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Direct Detection of the Excited Triplet State of Diphenylmethylene by Time-Resolved EPR Spectroscopy

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Although the chemistry and spectroscopy of carbenes in their ground states have been extensively studied over the past decades,[1] little attention has been focused on the excited states of these carbenes. Electron paramagnetic resonance (EPR)[2] and electron nuclear double resonance techniques[3] have made a significant contribution to our understanding of the electronic structure of diphenylmethylene (DPM) (Figure 1). It has been established that DPM is a triplet in the electronic ground state. Theoretical calculations[4] and anisotropic ^{13}C hyperfine coupling[2] suggest that DPM has the bent geometry with a methylene bond angle of about 140−150°.

The lowest excited triplet state (T$_1$) was detected by triplet−triplet (T−T) fluorescence and transient absorption measurements.[5] The zero field splitting (ZFS) parameter of D in the T$_1$ state of DPM has been estimated on the basis of the results of the external magnetic field effects on the T−T fluorescence decay.[6] However, there are no reports on the EPR spectrum of the T$_1$ state of carbenes. Time-resolved (TR) EPR technique has been successfully applied to the investigation of the short-lived T$_1$ state. In the present paper, we report the first observation of the TREPR spectrum of the T$_1$ state of DPM and determine the ZFS parameters (both $|D|$ and $|E|$) directly.

The precursor of DPM, diphenyldiazomethane (DPDM), was prepared by the method reported previously.[7] The T$_0$ state of DPM was generated by photodissociation of DPDM (2×10^{-3} M) in degassed methylcyclohexane (MCH) upon excitation by a Nd:YAG laser (third harmonics, 355 nm) at low temperature. The method to detect transient EPR signals has been described previously.[8] A dye laser (Lumonics model HD-300, C460, 465 nm) was used as the light pulse source. Measurements at cryogenic temperatures were performed using an Oxford ESR 900 helium-flow cryosystem.

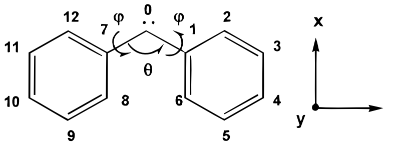

Figure 1. Numbering of the atoms and the principal axes of DPM together with bent (θ) and twist (φ) angles.

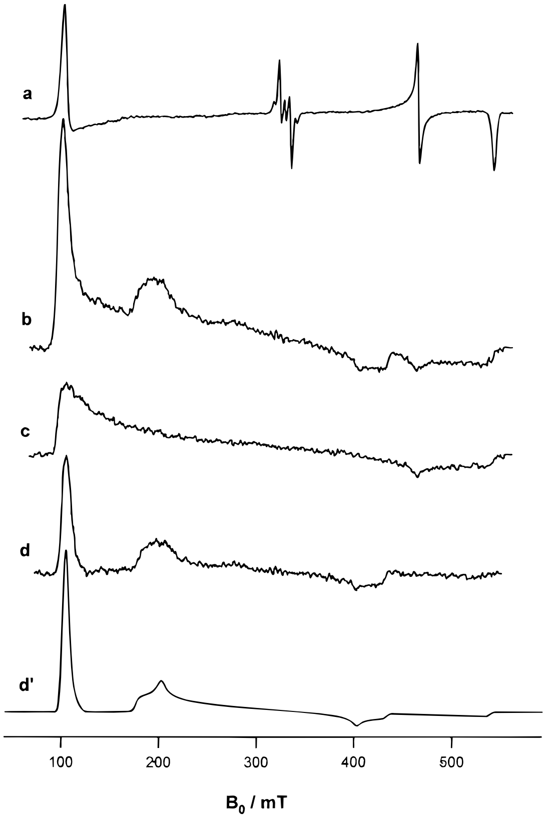

Figure 2. Steady-state (a) and time-resolved EPR spectra (b, c) in a MCH glassy matrix at 16 K. TREPR spectra were observed at 100 ns (b) and 1 μs (c) after the laser pulse irradiation. The spectrum of the T$_1$ state of DPM (d) was obtained by the subtraction of (c) from (b) with the appropriate weighting. The simulated spectrum (d′) was calculated by using the parameters in the text.

