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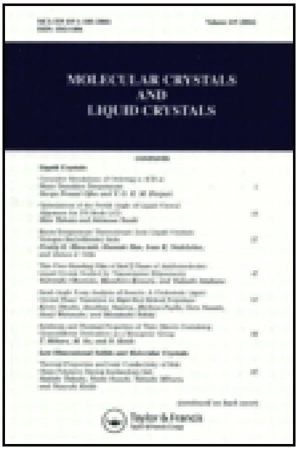

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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High-Spin Polycarbenes as a Model for Organic Ferromagnets

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Version of record first published: 17 Oct 2011.

To cite this article: Hiizu Iwamura , Tadashi Sugawara , Koichi Itoh & Takeji Takui (1985): High-Spin Polycarbenes as a Model for Organic Ferromagnets, Molecular Crystals and Liquid Crystals, 125:1, 251-260

To link to this article: http://dx.doi.org/10.1080/00268948508080104

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Mol. Cryst. Liq. Cryst. 1985, Vol. 125, pp. 251-260
0026-8941/85/1254-0251/$15.00/0
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HIGH-SPIN POLYCARBENES AS A MODEL FOR ORGANIC FERROMAGNETS

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Abstract High-spin polycarbenes (1 and 2) have been designed by using the triplet diphenylcarbene molecule as a repeating unit. The corresponding polydiazo compounds were prepared and photolyzed in 2-methyltetrahydrofuran matrices and in single crystals of a benzophenone host at cryogenic temperatures. The ESR fine structures and magnetic susceptibilities were measured and analyzed to show that the highest spin states were generated as the electronic ground state of the polycarbenes. Relevance of these results to organic ferromagnets is discussed.

INTRODUCTION

Organic molecules are characterized by their closed shell electronic structures. Many organic compounds are therefore diamagnetic. There are still quite a few organic free radicals that have an odd electron and $S = 1/2$. These radicals are paramagnetic. Only a few organic molecules are in the ground triplet state. They are classified into three groups: antiaromatic annulenes, non-Kekulé alternant hydrocarbons, and monocentric diradicals. These structures serve as a good starting point for designing high-spin organic molecules. We designed, generated and characterized a series of high-spin hydrocarbons 1 and 2 on the basis of a structural combination of the last two groups. The high-spin

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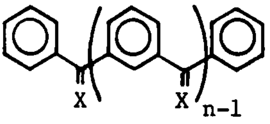
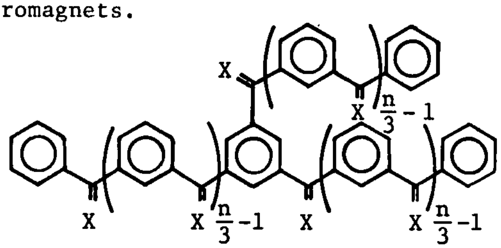
polycarbenes are expected to function as a model for hitherto unknown organic ferromagnets.



1(X = :)
3(X = H, •)
5(X = N_2)
6(X = NNH_2), 7(X = O)



2(X = :)
4(X = H, •)

