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Electron Paramagnetic Resonance Studies of the Lowest Triplet States of Polyphenyl Molecules in Rigid Glasses

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Electron paramagnetic resonance (EPR) on the lowest excited triplet (T_1) states of polyphenyl [diphenyl(polyphenylene)] molecules were studied in rigid organic glasses at 77 K. We observed the very interesting differences among their three groups of *o*-, *m*-, and *p*-polyphenyls [diphenyl(poly(1,2-, 1,3-, and 1,4-phenylene)), respectively]. For *p*-polyphenyls, the $|D|$ value decreases with the increase of the number of the composed benzene rings, whereas it is scarcely changed at about 0.109 cm^{-1} for *m*-polyphenyls and at about 0.086 cm^{-1} for *o*-polyphenyls except for *o*-quaterphenyl. Because there are several conformers for *o*- and *m*-polyphenyls composed of more than three benzene rings, the $|E|$ values obtained are distinguishable in some cases of *m*-polyphenyls with planar conformations but could not generally be separable for *o*-polyphenyls with nonplanar conformations which have changeable twist angles around the C−C bond connecting the adjacent benzene rings. For the quaterphenyls having two different groups, the EPR spectra of *o*,*p*- and *m*,*p*-quaterphenyls [$C_6H_5-(1,2\text{-}C_6H_4)-(1,4\text{-}C_6H_4)-C_6H_5$ and $C_6H_5-(1,3\text{-}C_6H_4)-(1,4\text{-}C_6H_4)-C_6H_5$, respectively] are relatively close to that of *p*-terphenyl, whereas that of *o*,*m*-quaterphenyl [$C_6H_5-(1,2\text{-}C_6H_4)-(1,3\text{-}C_6H_4)-C_6H_5$] appears approximately to be a superposition of those of *o*- and *m*-terphenyls. These relations can be elucidated from the viewpoints of the geometrical and electronic structures. The lifetimes of their T_1 states (τ_p's) were measured from the decay curves of their EPR $B_{\min}$ signals. For *p*-polyphenyls, the τ_p decreases with the increase of the number of the composed benzene rings, whereas it is scarcely changed at about 5.0 s for *m*-polyphenyls and at about 2.2 s for *o*-polyphenyls except for *o*-terphenyl. These trends are generally similar to those of the $|D|$ values.

Introduction

Polyphenyl [diphenyl(polyphenylene)] molecules are composed of benzene rings (phenyl and phenylene groups) only without any other constituents. As a result, their lower excited states may be well elucidated by taking an account of both the local excitation of each benzene ring and some groups composed of a few benzene rings, in addition to the electron transfer between the above adjacent groups. Especially for the lowest excited triplet (T_1) state of these molecules, therefore, the zero-field splitting (ZFS) parameters obtained from the electron paramagnetic resonance (EPR) measurements are very interesting from the viewpoint of the dependence upon the molecular structure, in connection with the conjugation between the adjacent benzene rings. Nevertheless, these experimental values have not yet been published except for biphenyl,[1−7] terphenyls,[1,8] and 1,3,5-triphenylbenzene.[1]

Although there are several conformers for many kinds of polyphenyl molecules, their T_1 states can be classified into the following three types by taking the molecular structures into consideration: (1) molecules possessing a *p*-terphenylene group [$-C_6H_4-(1,4\text{-}C_6H_4)-C_6H_4-$], (2) those possessing a *m*-terphenylene group [$-C_6H_4-(1,3\text{-}C_6H_4)-C_6H_4-$], and (3) those possessing an *o*-terphenylene group [$-C_6H_4-(1,2\text{-}C_6H_4)-C_6H_4-$]. Actually, such a classification is not completely

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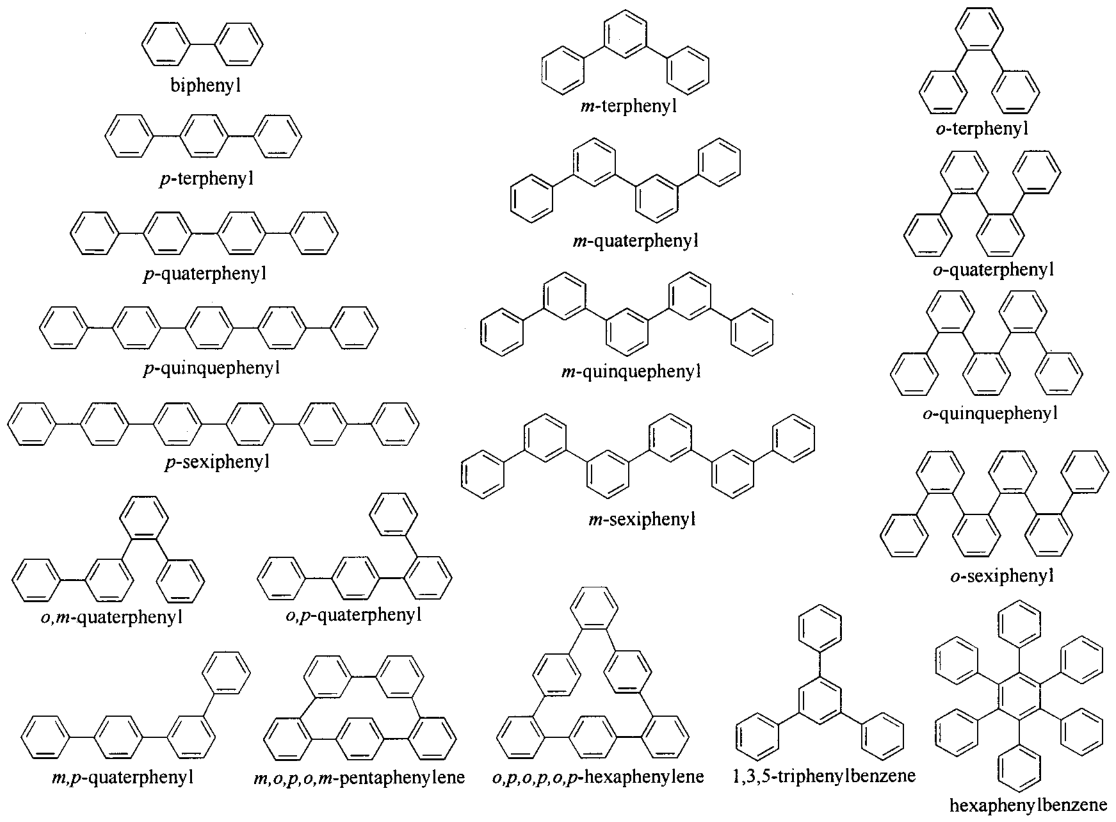

Figure 1. Typical structures of polyphenyl molecules studied in the present work.

separable, because some of the molecules have two or more different groups mentioned above. In the present work, the T_1 states of *o*-, *m*-, and *p*-polyphenyl molecules possessing only *o*-, *m*-, and *p*-terphenylene groups, respectively, are mainly treated by adopting the EPR method. Also some of the other polphenyls are briefly studied. The structures of the molecules studied are shown in Figure 1.

