

Molecular Design and Model Experiments of Ferromagnetic Intermolecular Interaction in the Assembly of High-Spin Organic Molecules. Generation and Characterization of the Spin States of Isomeric Bis(phenylmethylene)[2.2]paracyclophanes

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Abstract: The electron spin-spin interaction between the two triplet diphenylcarbene units incorporated in the [2.2]paracyclophane skeleton has been investigated by ESR spectroscopy. Pseudoortho, pseudometa, and pseudopara didiazo[2.2]paracyclophanes (**4a-c**) were prepared and photolyzed with Pyrex-filtered UV light in a 2-methyltetrahydrofuran glass at cryogenic temperatures to give the corresponding dicarbenes (**5a-c**). Intense quintet signals with $|D| = 0.0624$ and $|E| = 0.0190$ cm⁻¹ were obtained from **4a**. Their intensity obeyed the Curie law in the temperature range 11-50 K, showing that quintet **5a** was the ground state. A signal at 104.0 mT due to the thermally populated triplet was also detected at temperatures above 20 K. From the analysis of the temperature dependence of its intensity, the triplet state was located at the energy level 0.18 kcal/mol above the quintet state. Pseudometa bis(phenylmethylene)[2.2]paracyclophane (**5b**) did not show any ESR signal at 11 K. As the temperature was raised above 25 K in the dark, a set of triplet signals with $|D| = 0.1840$ and $|E| = 0.0023$ cm⁻¹ appeared. Thus it was found that **5b** was in the singlet ground state, and its thermally populated triplet was at 0.28 kcal/mol above the ground state. Intense quintet signals ($|D| = 0.1215$ cm⁻¹ and $|E| = 0.0085$ cm⁻¹) were detected at 15 K for **5c**, but it was too unstable chemically to study the Curie plots. Dipolar interaction tensors have been calculated for the resultant quintet states of dicarbenes **5a** and **5c** and the triplet state of dicarbene **5b**. The best fit of the computed zero-field splitting parameters with those of the experiments produced proposed conformations of the dicarbenes. McConnell's theory on the intermolecular magnetic interaction between two organic radicals has been demonstrated and a new strategy for increasing the dimension of the high-spin aromatic molecules was found.

Molecular design and construction of organic ferromagnets are the subject of great interest in modern theoretical and organic chemistry.¹ As an approach to this challenging goal, we have generated a series of high-spin polycarbenes by photolysis of the corresponding polydiazo compounds at cryogenic temperatures.² Magnetic susceptibility measurements have revealed that the nonent tetracarbene Ph $\dot{C}(m-C_6H_4\dot{C})_3$ Ph, for example, has the paramagnetic property of a very large magnetic moment, approaching superpara-magnetism.³ The logical extension of this finding is that it will be possible to construct "organic molecular magnets". Curie plots of the paramagnetic susceptibility of a sample in 2-methyltetrahydrofuran (2MTHF) glass or in neat crystal have shown, however, that the intermolecular interactions in the fortuitously formed aggregates are antiferromagnetic. Therefore, it is imperative for establishing the spin alignment in macroscopic scale throughout the molecular assembly that a system be designed in which intermolecular interactions could be ferromagnetic. One of the plausible methods for achieving this objective is a design of molecular stacking of the spin-containing aromatic rings in crystals and other organized molecular systems;⁴ this will be discussed in this paper.

Let us treat the problem of weak intermolecular interaction between two triplet molecules, generating the singlet, triplet, and quintet states.^{1c} When the exchange integral (J) between the two species is negative, as is often the case between organic open-shell molecules at a separation of the van der Waals distance, the singlet is the ground state. When J is positive, the quintet is the ground state of the interacting system (Figure 4). As a representative of the triplet species, we chose diphenylcarbene which is known to have the ground triplet state located 3-5 kcal/mol below the singlet state.⁵ Let us consider the simplest case of superimposable stacking of two benzene rings, one from each diphenylcarbene molecule. Since the benzene ring is monosubstituted, there are four kinds of idealized orientations for the possible stacking: pseudogeminal, pseudoortho, pseudometa, and pseudopara. We became interested in knowing if the effective exchange interaction

might be different depending on the orientation of the stacking pattern. As an operational test for this question, we have introduced the [2.2]paracyclophane skeleton to fix the orientation of the stacking modes of the two diphenylcarbene molecules.⁶ In this paper generation and ESR spectral characterization of three isomeric [2.2]paracyclophanedicarbenes are described and an intriguing transannular magnetic interaction is discussed as a model for the assembly of high-spin molecules.

Results and Discussion

A. Preparation of Isomeric [2.2]Paracyclophanedidiazole Compounds (4a, 4b, and 4c) and 4-(α -Diazobenzyl)[2.2]paracyclophane (7). Isomeric dibromocyclophanes (**1a-c**) were obtained by bromination of [2.2]paracyclophane.⁷ Pseudopara isomer **1c** was

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(2) (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. (b) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *Ibid.* **1986**, *108*, 2147. (c) Teki, Y.; Takui, T.; Yagi, H.; Itoh, K.; Iwamura, H. *J. Chem. Phys.* **1985**, *83*, 539. (d) Iwamura, H.; Sugawara, T.; Itoh, K.; Takui, T. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 251.

(3) (a) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *Ibid.* **1986**, *108*, 368.

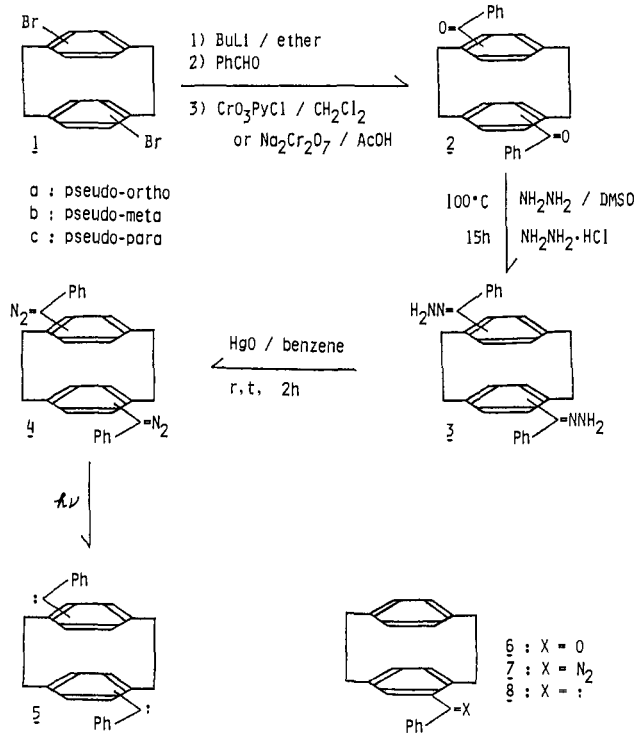
(4) The design of molecular assemblies of diphenylcarbenes with ferromagnetic interaction was advanced based on this study and is described in: (a) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. (b) Sugawara, T.; Tukada, H.; Izuoka, A.; Murata, S.; Iwamura, H. *Ibid.* **1986**, *108*, 4272.

(5) (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (b) Eienthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Heferson, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *Ibid.* **1980**, *102*, 6563. (c) Turro, N. J. *Tetrahedron* **1982**, *38*, 809. (d) Griller D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(6) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786.

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Scheme I



isolated by a fractional recrystallization, while pseudoortho **1a** and pseudometa **1b** were separated by liquid chromatography. A pseudogeminal isomer was not obtained under this bromination for steric reasons. Dilithio compounds obtained from **1a-c** were treated with benzaldehyde to give dialcohols. Pseudoortho and pseudometa diols were oxidized by pyridinium chlorochromate to afford diketones **2a** and **2b**. Pseudopara diol was oxidized to diketone **2c** by sodium dichromate in acetic acid. The isomeric configuration of the ketones was assigned by $^1\text{H NMR}$ (vide infra). Since the hydrazones could not be formed by usual procedures, the following modification was applied. Diketones **2a-c** in $(\text{CH}_3)_2\text{SO}$ were treated with excess anhydrous hydrazine and hydrazine monohydrochloride and allowed to react at 110°C for 10 h to give the corresponding dihydrazones (**3a-c**) in quantitative yield. The procedure turned out to be useful for converting reluctant ketones to hydrazones. Didiazo compounds **4a-c** were obtained by oxidation of the hydrazones with mercuric oxide (yellow) and purified by column chromatography on alumina.

4-Benzoyl[2.2]paracyclophane (**6**) was obtained by Friedel-Crafts reaction of [2.2]paracyclophane with benzoyl chloride and converted to 4-(α -diazobenzyl)[2.2]paracyclophane (**7**) via the hydrazone similarly to the above method.

