sought for $[Mo_2Fe_6S_{12}(SR)_6]^{4-}$. The solid isolated from the dropwise addition (30 min) of 23 mmol of $FeCl_3$ in 100 mL of methanol to a mixture of NaOMe (69 mmol), p-ClC_6H_4SH (54 mmol), and $(NH_4)_2MoS_4$[22] and Na_2S_2[23] (both 7.7 mmol) in 300 mL of methanol, followed by 16 h of reaction and addition of Et_4NCl (15 mmol), was extracted with 1 L of acetonitrile. The residue from solvent removal was thoroughly washed with acetone and recrystallized from acetonitrile to afford a black solid identical in all respects with $(Et_4N)_4$(**4**) prepared via **1**. Although the yield is moderate[24] (15–20%, nonoptimized), the procedure is simple and does not require the isolation of an intermediate.

Clusters **4** and **5** are new additions to the general class of $MoFe_3S_4$ double cubanes and are accessible through intermediate **1** and by spontaneous self-assembly. Disulfide decarbonylation of oxidizable clusters with accompanying thiolate coordination and core rearrangement may be a reaction of broader utility, in which case appropriate complexes of **3** would be precursors to new M–S–SR clusters. The conversion $2Fe_2S_2(CO)_6 \rightarrow [Fe_4S_4(SR)_4]^{2-}$ with PhSSPh/PhS^-[15] was the initial example of this type of reaction. Symmetrical $Mo(\mu_2\text{-}L)_3Mo$ bridges of double cubanes are not reactive under conditions that maintain subcluster structure.[3a] Disulfide bridges of $[Mo_2Fe_6S_{12}(SR)_6]^{4-}$ may be reactive, and the conceivable transformations $Mo(S_2)_2Mo \xrightarrow{L''} L''Mo(\eta^2\text{-}S_2) \xrightarrow{2H} L''Mo(SH)_2$ are under investigation. Addition across a *cis*-dithiol group incorporated in a redox-active cluster offers a potential new method for activation and reduction of unsaturated enzymic substrates.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank Drs. R. B. Frankel and G. C. Papaefthymiou for the Mössbauer spectral measurements.

Supplementary Material Available: Tables of atom coordinates and thermal parameters for $(Et_4N)_2[MoFe_3S_6(CO)_6]$ and $(Et_4N)_4[Mo_2Fe_6S_{12}(S\text{-}p\text{-}C_6H_4Br)_6]$ (9 pages). Ordering information is given on any current masthead page.

---

[22] McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.

[23] Feher, F.; Berthold, H. J. *Z. Anorg. Allg. Chem.* **1953**, *273*, 144.

[24] $(Et_4N)_2[Fe_4S_4(S\text{-}p\text{-}C_6H_4Cl)_4]$[15] and another paramagnetic cluster salt (unidentified), both acetone soluble, were observed as byproducts by ^1H NMR.

Ferro- and Antiferromagnetic Interaction between Two Diphenylcarbene Units Incorporated in the [2.2]Paracyclophane Skeleton

Akira Izuoka, Shigeru Murata, Tadashi Sugawara, and Hiizu Iwamura*

Division of Applied Molecular Science
Institute for Molecular Science, Okazaki 444, Japan

Received November 1, 1984

High-spin polycarbenes and polyradicals are considered to be a model for low-dimensional organic ferromagnets.[1] Most of the hitherto known examples, namely, *m*-phenylenebis(phenylmethylene),[2] its higher homologues,[3] 3,6-dimethyleneanthracenediyl-1,8-dioxyl,[4] etc., derive their high-spin multiplicity from the nonbonding molecular orbitals due to the symmetry of the alternant hydrocarbon skeleton. We wish to report here a novel system in which spin multiplicity of dicarbenes is controlled by the overlapping modes of spin-distributed benzene rings incorporated in the rigid [2.2]paracyclophane framework.