In the presence of a magnetic field (magnetic induction **B**), the EPR spectra of the T_1 states of molecules can well be interpreted by the following spin Hamiltonian:

$$\begin{aligned} H_S &= g\mu_B \mathbf{B}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} \\ &= g\mu_B \mathbf{B}\cdot\mathbf{S} + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \\ &= g\mu_B \mathbf{B}\cdot\mathbf{S} - XS_x^2 - YS_y^2 - ZS_z^2 \qquad (S = 1) \end{aligned} \tag{1}$$

Here, these symbols have their usual meaning and the anisotropy of g was disregarded. Because rigid organic glasses were used as hosts in the present work, the ZFS parameters are tentatively assumed as follows:

$$|X| \leq |Y| \leq |Z| = (2/3)|D| \tag{2}$$

For the magnetic axis system of planar molecules, therefore, the z axis is perpendicular to the molecular plane and the x and y axes are in the molecular plane. From the EPR experiments on biphenyl oriented in a single crystal[3,7] and in a stretched polymer-film,[9] it follows that the x and y axes are parallel to the short and long in-plane molecular axes, respectively, and the principal values of X, Y, and Z satisfy eq 2. However, in the present work, the directions of the x and y axes were not determined for the other polyphenyls because we used the sample solutions of randomly oriented molecules.

Experimental Section

Biphenyl; *o*-, *m*- and *p*-terphenyls (Tokyo Kasei); *m*-quaterphenyl (K & K Labs.); and 1,3,5-triphenylbenzene (Tokyo Kasei) were purified by recrystallization from ethanol (EtOH) solutions, and *p*-quaterphenyl (Tokyo Kasei) was purified from benzene. The other polyphenyls were prepared and purified by the methods described in papers by Ibuki and co-workers.[10] For examining the EPR spectra more carefully, *o*-quaterphenyl was newly synthesized using a different method from that described by Ibuki et al. as follows: The *o*-quaterphenyl was prepared by the coupling of 2-iodobiphenyl which was synthesized from 2-aminobiphenyl (Tokyo Kasei) by diazonium reaction with potassium iodide.[11] Then the *o*-quaterphenyl was purified by silica gel column chromatography with *n*-hexane, and by recrystallization from dry methanol (MeOH). The isolated white crystal (mp 118−119 °C) was formulated to be *o*-quaterphenyl (denoted hereafter as NS) on the basis of IR, mass spectroscopy (MS), and NMR experiments.[12]

2-Methyltetrahydrofuran (MTHF; Tokyo Kasei, G. R. Grade) was purified by passing through an activated alumina column eight times and thereafter by distillation. EtOH (Wako, S. S. Grade), MeOH, 2-methylcyclohexane, *n*-hexane (Dotite, Spectrosol), and 3-methylpentane (Tokyo Kasei, G. R. Grade) were used without further purification. All of the sample solutions were prepared at the concentration of 5×10^{-3} mol dm^{-3} except at that of 1×10^{-4} mol dm^{-3} for *p*-quaterphenyl and the saturated ones for *p*-quinquephenyl and *p*-sexiphenyl because of their low solubility in the solvents used.

Most of the EPR spectra were measured in MTHF at 77 K by a JEOL-JES-FE1XG spectrometer with 100 kHz magnetic

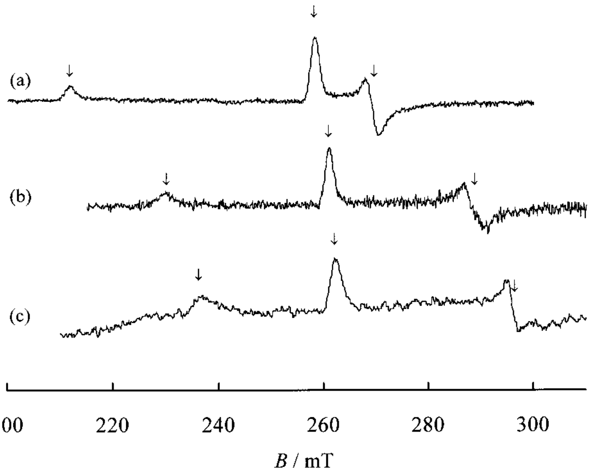

Figure 2. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of *p*-polyphenyl molecules in MTHF at 77 K: (a) biphenyl, (b) *p*-terphenyl, and (c) *p*-quaterphenyl.

TABLE 1: ZFS Parameters (cm^{-1}) and Lifetimes (s) Observed in Glassy Matrixes at 77 K

molecule	$\|D\|$	$\|E\|$	$D^{*\,a}$	$D^{*\,b}$	$\tau_p{}^c$
biphenyl	0.1090	0.0036	0.1092	0.1087	4.5
p-terphenyl	0.0924	0.0090	0.0937	0.0932	2.2
p-quaterphenyl	0.0864	0.0110	0.0884	0.0879	1.6
p-quinquephenyl				0.0856	
m-terphenyl	0.1094	0.0049	0.1097	0.1090	4.9
(*E*)-*m*-quaterphenyl	0.1086	0.0046	0.1089	0.1086	5.0
(*Z*)-*m*-quaterphenyl	0.1086	0.0006	0.1086		
m-quinquephenyl	0.1085	0.0047	0.1088	0.1084	5.0
	0.1084	0.0006	0.1085		
m-sexiphenyl	0.1085	0.0046	0.1088	0.1085	5.1
	0.1085	0.0007	0.1086		
o-terphenyl	0.0857	0.0156	0.0898	0.0902	1.4
o-quaterphenyl	0.0810	0.0195	0.0878	0.0899	2.2
	0.0795	0.0155	0.0839	0.0840	
	0.0675	0.0085	0.0691		
o-quinquephenyl	0.0864	0.0133	0.0894	0.0913	2.2
o-sexiphenyl	0.0865	0.0142	0.0899	0.0900	2.6
o,m-quaterphenyl A	0.0839	0.0170	0.0889	0.0883	1.3
B	0.1071	0.0054	0.1075	0.1067	4.0
o,p-quaterphenyl	0.0899	0.0088	0.0912	0.0896	2.3
m,p-quaterphenyl	0.0913	0.0092	0.0927	0.0928	2.6
m,o,p,o,m-pentaphenylene	0.1030	0.0060	0.1035	0.1026	3.0
o,p,o,p,o,p-hexaphenylene	0.0872	0.0079	0.0883	0.0874	2.0
1,3,5-triphenylbenzene	0.1107	0.0010	0.1107	0.1099	5.3

