Studies of the electronic structure of polyradicals by means of their magnetic properties

Hiizu Iwamura,[1]* Noboru Koga,[2] and Kenji Matsuda[1]

[1] *Institute for Fundamental Research in Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*
[2] *Faculty of Pharmaceutical Sciences, Kyushu University, Maedashi, Higashi-ku, Fukuoka 812-8582, Japan*

Abstract: Having identified the limitations of the commonly used ESR spectroscopic method, we have employed a versatile method of measuring magnetic susceptibility and magnetization for the characterization of the ground state spins of di-, oligo- and polyradicals. Under these subjects are specifically included such items as the determination of a small singlet-triplet energy gap of < 1 K in conformationally fixed tetramethyleneethane (**1**), the demonstration of spin frustration or competing interaction in the ground state of antiferromagnetically coupled spins in triradical **3** and the dinuclear Mn(II) complex **5**, and the analyses of super high-spin (S = 7~9) poly-carbenes **6** and **7**.

EPR SPECTROSCOPY VERSUS PARAMAGNETIC SUSCEPTIBILITY/ MAGNETIZATION STUDIES

EPR spectroscopy serves as a standard method for detecting triplet diradicals and higher spin polyradicals and for studying their electronic states (1). The fine structures due to the dipolar interaction of the spins within the polyradical molecules are analyzed and Δm_S = 2 or higher transitions are often detected in the g = 4 or higher regions. The D and E parameters of the zero-field tensor of the radical molecules thus obtained give a measure of the average distance between the unpaired electrons and the axial symmetry/asymmetry of the multidipolar tensor, respectively. The energy gap between the spin sub-levels, which corresponds to the transition energy, is in the microwave range (e.g., 9 GHz for a typical X-band spectrometer) and equivalent to the thermal energy k_BT at 0.4 K. Thus the signal intensity *Int* which should be dictated by the Boltzmann distribution of the spins between the spin sub-levels concerned becomes inversely proportional to T. When EPR active species under question is in thermal equilibrium with the other species that are EPR-silent or have EPR signals at different resonance positions, the concentration of the original species itself can become subject to a Boltzmann population. The temperature dependence of the *Int* due to a triplet diradical in equilibrium with the corresponding singlet species is expressed in terms of a product of the two factors, the transition probability and the population of the triplet (Eq. 1)

$$Int = \frac{1}{T}\frac{C\exp(-\Delta E_{ST}/k_BT)}{[1+3\exp(-\Delta E_{ST}/k_BT)]} \tag{1}$$

where C is a proportionality constant and ΔE_{ST} is the potential energy difference between the singlet and triplet states; plus and minus signs are defined to correspond to the ground triplet and singlet states, respectively. Some theoretical curves for representative ΔE_{ST} values are drawn in Fig. 1 (2). When ΔE_{ST} >> 0, a Curie law of inverse proportionality holds. A linear relationship with a slope 3/4 of the Curie law holds also for $\Delta E_{ST} = 0$. Unless the absolute signals intensities can be determined, which is experimentally not easy especially for photochemically generated samples in dilute, frozen solutions, the two linear relationships cannot, in principle, be differentiated. For the intermediate cases, the relationship between *Int* vs $1/T$ is sigmoidal between the two lines. It is difficult to identify any deviation from linearity and determine the ΔE_{ST} value in practice. The energy gap between the two states can be determined experimentally only for $\Delta E_{ST} < 0$. Still deviation of the curve from a line becomes conspicuous at low temperature where temperature control is difficult and the signal intensity becomes readily saturated. With experimental data obtained at $T > 10$ K, we cannot discuss $-\Delta E_{ST}$ smaller than 5 K (= 3.5 cm^{-1} = 41.6 J•mol^{-1}) (2).
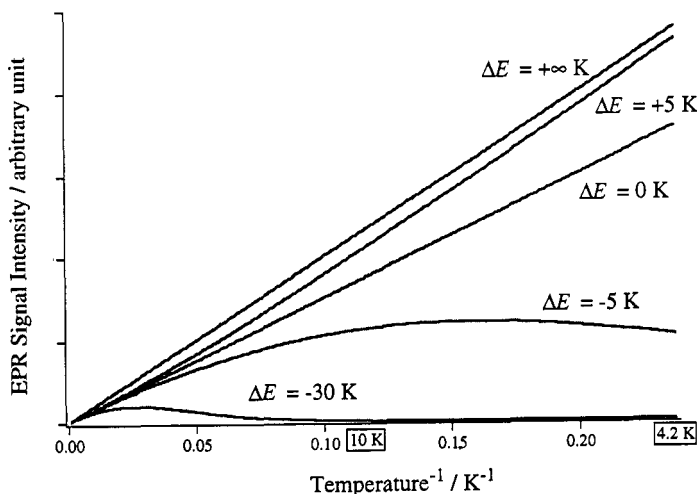