B. $^1\text{H NMR}$ Spectral Information. Characteristic spectral features were obtained from 400-MHz $^1\text{H NMR}$ spectra of diketones **2a-c** and didiazo compounds **4a-c**. For **2a-c** the hydrogens on the ethano bridges, the [2.2]paracyclophane aromatic rings, and the benzoyl groups appear in the δ 2.8–3.4, 6.4–7.0, and 7.35–7.75 regions, respectively (Figure 1). In the pseudometa and pseudopara diketones, **2b** and **2c**, two benzoyl groups appear to be independent of each other as judged from the fact that the chemical shift values of their H_o (δ 7.7–7.75), H_m (δ 7.39–7.44), and H_p (δ 7.52–7.57) are quite similar to those of the monobenzoyl derivative **6**. A large upfield shift of H_o (δ 7.5–7.55), a similar but smaller shift in H_m (δ 7.35–7.39), and an even smaller shift in H_p of the pseudoortho isomer **2a** are indicative of a mutual shielding effect of the two benzoyl groups. It is not clear from these data, however, if the conformation of the benzophenone unit in the pseudoortho isomer is different from those of the others.

In general, benzoyl substitution has the effect of shifting the pseudogeminal and pseudoortho hydrogens on the [2.2]paracyclophane ring to the lower and higher fields by ca. 0.2 ppm,

respectively. Two triplet and two doublet of triplet signals in the almost first-order spectra of the CH_2 region of the pseudoortho isomer clearly show that the ethano bridges take a staggered conformation in which the torsional angle is estimated from the Karplus relation to be ca. 30° . The staggering is presumed to be taken to avoid nonbonded interaction between the two pseudoortho benzoyl groups.

A diazomethyl group is ortho and para directing and, therefore, the H_o and H_p of the α -diazobenzyl group and H_a of the aromatic hydrogen of the [2.2]paracyclophane ring now appear in the higher field in contrast with those of the diketones. The H_a in the pseudoortho isomer is conspicuously upfield shifted, showing that the hydrogens are in the diamagnetic shielding zone of the other α -diazobenzyl group. The pseudogeminal and pseudoortho hydrogens on the [2.2]paracyclophane ring to the α -diazobenzyl group are shifted to lower field by 0.07 ppm and to higher field by 0.2 ppm, respectively. The similar shielding effects by the benzoyl and α -diazobenzyl groups of opposite electronic effect suggest that the effects are due to steric nature, and the benzene rings of these groups are probably situated nearer to the pseudoortho hydrogen and opposite to the ethano bridge.

C. ESR Detection of Bis(phenylmethylene)[2.2]paracyclophanes (5a**, **5b**, and **5c**) and Intramolecular Magnetic Interaction Revealed by the Temperature Dependence of Their Spectra.** Irradiation of pseudoortho didiazo compound **4a** in a rigid glass of 2-methyltetrahydrofuran at 11 K in an ESR cavity with Pyrex-filtered UV light gave a series of intense signals as shown in Figure 2a. The spectrum as a whole resembles the quintet spectrum of *m*-phenylenebis(phenylmethylene).⁸ The resonance positions are reproduced reasonably well by a second-order perturbational calculation as a quintet species (Q) with zero-field splitting (zfs) parameters of $|D| = 0.0624 \text{ cm}^{-1}$ and $|E| = 0.0190 \text{ cm}^{-1}$, although the fitting is not satisfactory for transitions at lower magnetic field than 200 mT because of the limitation of a high-field approximation used in the calculation.⁹ In addition to these quintet signals, triplet signals (T_G) were detected at 62.8, 463.0, 526.7, and 732.0 mT. The different origin of these lines from those of the quintet signals is confirmed by a different thermal behavior between them (vide infra). They are assigned to H_z , H_x , H_y , and H_z transitions of a triplet species, respectively. Its zfs parameters are calculated¹⁰ to be $|D| = 0.3730 \text{ cm}^{-1}$ and $|E| = 0.0156 \text{ cm}^{-1}$, which are close to those of 4-phenylmethylene[2.2]paracyclophane (**8**) ($|D| = 0.3720 \text{ cm}^{-1}$ and $|E| = 0.0161 \text{ cm}^{-1}$). Another triplet species with small zfs parameters ($|D| = 0.0134 \text{ cm}^{-1}$ and $|E| \approx 0.0 \text{ cm}^{-1}$) was detected in the central region of the spectrum. This is assigned to a triplet biradical (R) presumably formed from the dicarbene species by way of partial chemical reactions.

In order to determine the ground-state spin multiplicity and thermal stability of the observed species, the temperature dependence of the intensities of these signals was studied (Figure 3). The signal intensities of Q were found to obey the Curie law in the temperature range 11–50 K, indicating that the pseudoortho dicarbene **5a** has the quintet ground state. This is the first experimental demonstration that the magnetic interaction between two diphenylcarbene moieties is ferromagnetic when two spin-containing benzene rings, one from each diphenylcarbene, are stacked in the proper mode (vide infra). Since the signals of T_G also obeyed the Curie law in the temperature range of 11–85 K, it was assigned to the ground-state triplet monocarbene monodiazo species formed by failure to remove the second diazo group. While the signals of R obeyed the Curie law in the temperature range 11–50 K, their intensity increased irreversibly at above 50 K at the expense of the Q species, suggesting generation of R from Q.

(8) Takui, T.; Teki, Y.; Itoh, K. ESR spectrum in glass will be shown elsewhere.

(9) The zero-field parameters for quintet species were calculated based on a second-order perturbation method. See: Itoh, K. *Chem. Phys. Lett.* **1963**, *1*, 235. The ESR spectra of [2.2]paracyclophanedicarbene are well reproduced by using a simulation program by exact diagonalization of the spin Hamiltonian: Teki, Y.; takui, T.; Itoh, K.; Izuoka A.; Murata, S.; Sugawara, T.; Iwamura, H. to be submitted for publication.

(10) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

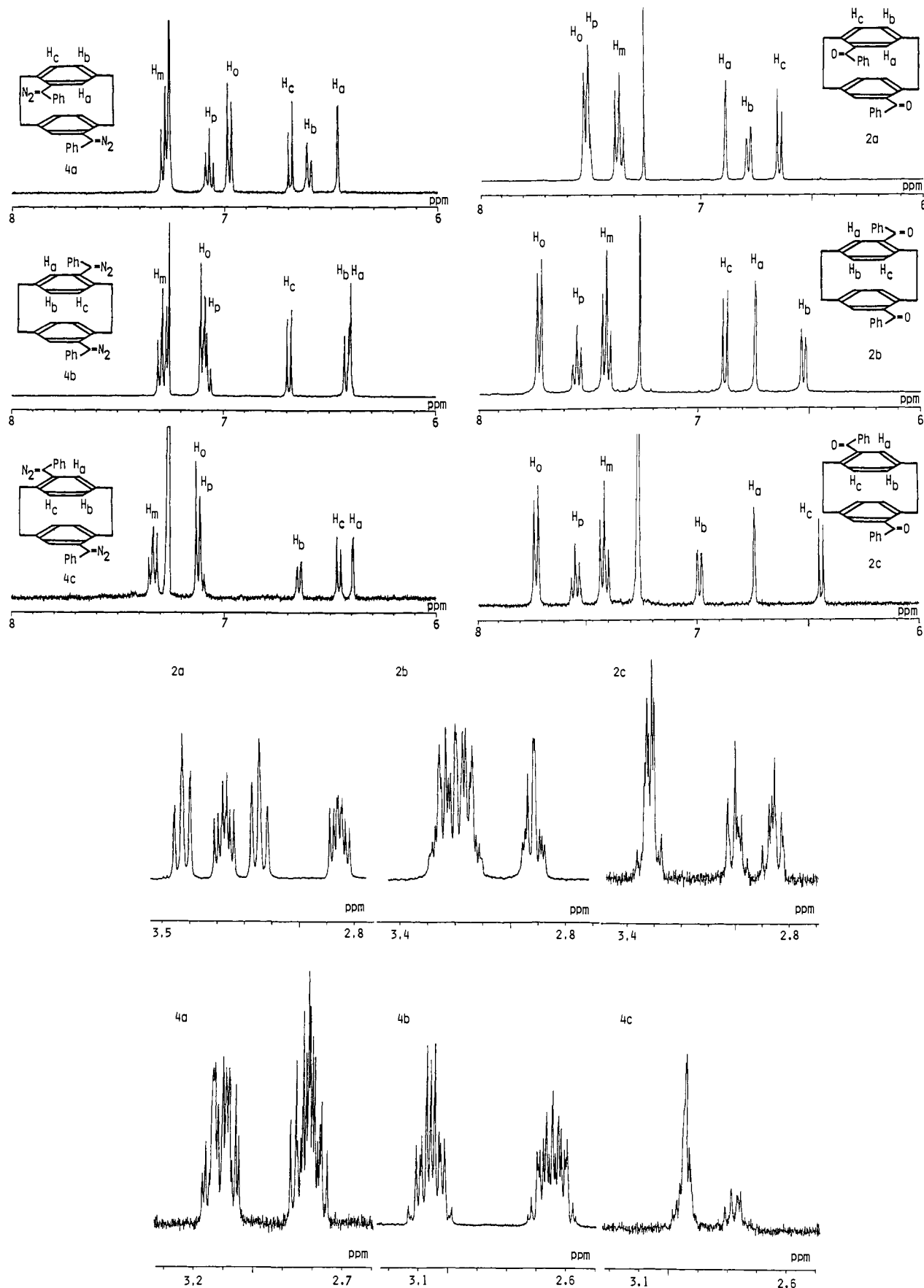


Figure 1. ^1H NMR spectra (400 MHz) of diketones **2a-c** and didiazo compounds **4a-c**.

