J. Phys. Chem. A **2002,** *106,* 8609−8618

Conformations and Zero-Field Splittings in the Lowest Excited Triplet States of *meta*- and *para*-Polyphenyl Molecules

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Received: April 29, 2002; In Final Form: July 13, 2002

Using a stretched-polymer-film technique, we could assign the resonance fields in the electron paramagnetic resonance (EPR) spectra of the lowest excited triplet (T_1) states of *p*- and *m*-polyphenyl molecules [$C_6H_5-(1,4\text{-}C_6H_4)_{n-2}-C_6H_5$, $C_6H_5-(1,3\text{-}C_6H_4)_{n-2}-C_6H_5$, respectively] relative to the spin axes. In this case, the set of the zero-field splitting (ZFS) parameters is unique for a *p*-polyphenyl molecule but not for a *m*-polyphenyl molecule composed of more than three benzene rings. Taking the z axis as being perpendicular to the molecular plane and the x axis as being rather close to the longest direction of the molecule, we obtained interesting relations of the ZFS parameters to the conformation. The present calculations showed that for *p*-polyphenyl molecules the conjugated system is delocalized along the longest molecular axis and the $|Z|$ values decrease by an increase of the composing benzene rings and that for the *m*-polyphenyl molecules the T_1 character is localized at every composing biphenyl skeleton and the $|Z|$ values are almost unchanged. Concerning the relative values of ZFS parameters, we obtained that $|X| > |Y|$ for *p*-polyphenyl molecules whereas $|X| < |Y|$ for *m*-polyphenyl molecules. Adopting both the valence-bond and the molecular-orbital approximations, we clarified that such a difference arises from the deformation of the molecular structure by the steric hindrance among the composing benzene rings. In this case, we emphasized that the influence of the bond angles of the composing benzene rings is especially important in discussing the ZFS parameters of polyphenyl molecules in their T_1 states. Such a relation is illustrated by using the ZFS parameters of the deformed biphenyl molecule. Comparing the different sets of the ZFS parameters of a *m*-polyphenyl molecule, we clarified the existence of its conformers, which were assigned to their respective conformations, although the observed set of the ZFS parameters cannot always correspond to the single conformation.

Introduction

Polyphenyl [diphenyl(polyphenylene)] molecules are composed of benzene rings (phenyl and phenylene groups) without any other kinds of substituents. As a result, their lowest excited triplet (T_1) states can be well discussed by taking each composing benzene ring as a unit. Especially for the zero-field splitting (ZFS) parameters, the theoretical consideration is very interesting from the viewpoint of the dependence upon the molecular structure in connection with the conjugation between the adjacent benzene rings.[1] Nevertheless, the recent papers are mainly concerned about the Raman spectroscopy of *p*-polyphenyl molecules.[2]

In the previous paper,[1] we reported many interesting characteristic features on the T_1 states of polyphenyl molecules obtained through the electron paramagnetic resonance (EPR) measurements at 77 K. Because these experiments were carried out in rigid glasses in which the sample molecules are randomly oriented, each component of their ZFS tensors could not be assigned in connection with their molecular spin axes. From the sets of the ZFS parameters so obtained, therefore, the assignment of the corresponding conformers was not always possible.

To overcome these difficulties, the present work adopted the stretched-polymer-film technique[3] for the EPR measurements of the *p*- and *m*-polyphenyl molecules [$C_6H_5-(1,4\text{-}C_6H_4)_{n-2}-C_6H_5$, $C_6H_5-(1,3\text{-}C_6H_4)_{n-2}-C_6H_5$, respectively] in their T_1 states. Such an experiment has not yet been carried out for these molecular species, except for the biphenyl molecule.[4] Also, the work using a single crystal as a host was restricted to the biphenyl molecule.[5,6] The ZFS parameters thus obtained can be discussed in connection with the geometry of their conformers with aid of the theoretical consideration. Because the structures of these molecules in their T_1 states are expected to be nearly planar, the approximation within the π-electron framework can be adopted. This makes it possible to discuss the experimental behavior rather more easily compared with the cases of the nonplanar *o*-polyphenyl molecules [$C_6H_5-(1,2\text{-}C_6H_4)_{n-2}-C_6H_5$] in which every adjacent benzene ring is twisted around the C−C bond connecting these rings. The main conformations of the molecules treated in the present work are shown in Figure 1. In the present paper, the conformations of *m*-quinquephenyl and *m*-sexiphenyl are classified by using notations UV-*m*-quinquephenyl and UVW-*m*-sexiphenyl, re-

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10.1021/jp026038a CCC: \$22.00

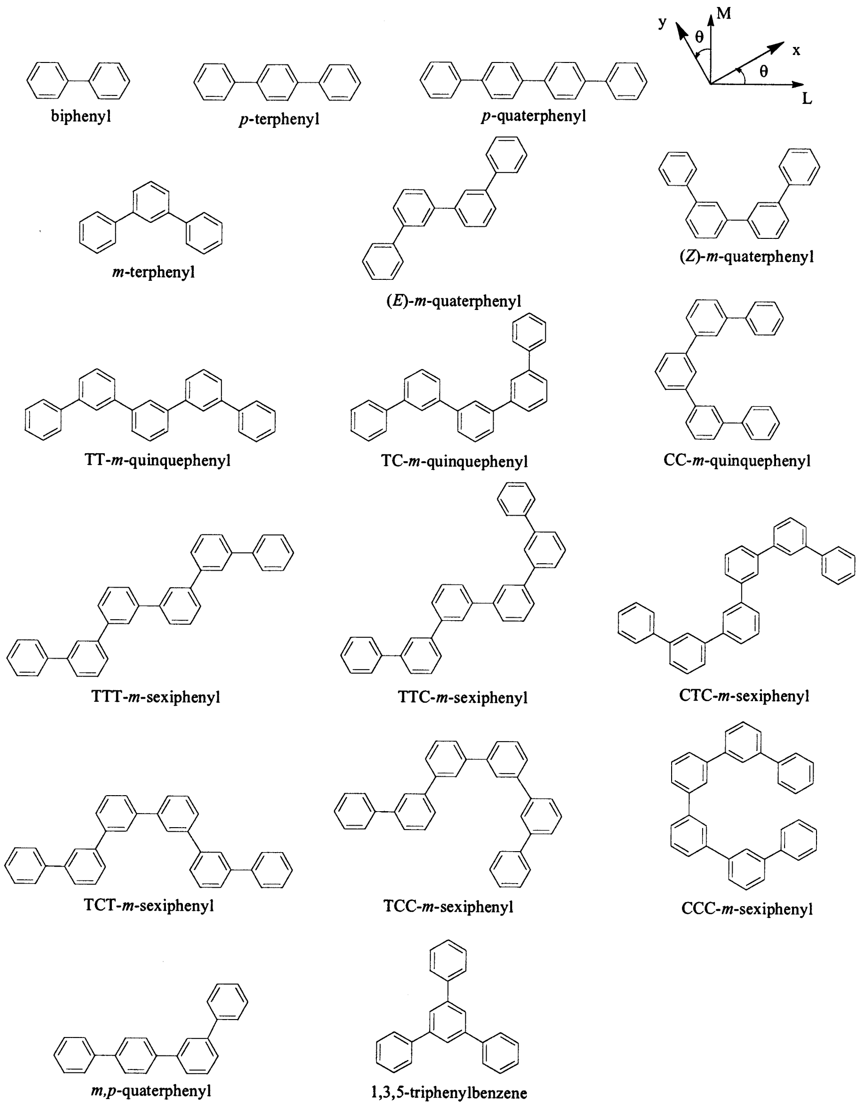

Figure 1. Main conformations of *m*- and *p*-polyphenyl molecules treated in the present work.

spectively. Here, U, V, and W indicate T (or C), which means the trans (or cis) conformation concerning the C−C single bond connecting the second−third, third−fourth, and fourth−fifth benzene rings, respectively, as shown in Figure 1.

