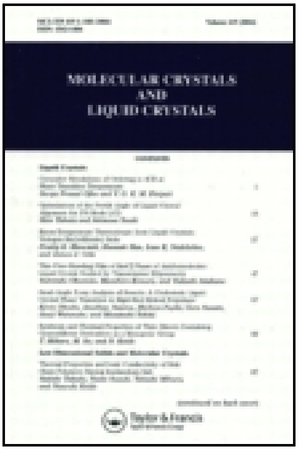

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Ab Initio Calculations of Effective Exchange Integrals. Possibilities of Superparamagnetic, Mictomagnetic and Amorphous Feromagnetic States for Aggregates of Aromatic Free Radicals and Polymer Radicals

Kizashi Yamaguchi [a] , Hideo Namimoto [a] & Takayuki Fueno [a]
[a] Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560, Japan

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AB INITIO CALCULATIONS OF EFFECTIVE EXCHANGE INTEGRALS. POSSIBILITIES OF SUPERPARAMAGNETIC, MICTOMAGNETIC AND AMORPHOUS FEROMAGNETIC STATES FOR AGGREGATES OF AROMATIC FREE RADICALS AND POLYMER RADICALS

KIZASHI YAMAGUCHI, HIDEO NAMIMOTO and TAKAYUKI FUENO
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract The intermolecular effective exchange integrals (J_{ab}) for clusters of aromatic free radicals were calculated by the ab initio spin-projected unrestricted Hartree-Fock (UHF) Møller-Plesset (APUMP) method. It was found that the sign and magnitude of the calculated J_{ab}-values vary with the stacking modes of the species. Implications of the ab initio results were discussed in relation to possibilities of spin glass, superparamagnetic, mictomagnetic and amorphous ferromagnetic states for aggregates of aromatic free radicals and polymer radicals.

INTRODUCTION

Theoretical calculations of effective exchange interactions between open-shell molecules provide a useful guide for molecular designing of organic ferromagnets. Previously, the approximately projected unrestricted Hartree-Fock (APUHF) method was applied to non- and semi-empirical calculations of effective exchange integrals (J_{ab}) for dimer and clusters of free radical species.[1-3] It was shown that ferromagnetic intermolecular effective exchange interactions are feasible between free radicals with capto-dative stabilization[4] if the stacking modes of the species are controlled so as to guarantee the intermolecular spin polarization (ISP) rule, which is expressed by the spin density product (SDP) term[1] first introduced by McConnell.[5]

As a continuation of previous work,[1-3] APUHF and approximately projected UHF Møller-Plesset (APUMP) calculations will be performed for clusters of aromatic free radicals in order to elucidate effects of stacking modes, local conformations and other geometrical factors on the effective exchange interactions of these species. Implications of the ab initio results will be also discussed in relation to possibilities of spin glass, superparamagnetic, mictomagnetic and amorphous feromagnetic states for aggregates of aromatic free radicals and one- and two-dimensional polymer radicals.

AB INITIO CALCULATIONS OF THE EFFECTIVE EXCHANGE INTEGRALS

Basis Set Dependency and Correlation Correction

It is experimentally known that the magnetic interactions between free radicals are usually described on the basis of the isotropic Heisenberg (HB) Hamiltonian instead of the Ising model[6-10]

$$\mathbf{H}\,(\mathrm{HB}) = -2 \sum J_{ab}\, \mathbf{S}_a \cdot \mathbf{S}_b \qquad (1)$$

where $\mathbf{S}_a$ is the spin at molecule a. The effective exchange integral (J_{ab}) for the HB model can be calculated by the ab initio n-th order APUMP (APUMPn) method as described previously[1-3,11-13]

$$J_{ab} = \frac{[\,{}^{LS}E(\mathrm{UMPn}) - {}^{HS}E(\mathrm{UMPn})\,]}{[\,{}^{HS}\langle\hat{S}^2\rangle(\mathrm{UMPn}) - {}^{LS}\langle\hat{S}^2\rangle(\mathrm{UMPn})\,]} \qquad (2)$$

where ${}^{X}E(\mathrm{UMPn})$ and ${}^{X}\langle\hat{S}^2\rangle(\mathrm{UMPn})$ denote, respectively, the total energy and total spin angular momentum calculated for the lowest (X=LS) or the highest (HS) spin state by the UHF MP (UMP) method. The second term in the denominator in Eq. (2) is a spin projection term, which is related to the isotropic nature of the HB model.[10-13]

First, the APUMPn (n=1-4) calculations were carried out for the face-to-face dimer of methyl radicals in order to elucidate the basis set dependency and correlation correction for the J_{ab}-values. Figure 1 illustrates the staggered geometry assumed for the dimer. Table I summarizes the calculated results. From Table I, the following notices are available:

(1) The J_{ab}-values for the dimer of methyl radicals are negative in sign by all the APUMPn calculations. Therefore the magnetic interactions between methyl radicals are antiferromagnetic in nature.