[a] $D^* = (D^2 + 3E^2)^{1/2}$. [b] Obtained from the $B_{\min}$ signal. [c] Obtained from the decay of the $B_{\min}$ signal.

field modulation at microwave frequencies close to 9.2 GHz. The excitations were carried out using an Ushio USH-500D 500 W mercury arc lamp or a Canrad-Hanovia 1 kW Xe−Hg arc lamp through 5 cm of distilled water and a Toshiba UV-D33S glass filter.

Experimental Results and Discussion

***p*-Polyphenyls.** For the T_1 states of biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl, the EPR spectra were measured in MTHF glasses. Only a $B_{\min}$ signal was observed for *p*-quinquephenyl, and any signal of the triplet state was not detectable for *p*-sexiphenyl. With increasing the number of the composed benzene rings, the intensity of the phosphorescence decreases, whereas that of the fluorescence increases. The observed spectra of the low-field $\Delta M_S = \pm 1$ transitions are shown in Figure 2. The ZFS parameters obtained are listed in Table 1. For the low-field $\Delta M_S = \pm 1$ transitions, the resonance field of the *Z* signal observed is lowest for biphenyl[9] and increases with an increasing number of the composed benzene rings. As a result, the $|D|$ (or D^*) value of ZFS parameter decreases in the same sequence, whereas the $|E|$ (or $|X - Y|$) value increases. This indicates that the spin delocalization increases with an increase in the size of the molecule along the long molecular axis because of the expansion of the conjugated system along the same direction. This is a quite different situation from the cases of *m*- and *o*-polyphenyls in which the spin localization occurs, as is discussed later. The line widths in these triplet signals scarcely changed. This is mainly because of the fact that the stable conformation is unique in the observed temperature range for each molecular species. This is also a different situation from the cases of *m*- and *o*-polyphenyls, with several conformers discussed later.

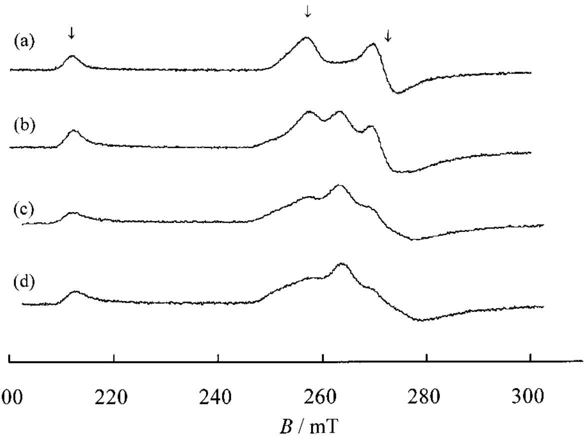

Figure 3. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of *m*-polyphenyl molecules in MTHF at 77 K: (a) *m*-terphenyl, (b) *m*-quaterphenyl, (c) *m*-quinquephenyl, and (d) *m*-sexiphenyl.

***m*-Polyphenyls.** For the T_1 states of *m*-terphenyl, *m*-quaterphenyl, *m*-quinquephenyl, and *m*-sexiphenyl, the EPR spectra were observed in MTHF glasses, and those of the low-field $\Delta M_S = \pm 1$ transitions are shown in Figure 3. The ZFS parameters obtained are listed in Table 1. Comparing these EPR spectra with those of *p*-polyphenyls, they showed the following different characteristic features: (1) the resonance fields of *Z* signals are observed at about 213 mT and scarcely change among *m*-polyphenyls studied; (2) for the molecules possessing at least four benzene rings, a signal near 265 mT is observable, and its intensity increases with increasing the number of the composed benzene rings *n*; and (3) all of the line widths are fairly broad compared with those of *p*-polyphenyls. For example, the well-fitted EPR spectra can be obtained using a Gaussian curve with a line width of 4 mT for *m*-terphenyl and with a line width of 3 mT for biphenyl.

In general, the line shape of the EPR spectrum changes more with increasing the number of the composed benzene rings. In that case, such a change is most remarkable between *m*-terphenyl and *m*-quaterphenyl and second between *m*-quaterphenyl and *m*-quinquephenyl. However, the difference in the EPR spectra between *m*-quinquephenyl and *m*-sexiphenyl is hardly appreciable. In this case, the samples were confirmed by their MS.

As shown by the EPR spectrum of *m*-quaterphenyl in Figure 3, a signal near 265 mT was clearly detected, in addition to the peaks corresponding to those observed for *m*-terphenyl. To clarify the origin of this peak, the EPR spectra were examined by using various solvents (MTHF, EtOH, MeOH, cyclohexane, *n*-heptane, and *n*-octane). The line shapes, the intensity ratios among the detected signals, and the observed resonance fields changed according to the solvent used. Further, the dependence of the line shapes upon the sample-cooling rate was observed

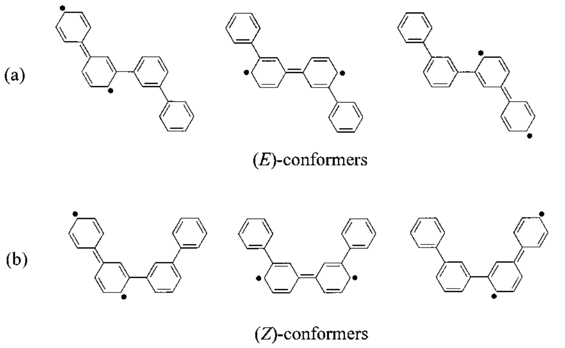

Figure 4. Main canonical structures of the T_1 state of *m*-quaterphenyl: (a) (*E*) conformer and (b) (*Z*) conformer.

by using EtOH glasses. In this case, the sample-cooling rate was controlled by changing the penetration rate of a quartz sample tube (5 mm o.d.) into liquid nitrogen. By reducing the penetration rate (1 mm/min), the line shape was remarkably changed from that of the rapidly frozen sample. These facts mean that the signals observed should be attributed to the conformers, not to the impurities.[13]

