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MO-Theoretical Description of Electronic Structures of Tricentric Bisdesmiphiles in the Ground and Excited States

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A systematic MO-theoretical description of electronic structures of tricentric bisdesmiphiles in the ground state is presented in response to contradictory arguments on the biradical character of the species by Huisgen, Firestone, and others. The approximately spin-projected but size-consistent (AP) UHF and UMP methods remedy artifact arising from the spin contamination effect involved in the singlet UHF and UMP wavefunctions, giving reasonable a different-orbitals-for-different-spins (DODS) MO description for oxygenated dipoles such as O_3 and CH_2OO and 1,3-biradicals without octet stabilization such as OCH_2O and $CH_2CH_2CH_2$. The RHF method provides well-accepted MO description for diszonimum and nitrilium betaines having little biradical character, and the RMP method works well even for species with weak biradical character. They are successfully applied to calculating relative energies between nonradical ring- and biradical open-forms of tricentric species, singlet–triplet energy gaps of tricentric biradicals, and high- and low-spin energy gaps of polyradicals constructed of 1,3-biradical units. Reliability of the projected UHF and UMP scheme for biradical species was confirmed by the complete active space (CAS) configuration interaction (CI) by the use of UHF natural orbitals (UNO). The UNO CASCI calculations are also carried out both for the ground and excited of 1,3-biradicals. The energy gradient technique based on UNO CASSCF is applied to the full geometry optimizations of tricentric systems, followed by the UNO CASSCF MP2 calculations for dynamical correlation corrections. On the other hand, the UNO MR SDCI method by the use of the UNO CASCI reference gives a well-balanced MO-theoretical description of the ground and excited states. Comparisons of different definitions of biradical character are given in relation to theoretical explanations of 1,3-dipoles and 1,3-dipolar reactions. It is shown that the present MO-theoretical description based on both delocalized and localized natural orbitals is wholly compatible with experimental data obtained by Huisgen and others.

Reactions of organic compounds are classified into four categories. One is the so-called concerted reactions which proceed without well-defined intermediates, while the other three reactions proceed stepwisely involving radical, ionic, and ion-radical intermediates (Chart 1), respectively. The charge and spin density populations obtained by theoretical calculations are utilized for characterization of these intermediates.[1)] There are two different theoretical methods for studies of electronic mechanisms of organic reactions (Chart 2): One is a molecular orbital (MO) approach; the other is a valence bond (VB) method. In previous series of papers,[2)] we have carried out the symmetry and stability analysis of molecular orbitals in order to elucidate the biradical (BR) character in organic intermediates from the MO-theoretical view point. It has been shown that the closed-shell MO bifurcates into the different orbitals for different spins (DODS) type MO responsible for BR character, if the triplet instability takes place in RHF solution.

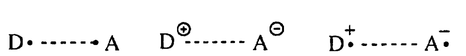


Chart 1.

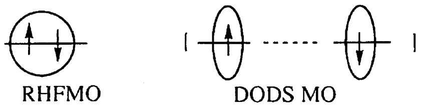


Chart 2.

A systematic MO-theoretical description of unstable intermediates based on these MO$_s$[2)] has been feasible to characterize electronic mechanisms of the above four categories. This has explored three selection rules in the ground state: (1) orbital symmetry rule for concerted reactions, (2) orbital stability rule for ionic and zwitterionic (ZW) reactions and (3) orbital pairing rules for radical and ion-radical reactions.[3)]

In order to derive these selection rules,[3)] semiempirical MO calculations[2,4)] for many unstable reaction intermediates and transition structures were carried out, and the calculated results for tricentric systems were summarized in a review article.[5)] Semiempirical calculations have several limitations for quantitative purposes. The computational methodologies are, however, equally applicable to ab initio computations. In fact, developments of the ab initio program package and computer technologies enable us to carry out the symmetry-stability analysis at ab initio level and DODS MO computations followed by several post HF computations for organic reaction intermediates. As a continuation of the semiempirical calculations,[5] ab initio calculations of some three center systems were carried out.[6] These studies indicated that the species which can be represented by the general formula, A–B–C, may range in behavior from transient intermediates such as trimethylene, $\cdot CH_2CH_2CH_2\cdot$, which may not be energy minima, through stable and highly reactive molecules such as $\cdot O–O–O\cdot$, to stable and unreactive species.[7,8] All of these molecules may be regarded as tricentric bisdesmiphiles, since they prefer to form two bonds at the termini of three atom systems in chemical reactions. Many theoretical treatments[9] of such species have been reported, (1) because calculations are the only method for determining directly the details of geometries and electronic structures of transient species (which in some cases may be saddle points), (2) because reactivities of intermediates are the well-known class of "1,3-dipoles", which are valuable synthetic intermediates, and, (3) because the general question of biradical versus zwitterionic, or covalent, character in these and other species is of general interest for understanding the chemistry of this group of molecules. The last point has been addressed by a variety of computational techniques where the electronic structures of these tricentric bisdesmiphiles are partitioned into biradical (BR) and zwitterionic (ZW) parts, but the results are not in general agreement. For example, ozone and diazomethane are considered as biradicals by Goddard[10] and Firestone.[11] The diazomethane and related diazonium betaines, however, are considered to be nonradical by Huisgen[7] and others[5] because no radical type behavior is observed in their 1,3-dipolar cycloadditions.

The BR and ZW characters of tricentric bisdesmiphiles have been experimentally studied by Huisgen and his collaborators (Chart 3).[7] In fact, Huisgen has explained many experimental results on 1,3-dipolar cycloadditions by using the MO concept and zwitterionic structures of A–B–C species. On the other hand, Firestone[11] has utilized the VB descriptions of 1,3-dipolar species presented by Linnett[12] to explain the mechanism of 1,3-dipolar cycloaddition. The discrepancies between the arguments by Firestone and by Huisgen are partly ascribed to the difference in definition of biradical (BR) character. Since the MO and VB approaches to unstable intermediates are apparently different, a common criterion should be introduced in order to elucidate electronic mechanisms of 1,3-dipolar reactions, leading to a proposal based on the natural orbitals.[13] The natural orbitals and occupation numbers are indeed obtained by diagonalyzing the first-order density matrices given by both MO- and VB-type wavefunctions and these are used for definition of BR character. The discrepancies between the Huisgen[7] and the Firestone[11] arguments are removed from the natural orbital (NO) CI view.[13]

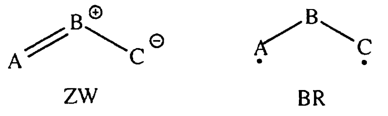


Chart 3.

