

ELECTRONIC STRUCTURES OF AROMATIC HYDROCARBONS WITH HIGH SPIN MULTIPLICITIES IN THE ELECTRONIC GROUND STATE

Koichi Itoh

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

Abstract - It has been established experimentally that there are alternant hydrocarbons (AH) with high spin multiplicities in the electronic ground state, the highest multiplicity known up to date being septet. Such electronic structures are rationalized by utilizing the degeneracy of non-bonding pi molecular orbitals (NBMO) predictable from the theory of Longuet-Higgins in conjunction with the non-bonding orbitals of divalent carbon atoms which are perpendicular to p_π orbitals and are nearly degenerate with NBMO. The degeneracy of NBMO is determined by the topological nature of molecules which permits the ground state with high spin multiplicities according to Hund's rule in spite of their low molecular symmetries. The nature of AH having high spin multiplicities in the ground state reported so far is understood in this manner. It was found, however, that for some AH the high spin multiplet states are unexpectedly not the ground states although they lie very close to the singlet ground state. The difference between these two types of AH with high spin multiplicities is associated with the fact that the spin distribution of NBMO is alternant in the former AH, but not in the latter. To the latter AH the weak interaction model was found to apply in which a molecule is divided into two units weakly interacting with each other.

INTRODUCTION

For a long time it was an open question whether there were organic molecules with spin multiplicities higher than triplet in the electronic ground state. This did not seem possible because the molecular symmetry of organic compounds is generally low in contrast to the case of ions of the transition-group elements in crystals or in ligands of metal complexes: From the group theoretical point of view, the number of the degeneracy of occupied molecular orbitals of organic compounds cannot be larger than two, which seems to violate Hund's rule.

In 1967, however, the author (1) and independently Wasserman et al. (2) found that the electronic ground state of the aromatic hydrocarbon, *m*-phenylene-bis-phenylmethylene, is the quintet state ($S=2$). This unusual molecule has the structure of type I in Fig. 1 with the phenyl group (C_6H_5) substituted for R.

Thereafter, a series of similar hydrocarbons with high spin multiplicities have been reported; *m*-phenylene-bis-methylene (I with $R=H$) in the quintet ground state (2), benzene-1,3,5-tris-phenylmethylene (II with $R=C_6H_5$) in the

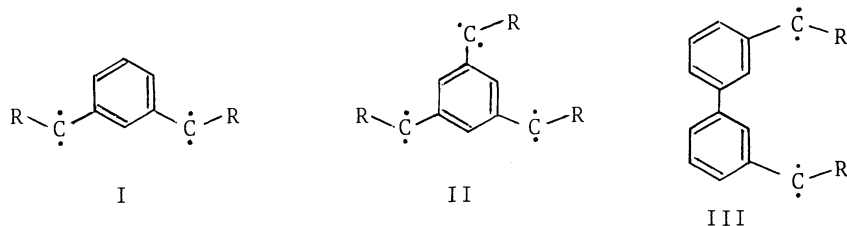


Fig. 1. Structures of aromatic hydrocarbons with high spin multiplicities.

septet ground state (3), and 1,3,5-benzenetriyl[di(*p*-biphenyl)methyl] (II with $\dot{C}(\text{biphenyl})_2$ substituted for $\dot{C}-R$) in the quartet ground state (4). The first two as well as *m*-phenylene-bis-phenylmethylene have divalent carbon atoms each having two unpaired spins. The investigations (1-3) by electron spin resonance (ESR) have shown that half of the parallel spins belong to the pi orbitals, while the other half is mainly localized in each of the non-bonding orbitals "n" of the divalent carbon atoms perpendicular to the pi orbitals. On the other hand, the last-mentioned hydrocarbon has parallel spins all of which belong to the pi electron system. The two high spin multiplet nitrenes iso-electronic to I and II were also reported (2,7). We are interested particularly in the hydrocarbons because they are of fundamental importance in quantum chemistry and can be dealt with using least ambiguous parameters in the calculation of the electronic structures.

GUIDING PRINCIPLE

The unusual spin multiplicity arises from the particular properties of zero-energy molecular orbitals or non-bonding molecular orbitals (NBMO's) in the pi system of conjugated alternant hydrocarbons which were already pointed out in 1950 by Longuet-Higgins (5), but the importance of the implication in molecular magnetism seems to have been overlooked until the discovery of the hydrocarbons described above. The rule of Longuet-Higgins states:

- (1) An alternant hydrocarbon has at least $N - 2T$ NBMO's where N denotes the number of carbon atoms in the conjugated system and T the maximum number of double bonds occurring in any resonance structure.
- (2) In the ground state there will be just one electron in each NBMO, and if there are two or more such electrons, their spins will be parallel.

