

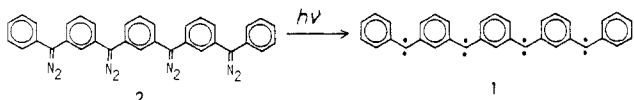
Magnetic Behavior of Nonet Tetracarbene as a Model for One-Dimensional Organic Ferromagnets

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Abstract: Tetracarbene (**1**) was generated by photolysis of the corresponding tetradiazo compound (**2**) in a 2-methyltetrahydrofuran glass or a single crystal of benzophenone at cryogenic temperatures. The temperature dependence of paramagnetic susceptibility revealed its nonet spin multiplicity in the ground state. A behavior suggesting the presence of antiferromagnetic intermolecular interaction was also found when generated in the glass. The field dependence of magnetization of **1** was analyzed in terms of the Brillouin function and the experimental data fit closely to that of the theoretical value for $J = 8/2$. This is independent evidence for the nonet spin multiplicity of **1**. The characteristic saturation behavior of magnetization in **1** was found to be due to its high spin multiplicity. Thus **1** may be regarded as a molecular superparamagnet. In the polycarbenes, the localized n spins at carbenic centers are aligned all in parallel through the electron correlation between the mobile π spins, resulting in the intramolecular ferromagnetic spin ordering. Although the mechanism of spin ordering of π spins in polycarbenes is entirely different from that in metallic ferromagnets, the interaction between n and π spins resembles s - d interaction in dilute alloys. The potentiality of polycarbenes as a microdomain in macroscopic ferromagnets will be discussed.

The explosive growth in the number of reports on organic conductors and superconductors has arisen from genuine interests in mobility of electrons in organic molecular crystals, components of which are insulators in themselves.¹ On the other hand, molecular design of organic ferromagnets which is becoming the current topic of theoretical interest in organic material science deals with the behavior of electron spins in organic molecules.² One of the strategies toward this goal is to construct organic molecules with high-spin multiplicity as domains in ferromagnets and to introduce ferromagnetic intermolecular (interdomain) interaction among them. High-spin organic molecules are accessible when nonbonding molecular orbitals are present due to the symmetry of the alternant hydrocarbon skeleton. Examples of the above category are *m*-phenylenebis(phenylmethylene),³ its higher homologues, 3,6-dimethylenanthracenediyl-1,8-dioxyl,⁴ etc. Recently we have generated tetracarbene, *m*-phenylenebis((diphenylmethylene-3-yl)methylene) (**1**) and proved its nonet spin multiplicity in the ground state by analyzing ESR fine structures of the sample oriented in a host single crystal of benzophenone.⁵ Now we have studied the magnetic behavior of this highly important tetracarbene **1** by means of magnetic susceptibility measurements.⁶



This paper describes the temperature dependence of paramagnetic susceptibility of **1** and its saturation behavior of magnetization in full detail to conclude the nonet spin multiplicity of **1** in the ground state independently from ESR spectroscopy. In addition the measurement was able to inform us of the character of intermolecular interaction which did not appear in ESR spectra of glassy matrices. The polycarbenes in this series have localized n spins at each carbenic carbon atom and delocalized π spins. These two types of spins can be compared with localized d and conducting s spins, respectively, in ferromagnetic dilute alloys. The unique magnetic behavior of **1** as a molecular superparamagnet is also discussed.

Experimental Section

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.

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. Inhomogeneity of the main magnetic field (H_M) was less than 0.2 T/m at the center of the main coil with the accuracy of 10^{-3} . The accuracy of the field gradient ($\partial H_G/\partial z$) is better than 10^{-3} which was calibrated by a GaAs Hall device. The temperature of the cryostat (300–20 K) was regulated by the microcomputer, and data were recorded 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. These temperature readings were calibrated in the whole temperature range with a magnetic thermometer with use of paramagnetic $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$ salt at the sample position. The absolute accuracy of the temperature was checked against the superconducting transition temperature of Nb ($T_c = 9.25$ K). Since T_c depends on the external magnetic field, the T_c value at zero field was obtained by extrapolating the T_c readings at several magnetic fields (less than 10 mT) to that of zero field. The difference was 0.2 K (2%) at this temperature. The predominant source of the error was found in magneto-resistance of the carbon thermometer.^{6b} A cylindrical quartz sample cell (10 mm in diameter, 12 mm in depth, and 135 mg in weight) was used for the measurement. The magnetic susceptibility measurement of tetracarbene **1** was performed in host crystals or in glassy matrices. A benzophenone single crystal (74.4 mg) doped with tetradiazo compound **2** (5.0×10^{-4} M) was placed in the cell, and liquid paraffin (41.5 mg) was added to fix the crystal. For the glassy matrix measurement,