Fig. 1. Theoretical curves for the EPR signal intensity vs. reciprocal of temperature.

Having identified the limitations of the conventionally used ESR spectroscopic method, we have employed a versatile method for characterizing the ground state spins of di-, oligo- and polyradicals by measurement of their magnetic susceptibilities and magnetization (3,4). The spin of an unpaired electron having the magnetic moment μ at finite temperature T tries to orient itself in the direction of the applied field H against its random orientation in the absence of the field. Since the energy of the former interaction μH is not necessarily stronger than the latter thermal fluctuation $k_B T$, the magnetization due to an assembly of N spins should be governed by their Boltzmann distribution. The magnetization M is described by a Langevin function for classical spins and a Brillouin function $B(x)$ for quantum spins in which the available directions of the spins under thermal fluctuation are spatially quantized to $(2S + 1)$ directions of $S_z = S$, $S-1$, •••, $-(S-1)$, $-S$:

$$M = Ng^2 S \mu_B B(x) \tag{2}$$

where

$$B(x) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x - \frac{1}{2S} \coth \frac{x}{2S}$$

and $x = gS\mu_B H/k_B T$. Thus, the spin quantum number S can be obtained from the measurement of M as a function of H and/or T. M saturates at $M_S = NgS\mu_B$ under high field ($H \to \infty$) (Fig. 2).
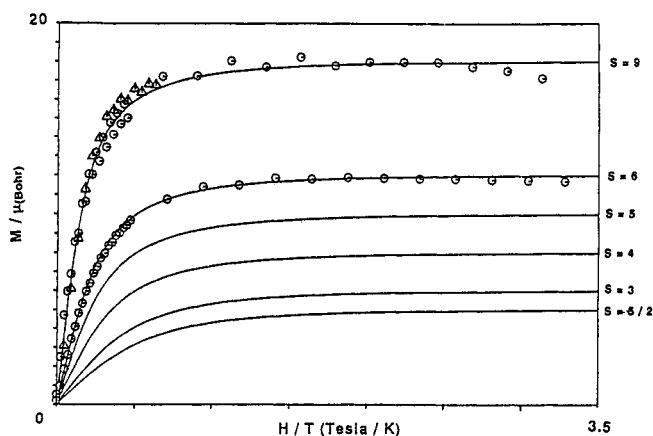

Fig. 2. Theoretical magnetization curves for various S values as a function of applied field H and temperature T. The observed values for a hexacarbene and a nonacarbene 6 are also added.

When $x \ll 1$, $B(x)$ can be expanded into a power series of x and, if only the first term is employed, Eq. 2 is simplified into $M = Ng^2 S(S+1)\mu_B^2 H/3k_B T$ and the paramagnetic susceptibility χ is given by Eq. 3:

