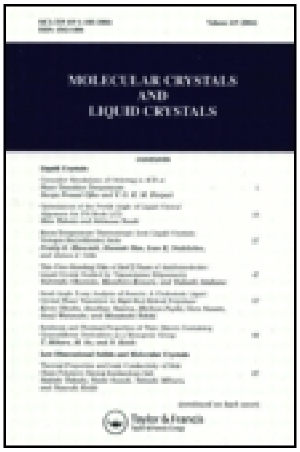


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Casscf Calculations for Neutral and Anion Radical States of Several π-Conjugated Bis-Methylene Systems

Daisuke Yamaki [a] , Sadamu Takeda [a b] , Wasuke Mori [a c] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki Aichi, 444, Japan

[c] Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-12, Japan

Version of record first published: 04 Oct 2006

To cite this article: Daisuke Yamaki, Sadamu Takeda, Wasuke Mori & Kizashi Yamaguchi (1997): Casscf Calculations for Neutral and Anion Radical States of Several π-Conjugated Bis-Methylene Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 475-486

To link to this article: http://dx.doi.org/10.1080/10587259708044603

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 475–486
Reprints available directly from the publisher
Photocopying permitted by license only

CASSCF CALCULATIONS FOR NEUTRAL AND ANION RADICAL STATES OF SEVERAL π-CONJUGATED BIS-METHYLENE SYSTEMS

DAISUKE YAMAKI[1], SADAMU TAKEDA[1,2], WASUKE MORI[1,3] AND KIZASHI YAMAGUCHI[1]
[1]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan; [2]Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan; [3]Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan

Abstract The CASSCF calculations were carried out for the neutral and anionic states of several model systems including two carbenes linked together through π-conjugation to investigate variations of the ground spin states induced by π- or σ- electron doping. The full geometry optimizations of these anion radical species were performed by the CASSCF energy gradient technique. It was found that the optimized geometries for the bis-methylene moieties largely depend on the electron configurations, particularly the number of σ-electrons, and the ground spin states for the anion radicals are also sensitive to the symmetry of the SOMO.

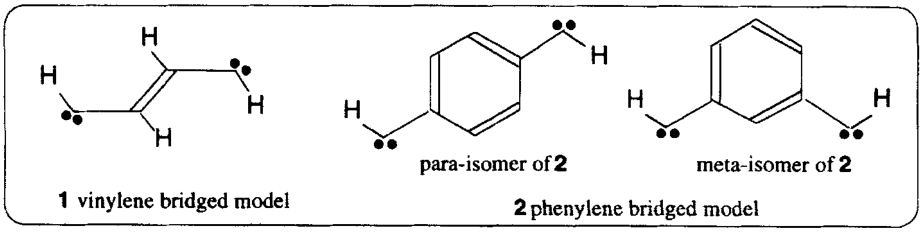
INTRODUCTION

New phenomena[1-8] arising from the interplay between localized spins and itinerant electrons have received continuous interest in relation to spin-mediated high T_c superconductivity,[9] magnetic conductivity, Kondo effect,[10-12] etc. About ten years ago, the hole or electron doping into polycarbene systems were investigated theoretically concerning with molecular design of organic magnetic metals, high T_c organic superconductors, so on.[1-9] It was shown that the conversions from the low-spin (LS) to the high-spin (HS) (vice versa) are theoretically feasible because of the spin delocalization and/or double exchange mechanisms. Recently,[13-16] we carried out *ab initio* CASSCF calculations for the neutral and π-hole doped states of several bis-methylene model systems. The ground state of these species is the high spin (HS) state because of double exchange, under the assumption that the triplet-carbene type electronic configurations are maintained upon the hole doping. However, it was demonstrated by the recent experiments that some electron doped bis-methylenes are low spin in the ground states.[17-19] This contradiction urged us to re-perform the CASSCF[20,21] calculations for the typical bis-methylene molecules with and without the doped σ- or π- electron. The full geometry optimizations of the anion radical states were carried out to elucidate variations of the ground spin states with the geometry changes, particularly for the carbene groups.