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

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

Here, these symbols have their usual meaning and the anisotropy of *g* was disregarded. In the present paper, the magnetic axis system is taken as follows: the *z* axis is perpendicular to the molecular plane, the *x* axis is rather close to the longest direction of molecule in the molecular plane, and the *y* axis is perpendicular to the other axes.

Experimental Section

Samples of polyphenyl molecules and solvents used are the same as those used in the previous work.[1] The poly(vinyl alcohol) (PVA) films were obtained by the same method as described previously.[3,4] After the heat treatment, the swollen films were soaked in methanol (MeOH) solutions of samples until their appropriate amount was penetrated by diffusion. Thereafter, the films were stretched with about 200% of stretch in the stretched direction, **s**.

The EPR spectra were measured at 77 K by a JEOL-JES-FE1XG spectrometer. 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. The details of the experiments were almost the same as those in the previous works.[3,7]

Experimental Results

***p*-Polyphenyls.** The observed EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of biphenyl, *p*-terphenyl, and *p*-quaterphenyl in stretched PVA films are shown in Figures 2, 3, and 4, respectively. It is difficult to obtain PVA films containing a sufficient amount of the other *p*-polyphenyl molecules by diffusion in their MeOH solutions. For the *p*-polyphenyl molecules in their T_1 states, each stable conformation is restricted to be only one with planar form, as can be supposed from their canonical structures.

To determine the directions of the magnetic principal axes, the EPR spectra were measured in stretched PVA films by

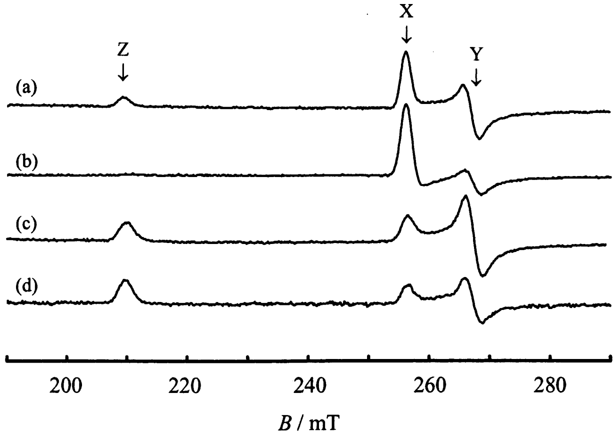

Figure 2. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of biphenyl molecule in (a) MeOH glass and stretched PVA films (b) **B**||**s**, (c) **B**||**c**, and (d) **B**||**n**.

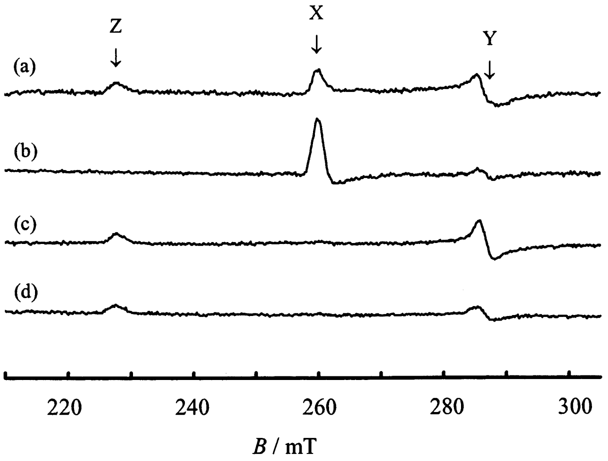

Figure 3. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of *p*-terphenyl molecule in (a) MeOH glass and stretched PVA films (b) **B**||**s**, (c) **B**||**c**, and (d) **B**||**n**.

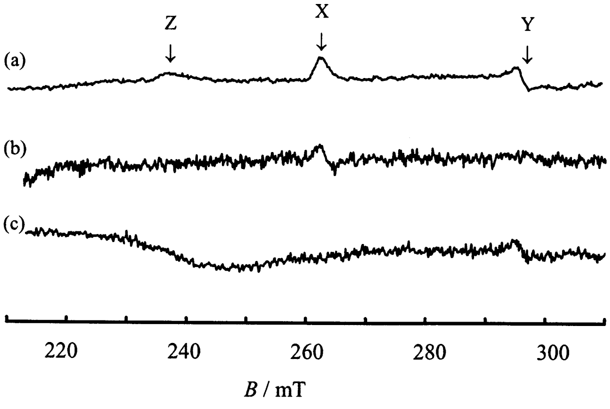

Figure 4. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of *p*-quaterphenyl molecule in (a) 2-methyltetrahydrofuran glass and stretched PVA films (b) **B**||**s** and (c) **B**||**c**.

TABLE 1: ZFS Parameters of *p*- and *m*-Polyphenyls[a]

molecule	*X*	*Y*	*Z*	*D*	*E*
biphenyl	0.0399	0.0327	−0.0727	0.1090	−0.0036
p-terphenyl	0.0398	0.0218	−0.0616	0.0924	−0.0090
p-quaterphenyl	0.0398	0.0179	−0.0576	0.0864	−0.0111
m-terphenyl	0.0312	0.0410	−0.0729	0.1094	0.0049
(*E*)-*m*-quaterphenyl	0.0313	0.0406	−0.0724	0.1086	0.0046
(*Z*)-*m*-quaterphenyl	0.0356	0.0368	−0.0724	0.1086	0.0006
m-quinquephenyl	0.0311	0.0405	−0.0723	0.1085	0.0047
	0.0356	0.0368	−0.0723	0.1084	0.0006
m-sexiphenyl	0.0313	0.0405	−0.0724	0.1085	0.0046
	0.0355	0.0369	−0.0724	0.1085	0.0007
m,*p*-quaterphenyl	0.0397	0.0213	−0.0609	0.0913	−0.0092
1,3,5-triphenylbenzene	0.0355	0.0375	−0.0738	0.1107	0.0010

[a] Experimental values in units of cm^{-1} are given.

applying the magnetic field parallel to the various directions of the films. According to the general relations concerning the orientation of guest molecules,[7] the assignment of the resonance field is straightforward. The intensity of the *X* signals is strong when the external **B** is parallel to the stretched direction of the film **s**, as shown in Figures 2b, 3b, and 4b. On the other hand, the intensity of *Y* signals is strong when the **B** is perpendicular to **s** in the film plane **c**, as shown in Figures 2c, 3c, and 4c. Further, the intensity of the *Z* signals is strong when the **B** is perpendicular to the film plane **n**, as shown in Figures 2d and 3d. Accordingly, all of the observed signals could reasonably be assigned. For the low-field $\Delta M_S = \pm 1$ transitions, the resonance field of the *Z* signal is observed to be the lowest and increases with increasing the number of the composing benzene rings. As a result, the $|Z|$ value of ZFS parameter decreases in the same sequence. On the other hand, the *X* signal is observed at lower field compared with the *Y* signal ($|Y| < |X| < |Z|$), as in the case of the T_1 state of biphenyl.[4−6] The ZFS parameters thus determined are listed in Table 1.