$$\chi = M/H = Ng^2 S(S+1)\mu_B^2/3k_B T \tag{3}$$

The proportionality of χ to reciprocal of T is called the Curie law. The product of χ times T should be independent of temperature and has a value of 0.375, 1, 1.875, and 4.375 emu•K•mol^{-1} for $S = 1/2$, 1, 3/2, and 5/2, respectively, when N is equal to the Avogadro number and $g = 2$. For a diradical, its singlet, triplet and degenerate states may be differentiated either by the slope of the χ vs $1/T$ plot or by their χT values of 0, 1 and 0.75 emu•K•mol^{-1}, respectively. Any deviation from a horizontal relationship of the χT vs. T plots often observed at low temperature is indicative of an interradical interaction; upward and downward shifts correspond to the interactions leading to parallel and antiparallel alignment of the spins and are termed ferro- and antiferromagnetic interactions, respectively (see Fig. 7 as an example). χT values for a diradical that is in equilibrium between singlet and triplet states change between 0 and 1 emu•K•mol^{-1} and are described by the Bleaney-Bowers equation similar to Eq. 1 (5).

Quantum Design MPMS$_2$ (1 T) or MPMS-5S (5 T) SQUID susceptometer/magnetometers equipped with a sample holder containing an optical fiber were used in the present study. A Hoya-Continuum Q-switched Nd/YAG laser Surelight I-10 (200 mJ at 532 nm) or a Xenon lamp in combination with Kenko sharp-cut filters and an OCL1 B cold mirror was used for the photolysis.

REPRESENTATIVE STUDIES FROM PARAMAGNETIC SUSCEPTIBILITY/MAGNETIZATION MEASUREMENTS

1. Determination of small singlet-triplet energy gaps in diradicals

Trimethylenemethane (TMM) and tetramethyleneethane (TME) are the simplest non-Kekulé alternant hydrocarbons (AH's) where Longuet-Higgins' rule dictates the occurrence of two non-bonding molecular orbitals (NBMO) that have zero π-bond energy and therefore both are diradicals. The two NBMO's each of

which is represented by a linear combination of 2p atomic orbitals have atoms in common in TMM and can be confined to different sets of atoms in TME,' and Hund's rule can not therefore be applicable straightforwardly to the latter. Pointing out this difference, Borden and Davidson predicted in their perturbational MO theory that, while TMM should have a ground triplet state, singlet and triplet states are nearly degenerate and higher order terms favor the singlet ground state for TME (6). Dowd and coworkers studied the EPR spectra of TME and 2,3-dimethylenecyclohexane-1,4-diyl (1), a conformationally restricted analog, to find that their triplet signal intensities obeyed Curie law in the temperature ranges 16-65 (7d) and 15-53 K (7f), respectively. While the possibility that the singlet and triplet states are degenerate within 125-170 J•mol^{-1} was taken into account, their triplet ground states were concluded on a basis that it was clearly less likely that both TME and 1 of different planarity showed similar degeneracy.

Diradical 1 was produced by the photolysis of 5,6-dimethylene-2,3-diazabicyclo[2,2,2]oct-2-ene in MTHF with light $\lambda > 320$ nm from a Xenon lamp at 9 K (7b). The field-dependence of magnetization of 1 at 2.0 K is shown in Fig. 3. Eq. 2 is modified into Eq. 2' for a triplet diradical ($S = 1$) that is in equilibrium with a singlet state lying near its Zeeman levels (8).

$$M = Ng\mu_B \frac{\exp(x') - \exp(-x')}{\exp(x') + 1 + \exp(-x') + \exp(\frac{-\Delta E_{ST}}{k_B T})} \qquad (2')$$