For example, with the three hypothetical molecules, *o*-, *m*-, and *p*- $C_6H_4(\dot{C}H_2)_2$, the number of NBMO's is 2 for meta compound, while zero for para or ortho compounds. This is a clear demonstration that this orbital degeneracy of NBMO is determined by the sequence of carbon atoms forming the conjugated system. In this sense we may call this the topological symmetry and this degeneracy the topological degeneracy. This is an accidental degeneracy in view of the group theory but has some mathematical meaning within the simple LCAO-MO approximation. It is to be noted that this degeneracy does not depend on the assumption of equal or related resonance integrals for the various bonds, i.e., this rule is little affected by changes of molecular configurations. The above-mentioned rule for the simplest case of $N - 2T = 1$ is justified by the LCAO-SCF-MO calculation (7).

This theory has been found to apply remarkably well to the before-mentioned molecules. But our recent investigation has shown that it is too simple to account for all the experiments. The limitation of the theory will be discussed later.

Meanwhile, the electronic structure of methylene, $\dot{C}H_2$ is well known. Its stable spin multiplicity depends on the bond angle θ . In the gaseous phase the triplet state $^3\Sigma_g^-$ (or 3B_1) is stable for nearly linear methylene ($\theta \sim 180^\circ$), while the singlet state 1A_1 is stable for bent methylene ($\theta = 103^\circ$) (8). According to the theoretical calculation by Dixon using the intra-atomic correlation correction, the two spins occupying the pi orbital ($1b_1$) and the non-bonding orbital n ($3a_1$) are parallel for θ larger than ca 140° because the orbital energies are nearly degenerate (9). Recent *ab initio* calculations indicate that the ground state is the triplet (3B_1) with the bond angle of $132 \sim 138^\circ$ (10, 11). On the other hand, the ESR measurement of methylene- d_2 in xenon matrix at 4.2 K gave $\theta = 137.7^\circ$ from the ^{13}C hyperfine structure (12) and 136° from the E/D value (13). These results indicate that the energy difference between the n and pi orbitals of the divalent carbon atom is small enough to align the two spins parallel. Therefore, if the topological degeneracy of NBMO's and the near degeneracy of n orbitals of divalent carbon atoms are taken into account, the number of parallel spins may be doubled provided that the bond angle is favorable to parallel spins.

ELECTRONIC STRUCTURES AND ESR SPECTRA OF ALTERNANT HYDROCARBONS WITH THE QUINTET AND SEPTET GROUND STATES

Figure 2 shows the electronic structure of the quintet molecule detected first in a series of similar molecules. R of I in Fig. 1 is replaced by the phenyl group in order to stabilize the molecule. Here the number of NBMO's is two and there are four nearly degenerate orbitals since the energy difference between the n orbital and NBMO may be small. Thus four spins are

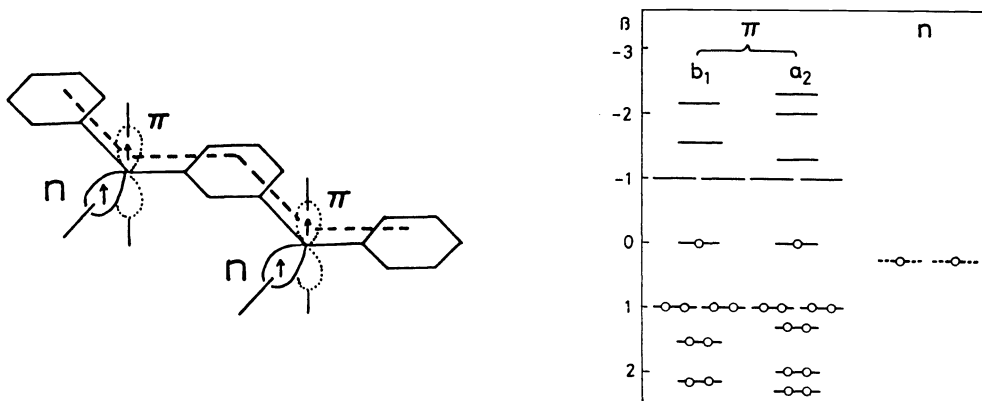


Fig. 2. Electronic structure of *m*-phenylene-bis-phenylmethylene

expected to be parallel according to Hund's rule. Two of them are localized in the *n* orbitals of the divalent carbon atoms, and the other two are delocalized over the whole molecule and exchange coupled strongly on the divalent carbon atoms, all the spins interacting in a common molecular space. It is interesting that this is similar to the *s*-*d* interaction of ferromagnetic metals.