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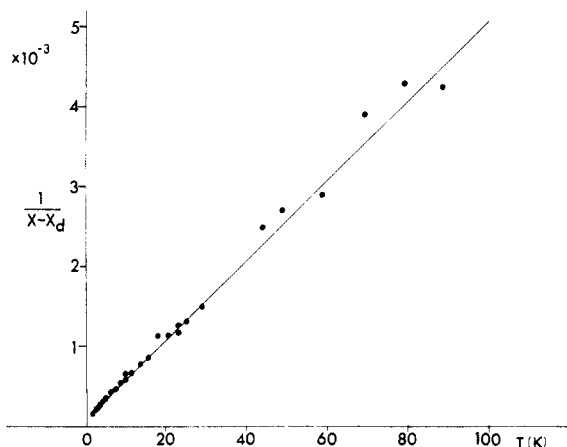


Figure 1. The temperature dependence of paramagnetic susceptibility of tetracarbene **1** in a single crystal of benzophenone (5.0×10^{-4} M).

tetradiazo compound **2** (0.409 mg) was dissolved in 0.2 mL of 2-methyltetrahydrofuran and the solution was degassed by bubbling an Ar stream for 3 min before setting in the cryostat. 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 10^3 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 to be 0.598×10^{-6} g $^{-1}$ from the intercept of the overall χ vs. $1/T$ plot. The contribution of the diamagnetic term to the operating force (ΔF) was then subtracted to give the force purely for the paramagnetic term (ΔF_{para}). The ΔF_{para} was then divided by the amount of the generated carbene species determined by an UV analysis (vide infra) and by $H_M(\partial H_G/\partial z)$ to give the paramagnetic susceptibility (χ_p) at each temperature.

The slopes of the linear plots and the parameters of the nonlinear plots in Figure 3 were obtained by the least-squares methods. The latter 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.

Formation of Tetracarbene 1. The photolysis of the sample was carried out to form tetracarbene **1** with an ultra-high-pressure mercury lamp (Philips SP 500W) through a quartz window at the bottom of the cryostat at 4 K. The progress of formation of the paramagnetic species was monitored by an increase in force on the sample. This photodecomposition was completed within 3 min for the single crystal sample, and 23% conversion was obtained after 30 min of irradiation for the glassy matrix. Although 100% conversion was obtained for the sample in the benzophenone single crystal, the amount of tetracarbene **1** was only 3.38×10^{-8} mol, which is almost the limit of detection in our magnetic balance system. This is because of a low solubility of **2** in benzophenone crystals. The conversion yield was determined by an UV analysis (Hitachi 340 spectrometer) at 520-nm absorption after the magnetic measurement. Magnetization of the photolyzed sample was recorded at various temperatures. A main field of 0.5 T 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 0.5 T/m.

Results and Discussion

(a) Temperature Dependence of Paramagnetic Susceptibility of Tetracarbene 1. The inverse of paramagnetic susceptibilities ($\chi_p = \chi - \chi_d$) of tetracarbene **1** was plotted against temperatures. The $1/(\chi - \chi_d)$ vs. T plots in this system gave a straight line ($r = 0.997$) in the whole temperature range (2–100 K) as shown in Figure 1. According to the Curie law $1/\chi_p = 3kT/(N\mu_{\text{eff}}^2\beta^2)$, where $\mu_{\text{eff}} \propto [J(J+1)]^{1/2} = 1/2[n(n+2)]^{1/2}$, the slope of the line gave $\mu_{\text{eff}} = 9.08 \mu_B$, and the spin number n of 8.1 is in good agreement with the theoretical value of 8.0. These results clearly show that **1** has the nonet spin multiplicity in the ground state

