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Time-Resolved Electron Paramagnetic Resonance Study of the First Excited Triplet States of Dibenzocycloheptadienylidene and Diphenylmethylene Derivatives

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Transient triplet electron paramagnetic resonance (EPR) spectra of dibenzocycloheptadienylidene (DBC) and substituted diphenylmethylenes were observed in a rigid glassy matrix at low temperatures. On excitation with the wavelength of the T−T transition of DBC, polarized EPR spectra due to the both ground (T_0) and excited (T_1) states were observed at a short delay time (180 ns) after the laser pulse. The T_1 components in the spectrum decayed faster than the other and diminished at 1 μs after the laser pulse irradiation. The remaining signals after the decay of the T_1 state were unambiguously assigned to the T_0 state, taking into account the steady-state (SS) EPR results. From analysis of the spectrum of the short-lived triplet species, the zero-field splitting (ZFS) parameters, $|D| = 0.201$ and $|E| = 0.008$ cm^{-1}, were determined for the T_1 state directly. The parameters obtained were comparable to those of the T_1 state of diphenylmethylene (DPM). The polarization patterns of the transient spectra match well with interpretation as anisotropic intersystem crossing induced by the spin−orbit couplings between the S_n and the triplet states. On the basis of the results of magnetophotoselection experiments, we also confirmed that the principal axes in the T_0 and T_1 states did not differ significantly from each other. The behavior of the methyl-substituted DPM resembles that of DPM and DBC, indicating that the methyl group does not affect the photophysical and photochemical properties of the T_0 and T_1 states. Although the SS EPR spectra were observed for the T_0 state of substituted DPM derivatives, the chemical properties of the excited states were affected by substitution of electron-donating (OCH_3) or -withdrawing (CN) groups.

Introduction

Recently we reported a study on the first excited triplet state of diphenylmethylene (DPM, Figure 1) employing time-resolved electron paramagnetic resonance (TREPR) spectroscopy.[1] The reduction of $|D|$ value in the T_1 state was discussed in terms of the significant delocalization of the unpaired electron to the phenyl ring. The electron polarization was ascribed to anisotropic intersytem crossing (ISC) between the singlet and triplet state of DPM. These results are consistent with those obtained from the magnetic field effect on the fluorescence decays.[2] Because the degree of Zeeman mixing among the triplet eigenstates is a function of the ZFS at low external field, the ZFS parameters of the emitting state can be extracted from the analysis of the fluorescence decay. Although the method for determining the parameters is indirect, the estimated $|D|$ value agreed well with the TREPR result.

Dibenzocycloheptadienylidene (DBC) has triplet spin multiplicity in the electronic ground state.[3] Although the photophysical and magnetic properties of DBC, including fluorescence lifetime of the T_1 state and ZFS parameters in the ground state, closely resemble those of DPM, the magnetic field effects on the fluorescence decay differed due to the small |D| value for the T_1 state.[4] As the lifetime of the T_1 state of DBC is in the

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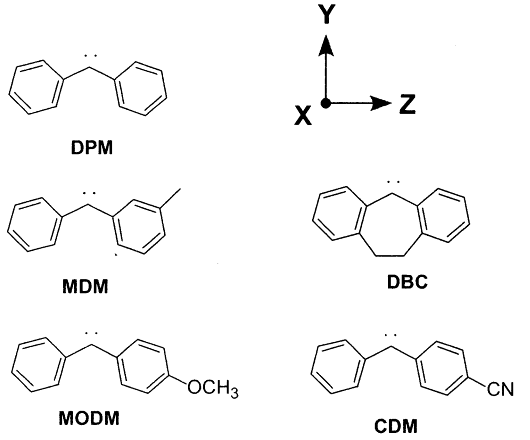

Figure 1. Structure and coordination systems of the methylenes studied in this paper.

range of the time resolution of TREPR technique, we applied TREPR to determine the ZFS parameters of the T_1 state of DBC directly.

TREPR experiments were also carried out for excitation of substituted diphenylmethylenes. Substitutions with electron-donating (OCH_3) and -withdrawing (CN) groups caused a photoreaction with T−T excitation indicating changes in properties of the excited states.