(2) The magnitude of the J_{ab}-value becomes about twice at the intermolecular distance (R=3.0 Å) if the 4-31G and more flexible basis sets are utilized instead of the STO-3G basis set. The magnitude becomes about three and half times that of the STO-3G basis set at R=3.4 Å by such an extension of the basis set.

(3) The magnitude of the J_{ab}-value by APUMP1 (=APUHF) method increases by about 23 % after the dynamical correlation correction by the APUMPn

TABLE I Effective exchange integrals (J_{ab}) calculated for dimer of methyl radicals by the ab initio APUMP method

Method		J_{ab}(cm^{-1})			
	R(Å)	STO-3G	4-31G	6-31G*	6-311G**
APUMP1	3.0	-767	-1585	-1625	-1656
	3.4	-158	-551	-578	-595
APUMP2	3.0	-878	-1923	-1954	-2004
	3.4	-182	-680	-705	-728
APUMP3	3.0	-877	-1902	-1916	-1957
	3.4	-181	-673	-692	-712
APUMP4	3.0	-885	-1973	-1990	-2042
	3.4	-182	-694	-714	-739
APUMPI	3.0	-883	-1988	-2004	-2057
	3.4	-182	-699	-718	-744

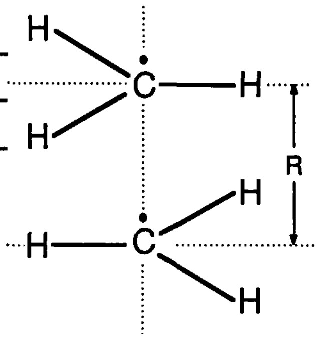


FIGURE 1. The anti conformation for the dimer of methyl radical.

method ($n \geq 2$) by use of the extensive basis sets. However, it is not so improved by the MP correction if the STO-3G basis set is utilized.

The results (1)-(3) indicate that the APUMP2 4-31G procedure is desirable for semiquantitative calculations of the effective exchange integrals of radical clusters. However, the APUHF (i.e., mean-field approximation) STO-3G method is useful for qualitative calculations of the J_{ab}-values for relatively larger systems.

The J_{ab}-value for the linear pentamer of methyl radical was calculated to be -915 cm^{-1} at R=3.0 Å by the APUHF STO-3G method. Judging from the calculated J_{ab}-values, the nearest neighbour approximation is reliable enough for linear-like clusters of free radicals.[13]

Dependency of the J_{ab}-Values on the Stacking Modes and Distances

The effective exchange interactions between organic radicals are usually dependent on the stacking modes.[1-3,10-13] In order to examine the conformational effect, the APUHF calculations were carried out for dimers of benzyl radicals at the geminal (Θ=0°), ortho (Θ=60°), meta (Θ =120°) and para (Θ=180°) conformations as shown in Figure 2. Table II summarizes the J_{ab}-values calculated for these conformers by the

TABLE II Effective exchange integlals (J_{ab})[a] calculated for dimer of benzyl radicals by the ab initio APUHF method

R(Å)	Gemi	Ortho	Meta	Para
3.4	-363	220	-225	218
3.5	-233	141	-143	140
3.6	-148	90	-91	89
3.7	-93	57	-57	56
3.8	-58	35	-35	35
3.9	-36	22	-22	21
4.0	-22	13	-13	13
4.1	-13	8	-8	8

a) cm^{-1}

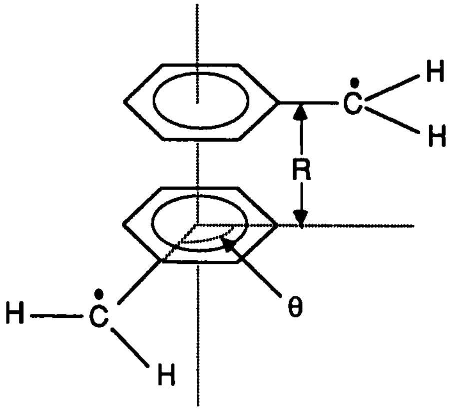


FIGURE 2. The geometry for the dimer of benzyl radical.