AB INITIO CALCULATIONS

Neutral Systems

We considered three model systems, in which two carbenes are linked together by three types of π-conjugation, i.e., vinylene bridged model (**1**), p-phenylene bridged model (para-**2**) and m-phenylene bridged model (meta-**2**), as illustrated in Figure 1. In order to investigate the variations of the ground spin state induced by π- or σ- electron doping, *ab-initio* CASSCF calculations were carried out for the neutral and ionic states of the respective model system. There are four single occupied molecular orbitals (SOMO) for all the models of neutral bis-carbenes, since each carbene has two SOMOs. These four SOMOs should be taken into account at least for the active space of the CASSCF calculations of **1** and **2**. Two kinds of active spaces for the CASSCF calculation were used for the neutral molecules of both models **1** and **2** as show in Figure 2. One {4 MOs, 4 electrons} of the active spaces consists of only the four SOMOs. The other, i.e., {6, 6} for **1** or {10, 10} for **2**, involves four SOMOs and all the π-MOs. The CASSCF method with minimal active space, namely CASSCF{4,4}, takes account of SOMO-SOMO interactions. The CASSCF method with extended active space includes both the spin polarization (SP) and electron correlation correction (EC) in addition to the SOMO-SOMO interactions. The total energies calculated by these methods are listed in Table I and the ground state of each model is indicated by under line. The ground state of **1** and para-**2** is low spin (LS), whereas that of meta-**2** is high spin (HS). The singlet state of singlet-carbene dimer is the most unstable. Table I indicates that SOMO-SOMO interactions are dominant for determination of the singlet-quintet energy gap in **1** and para-**2**, while the SP and EC contributions are important in meta-**2**.



para-isomer of **2**

meta-isomer of **2**

1 vinylene bridged model

2 phenylene bridged model

FIGURE 1 The model systems under investigation

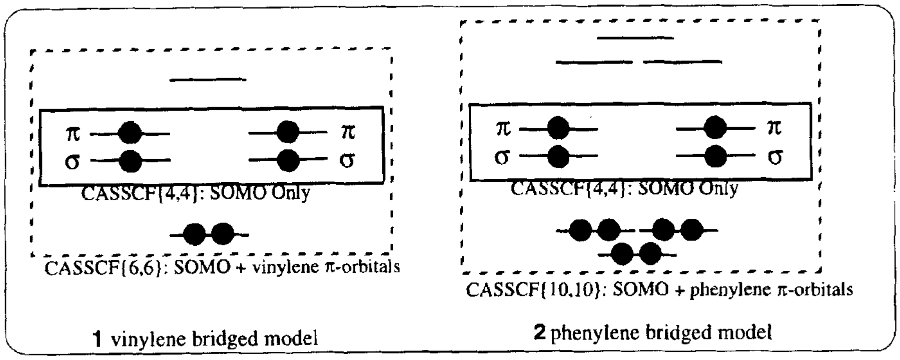


FIGURE 2 Active spaces for neutral model systems

TABLE I the energies (a.u.) for neutral state of the model systems

model	CASSCF[a)]	singlet[b)]	quintet	triplet	singlet	ground state
1	{4,4}	-153.29794	-153.35916	-153.41599	**-153.42415**	LS
	{6,6}	-153.35756	-153.39233	-153.46414	**-153.47087**	LS
para- **2**	{4,4}	-305.76445	-305.81557	-305.82672	**-305.83229**	LS
	{10,10}	-305.84063	-305.89742	-305.93516	**-305.93816**	LS
meta- **2**	{4,4}	-305.77052	**-305.81916**	-305.81726	-305.81647	HS
	{10,10}	-305.84063	**-305.91086**		-305.89742	HS