The observed ESR spectra can be completely reproduced by the spin Hamiltonian

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

with $S=2$, $g=2.0038$, $D=0.07137 \text{ cm}^{-1}$, and $E=0.01963 \text{ cm}^{-1}$ (1). The terms of the type S_i^4 , and $S_i^2 \cdot S_j^2$ ($i, j=X, Y, Z$) were found to be negligibly small in this case. This is reasonable because the spin orbit interaction in hydrocarbons is much smaller than that in transition-metal ions for which these terms have some contribution. The observed parameters were in fair agreement with the theoretical prediction by Higuchi (14) for this electronic structure. In addition, temperature dependence of the ESR spectra confirmed this quintet state to be the ground state.

On the other hand, the topological isomer, *p*-phenylene-bis-phenylmethylene, showed an ESR signal indicating the triplet state (15). However, our recent investigation (16) revealed that this state is the thermally excited one located 202 cm^{-1} above the singlet ground state. The spin Hamiltonian is also given by Eq. (1) with $S=1$, $g=2.0025$, $D=+0.05005 \text{ cm}^{-1}$ and $E=+0.00159 \text{ cm}^{-1}$. These parameters are reasonable for a triplet state in which two localized spins occupy the two different *n* orbitals. This is called the triplet state of the *nn* type (17). Thus this molecule has no singly occupied pi NBMO in contrast to the meta isomer. The meta and para isomers that have been detected experimentally constitute a good example of the theory of Longuet-Higgins described in the preceding chapter.

As an extension of this work, we have synthesized and detected benzene-1,3,5-tris-phenylmethylene (3) which has the structure II with $R=C_6H_5$ in Fig. 1. The ground state of this molecule is the septet which is the highest spin multiplicity amongst not only hydrocarbons but also a vast number of organic molecules known to date, together with the septet nitrene, *sym*- $C_6(\dot{C}N)_3$ (6). It will be seen how well the spin Hamiltonian for the septet state reproduces the experimental results for this molecule which is dissolved in a single crystal of 1,3,5-tribenzoylbenzene.

Figure 3 shows the ESR spectrum recorded in the dispersion mode at liquid helium temperature after photolysis of the diazo precursor. The six lines A^\pm , B^\pm , and C^\pm correspond to the six allowed transitions of the septet state. The other lines are due to the byproducts of the photolysis. The apparent deviation from the theoretical transition probabilities (3:5:6:6:5:3) is due to the Boltzmann distribution, from which the absolute sign of D was determined. The angular dependence of the six lines is shown in Fig. 4 as a function of the magnetic field. Here the solid line represents the calculated values using the spin Hamiltonian given by Eq. (1) with $S=3$, $g=2.0038$, $D=+0.104158 \text{ cm}^{-1}$, and $E=+0.01026 \text{ cm}^{-1}$ (the group theory allows terms up to the sixth

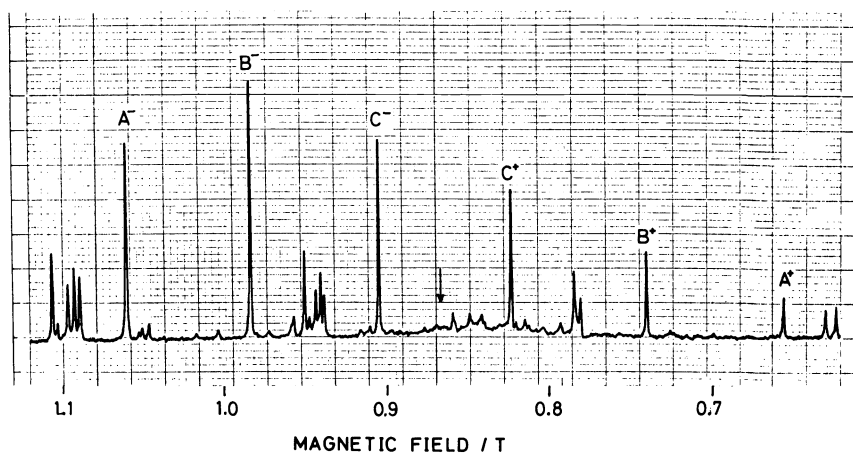


Fig. 3. ESR spectrum of benzene-1,3,5-tris-phenylmethylene recorded in the dispersion mode at 4.2 K. The magnetic field is parallel to the Z principal axis. The arrow indicates the position for $g=2.0040$.