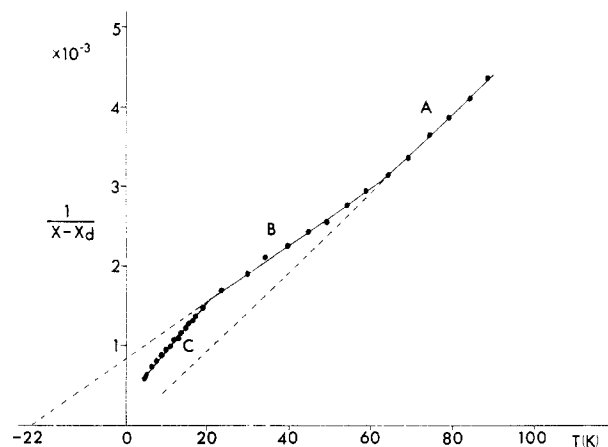


Figure 2. The temperature dependence of paramagnetic susceptibility of tetracarbene **1** in a glassy matrix of 2-methyltetrahydrofuran (8.7×10^{-4} M).

and is magnetically isolated in the host crystal, as previously shown by the ESR spectra.⁵

The magnetic susceptibility of **1** was then measured in a glassy matrix of 0.2 mL of a 2-methyltetrahydrofuran (2-MTHF) solution of **2** (3.78×10^{-3} M). The formation of **1** from **2** is known to be a one-photon process under these conditions. This was shown by the following experimental evidence. The ESR signals due to the nonet spin multiplicity come out first when irradiation is started in matrices and single crystals at cryogenic temperatures, and the initial rates of the formation of the nonet species are linearly dependent on the incident light intensity.^{5b,7} Thus, the presence of carbene species carrying the unreacted diazo groups and therefore of lower spin states is excluded. Plots of $1/\chi_p$ vs. temperature are not represented by a single line (Figure 2), suggesting that the magnetic interaction between the tetracarbene molecules is now important. The straight line in region A passes through the origin when extrapolated. The line has the first break point at 65 K and the line in region B has a negative Weiss temperature of -22 K in the Curie-Weiss relation: $1/\chi_p = (T - \theta)/C$, indicating that the paramagnetic species feels the anti-ferromagnetic molecular field at temperatures lower than 65 K. After the second break point, the inverse of the paramagnetic susceptibility nearly aims at the origin when plotted against temperature (region C). At temperatures higher than 65 K, the individual magnetic moment is considered not to suffer from the molecular field made by the other paramagnetic species presumably because thermal fluctuation becomes larger than magnetic interaction. The slope of line A was found to give $\mu_{\text{eff}} = 9.33 \mu_B$ and $n = 8.4$, the latter being reasonably close to the theoretical value. Since neither intra- nor intermolecular interaction was detected in benzophenone host crystals, the magnetic interaction found in 2MTHF at lower temperatures should be ascribed to intermolecular origin, unless the conformation of **1** in 2MTHF differs significantly from that in benzophenone host crystals.^{5b} The results suggest that **2** was not uniformly dispersed in 2-MTHF but formed an aggregate when frozen at higher concentrations,⁸ generating carbene molecules of **1** close enough to induce anti-ferromagnetic interaction between them. The same tendency was observed when the initial concentration of **2** was raised to 3.56×10^{-2} M in 2-MTHF or microcrystals of neat **2** were photolyzed. These results are consistent with the above interpretation. The observed behavior of the plots cannot be rationalized by anti-ferromagnetic dinuclear model, since a $1/\chi_p$ vs. T plot is supposed

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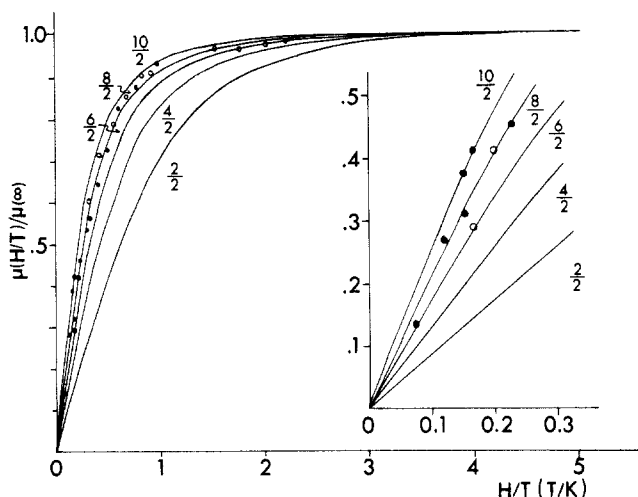