At temperatures higher than 20 K a new signal started to appear at 104.0 mT (Figure 2b). The intensity of the signal increased as the temperature was elevated and showed a maximum at 55 K (Figure 3). The signal decayed irreversibly at temperatures

higher than 50 K. The thermal behavior of the peak is characteristic of a thermally populated species (T_T). Since the relation $D_T = -3D_Q$ holds for two equivalent weakly interacting triplet species,^{1c} the zfs parameters can be estimated to be $|D| = 0.1872$

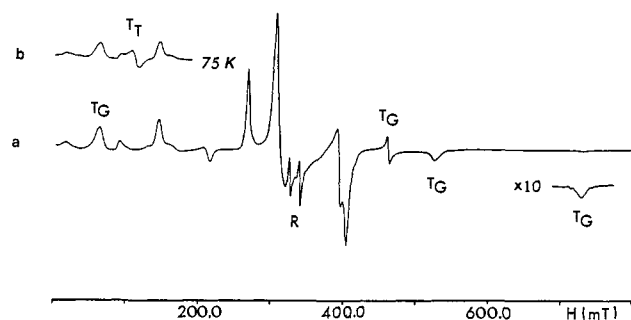


Figure 2. ESR spectra (9.3310 GHz) obtained (a) after photolysis of **4a** in 2MTHF at 11 K and (b) when (a) was warmed to 75 K.

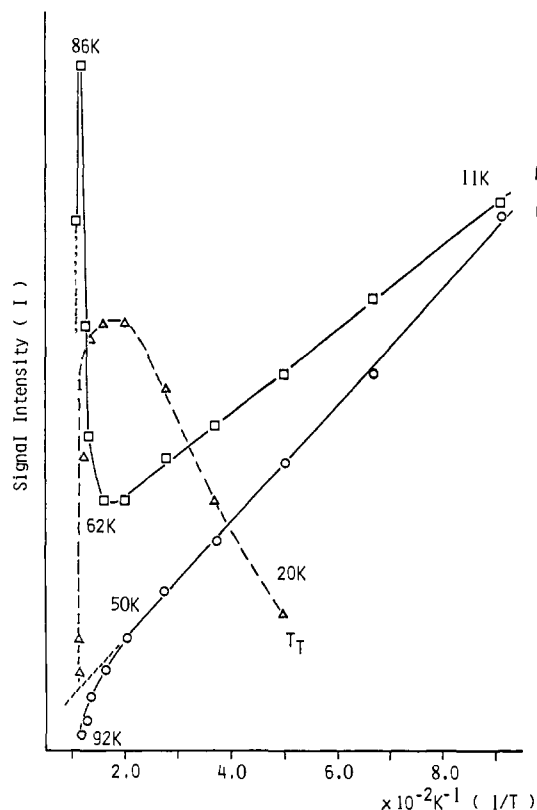


Figure 3. Plots of ESR signal intensities due to biradical R and dicarbene species Q and T_T obtained by irradiation of **4a** in 2MTHF vs. reciprocal temperature.

cm^{-1} and $|E| = 0.0570 \text{ cm}^{-1}$. The transition field of H_{\min} for T_T is calculated to be 104.9 mT from the estimated D and E values, in good agreement with the observed value of 104.0 mT.¹⁰ Since signals due to the other transitions of T_T were not observed for their weak intensities, they could not be identified precisely.

Let us consider relative energy levels of the spin states in two weakly interacting triplet carbene species.^{1c} The energy splittings caused by the magnetic interaction of a pair of carbenes can be expressed by eq 2 by using the Heisenberg spin Hamiltonian (eq 1), where S_i is the total spin quantum number. The energy of

$$\mathcal{H} = -2J\mathbf{s}_1\mathbf{s}_2 \quad (1)$$

$$E(S_i) = -J[S_i(S_i + 1) - 4] \quad (2)$$

the quintet state ($S_i = 2$) is $-2J$, and those of the triplet ($S_i = 1$) and the singlet state ($S_i = 0$) are $2J$ and $4J$, respectively. The energy levels of a ferromagnetically interacting pair with a positive J value is shown in Figure 4a. Since the energy difference (ΔE) between the spin states has a relation $\Delta E_{QT} = 2\Delta E_{TS}$, the temperature dependence of the signal intensities (I_T) for T_T in the ESR spectrum can be expressed by eq 3, assuming a Boltzmann

$$I_T = \frac{C \exp(-\Delta E_{QT}/RT)}{5 + 3 \exp(-\Delta E_{QT}/RT) + \exp(-3\Delta E_{QT}/2RT)} \frac{1}{T} \quad (3)$$

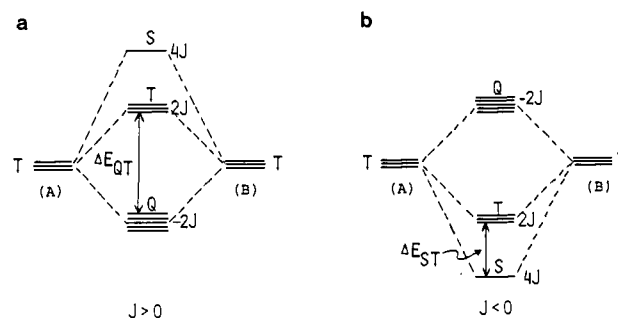


Figure 4. Weak-interaction diagrams between two triplet carbenes A and B. Ferro- and antiferromagnetic interactions are shown in (a) and (b), respectively.

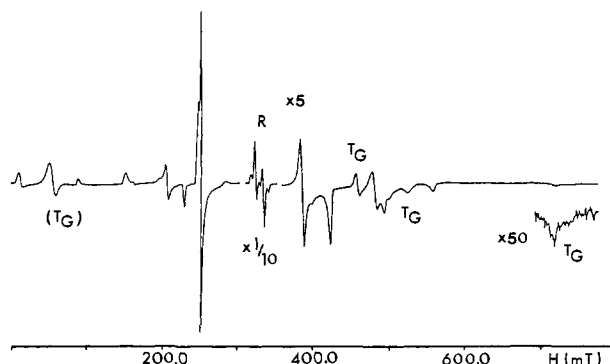


Figure 5. ESR spectrum (9.3352 GHz) obtained after irradiation of **4c** in 2MTHF at 15 K.

distribution among the three states.¹¹ From the observed thermal behavior of the thermally populated triplet species (T_T) in **5a**, ΔE_{QT} is estimated to be 0.18 kcal/mol ($=63 \text{ cm}^{-1}$) and J is calculated to be $+16 \text{ cm}^{-1}$ from eq 2.

ESR spectrum of the photolysate of pseudopara didiazo **4c** in 2-methyltetrahydrofuran at 15 K is shown in Figure 5. The zfs parameters of **5c** are determined to be $|D| = 0.1215 \text{ cm}^{-1}$ and $|E| = 0.0085 \text{ cm}^{-1}$.⁹ Besides the quintet signals, strong triplet signals due to a biradical species (R) were observed at around 330 mT with zfs parameters of $|D| = 0.0110 \text{ cm}^{-1}$ and $|E| \approx 0.0 \text{ cm}^{-1}$. A series of signals at 464.4, 530.1, and 742.4 mT are again assigned to the triplet monodiazo monocarbene species (T_G) ($|D| = 0.3837 \text{ cm}^{-1}$ and $|E| = 0.0168 \text{ cm}^{-1}$). The thermal behavior of Q and R is shown in Figure 6. The intensity of Q signals decreased as the temperature was raised from 15 to 41 K, apparently obeying the Curie law. However, the intensity was not reproducible when the temperature was lowered from 41 K back to 15 K; about 60% of the original intensity was lost presumably by chemical reactions. On the other hand, the intensity of R increased higher than the original intensity at 15 K, suggesting that Q is not stable and converted to R gradually, even at 15–41 K. Although it was not possible to obtain energetical information from the temperature dependence of the signal intensities, observation of the intense Q signals strongly suggest that the quintet is the ground state of **5c**. A thermally populated triplet species was not detected in the temperature range 15–57 K. The zfs parameters of T_T can be estimated to be $|D| = 0.3645 \text{ cm}^{-1}$ and $|E| = 0.0255 \text{ cm}^{-1}$ from the relation $\mathbf{D}_{T_T} = -3\mathbf{D}_Q$. Although the expected transitions of T_T were to appear in the fields near the signals of T_G , the latter obeyed the Curie law and their line shapes did not change in the above temperature range. No appearance of T_T signals seems to suggest that the energy difference between the ground quintet state and thermally populated triplet (ΔE_{QT}) of **5c** must be even larger than that of **5a**.

