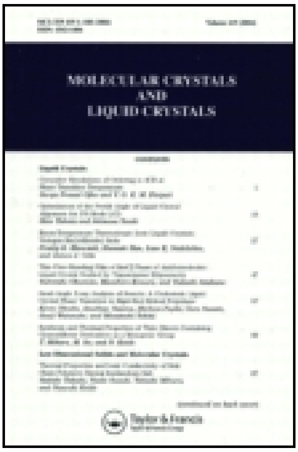

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# AN ESR AND MO STUDY OF STABLE TRIPLET DIPHENYLMETHYLENE WITH PERPENDICULAR CONFORMATIONS

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Abstract A ground-state triplet diphenylmethylene derivative, 2,2',3,3',5,5',6,6'-octamethyldiphenylmethylene (OMDPM) is a model for chemically stable organic high spin molecules. The electronic structure and the stability of OMDPM have been investigated by electron spin resonance, and the molecular conformation responsible for this stability has been shown by AM1 UHF MO calculations and LCAO MO calculations for zero-field splitting parameters. OMDPM was generated by photolysis of the corresponding diazo precursor in organic solvents or single crystals of the precursor at cryogenic temperatures. Based on the simulation of the fine-structure spectra from random orientation, the zero-field splitting parameters have been determined. The single-crystal experiment showed that OMDPM survived up to 250K. The AM1 UHF MO calculations and the LCAO MO calculations made clear the reason of this stability. Both calculations indicated that the phenyl rings of OMDPM were perpendicular to each other and that the reactive center was protected by the eight methyl groups.

## INTRODUCTION

In general carbenes are regarded as short-lived and highly reactive intermediates. During the last three decades chemists have attempted to synthesize and detect chemically stable carbenes at ambient temperature. Zimmerman et al. demonstrated the stability of carbenes by use of the introduction of substitutional groups, and synthesized a diphenylmethylene derivative with six methyl groups, dimesitylmethylene.1) This carbene is chemically stable in comparison with other diphenylmethylene derivatives. Since then Griller et al. gave a qualitative interpretation of this stability in terms of ESR measurements2) of randomly oriented dimesitylmethylene and crystal structure analysis3) of the

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corresponding diazo precursor. They indicated that the steric hindrance due to the methyl groups gave rise to the stability.

If the steric hindrance is workable, an analogous compound of dimesitylmethylene 2,2',3,3',5,5',6,6'-octamethyldiphenylmethylene (OMDPM) which has eight methyl groups at ortho and meta-positions of two phenyl rings is expected to be as chemically stable as dimesitylmethylene. The aim of this work is to find models for chemically stable organic high-spin molecules. In this paper, we report the zero-field splitting parameters and chemical stability of OMDPM by use of ESR spectroscopy. The relation between the chemical stability and molecular conformation of OMDPM was made clear in terms of Higuchi's work[4)] and AM1 UHF MO calculations.

## EXPERIMENTAL

### Materials

The preparation of the diazo precursor of OMDPM will be described elsewhere. Trans-decalin and 2-MTHF were purified according to usual methods and methylcyclohexane (spectral grade) was used without further purification.

### Electron Spin Resonance Measurements

The diazo precursor of OMDPM was fairly soluble in 2-MTHF or trans-decalin/methylcyclohexane (volume ratio 2:1) mixed solvent. The solution was degassed and sealed off on a vacuum line. The solution yielded a dark red glass at 77K. The glassy sample was irradiated with light of 405 nm wave length. The irradiated sample was transferred to the sample site of a cryostat at cryogenic temperature. ESR measurements were carried out at X band microwave frequencies by use of magnetic field modulation of 100kHz. The temperature dependence of the ESR spectral intensity was observed in the range of 1.7 to 110K. The temperature was controlled by an Oxford ESR 910 helium gas flow system. Numerical calculations were carried out with a HITAC M680 at Computer Center of IMS (the Institute for Molecular Science) and a HITAC M660/180E at Osaka City University Computer Center.