In the T_1 state of planar *m*-quaterphenyl, there are two kinds of conformers as shown in Figure 4. For these conformers, the *z* components of the **D** tensors (in the perpendicular direction to the molecular plane) are not much different from each other, because the interactions among the adjacent atoms, and also those among the second-nearest atoms, which make the most important contributions to the **D** tensor, scarcely change. As a result, the *D* (or *Z*) values of these conformers are nearly the same. On the other hand, the electron spin distribution of the (*E*) conformer is rather slender compared with that of the (*Z*) conformer, as can be supposed from their molecular conformations, and the $|E|$ value of the (*E*) conformer is expected to be larger than that of the (*Z*) conformer, as in the cases of 2,2′-bipyridine[14] and 3,3′-disubstituted biphenyls.[15,16] Although the observed EPR spectra are not well resolved, the ZFS parameters were determined by using the traceless relation of **D** tensors as follows: the *Z* peaks of these conformers almost coincide with each other, and the outer *X* and *Y* peaks are attributed to the (*E*) conformer, whereas the inseparable inner peaks near 265 mT are due to both the *X* and *Y* signals of (*Z*) conformer. As a result, the *E* value of (*Z*) conformer is close to zero. The intensity ratio between the peaks of the (*E*) and (*Z*) conformers does not change by using any selection of UV filters. Also, the decay curves of these peaks coincide with each other within our measurement. It is noted here that in EtOH or MTHF glasses another peak was detected as a shoulder of a *Y* signal near 250 mT, although it could not be observed in an *n*-heptane glass. Actually, this peak can be observed clearly when the sample-cooling rate was relatively slow (1 mm/min). Such a peak is possibly due to a nonplanar conformer, as was found for the T_1 state of 2,2′-bipyridine in 1-propanol−H_2O (*n*-PrOH−H_2O; 35 wt % of *n*-PrOH) at 77 K.[13]

For the T_1 state of a *m*-polyphenyl molecule which is composed of *n* benzene rings ($C_{6n}H_{4n+2}$), one should point out the fact that the main homopolar canonical structures can be constructed only from $(n - 2)$ benzene skeletons in their ground (G) states and a biphenyl one in its T_1 state. The typical example is illustrated for *m*-quaterphenyl in Figure 4, although a similar manifestation was already shown in the main resonance forms of *m*-terphenyl by Orloff and Brinen (Figure 5).[17] Similarly with the case of *m*-quaterphenyl, such canonical structures for the T_1 state of *m*-polyphenyls are stable in their planar forms because all of the benzene rings are constituents of the same conjugated system. Because the wave functions (WFs) of the T_1 states can approximately be constructed from the superposition of those corresponding to these canonical structures, the T_1 states of *m*-polyphenys are generally planar. Further, one can deduce the fact that the $|D|$ (or $|Z|$) values of *m*-polyphenyls are nearly the same as that of biphenyl, if the overlaps (or cross terms) among the WFs corresponding to these canonical structures are very small. Actually, such a condition is satisfied for the T_1 states of *m*-polyphenyls, as can be supposed from the case of *m*-terphenyl. That is, using the valence-bond method, the overlap between the WFs of the two most important canonical structures, Ψ_A and Ψ_B (shown in Figure 5), is only $\langle\Psi_A|\Psi_B\rangle = 1/64$ on the condition that the benzene rings are regular hexagonal, all of the C−C bond distances are equal, and all of the overlap integrals among the 2pπ atomic orbitals of carbon atoms are disregarded.[18] This value is supposed to be the largest value among *m*-polyphenyls. In evidence of this, the observed resonance fields of *Z* signals for *m*-polyphenyls scarcely change from near 212 mT of biphenyl, as described in the above feature of (1).

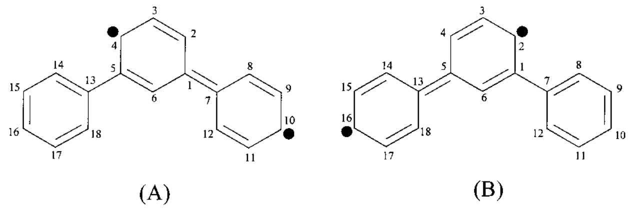

Figure 5. Two canonical structures of the T_1 state of *m*-terphenyl used in the VB calculation.

For *m*-polyphenyls composed of more than four benzene rings, the population of conformers possessing cis type structures increases upon increasing the number of the composed benzene rings *n*. As a result, the intensity of peak near 265 mT increases upon increasing the number of the composed benzene rings, as was described in the above feature (2). In these conformers, the $|E|$ values should be smaller than that of all-trans conformer, as in the case of (*Z*)-*m*-quaterphenyl, although each set of their ZFS parameters is slightly different from each other. Further, the conformations of the respective composed benzene rings for each conformer of *m*-polyphenyl molecule is not always quite the same. Also the existence of nonplanar conformers should not be negligible, as was detected as a peak near 250 mT for *m*-quaterphenyl. In consideration of these facts, the structures of *m*-polyphenyls in their T_1 states are not perfectly stiff in rigid glasses and the line widths become relatively broad compared with those of *p*-polyphenys, as described in the above feature (3).

***o*-Polyphenyls.** For the T_1 states of *o*-terphenyl, *o*-quaterphenyl, *o*-quinquephenyl, and *o*-sexiphenyl, the EPR spectra were observed in MTHF glasses, and those of the low-field $\Delta M_S = \pm 1$ transitions are shown in Figure 6. The ZFS parameters obtained from these peaks are listed in Table 1.[19] In these EPR spectra, we observed the following general characteristic features: (1) for the low-field $\Delta M_S = \pm 1$ transitions, the resonance fields of *Z* signals are apparently close to each other except for *o*-quaterphenyl and are distinctly high compared with those of *m*-polyphenyls and (2) the line widths are fairly broad compared with those of *p*-polyphenyls, especially for *o*-quaterphenyl.