a) 4-31G basis set is used

b) The states of singlet-carbene dimer

Anion Systems

(A) Classification of Anion States

The symmetry of the electronic state depends on the symmetry of the singly occupied molecular orbitals (SOMO). We assumed the C_{2h} symmetry for the geometries of **1** and para- isomer of **2** and the C_{2v} symmetry for that of meta-isomer of **2**. The electronic states of **1** and para-**2** belong to the symmetry species of C_{2h}, i.e., A_g, A_u, B_g and B_u, while those for meta-**2** are classified into the A_1, A_2, B_1 and B_2 states of the C_{2v} symmetry. We summarize the group-theoretical notations of all the four types of possible electronic states in Table II. For example, the notation of "σ^*-type" means that an odd number of electrons occupy the σ-orbital-space (σ, σ^*) and σ^*-orbital is singly occupied in the reference electronic configuration. Hereafter, we call the doublet state of σ^*-type as D(σ^*). The reference electronic configuration of each type is illustrated in Figure 3.

TABLE II The symmetries of SOMO and the electronic states

	radical-MO			doublet			quartet		
model	**1**	**2**		**1**	**2**		**1**	**2**	
		para	meta		para	meta		para	meta
σ-type	A_u	B_1	B_g	^2A_u	$^2B_1$	^2B_g	^4B_g	$^4A_2$	^4A_u
σ*-type	B_g	A_2	A_u	^2B_g	$^2A_2$	^2A_u	^4A_u	$^4B_1$	^4B_g
π-type	A_g	B_2	B_u	^2A_g	$^2B_2$	^2B_u	^4B_u	$^4A_1$	^4A_g
π*-type	B_u	A_1	A_g	^2B_u	$^2A_1$	^2A_g	^4A_g	$^4B_2$	^4B_u

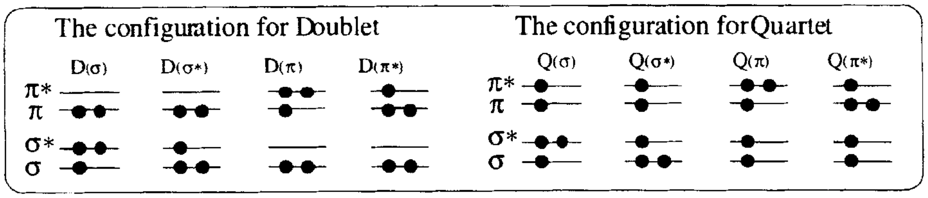


FIGURE 3 The reference electronic configuration of each type

(B) Ab initio Calculations of Anion Systems

The CASSCF calculations of the anion radical states of model systems were carried out for each symmetry state shown in Table II to elucidate the relative stability between the doublet and quartet states. Three kinds of active spaces were used, {3, 3}, {4, 5} and {6, 7} for **1**, while {10, 11} was used instead of {6, 7} for **2** as shown in Figure 4. All the geometries were optimized for each spin state and for each active space. Tables III summarizes the total energies for the doublet and quartet states of each symmetry state.

As shown above, the neutral state of **1** and **2** has four SOMOs. The doped electron occupies one of the four SOMOs and the SOMO becomes a doubly occupied MO. Thus the minimal active space for the anion radical state of the model systems consists of three SOMOs and three electrons, {3, 3}. The CASSCF method with this minimal active space also takes account of the SOMO-SOMO interactions. There are four different selections of the active spaces for CASSCF{3, 3}.

The active space {4, 5} consists of the corresponding four SOMOs of the neutral system. For the doublet state, the active space {4, 5} consists of several SP and EC type configurations in addition to that of {3, 3}, while the configuration for the active space {4, 5} is the same as that of {3, 3} for the quartet state. Therefore the CASSCF{4, 5} calculations generally favor the LS (doublet) state.

From Tables III, the ground quartet state is of π*-type for all the three models. It becomes the most stable state for meta-**2**. However, the doublet σ*-state is more stable than the quartet π*-state in the case of **1** and para-**2**.