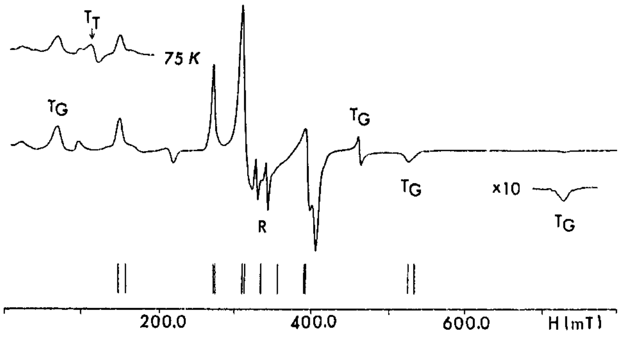


Figure 1. ESR spectrum obtained after irradiation of **1a** in 2-methyltetrahydrofuran at 11 K. Lines indicate the calculated transition of the quintet state based on the third-order perturbation method. T_G is assigned to a monocarbene which presumably was formed by failure in removal of the second diazo group or by further reaction with solvent molecules at one of the carbenic centers (for T_T; see text).

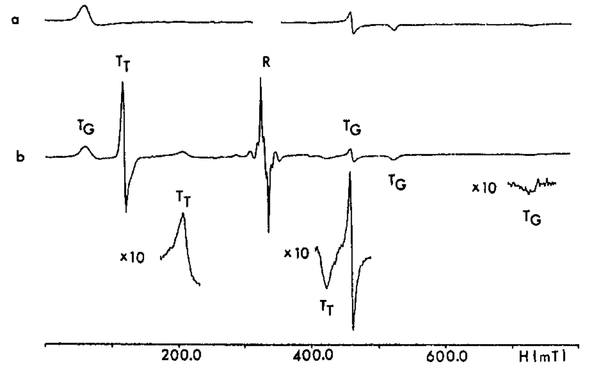
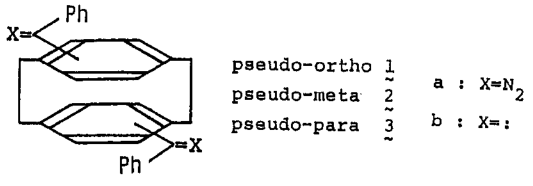


Figure 2. ESR spectra obtained (a) in the dark after generation of **2b** by irradiation of **2a** at 11 K and (b) when (a) was warmed to 60 K. T_G is assigned to a monocarbene as explained in Figure 1. R is a triplet biradical species formed adventitiously (for T_T; see text).

According to McConnell's theory on intermolecular magnetic interaction,[5] exchange interaction between two aromatic radicals can be ferromagnetic when the product of spin densities at two interacting sites on different molecules is negative in sign, since the exchange integral is negative between organic radicals at a distance of the van der Waals contact. The spin distribution of diphenylcarbene is given by the ENDOR experiment.[6]

Among the three isomers of bis(phenylmethylenyl)[2.2]paracyclophanes (**1b**–**3b**) with different orientation of the two phenylmethylenyl substituents, we note that only the pseudoortho and pseudopara isomers satisfy McConnell's condition. The sign of the spin density product at each interacting site between the two benzene rings is all negative in pseudoortho and pseudopara isomers and all positive in the pseudometa one.[7] Thus the different spin distribution is expected to result in the quintet ground state for **1b** and **3b** and in the singlet ground state for **2b**.



---

[1] (a) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (b) Ovchinnikov, A. A. *Ibid.* **1978**, *47*, 297. (c) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. (d) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Ito, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449.

[2] (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (b) *Pure Appl. Chem.* **1978**, *50*, 1251. (c) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

[3] Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722.

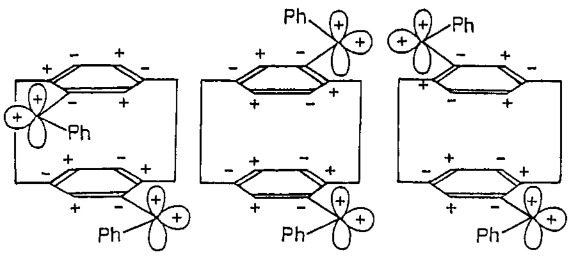
[4] (a) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5144. (b) *Ibid.* **1983**, *105*, 5146.

