

is manifested by a very small σ_{ii}^{CC} term and modest off-diagonal elements encountered in this study. Even bonds associated with considerable strain still exhibit a relative modest σ_{ii}^{CC} along the internuclear axis.

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Magnetic Interaction among Diphenylmethylene Molecules Generated in Crystals of Some Diazodiphenylmethanes

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Abstract: When polycrystalline solid samples of *p*-methoxy- and *p,p'*-dimethoxydiphenyldiazomethanes (3 and 4, respectively) were photolyzed in an ESR cavity at 10 K, fine structures due to triplet (T), quintet (Q), and higher multiplet species (M) were observed. The Q signals, e.g., $|D| = 0.136$ and $|E| = 0.015 \text{ cm}^{-1}$ from 4, were always most conspicuous and interpreted as arising from the pairwise interaction of the triplet *p,p'*-dimethoxydiphenylmethylene (2) formed in the host crystals of 4. The Curie plot of the ESR signal intensities and $1/\chi_p$ vs. T plot have shown that Q is the ground state for the pair of T carbenes. From the light intensity dependence, the formation of the Q pair in polycrystalline 4 was found to be one-photonically especially at shorter wavelength. In sharp contrast with the case of 3 and 4, photolysis of *p,p'*-dichlorodiphenyldiazomethane (6) gave predominantly an ESR spectrum of a triplet *p,p'*-dichlorodiphenylmethylene (5), accompanied by a weak signal of a thermally populated quintet species. The magnetic susceptibility measurement also showed a presence of very weak magnetic interaction among triplet species 5. The average spin multiplicity determined by the magnetic field dependence on the magnetization was $S = (3.8 \pm 0.4)/2$ for 2 and $S = (1.9 \pm 0.2)/2$ for 5, respectively. The pairwise ferromagnetic interaction between the T carbenes generated in the crystals of 4 was explained in reference to their crystal packing estimated from that of the corresponding *p,p'*-dimethoxybenzophenone. The magnetic model for 5 is also discussed based on the crystal packing of 6 determined by an X-ray analysis.

Since the advent of dicarbenes in the ground quintet state,¹ the possibility of constructing organic ferromagnets has been discussed from a theoretical point of view.² However, it is only of recent date that experimental approaches to organic ferromagnets have been started by investigators in various fields.³ In order to simulate macroscopic ferromagnets by organic molecular assemblies, it is imperative to introduce ferromagnetic intermolecular interaction among open-shell organic molecules and connect them magnetically to form domain structures.⁴ High spin hydrocarbons,⁵ such as *m*-phenylenebis(phenylmethylene) and its homologues, seem to be the most efficient building blocks to constitute magnetic domains. We have already shown the "superparamagnetic" behavior of the ground state nonet carbene, *m*-phenylenebis((diphenylmethylene-3-yl)methylene).⁶ Its intermolecular interaction however turned out to be weak and antiferromagnetic in fortuitously formed aggregates and neat polycrystals.

McConnell's theory serves as a guiding principle to design intermolecular magnetic interaction of π -spin-containing hydrocarbons.⁷ According to the theory, the intermolecular magnetic interaction is governed both by the intermolecular exchange integral, J_{ij}^{AB} , between the most interacting sites *i* and *j* on molecules A and B, respectively, and by the product of spin densities $\rho_i^A \rho_j^B$ at *i* and *j* where S^A, S^B are the total spin operator of molecules A and B, respectively. Since J_{ij}^{AB} is usually negative in sign, the sign of $\rho_i^A \rho_j^B$ is crucial to determine the character of magnetic interaction (eq 1).

$$\mathcal{H}^{AB} = -S^A \cdot S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \quad (1)$$

Let us consider the interaction between two superimposable benzene rings one from each diphenylcarbene molecule. There are four modes of overlap in reference to the relative orientation of phenylmethylene substituents as depicted below. The sign of ρ_i is established to alternate on the benzene rings of the diphenylcarbene molecules.⁸ The ferromagnetic interaction is predicted for pseudo-ortho or -para orientation, since spin densities have opposite signs at the most interacting sites. The interaction becomes antiferromagnetic in pseudo-geminal or -meta orientation.

By taking advantage of the [2.2]paracyclophane skeleton we have recently shown that the spin multiplicity of two interacting

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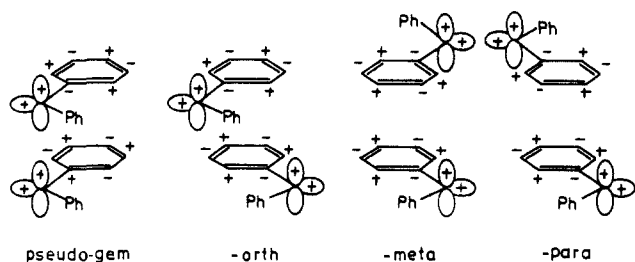
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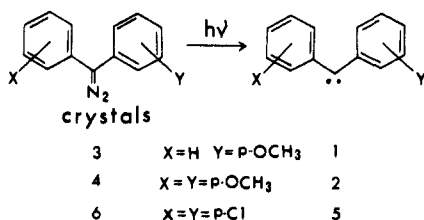
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triplet diphenylcarbenes in three isomeric bis(phenylmethylene)[2.2]paracyclophanes is controlled by the orientational modes of overlap as predicted. Namely, the ground-state quintet ESR signals were observed in the pseudo-ortho and -para isomers, and the singlet is the ground state for the pseudo-meta.⁹ These findings have encouraged us to investigate intermolecular magnetic interaction among diphenylcarbene derivatives generated in the host crystals of diazo precursors. Intermolecular interaction between carbene species can be ferromagnetic if favorable molecular orientation is realized in the crystals. The results could be interpreted on the assumption that the relative orientation of the generated carbene molecules may not change significantly from that of host diazo molecules. We have photolyzed a series of substituted diphenyldiazomethanes¹⁰ and found that *p*-methoxy- and *p,p'*-dimethoxydiphenylmethylenes (**1** and **2**, respectively) give



very intense quintet signals due to a pairwise intermolecular interaction between the ground-state triplet carbenes.¹¹ A contrasting result was obtained in the photolysis of *p,p'*-dichlorodiphenyldiazomethane (**6**). The magnetic interaction of the triplet carbene species was also studied by means of the magnetization measurements and will be discussed based on the molecular packing of the diazo compounds.