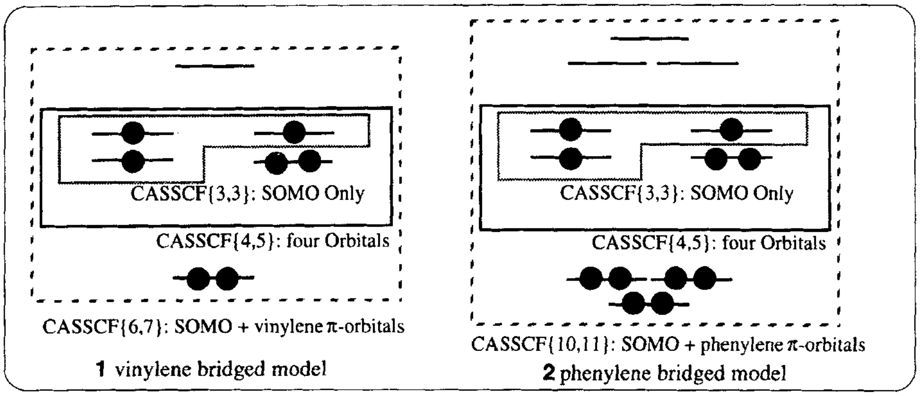


FIGURE 4 Active spaces for anion model systems

TABLE IIIa The total energies(a.u.) for model **1**

state	CASSCF{3,3}$^{a)}$	CASSCF{4,5}$^{a)}$	CASSCF{6,7}$^{a)}$
D(σ)	-153.29049	-153.34067	-153.37639
D(σ*)	**-153.32871**	**-153.36519**	**-153.40262**
D(π)	-153.32400	-153.32808	-153.35756
D(π*)	-153.29895	-153.30212	-153.33957
Q(σ)	-153.22297		-153.28205
Q(σ*)	-153.25106		-153.30600
Q(π)	-153.15223		-153.24116
Q(π*)	**-153.31295**		**-153.35024**

a) 4-31G basis set is used

TABLE IIIb The total energies(a.u.) for para-isomer of **2**

state	CASSCF{3,3}$^{a)}$	CASSCF{4,5}$^{a)}$	CASSCF{10,11}$^{a)}$
D(σ)	-305.71919	-305.77861	-305.87252
D(σ*)	-305.72447	**-305.78183**	**-305.87600**
D(π)	**-305.76724**	-305.77079	-305.85602
D(π*)	-305.75051	-305.75310	-305.85215
Q(σ)	-305.69392		-305.80785
Q(σ*)	-305.69991		-305.81220
Q(π)	-305.64273		-305.78671
Q(π*)	**-305.76351**		**-305.86291**

a) 4-31G basis set is used

TABLE IIIc The total energies(a.u.) for meta-isomer of **2**

state	CASSCF{3,3}$^{a)}$	CASSCF{4,5}$^{a)}$	CASSCF{10,11}$^{a)}$
D(σ)	-305.68063	-305.72011	-305.82377
D(σ*)	-305.68380	-305.72099	-305.82385
D(π)	**-305.74517**	**-305.74768**	-305.83685
D(π*)	-305.73616	-305.73764	**-305.84080**
Q(σ)	-305.70228		-305.82561
Q(σ*)	-305.70571		-305.82881
Q(π)	-305.72663		-305.83350
Q(π*)	**-305.74343**		**-305.84606**

a) 4-31G basis set is used

(C) Main Configurations

The CASSCF {4, 5} and {3, 3} methods distinguish π-electron doped states from σ-electron doped ones. The exact discrimination between the σ- and π-electron doped states becomes difficult at the CASSCF {10,11} ({6, 7} for **1**) level. For example, it is noteworthy that these σ-doped states have spin densities in π space because of spin polarization effect. However, we can understand the characteristic of π-electron doped or σ-electron doped state through the occupation numbers and main configurations.