***m*-Polyphenyls.** In the previous work,[1] we obtained the following two distinct characteristic features of *m*-polyphenyl molecules: (1) The resonance fields of the *Z* signals are scarcely changed, and (2) for the molecules composed of at least four benzene rings, a signal near 265 mT was also observed. Such a signal shows the existence of at least two conformers. For the two conformers of *m*-quaterphenyl, their *Z* peaks are almost overlapped with each other and the outer *X* and *Y* peaks are attributed to the (*E*) conformer, whereas the inner peak near 265 mT is due to the *X* and *Y* signals of the (*Z*) conformer as mentioned in the previous work.[1]

To determine the directions of the magnetic principal axes, the stretched-PVA film technique was applied, as in the case of *p*-polyphenyls. For *m*-polyphenyls, the intensities of the detected EPR signals are not always sufficiently strong for the assignment, because the sample molecules are generally difficult to penetrate into the host PVA films. Exceptionally, the resolved EPR spectra could be observed only for *m*-terphenyl and *m*-quaterphenyl, as shown in Figures 5 and 6, respectively. For their low-field $\Delta M_S = \pm 1$ transitions, the resonance field of the *Z* signal is the lowest and is close to that of biphenyl. However, the *X* signal is observed at a higher field than the *Y* signal ($|X| < |Y| < |Z|$), as shown in Figures 5 and 6. This is a quite different feature from the results of biphenyl and *p*-polyphenyls in which the relation of $|Y| < |X| < |Z|$ is satisfied. In actuality, such a relation could not be explained without the deformations of the composed benzene rings from those of *p*-polyphenyls. The details of these reasons will be discussed carefully in the succeeding sections. For the other *m*-polyphenyls observed in the previous work,[1] the resonance fields were assumed to be in the same sequence. In the present experiment, however, we could not obtain any information about the difference in the direction of the spin axes, *x* and *y*, between (*E*) and (*Z*) conformers of *m*-quaterphenyl because of the low resolution of the EPR spectra shown in Figure 6. The ZFS parameters thus obtained are also listed in Table 1.

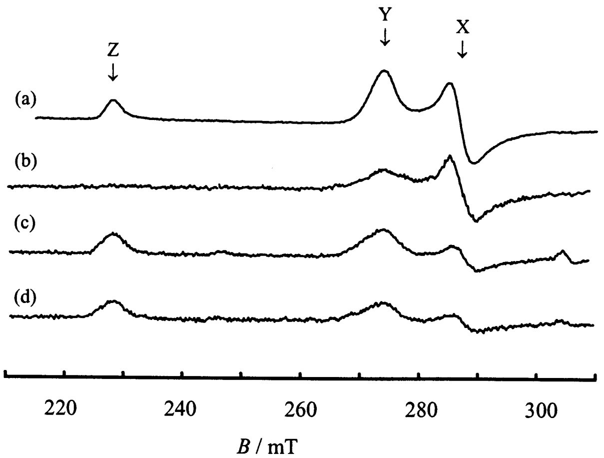

Figure 5. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of *m*-terphenyl molecule in (a) MeOH glass and stretched PVA films (b) **B**||**s**, (c) **B**||**c**, and (d) **B**||**n**.

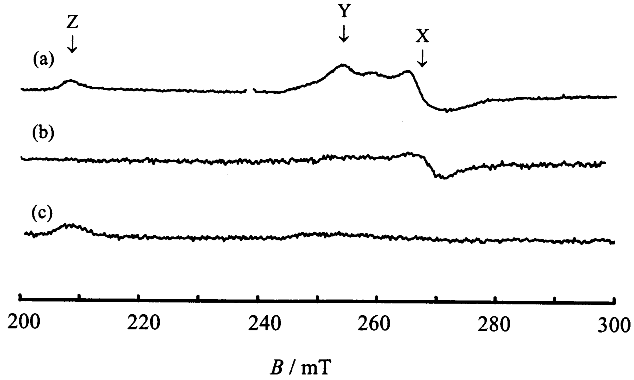

Figure 6. EPR spectra of the low-field $\Delta M_S = \pm 1$ transitions for the T_1 state of *m*-quaterphenyl molecule in (a) MeOH glass and stretched PVA films (b) **B**||**s** and (c) **B**||**n**.

Simplified Assignment Based on Valence-Bond Method for ZFS Parameters and Conformers in *m*-Polyphenyl Molecules

For the T_1 state of *m*-polyphenyl molecules, the number of their conformers increases with an increase of the composing benzene rings, as shown the typical conformations in Figure 1. However, the assignment of resonance fields was not possible for each conformer in the previous work,[1] because the molecules measured were randomly oriented in organic rigid glasses.

In the previous experiments,[1] we showed that the *Z* (or *D*) values of *m*-polyphenyl molecules are very close to that of the biphenyl molecule in its T_1 state. This fact can be well explained by taking the following main electronic structures into consideration.[1] First of all, we should remember the fact that the $T_1(\pi\pi^*)$ state of the benzene molecule is fairly high compared with that of biphenyl relative to each ground (G) state and the contributions of the T_1 state of the single benzene skeleton in the *m*-polyphenyl molecules are very small. For the T_1 states of *m*-polyphenyls (T_1 *m*-polyphenyls), which are composed of *n* benzene rings ($C_{6n}H_{4n+2}$), therefore, the main $(n-1)$ electronic structures can be well constructed from $(n-2)$ benzene skeletons in their G states and a biphenyl one in its T_1 state (T_1 biphenyl skeleton). In the present work, such structures are expressed as $[H-(C_6H_4)(G)_{i-1}-(C_6H_4-C_6H_4)(T_1)-(C_6H_4)(G)_{n-i-1}-H]$ $(1 \le i \le n-1)$. The corresponding wave functions (WFs) are denoted by Ψ_i's $(1 \le i \le n-1)$. Because the contributions of overlaps (or cross terms) among the canonical structures with the lowest energy (Ψ_i's) are very small in these molecules,[1] the total WF Ψ of the T_1 state in these molecules can be well constructed from these $n-1$ electronic structures with each nearly equivalent contribution.

$$\Psi \cong (n-1)^{-1/2}\sum \Psi_i \tag{2}$$

For simplicity, we assumed that the molecules treated are planar and all of the angles between the long axes of the two biphenyl skeletons sharing the same benzene ring are 120°. The ZFS tensors of the T_1 biphenyl skeletons in all of the structures Ψ_i's are transformed to the common magnetic axis system, and the ZFS tensor of a whole T_1 *m*-polyphenyl molecule is well obtained by superposing the transformed ZFS tensors of the T_1 biphenyl skeletons with each equivalent weight. After the transformation of the above ZFS tensor of the whole molecule to the principal axis system, the ZFS parameters and the directions of the principal spin axes of a T_1 *m*-polyphenyl molecule are easily obtainable.

Because the above transformation of magnetic axes can be carried out in the molecular plane, the *z* axis is preserved to be perpendicular to this plane as a rule. Therefore, the $|Z|$ (or *D*) value is unchanged from that of the T_1 biphenyl skeleton within the present approximation. This shows the fact that the $|Z|$ (or *D*) values of *m*-polyphenyls are nearly the same as that of the T_1 state of a free biphenyl (free T_1 biphenyl) molecule. However, as far as only the ZFS values of free T_1 biphenyl are used, the relation of $|X| > |Y|$ is still preserved after the above transformation of magnetic axes, as numerically given by the values marked (B) in Table 2.