In the case of *o*-quaterphenyl, the line shape of the spectrum is considerably deformed from those of the other *o*-polyphenyls, and a slight deformation is also observed in *o*-quinquephenyl. Such a situation was not improved even in the use of *o*-quaterphenyl-d_{10} ($C_6D_5-C_6H_4-C_6H_4-C_6D_5$). Thereupon, the

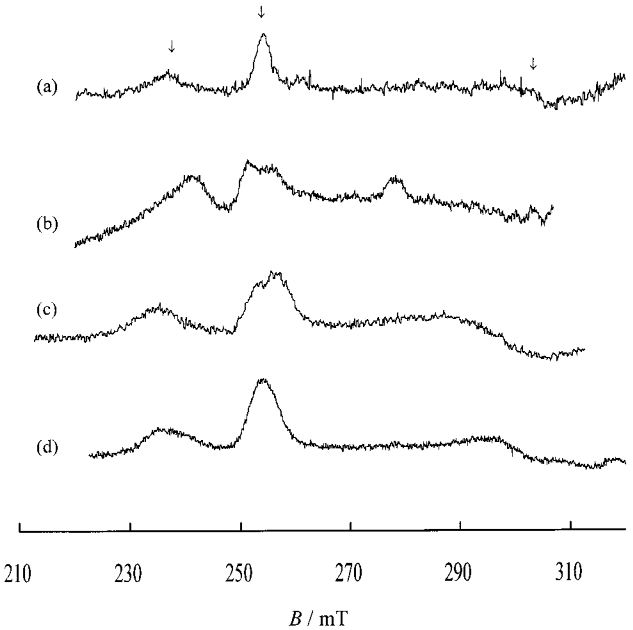

Figure 6. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of *o*-polyphenyl molecules in MTHF at 77 K: (a) *o*-terphenyl, (b) *o*-quaterphenyl, (c) *o*-quinquephenyl, and (d) *o*-sexiphenyl.

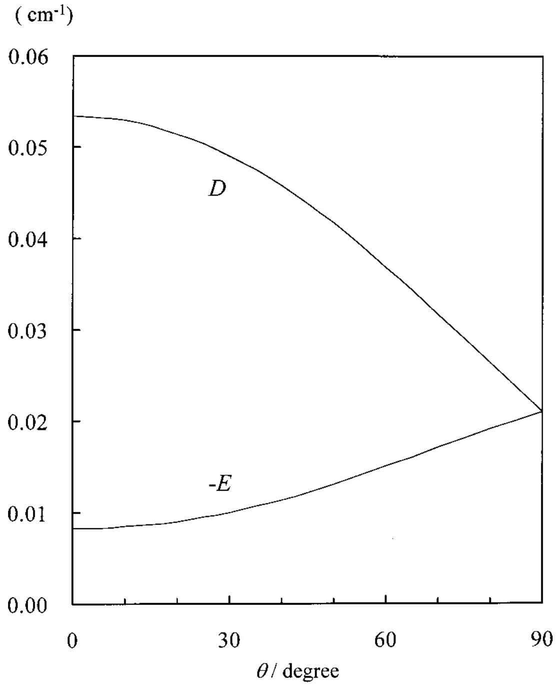

Figure 7. Angular dependence of the ZFS parameters of the T_1 state of the biphenyl molecule.

EPR spectra were examined by using various solvents (MTHF, EtOH, 3-methylpentane, *n*-hexane, and 2-methylcyclohexane). Consequently, the line shapes were a little changed, and some of the peaks with $\Delta M_S = \pm 1$ transitions were slightly separated depending on the solvents used. Using the sample of NS in an MTHF glass, the $B_{\min}$ signal was separated into two peaks giving $D^* = 0.0899$ and 0.0840 cm^{-1}. The former signal is fairly strong and relatively close to that of the other *o*-polyphenyls, whereas the latter is relatively weak and different from that of the other *o*-polyphenyls[20] and also *p*-quaterphenyl. The EPR spectrum of the low-field $\Delta M_S = \pm 1$ transitions observed in an MTHF glass is shown in Figure 6b.[21] By trying to reproduce this EPR spectrum as a superposition of Gaussian curves, we learned that the spectrum should be simulated using at least three fairly broad curves with different sets of ZFS parameters. One of the probable sets of the ZFS parameters listed in Table 1 shows that a set with the largest contribution is relatively close to that of the other *o*-polyphenyls, the next one gives $D^* = 0.0839$ cm^{-1}, whereas the other one is the origin of the peak near 278 mT. These facts suggest that the observed signals should not be attributed to impurities but to the various conformers, the mixing ratios of which are changeable according to the procedure adopted in the synthesis.

The *o*-polyphenyl molecules are nonplanar because of the steric hindrance among the composed phenyl and/or phenylene groups. Therefore, the overlaps between the π orbitals of the carbon atoms connecting the adjacent benzene rings are relatively small, compared with the cases of *m*-polyphenyls with planar structures. As can be seen in the T_1 states of *s-cis*-2,2′-dimethyl- and difluoro-biphenyls without coplanar benzene rings, the lack of the planar structure makes the decrease of $|D|$ (or $|Z|$) value with increasing the twist angle around the C−C bond connecting the adjacent benzene rings.[15,16] Such a tendency is illustrated for the T_1 state of the twisted biphenyl in Figure 7 using a simple calculation that the ZFS parameters are evaluated from the highest occupied and the lowest unoccupied orbitals obtained from Hückel MO method.[22,23] Although the obtained D values are actually smaller than the experimental value mainly because of the disregard of the configuration interaction (CI), the relative relation of the ZFS parameters can well be elucidated. Because the twist angles of *o*-polyphenyls are remarkably large compared with those of the above-mentioned cases of *s-cis*-2,2′-disubstituted biphenyls, the $|D|$ (or $|Z|$) values are considerably smaller than those of these molecules and also of *m*-polyphenyls. As a result, the resonance fields of the Z signals in the low-field transitions are distinctly high compared with those of *m*-polyphenyls, as described in feature (1).

Although all of the composed benzene rings should not be coplanar because of the steric hindrance, there remains faint conjugation among the π-electrons involved in the composed benzene rings. As a result, the D value of *o*-polyphenyl molecules should decrease upon increasing the number of the composed benzene rings if all of the twist angles around the C−C bonds connecting the adjacent benzene rings are nearly the same. Such a tendency is also obtainable by using the above simple evaluation as given in Table 2. However, this situation clearly disagrees with the observed D values which are generally close to each other. This may suggest the fact that in the T_1 states of *o*-polyphenyl molecules the T_1 character is mainly localized at a few benzene rings (possibly a biphenyl or an *o*-terphenylene group) and isolated from the other sites with near singlet character in the molecule. In this case, the twist angles around the C−C bonds connecting the moiety with near singlet character and the one with triplet character should be fairly large and near right angles, and the conjugation of the π-electron system between these two kinds of sites almost disappears.