APUHF STO-3G method. It is seen from Table II that the signs of the J_{ab}-values are positive for the ortho and para conformers, whereas they are negative for geminal and meta conformers. However, the sign for each conformer does not change with variation of the intermolecular distance (R). The J_{ab}-value for the para conformer was calculated to be 412 cm^{-1} at R=3.4 Å using the 4-31G basis set, being about twice as compared with that of the STO-3G basis set. This may indicate that the conclusions (1)-(3) are applicable to dimers of relatively larger organic radicals. For example, the J_{ab}-value for the para conformer of benzyl radical dimer by the APUMP4 6-311G** method is estimated to be about 517 cm^{-1} at R=3.4 Å.

Figure 3 illustrates the variation of the J_{ab}-value for the para and geminal conformers with the intermolecular distance (R). From Figure 3, the J_{ab}-value decreases with R in an exponential manner.

$$J_{ab} = t \exp (p - qR) \qquad (3)$$

where the parameter sets (t, p, q) are (-3.66, 20.7, -4.73) for the geminal and (2.32, 20.7, -4.75) for the para conformer, respectively. The situations were the same in other conformers. This indicates that the orbital overlap determines the magnitude of the J_{ab}-values as discussed previously[10-13], although the J_{ab}-values are expressed by the

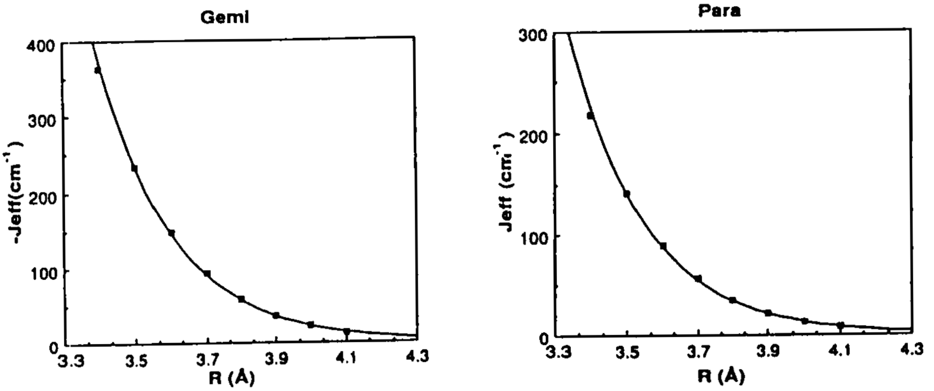


FIGURE 3. Variations of the J_{ab}-values for geminal and para conformers.

spin density product (SDP) terms in an extended McConnell model.[1-3]

The variations of the signs of the J_{ab}-values can be explained by the extended McConnell model proposed previously[1-3]

$$J_{ab} = J_{ab}(OO) + J_{ab}(SDP) \qquad (4)$$

where the former and latter denote the orbital overlap (OO) and spin-density-product (SDP) terms, respectively. For example, the OO-term between the singly occupied (SO) and singly unoccupied (SU) orbitals are not zero for the geminal and meta conformers, whereas it diminishes at the para and ortho conformations. Figures 4A and 4B ilustrate the OO-terms for the meta and para-conformers, respectively. From the figure, the OO-term favors the singlet state for the geminal and meta

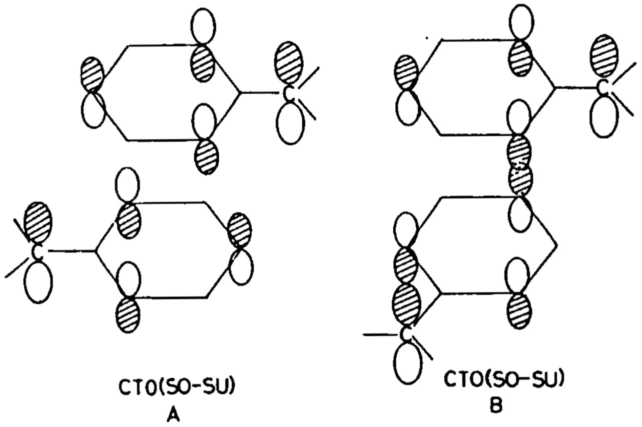


FIGURE 4. The orbital-overlap (OO) terms for para (A) and meta (B) conformers of benzyl radical.