The main configurations for the eight states for each system were selected from the CASSCF data. For all the three systems, each state except for the quartet state of π-type has the same main configurations even if the size of the active space is expanded. The main configurations are illustrated in Figure 4. The doublet state of π-type dropped in more stable state $\{\sigma^2 \sigma^{*2} \pi\}$. This state actually corresponds to π-electron doped singlet-carbene dimer. The state of π*-type corresponds to π-electron doped triplet-carbene dimer, and that of σ-type and σ*-type corresponds to σ-electron doped triplet-carbene dimer. Thus the local triplet configurations for the carbene groups are not changed upon the electron doping except for the doublet π-state.

(D) Optimized Geometries

The geometries of the bis-methylene should be sensitive to the types of the main configurations. Table IV summarizes the angles of the carbene groups in the anion radical states optimized by the CASSCF energy gradient technique: CASSCF {6, 7} for **1** and CASSCF {10, 11} for **2**. The corresponding data for the neutral state are also given in Table IV. It is clear that the angles of the carbene group depend on the electron occupation of its σ-orbital. The angles of the carbene groups with four σ-electrons are about 108 degree both in the neutral and in the anion radical states. This angle corresponds to that of singlet carbene. On the other hand, the angles become about 120 and 130 degree for the three and two σ-electron states, respectively. The last value corresponds to the angle for triplet phenyl methylene. Thus, the occupation number of the σ-orbital determines the bending angle for the carbene group. The optimized geometries are parallel to the main configurations in Figure 5.

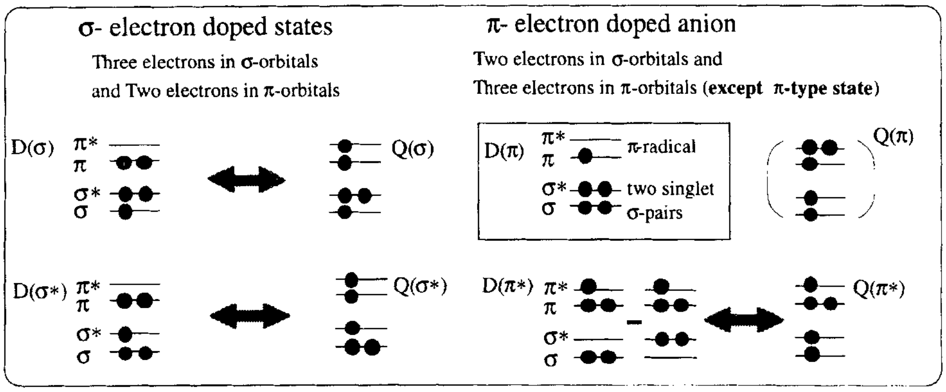


FIGURE 5 The main configurations for the model systems

TABLE IV The angles of carbene group in neutral and anion radical systems

states	neutral				anion							
	(S)†	S	T	Q	D(σ)	D(σ*)	D(π)	D(π*)	Q(σ)	Q(σ*)	Q(π)	Q(π*)
occupation of σ orbitals	4	2	2	2	3	3	4	2	3	3	2	2
1	107	134	134	130	119	120	107	132	118	117	130	131
p-**2**	108	133	133	130	119	119	108	131	117	118	130	130
m-**2**	108	130		131	119	119	108	131	118	119	130	131

† The states based on singlet-carbene dimer

(E) Doublet-Quartet Gaps for Anion Radical States

The doublet-quartet energy gaps for each anion radical state are summarized in Table V, and the following conclusions are drawn:

(1) The three-different CASSCF methods {3, 3}, {4, 5} and {10, 11} or {6, 7} gave the same sign for the doublet-quartet (D-Q) energy gaps of **1** and para-**2**. The D-Q gaps can be qualitatively explaind by the SOMO-SOMO interactions.

(2) The doublet state is more stable than the quartet state in the σ-, σ*- and π-states of 1 and para-**2**, while the tendency is reversed in their π*-state.