where $x' = g\mu_B H/k_B T$. When fitted to the observed data, the analysis gave ΔE_{ST} = -0.76 ± 0.16 K (= -6.3 ± 1.3 J mol^{-1}), indicating that the triplet and singlet states are nearly degenerate (8). The initial slope of the curve is nearly 3/4 that of a theoretical $S = 1$ curve. This finding resolved the ambiguity inherent in the EPR results, as to whether the triplet is the ground state of 1 or whether the singlet and triplet states have nearly the same energy (8,9).
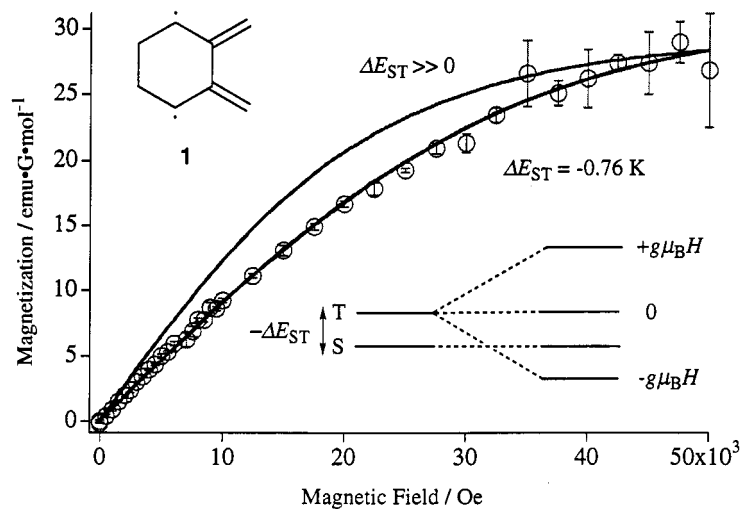

Fig. 3. Field dependence of magnetization of 1 measured at 2.0 K. Two curves are a theoretical S = 1 curve (top) and a best-fit curve (bottom) of Eq. 2'.

9-Fluorenylidene (2) and its 3,6-dimethoxy derivative have triplet and singlet ground states, respectively (10). Singlet and triplet states of 3-methoxy-9-fluorenylidene were recently found to have nearly the same energy (Fig. 4) (11).
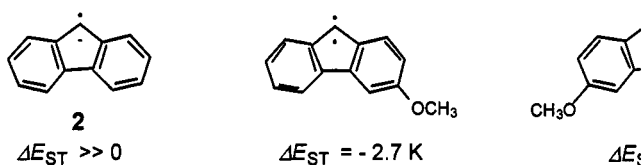
2

$\Delta E_{ST} \gg 0$ $\Delta E_{ST} = -2.7$ K ΔE_S

Fig. 4. The observed ΔE_{ST} values for 9-fluorenylidenes.

2. Spin frustration and competing interaction

When local spins S_A, S_B and S_C are placed at the corner of a triangle (Fig. 5) and the exchange coupling represented by J's between any two of them is ferromagnetic, namely, J_{AB}, J_{BC}, and J_{CA} are positive in the Heisenberg spin Hamiltonian (Eq. 4):

$$H = -2 (J_{AB}S_A \cdot S_B + J_{BC}S_B \cdot S_C + J_{CA}S_C \cdot S_A) \qquad (4)$$

nothing is special about the electronic structure of the system; the quartet ground state is a unique solution. On the other hand, when they are antiferromagnetic, the spins would find it difficult to decide which way to align in the ground state. For $|J_{AB}| = |J_{BC}| > |J_{AC}|$ or $|J_{AB}| = |J_{BC}| < |J_{AC}|$, the ground state spins will be illustrated as in Fig. 4b and 4c. For $J_{AB} = J_{BC} = J_{CA} < 0$, by symmetry or accidental degeneracy, the ground state of the triradical will be doubly degenerate. The energy level diagram obtained by solving Eq. 5 for three $S = 1/2$ spins and $J_{AB} = J_{BC} = J_{CA}/a < 0$ is given in Fig. 6 (12).

a)

b)

c)

or

a)