## RESULTS AND DISCUSSION

Figure 1a shows the ESR spectrum observed at 40K after the irradiation of the diazo precursor of OMDPM. This ESR spectrum is typical for randomly oriented triplet molecules with $D \sim 0.4\text{cm}^{-1}$, except for the signal observed at 0.34T. This signal originates from by-products during the sample preparation and/or photochemical decomposition of the diazo precursor. Numerical calculations were carried out to simulate the ESR fine structure spectra of these randomly oriented triplet molecules. In the calculations all the resonance fields and transition probabilities were obtained by an exact diagonalization[5)] of the following spin Hamiltonian

$$\begin{aligned}\mathcal{H} &= \beta\,\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}\\ &= \beta\,\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2),\end{aligned}$$

where the terms are defined in the usual manner. We assumed a Gaussian line-shape function for each transition. The number of orientations in the simulation for a single spectrum was 16606.

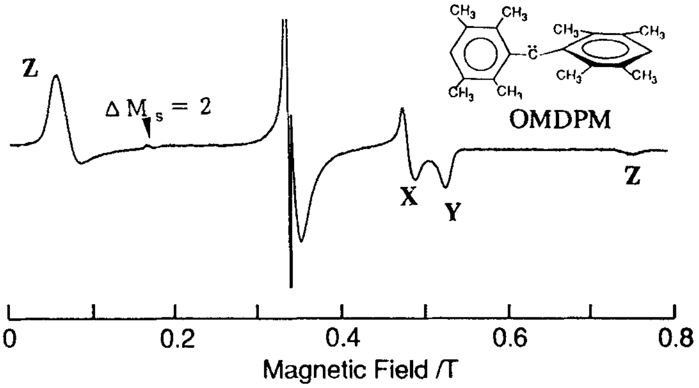
Figure 1b is the simulated spectrum for the ESR spectrum observed in 2-MTHF glass before annealing. The spin Hamiltonian parameters employed in the calculations are summarized in Table I. Assuming that the spin Hamiltonian parameters are constant unless molecular conformation changes of OMDPM occur, they were determined on the basis of spectra obtained at 40K at a microwave frequency of 9.5707GHz. The effect of the Boltzmann distribution was ignored in the calculations. The best fit spin Hamiltonian parameters were found to be $g=2.003$ (isotropic), $D=+0.3848\text{cm}^{-1}$, $E=-0.0128\text{cm}^{-1}$.

To determine the lowest energy state, we observed the temperature dependence of the ESR signal intensity. The ESR spectra were recorded in the range from 1.7 to 110K. Figure 2 shows the temperature dependence of ESR spectra of randomly oriented OMDPM in trans-decalin/methylcyclohexane (2:1) glass after annealing, indicating the absence of molecular conformation changes of OMDPM during the process of increasing temperature. The temperature dependence of the ESR signal intensity (I) of the Z transition (low magnetic field) in trans-decalin/methylcyclohexane (2:1) glass after annealing is shown in Figure 3. The plot of I vs. the reciprocal of temperature in the range from 40 to 80K indicates that it follows Curie law dependence over that temperature range. The points denote the observed values, and the solid curve represents the following expression

$$I = \frac{A}{T}\cdot\frac{1}{3+\exp(-\Delta E/kT)}$$

where A stands for the normalization constant and $\Delta E$ the energy gap between the singlet and triplet states. From these results it is concluded that the observed triplet is the electronic ground state and the singlet state is located far above the triplet state.

