Bull. Chem. Soc. Jpn., **55**, *1357—1361 (1982)*

Relation between Exchange Interaction and Crystal Structure of Verdazyl Radicals. As Studied by Means of McConnell's Spin Density Hamiltonian*

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(Received July 15, 1981)

The exchange interactions in four kinds of verdazyl crystals, 2,4,6-triphenylverdazyl (TPV), 2,4,6-triphenyl-3-methylverdazyl (MeTPV), 2,4,6-tri-*p*-tolylverdazyl (TTV), and 2,6-di-*p*-tolyl-4-phenylverdazyl (DTPV), have been studied by means of McConnell's spin density Hamiltonian. The calculated exchange parameters, J, have been compared with the experimental values derived from the magnetic susceptibilities. The observed order of J's, $J/k = -5.4$ (TPV), -9.1 (MeTPV), -11.1 (DTPV), and 0—-0.3 K (TTV), can be qualitatively explained by the following equation:

$$J \propto \sum_{ij} (-1/r_{ij})\rho_i^l \rho_j^{l+1},$$

where ρ_i^l and ρ_j^{l+1} are π-spin densities on atoms i and j of the l-th and $(l+1)$-th molecules in the *crystallographic column* and r_{ij} is the interatomic distance between atoms i and j. The magnetic susceptibility data of MeTPV and TTV between 1.6 and 300 K are presented and interpreted with the Heisenberg linear chain model. The susceptibility of DTPV is re-interpreted in the same framework as above.

The magnetic susceptibilities of some organic free-radical solids show a characteristic temperature dependence[1] which can be well explained based on the Heisenberg-type magnetic linear chain model.[2] The spin Hamiltonian for the exchange interaction in the magnetic linear chain can be given by a familiar form:

$$H = -2J \sum_l S_l S_{l+1}, \tag{1}$$

where S_l and S_{l+1} are the spin operators for the l-th and $(l+1)$-th magnetic electrons, and J is the exchange interaction parameter which depends on the crystal structure. However, the relation between J and the crystal structure has not been understood well.

The verdazyls first synthesized by Kuhn and Trischmann[3] are a series of stable organic radicals containing four nitrogen atoms per molecule with unpaired electrons over the entire molecules. The magnetic susceptibility of 2,4,6-triphenylverdazyl (TPV) between 77 and 300 K[4] has indicated existence of the substantial exchange interaction between the unpaired electrons. We have studied the magnetic susceptibilities of TPV, 2,4,6-triphenyl-3-methylverdazyl (MeTPV), 2,4,6-tri-*p*-tolylverdazyl (TTV), and 2,6-di-*p*-tolyl-4-phenylverdazyl (DTPV) (*cf.* Fig. 1) in order to understand the relationship between J and the crystal structure. J's determined from the magnetic susceptibilities are very different depending on the radicals in spite of the similarity in their spin distributions. X-Ray studies have shown that the crystal structures of these radicals are different from one another. Therefore, these four verdazyls form a suitable set for such a study.

In order to understand the observed J from the crystal structure, we have calculated the exchange parameter using McConnell's spin density Hamiltonian:[5]

$$H^{AB} = -S^A S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B, \tag{2}$$

where S^A and S^B are the spin operators for Molecules A and B, and where ρ_i^A and ρ_j^B are the π-spin densities on Atoms i of Molecule A and j of B, respectively. In evaluating the two-center exchange integral J_{ij}^{AB}, four trial functions of the distance, r_{ij}^{AB}, between Atoms i and j were used. The observed order of J's was qualitatively explained when J_{ij}^{AB} was assumed as a function of $1/r_{ij}^{AB}$.

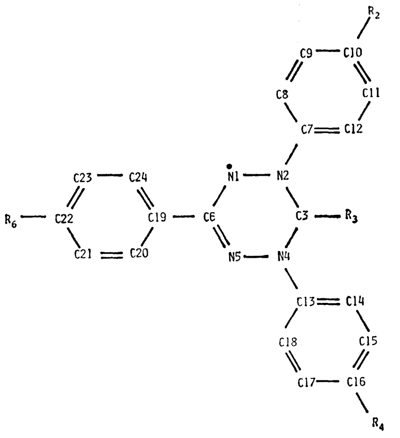

Fig. 1. Chemical structures and numbering system of verdazyls.