Experimental Section

Materials. Diphenyldiazomethanes (**3**, **4**, and **6**) were prepared according to the literature. *p*-Methoxydiphenyldiazomethane (**3**):^{12a} purple thin plates; mp 51–52 °C; ¹H NMR (CDCl₃) δ 3.85 (3 H, s), 6.96, 6.98 (2 H, d, *J* = 8.9 Hz), 7.11, 7.13, 7.15 (1 H, t, *J* = 7.3 Hz), 7.19, 7.20 (2 H, d, *J* = 7.3 Hz), 7.25, 7.28 (2 H, d, *J* = 8.7 Hz), 7.34, 7.36, 7.38 (2 H, t, *J* = 7.4 Hz); IR (Nujol) 2020 cm⁻¹. *p,p'*-Dimethoxydiphenyldiazomethane (**4**):^{12b} purple thin plates; mp 115–116 °C dec; ¹H NMR (CDCl₃) δ 3.82 (6 H, s), 6.93, 6.95 (4 H, d, *J* = 8.85 Hz), 7.17, 7.19 (4 H, d, *J* = 8.85 Hz); IR (Nujol) 2020 cm⁻¹. *p,p'*-Dichlorodiphenyldiazomethane (**6**):^{12c} purple needles; mp 111–113 °C dec; ¹H NMR (CDCl₃) δ 7.17, 7.19 (4 H, d, *J* = 8.85 Hz), 7.35, 7.37 (4 H, d, *J* = 8.85 Hz); IR (Nujol) 2025 cm⁻¹.

ESR Measurement. ESR spectra were measured on a Varian E-112/V7800 spectrometer (X-band microwave unit, 100 kHz field modulation) equipped with an Air Products LTD-3-110 liquid helium transfer system. Single crystals of diazo compounds were ground by mortar and

pestle made of agate, and the powdered crystals were placed in a quartz sample tube (5 mm o.d.). The sample was degassed and sealed under a nitrogen atmosphere. For a glassy matrix sample, the diazo compound (ca. 1 mg) was dissolved in 2-methyltetrahydrofuran (0.5 cm³), and the solution was degassed in a quartz cell by three freeze-thaw cycles. The sample was rapidly cooled in a precooled ESR cavity and irradiated with a high-pressure mercury lamp (500 W) at 10 K through a cylindrical cell (50 mm in diameter and 50 mm in depth) filled with distilled water and through a quartz lens (*f* = 100 mm, 50 mm in diameter). The light intensity was varied by neutral density filters (Oriental corporation: model G-66), and a band-pass filter (Hoya color filter glass: U340) was used for 366-nm irradiation. The microwave frequency was measured with a Takeda Riken 5201M frequency counter, and the resonance magnetic field values of the signals were measured with the aid of a Varian E500 NMR G meter. The dependence of the signal intensities on temperatures was measured by the use of a temperature-controlling accessory.

Measurement of Magnetic Susceptibility. Magnetic susceptibility was measured by an Oxford's Faraday-type magnetic balance system equipped with a superconducting magnet (5 T) and with a microprocessor.^{6c} The magnet was composed of a main coil and a pair of reverse Helmholtz coils for the field gradient. The main field gradient, the temperature of a sample, and the weight change were carefully calibrated to enable the absolute magnetic susceptibility measurement. The temperature of the cryostat (300 ~ 20 K) was regulated by the microcomputer, and data were collected when the temperature stabilized within 0.1%/min. The temperatures between 20 and 4 K were controlled manually by adjusting the flow of liquid helium, and lower temperatures than 4 K were obtained by pumping liquid helium. A platinum-resistance thermometer was used to read temperatures higher than 25 K and a carbon-resistance thermometer for lower temperatures. A cylindrical quartz sample cell (10 mm in diameter, 12 mm in depth, and 135 mg in weight) was used for the measurement. Polycrystals of a diazo compound (ca. 4 mg) was placed in the cell, and liquid paraffin (ca. 40 mg) was added to fix the crystals. The force loaded on the sample was measured by the electrobalance with the accuracy of 10⁻⁶ g. The cell was hung from an electrobalance with a quartz string (1.18 m in length and 0.2 mm in diameter) in a sample chamber of the cryostat. The sample was evacuated to remove oxygen at 100 K and cooled to 4 K by letting a heat exchange gas of 10³ Pa into the sample chamber. The cell was located in the center of the gradient coils where the operating force to the sample is expressed by $\Delta F = m\chi H_M(\partial H_G/\partial z)$.

The operating force of the photolyzed sample was divided by the total weight of the sample including the cell and by the product of the H_M and $\partial H_G/\partial z$ values to give the overall magnetic susceptibility (χ) at each temperature. The diamagnetic susceptibility (χ_d) of the photolyzed sample was determined from the intercept of the overall χ vs. $1/T$ plot. The contribution of diamagnetic term to the operating force (ΔF) was then subtracted to give the force purely for paramagnetic one (ΔF_{para}). The ΔF_{para} was then divided by the amount of the generated carbene species determined by an UV analysis and by $H_M(\partial H_G/\partial z)$ to give the paramagnetic susceptibility (χ_p) at each temperature.

The photolysis of the sample was carried out by an ultrahigh pressure mercury lamp (Philips SP 500W) through a quartz window at the bottom of the cryostat at 4 K. The conversion yield was determined by a UV analysis (Hitachi 340 spectrometer) of absorbances at 520 nm after the magnetic measurement. Magnetization of the photolyzed sample was recorded at various temperatures. Main field of 0.5T was applied by a persistent current mode of the superconducting magnet in order to avoid saturation of magnetization at lower temperatures, a field gradient being kept constant at 0.5T/m.

The parameters of the nonlinear plots were obtained by the least-square methods. This was performed on a Hitachi M-200H computer with the program ID SALS written by Dr. Toru Nakagawa (University of Tokyo) and Dr. Yoshio Oyanagi (Tsukuba University) and filed in the Program Library of the Computer Center of Institute for Molecular Science.