(a) Observed (2-MTHF; before annealing)



(b) Simulated

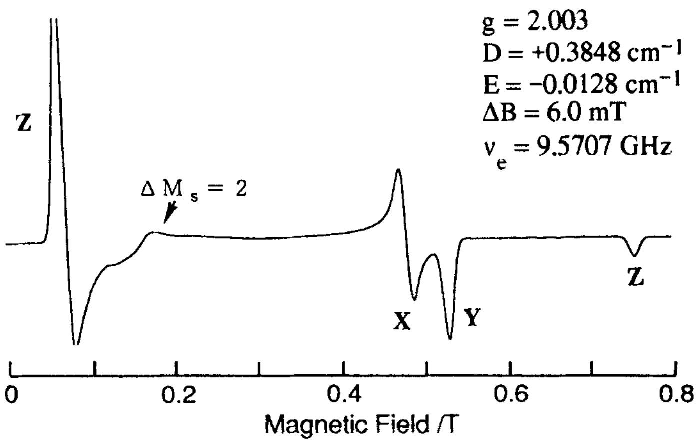


FIGURE 1 The X-band ESR spectra from the triplet state of OMDPM in 2-MTHF glass before annealing. (a) the observed spectrum at 40K,$\nu_e$=9.5707GHz (b) the simulated spectrum.

When the 2-MTHF glass was warmed to 130K for 10 seconds, there was a striking shift in the positions of the X and Y lines, which moved closer to each other. This is due to the reduction in E of OMDPM by annealing. On the other hand, the position of the Z line slightly shifted to lower magnetic field, indicating a small amount of the reduction in D. Re-cooling the sample did not reverse this change. As can be seen in Table I, the annealing process decreased the zero-field splitting parameters (especially E) by about 50%. It means that a structural irreversible change of OMDPM occurred in 2-MTHF glass by annealing. The reduction in D shows an increase in the delocalization of the spin density from the divalent carbon atom, and the reduction in E an increase of axial symmetry of OMDPM.

In 1971 Higuchi predicted the relation between the zero-field splitting parameters and molecular conformations of diphenylmethylene (DPM) on the basis of LCAO-MO calculations.[4] Figure 4 shows the calculated D and E values of DPM as a function of the $\dot{\underset{\cdot}{C}}$- bond angle (θ) assuming the planar structure (α=0°) and the structure with the two phenyl groups perpendicular to the plane of the -$\dot{\underset{\cdot}{C}}$- bond (α=90°). It is well known that this result coincides with the observed values of $D=0.4050cm^{-1}$, $E=0.01918cm^{-1}$. Because molecular conformation changes affect the zero-field splitting parameters more than functional group substitutions do, it is reasonable that the relation shown in Figure 4 applies to the case of OMDPM. Broken lines in Figure 4 are for the observed D and E of OMDPM in 2-MTHF glass after annealing. According to Higuchi's model, θ and α of OMDPM are 148.6° and 90°, respectively.

TABLE I Zero-field splitting parameters of OMDPM.

| matrix | temp,K | $D,cm^{-1}$ | $E,cm^{-1}$ |
|---|---|---|---|
| OMDPM | | | |
| before annealing | | | |
| 2-MTHF | 40 | +0.3848 | −0.0128 |
| after annealing ($T_a$=130K) | | | |
| 2-MTHF | 40 | +0.3520 | −0.0060 |
| decalin/methylcyclohexane | 40 | +0.3508 | −0.0067 |

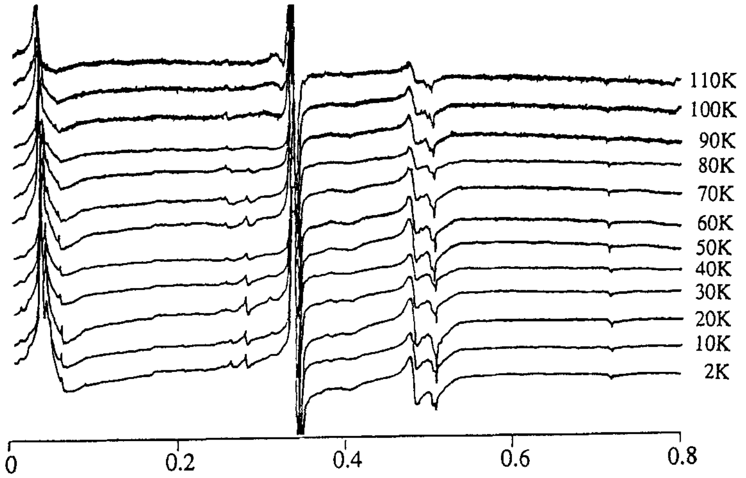


FIGURE 2 Temperature dependence of randomly oriented ESR spectrum of OMDPM in trans-decalin/methylcyclohexane (2:1) glass after annealing.