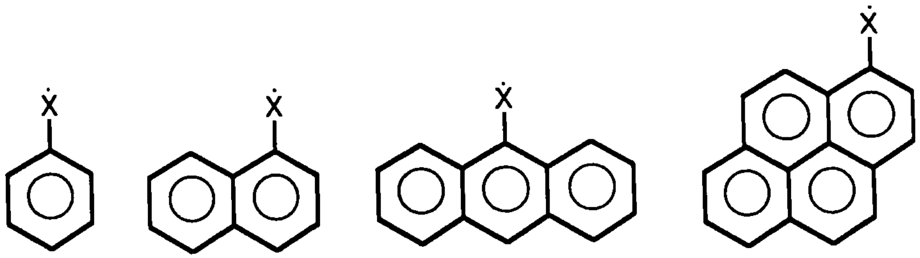
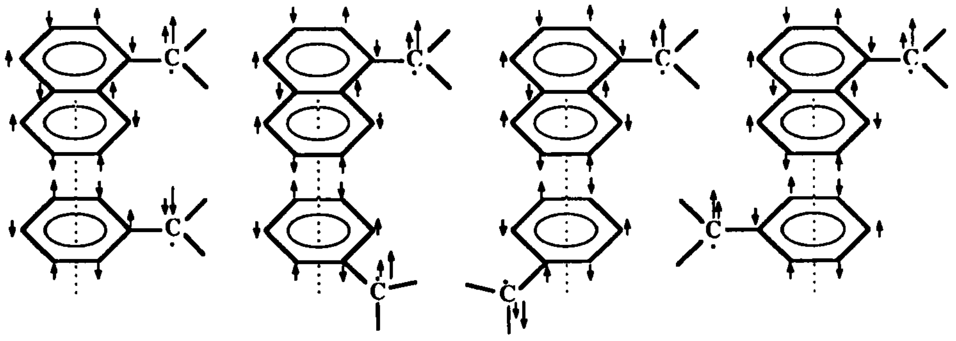


FIGURE 5. Aromatic free radicals with spin polarized π-networks. These are used as components of organic ferromagnets (see also Figs. 6 and 8).

conformers. The SDP term, on the other hand, plays a dominant role to determine the sign of the J_{ab}-value for the ortho and para dimers (see also Fig. 6).

Remote Intermolecular Interactions between Aromatic Radicals

The ab initio results in Table II indicate the important role of the spin polarization of π-networks for ferromagnetic intermolecular interaction. Figure 5 illustrates some of aromatic free radicals with large spin polarizations of π-networks. Anthracene and pyrene derivatives involve the naphthalene skeleton. Therefore the intermolecular effective exchange interactions between benzyl and naphthyl methyl radicals was examined as an model for remote interactions of aromatic free radicals via benzene rings as illustrated in Figure 6. The APUHF STO-3G calculations were performed for the pair of these radicals in



A (-211) B (206) C (-210) D (206)

FIGURE 6. Remote intermolecular interaction between naphthyl methyl radical and benzyl radical.

pseudo geminal (A), ortho (B), meta (C) and para (D) conformations, under the assumption of the intermolecular distance R=3.4 Å. The calculated J_{ab}-values are given in Figure 6. The signs vary alternately (-, +, - and +), depending on the conformations. The situation was the same in the case of benzyl radical dimer. The ab initio calculations provides the following conclusions:

(4) the remote (or indirect) effective exchange interaction via benzene rings is strong enough for intermolecular spin alignments of aromatic free radicals.

(5) the stacking modes are of particular importance for ferromagnetic intermolecular interaction between aromatic free radicals.

Further Investigations of Stacking Modes of Aromatic Free Radicals

Figures 5 and 6 clearly show the importance of stacking modes of benzyl radicals and aromatic free radicals for ferromagnetic inter-