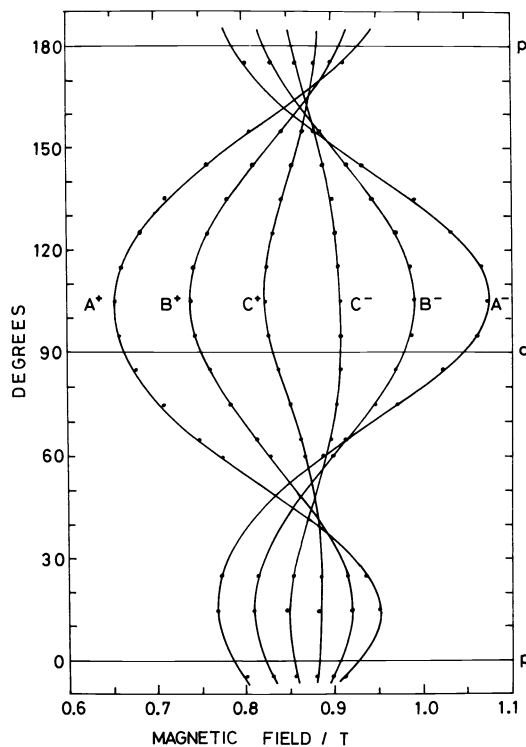


Fig. 4. Angular dependence of the resonance fields of the six lines for rotation of the magnetic field applied in the pq plane. The points represent the observed values, and solid lines the calculated ones.

power in \vec{S} which were found, however, negligibly small similarly to the case of the quintet hydrocarbon). The remarkable agreement proves the existence of the septet state. In addition, the measurement of temperature dependence confirmed this to be the ground state.

The molecular configurations of the quintet and septet hydrocarbons have been found unsymmetrical from the ESR experiments. The most probable configurations are shown in Fig. 5. Higuchi estimated the bond angles of the divalent carbon

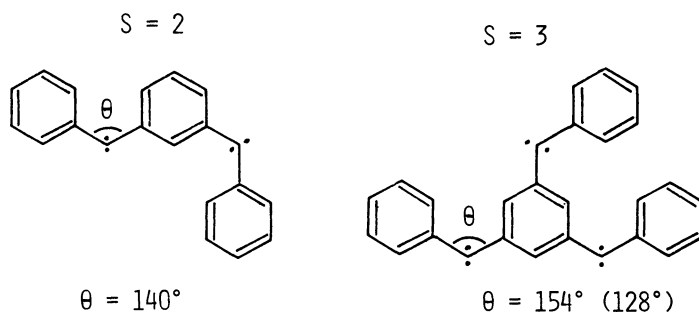


Fig. 5. Most probable configurations of the quintet and septet hydrocarbons.

atoms which are consistent with the observed fine structure parameters D and E . They are about 140° (18) and 154° (19) for the quintet and septet hydrocarbons, respectively, which are to be compared with the values for the 1B_1 state of methylene (10-13).

It may be interesting at this stage to classify the molecules with high spin multiplicities according to their magnitude of the spin-spin interaction. Most of the molecules mentioned before belong to the $n\pi$ type, and their $(2S-1)|D|$ value ranges from 0.2 to 0.3 cm^{-1} . In contrast to these, the $\pi\pi$ type molecule, 1,3,5-benzenetriyl [di(*p*-biphenyl)methyl], has a very small value of 0.00824 cm^{-1} (4). Yang's biradical ($S=1$) having oxygen atoms in the pi system also belongs to this category, and has a value of 0.0032 cm^{-1} (20). These small values are due to the particular property of the spin distribution of the NBMO where the spin density appears on alternating carbon atoms, so that the $\pi\pi$ interaction between the spins occupying the NBMO's is of long-range type and small. This is the same for the $n\pi$ type molecules as far as the $\pi\pi$ interaction is concerned. The large values for the $n\pi$ type molecules are, however, essentially due to the one-center $n\pi$ type interaction on the divalent carbon atoms. On the other hand, in the case of the nn type molecule, *p*-phenylene-bis-phenylmethylene, the interaction (0.05005 cm^{-1}) is simply a long-range one between the two localized spins.

It seems natural to extend this theory to polymers which are composed of these unusual molecules as units. The possible electronic structure of these polymers was discussed by Mataga previously (21).