Radical	R_2	R_3	R_4	R_6
TPV	H	H	H	H
MeTPV	H	CH_3	H	H
TTV	CH_3	H	CH_3	CH_3
DTPV	CH_3	H	H	CH_3

Experimental

Following the process of Kuhn and Trischmann,[6] the samples were prepared by the ring formation of the corresponding formazans with formaldehyde or acetaldehyde, followed by reduction with alkaline solutions of these aldehydes. The radicals were purified a few times through

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* Part XIV of "The Magnetic Properties of Verdazyl Free Radicals."

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Table 1. Spin density distribution in TPV

Atom[a]	π-Spin density
N1, N5	0.1944
N2, N4	0.2040
C6	−0.0461
C7, C13	−0.0345
C8, C12, C14, C18	0.0473
C9, C11, C15, C17	−0.0179
C10, C16	0.0505
C19	0.0032
C20, C24	−0.0179
C21, C23	0.0067
C22	−0.0131

a) The numbering system refers to Fig. 1.

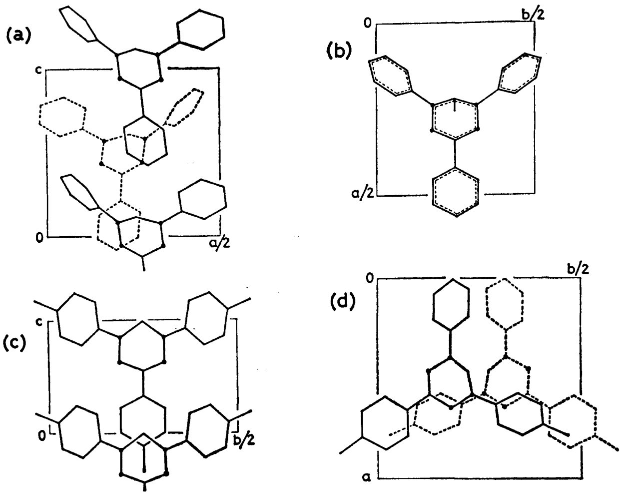

Fig. 2. Molecular packings of TPV(a),[13] MeTPV (b),[9] TTV(c),[10] and DTPV(d)[11] viewed along the b, c, a, and c axes, respectively.
Solid circle stands for the nitrogen atom. The molecule drawn with broken line is lower than one with solid line respective to the axis perpendicular to the projected plane.

recrystallization from a mixture of acetone and methanol. The results of the elementary analyses were in agreement with the calculated values within experimental errors.

The magnetic susceptibilities from 1.6 to 300 K were measured on the powdered samples of MeTPV and TTV by means of a magnetic torsion balance with an accuracy of 3%.[7] The temperature was measured with a carbon resister and an AuCo–Cu thermocouple calibrated by measurements of the susceptibility of manganese Tutton salt and of the vapour pressure of liquid helium.

The experiments of ESR and ENDOR in solution have been described elsewhere.[8] The analyses of the crystal structures of MeTPV, TTV, and DTPV by X-ray diffraction have been reported previously.[9–11]

Summary of Previous Results

Spin Density Distribution. The present radicals in dilute solution have exhibited nine-line ESR spectra due to four nearly equivalent nitrogen nuclei.[8] The nitrogen hyperfine coupling constants have ranged from 0.56 to 0.58 mT. The proton hyperfine coupling constants of TPV, MeTPV, and TTV have been measured by means of the ENDOR technique.[8] The changes in the proton coupling constants caused by methyl substitutions are less than 5%. The spin densities in TPV calculated by Fischer[12] are given in Table 1. As these values explain the hyperfine coupling constants, we use these values for the calculation of the exchange parameters.