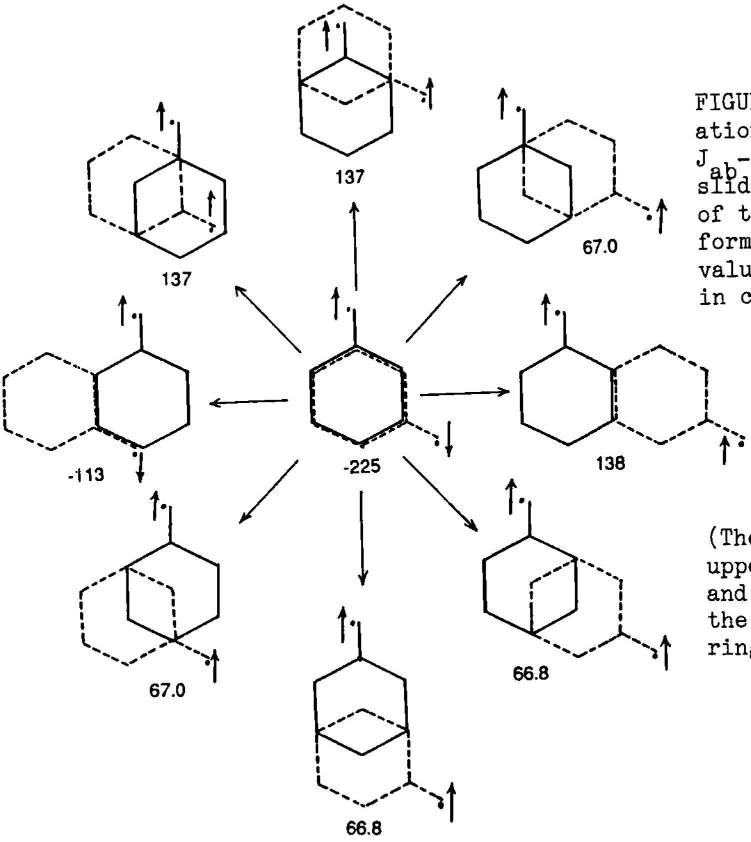


FIGURE 7. Variations of the J_{ab}-values with slid deformations of the meta conformer. The J_{ab}-values are given in cm^{-1}.

(The solid line for upper benzene ring and dotted line for the lower benzene ring.)

molecular effective exchange interaction. However, the face-to-face stackings of neutral aromatic free radicals are hardly realized because of the steric repulsions. Therefore, further investigations of stereochemical factors are necessary. Figure 7 shows variations of the J_{ab}-values with slip deformations of the meta conformer. From Figure 7, the negative J_{ab}-value for the meta conformer was converted into the positive values in the case of several stacking modes. The ab initio results clearly indicate that the three dimensional structures are very important for introduction of ferromagnetic long-range orders in the case of aggregates of benzyl radicals. This in turn suggests the necessity of stereochemical control for synthesis of organic ferromagnets.

DISCUSSION AND CONCLUDING REMARKS

Possible Magnetic States of Organic Radicals

Ab initio results indicate that the pure organic ferromagnets are feasible if the stacking modes of aromatic free radicals are well-controlled. However, the organic synthesis of such a crystalline organic ferromagnet is not so easy at the present stage. On the other hand, several magnetically ordered states are conceivable for aromatic radical solids with amorphous structures. Figure 8 illustrates schematically possible magnetic states concluded from the ab initio results: namely paramagnetic (PM), spin glass (SG), superparamagnetic (SPM), mictomagnetic (MMG) and amorphous ferromagnetic(AMFM) states. An AMFM state is here defined as the ferromagnetically ordered state of spins

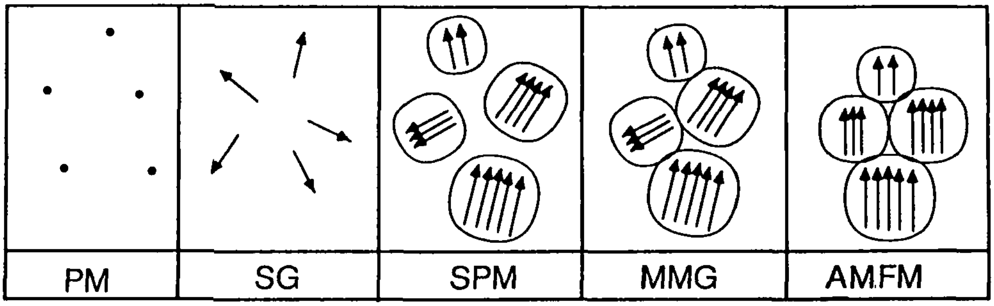


FIGURE 8. Possible magnetic orders for amorphous solids of organic radicals and polymer radicals.

realized in spatially random aggregates of organic radicals. The amorphous ferromagnetism is conceivable theoretically since the sign of the calculated effective exchange integrals (J_{ab}) is positive in sign for clusters with appropriate conformations as illustrated in Figure 7. However, it is well known that three-dimensional magnetic interactions are necessary for the ferromagnetism, i.e., long-range order of spins.