(11) Although the exact equation for the temperature dependence of the ESR signal intensities contains the factor for the each spin state sublevels, it can be approximated by eq 3 if the energy difference ΔE between the spin states are much larger than the energy separation among spin sublevels. Equation 4 is also given by the same approximation.

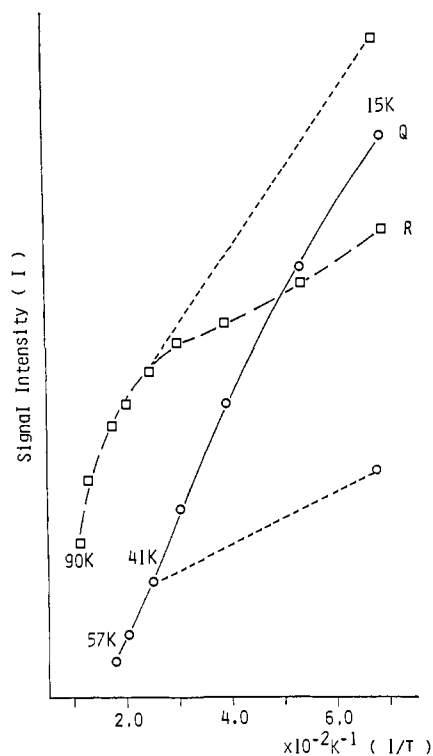


Figure 6. Plots of ESR signal intensities of biradical R and quintet dicarbene Q obtained by irradiation of **4c** in 2MTHF vs. reciprocal of temperature. The broken lines show the gain and loss of the original intensities at 15 K after warming up to 41 K.

Irradiation of pseudometa didiazo **4b** at 12 K afforded only the ground-state triplet signals of monodiazomethylcarbene and those of a biradical (Figure 7a). However, when the temperature was raised to 25 K after the photolysis, a new signal (T_T) started to appear at 119.4 mT, and the intensity of the signal increased with temperature, giving a maximum at 65 K. Two other peaks (209.1 and 425.4 mT) assignable to T_T were also detected at 65 K (Figure 7b). The species T_T started to decay at temperatures higher than 70 K and disappeared at 90 K (Figure 8). The thermal behavior of the peaks can well be explained as a thermally populated species. The zfs parameters of T_T are estimated to be $|D| = 0.1840 \text{ cm}^{-1}$ and $|E| = 0.0023 \text{ cm}^{-1}$. Since the quintet signals were not detected, and the triplet was thermally populated, the two diphenylcarbene units in **5b** are concluded to interact antiferromagnetically to give the singlet ground state. The energy levels of the antiferromagnetically interacting triplet species with a negative J value are shown in Figure 4b. The energy difference (ΔE_{ST}) between the ground-state singlet and the thermally populated triplet state can be calculated by eq 4. Using the thermal behavior of signal

$$I_T = \frac{C \exp(-\Delta E_{ST}/RT)}{1 + 3 \exp(-\Delta E_{ST}/RT) + 5 \exp(-3\Delta E_{ST}/RT)} \frac{1}{T} \quad (4)$$

intensities of T_T at temperatures lower than 65 K, ΔE_{ST} is estimated to be 0.28 kcal/mol ($=98 \text{ cm}^{-1}$), J being -49 cm^{-1} . The quintet state appears to be too highly lying to detect by thermal population.

D. Information on the Quintet [2.2]Paracyclophanedicarbene 5a by UV Irradiation in a Glassy Matrix at Cryogenic Temperature. Photolytic formation of the quintet *m*-phenylenebis(phenylmethylene) from *m*-bis(α -diazobenzyl)benzene in benzophenone host crystals has been reported to be one-photon.¹² Recently we found that a quintet carbene pair is generated photolytically in crystals of diazo compounds through a one-photon process especially at shorter wavelength irradiation.^{4b} The latter phe-

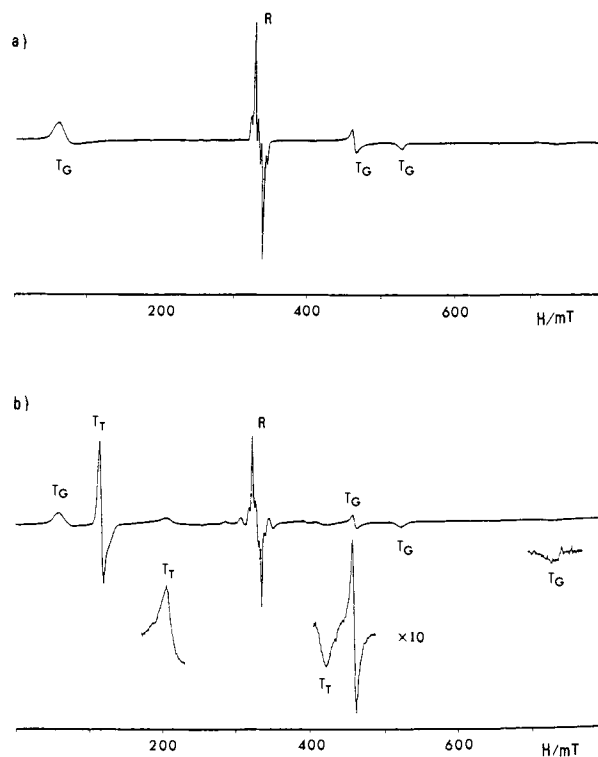


Figure 7. ESR spectra (9.3272 GHz) obtained (a) after photolysis of didiazo compound **4b** in 2MTHF at 12 K and (b) when (a) was warmed to 65 K.

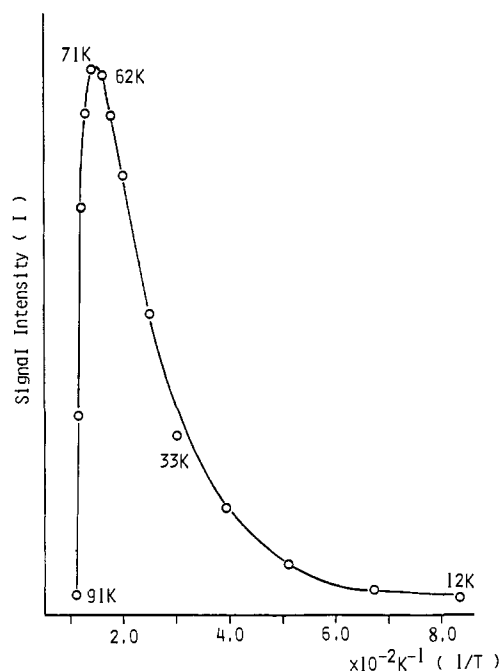


Figure 8. Plots of ESR signal intensities due to thermally populated triplet dicarbene T_T of **5b** in 2MTHF glass vs. $1/T$.

nomenon may be rationalized by intermolecular energy transfer among diazo molecules coupled with removal of nitrogen molecules, the latter process being known to be exothermic.¹³ These findings prompted us to study photolytic behavior of pseudoortho didiazocyclophane **4a**.

The initial rates of formation of the quintet dicarbene (Q) **5a** and the triplet species (T_G) under steady-state irradiation with Pyrex-filtered light were monitored in a 2-methyltetrahydrofuran glass at cryogenic temperature by an increase in intensities of

(12) Itoh, K.; Takui, T.; Teki, Y. Abstracts of Papers, 46th Annual Meeting of the Chemical Society of Japan, Niigata, Oct 1982, p 17. See also ref 2b.

(13) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 5156.