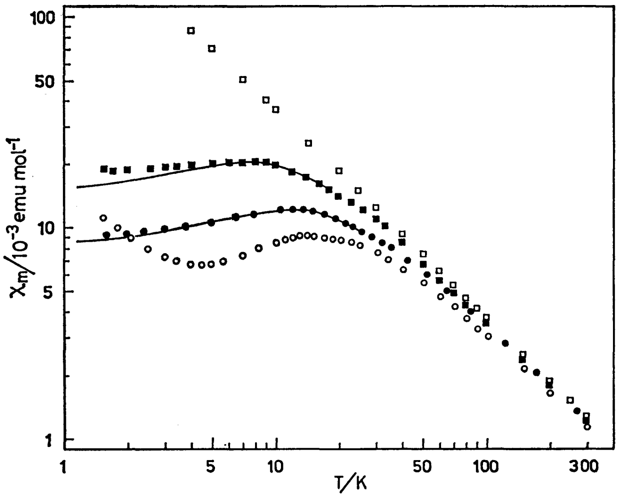

Fig. 3. Molar paramagnetic susceptibilities of crystalline verdazyls.
The solid square stands for the observed susceptibility of TPV, the solid circle of MeTPV, the open square of TTV, and the open circle of DTPV. The solid lines are theoretical susceptibilities calculated with the Heisenberg linear chain model.

Crystal Structure. The molecular overlappings of four verdazyls are compared with one another in Fig. 2. TPV and DTPV molecules are arranged in zigzag chains along the respective c axes, and MeTPV and TTV ones form Venetian blinds along the respective c axes. No alternation is observed in the intermolecular distances in these chains and blinds (columns). The angular orientation of $p_z\pi$-orbitals in TTV crystal is much more unfavourable for overlapping than that in the MeTPV crystal. The order of the mean values of the interatomic distances between the π-frameworks of the neighbouring molecules in the columns is as follows: DTPV<MeTPV<TTV<TPV (see Table 3).

Magnetic Susceptibility

The susceptibility data were corrected for the diamagnetic contribution using Pascal's constants.[14] The molar paramagnetic susceptibility, χ_m, of MeTPV follows the Curie-Weiss law with the negative Weiss constant of $\theta=-10.3$ K in the high temperature region. In the low temperature region, however, it deviates from the Curie-Weiss law and exhibits a broad maximum, χ_{max}, at T_m ($=11.7$ K). When the temperature, T, is lowered below T_m, χ_m decreases towards a non-zero value at 0 K. This finite value, $\chi_{T=0}$, was estimated by extrapolation. The susceptibility of TTV complies with the Curie-Weiss law

TABLE 2. RESULTS FROM SUSCEPTIBILITY MEASUREMENTS

	TPV	MeTPV	TTV	DTPV
θ/K	-8.0	-10.3	-0.3	-14.6
T_m/K	6.9	11.7		14.2
T_n/K	1.7			
$\chi_{\max}/10^{-3}$ emu mol^{-1} [a)]	20.3	12.1		9.15
$\chi_{T=0}/10^{-3}$ emu mol^{-1} [a)]	17.0	8.5		2.5
(J/k)/K	-5.4	-9.1	$0 — -0.3$	-11.1

a) The value of the molar susceptibility in m^3 mol^{-1} (SI) can be obtained by multiplying the value in emu mol^{-1} (cgs) by $4\pi \times 10^{-6}$.

with a small negative Weiss constant of -0.3 K over the whole temperature region examined. The spin concentrations of MeTPV and TTV, as determined from the susceptibilities in the Curie-Weiss region, were 100% within the experimental accuracy.

The susceptibilities of TPV[15)] and DTPV[16)] have been reported previously. However, the susceptibility of DTPV, which has been explained tentatively by the Ising model, is re-interpreted in the framework of the Heisenberg model in this paper. The susceptibility of DTPV displays a round maximum and a broad minimum at 4 K. An approximated $\chi_{T=0}$ is estimated by the extrapolation of the curve between the maximum and minimum. The susceptibilities of the verdazyls and the results obtained from the susceptibilities are shown in Fig. 3 and Table 2, respectively, together with the data of TPV. In Table 2, T_n for TPV shows the temperature at which χ_m-T curve exhibits a discontinuity in its slope.