(3) The CASSCF methods {3, 3}and {10, 11} predict that the quartet state is more stable than the doublet state in the σ-, σ*- and π*-states of meta-**2**, while the tendency is reversed in its π-state because of the formation of singlet carbene sites.

(4) The low-spin (doublet) state is more stable than the high-spin (quartet) state at the CASSCF {4, 5} level for the σ- and σ*-states of meta-**2**, since it is biased to overestimate the stability of the LS state.

TABLE V Doublet-quartet energy gap (a.u.) of each type by CASSCF/4-31G

system	type	{3,3}	{4,5}	{6,7}
model **1**	σ	-0.06752	-0.11770	-0.09434
	σ*	-0.07765	-0.11413	-0.09662
	π	-0.17176	-0.21296	-0.11640
	π*	0.01400	0.01083	0.01067
	type	{3,3}	{4,5}	{10,11}
p-isomer of model **2**	σ	-0.02527	-0.08469	-0.06467
	σ*	-0.02456	-0.01528	-0.06380
	π	-0.12451	-0.12807	-0.06931
	π*	0.01300	0.01041	0.01076
m-isomer of model **2**	σ	0.01165	-0.01783	0.00164
	σ*	0.02191	-0.08192	0.00496
	π	-0.01854	-0.02105	-0.00335
	π*	0.00727	0.00579	0.00526

ORBITAL INTERACTIONS FOR NEUTRAL AND ANIONIC SYSTEMS

The preceding CASSCF results indicated that the relative stability between the LS and HS states for the model compounds can be qualitatively explained by using the CAS {3, 3}. There are in principle four kinds of the inter-site SOMO-SOMO interactions, i.e., π-π, σ–σ, intra-carbene π-σ and inter-carbene π-σ. The π-π interaction depends on π-conjugation bridge between the two carbenes. This interaction for model **1** and para-isomer of **2** is anti-ferromagnetic, while it is ferromagnetic for the meta-isomer of **2**. On the other hand, the intra-carbene π-σ interaction is usually ferromagnetic because of the orthogonality of these orbitals. Similarly, the inter-carbene π-σ interaction is ferromagnetic but it is weaker than the intra-carbene π-σ interaction . Judging from the previous CASSCF results for meta-**2**, the σ-σ interaction is small and can be ignored for the qualitative discussions. Figure 5 illustrates the SOMO-SOMO interaction schemes.