On the other hand, molecular magnetism has received current interest. Clusters of reactive intermediates such as triplet carbenes have been investigated as typical examples of high-spin molecules.[14] 1,3-Biradical species have also received current interest as building blocks of polyradicals and magnetic polymers. In fact, the methylene ($–CH_2–$) and oxygen (–O–) units have been used as the ferromagnetic and antiferromagnetic coupling units for constructing these species.[15c] For example, the ground states of trimethylene ($\cdot CH_2CH_2CH_2\cdot$) and bis(methylene)oxyl ($\cdot CH_2OCH_2\cdot$) are triplet (high-spin) and singlet (low-spin), respectively. The singlet (S)–triplet (T) intersystem crossing by the spin-orbit interaction and by the external magnetic fields is a key factor in the spin dynamics experiments. Thus the S–T energy gap in 1,3-biradical species is an the important theoretical aspect in molecular magnetochemistry.[14,15]

Our basic ideas and computational procedures for a systematic MO-theoretical description of unstable species were already presented in several letter articles.[2,4,6,15] In this full paper we extend such ideas and fully examine related theoretical aspects. We also clarify the proposed computational procedures, which are partly implemented in GAUSSIAN 94[16] and EFCI[17] program packages. To this end, ab initio computations are carried out in order to obtain the MO-theoretical description of electronic structures of tricentric bisdesmiphiles in both the ground and excited states. Implications of the calculated results are discussed in relation to several theoretical explanations of electronic structures of the species by Husigen, Firestone, Goddard and others.

Theoretical Backgrounds

The theoretical background is briefly considered in this section. As examined previously,[18] a potential curve for the dissociation process of covalent bond in a bicentric system is divided into three characteristic regions, as illustrated in Fig. 1: (I) stable region, (II) intermediate (transition) region and (III) unstable (magnetic) region. As is well known, the full configuration interaction (FCI) provides a reasonable potential curve over the whole region, as illustrated in Fig. 1. The restricted Hartree–Fock (RHF) and RHF Moller–Plesset (RMP) perturbation methods are applied to species in region I, but RHF and RMP provide usually the rise-up and fall-off curves, respectively, in region III, as illustrated in Fig. 1A. Such fall-off phenomena cannot be removed out even if the RHF coupled-cluster (RCC) method is employed, although RCC is usually reliable in the region II. On the other hand, the unrestricted Hartree–Fock (UHF) method provides a proper dissociation curve but it suffers the so-called spin contamination error. However, the full CI (FCI) wavefunction does not involve any spin contamination error, even if the UHF solution is employed as a starting wavefunction as illustrated in Fig. 1B. Therefore, the spin contamination effect should become less predominant if the UHF-based correlated wavefunctions are close to the FCI wavefunction. For example, the UHF coupled-cluster (UCC) wavefunction is given by the exponential form of the excitation operators[18] as

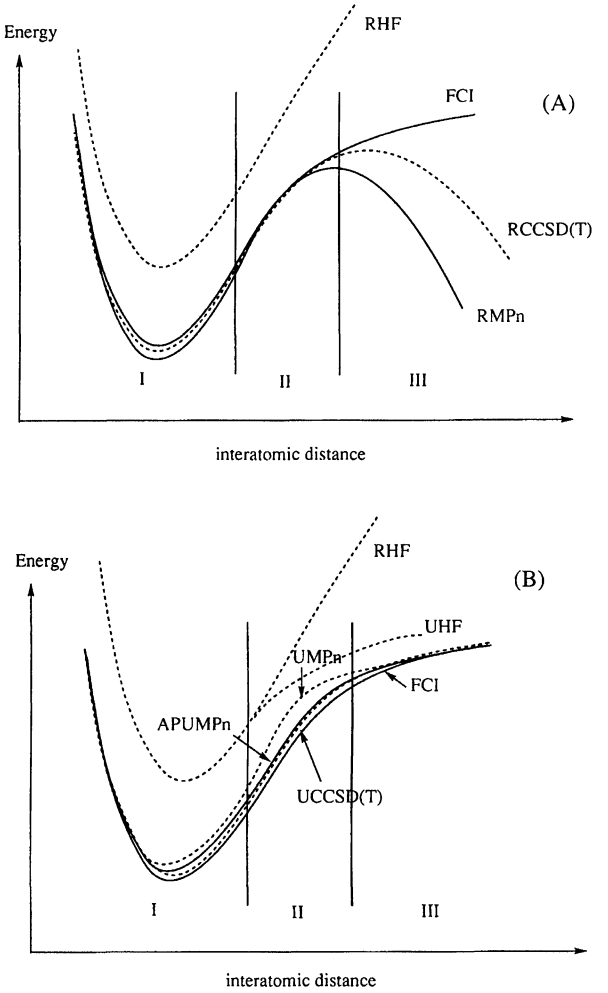


Fig. 1. (A) Typical potential curves for dissociation process of a covalent bond obtained by the RHF MP*n* and CC SD-(T) methods, whereas (B) the corresponding curves by the UHF MP*n* and CC SD(T), and APUHF MP*n* methods. The regions I, II, and III denote the nonradical, intermediate, and magnetic regions with weak, intermediate, and biradical characters, respectively.

$$\Psi_{\mathrm{FCI}} = \Psi_{\mathrm{UCC}} = \exp\{\textstyle\sum T_i\}\,\Phi_0(\mathrm{SR})(\Phi_0(\mathrm{SR}) = \Phi_{\mathrm{UHF}}), \quad (1)$$

where SR denotes the single reference and T_i is the *i*-tuple excitation operator such as single (T_1), double (T_2), triple (T_3) or quadruple (T_4) excitation operator. The UCC wavefunction should be very close to the FCI if the exponential part in Eq. 1 is taken to involve sufficient higher excitation operators. In fact, the spin contamination errors on the potential curve were not serious even at the truncated UCC SD(T) level in the bicentric systems examined before.[18]

The UHF Moller–Plesset (UMP) method[19] was used to investigate electronic structures of biradical species. However, these wavefunctions suffered from the spin contamination errors arising from the higher spin states, leading to the full Löwdin-type[20] spin projection scheme (PMP)[21] or approximate spin projection scheme (APUMP).[22] The PMP and APUMP methods were used for calculations of heats of formations in biradical reactions. They are used as an alternative method to UCC SD(T) since the latter is time-consuming in large organic systems.