For the steric interaction between the *ortho*-hydrogen atoms belonging to the adjacent benzene rings, there are $(n-2)$ hydrogen atoms concerned simultaneously with those of the two different adjacent benzene rings in the *m*-polyphenyls ($C_{6n}H_{4n+2}$) $(n \ge 3)$, whereas there is no such hydrogen atom in the *p*-polyphenyls. This fact suggests that the conformations of the composing benzene rings in the *m*-polyphenyls are essentially different from those of the *p*-polyphenyls. To confirm this fact, the ZFS parameters of the T_1 biphenyl skeleton were tentatively deduced from the experimental values for the T_1 state of *m*-terphenyl (T_1 *m*-terphenyl) by adopting the above transformation in the reverse order. In this case, the WF used was constructed from the two electronic structures corresponding to $[(C_6H_5-C_6H_4)(T_1)-(C_6H_5)(G)]$ and $[(C_6H_5)(G)-(C_6H_4-C_6H_5)(T_1)]$. If the angle between the long axes of these biphenyl skeletons is assumed to be 120°, the ZFS parameters obtained for the T_1 biphenyl skeleton in the T_1 *m*-terphenyl are as follows: $X = 0.0263$, $Y = 0.0459$, and $Z = -0.0729$ cm^{-1}. These values distinctly satisfy the relation of $|X| < |Y|$ for *m*-polyphenyls.

Hereupon, the *X* and *Y* values of all of the planar conformers for the other *m*-polyphenyls $C_{6n}H_{4n+2}$ were intended to be evaluated by using the *X* and *Y* values obtained from the T_1 biphenyl skeleton in the T_1 *m*-terphenyl described above. The ZFS parameters thus obtained generally satisfied the relation of $|X| < |Y|$ as given by the values marked (T) in Table 2, although there remains some ambiguity when *X* is close to *Y*. However, some sets of these ZFS parameters are not always different among the respective conformers of the same molecular species. For the conformers giving the same calculated ZFS values, only a single set of the EPR peaks was apparently observed within the resolution of our EPR equipment, possibly because the ZFS parameters of these conformers are indistinguishably different from each other. These facts suggest that the T_1 biphenyl skeletons in the T_1 *m*-polyphenyls are essentially different from that of the free T_1 biphenyl. The origin of such

TABLE 2: Calculated ZFS Parameters (cm^{-1}) and the Direction of the *x* Axis, θ (deg)[a], for *m*-Polyphenyls Assigned by Using the Simplified VB Method

molecule			X	Y	Z	D	E	θ
biphenyl		expt	0.0399	0.0327	−0.0727	0.1090	−0.0036	
		(T)	0.0263	0.0459	−0.0729	0.1094	0.0098	0.0
m-terphenyl		expt	0.0312	0.0410	−0.0729	0.1094	0.0049	
		(B)	0.0381	0.0345	−0.0727	0.1090	−0.0018	0.0
m-quaterphenyl		expt	0.0313	0.0406	−0.0724	0.1086	0.0046	
	(*E*)	(T)	0.0304	0.0418	−0.0729	0.1094	0.0057	45.0
		(B)	0.0384	0.0342	−0.0727	0.1090	−0.0021	45.0
		expt	0.0356	0.0368	−0.0724	0.1086	0.0006	
	(*Z*)	(T)	0.0361	0.0361	−0.0729	0.1094	0.0000	0.0
		(B)	0.0363	0.0363	−0.0727	0.1090	0.0000	0.0
m-quinquephenyl		expt	0.0311	0.0405	−0.0723	0.1085	0.0047	
	TT	(T)	0.0312	0.0410	−0.0729	0.1094	0.0049	0.0
		(B)	0.0381	0.0345	−0.0727	0.1090	−0.0018	0.0
		expt	0.0356	0.0368	−0.0723	0.1084	0.0006	
	TC	(T)	0.0336	0.0386	−0.0729	0.1094	0.0025	30.0
		(B)	0.0372	0.0354	−0.0727	0.1090	−0.0009	30.0
	CC	(T)	0.0336	0.0386	−0.0729	0.1094	0.0025	0.0
		(B)	0.0372	0.0354	−0.0727	0.1090	−0.0009	0.0
m-sexiphenyl		expt	0.0313	0.0405	−0.0724	0.1085	0.0046	
	TTT	(T)	0.0309	0.0413	−0.0729	0.1094	0.0052	20.4
		(B)	0.0382	0.0344	−0.0727	0.1090	−0.0019	20.4
	TCT	(T)	0.0322	0.0400	−0.0729	0.1094	0.0039	0.0
		(B)	0.0377	0.0349	−0.0727	0.1090	−0.0014	0.0
		expt	0.0355	0.0369	−0.0724	0.1085	0.0007	
	TTC	(T)	0.0341	0.0381	−0.0729	0.1094	0.0020	30.0
		(B)	0.0370	0.0356	−0.0727	0.1090	−0.0007	30.0
	TCC	(T)	0.0341	0.0381	−0.0729	0.1094	0.0020	−30.0
		(B)	0.0370	0.0356	−0.0727	0.1090	−0.0007	−30.0
	CTC	(T)	0.0341	0.0381	−0.0729	0.1094	0.0020	0.0
		(B)	0.0370	0.0356	−0.0727	0.1090	−0.0007	0.0
	CCC[b]	(T)	0.0341	0.0381	−0.0729	0.1094	0.0020	0.0
		(B)	0.0370	0.0356	−0.0727	0.1090	−0.0007	0.0

[a] Angle of the *x* axis from the *L* axis (see Figure 1). [b] Hypothetical planar conformation in which the interactions among the hydrogen atoms are disregarded: (T) using the ZFS parameters of the composing biphenyl skeletons obtained from those of *m*-terphenyl and (B) using the ZFS parameters of the composing biphenyl skeletons obtained from those of the free biphenyl.

differences can adequately be explained from the deformation of benzene rings, as in the case of quinoid and antiquinoid forms in the T_1 state of benzene molecule[8] (see also Appendix). As a result, all of the benzene rings approximately become close to the structures of the T_1 *m*-terphenyl rather than those in the free T_1 biphenyl, as will be described in the succeeding section.[9] In this case, it is possible to improve partly the present results by changing the molecular geometry, especially by changing the angles between the long axes of the biphenyl skeletons sharing the same benzene ring from 120° and by taking account of slightly different ZFS parameters of the inner biphenyl skeletons from those of the side ones and so on. However, we did not carry out such modifications extensively, because the present purpose is obtaining the general trend of the ZFS parameters not the apparent numerical agreement with the experimental values within the present simple treatment.

Molecular Orbital Considerations

Biphenyl. Biphenyl is the simplest polyphenyl molecule and the T_1 state of its skeleton is one of the fundamental units of the planar T_1 *m*-polyphenyl molecules, as described in the previous paper.[1] Before discussing the T_1 states of polyphenyl molecules extensively, the T_1 state of the biphenyl molecule should carefully be examined from the theoretical viewpoint. Because the molecular structure of the free T_1 biphenyl is planar or nearly planar, the ZFS parameters were evaluated from the electron spin−spin interaction by the molecular orbital (MO) method adopting the treatment within π-electron framework as was used in the previous work of the T_1 states of benzene, triphenylene, and coronene.[8] The calculations were performed using the Pariser−Parr−Pople-type (PPP-type) approximation[10,11] with the zero-differential overlap (ZDO) treatment[10] by including configurations arising from all of the single excitations relative to the G state. In this case, the molecular structure was assumed to belong to the symmetry D_{2h} and the composing benzene rings are regular hexagons. The adjacent C−C bond distances of the benzene rings are 1.397 Å, and the distance of the central C−C bond, which connects the two benzene rings, $R(C_1{-}C_{1'})$, is 1.400 Å. As a result, the relation of $|X| < |Y| < |Z|$ was obtained in disagreement with the experimental result as listed in Table 3, although the difference between X and Y was very small.