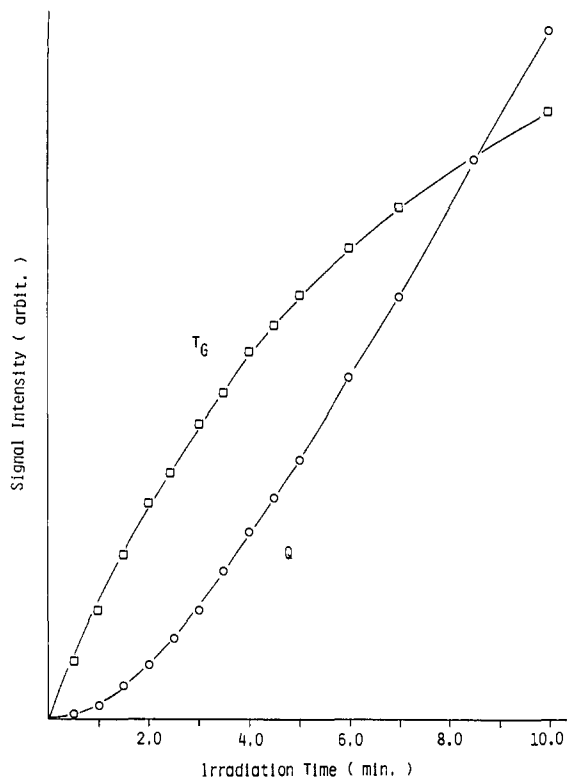


Figure 9. Growth of ESR signals due to quintet dicarbene Q and triplet carbene T_G during photolysis of didiazo compound **4a** in 2MTHF glass (1.81 mM) at 20 K.

transitions at 250 and 450 mT for Q and T_G , respectively (Figure 9). These signals were chosen because they were well resolved from other transitions. The formation of Q was found to have an obvious induction period, increasing linearly thereafter. On the other hand, the rise of T_G gave a concave curve, showing a gradual saturation in its concentration. The trend is best explained by a scheme in which Q is formed through T_G as an intermediate species. Thus T_G is assigned to monodiazomonocarbene species. The result resembles a stepwise photodecomposition of *m*-bis(α -diazobenzyl)benzene in a fluid solution at room temperature¹⁴ and suggests that one-photon decomposition of two diazo groups at cryogenic temperature is not necessarily a general process, at least in glassy matrices.

E. Conformational Analysis of [2.2]Paracyclophanedicarbenes (5a, 5b, and 5c) Based on the zfs Parameters. In order to discuss the magnetic interaction between two diphenylcarbene units in the [2.2]paracyclophane skeleton in some detail, determination of the predominant conformation in each isomeric model system is worthwhile. Several conformers are possible in each dicarbene isomer with respect to rotation around the bond connecting the carbenic carbon to the cyclophane benzene ring. In the conformer which has two phenyl groups overlapped in **5a** (see conformation II in Table I), for example, the magnetic interaction could be approximately doubled by the additional interaction of the two phenyl groups. Therefore, a computational effort has been made to determine which conformer is mainly responsible for the zfs parameters observed in the ESR spectra.

It has been established that the zfs parameters of the quintet dicarbene reflect a relative orientation of the two carbene units.^{1c} A dipolar interaction tensor (D_Q) of a quintet dicarbene can be expressed by a sum of dipolar tensors (D_{T1} , D_{T2}) of the individual triplet carbene units under the conditions of weak interaction (eq 5),^{1c} where the dipolar tensors are described in the same coordinate

$$D_Q = (1/6)(D_{T1} + D_{T2}) \quad (5)$$

system. In the case of the cyclophanedicarbene, a unit dipolar

Chart I

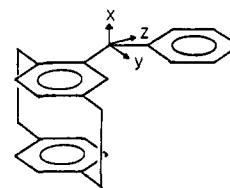


Table I. Conformations and Calculated Zfs Parameters of Quintet Pseudortho (**5a**) and Pseudopara (**5c**) Dicarbene

I (syn-anti) $\theta = 60$	II (syn-syn) $\theta = -60$	III (anti-anti) $\theta = 60$
$\phi = 0$ D = 0.0755 E = 0.0108	$\phi = 180$ D = 0.1130 E = 0.0017	$\phi = 180$ D = 0.0539 E = 0.0027
$\phi = 72$ D = 0.0624 E = 0.0194	$\phi = 108$ D = 0.1012 E = 0.0087	$\phi = 108$ D = 0.0616 E = 0.0093
IV (syn-syn) $\theta = 180$	V (anti-anti) $\theta = 180$	VI (syn-anti) $\theta = 180$
$\phi = 0$ D = 0.1240 E = 0.0054	$\phi = 0$ D = 0.1240 E = 0.0054	$\phi = 180$ D = 0.1089 E = 0.0003
$\phi = 72$ D = 0.1191 E = 0.0035	$\phi = 72$ D = 0.1191 E = 0.0035	$\phi = 108$ D = 0.1144 E = 0.0085

Table II. Conformations and Calculated Zfs Parameters of Triplet Pseudometa Dicarbene **5b**

VII (syn-syn) $\theta = 120$	VIII (syn-anti) $\theta = -120$	IX (anti-anti) $\theta = -120$
$\phi = 180$ D = 0.3390 E = 0.0051	$\phi = 0$ D = 0.2265 E = 0.0324	$\phi = 180$ D = 0.1617 E = 0.0081
$\phi = 108$ D = 0.3036 E = 0.0261	$\phi = 72$ D = 0.1872 E = 0.0582	$\phi = 108$ D = 0.1848 E = 0.0279

interaction tensor of 4-phenylmethylene[2.2]paracyclophane (**8**) can be chosen as D_{T1} and D_{T2} in order to take into account the delocalization of spins to the other part of the molecule. The principal values of its D tensor are calculated to be $D_{xx} = \pm 0.1079$, $D_{yy} = \pm 0.1401$, and $D_{zz} = \mp 0.2480$ cm⁻¹, from the zfs parameters of **8** determined by ESR spectrum in a 2-methyltetrahydrofuran glass at 14 K (vide supra).

The nonplanar structure with C_2 symmetry of a diphenylcarbene molecule has been established by ENDOR experiments: the bond angle around the carbenic carbon atom is 147.6° and the dihedral angle between the benzene rings is 72.0°.¹⁵ We assume these fundamental structural parameters to be applicable to our di-

(14) Sugawara, T.; Inada, M.; Iwamura, H. *Tetrahedron Lett.* **1984**, 25, 2375.

(15) (a) Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, 51, 3327. (b) Anderson, R. J. M.; Kohler, B. E. *Ibid.* **1976**, 65, 2451.

carbenes. For each of the pseudoortho, pseudometa, and pseudopara isomers, the [2.2]paracyclophane skeleton gives rise to ten possible conformations of which six have different mutual orientations of the two magnetic dipoles due to the two phenylmethylene units. These six conformations are amenable to analysis by eq 5. There is a set of two operations generating these conformers: syn-anti disposition defined by angle θ and conrotatory-disrotatory torsion defined by angle φ as shown in Tables I and II. In the syn conformer, the phenyl group is placed away from the ethano bridge, while in the anti conformer the phenyl groups are placed close to the bridge. A conrotatory twisting results in a parallel orientation between the rotated phenylmethylene groups, while a disrotatory twisting generates the dihedral angle of 72° or the angle of 108° between the planes containing the carbenic bonds. The bond connecting the carbenic center and the phenyl group is considered to be rotated to keep the local C_2 symmetry of the diphenylcarbene unit. The zfs values of the quintet dicarbenes were calculated for the pseudoortho and pseudopara isomers using these parameters on the basis of eq 5 and are listed in Table I. Triplet zfs parameters of T_T for the pseudometa isomer were also calculated from a similar equation (eq 6)^{1c} as in the quintet case, and the results are listed in Table II.

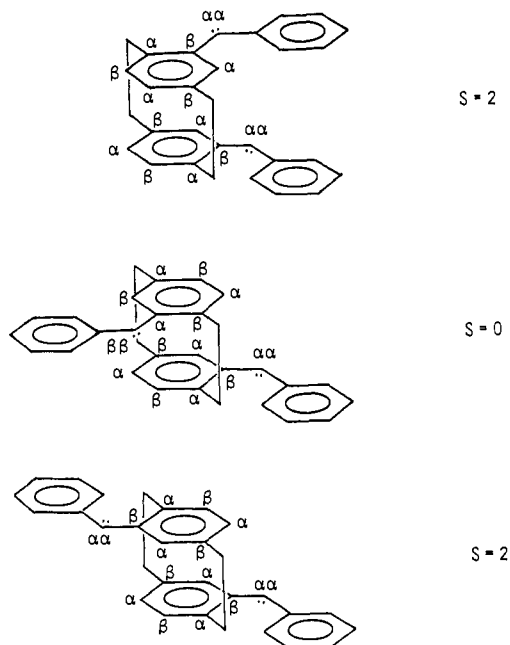
$$D_T = -(1/2)(D_{T1} + D_{T2}) \quad (6)$$

For the pseudoortho isomer, the calculated zfs values of a disrotatory twisted-I conformer fit best to the observed zfs values. In this conformation, an additional through-space magnetic interaction due to the two phenyl groups in **5a** is not significant. Unfortunately, conformers IV and V of the pseudopara isomer cannot be distinguished with the θ and φ parameters. Moreover, the two twisted conformers of them have similar zfs values to the observed one. Therefore, the conformation of the pseudopara cyclophanedicarbene corresponding to the observed ESR spectrum cannot be uniquely determined by this method, but conformer VI is excluded. For the pseudometa isomer, the disrotatory twisted-IX is the most probable conformer.