On the other hand, the multiconfiguration approach is inevitable for more quantitative MO-description of both the ground and excited states of tricentric bisdesmiphiles. The complete active space (CAS) configuration interaction (CI) calculation by the use of UHF natural orbitals (UNO) are carried out for MO-theoretical descriptions of both the ground and excited states.[6,23] The UNO CASCI vector is a good trial for the UNO CASSCF calculations of the species.[18,24,25] The energy gradient technique based on UNO CASSCF is applied to the full geometry optimizations, followed by the UNO CASSCF MP2 calculations for dynamical correlation corrections.[26] On the other hand, the UNO MR SDCI method by the use of the UNO CASCI reference[17] gives a well-balanced MO-theoretical description of the ground and excited states. These theoretical aspects are thoroughly investigated below using tricentric systems as appropriate examples.

MO Description of Tricentric Bisdesmiphiles

1. Symmetric A–B–C Systems: Ozone, Methylenebis(oxyl), and Trimethylene. Huisgen[7] classified tricentric bisdesmiphiles into four groups on experimental grounds, particularly in relation to biradical type behavior in 1,3-dipolar cycloadditions. (1) type A: diazonium betaines, (2) type B: azomethinium betaines and carbonyl betaines, (3) type C: nitrilium betaines, and (4) type D: 1,3-dipoles without octet stabilization, as illustrated in Fig. 2, where the appropriate computational procedures are also illustrated. In order to elucidate the BR character (y) of tricentric bisdesmiphiles, some aspects of MO theory should be explored. As shown previously,[5] the restricted Hartree–Fock (RHF) MO method cannot be used for molecules with appreciable biradical character. In such biradical systems, quasidegeneracy of the highest occupied (HO) and the lowest unoccupied (LU) molecular orbitals (MO) induces a triplet instability of the RHF closed-shell orbital description, which indicates the breakdown of the description.[2] However, this defect can be removed by using the more flexible unrestricted Hartree–Fock (UHF) method without the double occupancy constraints.[2—4] This paper uses a method allowing DODS MO for the MO-theoretical description of tricentric bisdesmiphiles, A–B–C.[5]

Since the RHF 3×3 CI[5,27] was first utilized for MO-theoretical description of biradical species, let us clarify the mutual relationship between 3×3 CI and DODS MO.[4] Ozone (**1**) is an appropriate molecule for the purpose of explanation and illumination of a MO-theoretical description[5] for reactive intermediates. The ground state of O_3 (**1**) can be represented by the ground configuration $G=|K\pi_{S1}{}^2\pi_A{}^2\pi_{S2}{}^0|$ in the RHF approximation, where K represents the doubly-occupied inner shell (core) orbitals and S1, A, and S2 denote the bonding(symmetric), nonbonding(antisymmetric), and antibonding(symmetric) π-MOs. This configuration corresponds to a nonradical closed-shell shell structure of O=O=O, **1a**. However, 3×3 RHF CI[27] indicated that the contribution from the doubly excited configuration $D=|K\pi_{S1}{}^2\pi_A{}^0\pi_{S2}{}^2|$ cannot be neglected even in a qualitative sense because of

System	$N\equiv N^{\oplus}-Z^{\ominus}$ diazonium betaines $R-C\equiv N^{\oplus}-Z^{\ominus}$ nitrilium betaines	$R_2-C=N^{\oplus}(R)-Z^{\ominus}$ azomethinium betaines	$R_2-C=O^{\oplus}-Z^{\ominus}$ carbonyl betaines	$R_2-C(R_2)-R$ 1,3-dipoles without octet stabilization
Region	I	II		III
y(%)	0~10	20~50		80~90
MPn	RMPn	RMPn	RMPn, APUMPn	PMPn, APUMPn
CC	RCCSDT	RCCSDT	UCCSD(T)	APUCCSD(T)
CI	RHF CI	UNO CI	UNO CI	UNO CI
CAS	CASMP2	CASMP2		CASMP2
MRCC	CASCC SD(T)	CASCC SD(T)		CASCC SD(T)

Fig. 2. Classifications of 1,3-dipolar species into five different groups by Husigen on the experimental grounds. Relations between his classification and present theoretical modelings are illustrated schematically. Notations of y, MPn, CC, and CAS are given in the text.

the instability of the ground RHF configuration.[4] In fact, the singlet closed-shell RHF solution for **1a** is less stable than the triplet UHF solution for the triplet biradical state: the RHF solution of O_3 involves a triplet instability.[4] The singlet UHF solution given by

$$ {}^1\Psi_{\mathrm{UHF}} = |K\pi_{\mathrm{S1}}{}^2\chi_\pi\eta_\pi|, \qquad (2)$$

where χ_π and η_π are the singly occupied MOs (SOMOs) of O_3, is more stable. Since they are largely localized on the terminal O-atoms, as illustrated in Fig. 3, the UHF electronic orbital configuration given by Eq. 2 expresses the singlet ππ-biradical (BR) structure **1b** of O_3. The broken-symmetry SOMOs χ_π and η_π are almost identical to those calculated by generalized VB (GVB) method.[28] The orbital overlap $T_{\mathrm{HO}} = \langle\chi_\pi|\eta_\pi\rangle$ is defined as a measure of π-electron localization in the BR state. The biradical character (y) is defined by the weight of doubly excited configuration in the configuration interaction (CI) theory, and it is rewritten by T_{HO} in the DODS UHF MO theory followed by spin projection[13] as

$$y = 1 - 2T_{\mathrm{HO}}/(1+T_{\mathrm{HO}}^2). \qquad (3)$$

On the other hand, the core part K in Eq. 2 is constructed from the RHF-type delocalized MO with full C_{2v} symmetry, while the σ-orbitals in the GVB theory are essentially localized in bond regions, in conformity with the VB theory.[29] Therefore, the DODS MO and GVB descriptions of ozone are different in the core part K because of the small spin polarization effect.[30]