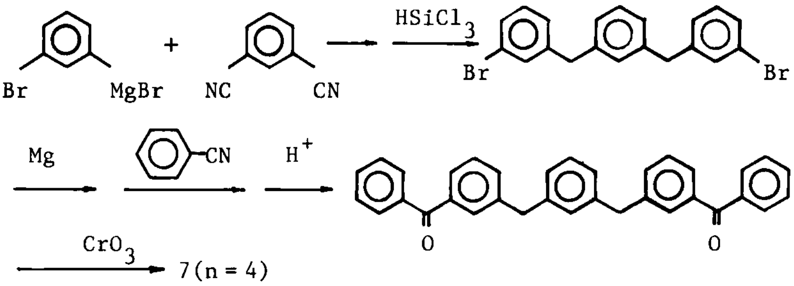
MOLECULAR DESIGN

According to the MO theory on the non-bonding molecular orbitals in alternant hydrocarbons,[1] structures 3 and 4 are predicted to have *n* degenerate non-bonding MO's and therefore the ground state of the neutral hydrocarbons will be of high spin, i.e., $S = n/2$.[2] The VB theory also gives the same high spin multiplicity.[3] Let us replace each doublet center >CH• with a divalent >C: which has an n-orbital being nearly degenerate with the π-orbital and as a result has a triplet character. We expect to obtain a series of systems 1 and 2 where $S = n$, doubling the structural efficiency for increasing the total electron spin quantum number. In theory we can put $n \to \infty$ and predict one-dimensional and two-dimensional macroscopic spins for 1 and 2, respectively. The n-π interaction between the localized n spins and the delocalized π spins in 1 and 2 is reminiscent of the s-d interaction in ferromagnetic dilute alloys. The theoretical prediction of ferromagnetic polymers of these series was put forward by Mataga in 1968,[4] and the lower homologs were reported by Itoh[5] and Wasserman[6] in 1967. We have been engaged for sometime in the study of the higher homologs of these series and describe here some properties of 1(n = 4).

PREPARATION OF THE PRECURSORS

The corresponding polydiazo compounds (5) are good precursors of choice, since the polycarbenes are cleanly generated by photolysis. The polydiazo compounds were obtained by oxidation with metal oxides of the corresponding polyhydrazones (6) which in turn were obtained by the reaction of polyketones 7 with hydrazine hydrate. We have so far employed a stepwise route to 7 as exemplified by 7(n = 4) in Scheme 1.

Scheme 1



ESR SPECTRA

The diazo precursor 5(n = 4) in a glassy matrix of 2-methyltetrahydrofuran (2-MTHF) was photolyzed in an ESR cavity to give complex ESR fine structure due to unoriented 1(n = 4). The spectrum amenable to a rigorous analysis was obtained by orienting 5(n = 4) in single crystals of benzophenone and photolyzing the sample at 4.2 K with the 405-nm mercury line. The eight observed lines (Figure 1) were found to be the fine structure due to the following $\Delta M_S = \pm 1$ allowed transi-

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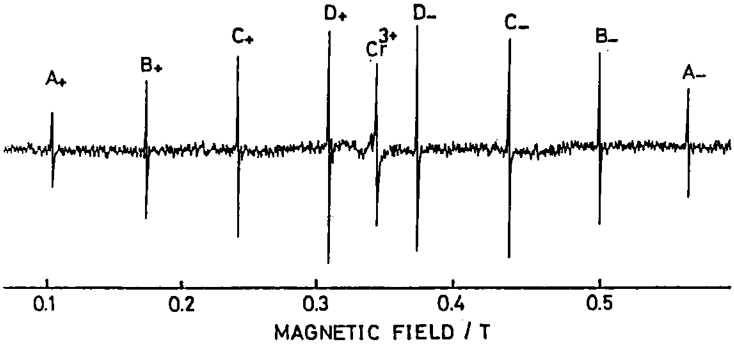

FIGURE 1. ESR spectrum of 1(n = 4) obtained at 4.2 K with the magnetic field along the direction 26° from the *a* axis in the *ab* plane of the host crystal. The microwave frequency was 9550.6 MHz.

tions: $A_\pm$(M_s = ±4↔±3), $B_\pm$(M_s = ±3↔±2), $C_\pm$(M_s = ±2↔±1), and $D_\pm$(M_s = ±1↔±0). The relative separations are nearly (A_--A_+):(B_--B_+):(C_--C_+):(D_--D_+) = 7 : 5 : 3 : 1, and the relative integrated intensities are nearly $A_\pm$:$B_\pm$:$C_\pm$:$D_\pm$ = 4 : 7 : 9 : 10 as expected of $S = 4$ in the high-field approximation. The magnetic field is approximately parallel to the Z principal axis of the fine-structure tensor, the deviation being 9.8°, which gives the largest fine-structure splittings.