Experimental Section

The diazo precursor of DBC and diphenylmethylenes were synthesized and purified as reported previously.[3,5] The sample solutions were prepared at concentrations of 10^{-5} mol dm^{-3} for fluorescence measurements and 10^{-3} mol dm^{-3} for TREPR measurements, and were deaerated using a vacuum line technique. The fluorescence and excitation spectra were measured at 77 K using a fluorescence spectrometer (Hitachi 850). The TREPR spectra were obtained using an X band EPR spectrometer (Varian E-12) without field modulation, as previously described.[6] A dye laser (Lumonics model HD-300) was used as the light pulse source. Measurements at cryogenic temperatures were performed using an Oxford ESR 900 helium-flow cryosystem. The magnetophotoselection (MPS) experiments were performed by passing the polarized dye laser light through a Glan-Thompson prism to remove the depolarized components.

Results and Discussion

Dibenzocycloheptadienylidene (DBC). In Figure 2 the fluorescence and related excitation spectra of DBC are shown observed at 77 K in an ethanol (EtOH) matrix. The emission is observed as mirror image of its excitation spectrum. The T_1 state energy, obtained from the intersection point of the fluorescence and its excitation spectra, was determined to be 2.46 eV (503 nm) for DBC. The fluorescence decay was analyzed using by the sum of two exponential functions leading to the component lifetimes of 52 and 135 ns.[7]

Upon irradiation by dye laser light (Coumarin 500, 503 nm) of the diazo-precursor of DBC in EtOH, a characteristic triplet EPR signal is formed. This powder pattern spectrum corresponds unambiguously to the T_0 state of DBC. Confirmation for this assignment is based on simulation of the EPR spectrum using the ZFS parameters of $|D| = 0.393$ and $|E| = 0.017$ cm^{-1}, which showed that the parameters are in good agreement with literature data.[3]

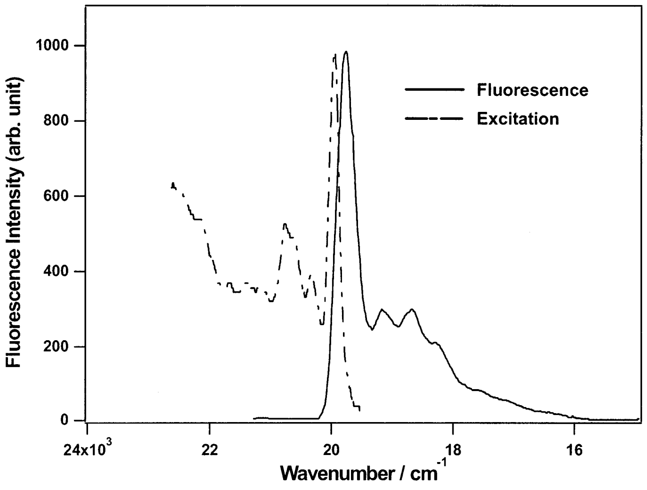

Figure 2. Fluorescence and excitation spectrum of DBC in a ethanol glassy matrix at 77 K. The fluorescence spectrum was recorded by 350 nm excitation, and the excitation spectrum was observed by monitoring at 535 nm.

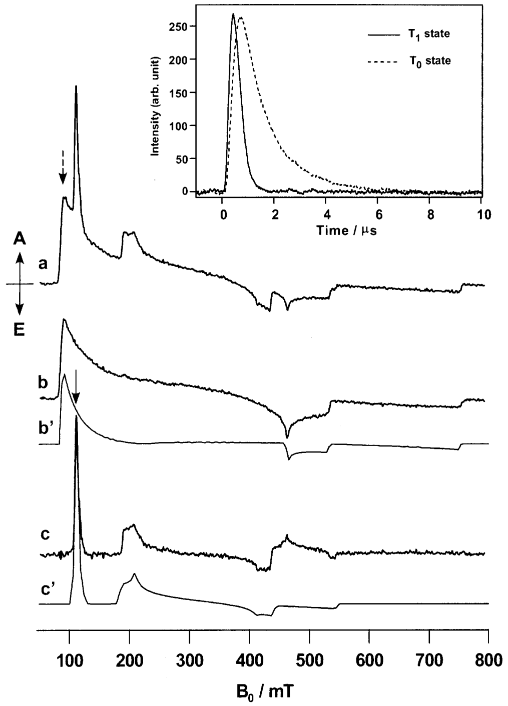

Figure 3. TREPR spectra of DBC were observed at 180 ns (a) and 1 μs (b) after laser pulse irradiation in an ethanol glassy matrix at 20 K. The spectrum of the T_1 state of DBC (c) was obtained by subtraction of (b) from (a) with the appropriate weighting. The simulated spectrum (c′) was calculated using the parameters in the text. Inset: time profiles of the transient triplet EPR signals observed at 100.015 (a) and 116.30 mT (b) in an ethanol glassy matrix.