NEW TYPE OF ALTERNANT HYDROCARBON

The electronic structure of the alternant hydrocarbon having the structure of type III in Fig. 1 is interesting because the spins on the divalent carbon atoms couple through a biphenyl ring in contrast to the case treated in the preceding chapter where spins couple through a benzene ring. According to the above-mentioned rule and experimental results, molecules of type III are also expected to have the quintet ground state. Recently, we have investigated the ESR of biphenyl-3,3'-bis-phenylmethylene (BBPM) with the structure shown in Fig. 6a (22). This alternant hydrocarbon was formed at 4.2 K or 20 K by the photolysis of its diazo precursor, 3,3'-bis(α -diazobenzyl)biphenyl, oriented in single crystals of benzophenone. By the analysis of angular dependence and

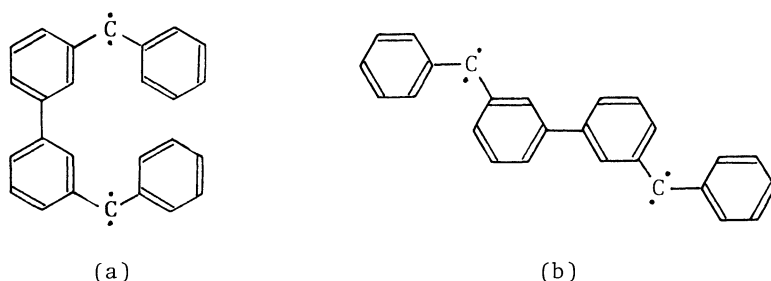
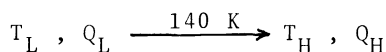


Fig. 6. Chemical structure (a) and molecular configuration (b) of biphenyl-3,3'-bis-phenylmethylene.

temperature dependence of the ESR spectra, we confirmed that the lowest energy levels are nearly degenerate singlet, triplet, and quintet states in the order of increasing energy in spite of the above-mentioned simple expectation. In addition, there are two isomers of BBPM with different configurations in the host crystal. The isomer designated L is stable at low temperature and changes irreversibly into another isomer H at 140 K. Therefore, the irreversible spectral change corresponding to



was observed, where T and Q stand for the triplet and quintet states, respectively.

As before the spin Hamiltonian given by Eq. (1) fully accounts for the angular dependence of the ESR spectra of all the four paramagnetic species. The parameters experimentally determined are listed in Table 1. This table indicates

TABLE 1. Fine structure parameters and g values for T_L , Q_L , T_H , and Q_H of biphenyl-3,3'-bis-phenylmethylene. The principal axes of the fine structure tensors for T_L and Q_L and also for T_H and Q_H coincide with each other.

$S = 1$	$S = 2$
$T_L: D = -0.29583 \pm 0.00010 \text{ cm}^{-1}$ $E = 0.06032 \pm 0.00010 \text{ cm}^{-1}$ $g = 2.0040$	$Q_L: D = 0.10349 \pm 0.00009 \text{ cm}^{-1}$ $E = -0.01457 \pm 0.00009 \text{ cm}^{-1}$ $g = 2.0040$
$T_H: D = +0.23895 \text{ cm}^{-1}$ $E = +0.06452 \text{ cm}^{-1}$ $g = 2.0040$	$Q_H: D = +0.08329 \pm 0.00008 \text{ cm}^{-1}$ $E = +0.02114 \pm 0.00008 \text{ cm}^{-1}$ $g = 2.0040$

the three characteristic features of the fine structure tensors. Firstly, the principal axes of the fine structure tensors for $T_{L(H)}$ and $Q_{L(H)}$ coincide with each other. Secondly, the D and E values of $T_{L(H)}$ are almost three times as large as those of $Q_{L(H)}$. Thirdly, the absolute signs of the D and E values are opposite between T_L and Q_L (unfortunately the absolute sign for T_H and Q_H could not be determined because of the small population at low temperature). In addition, the g values of the triplet and quintet states are almost isotropic and equal.

These features were found to be nicely accounted for by the following weak interaction model. BBPM may be regarded as composed of two diphenylmethylene units connected with each other at the meta position of each benzene ring (see Fig. 6a). The spin densities at the bridge carbon atoms connecting these units are zero for the spins occupying the NBMO's. Therefore, concerning the four spins occupying the two NBMO's and the two n orbitals, their interactions between the two diphenylmethylene units may be considered to be much smaller than the $\pi\pi$ interaction within each unit in good approximation. Since the ground state of diphenylmethylene is the triplet state(23), the composite system is expected to have one quintet, one triplet, and one singlet state as low-lying energy levels.