By the irradiation of DPDM with the light of 355 nm, its typical violet color changed to light green, and the characteristic triplet continuous wave EPR spectrum of DPM was observed as shown in Figure 2a. The signals were easily assigned to the T$_0$ state of DPM on the basis of the ZFS parameters ($|D| = 0.4088$ and $|E| = 0.0170$ cm^{-1}).[2] Relatively complicated signals observed around the $g = 2$ region are attributed to the radicals and/or the radical pairs formed by both thermal and secondary photochemical reactions of DPM.[9]

As the continuous wave EPR signal intensity reached a plateau with the prolonged irradiation, TREPR measurements were started from this condition. The excitation with the light of 465 nm, which corresponded to T−T absorption of the T$_0$ state of DPM, gave the polarized spectra as shown in Figure 2b−d. The transient triplet spectrum observed at 100 ns after the laser pulse at 16 K was rather complicated, indicating the contributions of two polarized species. One component decayed faster than the other and vanished at 1 μs (Figure 2c). The polarized species remaining at 1 μs is assigned to the T$_0$ state because the ZFS parameters completely coincide with the steady-state EPR. By the subtraction

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of this component from the spectrum observed at 100 ns we obtained the difference TREPR spectrum corresponding to the faster decay component as shown in Figure 2d. The spectrum was well reproduced by computer simulation (Figure 2d′) resulting in the ZFS parameters of $|D| = 0.201$ and $|E| = 0.0085$ cm^{-1}. The decay rate of this component is ∼160 ns at 16 K and unaffected by the incident microwave power, indicating that the polarization decay corresponds to the lifetime of the transient species. From the lifetime and rather small $|D|$ value we assigned this species to T_1 state DPM. The values of half-life and $|D|$ agree well with the results of the fluorescence measurements.

Despres et al. have shown from the T−T fluorescence experiments that there are two conformers (C_1 and C_{2v} symmetry species) in a glassy matrix, and their decays have three components in the absence of an external magnetic field. The component lifetimes are 4.2, 8.0, and 26 ns for the C_{2v} species, and 26, 92, and 163 ns for the C_1 species at 20−30 K.[6] The T_1 state TREPR signals in the present work would be due to the species having a relatively longer lifetime. As depicted in Figure 2d, the electron spin polarization of an AAA/EEE pattern was observed for the $|\Delta M_s| = 1$ transitions in the T_1 state of DPM, where A and E denote enhanced absorption and emission of microwave radiation, respectively. The spin polarization suggests that the highest sublevel is almost exclusively depopulated at the delay time of 100 ns, indicating the highest sublevel corresponds to that showing the fastest decay. The spin−orbit coupling (SOC) interaction between the T_1 and S_n states would induce the selective decay from the highest sublevel through the anisotropic nonradiative decay.

In the $T_0(n\pi_0)$ state of DPM, the one-center electron spin dipolar interaction governs the ZFS parameters. The $|D|$ value of the T_1 state is nearly $^1/_2$ that of the T_0 state of DPM, indicating the delocalization of π electron spin densities on the phenyl rings by excitation. Using a simple Hückel approximation, the LCAO MOs for the SOMOs in the $T_0(n\pi_0)$ and $T_1(n\pi_1{}^*)$ states are roughly expressed in a small φ region as follows:

$$\psi_n = a\chi_{\mathrm{lo}} - b(\chi_2 - \chi_4 + \chi_6 - \chi_8 + \chi_{10} - \chi_{12})$$

$$\psi_{\pi_0} = c\chi_{\mathrm{2pyo}} - d(\chi_2 - \chi_4 + \chi_6 + \chi_8 - \chi_{10} + \chi_{12})$$

$$\psi_{\pi_1{}^*} = {}^1/_2\sqrt{6}(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6 - 2\chi_7 + \chi_8 + \chi_9 - 2\chi_{10} + \chi_{11} + \chi_{12})$$