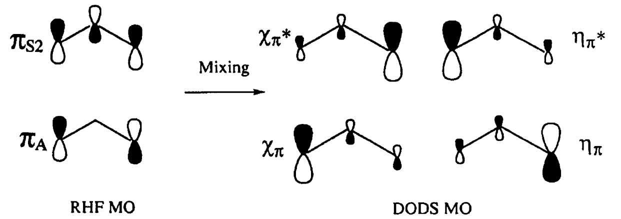


Fig. 3. Schematic illustrations of RHF HOMO and LUMO for closed-shell 1,3-dipoles, and DODS MOs for up- and down-spins for 1,3-biradical species. DODO MOs are given by the mixing of RHF HOMO and LUMO.

Although the singlet UHF solution provides a DODS MO description of singlet ozone, the singlet UHF wavefunction involves the triplet excited wavefunction as a contaminant. As described elsewhere,[4,15,21] the fraction (f_{sc}) of the triplet component can be estimated from the expectation value of the total spin angular momentum operator $\langle S^2\rangle$ for the singlet UHF wavefunctions as

$$\begin{aligned} f_{\mathrm{sc}} &= m/(1-m); \\ m &= {}^1\langle S^2\rangle(\mathrm{UHF})/{}^3\langle S^2\rangle(\mathrm{UHF}). \end{aligned} \qquad (4a)$$

Quantities for the pure singlet biradical state can be calculated approximately by:

$$ {}^1Q_{\mathrm{APUHF}} = {}^1Q_{\mathrm{UHF}} + f_{\mathrm{sc}}({}^1Q_{\mathrm{UHF}} - {}^3Q_{\mathrm{UHF}}). \qquad (4b)$$

The ${}^a\langle S^2\rangle$ values (a=1 or 3) easily be calculated by ab-initio program package such as GAUSSIAN 94.[16] Equation 4b can be used in the following for projecting out the unwanted spin state(s). It is also noteworthy that the approximate spin projection scheme in Eq. 4b can be applicable to the singlet unrestricted Kohn–Sham (UKS) density functional theory (DFT).[31] Therefore, it is useful in any practical computational scheme given by the hybrid of the UHF- and UKS-based methods.[32]

As a typical example, the instability of the RHF solution of O_3 (**1**) with the experimental geometry was examined by changing the quality of the basis sets. Table 1 summarizes the relative energies obtained by the difference between UHF (or APUHF) and RHF total energies. The total energy

Table 1. Correlation Corrections (kcal mol^{-1}) Calculated for Ozone by Several Computational Methods with Different Basis Sets

Methods	4-31G	6-31G*	6-311G*	6-311G(2df)
RHF	0.0[a)]	0.0[b)]	0.0[c)]	0.0[d)]
UHF	−63.3	−55.6	−58.2	−56.6
APUHF	−68.7	−62.5	−64.6	−63.3
UNO CASCI {2,2}	−66.9	−57.9	−61.1	−50.4
UNO CASCI {4,4}	−78.4	−66.4	−69.4	
UNO CASCI {6,6}	−99.9	−76.9	−80.3	
UNO CASCI {8,8}	−123.1	−93.0	−94.2	
UNO CASSCF {2,2}	−67.7	−59.5	−66.1	−59.4
UNO CASSCF {4,4}	−82.6	−83.1		
UNO CASSCF {6.6}	−123.7	−111.0		
UNO CASSCF {8,8}	−151.6			
RMP2	−300.1	−389.0	−422.7	
UMP2	−264.1	−351.8	−385.8	
PMP2	−273.0	−364.0	−397.7	
APUMP2	−276.6	−367.0	−400.1	
RMP4	−302.6	−401.9	−439.2	
UMP4	−279.8	−377.0	−412.4	
PMP4	−288.4	−388.7	−423.8	
APUMP4	−294.2	−393.6	−428.3	
RCCSD(T)	−297.4	−395.4	−429.5	
UCCSD(T)	−293.8	−390.2	−423.8	
UNO MR SDCI {2,2}	−270.3			
UNO MR SDCI[e)] {2,2}	−292.1			
UNO CASMP2 {2,2}[f)]	−268.4	−359.8		
UNO CASMP2 {2,2}[g)]	−299.2	−393.3		

a) −223.90715, b) −224.246674, c) −224.303995, d) −224.328564 (a.u.), e) after Devidson's correction, f) by GAUSSIAN94, g) by HONDO95.

of closed-shell ozone (**1a**) is −223.9072 a.u. at the RHF/4-31G level, whereas the energy of the $\pi\pi$-biradical state (**1b**) with the APUHF/4-31G wavefunction is −224.0166 au. The energy difference between **1a** and **1b** is about 69 kcal mol^{-1}, which is considered to be the correlation correction for the biradical pair. As is well known, this type of correlation is referred to as a non-dynamical correlation,[33)] and the remaining electron correlation for the closed-shell part is referred to as the dynamical correlation, as will be described below. The non-dynamical correlations by the 6-31G*, 6-311G*, and 6-311G(2df) basis sets are 63, 65, and 63 kcal mol^{-1}, respectively, showing that they are not so sensitive to the basis sets employed. The orbital overlaps T_{HO} are 0.249, 0.266, 0.257, and 0.279, respectively, by 4-31G, 6-31G*, 6-311G*, and 6-311G(2df), and therefore the corresponding biradical characters (y) are 53, 50, 52, and 48 (%), respectively: These are not sensitive to the basis sets, at least to those examined here. These results suggest that the 4-31G basis set can be utilized for qualitative discussions of the instability of covalent bonds[4)] and biradical characters in 1,3-biradical species, even if large basis sets are crucial in evaluating binding energies.