Equation 5 shows that the zfs parameters of quintet dicarbenes are affected by the relative orientation of two triplet carbenes. Therefore, it is very often the case that ESR spectra of quintet dicarbenes in glassy matrices are complicated by the presence of more than one conformer of precursor didiazo compounds in such media. The ESR spectra of cyclophanedicarbenes (**5a**, **5b**, and **5c**) are, on the contrary, well explained by a single set of zfs parameters (vide supra), suggesting that these dicarbenes should exist in a single preferred conformation in 2-methyltetrahydrofuran glassy matrices. It is not probable that the didiazo molecules (**4a**, **4b**, and **4c**), the precursors of the dicarbenes (**5a**, **5b**, and **5c**), exist in a single conformation in glassy matrices. A clue to rationalizing the observed phenomena is obtained by observation of the intense lines of the triplet biradical in the photolysate of the pseudometa and pseudopara didiazo compounds. It is usually the case that dicarbenes are stable at temperatures lower than 80 K in 2-methyltetrahydrofuran glassy matrices and that a biradical species is not detected in this temperature range. Thus it is more likely that some conformers of the dicarbenes **5b** and **5c** are kinetically unstable. Based on the structural feature of the pseudometa dicarbene **5b**, the half-filled σ -type orbital on the carbenic carbon atom is located in the proximity of the ethano bridge. Thus the chance of abstracting hydrogen from the ethano bridge in dicarbene **5b** with conformations VII or VIII might be reasonably high. If this is the case,¹⁶ only the remaining conformer IX of **5b** would be detected. On a similar basis, it is presumed that the observed conformation of the pseudopara cyclophanedicarbene is the disrotatory twisted-V form.

F. Significance of Magnetic Interaction in [2.2]Paracyclophanedicarbenes (5a**, **5b**, and **5c**).** A possibility of ferromagnetic intermolecular interaction has been pointed out by McConnell between two odd-alternant radicals in which π -spin distribution is characterized by an alternation in signs.¹⁷ The interaction is

Chart II



described as the expanded form of the Heisenberg Hamiltonian (eq 7), where s^A and s^B are the total spins on molecules A and

$$\mathcal{H}^{AB} = -2 \sum_{ij} J_{ij}^{AB} s_i^A s_j^B = -2 s^A s^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \quad (7)$$

B, ρ_i^A and ρ_j^B are the π -spin densities on the i and j atoms of molecules A and B, and J_{ij}^{AB} is the exchange integral between i and j . When the sum in eq 7 is negative, the interaction is ferromagnetic. Whereas these equations are sometimes referred to interpreting complicated intermolecular interactions found in crystals of stable organic radicals,¹⁸ the theory has never been tested for a straightforward model system.

The cyclophanedicarbenes (**5a**, **5b**, and **5c**) provide a reasonably good model for examining the intermolecular magnetic interaction¹⁹ in reference to this theory, since the spin-containing benzene rings of two diphenylcarbene molecules are stacked in parallel in the [2.2]paracyclophane skeleton.²⁰ The transannular interactions found in the cyclophanes have been considered to be good models for the intermolecular interactions of the aromatic rings stacked face-to-face since the middle 50's when a renaissance of the interest in cyclophane chemistry took place.²¹

(17) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(18) (a) Nakajima, A.; Nishiguchi, H.; Deguchi, Y. *J. Phys. Soc. Jpn.* **1968**, *24*, 1174. (b) Mukai, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 40. (c) Mukai, K.; Ishizu, K. *J. Phys. Soc. Jpn.* **1969**, *27*, 783. (d) Mukai, K.; Oishi, K.; Ishizu, K.; Azuma, N. *Chem. Phys. Lett.* **1973**, *23*, 522. (e) Azuma, N.; Yamauchi, J.; Mukai, K.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2728. (f) Azuma, N.; Ishizu, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294. (g) Mukai, K.; Nagai, H.; Ishizu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2381. (h) Awaga, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211.

(19) In the [2.2]paracyclophanedicarbene system, there is a possibility of through-bond interaction via ethano bridges in addition of the through-space interaction. However, a preliminary ESR study on isomeric [3.3]paracyclophanedicarbenes gave similar results indicating that the contribution of the through-bond interaction must not be significant. Details on these results will be reported elsewhere.

(20) Strictly speaking, the model is far from ideal. For instance, the benzene rings incorporated in the [2.2]paracyclophane structure are not planar but bent into a boat form; the inter-ring distances are therefore not even (~ 2.8 – 3.1 Å), and the two rings are deplaned by 3.2° to avoid the ethano-type eclipsing in the side chains. (a) Brown, C. J. *J. Chem. Soc.* **1953**, 3265. (b) Lonsdale, K.; Milledge, H. J.; Rao, K. V. K. *Proc. R. Soc. London, Ser. A* **1960**, *555*, 82. (c) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204.

(21) (a) Cram, D. J.; Allinger, N. L.; Steinberg, H. *J. Am. Chem. Soc.* **1954**, *76*, 6132. (b) Cram, D. J.; Bauer, R. H. *Ibid.* **1959**, *81*, 5971. (c) For transannular spin exchange interaction, see: Forrester, A. R.; Ramasseul, R. *J. Chem. Soc. B* **1971**, 1638, 1645.

(16) A products analysis is in progress.

The π -spin distribution in diphenylcarbene is known to alternate as revealed by ENDOR experiments.¹⁵ We note that the signs of the spin density product $\rho_i^A \rho_i^B$ at each most strongly interacting site between the two benzene rings are all negative in the pseudoortho and pseudopara isomers (**5a**, **5c**) and all positive in the pseudometa (**5b**). It may be adequate to consider only the interaction between the facing carbon atoms in this particular system. Then eq 7, where the interactions among all the spin-distributed carbon atoms are considered, will be simplified as in eq 8. The ferromagnetic condition in eq 8 is satisfied in **5a** and

$$\mathcal{H}^{AB} = -2J_{\text{eff}} s^A s^B \sum \rho_i^A \rho_i^B \quad (8)$$

5c and the interaction should be antiferromagnetic in **5b**. In fact, the magnetic interaction delineated in this study by ESR spectroscopy is in accord with this prediction.²²

In order to estimate the transannular magnetic interaction quantitatively, we assume that the spin distribution in the cyclophane skeleton is not significantly different from that of diphenylcarbene itself. The sum of the products of spin densities ($\sum \rho_i^A \rho_i^B$) at the most strongly interacting sites is calculated to be -0.022 , 0.040 , and -0.022 for pseudoortho, pseudometa, and pseudopara isomers, respectively. The relative energy of the spin states of weakly interacting dicarbenes is expressed as in eq 9,

$$E(S_T) = -J_{\text{eff}} [S_T(S_T + 1) - 4] \sum \rho_i^A \rho_i^B \quad (9)$$

involving the contribution of spin densities. Since the energy difference between the ground singlet and the thermally populated triplet states in the pseudometa isomer is expressed by eq 10, the

$$\Delta E_{S_T(\text{meta})} = -2J_{\text{eff}} \sum \rho_i^A \rho_i^B \quad (10)$$

effective exchange interaction (J_{eff}) can be estimated to be -3.5 kcal/mol (1220 cm^{-1}) using the experimental $\Delta E_{S_T(\text{meta})}$ value of 0.28 kcal/mol. Provided that J_{eff} is constant in the three isomers of the cyclophanedicarbenes, the energy difference between the ground quintet and the thermally populated triplet states of **5a** and **5c** can be estimated to be 0.31 kcal/mol. The value is appreciably larger than the experimental value for **5a** (0.18 kcal/mol). The discrepancy may be due to the presence of the anti-ferromagnetic interaction between the two carbenic carbon atoms which are located in a relatively short distance (ca. 4.2 \AA) in **5a**. On the other hand, the estimated value may be more realistic for **5c** in which two carbenic centers are farther apart, although the experimental value is not available for the moment.