According to the calculation of MOPAC97−PM3 including the CI arising from the single excitations from the first or second highest occupied orbital to the first or second lowest unoccupied orbital, the triplet sites in the T_1 states of *o*-polyphenyls are mainly localized at one of the side-biphenyl group in which the twist angle around the central C−C bond is about 20°. Further, the twist angle around the C−C bond connecting the second benzene ring belonging to the above side-biphenyl group with the T_1 character and the adjacent third benzene ring is about

TABLE 2: Calculated ZFS Parameters (cm^{-1}) of *o*-Polyphenyls

molecule	twist angle (degrees)	*D*	*E*	*D** [a]
biphenyl	0.0	0.0534	−0.0083	0.0552
	45.0	0.0438	−0.0122	0.0487
	60.0	0.0369	−0.0151	0.0452
o-terphenyl	0.0−0.0[b]	0.0451	−0.0067	0.0466
	45.0−45.0	0.0355	−0.0059	0.0369
	60.0−60.0	0.0311	−0.0060	0.0328
	23.5−71.8[c]	0.0483	−0.0080	0.0503
o-quaterphenyl	0.0−0.0−0.0[b]	0.0391	−0.0074	0.0412
	45.0−45.0−45.0	0.0285	−0.0076	0.0314
	60.0−60.0−60.0	0.0218	−0.0081	0.0259
	20.6−70.3−70.2[c]	0.0478	−0.0073	0.0494
o-quinquephenyl	0.0−0.0−0.0−0.0[b]	0.0348	−0.0072	0.0370
	45.0−45.0−45.0−45.0	0.0249	−0.0077	0.0283
	60.0−60.0−60.0−60.0	0.0192	−0.0074	0.0231
	24.3−71.1−63.0−67.2[c]	0.0455	−0.0071	0.0471

[a] $D^* = (D^2 + 3E^2)^{1/2}$. [b] Hypothetical conformation in which the interactions among the hydrogen atoms are disregarded. [c] Twist angles were obtained from the optimized T_1 structure by using MOPAC97-PM3.

70°. This is a quite different conformation from that of the respective ground state in which all the twist angles obtained are within the range of 60 ± 12° by using the MOPAC97-PM3 calculation.[24] As a result, the conjugation between the side-biphenyl group with the T_1 character and the adjacent third benzene ring almost disappears, as was inferred from the above experimental evidence. Although such a calculated result is not always final, this may suggest the trend obtained in feature (1). In Table 2, the twist angles evaluated for the *o*-polyphenyls in their T_1 states are listed, together with the ZFS parameters calculated using these twist angles adopting the above simple treatment. Although the ZFS parameters so obtained are fairly smaller than the experimental values, the trend of the dependence upon the number of the composed benzene rings is roughly elucidated.

From the above evidence, one may infer the fact that in *o*-quaterphenyl the change in the mixing ratio of the plural conformers makes the different line shape from the other *o*-polyphenyls. In this case, the peaks giving $D^* = 0.0899$ cm^{-1} are attributed to a conformer which has a triplet site localized mainly in a slightly twisted side-biphenyl group, whereas those giving $D^* = 0.0840$ cm^{-1} arise from another one in which some delocalization of π-electron spin occurs in the whole molecule. One of the possible models for the latter case is that a triplet conformer has two slightly twisted side-biphenyls and the twist angle around the C−C bond connecting these two groups is fairly large. With an increasing number of the composed benzene rings in the latter-type conformers, the distance between the above two side-biphenyl sites increases by the inserted benzene rings in the bridged part. As a result, the interaction between the side-biphenyl sites decreases rapidly and the *D* value appears to be close to that of the single slightly twisted side-biphenyl site. Nevertheless, a little deformation of the line shape still remains for *o*-quinquephenyl. For large *o*-polyphenyls, therefore, the B_{min} peak giving a smaller D^* value may be easily hidden in the peaks of the other conformers.

In the case of the ground (G) state of *o*-terphenyl in its crystal, the twist angles between the mean plane of the central phenylene ring and the two side phenyl rings are 62.1 and 42.5°.[25] This may show the fact that the twist angles in the *o*-polyphenyls are changeable because of the environmental effect even in the ground state. Further, the conformations of the composed benzene rings are also slightly changeable by the steric hindrance. Accordingly, the *o*-polyphenyls in their T_1 states are possible to take slightly different conformations in rigid glasses. As a result, the EPR spectra observed are not attributable to a pure species with a single conformation and give fairly broad line widths of the peaks, as described in feature (2). Therefore, the ZFS parameters of large *o*-polyphenyls given in Table 1 may generally represent the averaged values for the several conformers with slightly different structures.

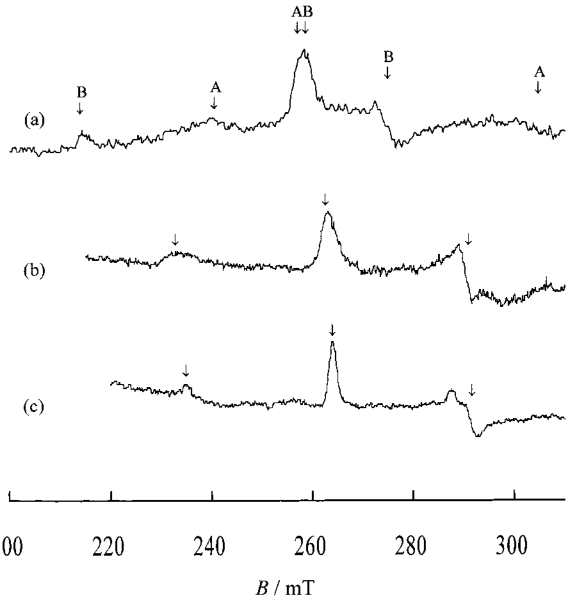

Figure 8. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of (a) *o*,*m*-quaterphenyl, (b) *o*,*p*-quaterphenyl, and (c) *m*,*p*-quaterphenyl in MTHF at 77 K.