The conventional EPR signal intensity reached a plateau with prolonged irradiation, indicating that the decomposition of the diazo precursor was complete. Excitation at a wavelength of 503 nm, corresponding to the T−T transition of the T_0 state of DBC, gave the transient EPR spectra as shown in Figure 3a−c. The spectrum observed at 1 μs after the laser pulse corresponds to the T_0 state of DBC because the ZFS parameters completely coincide with the steady-state EPR.

Other signals appeared in the spectrum observed at 180 ns after the laser pulse (Figure 3a), in addition to those of the T_0 state of DBC. After subtraction of the T_0 component from the spectrum observed at 180 ns we obtained the difference TREPR

TABLE 1: Zero Field Splitting Parameters of the T_0 and T_1 States of DBC, DPM, and Its Derivatives

	T_0			T_1		
	$\|D\|$/cm^{-1}	$\|E\|$/cm^{-1}	$\|E\|/\|D\|$	$\|D\|$/cm^{-1}	$\|E\|$/cm^{-1}	$\|E\|/\|D\|$
DBC	0.393	0.017	0.043	0.201	0.0080	0.040
DPM [1]	0.408	0.018	0.042	0.200	0.0080	0.040
MDM	0.405	0.018	0.044	0.200	0.0081	0.040
MODM	0.406	0.019				
CDM [5]	0.3906	0.0193				

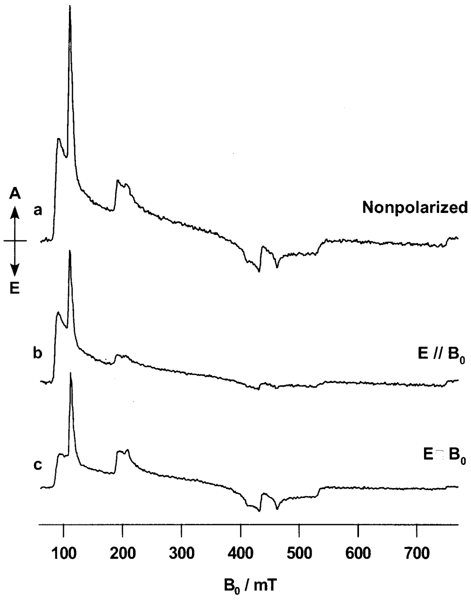

Figure 4. TREPR spectra of DBC obtained by excitation using polarized light in an ethanol glassy matrix at 20 K. The orientations of the polarized light with respect to the external magnetic field are depicted in the figure.

spectrum corresponding to the faster decay component, as shown in Figure 3c. To remove the T_0 component from the spectrum, the signal intensities in the low field area of the Z canonical orientation were normalized in each spectrum but, under this condition, the X and Y components were not eliminated in the difference spectrum. The results may be rationalized in terms of a sublevel-dependent spin relaxation in the T_0 state of DBC. Analysis of the spectrum of the T_1 state of DBC was carried out to put these remaining components of the T_0 state aside. The spectrum was well reproduced by computer simulation (Figure 3c′) using the ZFS parameters of $|D| = 0.201$ and $|E| = 0.008$ cm^{-1}.

The assignment of T_1 state DBC was also confirmed by the measurement of the time profiles of T_0 and T_1 state DBC. Temporal behaviors were observed at the resonance field of Z canonical orientations, as shown in the insert of Figure 3. The polarization decay of the T_1 component was independent of incident microwave power, indicating that the decay rate of 160 ns corresponded to the lifetime of this state. The rise time for the T_0 state polarization is in good agreement with the decay of the T_1 state of DBC. Detailed analysis of the EPR time profiles at each canonical orientation, which will be given elsewhere, is necessary for quantitative treatment of kinetics and spin relaxation, including the interactions of the electron spin system with the microwave field.