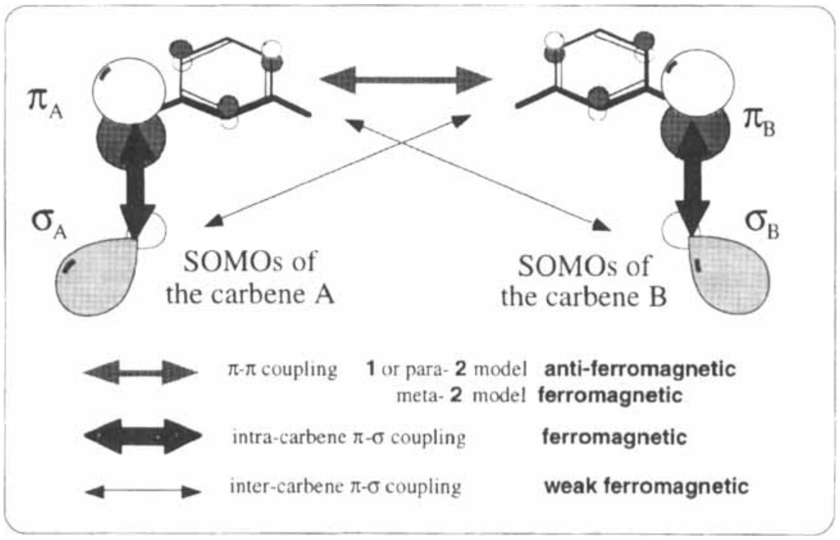


FIGURE 6 SOMO-SOMO interactions

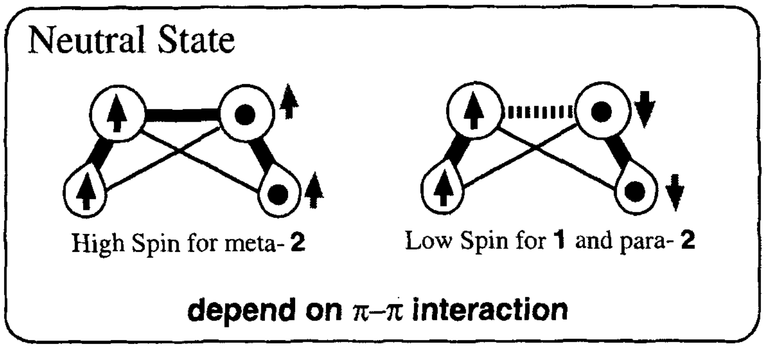


FIGURE 7a SOMO-SOMO interactions for the neutral system

Neutral Systems

Let us consider the neutral systems by using the orbital interaction picture illustrated in Figure 7a. In the case of the neutral systems, each SOMO of the carbene groups has one spin (one radical electron). The most stable state for meta-isomer of **2** is HS (quintet), because all the inter SOMO interactions are ferromagnetic. On the other hand, the most stable state of model systems **1** and para-isomer of **2** is LS (singlet), because anti-ferromagnetic π-π interaction is stronger than the ferromagnetic inter-carbene π-σ interactions . The ground spin state of the neutral systems is determined mainly by the π-π interaction.

Anion Radical Systems

In the case of the σ-doped systems (Figure 7b), we consider the remaining three spins, i.e., two in each π and one in σ. The orbital interactions concerning with the electron doped σ-orbital are vanished. The most stable state of meta-isomer of **2** is HS (quartet), because all three (π-π, intra and inter π-σ) interactions are ferromagnetic. On the other hand, the ground spin state of model system **1** and para-isomer of **2** are LS (doublet), because anti-ferromagnetic π-π interaction is stronger than the ferromagnetic inter-carbene π-σ interactions. The σ-electron doping does not change the spin arrangements of the neutral systems.

There are two different types of anion radical states generated by the π-electron doping. One is the electron-doped state of the triplet-carbene dimer and the other is that for the singlet-carbene dimer. In the former case, the interactions concerning with the electron doped π-orbital are vanished and we consider only the remaining three spins, i.e., two in each σ and one in π. The most stable state of all the three model systems is HS (quartet), because the π-π interaction is vanished and only the ferromagnetic interactions are remaining. In the latter case, there are no corresponding quartet state, and in this case, the spin state should be always LS (doublet).