Figure 3. Plots of magnetization of **1** at 2.1 and 4.2 K (represented by open (○) and black (●) circles, respectively) in a single crystal of benzophenone vs. temperature-normalized field strength (H/T), the saturated values being normalized to 1.0. Theoretical magnetization curves are given by the Brillouin function in which $J = S = 2/2, 4/2, 6/2, 8/2$, and $10/2$.

to show a concave curve for the two-centered interaction. The plot is highly reminiscent of the antiferromagnetic interaction in the trinuclear cluster of paramagnetic species.⁹ Therefore, magnetic interaction among tetracarbene molecules seems not to be dimeric but of a cluster-type and can be described by general trinuclear interaction. Several examples of intermolecular magnetic interaction among stable free radicals are reported in the literature, and it is usual that antiferromagnetic interaction with a negative Weiss temperature is detected.¹⁰ The present result is consistent with those examples. We may also have to take intramolecular interaction among the carbenic centers into account when we investigate longer homologues of the polycarbenes which have higher chances of coiled conformations.

(b) Field Dependence of Magnetization of 1. Magnetization of **1** in a benzophenone crystal was determined as a function of the main field at 2.1 and 4.2 K by subtracting the corresponding values obtained before irradiation. It is an advantage of this system to measure the difference in magnetization before and after irradiation, since paramagnetic impurities, if any, can be cancelled by this treatment. Paramagnetic species generated by photolysis have been well defined by ESR spectroscopy to show that the contribution of paramagnetic species with lower spin multiplicities is negligibly small.^{5a,b} The experimental values plotted against the temperature-normalized field strength (H/T) were found to form a smooth curve (Figure 3), although data were rather scattered. The striking feature is a large saturation effect on the magnetization of **1** at lower temperatures. Especially a complete saturation was observed in the magnetic field higher than 2.5 T at 2.1 K. The plot is rationalized in terms of the Brillouin function $B_J(x)$ for magnetization:

$$M = NgJ\mu_B B_J(x)$$

where

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

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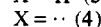
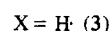
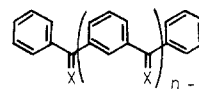
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and $x = gJ\mu_B H/(k_B T)$. The theoretical magnetization curves normalized to the saturated values, M/M_{∞} , are equal to $B_J(x)$ and given in Figure 3 for five high-spin states $J = 2/2, 4/2, 6/2, 8/2$, and $10/2$. The experimental data are found by the nonlinear least-squares method to fit the theoretical curve with $J = (8.12 \pm 0.62)/2$. The standard deviation of the plots is considered to originate from the insufficient amount of **1** (3.38×10^{-8} mol) generated in the sample cell and the consequent inaccuracy of the weight measurements. The temperature drift during the field dependence at certain temperatures was kept within 2%, and the absolute accuracy in the temperature reading was reasonably high (see Experimental Section). Thus the characteristic behavior of the saturation can be ascribed to the high-spin multiplicity of **1**. Since the orbital angular momentum may be neglected for hydrocarbon **1** and therefore $J = S$, the above correlation provides more evidence for the nonet ground state of **1**. This analysis proved to be a simple and versatile method for determining the high-spin multiplicity of paramagnetic samples even when the concentration is not known.¹¹ It is, to our knowledge, the first example of such facile saturation behavior in magnetization ever reported for organic compounds.

Magnetization behavior of **1** was measured also in 2-MTHF at 2.1, 4.2, 9.0, 17.5, and 31 K. These data turned out to fit practically with a single curve of $J = 8/2$ only for the small H/T region where intermolecular magnetic interaction was not significant. This means that, although magnetic interaction is suggested in the $1/\chi_p$ vs. T plot, the magnitude of the interaction is not large enough to give different saturation curves at each temperature range.

The most conspicuous feature of ferromagnets is the residual magnetization and hysteresis in magnetization curves. The hysteresis of ferromagnetic materials is due to the irreversible movement of domain walls. Since we are dealing with a finite system, a better example to compare with may be metal fine particles. When the size of metal fine particles becomes less than 30 Å in diameter, the particles are known to have a single domain structure.¹² The direction of magnetization can be varied only by rotation of the domain in those instances. The magnetic anisotropy plays a major role in determining the coercive force. If the anisotropic energy is large enough, fine particles show hysteresis and behave as a tiny ferromagnet, whereas particles with small anisotropy will be magnetized at any direction without the coercive force. The particles in the latter case are called superparamagnets, which means that electron spins within a particle are aligned all in parallel by the ferromagnetic exchange interaction, but the particle as a whole behaves independently of each other like a paramagnet. Thus magnetic behavior of **1** can be regarded as an organic molecular superparamagnet.