To examine such a disagreement, at first we took up the influence of the many molecular spin−spin interaction integrals, which were neglected by the use of the ZDO approximation. Thereupon, all of the two-, three-, and four-center spin−spin interaction integrals were evaluated[12] by using the Gaussian expansions of Slater-type atomic orbitals (GE-STAOs) of O-ohata, Taketa, and Huzinaga (the orbital exponent of 2p STAO of carbon used is 1.59).[13] Then, the ZFS parameters were calculated by including these spin−spin interaction integrals using the WFs obtained by PPP-type approximation described above.[10,11] Such a treatment is generally similar to that used for the T_1 state of naphthalene molecule by Godfrey, Kern, and Karplus.[14] However, we could not still obtain the relation of $|Y| < |X| < |Z|$ as shown in Figure 7. This means that the approximation with the ZDO adopted in the present work does not have a significant influence upon the evaluated ZFS parameters, especially upon the relative magnitude of X and Y. The absolute values of ZFS parameters thus obtained are

TABLE 3: Calculated ZFS Parameters (cm^{-1}) and the Direction of *x* Axis, θ (deg)[a], for *p*-Polyphenyls Adopting the Semiempirical MO Method with Zero-Differential Overlap Approximation[b]

molecule		X	Y	Z	D	E	θ
biphenyl	(P)	0.0410	0.0338	−0.0748	0.1121	−0.0036	0.00
	(R)	0.0317	0.0431	−0.0748	0.1122	0.0057	0.00
p-terphenyl	(P)	0.0406	0.0277	−0.0683	0.1024	−0.0064	0.00
	(R)	0.0327	0.0356	−0.0684	0.1025	0.0014	0.00
p-quaterphenyl	(P)	0.0413	0.0247	−0.0660	0.0990	−0.0083	0.00
	(R)	0.0340	0.0321	−0.0661	0.0992	−0.0010	0.00
p-quinquephenyl	(P)	0.0420	0.0231	−0.0651	0.0977	−0.0095	0.00
	(R)	0.0349	0.0303	−0.0652	0.0978	−0.0023	0.00
p-sexiphenyl	(P)	0.0425	0.0222	−0.0647	0.0971	−0.0102	0.00
	(R)	0.0356	0.0292	−0.0648	0.0972	−0.0032	0.00
m,p-quaterphenyl	(1)	0.0331	0.0354	−0.0685	0.1028	0.0011	8.57
	(2)	0.0406	0.0279	−0.0685	0.1027	−0.0063	1.80
	(3)	0.0371	0.0314	−0.0684	0.1027	−0.0029	18.97

[a] Angle of the *x* axis from the *L* axis (see Figure 1). [b] Treatment of ref 8 (treatment A) was adopted: (P) all of the composing benzene rings were prolate-hexagonal form ($\angle C_6C_1C_2 = \angle C_3C_4C_5 = 115°$); (R) all of the composing benzene rings were regular-hexagonal form; (1) same as (R); (2) composed of a *p*-terphenyl skeleton with structure (P) attaching a regular hexagonal benzene ring; (3) composed of two biphenyl skeletons with structure (P).

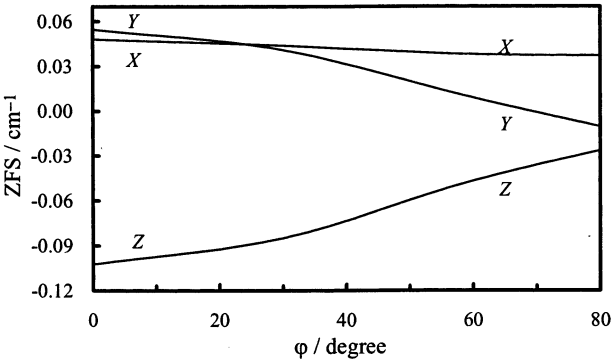

Figure 7. Variation of the calculated ZFS parameters of biphenyl molecule with symmetry C_{2h} as a function of the twist angle between the two benzene rings, φ. All of the spin−spin interaction integrals were included, and the two regular hexagonal benzene rings with R(C−C) = 1.400 Å and $R(C_1-C_{1'})$ = 1.500 Å were assumed for the purpose of the easier evaluation of the spin−spin interaction integrals.

relatively large compared with the calculated ones marked (P) in Table 3. This is mainly because the 2p AO used was the expansions (four Gaussians) of the STAO with an orbital exponent of 1.59, whereas the previous calculation used the double-ζ SCF-AOs.[8] Next, we examined the influence of the ZFS parameters upon the rotation around the central $C_1-C_{1'}$ bond. As a result, the relation of $|Y| < |X| < |Z|$ was obtained at the twist angles more than about 20°, although such structures are less-stable in the T_1 state of biphenyl.[15] In this range, the $|Z|$ value rapidly decreases with an increase of the twist angle, although the MOs used become less reliable with an increase of the twist angle because of the increase of the mixing between the so-called σ orbitals with the unpaired electron orbitals. These results are shown in Figure 7.[16] Hereafter, the ZFS parameters were calculated using the treatment of the previous work[8] to reduce the tedious evaluations with all of the spin−spin interaction integrals, and the numberings of atoms used in biphenyl are shown in Figures 8 and 9.

Owing to the interaction between the *ortho*-hydrogen atoms, the benzene rings of biphenyl in crystalline state are actually deformed from the regular hexagon, although the molecule is not perfectly planar.[17,18] Therefore, the dependence of the ZFS parameters upon the bond lengths and the bond angles was examined within the assumption that the molecule and each composed benzene ring belong to the symmetry D_{2h} [C_1-C_4 and $C_{1'}-C_{4'}$ are in one of the C_2 axes (the long axis) in the molecular plane]. As a result, we can express that $RA = R(C_1-$

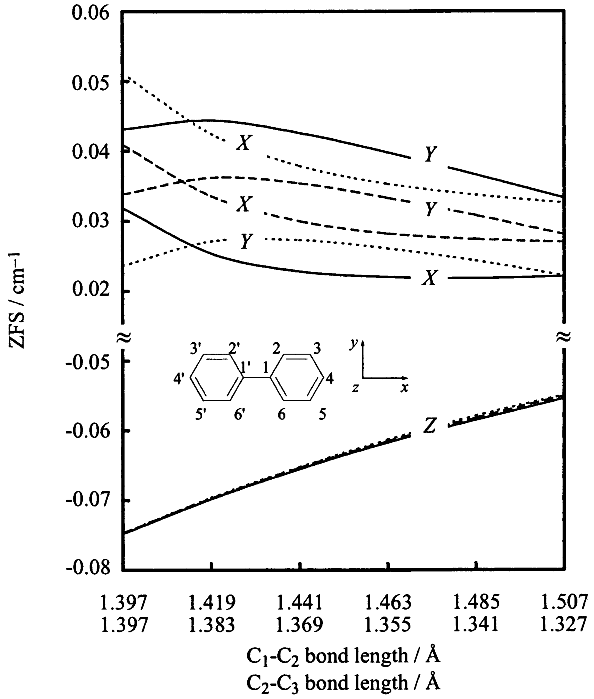

Figure 8. Variation of the calculated ZFS parameters of biphenyl molecule with symmetry D_{2h} as a function of the bond lengths in the benzene rings. The two hexagonal benzene rings with symmetry D_{2h} with $R(C_1-C_{1'})$ = 1.400 Å were assumed. The dotted, broken, and solid lines show the cases when the bond angle of $\angle C_6C_1C_2$ (= ΘA) used in the benzene rings is 110°, 115°, and 120°, respectively.