It can be seen from Table 1 that the differences between total energies by RHF and ^{1}APUHF methods are almost equal to the differences obtained from CAS CI[18)] using the quasi-degenerate UHF natural orbitals (UNO) and two biradical electrons {2,2} of **1**. However, the APUHF values are slightly larger than the corresponding UNO CASCI {2,2} values, since the former involve the so-called spin-polarization (SP) effects for closed-shell pairs. Judging from the present numerical results, it appears that the APUHF method is approximately an effective alternative to the UNO CASCI {2,2} method satisfying the simple relation:

$$^1\phi_{\mathrm{UNO\ CASCI}\ \{2,2\}} \cong {}^1\phi_{\mathrm{APUHF}}. \tag{5}$$

The nondynamical correlation corrections of **1** at the APUHF level is quite close to that of UNO CASSCF {2,2}, as shown below.[18)]

In order to confirm Eq. 5, the RHF, UHF, and APUHF calculations were carried out for methylenebis(oxyl) $\mathrm{OCH_2O}$ (**2**) and iminobis(methylene) $\mathrm{CH_2NHCH_2}$ (**6**), assuming the geometries fully optimized by the CASSCF {6,6}/6-31G** method (see below).[23)] Table 2 summarizes the energy differences between total energies by RHF and other computational methods. From Table 2, the stabilization energy from RHF by APUHF is close to those of UNO CASCI {2,2} and CASSCF {2,2} in all the biradical species examined here. It is probable that the situation is the same for other 1,3-biradical species.[5,7)]

2. Unsymmetrical A–B–C Systems: Methyleneperoxyl, Ethyleneoxyl, and Iminoperoxyl. Equation 4b is here used to elucidate the low-lying energy levels of methyleneperoxyl (**4**), ethyleneoxyl (**5**), the CO ring-opened form of oxirane, and iminoperoxyl (**7**) (Chart 4). There are four different UHF electronic orbital configurations for **4**, **5**, and

Table 2. Correlation Corrections (kcal mol^{-1}) Calculated for 1,3-Biradicals by Several Computational Methods with the 6-31G* Basis Set

Methods	CH_2NHCH_2	CH_2OO	OCH_2O	CH_2CH_2O
RHF	0.0$^{a)}$	0.0$^{b)}$	0.0$^{c)}$	0.0$^{d)}$
UHF	−16.0	−20.0	−115.6	−77.1
APUHF	−26.1	−25.3	−116.6	−79.7
UNO CASCI {2,2}	−25.3	−23.7	−111.7	−71.8
UNO CASCI {4,4}	−29.5	−30.0	−117.1	−78.1
UNO CASCI {6,6}	−36.3	−39.5	−124.0	−84.0
UNO CASSCF {2,2}	−26.2	−26.7	−111.9	−71.9
UNO CASSCF {4,4}	−33.1	−38.2	−117.1	
UNO CASSCF {6,6}	−48.8	−46.0	−141.5	
RMP2	−279.3	−315.2	−386.5	−276.5
RMP4	−307.3	−340.5	−410.0	−317.3
RCCSD(T)	−307.8	−339.7	−399.3	−441.4
UMP2	−264.4	−297.4	−366.1	−308.5
PMP2	−278.6	−311.2	−371.4	−312.4
APUMP2	−279.3	−315.0	−368.4	−312.3
UMP4	−293.8	−322.3	−393.6	−338.6
PMP4	−307.0	−335.4	−398.9	−342.4
APUMP4	−309.2	−340.1	−396.3	−342.5
UCCSD(T)	−304.8	−335.3	−396.6	−341.2
UNO CASMP2 {2,2}	−292.8	−329.5	−388.7	−323.7

a) −132.96764, b) −188.53902, c) −188.47370, d) −152.70365 (a.u.).

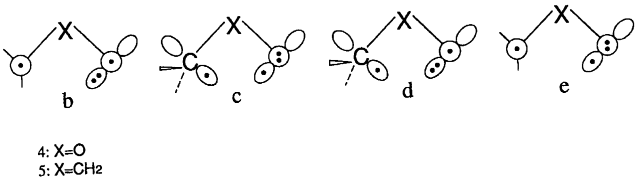


Chart 4.

7 and four different biradical forms, (**4b**)—(**4e**), are possible in each spin state. The energy levels and fully-optimized geometries of **4** and **5** at the UHF level have been reported previously.[15] Tables 3 and 4 summarize the relative energies of these biradicals states as calculated by Eqs. 4a and 4b.

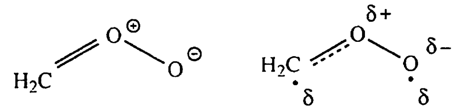
Table 4. Relative Enegies (eV) of Eight Biradical States of Iminoperoxyl Calculated by the UHF, APUHF, and UNO MR SDCI/4-31G Method

States	UHF	APUHF	CI$^{a)}$				
			R$^{b)}$	100	50	10	5
$^1\pi\pi$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$^1\pi\sigma$	0.647	0.778	0.828	0.459	0.466	0.699	1.029
$^1\sigma\pi$	3.115	3.330	3.379	3.857	3.650	3.752	3.823
$^1\sigma\sigma$	3.976	4.015	4.020	4.486	4.309	3.856	4.012
$^3\pi\pi$	0.076	0.151	0.204	0.739	0.793	0.745	0.538
$^3\pi\sigma$	0.592	0.666	0.723	0.847	0.875	0.982	1.051
$^3\sigma\pi$	2.975	3.049	3.157	4.329	4.614	4.320	3.762
$^3\sigma\sigma$	4.016	4.091	4.172	4.361	4.320	4.272	4.430

a) Threshhold values (μh) for perturbation selections are given.
b) Reference 3×3 CI.

As seen from Tables 2, 3, and 4, the energy splittings between the singlet biradical states become larger after the symmetry projections of the UHF solutions. The relative energies obtained by the ^{1}APUHF method are almost parallel to those from a 3×3 CI[27] using the UHF natural orbitals (UNO) and two biradical electrons {2,2} of **4**, **5**, and **7**, supporting the simple relation given by Eq. 5.