The ZFS parameters were obtained from the analysis of the spectra and summarized in the Table 1 with those of DPM and its derivatives. The differences of the ZFS parameters between DPM and DBC in their ground states were attributable to change in geometry and delocalization of unpaired electrons on the phenyl moieties. In their T_1 states, however, the differences were small for both $|D|$ and $|E|$ values, indicating that the geometry for DPM and DBC is very similar in this state. The small $|D|$ values in the excited state were interpreted as due to the delocalization of π electrons and agreed with the result of the MO calculation reported previously.[1]

The polarization pattern was A/EEE for the T_0 state and AAA/EEE for the T_1 state for DBC from low to high magnetic field (A denotes the enhanced absorption and E the emission of the microwave radiation). It is well-known that the long axis T_z sublevel is the lowest in the T_0 state: $T_y > T_x > 0 > T_z$. The polarization pattern of the T_0 state is well reproduced by the population differences of $P_z - P_y$:$P_z - P_x = 0.2$:0.8, indicating the preferential population in the lowest sublevel. One center SOC interaction between the $S_{1\text{ or }2}(\pi_0\pi_0)$ and $T_0(n\pi_0)$ states involves matrix elements of the z orbital angular momentum components, leading to preferential ISC into the T_z sublevel. The spin polarization of the T_1 state of DBC suggests that the highest sublevel is almost exclusively depopulated at a delay time of 180 ns, indicating that the highest sublevel corresponds to that showing the fastest decay. Spin−orbit coupling (SOC) interaction between the T_1 and S_3(nn) states would induce selective decay from the highest sublevel through anisotropic nonradiative decay. If the ordering of the triplet sublevels for the T_1 state is similar to that of the T_1 state of DPM, the simulated TREPR spectrum shown in Figure 2c′ can be fitted with the population differences $P_x - P_z$:$P_y - P_z = 0.60$:040. The present study indicates that the $T_1(n\pi^*)$ state of methylene has a very large radiationless rate from the long axis T_z sublevels. This agrees well with observation of the external magnetic field effects on the fluorescence decays.

Taking all of this into consideration, we assumed that the principal axes in the ground and excited states did not differ significantly from each other. To confirm this assumption, we carried out magnetophotoselection experiments. Because polarized light selectively excites the molecules when the transition dipole moment of the T_0 state is parallel to the electric field vector (**E**) of the light, the spectral pattern of the T_1 state is expected to reflect the selective excitation of the T_0 state.

Figure 4 shows the magnetophotoselection spectra of DBM in methylcyclohexane (MCH) obtained by excitation with polarized light from a dye laser (503 nm) at 20 K. When **E** of the exciting light was parallel to $\mathbf{B}_0$, the outermost pairs of the peaks were intensified for the T_0 state, but for photoexcitation with $\mathbf{E}\perp\mathbf{B}_0$, the signals of the X and Y canonical orientations became intense, as shown in Figure 4b,c.

As the transition moment of the electronic excitation of the T_0 state at 503 nm is aligned along the in-plane long molecular axis (Z), irradiation with light polarized parallel to the external magnetic field ($\mathbf{E}\|\mathbf{B}_0$) preferentially excites molecules aligned with the Z axis along $\mathbf{B}_0$.[2] The relative intensities of the X and Y components became weak in the spectra of both the T_0 and T_1 states of DBC. In contrast, the $\mathbf{E}\perp\mathbf{B}_0$ spectrum showed opposite behavior to that of the $\mathbf{E}\|\mathbf{B}_0$ spectrum. The dependencies of the T_1 state spectra on excitation with polarized light closely resemble those of the T_0 state of DBC. These results indicated the principal axis systems are unchanged in the T_0 and T_1 states of DBC.