[5] McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

[6] Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327.

[7] The spin distribution may be also caused by the through-bond mechanism via the strained ethano bridges. The direction of spin distribution, however, is the same as the through-space p_σ–p_σ interaction. Therefore this mechanism is not explicitly mentioned in the above argument.

0002-7863/85/1507-1786$01.50/0



Irradiation of pseudoortho didiazo compound **1a**[8] in a rigid glass of 2-methyltetrahydrofuran at 11 K in an ESR cavity (Varian E112/V7800, X-band spectrometer) with Pyrex-filtered UV light gave intense quintet signals as shown in Figure 1. The zero-field splitting parameters were evaluated to be $|D| = 0.0624$ and $|E| = 0.0190$ cm^{-1} on the basis of a third-order perturbational calculation.[9] The intensity of the quintet signals was found to obey the Curie law in the temperature range 11–50 K, indicating that the quintet is the ground state. A signal at 104.0 mT was detected at temperatures above 20 K. The signal intensity increased at elevated temperatures, suggesting that this species was a thermally populated triplet (T_T), although the rest of its signals were weak and not resolved well.

In sharp contrast with **1b**, signals due to the quintet species were not detected in the ESR spectrum obtained after irradiation of **2a** (Figure 2). A new set of triplet signals (T_T: $|D| = 0.1973$, $|E| = 0.0038$ cm^{-1}) started to appear when the temperature was raised to 20 K. The signal intensities increased as the temperature was raised but did not change with time at each temperature. The signal intensity of T_T started to decrease with time at about 70 K. The intensity behavior is unambiguously of the thermally populated triplet. Since 1,*n*-biradicals cannot have such large D value as observed in T_T, the signals should be due to the triplet state of **2b**. The absence of quintet signals together with the presence of thermally populated triplet ones lead us to conclude that the singlet is the ground state for pseudometa dicarbene **2b**.

A preliminary measurement was performed on pseudopara didiazo compound **3a** and the intense quintet signals were detected.[10] The result suggests the quintet ground state for pseudopara dicarbene **3b**.

These considerable differences in spin multiplicity of dicarbenes **1b**–**3b** observed here are the first experimental demonstration[11] that the spin distribution of the π-electron in the layered benzenoid moieties can determine the ferro- or antiferromagnetic interaction between the carbene species. The results also suggest that the mode of stacking of the benzene units can be crucial in increasing the dimension and determining the intermolecular interaction which should control the bulk magnetic properties of the high-spin aromatic molecules.

---

(8) Three isomeric dibromo[2.2]paracyclophanes were prepared and separated according to the literature method. See: Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527. Each isomer was dilithiated by *n*-butyllithium in ether and treated with benzaldehyde to give the corresponding diol, which was then oxidized by pyridinium chlorochromate in dichloromethane to give the dibenzoyl[2.2]paracyclophane. It was converted to the didiazo compound through the bis(hydrazone) by oxidizing with yellow HgO in benzene at room temperature. The crude product was purified by alumina column chromatography by rapid elution with benzene: peuedoortho, mp 107–109 °C dec; pseudometa, mp 136–138 °C dec; pseudopara, mp 147–148 °C dec. All the new compounds gave satisfactory elemental analyses and ^{1}H NMR data.

(9) (a) Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120. (b) Itoh, K., private communication.

(10) The dicarbene was found to be unstable and to be converted to the biradical ($|D| = 0.0108$, $|E| = 0.0005$ cm^{-1}) thermally. The thermal instability of the dicarbene **3b** prevented us from drawing the Curie plot in a wide temperature range.

(11) The ESR spectra of pseudoortho, pseudometa, and pseudopara [2.2]paracyclophanylenebis(*tert*-butyl nitroxide) in a glass of *o*-terphenyl are reported. See: Forrester, A. R.; Ramasseul, R. *J. Chem. Soc., Perkin Trans. 1* **1971**, 1645. The triplet signals are obtained in all cases including pseudometa one. The electron spins of these nitroxides are localized in the nitroxide groups rather than delocalized to the benzene rings because of the twisting of *tert*-butylnitroxyl groups. Therefore the exchange interaction of the electron spins between the benzenoid moieties in these cases is unfortunately too small to test McConnell's theory.