The angular dependence of the resonance fields (Figure 2) and of the signal intensities of the eight lines is well reproduced by the spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \qquad (1)$$

where $S = 4$, $g = 2.003$, $D = +0.0332$ cm^{-1} and $E = -0.0031$ cm^{-1}. Higher terms in S group theoretically allowed for $S = 4$ are negligibly small. This fact and the nearly isotropic g value close to that of free electron spin are consistent with 1(n = 4) composed of light atoms with small spin-orbit

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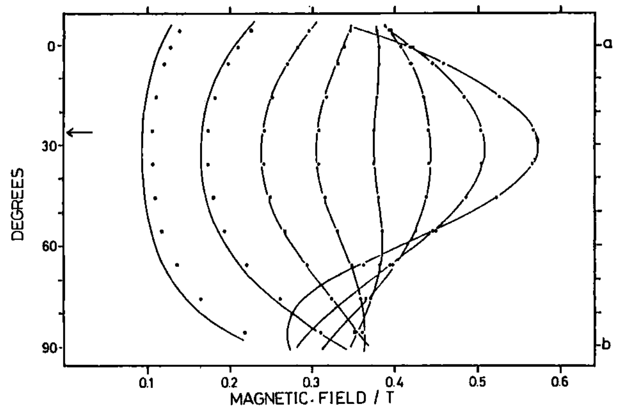

FIGURE 2. Angular dependence of the ESR signals due to 1(n = 4) at 4.2 K. The microwave frequency was 9550.2 MHz.

coupling. In addition, the D and E values fall in the range extrapolated from the known high-spin multiplet hydrocarbons. In order to determine the lowest energy level, we have measured the ESR spectra in the temperature range 1.8 - 150 K. No thermally populated triplet, quintet and septet signals were detected, indicating that the ground state is nonet. The temperature dependence of the total signal intensity confirmed that 1(n = 4) has been obtained in its nonet ground state.

In order to study the conformation of the 1(n = 4) molecule, a semi-empirical calculation of the fine structure parameters has been performed. One center n-π interaction was assumed to be most important and the fine structure parameters of triplet diphenylcarbene[7] was used for evaluating the interaction on the divalent carbon atom. Conformations A and B gave reasonably good fine structure parameters.

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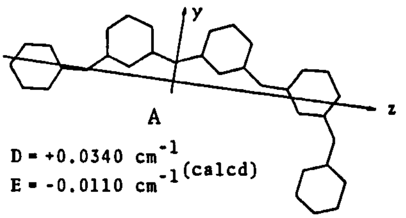
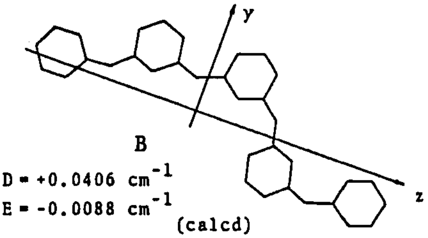
Whereas conformation A requires replacement of four benzophenone molecules in the host single crystals, it is necessary for form B to replace only three. The latter would fit better in the host crystals.

When the temperature was raised, 1(n = 4) suffered irreversible spectral changes at 64 and 92 K. They are interpreted in terms of the conformational changes of the guest molecule 1(n = 4). The phenomenon may have the significance of its own but we only point out here that 1(n = 4) has the nonet ground state irrespective of its different conformations.[8]





MAGNETIC SUSCEPTIBILITY

We have measured the magnetization of 1(n = 4) as a function of the magnetic field strength and temperature on an Oxford magnetic balance system.

1(n = 4) Doped in Crystalline Benzophenone

Crystals of benzophenone doped with 5(n = 4)(5.0 × 10^{-4} M) in a small quartz basket was photolyzed in a cryostat of a magnetometer. Magnetization of the photogenerated 1(n = 4) was meaured with the field gradient fixed at 5 T/m by separate coils from a main coil of 0.5 T. The amount of 1(n = 4) generated in the cell was determined by the decrease of a UV absorption at 520 nm due to the diazo group. The formation of 1(n = 4) from 5(n = 4) has been shown independently to be a one-photon process. The diamagnetic susceptibility (χ_d) of the photolyzed sample was determined by the χ vs 1/T plot and the value $-0.598 \times 10^{-6}\ g^{-1}$ was subtracted to obtain the paramagnetic susceptibility ($\chi_p = \chi - \chi_d$). The $1/\chi_p$ vs T plots in this system gave a straight line in the whole temperature range (2 - 100 K). The slope of the line gave $\mu_{eff} = 9.08\ \mu_B$ and the spin number n of 8.1 according to the Curie law (Eq. 2).

$$\chi_p = \frac{N\mu^2}{3kT} \qquad (2)$$

The latter value is in good agreement with the theoretical value of 8.