The spin Hamiltonian for a system consisting of weakly interacting units a and b may be written as

$$\mathcal{H} = \mathcal{H}^a(1) + \mathcal{H}^b(2) + \mathcal{H}^{ab}(1,2) \quad (2)$$

where the Hamiltonians for each unit are

$$\mathcal{H}^a(1) = \beta \vec{H} \cdot \vec{g}^a \cdot \vec{S}_1 + \vec{S}_1 \cdot \vec{D}^a \cdot \vec{S}_1 \quad (3)$$

$$\mathcal{H}^b(2) = \beta \vec{H} \cdot \vec{g}^b \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{D}^b \cdot \vec{S}_2 \quad (4)$$

and the Hamiltonian for the interaction is

$$\mathcal{H}^{ab}(1,2) = J\vec{s}_1 \cdot \vec{s}_2 + \vec{s}_1 \cdot \underline{D}^{ab} \cdot \vec{s}_2 \quad (5)$$

For the present model $S_1 = S_2 = 1$, and in good approximation $g^a = g^b = g$ (isotropic). If the exchange energy is large compared with the other spin energies, \mathcal{H} can be rewritten with the total spin $\vec{s} = \vec{s}_1 + \vec{s}_2$ as

$$\mathcal{H} = E_S + g\beta\hbar\vec{s} + \vec{s} \cdot \underline{D}_S \cdot \vec{s} \quad (6)$$

where

$$E_S = (J/2)[S(S+1) - 4] \quad (7)$$

$$\underline{D}_S = [(3S^2 + 3S - 11)/2(2S - 1)(2S + 3)](\underline{D}^a + \underline{D}^b) + [(S^2 + S + 8)/2(2S - 1)(2S + 3)]\underline{D}^{ab} \quad (8)$$

using the transformation properties of angular momentum and tensor operators (24). E_S is J , $-J$, and $-2J$ for $S = 2$, 1 , and 0 , respectively, and \underline{D}_S for $S = 2$, and 1 is given by

$$\underline{D}_2 = (1/6)(\underline{D}^a + \underline{D}^b) + (1/3)\underline{D}^{ab} \quad (9)$$

$$\underline{D}_1 = (-1/2)(\underline{D}^a + \underline{D}^b) + \underline{D}^{ab} \quad (10)$$

In this system \underline{D}^{ab} may be much smaller than \underline{D}^a and \underline{D}^b which are very large because of the large one-center $n\pi$ interaction, so that we finally obtain $\underline{D}_1 = -3\underline{D}_2$. All the above-mentioned characteristic features of the fine structure tensors are interpreted by this relation.

Consequently, if J values determined independently from the triplet and quintet signals are equal and positive, all the above-mentioned experimental results are explained by the weak interaction model. In order to confirm the mechanism the signal intensity for the H isomer times temperature is plotted in Fig. 7.