The semiquantitative estimation of J_{eff} in the cyclophane system has revealed the presence of a strong spin correlation between the two diphenylcarbene units. The result suggests that the appropriate stacking of diphenylcarbene, its higher homologues, and other high-spin organic molecules²³ is a practical method for increasing spin multiplicity in their molecular assemblies and promises the possibility of realizing macroscopic organic ferromagnets.

Experimental Section

A. General. Proton NMR spectra were recorded on a JNM GX-400 (400 MHz) spectrometer in CDCl_3 and are reported in δ from Me_4Si . IR spectra in KBr disks were recorded on a JASCO IR-810 infrared spectrometer. UV spectra were recorded on a JASCO UVIDEC-610 ultraviolet/visible spectrophotometer. High-resolution mass spectra were recorded on a JMS-D300 mass spectrometer equipped with a JMA-2000 computer system under electron impact (EI) conditions. Melting points were determined with a Mel-Temp apparatus and were uncorrected. For preparative chromatography, a Japan Analytical Industry Co., Ltd.,

Model LC-08 gel permeation chromatography (GPC) apparatus was used with a series of JAIGEL 1H and 2H columns and flow of 3.7 mL of chloroform/min. Lobar columns (Merck, Lichroprep Si60, size B or C) were used for the adsorption mode in conjunction with a Duramat pump and an Altex UV detector.

B. ESR Measurements. ESR spectra were measured on a Varian E-112/V7800 spectrometer (X-band microwave unit, 100-kHz field modulation) equipped with an Air Products LTD-3-110 liquid helium transfer system. The diazo compound (ca. 0.5 mg) was dissolved in 2-methyltetrahydrofuran (0.5 mL). The solution was placed in a quartz sample tube (5-mm o.d.) and degassed by three freeze-thaw cycles. The sample was rapidly cooled in a precooled ESR cavity and irradiated with a high-pressure mercury lamp (500 W) at $11\text{--}15 \text{ K}$ through a cylindrical cell (50 mm in diameter and 50 mm in depth) filled with distilled water and through a quartz lens ($f = 100 \text{ mm}$, 50 mm in diameter). The microwave frequency was measured with a Takeda Riken 5201M frequency counter and the resonance magnetic field values of the signals were measured with the aid of a Varian E500 NMR gauss meter. The dependence of the signal intensities on temperatures was measured by the use of a temperature-controlling accessory (Air Products, APD-E).

C. Materials. Dibromo[2.2]paracyclophanes (1a-c). The method of Reich and Cram by bromination of [2.2]paracyclophane⁷ was employed with the following modification. The crude reaction product from 4.00 g (19.2 mmol) of the starting material was dissolved in 65 mL of hot chloroform, 40 mL of ether was added, and the mixture was allowed to stand overnight at room temperature. The crystals were collected by filtration and washed with chloroform containing ether ($3:2 \text{ v/v}$). A second crop was obtained and the combined solids were recrystallized from chloroform-ether ($3:2 \text{ v/v}$) to give 1.85 g of pseudopara-dibromo-[2.2]paracyclophane **1c** (26.3%), mp $252\text{--}254 \text{ }^\circ\text{C}$ (lit.⁷ $250\text{--}251 \text{ }^\circ\text{C}$).

From the mother liquor were obtained a mixture of para, pseudoortho, and pseudometa isomers and a further crop of pseudopara isomer by a cycle of GPC. The mixture was diluted with 50 mL of ether and warmed. Insoluble crystals (0.12 g) of a mixture of para and pseudopara dibromides were collected and washed with ether. The combined ether solutions were concentrated by evaporation and chromatographed on a Lobar column with *n*-hexane. The first fraction gave 0.58 g (8.2%) of pseudo-*m*-dibromo[2.2]paracyclophane (**1b**) after recrystallization from petroleum ether (bp $30\text{--}70 \text{ }^\circ\text{C}$), mp $120\text{--}122 \text{ }^\circ\text{C}$ (lit.⁷ $123.5\text{--}125.5 \text{ }^\circ\text{C}$). The second fraction afforded 1.42 g (20.2%) of pseudo-*o*-dibromo-[2.2]paracyclophane (**1a**), mp $199\text{--}202 \text{ }^\circ\text{C}$ (from ether) (lit.⁷ $204\text{--}207 \text{ }^\circ\text{C}$).

pseudo-*o*-Dibenzoyl[2.2]paracyclophane (2a). To a solution of **1a** (1.00 g , 2.73 mmol) in dry ether (40 mL) 34.4 mL of 1.6 M *n*-butyllithium-hexane solution (55.0 mmol) was added under nitrogen at room temperature. After the solution was stirred for 5 h at room temperature and cooled to $0 \text{ }^\circ\text{C}$, a solution of benzaldehyde (5.89 g , 55.0 mmol) in dry ether (30 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 2 h . Ice was added to the solution at $0 \text{ }^\circ\text{C}$. The ethereal layer was separated and dried over MgSO_4 . After evaporation of the solvent, the residue was dissolved in dry dichloromethane (40 mL) and mixed with powdered pyridinium chlorochromate (12.9 g , 60.0 mmol) at room temperature. The mixture was stirred for 2 h . The dark brown reaction mixture was diluted with 50 mL of ether, the solvent was decanted, and the black tar was washed with ether. The organic extracts were filtered through Florisil (200 mesh) and concentrated by evaporation of the solvent. pseudo-*o*-dibenzoyl[2.2]paracyclophane (**2a**) was separated from the residue by GPC after three recyclings and recrystallized from ethanol: colorless needles (430 mg , 37.8%); mp $142\text{--}143 \text{ }^\circ\text{C}$; IR (KBr) 1645 , 1660 cm^{-1} (sh); MS, found M^+ 416.1777 ($\text{C}_{30}\text{H}_{24}\text{O}_2$ requires M^+ 416.1776).

pseudo-*m*-Dibenzoyl[2.2]paracyclophane (2b). This compound was prepared as above using **1b** (400 mg , 1.09 mmol), 13.6 mL of a 1.6 M hexane solution of *n*-butyllithium, benzaldehyde (2.33 g , 21.8 mmol), and pyridinium chlorochromate (5.39 g , 25.0 mmol). pseudo-*m*-Dibenzoyl[2.2]paracyclophane (**2b**) was separated from the residue by GPC after three recyclings and recrystallized from methanol to give a white powder (138 mg , 30.4%); mp $146\text{--}147 \text{ }^\circ\text{C}$; IR (KBr) 1655 , 1670 cm^{-1} ; MS, found M^+ 416.1778 ($\text{C}_{30}\text{H}_{24}\text{O}_2$ requires M^+ 416.1776).

pseudo-*p*-Dibenzoyl[2.2]paracyclophane (2c). Bis(α -hydroxybenzyl)[2.2]paracyclophane was prepared as above using **1c** (160 mg , 0.437 mmol), 2.0 mL of a 1.6 M hexane solution of *n*-butyllithium, and benzaldehyde (0.37 g , 3.5 mmol). The powdered crude dialcohol (115 mg) precipitated with petroleum ether (bp $30\text{--}70 \text{ }^\circ\text{C}$) was dissolved in acetic acid (5 mL) and treated with a solution of sodium dichromate (0.9 g , 3.0 mmol) in acetic acid (15 mL). The mixture was for 4 h at room temperature; then 30 mL of water was added to precipitate 86 mg (47.3%) of pseudo-*p*-dibenzoyl[2.2]paracyclophane. An analytical sample was recrystallized from CHCl_3 to give prisms: mp $286\text{--}289 \text{ }^\circ\text{C}$; IR (KBr) 1645 , 1650 cm^{-1} (sh); MS, found M^+ 416.1793 ($\text{C}_{30}\text{H}_{24}\text{O}_2$ re-

(22) Recently Yamaguchi, et al. examined this system by means of ab initio calculations. The total exchange interaction is divided into kinetic and potential terms, and the latter is expressed according to McConnell-type formalism. The potential term is found to be predominant over the kinetic one, having positive values in pseudoortho and pseudopara isomers, and negative in pseudometa. The result agrees with McConnell's treatment: Yamaguchi, K.; Fukui, H.; Fueno, T. *Chem. Lett.* **1986**, 625.

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quires $M^+ 416.1776$).