X-ray Crystal Determination. Crystal data: C₁₃H₉Cl₂N₂; *M* = 263.11. monoclinic *P*2₁/*a*, *Z* = 4, *a* = 19.59 Å, *b* = 3.98 Å, *c* = 16.65 Å, β = 114°, *D*_c = 1.47 g cm⁻³. A total of 919 independent reflections with *F*_o > 3σ(*F*_o) were collected on a Rigaku AFC-5R diffractometer with monochromatized Cu Kα radiation. The structure was solved by the Monte-Carlo direct method¹³ with the aid of MULTAN78 and refined on *F*² by a full-matrix least-squares program.¹⁴ The final *R* value was 0.148. Decomposition of the diazo crystal was observed under X-ray radiation, and this may be the reason for the large *R* value. All calcu-

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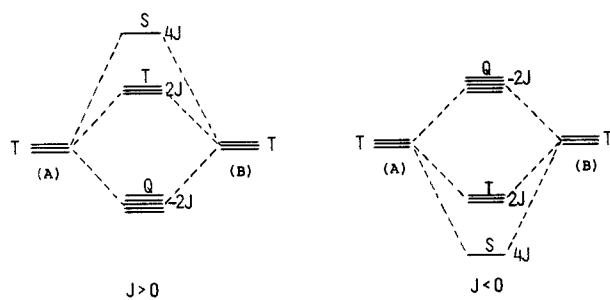
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Scheme I. Weak Interaction between two Triplet Species



lations were carried out on a FACOM M-382 computer at the computation center of Nagoya University.

Results and Discussion

(a) **Magnetic Interaction Model of a Triplet Carbene Pair.** While the radical pair theory¹⁵ is well-established and has been utilized in interpreting various chemical phenomena including CIDNP, CIDEF, or external field effect on chemical reactions, a theory on a triplet carbene pair^{1c,16} is less common in chemistry and may be worthwhile describing here in brief. In the valence bond model, the energy states derived from weakly interacting two triplets can be described by a Heisenberg Hamiltonian (eq 2) where s_i is a spin angular momentum operator for each triplet

$$\mathcal{H}_{\text{ex}} = -2Js_1 \cdot s_2 \quad (2)$$

state, and J is the exchange integral. The spin parts of the wave function of each triplet state are $\alpha\alpha$, $(1/\sqrt{2})(\alpha\beta + \beta\alpha)$, and $\beta\beta$. Thus the spin functions of the total system can be described by the products of these three spin functions. The eigenfunctions of the Hamiltonian (2), which are given as a linear combination of the nine spin functions, belong to three eigen values, $-2J$, $2J$, and $4J$. The state of eigen value $-2J$ has fivefold degeneracy with a total spin $S = 2$, which is a quintet state. The eigenfunctions of the quintet state is shown in eq 3, where the subscript of Q_i shows the eigen value of s_z . The state of the eigen value $2J$ is

$$Q_2 = \alpha\alpha\alpha\alpha$$

$$Q_1 = (1/2)[\alpha\alpha(\alpha\beta + \beta\alpha) + (\alpha\beta + \beta\alpha)\alpha\alpha]$$

$$Q_0 = (1/\sqrt{6})[\alpha\alpha\beta\beta + (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) + \beta\beta\alpha\alpha]$$

$$Q_{-1} = (1/2)[(\alpha\beta + \beta\alpha)\beta\beta + \beta\beta(\alpha\beta + \beta\alpha)]$$

$$Q_{-2} = \beta\beta\beta\beta \quad (3)$$

threefold degenerate (eq 4) with a total spin of $S = 1$, corresponding to a triplet state. The eigenfunction which belongs to

$$T_1 = (1/2)[\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha]$$

$$T_0 = (1/\sqrt{2})(-\alpha\alpha\beta\beta + \beta\beta\alpha\alpha)$$

$$T_{-1} = (1/2)[(\alpha\beta + \beta\alpha)\beta\beta - \beta\beta(\alpha\beta + \beta\alpha)] \quad (4)$$

the eigen value $4J$ is a singlet state ($S = 0$) and is given by eq 5. The relative energy of three states are calculated as in eq 6

$$S_0 = (1/\sqrt{3})[\alpha\alpha\beta\beta - (1/2)(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) + \beta\beta\alpha\alpha] \quad (5)$$

indicating that the quintet is the ground state when the sign of J is positive and that the singlet becomes the ground state for a negative J value. The energy gap between the triplet and the

$${}^5E - {}^3E = 4J, \quad {}^3E - {}^1E = 2J \quad (6)$$

quintet state is twice as large as that between the triplet and the

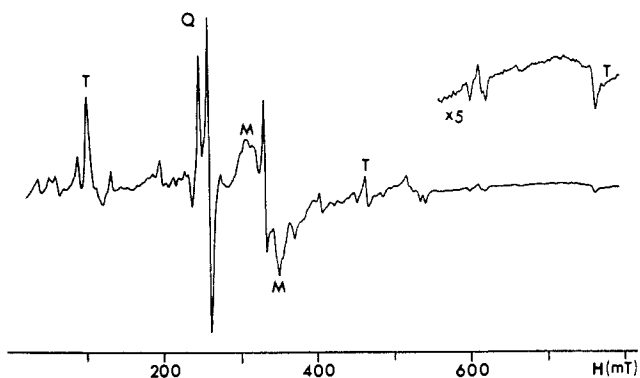


Figure 1. ESR spectrum obtained after irradiation of the polycrystalline sample of **4** at 10 K. T, Q, and M stand for the signals assigned to the triplet carbene, the quintet pair, and the interaction between quintet pairs, respectively.

Table I. Zero-Field Parameters of Triplet Diphenylcarbenes and Carbene Pairs with Quintet Ground State

diphenylcarbenes	media	triplet (cm^{-1})	quintet (cm^{-1})
<i>p</i> -OCH ₃ (1)	2-MeTHF	$D = 0.406$ $E = 0.0193$	
	crystals	$D = 0.408$ $E = 0.0180$	$D = 0.136$ $E = 0.013$
<i>p,p'</i> -(OCH ₃) ₂ (2)	2-MeTHF	$D = 0.407$ $E = 0.0198$	
	crystals	$D = 0.408$ $E = 0.0194$	$D = 0.136$ $E = 0.015$
<i>p,p'</i> -Cl ₂ (5)	2-MeTHF	$D = 0.399$ $E = 0.0198$	
	crystals	$D = 0.398$ $E = 0.0194$	<i>a</i>

^aThe amount of the quintet species was too small to determine the zero-field parameters.

singlet states (Scheme I). In the following sections magnetic interaction between triplet diphenylmethylene will be discussed based on the above model.