Other Polyphenyls. The T_1 states of polyphenyls possessing two kinds of different groups were studied as in the cases described above. For *o*,*m*-, *o*,*p*-, and *m*,*p*-quaterphenyls [C_6H_5−(1,2-C_6H_4)−(1,3-C_6H_4)−C_6H_5, C_6H_5−(1,2-C_6H_4)−(1,4-C_6H_4)−C_6H_5, and C_6H_5−(1,3-C_6H_5)−(1,4-C_6H_4)−C_6H_5, respectively; see Figure 1], the EPR spectra were observed in MTHF glasses, and those of the low-field $\Delta M_S = \pm 1$ transitions are shown in Figure 8. The ZFS parameters obtained are listed in Table 1. The EPR spectra of *o*,*p*- and *m*,*p*-quaterphenyls are fairly close to that of *p*-terphenyl, whereas that of *o*,*m*-quaterphenyl consists of two different sets; that is, one set of the spectrum is relatively close to that of the *o*-terphenyl and another is fairly close to that of the *m*-terphenyl (denoted by A and B, respectively, in Figure 8a and in Table 1). This fact can be elucidated by the energy differences among the T_1 states of *o*-, *m*-, and *p*-terphenyls relative to the respective ground states. Actually the T_1-G energy separation is largest for *m*-terphenyl, and subsequently large for *o*-terphenyl, whereas that of *p*-terphenyl is smallest.[26] For the *o*,*p*- and *m*,*p*-quaterphenyls, the *o*-substituted phenyl group is rather perpendicular to the *p*-terphenylene site because of the steric hindrance, whereas the influence of the *m*-substituent upon the *p*-terphenylene site is very small. Therefore, the conjugation of the *p*-terphenylene site with the substituted phenyl group is fairly weak in these two species and the T_1 characters are mainly localized at their *p*-terphenylene group site in their molecules. As a result, the EPR spectra of these two kinds of molecules in their T_1 states appear to be fairly close to that of the *p*-terphenyl, although each EPR spectrum is slightly affected by the respective substituent, as clearly shown in the relative magnitude of $|D|$ value.

On the other hand, *o*,*m*-quaterphenyl is difficult to take simultaneously both the most stable conformation of *o*-terphenylene group and that of *m*-terphenylene group, because the

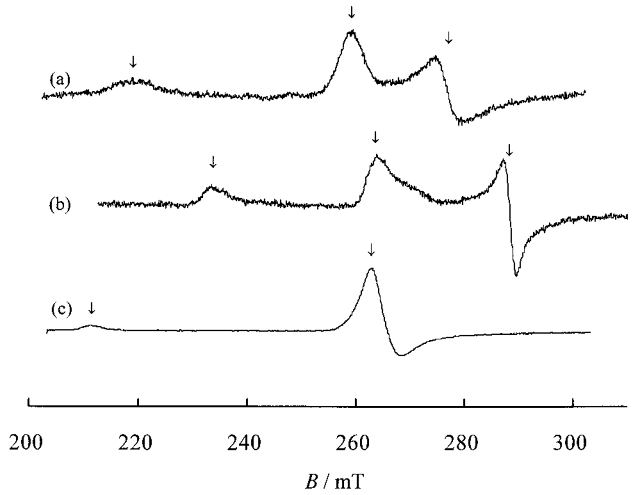

Figure 9. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 states of (a) *m,o,p,o,m*-pentaphenylene, (b) *o,p,o,p,o,p*-hexaphenylene, and (c) 1,3,5-triphenylbenzene in MTHF at 77 K.

benzene rings in the former structure are not coplanar with each other, whereas those in the latter one are generally coplanar. In this case, the side-phenylene parts of the *o*-terphenylene group are possible to twist rather easily around the C−C bond connecting the two benzene rings. As can be deduced from the results of biphenyl,[27,28] therefore, the T_1-G energy separation of the quaterphenyls possessing an *o*-terphenylene group is changeable and becomes close to or slightly larger than that possessing an *m*-terphenylene group when the twist angle around the C−C bond connecting the neighboring benzene rings changes. This suggests the fact that there are two typical conformers for *o,m*-quaterphenyl in the T_1 state; that is, one possesses a nearly planar *m*-terphenylene site connecting the *o*-substituted phenyl group near-perpendicularly, and another possesses a relatively stable nonplanar *o*-terphenylene site connecting the side-phenyl group at the *meta*-position where the influence of the substitution is not large. In a glassy matrix, such conformations are possible to appear especially for the molecules possessing large substituents, and the EPR spectrum of *o,m*-quaterphenyl becomes to be close to a superposition of those of *o*- and *m*-terphenyls. These facts suggest that the localization of the T_1 character at a small group site in a molecule is actually possible to occur for the T_1 states of many polyphenyl molecules.

In addition, the EPR spectra of the T_1 states of *m,o,p,o,m*-pentaphenylene and *o,p,o,p,o,p*-hexaphenylene were observed in MTHF glasses at 77 K, and those of the low-field $\Delta M_S = \pm 1$ transitions are shown in Figure 9. The ZFS parameters obtained are also listed in Table 1. The *p*-terphenylene groups in these molecules should not be planar because of the steric hindrance between the hydrogen atoms involved and these T_1-G energy separations are fairly larger than that of the free *p*-terphenyl molecule. As a result, the contribution of the *p*-phenylene group to the $|D|$ value of the molecules is apparently very small. The $|D|$ value obtained for the T_1 state of *m,o,p,o,m*-pentaphenylene is a little smaller than that of *m*-terphenyl possessing an *m*-terphenylene group. This may be due to the fact that the *m*-terphenylene groups in this molecule cannot perfectly take a planar conformation owing to the steric hindrance of one of the side benzene rings (the central benzene ring of the more twisted *o*-terphenylene group) against the central benzene ring of the *p*-terphenylene group. As a result, the T_1 character may mainly be localized at a deformed *m*-terphenylene site. On the other hand, the $|D|$ value obtained for *o,p,o,p,o,p*-hexaphenylene is a little larger than that of *o*-terphenyl and somewhat smaller than that of *p*-terphenyl, whereas the *E* value is not zero. This means that the T_1 state of *o,p,o,p,o,p*-hexaphenylne has no longer a trigonal axis, mainly because of the steric hindrance among the composed benzene rings. That is, in this nonplanar molecule, all of the three *o*-terphenylene groups are impossible to take simultaneously their most stable conformation that their side benzene rings are twisted in a same direction as that in the *o*-terphenyl crystal, because two of these *o*-terphenylene groups share the same side benzene ring (the central benzene ring in each *p*-terphenylene group). As a result of this, the molecule should deviate from a structure with C_3 symmetry and the T_1 character may mainly be localized at a deformed *p*-terphenylene site rather than a deformed *o*-terphenylene one.