$E(3/2, 2/2); -(1/2a+1)J$

$E(1/2, 2/2); -(1/2a-2)J$

$E(1/2, 0); 3/2aJ$

b)
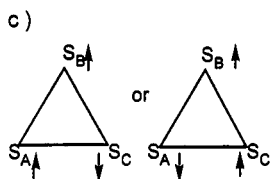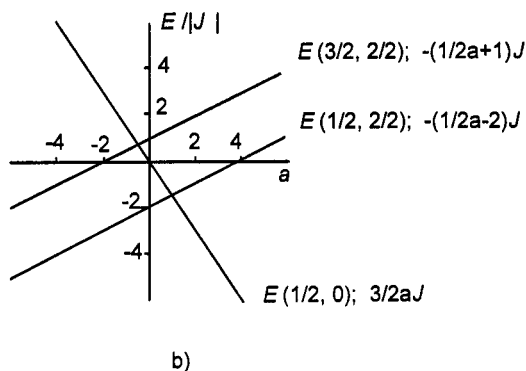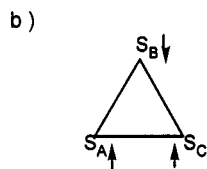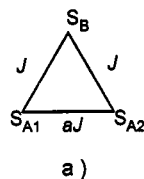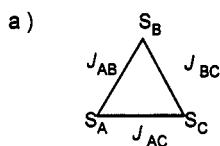
Figs. 5. Three spins in triangular, antiferromagnetic coupling.

Fig. 6. Variation of the spin state energies with asymmetric parameter a.

The χT value of a microcrystalline sample of 3 is 1.039 emu•K•mol^{-1} at 350 K and decreases to a value of 0.365 emu•K•mol^{-1} at 4K, suggesting that the antiferromagnetic interaction produces a doublet ground state. The equation derived from an isosceles triangular three spin model was fit to the experimental data to afford two sets of best-fit negative J's: J/k_B = -41.3 K, a =0.27 and J/k_B = -21.4 K, a = 2.4. The former J value is more consistent with J/k_B = -39.7 K for the reference biradical, 1-bromo-2,4-dimethoxy-3,5-benzenediylbis(N-tert-butyl nitroxide). In triradical 3, therefore, the ground spin state would be a doublet with the stronger antiferromagnetic interaction between the spins at 1- and 3-position and 3- and 5-position polarizing the ferromagnetic alignment of the 1- and 5-spins, providing the first demonstration of an organic triradical showing competing interactions (12).

3   4   5
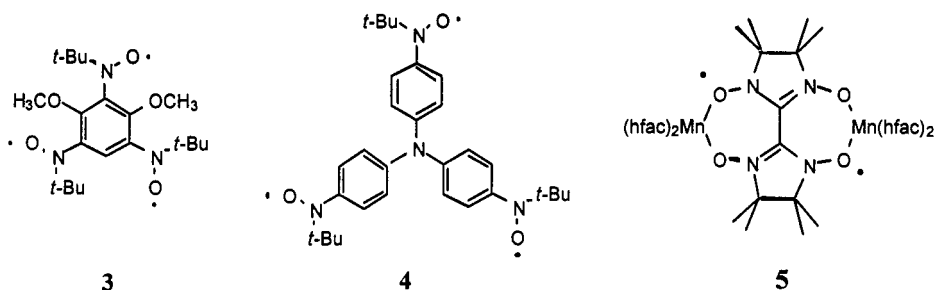
The temperature dependence of the molar paramagnetic susceptibility of 4 measured at 500 G showed that the χT values remained almost constant from 100 down to 20 K (Fig. 7) (13). The observed χT values are in good agreement with the theoretical value expected for a single isolated spin. As the temperature was decreased below 20 K, the χT values increased continuously to a maximum of 0.58 emu•K•mol^{-1} at 2 K. The continuous increase in the χT value did not show up in a sample of 4 diluted (5%) in poly(vinyl chloride), thereby suggesting that there is no intramolecular ferromagnetic interaction and the ground state must be a doublet state. The ground electronic structure is ascribed to the operation of a superexchange mechanism by polarization of a lone pair of pπ-electrons at the central nitrogen atom which effectively couple any two spins at the para positions antiferromagnetically, with the remaining one spin intact.
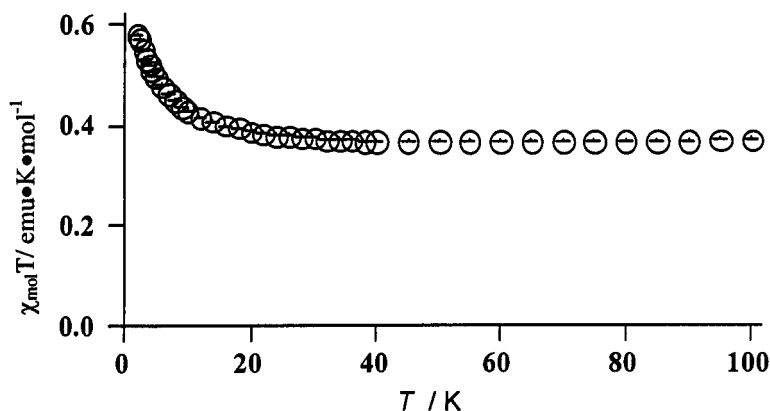