(b) **Magnetic Interaction of *p*-Methoxy- and *p,p'*-Dimethoxydiphenylmethylene Generated in Diazo Precursors.** Irradiation of polycrystalline samples of *p*-methoxy- and *p,p'*-dimethoxydiphenyldiazomethanes (**3** and **4**, respectively) was carried out in an ESR cavity at 10 K. The observed spectra were found to be entirely different from those obtained in glassy matrices. The spectra as a whole resembled closely that of the pseudo-para isomer of bis(phenylmethylene)[2.2]paracyclophane with the quintet ground state (Figure 1).⁹ Intense signals at 248.9 and 259.9 mT for **1** and 247.6 and 259.0 mT for **2** were observed immediately after the beginning of irradiation. These lines are characteristic of Q species.^{1b,9,17} The z line of the Q species was almost overlapped with that of T species. With these clues in hand the zero-field parameters of Q were estimated to be $|D| = 0.136 \pm 0.005$, $|E| = 0.013 \pm 0.004 \text{ cm}^{-1}$ for **1** and $|D| = 0.136 \pm 0.005$, $|E| = 0.015 \pm 0.003 \text{ cm}^{-1}$ for **2** based on a second order perturbational calculation.¹⁸ The observation of the intense Q signals suggests that a pair of the T carbenes generated in crystals of **3** and **4** interacts efficiently to give the Q species. The weak triplet lines were also observed in the photolysate of **3** and **4** with zero-field parameters of $|D| = 0.408$, $|E| = 0.0180 \text{ cm}^{-1}$, and $|D| = 0.408$, $|E| = 0.0194 \text{ cm}^{-1}$, respectively. The parameters of triplet species are very close to those obtained in a 2-methyltetrahydrofuran (2-MeTHF) glassy matrices (see Table I).¹⁹ Besides these lines, multiplet signals (M) were detected in the range 300–380 mT. The intensity of lines of Q species in this region should be much weaker than those of the observed multiplet, and

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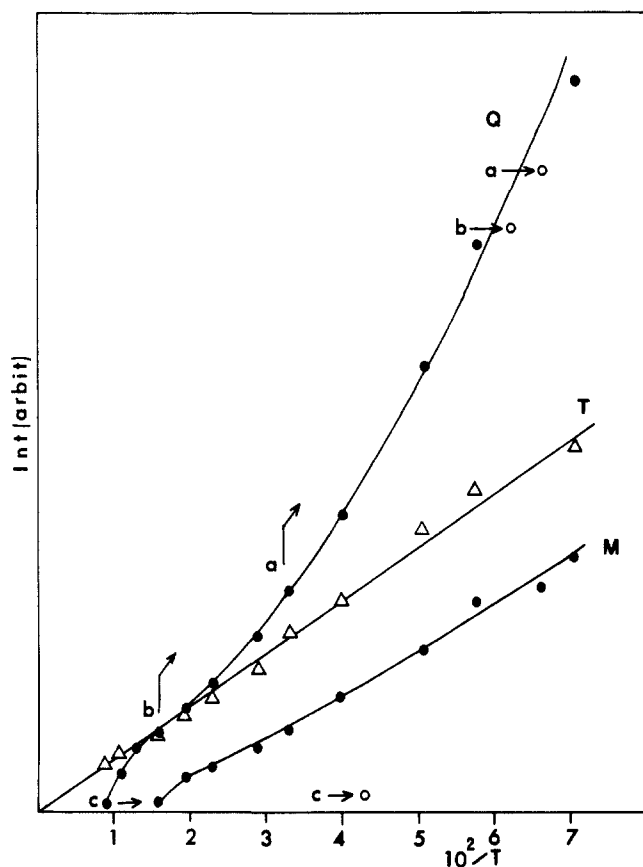


Figure 2. Curie plots of the quintet signals (Q) are due to the pairwise interaction between the triplet carbenes and those of multiplet (M) and of the triplet ones (T) observed in the photolysis of **4**. Open circles a and b indicate reproducibility of the intensity of Q after warming up to (a) 30 K and (b) 62 K, respectively. A point c (O) represents irreversible decomposition of Q after warming up to 110 K.

besides the thermal behavior of M was found to be different from that of Q (vide infra). Therefore, M was assigned to a species with higher spin multiplicity presumably formed by interaction between the Q pairs and/or the Q pair and the T carbene generated in the closest neighbors. The above spectral feature may be well-explained by postulating that various sizes of clusters of carbene species were formed photochemically in crystals of diazo molecules.

In order to obtain information on the ground-state multiplicity and the thermal stability of carbene pairs observed in the photolysate of **4**, temperature dependence of the intensities of M, Q, and T signals was measured in the range 14~120 K. Firstly, the multiplet signals (M) were observable only at temperatures lower than 60 K and irreversibly disappeared at higher temperatures presumably through a chemical reaction. Secondly, the temperature dependence of the Q signals showed no tendency that the Q species was a thermally populated one. The Curie plot was characterized by an upward deviation at lower temperatures from a straight line obtained in a higher temperature region (Figure 2). The deviation at lower temperatures from the first line is not consistent with the Boltzmann distribution of spins among the spin sublevels in a given amount of the Q species but suggests that the amount of Q species may change through an equilibrium with spin states (T and S) which are lying slightly above the ground Q state (Scheme I). The thermal behavior of Q signals may be reproduced qualitatively by calculating a Boltzmann distribution of electron spins among spin states (Q, T, and S), assuming that the energy difference among spin states is much larger than that of spin sublevels.²⁰ The calculated curve re-

