with different on rates, or CO could be trapped in different sites, in which case the slow on rate could conceivably be a rate-limiting protein conformational change preceeding recombination.

Optical studies indicate that ferroCCP undergoes a heme-linked, cooperative two-proton ionization with a $pK = 7.7$.[7] To determine if the kinetics were also pH dependent, we examined the recombination at pH 6–8. At pH 6.0 only the slow phase is observed; the fast phase predominantes at pH 8.0 with the decay being ~80% monophasic. In addition, a cooperative two-proton ionization ($7 < pK < 8$) appears to control the rate transition.[8] Since both the spectral and rate transitions exhibit similar pH dependencies, it is plausible that deprotonation of the same group or groups is involved in each case. This in turn would imply that the CO association rate is largely controlled by the properties of the heme pocket rather than the protein matrix.

However, the protein matrix must play a role in preventing the escape of CO to the solvent following photodissociation, since the crystal structure of CCP reveals that its ligation pocket lies ~10 Å below the protein surface.[2] In Mb the pocket is exposed allowing rapid CO escape at room temperature.[3a] To further probe the kinetic barriers to ligand binding in ferroCCP, we are currently investigating the temperature dependence of CO recombination. Also, to ascertain whether similar barriers are present in the ferric form of the enzyme which binds H_2O_2, flash studies on the NO complex of CCP are under way.

(7) Conroy, C. W.; Tyma, P.; Daum, P. H.; Erman, J. E. *Biochim. Biophys. Acta* 1978, *537*, 62.

(8) The rate transition between pH 7 and 8 is too sharp to arise from the ionization of a single proton. Kinetic titration in this pH region suggests that a cooperative 2.0 ± 0.3 proton ionization is involved (Taylor, K., unpublished results).

Magnetic Behavior of Nonet Tetracarbene, m-Phenylenebis((diphenylmethylen-3-yl)methylene)

Tadashi Sugawara, Shunji Bandow, Keisaku Kimura, and Hiizu Iwamura*

*Institute for Molecular Science, Myodaiji
Okazaki 444, Japan*

Koichi Itoh

*Department of Chemistry, Faculty of Science
Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan*

Received April 23, 1984

Recently we presented the ground-state nonet molecule *m*-phenylenebis((diphenylmethylen-3-yl)methylene) (**1**)[1] as a model for organic ferromagnets[2] and discussed the unique molecular structure which makes the high-spin ground-state accessible. Characterization of **1** was based on the ESR fine structures. We have now studied the magnetic behavior of this highly important tetracarbene **1** as a molecular ferromagnet and found that the

(1) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H. Kobayashi, K. *J. Am. Chem. Soc.* 1983, *105*, 3722.

(2) (a) McConnell, H. M. *J. Chem. Phys.* 1963, *39*, 1910. (b) McConnel, H. M. *Proc. Robert A. Welch Found. Conf. Chem. Res.* 1967, *11*, 144. (c) Mataga, N. *Theor. Chim. Acta* 1968, *10*, 372. (d) Ovchinnikov, A. A. *Dokl. Akad. Nauk SSSR* 1977, *236*, 928. (e) Ovchinnikov, A. A. *Theor. Chim. Acta* 1978, *47*, 297. (f) Buchachenko, A. L. *Dokl. Akad. Nauk SSSR* 1979, *244*, 1146. (g) Breslow, R.; Juan, B.; Kluttz, R. Q.; Xia, C. Z. *Tetrahedron* 1982, *38*, 863.
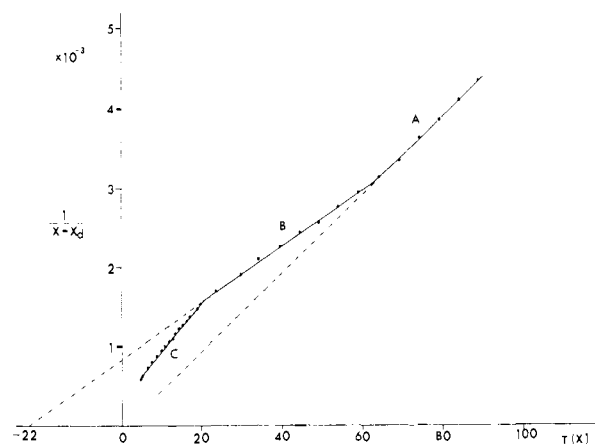

Figure 1. The temperature dependence of paramagnetic susceptibility of tetracarbene **1** in a glassy matrix of 2-methyltetrahydrofuran (8.7×10^{-4} M).

high-spin multiplicity of polycarbenes could be effectively determined by magnetic susceptibility measurements. An interesting behavior relevant to the magnetic interaction of the tetracarbene molecules has also been found.