The rotational energy barriers for the terminal methylene group of **4**, defined as the energy difference between the EE ($\pi\pi$)(**4b**)- and FE($\sigma\pi$)(**4d**)-biradical conformations (Chart 5), are 11.2 and 8.0 kcal mol^{-1}, respetively, for the singlet state by the APUHF 4-31G and 6-31G**methods. The rotational barrier of singlet methyleneperoxyl is very close to 11 kcal mol^{-1} calculated at the RHF CI level by Hiberty.[34] The barrier is much smaller than that of formaldehyde due to the biradical property of **4**. Judging from the rotational barrier, the carbonyl betaine structure $H_2C{=}O^+{-}O^-$ of **4** is partly destroyed, giving rise to the decrease of the



4a(ZW) **4b**(BR)

Chart 5.

Table 3. Relative Energies (kcal mol^{-1}) of Low-Lyging Biradical States of C–O Cleavaged Oxirane by the UHF, APUHF, and UNO CASCI {2,2}/6-31G* $^{a)}$ Method

States	CH_2CH_2O (**5**)			CH_2OO (**4**)		
	UHF$^{b,c,d)}$	APUHF$^{d)}$	CI	UHF$^{b)}$	APUHF	CI$^{b)}$
$^1\sigma\sigma$	2.0(2.4)	2.0(3.0)	(0.7)	13.0(14.3)	18.2(21.7)	(18.9)
$^1\sigma\pi$	1.0(1.0)	2.3(2.5)	(2.4)	2.9(4.5)	8.0(11.2)	(10.4)
$^1\pi\sigma$	3.3(3.5)	4.2(4.6)	(4.8)	11.5(13.5)	14.0(17.2)	(17.4)
$^1\pi\pi$	0.0(0.0)	0.0(0.0)	(0.0)	0.0(0.0)	0.0(0.0)	(0.0)
$^3\sigma\sigma$	1.6(1.1)	1.1(0.5)	(2.5)	9.4(9.6)	11.4(12.5)	(17.5)
$^3\sigma\pi$	−0.8(−1.2)	−1.2(−1.8)	(−0.3)	−0.2(0.5)	1.7(3.4)	(8.3)
$^3\pi\sigma$	1.8(1.8)	1.4(1.2)	(2.5)	10.9(12.6)	12.8(15.5)	(17.3)
$^3\pi\pi$	−0.5(−0.6)	−0.9(−1.2)	(0.1)	2.0(3.2)	3.9(6.0)	(8.5)

a) 3×3 CI, b) Ref. 30. c) The optimized geometry of the $^1\sigma\pi$-states, wherer the optimized geometry of the $^1\pi\pi$-states was assumed for the $^1\pi\sigma$-, $^3\pi\sigma$, and $^3\pi\pi$-states. d) Values by the 4-31G basis under the assumption$^{c)}$ are given in parentheses.

C–O double bond character. The generalized π-bond order P_i in the EE(ππ)-biradical state is defined by the occupation number (n) of the bonding and antibonding pairs i as

$$P_i = (n_i - n_i{}^*)/2 = 1 - y_i \qquad (i = \text{HO etc}). \tag{6}$$

From Eq. 6, the bond order decreases with the increase of the biradical character, in agreement with the tendency recognized for the calculated rotational barriers. On the other hand, for the triplet state with the zero π-bond order, the rotational barrier from ππ- to σπ-biradical state is about −2 kcal mol^{-1}. The terminal methylene group of CH_2OO (**4**) exhibits essentially free rotation in the triplet state. For ethyleneoxyl (**5**)[6c] the rotational energy barriers for the terminal methylene group as calculated by the UHF and APUHF methods are very small in both the singlet and triplet biradical states. This tendency is in agreement with the large biradical character (over 80%) for the singlet state of **5**. The C–C bond of **5** is essentially a single bond, like that of propanol. The APUHF procedure is thus utilized for qualitative MO-theoretical studies of nondynamical correlation effects arising from quasi-orbital degeneracies in biradical species.

3. Possible HF Solutions for Unstable Molecules. The ππ-BR states of **1** and **2** are isoelectronic to the antiaromatic cyclopropenyl anion.[4b] Therefore, there are in principle several possible Hartree–Fock solutions for tricentric bisdesmiphiles. In fact, both singlet- and triplet-type instabilities occur for the RHF solutions of **1**, and **2** (Chart 6). From the singlet instability, the so-called bond-order alternating RHF solution (NRHF or complex charge-density wave (CCDW))[4] is obtained. The bond-length alternating geometry, A=B–C, by NRHF(CCDW) has only C_s-symmetry. However, the NRHF solution is unstable due to triplet instability.[4b] The most stable HF solution is the DODS UHF for 1,3-biradical species **1** and **2**, which gives a C_{2v} symmetric geometry, in agreement with MCSCF result.[35] On the other hand, the triplet instability does not occur for the isoelectronic SO_2, indicating the nonradical structure. Thus, possible electronic structures of reaction intermediates can be systematically examined by using the instability conditions.[4]

The constructions of the several Hartree–Fock solutions for biradical species and polyradical species are now feasible according to the instability check[2] and the mix procedure[4] of the RHF solution which are implemented in GAUSSIAN 94 program package.[16] On the other hand, trial orbitals constructed for the fragment free-radical orbitals often become efficient for UHF SCF calculations when RHF SCF calculations are divergent for biradical species.[4]

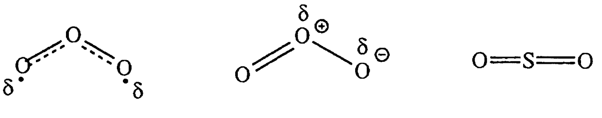

(UHF) (CCDW) (RHF)

Chart 6.

MP and CC SD(T) Calculations for Tricentric Bisdesmiphiles

1. MP and CC Corrections and Correlation Effects. As shown in Fig. 1, a systematic MO-theoretical description of both nonradical and biradical species is feasible on the basis of the Hartree–Fock solutions without instabilities. However, the major approximation in the Hartree–Fock MO method is the neglect of dynamical electron correlations between opposite spins. Such correlations are essential for investigations of relative stabilities between nonradical (NR) and biradical (BR) species. The RMP series are often largely oscillating if the zero-order RHF solution involves the triplet instability. On the other hand, UHF MP (UMP) energies for BR species are not oscillating but slow convergent since the UMP method for singlet biradical species suffers from spin contamination, indicating the necessity of spin projection.