The Temperature Dependence of χ_p of 1(n = 4) in 2-MTHF Matrix

The magnetic susceptibility of 1 was measured in a glassy matrix of 2-MTHF (3.77×10^{-3} M). Plots of $1/\chi_p$ vs T are not represented by a simple line (Figure 3), suggesting that the magnetic interaction between the tetracarbene molecules has to be taken into account. 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 molecules presumably because of the thermal 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 a 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 below 65 K. After the second break point at ca 20 K, the inverse of the paramagnetic susceptibility aims at the origin when plotted against temperature (region C). The observed behavior of the plots suggests the three-center antiferromagnetic inter-

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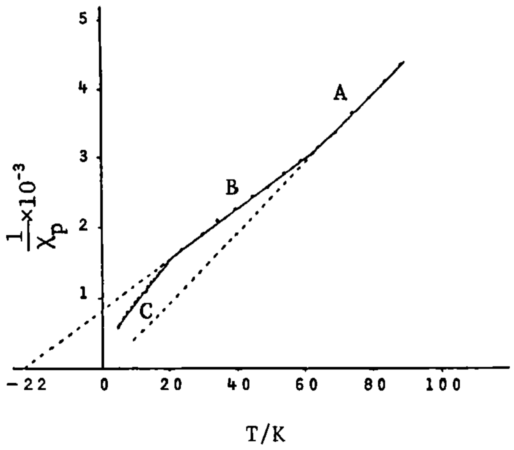

FIGURE 3. The temperature dependence of paramagnetic susceptibility of **1**(n = 4) in a glassy matrix of 2-MTHF (8.7×10^{-4} M).

action being present among the polycarbene molecules in the matrix as observed in the trinuclear cluster of paramagnetic species.[9]

The Field Strength Dependence of Magnetization of 1(n = 4) in 2-MTHF at Several Temperatures

Magnetization of **1**(n = 4) in 2-MTHF was measured as a function of the main magnetic field at 2.1, 4.2, 9.0, 17.5 and 31 K. The striking feature is a large saturation effect on the magnetization of **1**(n = 4) at lower temperatures. The characteristic behavior of the saturation should be due to the high spin multiplicity of **1**. When the experimental values are plotted against the field strength over temperature ($\underline{H}/\underline{T}$), the data fit with a single curve. The correlation is rationalized in terms of the Brillouin function for magnetization:

$$\underline{B}_J(\underline{x}) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\underline{x}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad (3)$$

where $x = gJ\ {}_{B}H/(k_{B}T)$. The experimental values 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(n = 4) and therefore $J = S$, the above correlation provides another evidence for the nonet ground state of 1(n = 4). Since Eq. 3 does not contain the concentration of the electron spins, we propose this analysis as a simple and versatile method for determining the high spin multiplicity of paramagnetic samples of unknown concentration.

CONCLUSION

The results from the susceptibility measurements suggest that, as n increases in 1, there is a high chance of obtaining a one-dimensional ferromagnet. Comparison with a typical example of inorganic one-dimensional ferromagnets will be worthwhile. In $CsNiF_3$[10] and $CoCl_2{\cdot}2C_5H_5N$,[11] the antiferromagnetic interchain interaction at low temperature is considered to be effective in stabilizing the ordering of the one-dimensionally localized spins. In polycarbenes 1, there are delocalized π electrons which can extend the spin correlation throughout the chain. The exchange interaction between the molecules of 1(n = 4) were found to be antiferromagnetic in the molecular aggregates formed in 2-MTHF. If we are able to design an appropriate molecular stacking of the polycarbenes so that the intermolecular exchange interaction might become ferromagnetic, the polycarbene molecules could serve as a magnetic domain and exhibit ferromagnetism as a macroscopic property.

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