Fig. 7. Temperature dependence of the observed χT values for 4.

The three spins coupled antiferromagnetically in a triangular disposition is reminiscent of the molecular structure of a cyclopropenyl radical in which the antiferromagnetic coupling is so strong by virtue of the π-orbital overlap that a covalent bond is formed and the radical consists of triply degenerate valence isomers.

In **3** and **4**, neighboring spins are exchange-coupled but the coupling is not strong enough to warrant the formation of a chemical bond.

In the dinuclear Mn(II) complex **5**, the ground state is degenerate among seven spin states and is thus spin-frustrated (14).

3. Super high-spin molecules

Whereas the field dependence of the magnetization revealed a $S = 9$ ground state for nonacarbene **6** (15), the highest spin ever reported for a purely organic compound, further experiments on the higher branched nona- and dodecadiazo compounds did not give M vs H/T curves corresponding to $S = 9$ and 12, respectively. The photolysate of the branched nonadiazo compound gave $S = 7$ with high reproducibility and was therefore assigned to have heptacarbene structure **7** as a result of the interbranch coupling in dilute solid solution (16). Such a limitation discouraged us from studying extensively branched dendritic structures. Instead, the carbene centers generated in the crystal of polymeric chain complexes of $Mn^{II}(hfac)_2$ with di(4-pyridyl)-diazomethane were intact up to 240 K and the photolyzed crystalline complex became a set of ferrimagnetic chains of S as high as 272 at 5 K (17).

6   **7**
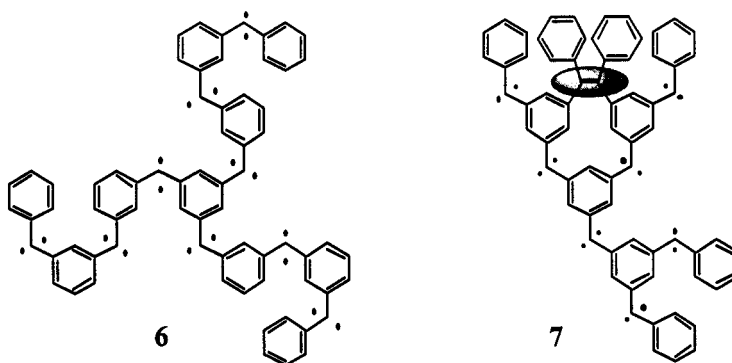
Conclusion

Determination of temperature dependence of the magnetic susceptibility and magnetic field dependence of the magnetization is the method of choice for studying the magnitude of the effective magnetic moments and the ground state spins of polyradicals. The method is not without demerits. We point out that, since the magnetic measurements are not spectroscopic and evaluate the paramagnetic samples as a whole, it is necessary to minimize any paramagnetic impurities which could be discriminated by EPR spectroscopy. This becomes especially serious when samples to be studied are generated at cryogenic temperature and the magnetic measurements are performed in situ; the conditions have to be optimized to minimize any side reaction giving paramagnetic impurities.

Acknowledgments

References and Notes

1. (a) W. Weltner, Jr. *Magnetic Atoms and Molecules*, Van Nostrand Reinhold, New York (1983). (b) T. Takui, K. Sato, D. Shiomi, K. Itoh. In *Molecule-based Magnetic Materials* (M. M. Turnbull, T. Sugimoto, L. K. Thompson. eds.), Chapter 6. ACS symposium series. 644 (1996).