In a previous study of the magnetic field effect on fluorescence decay of the triplet species, $|D| = 0.02$ cm^{-1} for the T_1 state of DBC was estimated.[4] To obtain the TREPR spectrum corresponding to this conformer, we measured TREPR spectra at different temperatures and excitation wavelengths. No new TREPR spectrum was observed at lower temperature (<10 K),

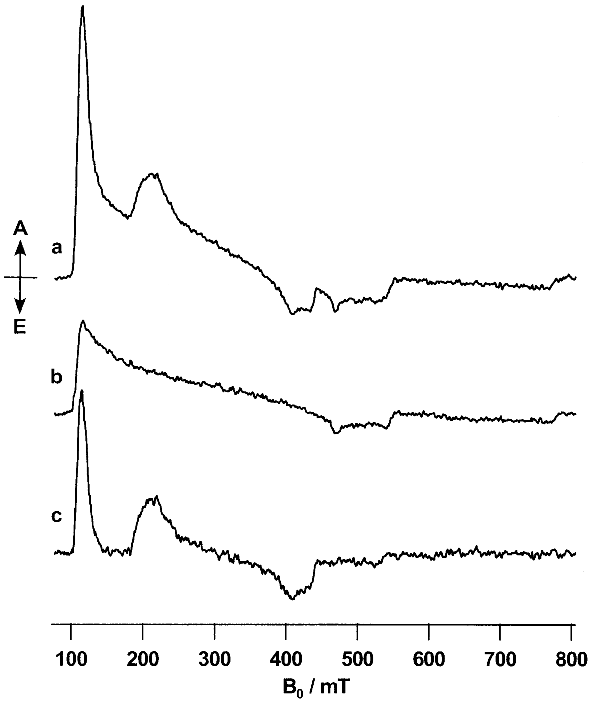

Figure 5. TREPR spectra of MDM were observed at 180 ns (a) and 1 μs (b) after laser pulse irradiation in an ethanol glassy matrix at 20 K. The spectrum of the T_1 state of MDM (c) was obtained by subtraction of (b) from (a) with the appropriate weighting.

nor by excitation with light of different wavelength (465, 470, 475 and 480 nm). Laser excitation at shorter wavelengths led to reduction of the signal intensities, reflecting the absorbances of T−T transitions.

The discrepancy between the EPR and the fluorescence measurement would be due to the difference of matrixes used for the experiments. Broad and sharp fluorescence spectra were observed in an *n*-hexane Shpolskii matrix between 4.2 and 77 K. These are tentatively assigned to two different conformers, the sharp signal corresponding to methylene in a quasi-planar geometry and the broad emitting species assigned to the nonplanar conformer. As shown in Figure 2, there is no correspondence with the sharp component in an ethanol glassy matrix. Under the current experimental conditions only the broad emitting species was present in the system and the ZFS parameters were same as those of the excited state of DPM. Consequently, on the basis of our TREPR experiments, the molecular structure of the broad emitting species should be assigned to the quasi-planar structure.

3-Methyldiphenylmethylene (MDM). Upon irradiation of a solution of the diazo precursor of MDM, the characteristic SS EPR spectrum of DPM derivatives was observed at low temperature. The spectrum was easily assigned to the T_0 state of MDM on the basis of ZFS parameters. Polarized EPR spectra were also observed with excitation of the T_0 state at a wavelength of 465 nm, as shown in Figure 5. The same procedures were adopted to obtain the TREPR spectrum of the T_1 state of MDM. The ZFS parameters, $|D| = 0.200$ and $|E| = 0.008$ cm^{-1}, of the T_1 state were determined by computer simulation. The polarization patterns were essentially the same as those of the DPM triplet states, indicating that the substitution of a methyl group at the meta position does not affect the distribution of the unpaired electrons of the triplet states of DPM. The differences of |D| values in the T_1 state of MDM and DBC were negligibly small, regardless of a slight reduction being obtained in the T_0 state of DBC. The bond angle in the central carbon atom of DBC is slightly wider than that of DPM in the ground state, inducing the change in the distribution of the unpaired electrons. The $|D|$ values of the T_1 states agreed, within experimental error. These results suggest that the molecular structures in the T_1 states were identical, especially around the central carbon atoms.