Discussion

Susceptibility. The susceptibilities of the verdazyls are discussed here in order to obtain the experimental parameters for the exchange interactions. The columnar structure with a uniform intermolecular distance suggests a linear chain spin system, that is, the Heisenberg linear chain model with an isotropic exchange interaction or the Ising linear chain model with an extremely anisotropic one. In our case, therefore, the former is more adequate than the latter in view of the practically isotropic *g*-values of the verdazyls, $g=2.003$.[17)] Edelstein[18)] employed the Ising linear chain model to interpret the susceptibilities of organic radicals of BDPA and PAC at an earlier date. Recently, however, those susceptibilities were interpreted quantitatively in terms of the Heisenberg-type interaction.[1a,b)]

According to the study of Bonner and Fisher,[2)] the susceptibility of the Heisenberg linear chain with an antiferromagnetic exchange coupling exhibits a round maximum of height

$$\chi_{\max}T_m = 0.142 \tag{3}$$

at

$$kT_m/|J| = 1.282, \tag{4}$$

where k is the Boltzmann constant. J parameters of TTV[15)] and MeTPV have been estimated from Eq. 4 (see Table 2). The observed $\chi_{\max}T_m$ values of TPV and MeTPV are 0.140 and 0.142, respectively. The ratios of $\chi_{\max}/\chi_{T=0}$ estimated for TPV and MeTPV are, respectively, 1.19 and 1.42, while theory predicts 1.45.[2)] These values indicate that the MeTPV crystal is a typical Heisenberg linear chain spin system. On the other hand, the TPV crystal is not an ideal one, which is indicated also by the discontinuity in the slope of the χ_m-T curve. However, the dominant exchange interaction is the Heisenberg-type one.

J value for TTV has been estimated by a familiar relation of $\theta=2\zeta JS(S+1)/3k$ given by the molecular field theory,[19)] where the nearest-neighbour parameter, ζ, is 2 and $S=1/2$.

DTPV Spin System: The susceptibility of DTPV exhibited a maximum and a broad minimum, and $J/k=-17$ K was obtained by means of the Ising linear chain model.[16)] However, application of the Ising model to such susceptibility may underestimate the contribution from magnetic chains with odd spins. Therefore, we re-interpreted the susceptibility of DTPV based on diamagnetic dilution.

When a magnetic linear chain with an infinite length is diluted by diamagnetic impurities, the resultant diluted system is composed of paramagnetic chains of various finite lengths; such finite chains will be called segments. When the interaction between the segments is disregarded, the susceptibility of the diluted system is given by

$$\chi_m = \sum_{n=1}^{\infty} P_{n,c}\chi_n, \tag{5}$$

where $P_{n,c}$ is a probability making the segment with n spins at c spin-concentration, and χ_n is the susceptibility of the n-spin segment. For random diamagnetic dilution of the linear chain, $P_{n,c}$ is approximately given by

$$P_{n,c} = nc^n(1-c)^2. \tag{6}$$

Because there is no analytical representation of χ_n, the susceptibility of DTPV is treated graphically in Fig. 4. The solid circles are the experimental values based on $J/k=-11.1$ K which is estimated from Eq. 4. The open circles were obtained by adjusting the experimental value at T_m to the theoretical value of the Heisenberg linear chain at the same temperature. The adjusting factor is 1.09; this corresponds to the spin concentration of 0.92, which is very close to 0.94 determined from the susceptibility measurement. The adjusted susceptibility is close to the mean of the theoretical values for 10- and 11-spin segments. This mean susceptibility is very similar to that of the Heisenberg linear chain except for the region below $kT/|J|=0.3$. On the other hand, $n=12$ is obtained from the equation derived by $\partial P_{n,c}/\partial n=0$ with $c=0.92$. These results suggest strongly that the DTPV spin system is characterized by the Heisenberg linear chain with $J/k=-11$ K.

Relationship between J and Crystal Structure. Comparing Eq. 2 with Eq. 1, the quantity in the summation in Eq. 2 is identified as $2J$ in Eq. 1, which is the exchange integral between the l-th and $(l+1)$-th radicals. In order to obtain a tractable form of J_{ij}^{AB}, we have calculated the summation for pairs of the