As an alternative method for PMP by Schlegel,[21] the n-th order UMP energy for singlet biradicals can be improved by projecting out the triplet UMP energy.[15,22]

$${}^1E(\text{APUMP}n) = {}^1E(\text{UMP}n) + f'_{\text{sc}}(n)[{}^1E(\text{UMP}n) - {}^3E(\text{UMP}n)], \tag{4c}$$

$$f'_{sc}(n) = {}^1\langle S^2\rangle(\text{UMP}n)/[{}^3\langle S^2\rangle(\text{UMP}n) - {}^1\langle S^2\rangle(\text{UMP}n)]. \tag{7}$$

The fraction $f'_{\text{sc}}(n)$ of the triplet contamination involved in the ^{1}UMP wavefunction is given by Eq. 7. Although Eq. 4c is approximate in nature, it satisfies the so-called size-consistency condition since it utilizes the UMPn values themselves. In fact, Eq. 4c works well for semiquantitative calculations of effective exchange integrals in polyradical systems.[15,22] The dynamical correlation corrections by the n-th order MP (RMP, UMP, or APUMP) series are defined by

$$\Delta E_{\text{corr}}(n) = E(n) - E(n-1); \quad (n > 2) \tag{8}$$

The correlation energy at the n-th order MP level is given by

$$E_{\text{corr}}(n) = \sum \Delta E_{\text{corr}}(i) = E(n) - E(1) \tag{9}$$

where $E(1)$ is the UHF (APUHF) energy. Then the total correlation energy is given by the sum of the above dynamical part E_{corr} (n) and the nondynamical one; E_{corr} $(0)=E(1)-E(\text{RHF})$. Thus, in our MO-theoretical description of unstable molecules, the correlation corrections for closed-shell pairs are considered to be dynamical in nature.

2. Convergence Behavior of MP Series for BR Species. The RHF 3×3[27] suggests that the doubly excited configuration responsible for the biradical character can be included by the Moller–Plesset perturbation procedure.[19,22] In fact, the MP perturbation based on the RHF wavefunction (RMP) has been successfully used as a method for introducing electron correlation in many nonradical cases and in the case of species with weak biradical characters.[5] However, the convergence of RMP series should be carefully examined in the case of biradical species, since it is largely dependent on the magnitude of the biradical character. Figure 4A illustrates variations of energy differences between RHF and RMPn/6-31G* of CH_2NHCH_2 (**6**) in order to elucidate the convergence behavior From Fig. 4A, the RMP series for **6** with the small biradical character ($y=15\%$) converges smoothly and the resulting RMP total energy is almost equivalent to that of RCCSD(T). On the other hand, the total energy by UMP*n* is less stable by about 15 kcal mol^{-1} than the corresponding RMP*n* value, suffering from the spin contamination error. However, the PMP*n*, APUMP*n*, and RMP*n* series provided quite similar energies, as shown in Fig. 4A. This in turn indicates that RMPn is reliable for total energy calculations of azomethynium betaines as well as diazonium and nitrilium betaines because weak biradical characters do not entail the fall-off behavior in energy as illustrated in Fig. 2.

Figure 4B illustrates convergence behavior of CH_2CH_2O (**5**) with the strong biradical character. The correlation corrections by RMP*n*/6-31G* series are smaller than those of UMPn series, and the RCCSD(T) energy indicates the fall-off behavior, as compared with that of UCCSD(T). The latter situation is similar to the region III of bicentric systems shown in Fig. 1. On the other hand, the convergence behaviors of UMP*n*, PMP*n*, and APUMP*n* series are smooth, and the correlation corrections by these methods are quite similar. The UHF-based methods are rather reliable for 1,3-biradicals without octet stabilization as shown in Fig. 2.

Equation 4c was applied to estimating the correlation corrections for ozone (**1**) with the intermediate biradical character. In order to confirm the above 6-31G* results, the basis set dependency was also examined. Table 1 summarizes the total energies and correlation corrections for ozone (**1**) by the RMP*n*, UMP*n*, and APUMP*n* methods with the three different basis sets. From Table 1, the dynamical correlation energies at each level of computations increase with the increase of quality of the basis sets employed. Therefore, very large basis basis sets would be necessary for quantitative discussions of observables, which are sensitive to dynamical correlation corrections. The selections of basis sets should be carried out based on problems under consideration. The magnitude of the correlation corrections varies in the order: UMP*n*<PMP*n*=APUMP*n*<RMP*n* and this tendency is independent on the basis sets used. The RMP4 total energy is much deeper, as compared with that of RCCSD(T), because of the intermediate BR character of **1**. On the other hand, the energy stabilizations after the spin projection are 6.9, 15.2, and 16.6 kcal mol^{-1} by MP1, MP2, and MP4/6-31G* levels, respectively, showing that elimination of spin contamination error is essential in the case of UMP*n* series. Apparently, the rigorous treatments based on CASSCF are desirable for species in the intermediate correlation region II, as shown in Fig. 2.

Table 2 summarizes the correlation corrections for iminobis(methylene) CH_2NHCH_2, methylenebis(oxyl) OCH_2O (**2**), methyleneperoxyl CH_2OO (**4**), ethyleneoxyl CH_2CH_2O (**5**) by using the 6-31G* basis set. From Table 2, the stabilization energies by the approximate spin projection for methyleneperoxyl (**4**) are 5.3, 17.6, and 17.8 kcal mol^{-1} at UMP1, UMP2, and UMP4 levels, respectively. Judging from the magnitudes of these energy corrections, the spin projection is crucial at the UMP level. The spin projection is also crucial for other biradical species examined in Table 2. The correlation corrections PMPn and APUMPn close, showing that the latter works well for qualitative purposes.