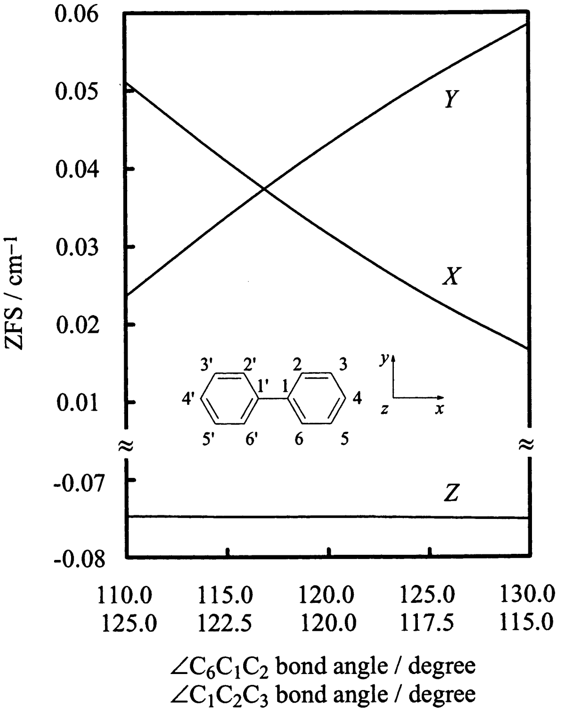

Figure 9. Variation of the calculated ZFS parameters of biphenyl molecule with symmetry D_{2h} as a function of the bond angles in the benzene rings. The two hexagonal benzene rings with symmetry D_{2h} and with R(C−C) = 1.397 Å and $R(C_1-C_{1'})$ = 1.400 Å were assumed.

$C_2) = R(C_3-C_4) = R(C_4-C_5) = R(C_6-C_1) = R(C_{1'}-C_{2'}) = R(C_{3'}-C_{4'}) = R(C_{4'}-C_{5'}) = R(C_{6'}-C_{1'})$, $RB = R(C_2-C_3) = R(C_5-C_6) = R(C_{2'}-C_{3'}) = R(C_{5'}-C_{6'})$, $RC = R(C_1-C_{1'})$, $\Theta A = \angle C_6C_1C_2 = \angle C_3C_4C_5 = \angle C_{6'}C_{1'}C_{2'} = \angle C_{3'}C_{4'}C_{5'}$, and $\Theta B = \angle C_1C_2C_3 = \angle C_2C_3C_4 = \angle C_4C_5C_6 = \angle C_5C_6C_1 = \angle C_{1'}C_{2'}C_{3'} = \angle C_{2'}C_{3'}C_{4'} = \angle C_{4'}C_{5'}C_{6'} = \angle C_{5'}C_{6'}C_{1'} = 180° - \Theta A/2$. In the free T_1 biphenyl, the central C−C bond distance *RC* should be shorter than that of the planar G state, in consideration of the main canonical structures in which the $C_1-C_{1'}$ is a double bond.[1] However, the steric hindrance between the *ortho*-hydrogen atoms increases with a decrease of the *RC*. In the following calculations, therefore, the *RC* was taken to be 1.400 Å instead of the 1.340 Å of the C=C double bond.

First, the dependence of the ZFS parameters upon the bond lengths was examined assuming that the bond angles of Θ*A*s are between 120° and 110°. Here, the deformed structures of benzene rings were chosen at regular intervals to be those between the regular hexagon and the hexagon with two C=C double bonds and four C−C single bonds [$1.397 \le RA \le 1.507$ Å and $1.327 \le RB \le 1.397$ Å]. In this range, the change of the *Z* value is rather remarkable, and the relative magnitude of the *X* and *Y* values is changed near $\Theta A = 115°$ at about $RA = 1.410$ Å, as shown in Figure 8. This means that the change of bond angles plays a more important role for the variation of the ZFS parameters compared with the change of bond lengths. The other structures were not numerically examined, because the *RB*s should not be larger than 1.397 Å, as can easily be deduced from the canonical structures of the T_1 state with the lowest energy.

Next, the dependence of the ZFS parameters upon the bond angles was examined more clearly assuming that all of the C−C bond lengths of benzene rings are equal, $RA = RB = 1.397$ Å, and $RC = 1.400$ Å. The bond angles are chosen within a range of $110° \le \Theta A \le 130°$. In this range, the *Z* values obtained are scarcely changed, and the relative magnitudes of the *X* and *Y* values are reversed near $\Theta A = 117°$, as shown in Figure 9. This is actually similar to the case of the T_1 state of the benzene molecule with the deviation of ∠CCC bond angles from 120° within D_{2h} symmetry, except that the structure of the benzene ring with $X = Y$ is the regular hexagon (see Appendix). In this case, the small variation of the central C−C bond distance *RC* is not significantly influenced upon the trend of ZFS parameters concerning the conformations of the composing benzene rings.

In the crystalline state of biphenyl, the bond angles of $\angle C_6C_1C_2 = \angle C_{6'}C_{1'}C_{2'}$ are 117.3° and 115.3° for the ground states of the neutral molecule[17] and of the anion,[18] respectively.[19] On the other hand, these angles of the neutral biphenyl in its T_1 state were obtained to be 114.8° by using the AM1 approximation.[20] In consideration of these facts, the composing benzene rings in the T_1 state of planar biphenyl molecule are prolate, probably with $\angle C_6C_1C_2 = \angle C_{6'}C_{1'}C_{2'} \le 115°$. In this condition, the relation of $|Y| < |X| < |Z|$ is distinctly satisfied. From these observations, one could learn that the variation of the bond angles plays an important role for the relative magnitude between *X* and *Y* compared with the variation of the bond distances, although these changes should not occur independently.[21] It appears that the origin of the relation of $|Y| < |X|$ is the deformation of the benzene skeletons arising from the steric hindrance between the *ortho*-hydrogen atoms of the adjacent benzene rings.

***p*-Polyphenyls.** The ZFS parameters of *p*-polyphenyl molecules in their T_1 states were calculated using the treatment adopted in the previous work[8] by assuming that the symmetry of both the total molecules and their composing benzene skeletons belongs to D_{2h}. In this case, all of the C−C bond distances connecting the adjacent benzene rings (*RC*s) were taken as 1.400 Å. As was supposed from the calculation of biphenyl in the previous section, however, the observed relation of $|Y| < |X|$ could not be obtained for *p*-terphenyl and *p*-quaterphenyl by assuming that all of the benzene rings are regular hexagons with the adjacent C−C bond lengths of 1.397 Å, as given the values marked (R) in Table 3. With reference to the previous calculation of the T_1 biphenyl molecule, the ZFS parameters were evaluated by assuming the deformed hexagonal benzene rings with the symmetry of D_{2h} and the same bond distances. In this case, the bond angles of every benzene ring were taken as $\Theta A = 115°$ and $\Theta B = 122.5°$ (C_1-C_4 is a C_2 axis for each benzene ring along the molecular long direction). As a result, we could obtain a relation of $|Y| < |X| < |Z|$ in agreement with the experimental results, as listed the values marked (P) in Table 3. This shows the fact that in the T_1 *p*-polyphenyls every benzene skeleton is deformed from the regular hexagonal structure because of the steric hindrance between *ortho*-hydrogens of the adjacent benzene rings, as in the case of the T_1 biphenyl. For the inner benzene skeletons, the structures should be slightly different from those of the side benzene rings in each of which two *ortho*-hydrogens are concerned. However, such a slight modification was not done in the present work. The $|Z|$ (or *D*) value obtained here decreases with an increase of the number of the composing benzene rings in agreement with the experimental relation. Therefore, these results can semiquantitatively elucidate the experimental results obtained in the present work and in the previous work,[1] as listed in Table 3.