A single crystal of benzophenone doped with tetrakis(diazo) compound (**2**) (5.0×10^{-4} M) in a cylindrical quartz cell (10 mm in diameter and 12 mm depth) was placed in a cryostat of an Oxford magnetic balance system. After evacuation to remove oxygen, no ferromagnetic impurities were detected at 4.2 K by the field dependence of magnetization of the sample. Irradiation of the diazo compound was performed through a quartz window at the bottom of the cryostat with an ultra-high-pressure mercury lamp (Philips SP 500W).[3] Magnetization of the photolyzed sample was recorded at various temperatures, the field gradient being fixed at 5 T/m by separate coils from a main coil (0.5 T).
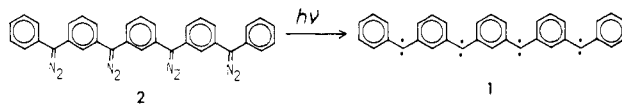
The amount of **1** generated in the cell was determined by the decrease of a UV absorption at 520 nm due to the diazo compound after the magnetic measurement. The diamagnetic susceptibility (χ_d) of the photolyzed sample was determined by the χ vs. $1/T$ plot and the value -0.598×10^{-6} g^{-1} was subtracted to obtain paramagnetic susceptibilities ($\chi_p = \chi - \chi_d$). The $1/(\chi - \chi_d)$ vs. T plots in this system gave a straight line in the whole temperature range (2–100 K). The slope of the line gave $\mu_{eff} = 9.08$ μ_B and the spin number n of 8.1 in good agreement with the theoretical values. These results clearly show that **1** has the nonet spin multiplicity in the ground state and is homogeneously dispersed in the crystal, as previously shown by the EPR spectra.[1]

The magnetic susceptibility of **1** was then measured in a glassy matrix of 2-methyltetrahydrofuran (2-MTHF) (3.77×10^{-3} M). Plots of $1/\chi_p$ vs. temperature are not represented by a simple line (Figure 1), 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 individual magnetic moment is considered not to suffer from the molecular field made by the other paramagnetic species presum-

(3) 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. The formation of **1** from **2** is therefore concluded to be a one-photon process under these conditions. This excludes the presence of carbene species carrying the unreacted diazo groups and therefore of lower spin states. The conversion of **1** from **2** was 23% after irradiation for 30 min. See: (a) Itoh, K.; Takui, T.; Teki, T. "Abstracts of Papers", 46th Annual Meeting of the Chemical Society of Japan, Niigata, Japan, Oct 1982; Chemical Society of Japan: Tokyo, 1982; p 17. (b) Sugawara, T.; Inada, M.; Iwamura, H. *Tetrahedron Lett.* 1983, *24*, 1723. (c) Sugawara, T.; Bethell, D.; Iwamura, H. *Ibid.* 1984, *25*, 2375.
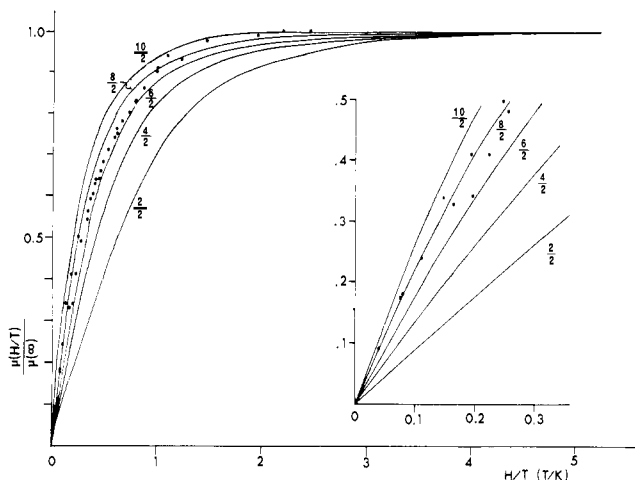
Figure 2. Plots of magnetization of **1** in 2-methyltetrahydrofuran vs. temperature-normalized field strength (H/T). Theoretical magnetization curves are given by the Brillouin function in which $J = S = {}^2/_2, {}^4/_2, {}^6/_2, {}^8/_2$, and ${}^{10}/_2$, the saturated values being normalized to 1.0.

ably because of the orientational fluctuation under these conditions. The slope of line A was found to give $\mu_{eff} = 9.33 \ \mu_B$ and $n = 8.4$. The line has the first break point at 65 K and the line in region B has a negative Weiss temperature of −22 K, indicating that the paramagnetic species now feels the antiferromagnetic molecular field at temperatures lower than 65 K. After the second break point, the inverse of the paramagnetic susceptibility aims at the origin when plotted against temperature (region C). The observed behavior of the plots is highly reminiscent of the antiferromagnetic interaction in the trinuclear cluster of paramagnetic species.[4] Similar results were obtained when the initial concentration of **2** was raised to 3.56×10^{-2} M or microcrystals of neat **2** were photolyzed. The results show that **2** was dispersed in 2-MTHF as an aggregate when frozen at higher concentrations, generating **1** close enough to induce antiferromagnetic interaction between the molecules of **1**.[5]

Magnetization of **1** in 2-MTHF was measured as a function of the main field at several temperatures (2.1, 4.2, 9.0, 17.5, and 31 K). 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 characteristic behavior of the saturation should be due to the high spin multiplicity of **1**. The experimental values plotted against the temperature-normalized field strength (H/T) were found to fit with a single curve (Figure 2). The correlation is rationalized in terms of the Brillouin function for magnetization:

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

where $x = gJ\mu_B H/(k_B T)$. The theoretical magnetization curves are given in Figure 2 for five high-spin states $J = {}^2/_2, {}^4/_2, {}^6/_2, {}^8/_2$, and ${}^{10}/_2$, the saturated values of each state being normalized to 1.0. Note that the curves are independent of the concentration of the electron spins. The experimental data are found to fit the theoretical curve with $J = {}^8/_2$ especially in the small H/T region where intermolecular magnetic interaction is not significant. Since

the orbital angular momentum may be neglected for hydrocarbon **1** and therefore $J=S$, the above correlation provides another evidence for the nonet ground state of **1**. We propose this analysis as a simple and versatile method for determining the high spin multiplicity of paramagnetic samples of unknown concentration.

Lastly, the saturation behavior of magnetization of **1** is somewhat similar to that of ferromagnetic materials. The result suggests that the nonet polycarbene can be regarded as a "micro" domain in ferromagnets and that, as the spin multiplicity of polycarbenes becomes higher, the magnetization behavior will resemble closer that of ferromagnets.[6]

(6) The Fe fine particles with a size of 30 Å show superparamagnetic behavior. Magnetization of these particles (μ_{eff} = ca. 160 μ_B) obeys the Brillouin function just like a paramagnetic species, but the $1/\chi_p$ vs. T plot reveals the transition to a ferromagnet at 30 K (Yatsuya, S.; Hayashi, T.; Akoh, H.; Nakamura, E.; Tasaki, A. *Jpn. J. Appl. Phys.* **1978**, *17*, 335). Nonet carbene **1** may be regarded as an organic counterpart of the above superparamagnet and to constitute the "micro" domain of the ferromagnets.

Synthesis of *in,out*-Bicyclo[4.4.4]tetradecane. Generation of a Stable μ-Hydrido-Bridged Carbocation

John E. McMurry* and Carl N. Hodge

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

Received June 25, 1984

Although small-ring bicycloalkanes such as bicyclo[2.2.1]-heptane (norbornane) and bicyclo[2.2.2]octane are well-known and much-studied, medium-ring bicycloalkanes, in which all rings are eight-, nine-, or ten-membered, are practically unknown. Only bicyclo[3.3.3]undecane (manxane) has been reported.[1,2] As pointed out by Alder,[3] however, this situation is unfortunate in view of the chemistry that might be expected for other medium-ring bicycloalkanes. For example, it has been predicted[4] that *out,out*-bicyclo[4.4.4]tetradecane (**1**) should have 60.5 kcal/mol
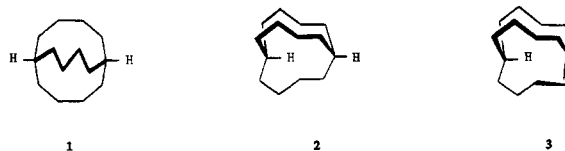
strain energy as a consequence of severe transannular interactions and that its bridgehead chloro derivative should be some 10^7–10^9 more reactive toward solvolysis than *tert*-butyl chloride.

Perhaps more interesting, however, is that bicyclo[4.4.4]tetradecane should be capable of existence in more than one isomeric form. Because of the size of the four-carbon bridges, in,out isomer **2** with an inverted bridgehead carbon should also be possible and may,[3] in fact, be less strained than out,out isomer **1**. We have now synthesized in,out isomer **2** and bridgehead olefin **3** by the route indicated in Scheme I.

The route, starting from the known[5] keto alcohol **4**, is self-explanatory, with the key titanium-induced cyclization[6] of keto

(4) (a) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48. (b) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Chem. Phys.* **1968**, *49*, 2183. (c) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1968**, *5*, 933. (d) Sinn, E.; Harris, C. M. *Coord. Chem. Rev.* **1969**, *4*, 391. (e) Sinn, E. *Ibid.* **1970**, *5*, 313. (f) Idogai, T.; Iwashita, T.; Uryû, N. *J. Chem. Phys.* **1971**, *54*, 817.

(5) (a) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1980**, *102*, 7637. (c) A quintet radical pair is formed in organic matrices containing triplet carbenes. Murai, H.; Torres, M.; Strausz, O. P. *Ibid.* **1980**, *102*, 5104. A referee suggested that a possible intramolecular interaction in the coiled conformation of **1** in a glassy matrix would account for the antiferromagnetic exchange interaction between the carbenic centers. An experimental work to explore the possibility is under way in these laboratories by taking advantage of the cyclophane dicarbene models.

(1) Doyle, M.; Parker, W.; Gunn, P. A.; Martin, J.; MacNicol, D. D. *Tetrahedron Lett.* **1970**, 3619.
(2) Leonard, N. J.; Coll, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 6685.
(3) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321.
(4) Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121.
(5) Holmquist, H. E.; Rothrock, H. S.; Theobald, C. W.; Englund, B. E. *J. Am. Chem. Soc.* **1956**, *78*, 5339.
(6) (a) McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655. (b) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.