4-Benzoyl[2.2]paracyclophane (6). Benzoyl chloride (0.680 g, 4.84 mmol) and 0.58 g of aluminum chloride (4.34 mmol) were dissolved in 4.5 mL of 1,1,2,2-tetrachloroethane at room temperature. To the solution cooled to -30°C , powdered [2.2]paracyclophane (0.500 g, 2.40 mmol) was added in one portion. The mixture was stirred at this temperature for 30 min and warmed to 0°C over a period of 1 h. The solution was again cooled to -40°C , 1.5 mL of 1N HCl was added, and the mixture was warmed slowly to 0°C . Dichloromethane (50 mL) and water (20 mL) were added and the organic layer was separated and washed twice with water. After dichloromethane was evaporated 1,1,2,2-tetrachloroethane and unreacted benzoyl chloride were removed in vacuo (0.1 mm) on a water bath at 70°C . The residue solidified and was recrystallized from ethanol to give colorless needles of 4-benzoyl[2.2]paracyclophane (717 mg, 96%): mp $126-128^\circ\text{C}$; IR (KBr) 1650 cm^{-1} ; MS, found $M^+ 312.1516$ ($\text{C}_{23}\text{H}_{20}\text{O}$ requires $M^+ 312.1517$); $^1\text{H NMR}$ (CDCl_3) δ 2.82-3.38 (m, 8 H), 6.34 (d, $J = 8.1\text{ Hz}$, 1 H), 6.53-6.58 (m, 3 H), 6.67-6.72 (m, 2 H), 6.75 (d, $J = 7.6\text{ Hz}$, 1 H), 7.40 (t, $J = 8.1\text{ Hz}$, 2 H), 7.53 (t, $J = 8.1\text{ Hz}$, 1 H), 7.71 (d, $J = 8.1\text{ Hz}$, 2 H).

Isomeric Cyclophane Dihydrazones (3a-c). Anhydrous hydrazine (2.0 mL) was added to the mixture of each dibenzoylcyclophane isomer (30 mg, 67.5 μmol), hydrazine monohydrochloride (50 mg, 1.37 mmol), and 3.0 mL of dry dimethyl sulfoxide. The mixture was heated at 110°C for 8 h. After hydrazine and dimethyl sulfoxide were removed in vacuo at 80°C , the residue was washed with water and dried in vacuo to give the corresponding dihydrazone in quantitative yield. For **3a**: mp $94-97^\circ\text{C}$; MS, found $M^+ 444.2319$ ($\text{C}_{30}\text{H}_{28}\text{N}_4$ requires $M^+ 444.2314$). For **3b**: mp $93-105^\circ\text{C}$; MS, found $M^+ 444.2319$ ($\text{C}_{30}\text{H}_{28}\text{N}_4$ requires $M^+ 444.2314$). For **3c**: mp $314-315^\circ\text{C}$; MS, found $M^+ 444.2317$ ($\text{C}_{30}\text{H}_{28}\text{N}_4$ requires $M^+ 444.2314$).

4-Benzoyl[2.2]paracyclophane hydrazone was obtained quantitatively as a gummy solid from ketone **6** using the above method: MS, found $M^+ 326.1786$ ($\text{C}_{23}\text{H}_{22}\text{N}_2$ requires $M^+ 326.1783$).

pseudo-o-Bis(α -diazobenzyl)[2.2]paracyclophane (4a). To a solution of pseudoortho dihydrazone **3a** (30 mg, 67.5 μmol) in 15 mL of benzene, 1.0 g (4.6 mmol) of mercuric oxide (yellow) and a few drops of a freshly prepared saturated solution of potassium hydroxide in absolute ethyl alcohol were added. After the mixture was stirred for 2 h at room temperature in the dark, the red solution was filtered through Celite and the residue washed with benzene. The combined benzene solutions were concentrated under reduced pressure in the cold. The residual solid was dissolved in 0.2 mL of benzene and placed on a disposable Pasteur pipet (146 mm, 5 mm i.d.) containing 1.6 g of alumina. The column was then rapidly washed with *n*-hexane-benzene (3:1) under moderate pressure.

The first eluted red solution was concentrated under reduced pressure in the cold to give 14 mg of pink powder of didiazo **4a** (47% yield). An analytical sample was recrystallized from *n*-hexane: mp $106-109^\circ\text{C}$; IR (KBr) 2035 cm^{-1} ; MS, found $M^+ - \text{N}_2 412.1952$ ($\text{C}_{30}\text{H}_{24}\text{N}_2$ requires $M^+ - \text{N}_2 412.1939$); UV-vis (2MTHF) $\lambda_{\text{max}} 521\text{ nm}$ ($\log \epsilon 2.44$).

pseudo-m-Bis(α -diazobenzyl)[2.2]paracyclophane (4b). Didiazo **4b** was prepared and purified as above. A red powder (12 mg, 40%) was obtained. An analytical sample was recrystallized from ether-petroleum ether (bp $30-70^\circ\text{C}$): mp $136-138^\circ\text{C}$ (dec); IR (KBr) 2035 cm^{-1} ; MS, found $M^+ - \text{N}_2 412.1950$ ($\text{C}_{30}\text{H}_{24}\text{N}_2$ requires $M^+ - \text{N}_2 412.1939$); UV-vis (2MTHF) $\lambda_{\text{max}} 528\text{ nm}$ ($\log \epsilon 2.39$).

pseudo-p-Bis(α -diazobenzyl)[2.2]paracyclophane (4c). Pseudopara dihydrazone **3c** (100 mg, 0.225 mmol) was dissolved in 50 mL of dichloromethane, and 4.0 g of mercuric oxide and a few drops of a freshly prepared saturated solution of potassium hydroxide in absolute alcohol were added to the solution. The mixture was stirred for 3 h at room temperature in the dark. After the solvent was removed by evaporation in the cold, the residual red solid was chromatographed on alumina deactivated water and eluted with dichloromethane to give 58 mg (59%) of scarlet crystals of didiazo **4c**. An analytical sample was recrystallized from CHCl_3 -ether: mp $133-135^\circ\text{C}$ (dec); IR (KBr) 2035 cm^{-1} ; MS, found $M^+ - \text{N}_2 412.1914$ ($\text{C}_{30}\text{H}_{24}\text{N}_2$ requires $M^+ - \text{N}_2 412.1939$); UV-vis (2MTHF) $\lambda_{\text{max}} 521\text{ nm}$ ($\log \epsilon 2.38$).

4-(α -Diazobenzyl)[2.2]paracyclophane (7). To a solution of 4-benzoyl[2.2]paracyclophane hydrazone (200 mg, 0.613 mmol) in 40 mL of benzene, 5.0 g of mercuric oxide and a few drops of a freshly prepared saturated solution of potassium hydroxide in absolute alcohol were added. After the red solution was worked up, the residue was chromatographed as above to give 155 mg (78% yield) of red solid of diazo **7**. An analytical sample was recrystallized from petroleum ether (bp $30-70^\circ\text{C}$): mp $103-105^\circ\text{C}$; IR (KBr) 2040 cm^{-1} ; MS, found $M^+ 324.1608$ ($\text{C}_{23}\text{H}_{20}\text{N}_2$ requires $M^+ 324.1626$); UV-vis (2MTHF) $\lambda_{\text{max}} 525\text{ nm}$ ($\log \epsilon 1.98$); $^1\text{H NMR}$ (CDCl_3) δ 2.73-3.13 (m, 8 H), 6.33 (s, 1 H), 6.37-6.41 (m, 1 H), 6.52-6.64 (m, 5 H), 7.08 (t, $J = 7.6\text{ Hz}$, 1 H), 7.11 (d, $J = 7.6\text{ Hz}$, 2 H), 7.32 (t, $J = 7.6\text{ Hz}$, 2 H).

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Carbon-13 Chemical Shielding Tensors in Polycyclic Aromatic Compounds. 1. Single-Crystal Study of Pyrene

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Abstract: The carbon-13 chemical shielding tensors measured in single-crystal pyrene are reported. The two internal bridgehead carbons have principal values of 197, 191, and -18 ppm and the four peripheral bridgehead carbons 213, 187, and -7 ppm with respect to liquid Me_4Si . The high field component of every tensor is determined to be perpendicular to the molecular plane, as in benzene. The protonated carbons have principal values similar to benzene, with the low-field components lying approximately along the C-H bonds. The rotation of the principal axes away from the C-H bond direction is measured experimentally and interpreted by quantum chemical calculations. By use of a MNDO wave function and the Pople model of chemical shielding, the magnitudes of the experimental in-plane components are reproduced very well and the calculated orientations of the principal axes are consistent with the experimental data. The results reported here demonstrate that the measurement of ^{13}C shielding tensors in polycyclic aromatic compounds can be used as a measurement of the aromatic character of bonds adjacent to ^{13}C nuclei.

With the advent of high-resolution ^{13}C NMR in solids, the chemical shielding tensors of carbon nuclei have been studied in a few chemical environments.¹⁻³ Since the anisotropy in shifts

results from nonspherical distribution of electrons surrounding the nucleus, chemical shift tensors give new information about electronic structure and present a detailed three-dimensional view of important features of chemical bonding. The measured tensor

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