Observation of a Novel Low-Lying Excited State in Zinc(II) Complexes

K. A. Truesdell and G. A. Crosby*

Chemical Physics Program
Washington State University
Pullman, Washington 99164-4620

Received May 10, 1984

Photoluminescence spectra of closed-shell zinc(II) complexes containing both N-heterocyclic and aromatic thiol ligands reveal the presence of a previously uncharacterized excited state. Modifications of the complexes by changing the π-donating strength of the substituents on the thiol moiety produce substances ranging from those in which the presence of the low-lying state is barely detectable to compounds whose emission spectra are dominated by the new transition. The experimental observations on a typical set of analytically pure compounds are reproduced in Figure 1.

When the $ZnCl_2$(phen) complex, a white solid, is illuminated by ca. 330-nm UV light in an organic glass at 77 K, strong fluorescence and phosphorescence characteristic of the phen ligand are observed.[1] Replacement of the chlorides by two pentafluorothiophenol anions (F_5PhS) produces a slightly offwhite solid that exhibits no phen fluorescence but does show a strong phen phosphorescence. Intensive studies of this latter emission reveal the presence of a new band maximizing at ca. 620 nm lying in the tail of the phen phosphorescence. The band shows up clearly in time-resolved spectra. Replacing the chlorides in $ZnCl_2$(phen) by the anions of 4-chlorothiophenol (4-ClPhS) produces a molecule in which the new band dominates the emission spectrum as is clearly seen in Figure 1. Phen phosphorescence is not entirely quenched, however. Finally, excitation of the Zn(4-MeOPhS)$_2$(phen) complex (4-MeOPhS = anion of 4-methoxythiophenol) produces only the broad new band maximizing ca. 620 nm. (The presence of an aromatic thiol is necessary; aliphatic thiols do not produce compounds exhibiting the new band.) Although the observed structured fluorescence and phosphorescence clearly originate from the phen ligand, the subtle differences both of the spectra themselves and, in the case of the phosphorescence, the measured lifetimes decisively show that the phen ligand is coordinated to the zinc ion.

Detailed spectroscopic measurements, including time-resolved studies, determine that the new band arises from an excited state that (a) is only present when *both N-heterocyclic and aromatic thiol* ligands are coordinated to the Zn(II) ion, (b) decays on the order of microseconds at 77 K, (c) is tunable to some extent by making judicious change in either or both types of ligand, (d) profoundly affects the radiationless degradation rates and pathways in the complexes, and (e) is a general property of these types of complexes of metal ions with filled d shells. We have in the laboratory analogous results from Cd(II)[2] and Sn(IV) systems.[3]

Absorption measurements of these types of complexes show the presence of a broad low-lying transition(s) that gradually shifts toward the visible (see Figure 1) as the electron-donating ability of the thiol ligand increases. This new band correlates with the presence of the novel emission band and is responsible for the progressive change in color of the complexes from white [$ZnCl_2$(phen)] to yellow [Zn(4-MeOPhS)$_2$(phen)] in the crystalline state. The behavior of this absorption band in Zn(II) complexes has been noted previously by Koester (dithiol ligands),[4] who assigned it to an interligand trans-metallic charge-transfer (ITCT) transition between the *thiol donor and the N-heterocyclic acceptor*. We tentatively assign the new emitting state(s) to an ITCT transition(s), although the new emission band is not the inverse of the absorption band. Both the ITCT orbital designation

---

(1) Bray, R. G.; Ferguson, J.; Hawkins, C. J. *Aust. J. Chem.* **1969**, *22*, 2091.

(2) Highland, R. G.; Crosby, G. A., manuscript in preparation.

(3) McGuire, B. R., unpublished results.

(4) Koester, V. J. *Chem. Phys. Lett.* **1975**, *32*, 575.

0002-7863/85/1507-1787$01.50/0