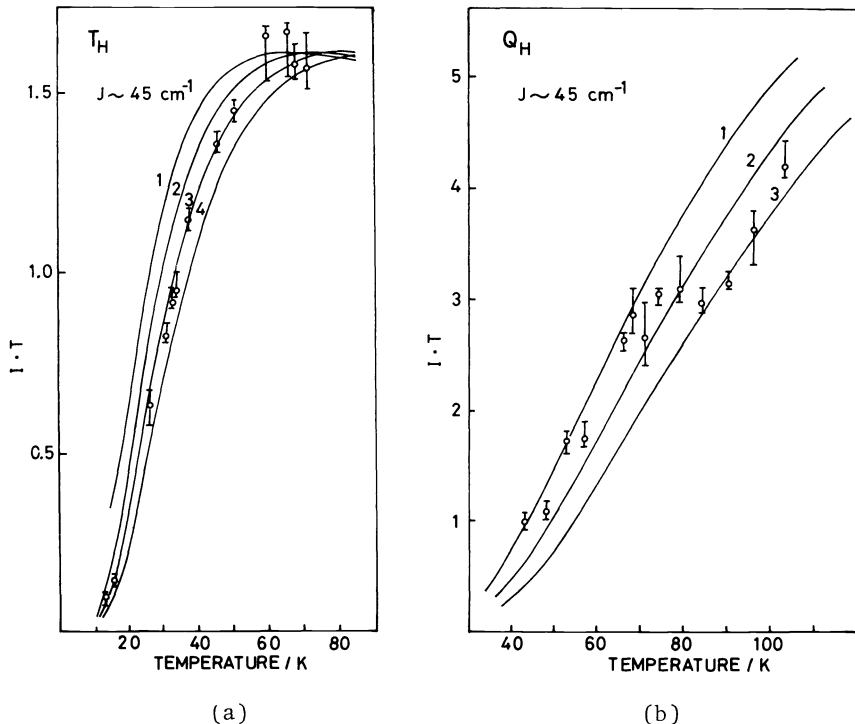


Fig. 7. Plots of the signal intensity for T_H and Q_H times temperature as a function of temperature. The circles and the vertical lines represent the experimental values and their uncertainties, respectively. The solid lines represent the theoretical values calculated from the above-mentioned model for the following J values: (a) 1(35 cm⁻¹), 2(40 cm⁻¹), 3(45 cm⁻¹), 4(50 cm⁻¹); (b) 1(40 cm⁻¹), 2(45 cm⁻¹), 3(50 cm⁻¹).

as a function of temperature and compared with the theoretical values calculated from the model. The plots for both T_H and Q_H give the same J value of $45 \pm 5 \text{ cm}^{-1}$ independently. Similarly, the J value for the L isomer was determined to be $+20 \text{ cm}^{-1}$.

As we have seen, every phase of the present experiment supports the weak interaction model. Therefore, it may be concluded that the four spins in this molecule couple strongly with ferromagnetic J , and that each pair of spins further couples weakly with antiferromagnetic J . As a result, the simple prediction by theory of Longuet-Higgins does not apply to this molecule.

The reason for the value of J being positive may be accounted for as follows. The spin distribution of NBMO for BBPM in the simple LCAO-MO approximation is such that there is no spin density on the bridge carbon atoms. However, since the direct long-range exchange interactions between carbon atoms other than the bridge carbons are very small, the observed weak exchange interaction is probably due to the spin densities induced on the bridge carbon atoms. If this is the case, the weak antiferromagnetic coupling seems reasonable from the nature of the exchange interaction between. Figure 8 shows the behavior of J between two p orbitals on adjacent carbon atoms

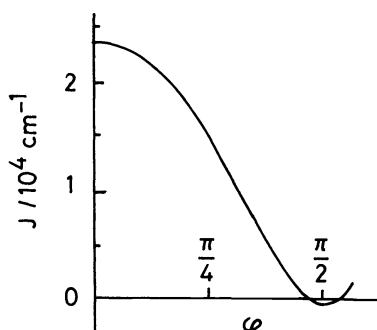


Fig. 8. J value vs. angle of bond twist φ between two p orbitals on adjacent carbon atoms. The value for $\varphi=0$ is estimated from the singlet-triplet transition energy of ethylene and that for $\varphi=\pi/2$ is from Kotani's table (about -200 cm^{-1}).

when the angle of bond twist is varied. Here the positive sign corresponds to the antiferromagnetic coupling from the definition of the exchange energy in the spin Hamiltonian given by Eq. (5). The J value for $\varphi=0$ may be approximated by the singlet-triplet transition energy of ethylene. As φ increases, J decreases and changes its sign at an angle very close to $\pi/2$. For $\varphi=\pi/2$ J reduces simply to the negative of the exchange integral, $-(pp'|e^2/r|p'p)$, which is very small between the p orbitals perpendicular with each other (about -200 cm^{-1} was estimated from Kotani's table). Negative J values would be obtained only if two benzene planes of the biphenyl group are very nearly perpendicular with each other. If we consider the size of BBPM molecule, such a configuration may be impossible not only in the host crystal but also in other matrices. Moreover, a recent *ab initio* CI calculation by Iwata (25) suggests that J is always positive if electron correlations are taken into account. The positive J value is, therefore, reasonable for other type-III molecules as well as BBPM. On the other hand, the calculation of the spin-spin interaction suggests that BBPM takes an unsymmetrical and stretched configuration as shown in Fig. 6b.