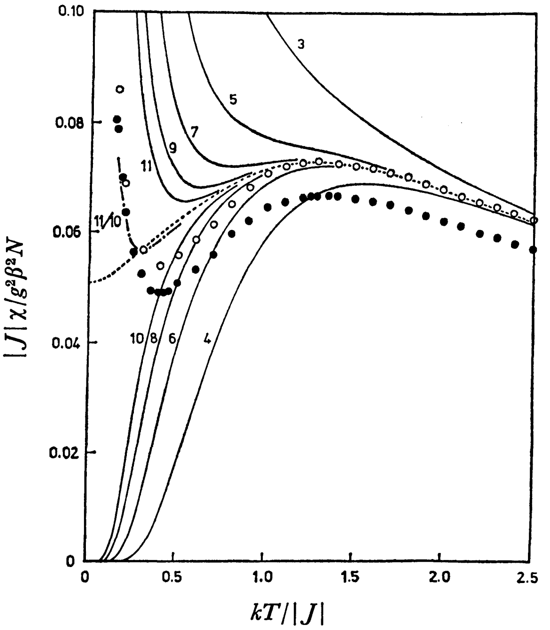

Fig. 4. Paramagnetic susceptibility of DTPV.
The solid circles are the experimental values. The open circles are the values corrected for the diamagnetic impurities. The broken line is the susceptibility of the Heisenberg linear chain.[2] The solid lines with n figures are the theoretical susceptibilities from rings of n Heisenberg-spins and dashed line is the mean of those of 10 and 11 spins.[2]

neighbouring molecules in the crystal. By analogy with the hydrogen molecule, the antiparallel spin-arrangement may be favourable with negative J_{ij}^{AB}. The negative J_{ij}^{AB} was assumed previously in this series[15] and also by Duffy *et al.*[20] in order to estimate J in DPPH-benzene crystal. Four trial functions with negative sign are adopted for J_{ij}^{AB}.

$$\text{Type A} \qquad J_{ij}^{\mathrm{AB}} = -C\exp\left[-Dr_{ij}^{\mathrm{AB}}\right], \tag{6}$$

where C and D are positive constants. This equation can be derived from the result of the numerical calculation made by Dulčić and Herak[21] who have treated two carbon atoms in a radical pair by using the explicit form for the exchange integral given by Löwdin.[22]

On the other hand, it has been considered that the overlap between the orbitals occupied by the unpaired electrons serves as the path of the exchange interaction and the overlap has been used as a measure of the magnitude of the exchange interaction.[23] Then, this measure is adopted as the second trial function:

$$\text{Type B} \qquad J_{ij}^{\mathrm{AB}} \propto -S_{ij}^{\mathrm{AB}}, \tag{7}$$

where S_{ij}^{AB} is the overlap integral between $\mathrm{p}_z\pi$-orbitals of atoms i and j. The overlap integral can be easily computed with the recurrence formulae.[24]

In order to obtain the third trial function, the Hamiltonian for hydrogen molecule written by using the familiar symbols is referred:

$$H = -(h^2\nabla_1{}^2/8\pi^2m + e^2/r_{\mathrm{a}1}) - (h^2\nabla_2{}^2/8\pi^2m + e^2/r_{\mathrm{b}2}) \\ + (-e^2/r_{\mathrm{a}2} - e^2/r_{\mathrm{b}1} + e^2/r_{12} + e^2/R).$$

The quantity in the last parentheses is known as the interaction operator, H'; $(H'-e^2/R)$ is the operator for the Heisenberg exchange interaction. The energy given by $(H'-e^2/R)$ approaches $-e^2/R$ when R becomes large. Then, the intermolecular exchange interaction may be approximated by

$$\text{Type C} \qquad J_{ij}^{\mathrm{AB}} \propto -1/r_{ij}^{\mathrm{AB}}. \tag{8}$$

Several investigators have noted the linear correlation between the singlet-triplet energy separation and the zero-field splitting parameter for a number of aromatic hydrocarbons and biradicals.[25] This correlation suggests that the exchange energy follows r^{-3} where r is the mean distance between the unpaired electrons, so we adopted the following trial function.

$$\text{Type D} \qquad J_{ij}^{\mathrm{AB}} \propto -1/(r_{ij}^{\mathrm{AB}})^3. \tag{9}$$

The exchange integral depends on both the distance and the angle between the $\mathrm{p}_z\pi$-orbitals. However, the angular dependence is neglected in Types A, C, and D. A possible angular correction can be made by multiplying the trial functions by $\cos\theta_i^{\mathrm{A}}\cos\theta_j^{\mathrm{B}}$ where θ_i^{A} and θ_j^{B} are the angles between the respective axes of the $\mathrm{p}_z\pi$-orbitals and the interatomic vector distance $\boldsymbol{r}_{ij}^{\mathrm{AB}}$.[20] However, we adopted the following correction factor, p,

$$p = \begin{cases} 1 & \text{when } r_{ij}^{\mathrm{AB}} \leq 6\,\text{Å} \\ 0 & \text{when } r_{ij}^{\mathrm{AB}} > 6\,\text{Å}. \end{cases} \tag{10}$$

Such a correction gives almost the same effect as that obtained by the cosine squared factors in our case.