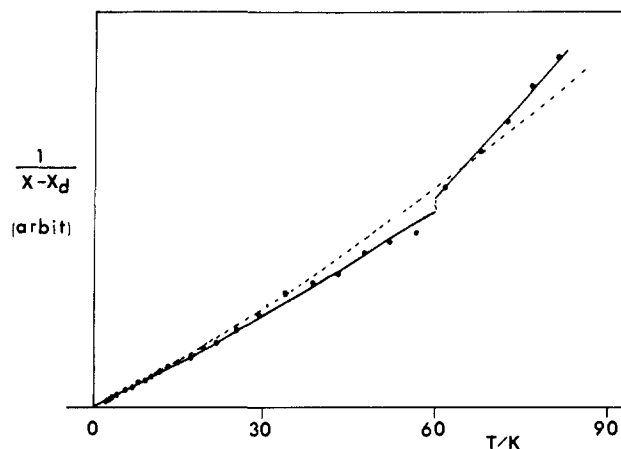


Figure 3. The temperature dependence of the reciprocal paramagnetic susceptibility of **2** generated in crystals of **4**. A solid line is a simulated curve using eq 7 and 8, the change in the amount of Q above 60 K being calibrated. A dotted line is a theoretical curve for Q species with $J = 30$ cal/mol.

produces 50% of the observed upward deviation at 10 K when the energy separation between Q and T (4 J) is assumed to be 30 cal/mol. The disagreement may be due to the inaccuracy of the above approximation. The Q signals showed good thermal reproducibility in the range 14–62 K, but they started to decay gradually at higher temperatures than 60 K, irreversibly disappearing at temperatures higher than 80 K. For a third, a Curie plot of the T signal intensities gave a straight line all through the temperature range, showing that the isolated T species is mainly responsible for the T signals. The thermally populated T species was not observed separately in the ESR spectra. The dipolar coupling tensor for weakly interacting two T carbenes can be expressed by the sum of those of individual ones (D_T^a, D_T^b) as follows, $D_T = 1/2(D_T^a + D_T^b)$.^{1c} Especially in the case of pseudo-gem or -para overlap, main axes of the pair coincide with those of each unit. Therefore zero-field parameters of T state of the pair becomes identical with those of the isolated T carbene; the observed T signals are considered to consist of the two T species. Since the energy difference between T and the ground Q state is estimated to be very small, the Curie plot of the thermally populated T may be approximated by a straight line at temperatures higher than 20 K. Thus it is difficult to estimate the contribution of the thermally populated T species to the observed overall T.

In short, the T carbene pair can be regarded as a combined molecule with the Q ground state from the view point of magnetic interaction and is chemically stable up to 60 K. The magnetic interaction within the carbene pair is however small and causes only small energy splittings among its spin states (Q, T, and S). The interaction between Q pairs is also detected.

A magnetic susceptibility measurement was carried out on the photolyzed crystals of **4**. Since the conversion yield of carbene species reaches to ca. 20%, probability of finding carbene species in the closest neighbors is expected to be reasonably high. The $1/\chi_p$ vs. T plots in the temperature range 14–62 K can be approximated by a straight line, and there is no tendency that χ_p decreases by an antiferromagnetic coupling. On raising the temperature, the plots exhibit a break point at around 60 K. The plots in the higher temperature range show a steeper slope than that obtained at the lower temperature region (<60 K), suggesting that the average spin multiplicity decreases at higher temperatures (Figure 3). The nonlinear behavior of the $1/\chi_p - T$ plots may be explained by the presence of different sizes of carbene clusters, a pair of T carbene (Q), and a dimer of Q pairs (M) with the nonet spin multiplicity in the ground state,²¹ which behave independently

(20) Assuming that the energy separation between Q–T (ΔE_1) and T–S (ΔE_2) is much larger than the energy separation among spin sublevels, the number of spins in the Q level can be given as follows. $N_Q = 5N / [\exp(-\Delta E_1/RT) + \Delta E_2/RT] + 3 \exp(-\Delta E_1/RT) + 5]$.

(21) The contribution of the isolated T carbenes (T) to the overall magnetic susceptibility is ignored since the temperature dependence of magnetic susceptibility of the isolated T is linear, if any, and does not affect the curvature of the plots.

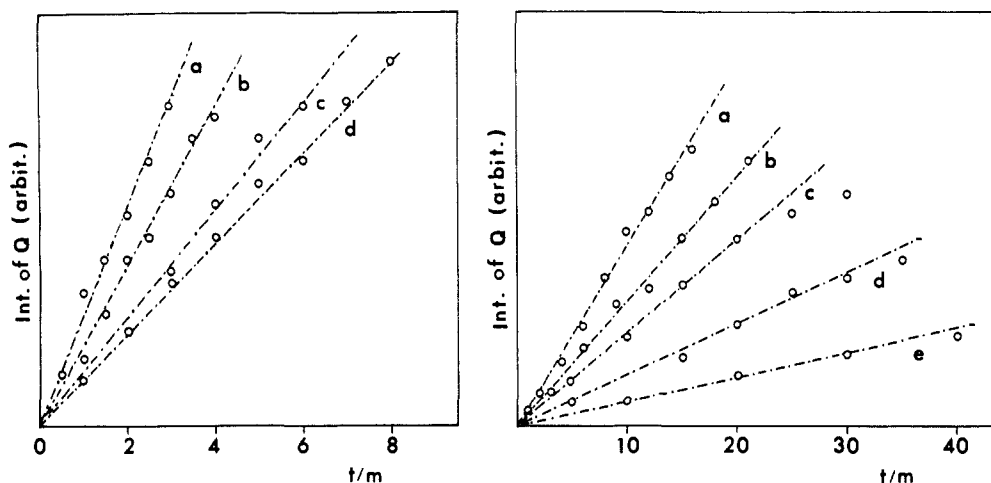


Figure 4. Rise of Q signals at various light intensities in the irradiation at 254 nm (left) and 340 nm (right). The light intensity was decreased for 254-nm irradiation as follows: $a = 1/1.32$, $b = 1/1.66$, $c = 1/2.34$, $d = 1/2.88$; for 340 nm: $a = 1/1.32$, $b = 1/1.62$, $c = 1/2.34$, $d = 1/3.09$, $e = 1/4.17$, respectively.