Our experimental results on the alternant hydrocarbons which are expected to have high spin multiplicities from their topological symmetry may be summarized as follows. The alternant hydrocarbons of the type (A) and (B) in Fig. 9 have parallel spins in the ground state. For these molecules the starred carbon atom coincides with the active carbon atom where "active" means the non-zero spin density on that carbon atom. On the other hand, for the type (C) molecule the set of the starred carbon atoms and that of the active carbon atoms do not coincide with each other. In other words, in this category of alternant hydrocarbons the spin distribution is not alternant, and there are always two adjacent carbon atoms with zero spin densities in NBMO's. The molecule may, therefore, be regarded as separated at the boundary concerning the interaction between the spins occupying the NBMO's. For this group of

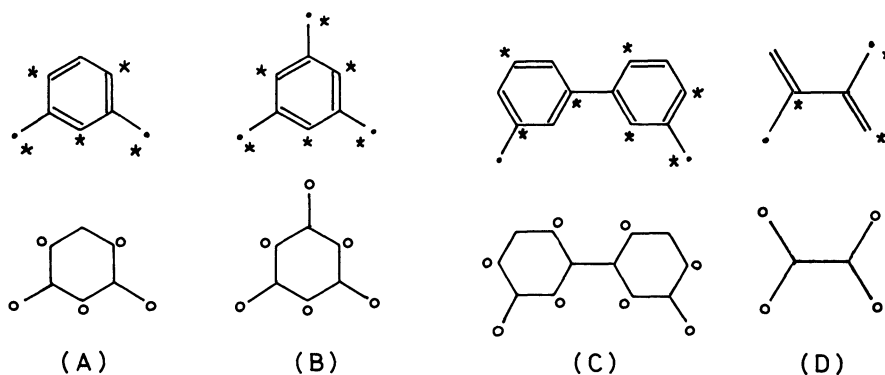


Fig. 9. Diagram showing the starred (*) and active (o) carbon atoms of the alternant hydrocarbons which are expected to have high spin multiplicities. Hydrogen atoms are neglected in this diagram.

molecules the weak interaction model is better suited and their ground states are expected to be singlet. The still hypothetical molecule, tetramethylene ethylene, shown as (D) in Fig. 9 and originally suggested by Longuet-Higgins, may also belong to this group.

Acknowledgements - The author wishes to acknowledge to Prof. J. Higuchi of Yokohama National University for his stimulating discussion. He is also indebted to Dr. T. Takui and to the several doctoral candidates who have done much of the experimental work described herein.

REFERENCES

1. K. Itoh, *Chem. Phys. Letters* **1**, 235 (1967).
2. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, *J. Am. Chem. Soc.* **89**, 5076 (1967).
3. T. Takui and K. Itoh, *Chem. Phys. Letters* **19**, 120 (1973).
4. J. Brickman and G. Kothe, *J. Chem. Phys.* **59**, 2807 (1973).
5. H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950).
6. E. Wasserman, K. Schueller and W. A. Yager, *Chem. Phys. Letters* **2**, 259 (1968).
7. H. C. Longuet-Higgins, A. J. Pople, *Proc. Phys. Soc. (London)* **A58**, 591 (1955).
8. G. Herzberg, *Proc. Roy. Soc. (London)* **A262**, 291 (1961).
9. R. N. Dixon, *Mol. Phys.* **8**, 201 (1964).
10. J. F. Harrison and L. C. Allen, *J. Am. Chem. Soc.* **91**, 807 (1969); J. F. Harrison and R. C. Liedtke, *J. Chem. Phys.* **58**, 3106 (1973).
11. C. F. Bender and H. F. Schaefer III, *J. Am. Chem. Soc.* **92**, 4984 (1970).
12. R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.* **54**, 3223 (1971).
13. E. Wasserman, V. J. Kuck, R. S. Hutton and W. A. Yager, *J. Am. Chem. Soc.* **92**, 7491 (1970).
14. J. Higuchi, *J. Chem. Phys.* **38**, 1237 (1963).
15. A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager and E. Wasserman, *J. Am. Chem. Soc.* **85**, 2526 (1963).
16. M. Asano, T. Takui and K. Itoh, to be published.
17. J. Higuchi, *J. Chem. Phys.* **39**, 1847 (1963).
18. J. Higuchi, *Bull. Chem. Soc. Japan* **43**, 3773 (1970).
19. J. Higuchi, private communication.
20. R. Kreilick, *J. Chem. Phys.* **43**, 308 (1965); K. Mukai, T. Mishina and K. Ishizu, *J. Chem. Phys.* **66**, 1680 (1977).
21. N. Mataga, *Theoret. Chim. Acta (Berl.)* **10**, 372 (1968).
22. Details will be published elsewhere.
23. E. Wasserman, A. M. Trozzolo, W. A. Yager, R. W. Murray, *J. Chem. Phys.* **40**, 2408 (1964); R. W. Brandon, G. L. Closs, C. E. Davoust, A. Hutchison Jr. B. E. Kohler, R. Silbey, *J. Chem. Phys.* **43**, 2006 (1965).
24. B. R. Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw-Hill (1963).
25. S. Iwata and K. F. Freed, to be published.