2. H. Iwamura. *Adv. Phys. Org. Chem.* 26, 179-253 (1990).

3. H. Iwamura, N. Koga. *Acc. Chem. Res.* 26, 346-351 (1993).

4. C. J. O'Connor, ed. *Research Frontiers in Magnetochemistry*. World Scientific, Singapore (1993).

5. B. Bleaney, K. D. Bowers. *Proc. Royal Soc. London*, Ser. A. 214, 451-465 (1952).

6. W. T. Borden, E. R. Davidson. *Acc. Chem. Res.* 29, 67-75 (1996).

7. (a) P. Dowd. *J. Am. Chem. Soc.* 92, 1066-1068 (1970). (b) W. R. Roth, G. Erker. *Angew. Chem. Int. Ed. Engl.* 12, 503-504 (1973). (c) T. Beetz, R. M. Kellogg. *J. Am. Chem. Soc.* 95, 7925-7926 (1973). (d) P. Dowd, W. Chang, Y. H. Paik. *J. Am. Chem. Soc.* 108, 7416-7417 (1986). (e) W. R. Roth, U.Kowalczik, G. Maier, H. P. Reisenauer, R. Sustmann, W. Müller. *Angew. Chem. Int. Ed. Engl.* 26, 1285-1287 (1987). (f) P. Dowd, W. Chang, Y. H. Paik. *J. Am. Chem. Soc.* 109, 5284-5285 (1987). (g) W. R. Roth, R. Langer, M. Bartmann, B. Stevermann, G. Maier, H. P. Reisenauer, R. Sustmann, W. Müller. *Angew. Chem. Int. Ed. Engl.* 26, 256-258 (1987).

8. (a) K. Matsuda, H. Iwamura. *J. Am. Chem. Soc.* 119, 7412-7413 (1997). (b) K. Matsuda, H. Iwamura. *J. Chem. Soc. Perkin 2*, 1023-1026 (1998).

9. For up-dated results and discussion, see several related papers in Keynote Collection in Memory of Professor Paul Dowd 1936-1993 in: *J. Chem. Soc. Perkin 2*, Number 5, pp 1007-1117 (1998).

10. C. Chuang, S. C. Lupin, A. K. Shurock, G. B. Schuster. *J. Am. Chem. Soc.* 107, 4238-4243 (1985).

11. K. Ueno, K. Matsuda, K. Hori, H. Iwamura. work to be published elsewhere.

12. J. Fujita, M. Tanaka, H. Suemune, N. Koga, K. Matsuda, H. Iwamura. *J. Am. Chem. Soc.* 118, 9347-9351 (1996).

13. T. Itoh, K. Matsuda, H. Iwamura. to be published elsewhere.

14. M. Tanaka, K. Matsuda, T. Itoh, H. Iwamura. *Angew. Chem., Internat. Ed. Engl..* 37, 810-812 (1998).

15. (a) N. Nakamura, K. Inoue, H. Iwamura. *Angew. Chem. Int. Ed. Engl.* 32, 872-874 (1993). (b) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura. *Bull. Chem. Soc. Jpn.* , 69, 1483-1494 (1996).

16. (a) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura. *J. Am. Chem. Soc.* 117, 5550-5560 (1995). (b) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, H. Iwamura. *Chem. Eur. J.* 2, 259-264 (1996).

17. (a) Y. Sano, M. Tanaka, N. Koga, K. Matsuda, H. Iwamura, P. Rabu, M. Drillon. *J. Am. Chem. Soc.* 119, 8246-8252 (1997). (b) N. Koga, Y. Ishimaru, H. Iwamura. *Angew Chem Int Ed Engl* . 35, 755-757 (1996). (c) N. Koga, H. Iwamura. *Mol Cryst Liq Cryst.* 305, 415-424 (1997).