where, $a = 2/(4 - 6\sin^2\varphi\cos\theta)^{1/2}$, $b = \sin\varphi\{-\cos\theta/(4 - 6\sin^2\varphi\cos\theta)\}^{1/2}$, $c = 2/(4 + 6\cos^2\varphi)^{1/2}$, $d = \cos\varphi/(4 + 6\cos^2\varphi)^{1/2}$, and $\chi_{\mathrm{lo}} = \{(1 + \cos\theta)/(1 - \cos\theta)\}^{1/2}\chi_{\mathrm{2so}} + \{-2\cos\theta/(1 - \cos\theta)\}^{1/2}\chi_{\mathrm{2pxo}}$.[10] Since the π^* orbital in the $T_1(n\pi_1{}^*)$ state has zero coefficients on the methylene carbon, we can predict that the one-center dipolar interaction is negligible in the T_1 state of DPM.

The electron spin−spin interaction part in the ZFS parameters was calculated by including all of the two-center Coulomb-type dipole−dipole interaction integrals. Details of the calculations are essentially the same as those in previous papers.[4,11] The principal ZFS parameters of $Z = 0.0946$, $X = -0.0399$, and $Y = -0.0466$ cm^{-1} [$D = -3Z/2 = -0.142$ cm^{-1}, $E = (Y - X)/2 = -0.0033$ cm^{-1}] were obtained for the T_1 state with a bent structure ($\theta = 150°$ and $\varphi = 15°$) by the calculation. The principal axes are shown in Figure 1. Taking into account the ordering of the triplet sublevels, we obtained the simulated TREPR spectrum shown in Figure 2d by the population differences of $(P_x - P_z)$:$(P_y - P_z) = 0.65$:0.35. The present study indicates that the T_1-$(n\pi^*)$ state of methylene has very large radiationless rate from the long axis T_z sublevels.

The spin polarization pattern observed in the T_0 state is the same as that in the T_1 state. It is well-known that the long axis T_z sublevel is the lowest one in the T_0 state: $T_y > T_x > 0 > T_z$. An A/EEE pattern is well reproduced by the population differences of $P_y - P_x$:$P_z - P_x = 0.2$:0.8, indicating the preferential population in the lowest sublevel. It has been reported that for DPM the radiative yield is relatively low ($\Phi_f = \sim 0.2$)[12] and the ISC rate between the $S_1(nn)$ and T_0 states is very large.[13] Therefore, the T_0 state would be reproduced via a radiationless process. The possible path for the spin polarization creation in the T_0 state may be the anisotropic ISC from the $S_1(nn)$ which populated by the process

$$T_1(n\pi_1{}^*) \xrightarrow{\text{ISC}} S_n \rightarrow S_1(nn) \xrightarrow{\text{ISC}} T_0(n\pi_0)$$

One center SOC interaction between the $S_1(nn)$ and $T_0(n\pi_0)$ states involves matrix elements of the z orbital angular momentum components, leading to the preferential ISC into the T_z sublevel. The decay time constant of 2.8 μs was observed for the polarization of the T_0 state DPM. Since the ground-state of DPM persists at 16 K, the polarization decay of the T_0 state is governed by the spin−lattice relaxation.

It has been suggested that the T_2 and T_3 states are closely located to the T_1 state. Therefore, the configuration interaction should be taken into account for the precise interpretation of the ZFS parameters in the T_1 state of DPM. SOC interaction also may contribute to the ZFS parameters as suggested in the T_0 state of methylene.[14] Further detailed investigations are in progress by modifications of the geometry and the energy difference between the T_1 and T_2 states by substituent groups.

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(10) Exactly speaking, the interaction with a configuration arising from one-electron excitation from one of the HOMOs with symmetry a to a π_0 MO should be included.

(11) A 2s electron was replaced by a unit charge at the nucleus, and a π electron was two $^1/_2$ point charges which located it at distance d from the center of an atom.[4] The d values were evaluated using SCF-2p$_x$ AOs given by Clementi. (Clementi, E. Tables of Atomic Functions. *IBM J. Res. Dev. Suppl.* **1965**, *9*, 2.).

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