Several methods such as crystallization, use of polymer networks, external magnetic field, paramagnetic impurities, etc. are possible for introduction of the three-dimensional ferromagnetic interactions between high-spin clusters as illustrated in Figure 9. If the magnetic interaction between the clusters are negligible, the superparamagnetic (SPM) state might be formed as illustrated in Figure 8. The giant spins of the clusters are paramagnetic in this SPM state, whereas they are anisotropic in the case of the mictomagnetic (MMG) state. The spin glass and mictomagnetic states[14] are also conceivable for amorphous solids of organic radicals at a low temperature because the signs of the J_{ab}-values are variable, depending on the stacking modes of the species.

Judging from the ab initio results, the site models developed in the solid state physics[15-17] seem applicable to the magnetic states in Fig. 8. The quantum Monte Carlo simulations are necessary for elucidation of macroscopic properties Q such as magnetic susceptibility expected for aggregates of aromatic free radicals

$$Q = \langle\langle \hat{Q} \rangle\rangle_c \qquad (5)$$

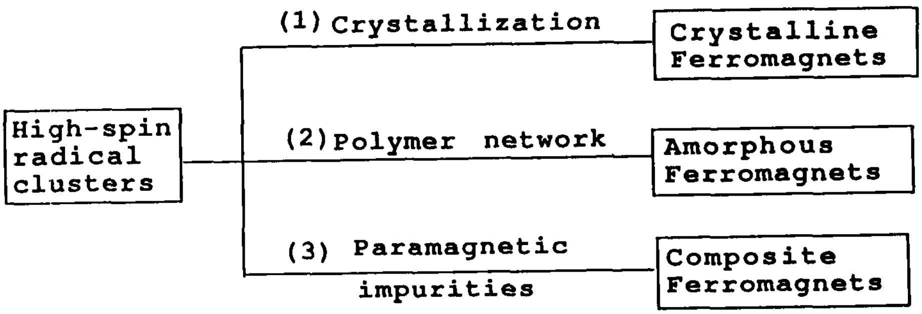


FIGURE 9. Introduction of the three-dimensional magnetic interactions for clusters of organic radicals.

where $<< >>_c$ denote the configuration average[17] of the expectation value $<\hat{Q}>$ of the observable $\hat{Q}$.

Relations to Experiments

Recently, several experiments have indicated (A) that the ferromagnetic intermolecular interaction[8] is operative for clusters of galvinoxyl radicals, (B) that the superparamagnetic state[9] is feasible in the case of substituted diphenyl carbenes and (C) that the superparamagnetic or amorphous ferromagnetic state[18] is feasible in the case of COPNA resin, which has the two-dimensional π-network. The present ab initio results are compatible with these findings A-C.

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APPENDICES

Details in computational methods

Derivations of Eq. 2 for dimers were carried out in refs. 1, 2, 10 and 11, and the extension to trimer - pentamer was given in refs. 3 and 13. Since the unrestricted Hartree-Fock (UHF) and UHF Møller-Plesset (UMP) solutions for the low spin (LS) state involve the so-called spin-contamination terms (i.e., intermediate spin (IS) and the highest spin (HS) components), the spin projection is necessary to obtain the spin-symmetry adapted wavefunction for the LS state. In the present scheme, the spin-projection was performed by the use of the UHF (or UMP) solution for the HS state on the assumption of Heisenberg-type (Eq. 1) energy splittings for the intermediate spin states. As shown in ref. 10, this procedure provides the approximately projected (AP) UMP scheme:

APUMP = approximately projected (AP) unrestricted Hartree-Fock (UHF) Møller-Plesset (MP).

The term ,APUMP, is equivalent to the SCMP (spin-corrected MP) used for monocentric diradicals in ref. 12. The utility and reliability of the APUMP method were discussed in refs. 1,2, 10-13, etc. (recent papers in Chem. Phys. Lett. 157, 211; 158, 95 (1989)). The details numerical data in this paper will be given later.

Geometries used for computations

Several assumptions were made for molecular geometries without full geometry optimizations.

(1) The conformations of methyl radical in Fig. 1 and aromatic radicals in Figs. 2, 5, 6 and 7 are planer.

(2) The C-C and C-H distances are 1.40 and 1.09 Å, respectively, for all the radicals examined in Figs. 1, 2, 5, 6 and 7.

(3) All the CCC, CCH and HCH angles are 120°.

(4) The interplane distances between aromatic rings are 3.4 Å in Figs. 6 and 7.

The full geometry optimizations of radicals and use of more flexible basis sets for larger molecules are necessary for further refinements of the J_{ab}-values determined by the APUMP method. These are future problems.