On the other hand, the structural optimization of OMDPM were carried out by AM1 UHF MO calculations. The calculations were performed for θ and α. The energy-optimized conformation of OMDPM is shown in Figure 5, indicating α=89.4° and θ=151.4°. This result agrees with one obtained in terms of the comparison with Higuchi's work. Both calculations indicated that the phenyl rings of OMDPM were perpendicular to each other and that the reactive center (the divalent carbon atom) was protected by the eight methyl groups of the two phenyl rings. Fully optimized calculations for the molecular conformation of OMDPM by use of ab initio MO calculations are under way.

Figure 6 shows the ESR spectra observed from a single crystal of OMDPM [(a) at 3K, (b) at 250K], indicating the remarkable chemical stability of OMDPM in comparison with the other diphenylmethylene derivatives. It can be concluded that the chemical stability is due to the perpendicular conformation of OMDPM, which is caused by the steric hindrance of the substituted methyl groups. This conformation prevents other molecules from approaching the reactive center.

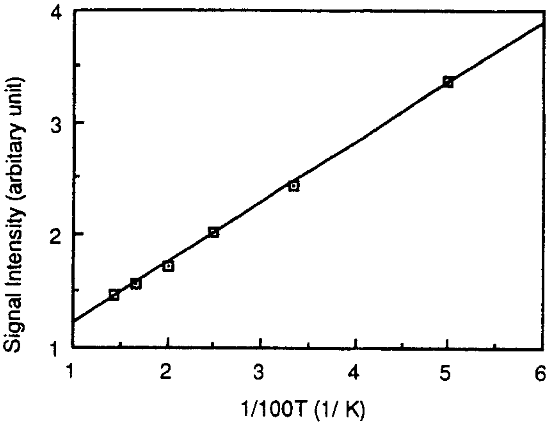


FIGURE 3 Temperature dependence of the signal intensity of the Z-transition (low magnetic field) of OMDPM in trans-decalin/methylcyclohexane (2:1) glass after annealing.

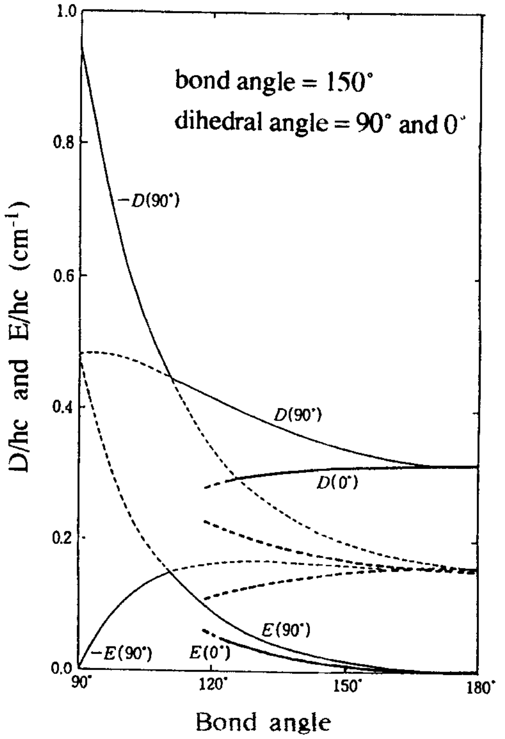


FIGURE 4 The relation between the fine-structure constants and molecular conformations. [J. Higuchi, Bull. Chem. Soc. Jpn., 44, 2634 (1971).]