For reference, the EPR study of 1,3,5-triphenylbenzene in its T_1 state was carried out under the same condition as described above. The ZFS parameters so obtained are fairly close to those observed in 3-methylpentane by Orloff and Brinen[17] except that the nonzero *E* value was obtained from the simulation of the EPR spectrum (see Table 1). The present result shows that 1,3,5-triphenylbenzene in the T_1 state actually loses a C_3 symmetry in the rigid glasses. The fact that the $|D|$ value is relatively close to that of *m*-terphenyl is distinctly due to the structure possessing the *m*-terphenylene-type groups. In a preliminary EPR measurement for the T_1 state of hexaphenylbenzene (Aldrich) observed in an MTHF glass at 77 K, the $|D|$ value is 0.092 cm^{-1} which is a little larger than that of *o*-terphenyl possessing an *o*-terphenylene group, possibly because the conformations of these *o*-terphenylene skeletons deform from that of the free T_1 *o*-terphenyl because of the steric hindrance among the phenyl groups. The $|E|$ value of 0.005 cm^{-1} showed that the molecule also loses not only a C_6 symmetry but a C_3 symmetry in its T_1 state.

Lifetimes. The T_1 lifetimes (τ_p's) for the polyphenyl molecules were measured from the decay curves of their $B_{\min}$ signals in MTHF glasses at 77 K. These values are also listed in Table 1. For *p*-polyphenyls, the τ_p decreases with increasing the number of the composed benzene rings. On the other hand, the τ_p's of *m*-polyphenyls are nearly the same values of about 5.0 s, whereas those of *o*-terphenyls are in a range of 2.4 ± 0.2 s, except that of *o*-terphenyl of 1.4 s. For the *o*- and *m*-polyphenyls, the values of τ_p's may be explained by the localization of the T_1 character within a small group site, possibly a biphenyl group, in the molecule, as was inferred from the *D* value in the last section. On the other hand, the S_1-T_1 energy separations of *p*-polyphenyls decrease upon increasing the number of the benzene rings involved owing to the expansion of the conjugated system, and the spin−orbit interaction between the S_1 and T_1 states increases because the magnitude of the small component of the S_1 character in the T_1 state depends inversely on the S_1-T_1 energy separation. As a result, the tendency of τ_p to the observed molecules are generally similar to that of the $|D|$ value.

For quaterphenyls possessing two different terphenylene groups, the τ_p's show a similar tendency to that of the $|D|$ values of these molecules. That is, the τ_p's of *o,p*- and *m,p*-quaterphenyls are slightly larger than that of *p*-terphenyl. On the other hand, the τ_p of *o,m*-quaterphenyl obtained from the $B_{\min}$ signal at the higher field ($D^* = 0.0883\ \text{cm}^{-1}$) is 1.3 s, which is fairly close to that of *o*-terphenyl, whereas that obtained from the $B_{\min}$ signal at the lower field ($D^* = 0.1067\ \text{cm}^{-1}$) is 4.0 s, which is rather close to that of *m*-terphenyl. This is due to the existence of two conformers as described in the previous section and also suggests the fact that the highest occupied and the lowest unoccupied orbitals are mainly localized approximately at some of small group site, possibly the side-biphenyl group, in a polyphenyl molecule, although they are influenced slightly by the other part of the molecule. By the way, the τ_p of 1,3,5-triphenylbenzene is fairly close to that of *m*-polyphenyl. For *m*,*o*,*p*,*o*,*m*-pentaphenylene and *o*,*p*,*o*,*p*,*o*,*p*-hexaphenylene, the τ_p's are distinctly different from that of *m*-terphenyl and *p*-terphenyl, respectively, possibly because of the fact that the benzene rings in these groups in their molecules are not coplanar.

Conclusion

From the EPR spectra and the T_1 lifetimes, the T_1 states of the polyphenyl molecules can generally be classified by three types with *o*- and *m*-terphenylene and *p*-polyphenylene groups. For *p*-polyphenyls, the $|D|$ value and τ_p decrease upon increasing the number of the composed benzene rings, wheras they are scarcely changed at about 0.109 cm^{-1} and 5.0 s, respectively, for *m*-polyphenyls possessing only *m*-terphenylene groups and at about 0.086 cm^{-1} and 2.4 ± 0.2 s, respectively, for *o*-polyphenyls possessing only *o*-terphenylene groups except $\tau_p = 1.4$ s of *o*-terphenyl. These facts can be rationalized by the localization of the T_1 character at some T_1 sites in these molecules. That is, the T_1 character of the *p*-polyphenyls is delocalized within the identical conjugated system extending over the whole molecules, and that of the *m*-polyphenyls is delocalized by the superposition of the T_1 states of biphenyl skeletons which are overlapping at one of the benzene rings in the biphenyl group with each other, whereas that of the *o*-polyphenyls is localized mainly at one of the side-biphenyl skeletons which is connected with the adjacent benzene ring so as to locate near-perpendicularly. Such a trend is also essentially preserved in the polyphenyl molecules possessing two different groups, although some structural deformation within these groups occurs.

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(12) The MS fragmentation revealed mother ion peak at $M = 306$, which agreed with the calculated value for *o*-quaterphenyl ($C_{24}H_{18}$). The ^1H NMR spectrum was assigned with the aid of NOESY spectrum as follows: (6.61 ppm, d,2H,2′,6′), (6.90 ppm, d,2H,3′,5′), (7.07 ppm, t,1H,4′), (7.16 ppm, d-d,1H,3), (7.33, m,2H,4,5), and (7.41 ppm, d−d,1H,6).

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(18) For example, $\Psi_A = A\chi_2\chi_3(\alpha\beta\text{-}\beta\alpha)\chi_4(\alpha)\chi_5\ \chi_6(\alpha\beta\text{-}\beta\alpha)\chi_1\ \chi_7(\alpha\beta\text{-}\beta\alpha)\text{-}\chi_8\ \chi_9(\alpha\beta\text{-}\beta\alpha)\ \chi_{10}(\alpha)\chi_{11}\ \chi_{12}(\alpha\beta\text{-}\beta\alpha)\chi_{13}\ \chi_{14}(\alpha\beta\text{-}\beta\alpha)\chi_{15}\ \chi_{16}(\alpha\beta\text{-}\beta\alpha)\chi_{17}\ \chi_{18}\text{-}(\alpha\beta\text{-}\beta\alpha)$, where χ_i ($i = 1-18$) is the 2pπ atomic orbital of carbon atom i shown in Figure 5A, A is the operator of antisymmetrization and normaliztion, and the assumption of $\int\chi_i\,\chi_j\,d\tau = 0$ ($i \neq j$) is made.

(19) In the case of *o*-quinquephenyl, the ZFS parameters were obtained by disregarding a slight splitting of the *Y* peaks.

(20) This situation is generally the same as that when the previous sample was purified by passing through a silica gel column with *n*-hexanes−ethyl ether (6:1), followed by recrystallization from petroleum ether, although these EPR spectra observed are slightly different from each other.

(21) This spectrum is fairly close to that using the previous sample in an EtOH glass.

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