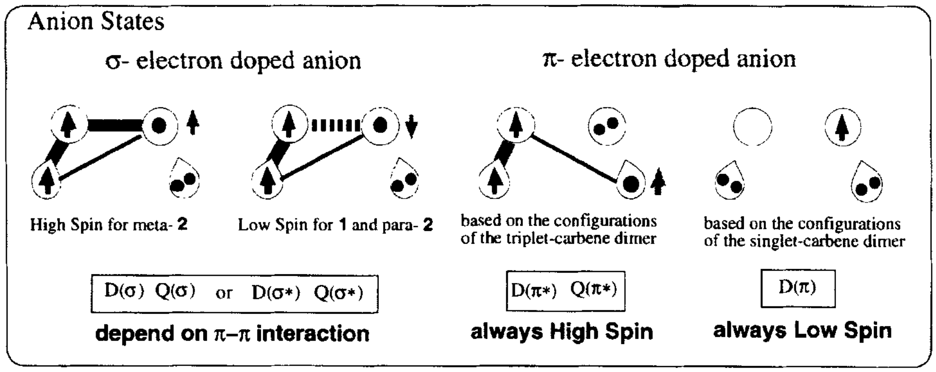


FIGURE 7b The SOMO-SOMO interaction pictures for anion radical states

CONCLUDING REMARKS

The present CASSCF calculations clearly indicated that the low-spin (LS) doublet state is feasible for the electron doped state of para-phenylene bis-methylene (para- **2**) if the electron is doped in the σ-orbital. The high-spin (HS) quartet state becomes the ground state for para-**2** by doping the π-electron, supporting the previous computational results.[13,14] However, the π-electron doped state becomes low-spin if the triplet carbene sites are collapsed into the singlet ones. Therefore, there are several possibilities in a theoretical view point to explain the experimental result [17-19] that the ground state of the electron doped para-phenylene bis(phenylcarbene) is doublet.

The ground spin state of the meta-phenylene bis-methylene (meta- **2**) becomes quartet after the full geometry optimization by the CASSCF energy gradient technique. The present and previous calculations[13,14] are consistent with the experiments available[17-19].

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas of Molecular Magnetism (No. 04242101). We are also grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 06101004).

REFERENCES

1. K. Yamaguchi, Y. Toyoda and T. Fueno, Kagaku, 41, 585 (1986) (in Japanese).
2. K. Yamaguchi, Y. Toyoda and T. Fueno, Funct. Mater., 5, 47 (1986) (in Japanese).
3. K. Yamaguchi, Y. Toyoda and T. Fueno, Synth. Metals, 19, 81 (1987).
4. K. Yamaguchi, Y. Toyoda, M. Nakano and T. Fueno, Synth. Metals, 19, 87 (1987).
5. K. Yamaguchi, Funct. Mater. 7, 5 (1987) (in Japanese).
6. K. Yamaguchi, Y. Takahara, T. Fueno, K. Nakasuji and I. Murata, Jpn. J. Appl. Phys., 27, L766 (1987).
7. K. Yamaguchi, Int. J. Quant. Chem., 37, 167 (1990).
8. K. Yamaguchi, H. Namimoto, T. Fueno, T. Nogami and Y. Shirota, Chem. Phys. Letters, 166, 408 (1990).
9. J. G. Bednort and K. A. Muller, Z. Phys., B64, 189 (1986).
10. K. Yamaguchi, M. Okumura, T. Fueno and K. Nakasuji, Synth Metals, 41-43, 3631 (1991).
11. T. Sugano, T. Kukasawa and M. Kinoshita, Synth Metals, 41-43, 3281 (1991).
12. R. Kumai, M. M. Matsushita, A. Izuoka and T. Sugawara, J. Am. Chem. Soc., 116, 4523 (1994).
13. S. Yamanaka, M. Okumura, H. Nagao and K. Yamaguchi, Chem. Phys. Lett., 233, 88 (1995).

14. S. Yamanaka, T. Kawakami, M. Okumura and K. Yamaguchi, Chem. Phys. Lett., 233, 257 (1995).
15. D. Yamaki, S. Yamada, G. Maruta, T. Kawakami, W.Mori and K.Yamaguchi, Mol. Cryst. Liq. Cryst., 279, 9 (1996).
16. G. Maruta, D. Yamaki, W. Mori, K. Yamaguchi and H. Nishide, Mol. Cryst. Liq. Cryst., 279, 19 (1996).
17. M. Matsushita, T. Momose, T. Shida, Y. Teki, T. Takui and K. Itoh, J. Am. Chem. Soc., 112, 4700 (1900).
18. M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, J. Am. Chem. Soc., 114, 7470 (1992).
19. M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, Bull. Chem. Soc. Jpn, 66, 1333 (1993).
20. S. Yamanaka, M. Okumura, K. Yamaguchi and K. Hirao, Chem. Phys. Lett., 225, 213 (1994).
21. M. Dupuis, A. Marquez and E. R. Davidson, HONDO 95. 3 from CHEM-Station, (1995) IBM Corporation, Neighborhood Road, Kingston, NY. 12401