The results of the calculation are shown in Table 3. Type A predicts J less than 1% of the observed one. This result arises from the short-range character of Eq. 6 which gives $J_{ij}^{\mathrm{AB}}/k = -3.9$ and -0.01 K for $r_{ij}^{\mathrm{AB}} = 3.4$ and 4.6 Å, respectively. Type B as well as Type A reverse the observed order of J's strikingly. Contrary to the case of Types A and B, Types C (and D) explain the order of the observed J's when the summation in Eq. 2 is performed over the pair of the neighbouring molecules in the column along the c axis of each crystal. This result shows that the magnetic chains in the present crystals are along the respective c axes and correspond to the *crystallographic columns*. The ratios of the interchain coupling to the intrachain one calculated by using Type C are 0.2, 0.04, 0.1, and 0.04 for TPV, MeTPV, TTV, and DTPV, respectively. This is consistent with the following fact based on the susceptibility: TPV crystal is not a typical Heisenberg linear chain spin system, while MeTPV and DTPV crystals are typical ones. Since the molecular packing along the column is generally different from those perpendicular to the column in the crystals of organic radicals, the ratios of the exchange coupling between the chains to the intrachain one may be hence more adequately estimated by using Type C than Types A and B.

Concluding Remarks

The susceptibilities of TPV, MeTPV, and DTPV can be explained in the framework of the Heisenberg linear chain model. The exchange parameters estimated from the susceptibilities are $J/k = -5.4$, -9.1, -11.1, and 0—-0.3 K for TPV, MeTPV, DTPV,

Table 3. Results of summation in McConnell's spin density Hamiltonian

Direction in the crystal	Type of J_{ij}^{AB}	Sum in Eq. 2[a]			
		TPV	MeTPV	TTV	DTPV
Along a axis	A	0.0012	0.00071	0.00019	0.00028
	B	−0.032	0.20	0.48	−0.013
	C	−1.0	0.22	0.18	−0.35
	D	−0.79	0.25	0.26	−0.33
	$\langle r \rangle$[b]	10.27	10.38	9.77	11.45
Along b axis	A	0.00037	0.00000	−0.0029	−0.0029
	B	0.41	0.00	−1.9	−0.14
	C	0.24	0.00	−0.33	0.38
	D	0.24	0.00	−0.54	0.38
	$\langle r \rangle$	8.85	12.61	11.40	9.43
Along c axis	A	−0.046	−0.00026	−0.00043	−0.071
	B	−1.1	−0.64	0.13	−11
	C	−5.8	−5.8	−2.7	−11
	D	−5.1	−4.2	−2.1	−11
	$\langle r \rangle$	7.86	7.76	7.82	7.15
Obsd (J/k)/K		−5.4	−9.1	0—−0.3	−11.1

a) The constants in Eq. 6 (Type A) were obtained from the exchange integrals (in [K]) in Ref. 21. Those in Eqs. 7—9 were adjusted to give −11 K for the DTPV pair along the c axis. b) $\langle r \rangle$ is the mean value of the relevant interatomic distances [l/Å].

and TTV, respectively. These differences arise from the differences in the crystal structures. The McConnell's spin density Hamiltonian with $-1/r_{ij}^{AB}$ in place of J_{ij}^{AB} may be useful in finding the direction of the dominant exchange interaction and in estimating the order of the exchange coupling between the magnetic chains in crystals of aromatic radicals.

The author is much obliged to Professors Hiroaki Ohya-Nishiguchi and Yasuo Deguchi for continuous encouragement throughout this work and also indebted to Professors Noboru Hirota and Kazuo Mukai for illuminating discussions. Encouraging advices have been given by Professor Kazuhiko Ishizu, to which the author's thanks are due. Thanks are also due to the co-authors in this series for hearty cooperation. The calculations were performed at the Computer Centers of Kyoto and Ehime Universities.

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