***m*-Polyphenyls.** The ZFS parameters of *m*-polyphenyl molecules in their T_1 states were calculated by the treatment used in the case of *p*-polyphenyls. The main difference in the structures of the T_1 *m*-polyphenyls from the T_1 *p*-polyphenyls arises from the steric interactions among the *ortho*-hydrogen atoms of the adjacent benzene rings. For *m*-polyphenyls, there are three closely located *ortho*-hydrogen atoms each of which is connected to the adjacent benzene rings, as was described previously, whereas for *p*-polyphenyls two *ortho*-hydrogen atoms only are concerned. As a result, the bond angles in each benzene ring for these two groups should be different. At first, the ZFS parameters of T_1 *m*-terphenyl were examined assuming the total molecule with symmetry C_{2v} and each benzene skeleton with symmetry D_{2h}. In this case, the long symmetry axis of each side benzene skeleton is parallel to the C−C bond connecting the central benzene ring to the side benzene ring. The adjacent C−C bond lengths in all of the benzene rings are 1.397 Å and the distances of the C−C bonds connecting to the adjacent benzene rings are 1.400 Å. The direction of each C−C bond connecting the two benzene rings is assumed to the opposite one of the bisection between the other two C−C bonds sharing the same carbon atom. Under these conditions, several calculations were carried out by changing the bond angles of the benzene skeletons. $|E| = |Y - X|/2$ becomes too small when Θ*S* increases and Θ*As* decreases. Here, Θ*S* denotes the ∠CCC bond angle of the carbon atom where the C_{2v} symmetry axis of the central benzene skeleton passes through, while Θ*As* denotes the one of the side benzene ring where the above-mentioned long symmetry axis of the side benzene passes through. (For example, $X = 0.0354$ and $Y = 0.0373$ cm^{-1} when $\Theta S = 120°$ and $\Theta As = 114°$, and $X = 0.0379$ and $Y = 0.0349$ cm^{-1} when $\Theta S = 123°$ and $\Theta As = 114°$). On the other hand, $|E|$ becomes too large when Θ*S* decreases (for example, $X = 0.0289$ and $Y = 0.0439$ cm^{-1} when $\Theta S = 115°$ and $\Theta As = 120°$). As a result,

TABLE 4: Calculated ZFS Parameters (cm^{-1}) and the Direction of the *x* Axis, θ (deg)[a], for *m*-Polyphenyls by Adopting the Semiempirical MO Method with Zero-Differential Overlap Approximation and the Regular Hexagonal Benzene Ring[b]

molecule		X	Y	Z	D	E	θ
m-terphenyl		0.0334	0.0394	−0.0728	0.1092	0.0030	0.00
m-quaterphenyl	(*E*)	0.0335	0.0390	−0.0724	0.1086	0.0027	30.73
	(*Z*)	0.0350	0.0374	−0.0725	0.1087	0.0012	0.00
m-quinquephenyl	TT	0.0336	0.0387	−0.0723	0.1085	0.0026	0.00
	TC	0.0347	0.0377	−0.0724	0.1085	0.0015	10.18
	CC	0.0364	0.0360	−0.0724	0.1086	−0.0002	0.00
m-sexiphenyl	TTT	0.0337	0.0386	−0.0723	0.1085	0.0024	29.83
	TTC	0.0344	0.0379	−0.0723	0.1085	0.0018	34.42
	TCT	0.0351	0.0373	−0.0723	0.1085	0.0011	0.00
	TCC	0.0354	0.0369	−0.0724	0.1086	0.0008	−23.23
	CTC	0.0350	0.0374	−0.0724	0.1085	0.0012	45.88
	CCC[c]	0.0358	0.0367	−0.0725	0.1088	0.0005	0.00
1,3,5-triphenylbenzene	(1)	0.0354	0.0354	−0.0708	0.1062	0.0000	0.00
	(2)	0.0295	0.0412	−0.0707	0.1061	−0.0058	0.00

[a] Angle of the *x* axis from the *L* axis (see Figure 1). [b] Treatment of ref 8 (treatment A) was adopted. [c] Hypothetical planar conformation in which the interactions among the hydrogen atoms are disregarded: (1) composed of four regular hexagonal benzene rings and (2) composed of a biphenyl skeleton with the deformed benzene rings ($\angle C_6C_1C_2 = \angle C_3C_4C_5 = 115°$) attaching two regular hexagonal benzene rings.

the preferable set of ZFS parameters is obtained approximately from the structure with three regular hexagonal benzene skeletons.

Then, the ZFS parameters of the T_1 *m*-polyphenyl molecules were calculated assuming that all of the benzene skeletons are regular hexagons in which the adjacent C−C bond lengths are 1.397 Å and the C−C distances connecting the adjacent benzene rings (*RC*s) are 1.400 Å. The results obtained satisfy the experimental relation of $|X| < |Y| < |Z|$, as listed in Table 4. From our measurements, some EPR spectra for every conformer are not always distinguishable from the others. The calculated ZFS parameters are fairly close to those evaluated in the previous section. In the present case, the slightly separated sets of ZFS parameters were actually obtained for the above experimentally indistinguishable conformers, although the differences among them are very small. However, these values should not be final, because the structures of the composing benzene rings should not always be the same with each other because they are influenced by the respectively different steric interactions. The ZFS parameters may possibly be obtainable more adequately by using the optimized structural constants, although the structures of the T_1 states in rigid glasses are almost impossible to determine exactly. Because the main purpose of the present work is obtaining the general trend of the ZFS parameters upon the conformation, especially upon some of the most sensitive factors among the structural constants, further calculations were not extensively carried out using the so-called optimized structures.

Other Polyphenyls. In the present experiment using the stretched-polymer-film technique, the EPR measurement for the T_1 state of *m*,*p*-quaterphenyl [$C_6H_5-(1,3\text{-}C_6H_4)-(1,4\text{-}C_6H_4)-C_6H_5$] was not performed for assigning their peaks with reference to the spin axes because of the difficulty in determining the direction of the spin axes exactly. On the other hand, only a calculation of the ZFS parameters similar to those of the previous sections was carried out by assuming the following three planar structures: (1) that composed of four regular hexagonal benzene rings; (2) that composed of a *p*-terphenyl skeleton with the deformed benzene rings used in the previous calculation ($\Theta A = 115°$) attaching a regular hexagonal benzene ring; (3) that composed of two biphenyl skeletons with the deformed benzene rings as was used in the calculation of biphenyl previously. In these models, the C−C internuclear distances of the benzene skeletons and those of the C−C bond connecting the adjacent benzene rings are taken as 1.397 and 1.400 Å, respectively. The direction of each bond was assumed to the opposite one of the bisection between the other two C−C bonds sharing the same carbon atom. As in the cases of the T_1 *p*-polyphenyls, the calculated ZFS values are not always close to the experimental ones. However, the result of model 2 is most satisfactory in explaining the previous observation that the EPR spectrum is fairly close to that for the T_1 *p*-terphenyl with $|Y| < |X|$. On the other hand, model 3 of the two-biphenyls form with $|Y| < |X|$ and model 1 of the four-regular-hexagonal-benzene form with $|X| < |Y|$ could not well elucidate the above observation. These results are listed in Table 3.