each other. The chemical stability of these clusters also has to be taken into account. The experimental plots now can be reproduced semiquantitatively by the above model and taking a population-weighted sum of the following two equations (eq 7 and 8) on the temperature dependence of paramagnetic susceptibility.²² The magnetic susceptibility of Q species is expressed by eq 7,

$$\chi_p^Q = (Ng^2\beta^2/kT) \times \frac{5 + \exp(-4J/kT)}{5 + 3 \exp(-4J/kT) + \exp(-6J/kT)} \quad (7)$$

assuming a Boltzmann distribution among spin states (Q, T, and S). The corresponding equation for the Q pair may be obtained by assuming that the magnetic interaction (J) between Q pairs is much weaker than that (J) within the Q pair. Thus the magnetic susceptibility of the nonet species could be expressed as a dimeric interaction between $S = 2$ species (eq 8). The best fit is obtained

$$\chi_p^N = (Ng^2\beta^2/kT) \{30 + 14 \exp(-8J'/kT) + 5 \exp(-14J'/kT) + \exp(-18J'/kT)\} / \{9 + 7 \exp(-8J'/kT) + 5 \exp(-14J'/kT) + 3 \exp(-18J'/kT) + \exp(-20J'/kT)\} \quad (8)$$

by the distribution of 95% Q with $J = 30$ cal/mol and 5% M with $J' = 5$ cal/mol, the contribution of the latter being considered only at temperatures lower than 60 K. The decrease in the number of the Q species at temperatures higher than 60 K is approximated by a linear function to reproduce the observed slope.²³

The magnetic field-dependence was also measured by changing an external field (0–5 T) at 2 and 4 K. The obtained plots were found to fit with the theoretical curve of Brillouin function with $S = (3.8 \pm 0.2)/2$ by the nonlinear least-squares method (Figure 7). The value of the average spin multiplicity larger than $S = 2/2$ suggests that the triplet carbene species is magnetically connected through the ferromagnetic interaction and is consistent with the results of ESR and magnetic susceptibility measurement.

The above result is quite in contrast with the precedents of stable organic radicals,²⁴ in most cases the interaction is characterized by negative Weiss constants. Even in the cases where weak ferromagnetic interaction is found, the interaction becomes an-

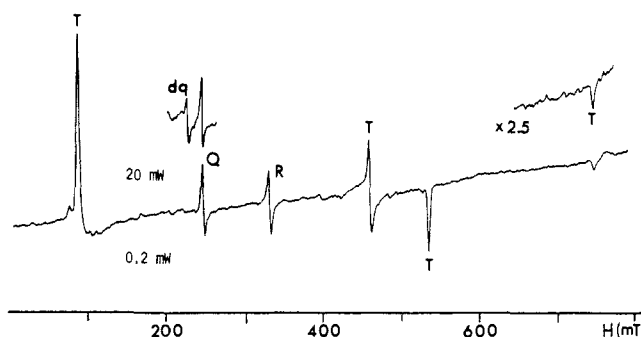


Figure 5. ESR spectrum obtained after irradiation of the powdered crystals of **6** at 10 K. T is assigned to the triplet carbene, accompanied by a dq transition at high microwave power (20 mW). Q is due to the thermally populated quintet species.

tiferromagnetic through a structural transition at lower temperatures.^{24b}

(c) Photolytic Behavior of *p,p'*-Dimethoxydiphenyldiazomethane (4**) in Crystals.** As stated above, the Q signals started to appear immediately after irradiation, making a sharp contrast to some precedents in which weak quintet signals if any were observed only after prolonged irradiation.^{11b} The initial rate constant (k) for formation of the Q signals from the polycrystals of **4** was studied as a function of the light intensity (I) at 20 K. The initial rise of Q signals is linear even at weakest light intensity (Figure 4). From the $\log k$ vs. $\log I$ plots, the photon number was determined to be 1.65 ± 0.27 and 1.14 ± 0.30 for the light of wavelengths 340 and 254 nm, respectively. The results suggest that a one-photon process may be involved in the formation of the Q species in the irradiation at 340 nm, and this process apparently predominates in 254-nm irradiation.²⁵ The results may be interpreted by assuming that the excess energy after removal of one nitrogen molecule from a diazo molecule could be efficiently transferred to the adjacent diazo molecule, resulting in the formation of the Q carbene pair. Because of the contribution of the stepwise two-photon process for formation of the Q pair in the 340-nm irradiation, the relative amount of Q over T is expected to be dependent on the light intensity. The Q/T ratio was measured by peak heights at 259.0 and 467.6 mT for Q and T species, respectively. The ratio turned out to decrease from 7.6 to 3.6 when the light intensity was decreased by one tenth. The dependence

(22) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: London, 1968; p 72.

(23) The following function was used to determine the number of Q species at T K: $N(T) = N(60)\{100 - 0.5(T - 60)\}/100$, where $T > 60$ K.

(24) (a) Nakajima, A.; Nishiguchi, H.; Deguchi, *J. Phys. Soc. Jpn.* **1968**, *24*, 1174. (b) Mukai, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 40. (c) Mukai, K.; Ishizu, K. *J. Phys. Soc. Jpn.* **1969**, *27*, 783. (d) Mukai, K.; Oishi, K.; Ishizu, K.; Azuma, N. *Chem. Phys. Lett.* **1973**, *23*, 522. (e) Azuma, N.; Ishizu, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294. (f) Mukai, K.; Nagai, H.; Ishizu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2381.

(25) The interpretation may have some ambiguity, since there is no diffusive process in photolysis of crystals. If the chance of receiving another photon is extremely high for the molecule adjacent to the photoreacted diazo molecule because of a local transparency or some unknown reason, the light-intensity dependence of the formation rate may mislead a one-photon conclusion.

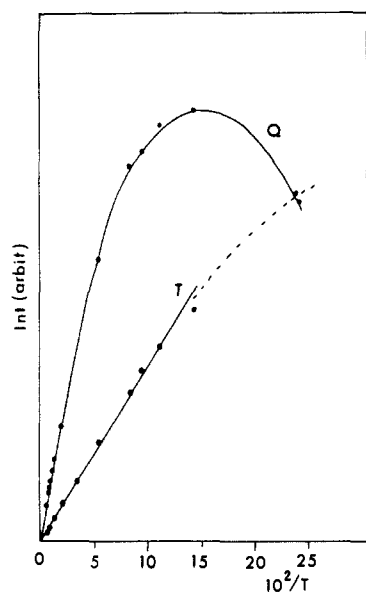


Figure 6. Curie plots of the quintet signals (Q) and triplet ones (T) observed after the photolysis of **6**.

of Q/T ratio on the light intensity and/or wavelength may have a possibility for interesting applications. This photochemical behavior can be considered as an intermolecular counterpart of the intramolecular single photon process found in the photolysis of *m*-phenylenebis(phenylmethylene) and its homologues in matrices and single crystals at cryogenic temperatures.^{5b,26}

