4d—4f. This shows that the two species trapped in the frozen media are scarcely different from each other in their absorption characteristics.

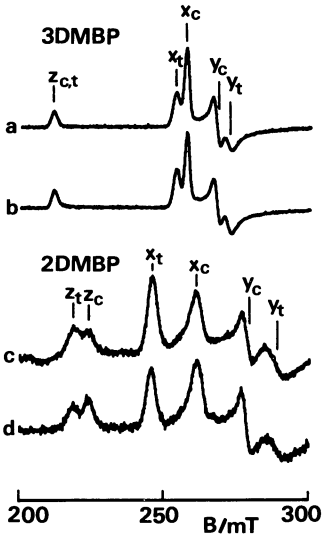

Fig. 5. ESR spectra of the low field $\Delta M_S=\pm1$ transitions for the T_1 state of 3DMBP in ethanol (a) and methylyclohexane (b), and 2DMBP in ethanol (c) and methylcyclohexane (d).

The phosphorescence spectra measured in this study did not give any information on the relative locations for the T_1 levels of the s-cis and s-trans conformers. The relative locations of the T_1 levels could be compared using the T_1–T_1 energy transfer from one conformer to the other, as has widely been admitted.[19–22] Regarding the ESR signal intensity ratio, the contribution of the energy transfer from the lowest singlet state of one conformer to that of the other is considered to be small owing to the relatively shorter lifetimes of the S_1 states than those of the T_1 states.

Figures 6a—6c show the ESR spectra of the low-field $\Delta M_S=\pm1$ transitions for 3DMBP in ethanol with concentrations of 5.4×10^{-2} to 8.9×10^{-5} mol dm^{-3}. The signal intensity ratio of the s-cis conformer to that of the s-trans one increased as the concentration of the samples increased. This indicates that the absorbed energy transfers from the T_1 level of the *s-trans*-3DMBP to that of *s-cis*-3DMBP. Thus, we can conclude that E_T(*s-trans*-3DMBP) locates higher in energy than E_T(*s-cis*-3DMBP).

For 2DMBP, the ESR spectra of the low-field $\Delta M_S=\pm1$ transitions were measured in ethanol, changing the concentration of 2DMBP from 8.3×10^{-2} to 8.3×10^{-5} mol dm^{-3}, as shown in Figs. 6d—6f. In this case the opposite trend to that for 3DMBP was obtained. As a result, we concluded that E_T(*s-trans*-2DMBP) locates lower in energy than E_T(*s-cis*-2DMBP).

Ortho methyl substituents were found to impede a coplanar conformation of the two aromatic rings, even in the T_1 state (especially for the s-cis conformer). *D* values and lifetimes were closely related to the twisting angle between the two phenyl rings. The results indicated that the $|D|$ value decreases with increasing the deviation of the twisting angles between the two

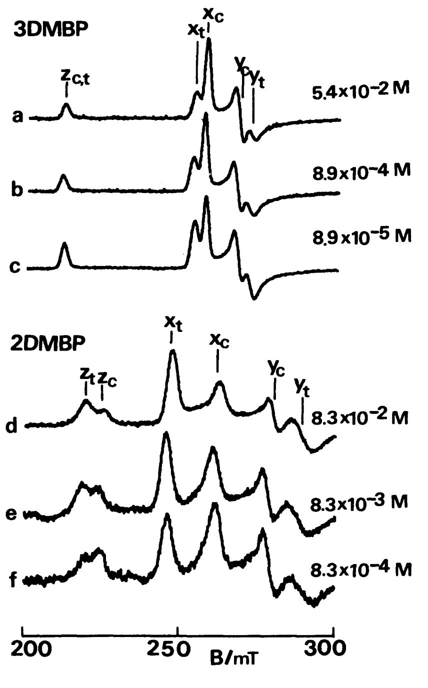

Fig. 6. ESR spectra of the low field $\Delta M_S=\pm1$ transitions for T_1 state of 3DMBP in ethanol of 5.4×10^{-2} mol dm^{-3} (a), 8.9×10^{-4} mol dm^{-3} (b), and 8.9×10^{-5} mol dm^{-3} (c), and for 2DMBP in ethanol of 8.3×10^{-2} mol dm^{-3} (d), 8.3×10^{-3} mol dm^{-3} (e), and 8.3×10^{-4} mol dm^{-3} (f). 1 M=1 mol dm^{-3}.

aromatic rings from zero, as was seen for *s-trans*-3,3′-dimethyl-2,2′-bipyridine.[11] This is quite the same conclusion as that deduced from a theoretical consideration on the spin delocalization in a biphenyl molecule. It should be noted here that in ESR spectroscopy the influence of methyl substitution in BP appears only for a change in the twisting angle. Further studies of other substituted biphenyls would systematically clarify the relationship between ZFS parameters and conformation, especially for the twisting angle.

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