(c) High-Spin Polycarbenes as a Microdomain in Organic Ferromagnets. It is of interest to discuss the mechanism of ferromagnetic spin ordering in the polycarbenes at the molecular level. According to the electronic structure of alternant hydrocarbons, meta-substituted polyradicals (**3**) are supposed to have n degenerate nonbonding MO's and therefore they will have the total spin quantum number $S = n/2$ based on Hund's rule. When each doublet center is replaced with divalent carbon to form polycarbenes (**4**), S should be doubled, since the divalent carbon has an n orbital being nearly degenerate with the π orbital.^{2c,3b}



Let us look at the spin ordering in the polycarbenes as a model for the one-dimensional organic ferromagnet. One will note that antiferromagnetic correlation of π spins plays an important role

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in ferromagnetic spin ordering.¹³ The sign of π spins at the carbenic carbons of which the spin density is the highest in each phenylmethylene unit becomes the same based on the π -spin correlation. The localized n spins at carbenic carbons will align to the same direction based on the one-center exchange interaction, resulting in ferromagnetic spin ordering. The latter interaction is also expected to stabilize the intramolecular ferromagnetic spin state¹⁴ and resembles s - d interaction in ferromagnetic dilute alloys.¹⁵ The above picture of the spin distribution in the polycarbenes is experimentally shown on some lower homologues, i.e., diphenylmethylene and m -phenylenebis(phenylmethylene), by ENDOR measurement.¹⁶

Although the ferromagnetically spin ordered state is the ground state for the polycarbenes of finite chain length, it is well-known that the ferromagnetic spin ordering in the pure one-dimensional system is destroyed by the thermal excitation of magnon.¹⁷

Therefore, the next step to approach macroscopic ferromagnetism is to introduce ferromagnetic intermolecular interaction among high-spin polycarbenes, regarding them as a microdomain in ferromagnets. Here McConnell's theory on the intermolecular magnetic interaction among the spin distributed π system will serve as the guiding principle.^{2a,18} The magnetic susceptibility measurement is expected to be a powerful technique in investigating intermolecular magnetic interaction and macroscopic magnetic properties.

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Registry No. 1, 85566-03-6; 2, 85566-04-7.

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Ab Initio Quantum-Chemical Study of the Unimolecular Pyrolysis Mechanisms of Formic Acid†

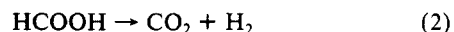
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Contribution from the School of Pharmacy, University of Lausanne, CH-1005 Lausanne, Switzerland. Received July 23, 1985

Abstract: The mechanisms of the two unimolecular competing reactions occurring during the pyrolysis of formic acid have been investigated by ab initio methods by using a variety of basis sets. The effects of valence electron correlation were included by Møller-Plesset (MP) perturbation theory to the fourth order. To explain the apparent inconsistency of the kinetic results, i.e., the lowest activation energy value for the decarboxylation process vs. the dehydration one and a CO/CO₂ ratio of product yield of 10, a new reaction mechanism has been proposed. That is, if the dehydration constitutes the main channel of formic acid pyrolysis with a calculated transition barrier of 67.1 kcal mol⁻¹, then some of the produced water molecules could serve as catalysts for the decarboxylation reaction, the computed activation energy of which amounts to 48.7 kcal mol⁻¹. The observed product ratio can furthermore be explained by the dependence of the decarboxylation process on the dehydration reaction.

I. Introduction

There are relatively few experimental investigations on the thermal decomposition of lower alkanolic acids the pyrolysis of which occurs by two parallel molecular eliminations, i.e., dehydration and decarboxylation. In the case of formic acid¹⁻⁴ the only products observed are CO, H₂O, CO₂, and H₂ from the simultaneous decompositions, the decarboxylation reaction being a relatively minor process with the ratio CO/CO₂ amounting typically to 10.²



By studies of gas-phase kinetics in both batch and flow systems between 457 and 780 °C, Blake et al.² found that decarboxylation was a first-order reaction over the whole temperature range ($k_2 = 10^{12.47} \exp(-48.5 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$), whereas the rate constant

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