(d) **Magnetic Interaction of *p,p'*-Dichlorodiphenylmethylene (**5**) Generated in Crystals of Diazo Precursor.** On the other hand, photolysis of *p,p'*-dichlorodiphenyldiazomethanes **6** gave predominantly an ESR spectrum for the triplet species ($|D| = 0.398$, $|E| = 0.0194 \text{ cm}^{-1}$) (Figure 5). The spectrum resembles closely that obtained for **6** in a 2-MeTHF glassy matrix, making a sharp contrast with the case of methoxy derivatives (**1** and **2**). An additional peak started to appear at 228.2 mT when microwave power was raised and was assigned to a double quanta transition (dq) of the T carbene for which the calculated peak position of 224.2 mT was obtained.²⁷ Besides the peak for the T species, a weak signal assigned to Q was detected at 280 mT. The temperature dependence of its intensity showed a concave curve with the maximum at 6 K (Figure 6).²⁸ From the thermal behavior of the peak intensity, the Q signal was ascribed to a thermally populated species, and the energy difference between the Q state and the ground state S is estimated to be $25 \pm 3 \text{ cal/mol}$.²⁹ The observation of the thermally populated Q species suggests that the T carbenes interact antiferromagnetically to give the singlet ground state for the carbene pair (Scheme I). The obtained energy difference may correspond to $6J$ in the antiferromagnetic interaction case of the T carbene pair model. The intensity ratio of T and Q signals remained constant during irradiation, and it was independent of the lots of ground single crystals of **6**. If most of the T signals are ascribable to isolated T carbenes formed by the

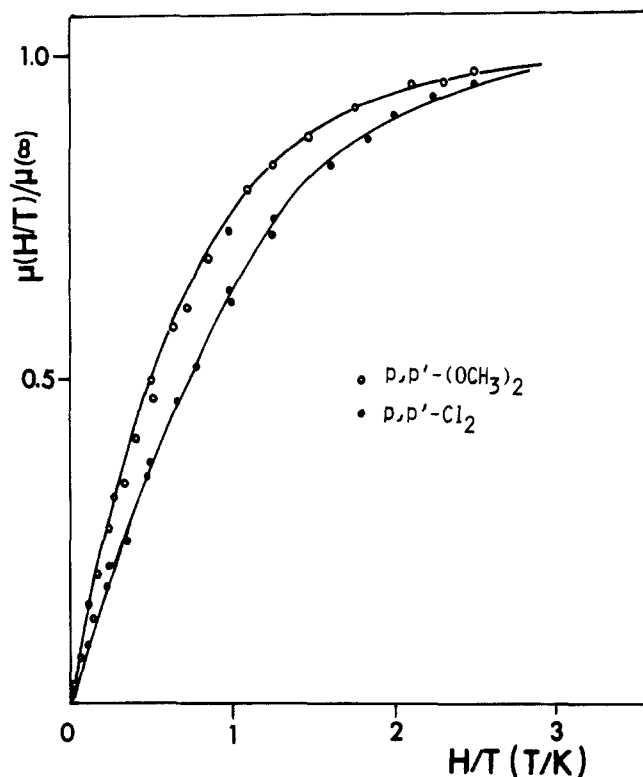


Figure 7. Plots of magnetization of **2** (O) and **5** (●) generated in diazo crystals vs. temperature normalized field strength (H/T).

failure in removing nitrogen from diazo molecules next to each other, the ratio may vary according to the irradiation time and/or to the condition of the surface of the powdered sample. It is not the case as described above. Therefore, the observed T species may be mainly due to a thermally populated T state of the T carbene pair.³⁰ The energy separation between the ground S state and observed T state is estimated to be only 8 cal/mol ($2J$). Then it seems difficult to obtain information from the thermal dependence of intensities of T species. In fact the Curie plot for the T signals showed a straight line in the temperature range 12–196 K, showing a slight deviation at temperatures lower than 9 K.

The magnetic susceptibility of **5** obtained by photolyzing crystals of **6** was recorded at various temperatures. The $1/\chi_p$ vs. T plot can be approximated by a straight line all through the temperature range 2–110 K, although a small deviation was detected at lower temperatures than 10 K. The feature of the plots could be interpreted by assuming that the T carbene **5** generated in the crystals of **6** shows very weak intermolecular antiferromagnetic interaction. The result is consistent with ESR data.

The field dependence of the magnetization of **5** was also measured, and the plots were fitted to a theoretical Brillouin function with $S = (1.9 \pm 0.2)/2$, meaning that the main species contributing to the magnetization is the T species (Figure 7).

(e) **Intermolecular Magnetic Interaction Model of Diphenylmethylene Derivatives.** The large difference in magnetic interaction between methoxy-substituted diphenylmethylenes **1** and **2** and dichloro derivative **5** may be rationalized by considering the relative orientation of each diazo precursor in the crystalline state. Neither **3** nor **4** gave good single crystals amenable to X-ray structural analyses. There are however several examples showing that carbonyl compounds have quite similar crystal packings as the corresponding diazo compounds. Therefore, the crystal structure of *p,p'*-dimethoxybenzophenone ($P2_1/a$)³¹ was taken as

(26) (a) Itoh, K.; Takui, T.; Teki, Y.; *Abstracts of Papers*, 46th Annual Meeting of the Chemical Society of Japan, Niigata, Japan, October, 1982; p 17. (b) Sugawara, T.; Inada, M.; Iwamura, H. *Tetrahedron Lett.* **1984**, *25*, 2375. (c) Sugawara, T.; Bethell, D.; Iwamura, H. *Tetrahedron Lett.* **1984**, *25*, 2375.

(27) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(28) The temperature dependence of the Q signal was carefully measured under low microwave power (0.5 mW) in order to avoid the saturation of signal intensities. The power dependence of the Q signal was checked in the range 0.05–5 mW at 4.2 K, and the linear dependence was confirmed in the range 0.05–2 mW.

(29) The temperature dependence of the peak intensity of the thermally populated Q is simulated by the following equation. $I_Q = 5cN/[\exp(\Delta E_1 + \Delta E_2)/RT] + 3 \exp(\Delta E_2/RT) + 5](1/T)$.²⁰ On the other hand, the energy difference between T and the ground S state is one third of that between S and Q. Thus the contribution of the thermally populated T to the Curie plots of the overall T is suspected to be negligibly small.