For the T_1 state of 1,3,5-triphenylbenzene, the ZFS parameters were similarly calculated by assuming the following two planar structures with the C−C bond distances of the benzene skeletons and those connecting the adjacent benzene rings being 1.397 and 1.400 Å, respectively. Model 1 with symmetry D_{3h} is composed of four regular hexagonal benzene rings, and model 2 with symmetry C_{2v} is a biphenyl skeleton with deformed benzene rings ($\Theta A = 115°$) attaching two regular hexagonal benzene rings. The agreement with the experimental values is better for model 1 despite $E = 0$, whereas the E value is about three times larger than the observed value for model 2. This may suggest that the deformation in the T_1 1,3,5-triphenylbenzene from model 1 is not so large as that assumed in model 2, that is, the deformed structure is changeable among three kinds of such structures with different biphenyl skeleton (model 2) at the experimental temperature. The numerical results are given in Table 4.

Some Remarks

In the present work, the T_1 states of *m*- and *p*-polyphenyl molecules were assumed to be near planar. This is because the conjugated systems in these T_1 molecules are expanded in the whole carbon skeletons. For the T_1 *p*-polyphenyls, therefore, the main origin of the relation of $|Y| < |X| < |Z|$ should not be the loss of the coplanarity among the composing benzene rings, although such a relation is obtained for biphenyl when the twist angle between the adjacent benzene rings fairly increases. For the overcrowded molecules such as *o*-polyphenyls, however, such an effect should be taken into consideration.

For the direction of the principal spin axes in the **D** tensor of the T_1 conformers without C_2 symmetry axis, the result of the simplified valence-bond (VB) treatment does not always coincide with that of the MO consideration. This is because of the difference of the contribution of the excited configurations included in these calculations. For the simplified VB treatment adopted, the excited configurations are relatively localized at every biphenyl skeleton and the spin−spin interactions and also the spin−orbit ones in this part are implicitly included extensively because of the use of the experimentally determined ZFS parameters. For the present MO consideration, all of the excited configurations included are those arising from the single excitations relative to the G state, although the long-range spin−spin interactions within this approximation are taken into account. In the directions of the calculated principal spin axes, therefore, some discrepancies arose between these two treatments, especially for the relatively large molecules. Actually, it is very difficult to find host crystals suitable for the experimental determination of the spin axis for each conformer. In consideration of these facts, the present work is generally successful for the assignment of the ZFS parameters within the present experimental condition.

Conclusion

For the T_1 states of *m*- and *p*-polyphenyl molecules, the assignment of the ZFS parameters relative to the spin axes are successfully carried out from both the experimental and the theoretical viewpoints. The fundamental difference in the ZFS parameters of these two kinds of species was experimentally found from the relatively small molecules using the stretched-polymer-film technique, that is, $|Y| < |X| < |Z|$ for *p*-polyphenyls and $|X| < |Y| < |Z|$ for *m*-polyphenyls. The origin of the relative magnitude of the X and the Y value can be satisfactorily explained from the different structures of the composing benzene rings between these species using the VB and MO methods. With an increase of the number of the composing benzene rings, the decrease of the $|Z|$ value in the *p*-polyphenyls is because of the delocalization of the conjugated system along the long axis of the molecule, whereas the scarce change in the *m*-polyphenyls is the localization of the T_1 character in the every composing biphenyl skeleton. In the course of the present elucidation of the T_1 polyphenyl molecules, the importance of the bond angles of the composing benzene rings in the ZFS parameters is emphasized by using the result for the T_1 state of biphenyl molecule.

Acknowledgment. The authors express their thanks to Professor Kazuhiko Ishizu of Ehime University for offering a chance of performing the present work and for providing sample molecules.

Appendix

The Dependence of the ZFS Parameters in the T_1 State of the Benzene Molecule (D_{2h}) upon the Variation of Bond Angles. In the previous paper,[8] the dependence of the ZFS parameters (D and E) for the T_1 state of the benzene molecule upon the variation of C−C bond distances was calculated from the electron spin−spin interactions using the Pariser−Parr−Pople-type approximation[10,11] with the zero-differential overlap (ZDO) treatment[10] by including configurations arising from all of the single excitations relative to the ground state. In the present note, the dependence of the ZFS parameters (X, Y, and Z) for the T_1 state of benzene molecule upon the variation of bond angles was evaluated adopting the same approximation used in the previous work (treatment C)[8] for reference to the T_1 state of biphenyl. In this calculation, the molecular structure was changed within D_{2h} symmetry (C_1−C_4 is one of the C_2 axes in the molecular plane) and the adjacent C−C bond distances are taken as 1.397 Å, as shown in Figure A1. The bond angles were changed within a range of $110° \leq \angle C_6C_1C_2 = \angle C_3C_4C_5 \leq 130°$. Comparing with the previous cases of the dependence of the C−C bond distances with $\Delta R(C_1-C_2) = \Delta R(C_3-C_4) = \Delta R(C_4-C_5) = \Delta R(C_6-C_1) = -\Delta R(C_2-C_3)/2 = -\Delta R(C_5-C_6)/2$ within D_{2h} symmetry shown in Figure A2, we learn that the present cases of oblate form with $\angle C_6C_1C_2 > 120°$ and of prolate form with $\angle C_6C_1C_2 < 120°$ are relatively similar to the cases of quinoidal and antiquinoidal form, respectively.

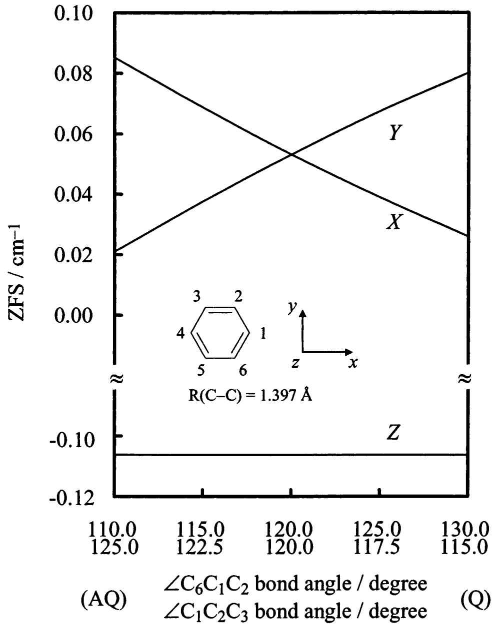

Figure A1. Variation of the calculated ZFS parameters of benzene molecule with symmetry D_{2h} as a function of the bond angles.

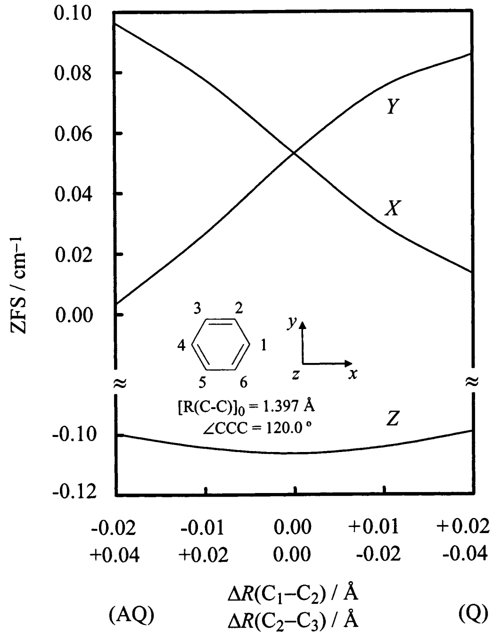

Figure A2. Variation of the calculated ZFS parameters of benzene molecule with symmetry D_{2h} as a function of the bond lengths.

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(21) From the evaluation of the T_1 state of biphenyl with AM1 approximation (ref 20), $R(C_1-C_{1'}) = 1.377$ Å, $R(C_1-C_2) = R(C_1-C_6) = 1.456$ Å, $\angle C_6C_1C_2 = 114.8°$, and $\angle C_1C_2C_3 = \angle C_5C_6C_1 = 122.0°$ were obtained.