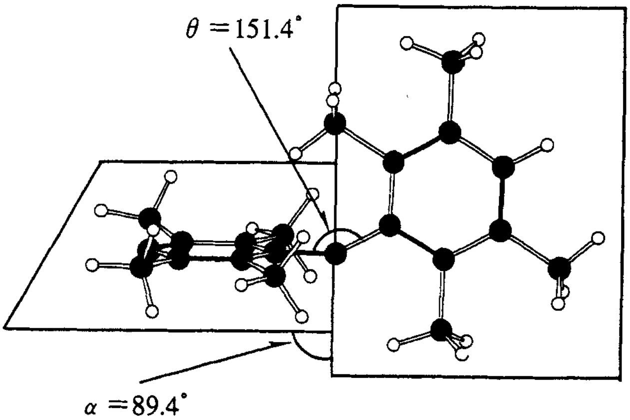


FIGURE 5 The energy-optimized conformation of OMDPM by AM1 UHF MO calculations (the optimization was carried out for θ and α).

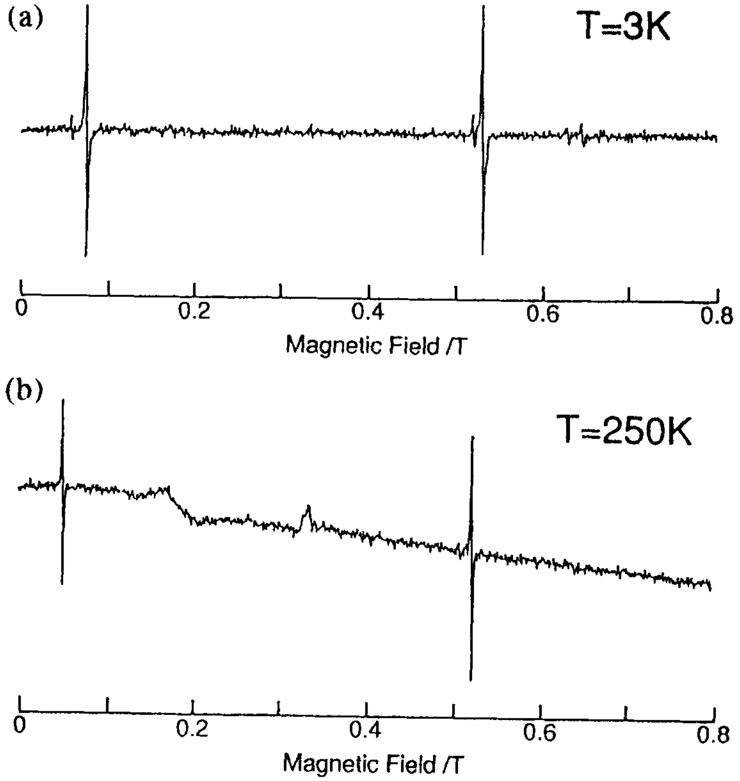


FIGURE 6 The ESR spectra observed from a single crystal of OMDPM [ (a) at 3K, $\nu_e$=9.5694GHz (b) at 250K, $\nu_e$=9.5683GHz]

## CONCLUSION

The electronic structure and the chemical stability of OMDPM were investigated by ESR spectroscopy, and the molecular conformation responsible for this stability was shown by AM1 UHF MO calculations and LCAO-MO calculations of the zero-field splitting parameters. All the resonance fields were well interpreted by an effective spin Hamiltonian with $S=1$, $g=2.003$ (isotropic), $D=+0.3848\text{cm}^{-1}$, $E=-0.0128\text{cm}^{-1}$ before annealing, $D=+0.3520\text{cm}^{-1}$, $E=-0.0060\text{cm}^{-1}$ after annealing in 2-MTHF glass, $D=+0.3508\text{cm}^{-1}$, $E=-0.0067\text{cm}^{-1}$ after annealing in trans-decalin/methylcyclohexane (2:1) glass. The temperature dependence of the signal intensity proved the ground state to be a triplet state. The single-crystal ESR experiment showed that OMDPM survived up to 250K in the neat crystal. The AM1 UHF MO calculations and LCAO-MO calculations indicated that the stability of OMDPM was due to the perpendicular conformation.

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