(30) The amount of the isolated T carbene in the photolysate of **6** seems smaller than that in **4**. The crystal packing of diazo molecules **6** is apparently more favorable to give a pair of carbenes through an energy transfer in the photolysis of diazo crystals, see: text.

(31) For the structure of the ketone, see: (a) Karle, I. L.; Hauptman, H.; Karle, L.; Wing, A. B. *Acta. Crystallogr.* **1957**, *10*, 481. (b) Karle, I. L.; Hauptman, H.; Karle, L.; Wing, A. B. *Ibid.* **1958**, *11*, 257.

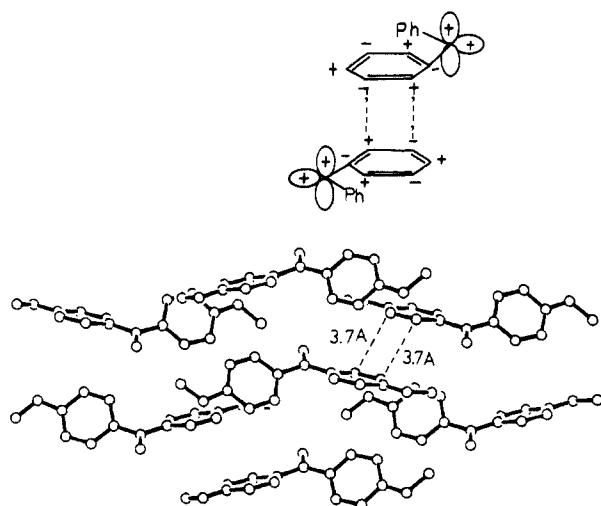


Figure 8. Packing arrangement of *p,p'*-dimethoxybenzophenone viewed in the *ab* plane. A magnetic interaction model of diphenylmethylenes is also shown.

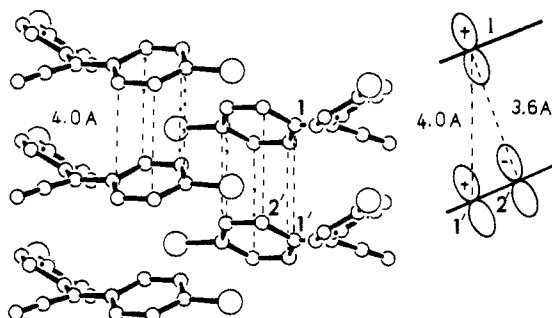


Figure 9. Packing arrangement of **6** viewed along the *a* axis. A schematic side view showing the magnetic interaction between C-1 and C-1', C-2' is also given.

a model for the crystal structure of diazo compound **4** and the generated carbene **2**. The magnetic model discussed above is in accord with the crystal structure. Among four independent molecules in the unit cell one benzene ring of the ketone molecule is nearly in parallel with the benzene ring of an adjacent molecule,

taking pseudo-para type orientation,⁹ although the center of the benzene ring is shifted and only two carbon atoms on the benzene ring are interacting effectively (Figure 8). The molecular orientation satisfies McConnell's theory⁷ in a sense that the carbon atoms with positive spin densities face those with negative ones at the interacting sites. The molecular packing also rationalizes weak interaction between Q pairs. The fact that the zero-field parameters were close to those of pseudo-para-bis(phenylmethylene)[2.2]paracyclophane is consistent with the above model.

The crystal structure of **6** ($P2_1/a$) was revealed by an X-ray analysis. The molecular packing was found to have a layered structure, and benzene rings are overlapped taking pseudo-geminal orientation (Figure 9). Thus antiferromagnetic intermolecular interaction is anticipated between the carbene species based on McConnell's relation, including direct interaction between carbene carbon atoms with the largest spin densities. The interaction however may not be very strong, because the inclination of benzene rings brings the distance, e.g., between C-1 and C-2' (3.6 Å) nearer than that of C-1 and C-1' (4 Å), the former having ferromagnetic interaction. This ferromagnetic interaction may reduce the antiferromagnetic coupling. Therefore, it may not be surprising that the quintet state of the carbene pairs is thermally accessible even at low temperatures.

The intriguing intermolecular magnetic interaction was found within clusters of diphenylmethylene molecules which were generated by irradiation on diamagnetic crystals of diazo molecules. The interaction was revealed to be well-explained by the crystal structure of diazo precursors based on McConnell's theory. The interaction however seems not to be extensive and strong enough to manifest macroscopic ferromagnetic property. Design of molecular assembly of diphenylmethylene derivatives with stronger and wider magnetic interaction is necessary. This is hoped to be achieved by introducing some additional intermolecular forces in order to bind carbene molecules tightly in favorable orientation in condensed phase. The project along this line is in progress in these laboratories.

Acknowledgment. We are indebted to Professor J. Tanaka, Dr. T. Katayama, and A. Kawamoto of Nagoya University for their skillful help in performing the X-ray diffraction analysis of *p,p'*-dichlorodiphenyldiazomethane **6**. We also thank Professor K. Itho, Dr. T. Takui, and Dr. Y. Teki for interpretation of ESR spectra of quintet species.

Fluorescence-Detected Circular Dichroism of Ethidium Bound to Nucleic Acids

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Abstract: Fluorescence-detected circular dichroism (FDCD) spectra of ethidium bound to poly(nucleotides), dinucleotides, tRNA, and DNA are reported. FDCD spectra show bands at approximately 275, 320, and 380 nm. All three bands are sensitive to base sequence at the ethidium binding site. For the bands near 320 and 380 nm, the largest magnitudes are observed for pyrimidine-purine sequences. In addition, the 275-nm band is sensitive to poly(nucleotide) structure near the ethidium binding site, and the 320-nm band is sensitive to spacing between ethidiums. FDCD spectra of ethidium bound to tRNA and DNA are consistent with an intercalative binding site and with a sequence preference for binding. FDCD spectra also indicate that ethidium binding to poly(dA-dG)-poly(dC-dT) is unusual.

Fluorescence-detected circular dichroism (FDCD)¹⁻³ is a spectroscopic technique for monitoring the local environment of

a fluorescent chromophore. FDCD combines the selectivity and sensitivity of fluorescence detection with the conformational