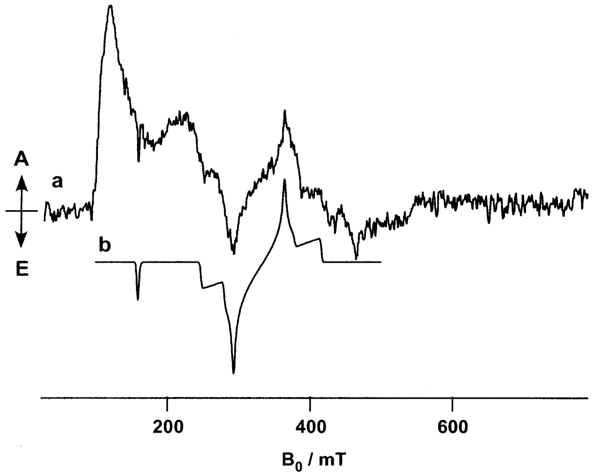

Figure 6. TREPR spectra were observed at 180 ns (a) in an ethanol glassy matrix at 20 K.. The simulated spectrum (b) was calculated using the parameters in the text

4-Methoxydiphenylmethylene (MODM). The methoxy derivatives of DPM were also well characterized through the observation of SS EPR and the optical measurements in their ground state.[5,8,9] The fluorescence decay rate increased with the substitution suggesting a change of properties in the T_1 state. Figure 6a shows the polarized EPR spectrum observed at 180 ns after the laser pulse irradiation of the ethanol solution of MODM at 20 K. In addition to the characteristic spectrum of the T_0 state of MODM, the polarized EPR signals were observed with the phase of E EEE/AAA pattern. The spectrum was reproduced by using the ZFS parameters of $|D| = 0.075$ and $|E| = 0.0043$ cm^{-1} as shown in Figure 6b. The decay rate of the signals was in the order of μs and significantly slower than that of the fluorescence of the T_1 state. The relative intensities of the signals of the T_0 components became weak with the prolonged irradiation with light at 470 nm whereas the intensities of the signals having opposite polarization to the T_0 state of MODM were gradually increased by the excitation. This can be ascribed to the conversion of MODM to a stable product through the excitation to the T_1 state. The resulting species has an absorption around 470 nm and produces the polarized triplet state through excitation at this wavelength.

In the course of transient absorption experiments of diazo compounds, the production of short-lived diphenyl carbenium ions has been identified in various hydroxylic solvents as a result of proton addition to the methylenes.[10,11] The reaction mechanism for the formation of carbenium ions has been proposed as diarylemethylene singlets interacting with hydroxylic molecules by abstracting a proton from them. Because the diphenyl carbenium ions have a strong absorption band around 470 nm, the polarized signals were assigned to the excited triplet state of the 4-methoxydiphenyl carbenium ion. Essentially identical results were observed for the stable carbenium ion. Excitation of the T_0 state of MODM produces the T_1 state followed by ISC to the S_n state. As the fluorescence quantum yield of MODM is an order of magnitude smaller than that of DPM, ISC occurred in the T_1 state, abstracting a proton from the solvent. The resulting carbenium ion was stable and accumulated with the T−T excitation of MODM at low temperature.

4-Cyanodiphenylmethylene (CDM). The reduction of the $|D|$ value of the T_0 state of CDM is significantly large and is interpreted as the electronic contribution of the CN group to the distribution of the unpaired electrons.[5,12] On irradiation of the diazo precursor of CDM in ethanol and MCH, the formation of CDM was confirmed by observation of the SS EPR spectrum at low temperature. Excitation corresponding to the T−T transition (478 nm) caused a rapid change in the color of the solution to black and gave no EPR spectrum even at 20 K. As CDM persists at low temperature, as do other DPM derivatives in the ground state, new reaction pathways were opened by excitation of CDM to the T_1 state.

Conclusion

Time-resolved EPR measurements of the diphenylmethylenes were carried out in rigid glassy matrixes at low temperatures. From the analysis of the spectra the ZFS parameters, $|D|$ and $|E|$, of the T_1 states were determined directly. The small $|D|$ values showed that the distribution of the unpaired electrons changes considerably upon T−T excitation. The introduction of a methyl or methylene unit to the aromatic rings did not affect the properties of the excited states, such as the anisotropy of the ISC, the distributions of unpaired electrons, and the reactivity. However, the substitution of an electron-donating or electron-withdrawing group changes the chemical properties after the excitation to the T_1 state regardless of the species persisting at low temperatures in the ground state. The formation of carbenium ion was suggested by the observation of polarized triplet spectrum for the methoxy derivative.

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