MP2 method, which is not a variational method, is not necessary to guarantee the upper limit for the true energy. The APUMP2 wavefunction involves partly the contributions of triple and quadruple excitations from the ground configuration in the sense of RHF CI since APUHF for 1,3-biradicals is almost equivalent to the 3×3 CI (see Eq. 5). However, if the APUMP2 series is not oscillating and reliable, it can reproduce the total correlation energy given by the variational UNO MR SDCI[17,36] setting the 3×3 CI as the reference. Furthermore, APUMP4 correlation energy should be close to that of UNO MR SDCI {2,2} with Davidson correction.[37] The total correlation energies for biradical species in Tables 1 and 2 demonstrate the above expected relations. Judging from these results, APUMP4 for biradical species should correspond to the sixth-order RHF MP (RMP6) approximation, whereas APUMP4 for tetraradicals is close to RMP8. The APUMP4 method by the use of large basis sets is therefore a practical alternative to UNO MR SDCI for larger systems such as 1,3-biradicals clustered with solvents and polyradicals[15] since large-scale CI and RMP approaches are impractical for such systems.

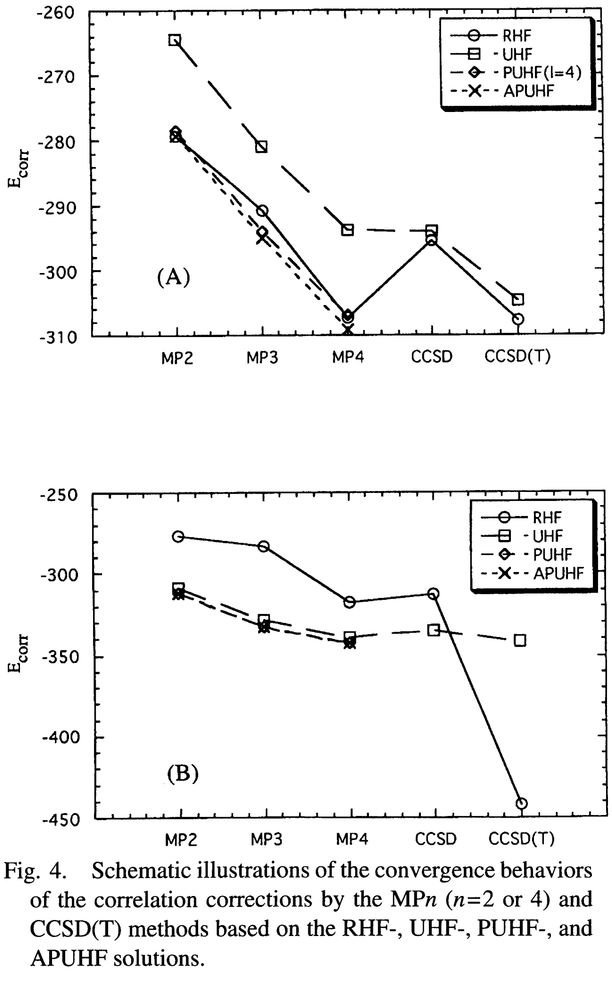


Fig. 4. Schematic illustrations of the convergence behaviors of the correlation corrections by the MP*n* (n=2 or 4) and CCSD(T) methods based on the RHF-, UHF-, PUHF-, and APUHF solutions.

3. Relative Stability between Ring and Open Forms of Tricentric Systems.

The open-form tricentric bisdesmiphiles A–B–C are usually formed by the ring-opening reactions of the corresponding ring compound (Chart 7). Since the three-membered ring compounds have three covalent bonds, the RHF MO description is feasible, showing the nonradical property in the present definition. Open forms are often biradicals described by DODS MO. Therefore, the relative energies ΔE_{RO} between the ring and open-forms should be sensitive to the computational methods employed, and these are defined by

$$\Delta E_{\mathrm{RO}}(\mathrm{X}) = E_{\text{open form}}(\mathrm{R(U)HF\ X}) - E_{\text{ring form}}(\mathrm{RHF\ X}), \qquad (10)$$

where X=MPn and CC SD(T). Table 5 summarizes the calculated results.

From Table 5, the following conclusions are drawn: (1) The RHF underestimates the stability of the biradical open-form of ozone (**1**), OCH_2O (**2**), CH_2OO (**4**), and CH_2CH_2O (**5**), while UHF, PUHF, and APUHF overestimate it. This is ascribed to the fact that these solutions involve the non-dynamical correlation energy for these species arising from the quasi-degeneracy of frontier orbitals, whereas the RHF solution of the ring form does not involve such a correction. (2) The RMP*n* (*n*=2 or 4) overestimate the stability of the biradical open-form of **1**, **2**, **4**, and **5**, and the UMP*n* (*n*=2 or 4) underestimate it. This is ascribed to the fact that the RMP*n* overestimate correlation energies for biradical species because of the fall-off phenomena (see Fig. 1), and the UMP*n* underestimate them because of slow convergence. (3) The RCCSD(T) method provides reasonable relative energies for **1**, **2**, and **4** except for **5**, as compared with the GVB-CI[38] The method is reliable enough for computations of relative stabilities between species with weak or intermediate biradical characters. (4) The relative energies by PMP and APUCCSD(T) are close for each species. The situation is similar between APUMP4 and GVB-CI[38] The PMP4 and APUMP4 can be used as convenient alternatives to GVB CI for biradical species. (5) Ozone (**1**) is a special molecule, since the biradical open-form is much more stable than the nonradical ring form.

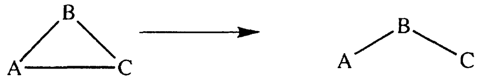


Chart 7.

Table 5. Relative Stabilities (kcal mol^{-1})[a] between the Ring and Open Forms by the RHF- and UHF-Based Methods

Methods	O_3 (**1**)	CH_2OO (**4**)	OCH_2O (**2**)	CH_2CH_2O (**5**)
RHF	1.2	41.8	82.8	101.4
UHF	−56.9	23.8	−32.8	24.2
PUHF	−69.2	9.7	−38.1	20.3
APUHF	−63.8	9.3	−33.9	21.7
RMP2	−34.6	35.6	5.3	100.0
UMP2	3.6	33.8	25.7	68.0
PMP2	−8.7	39.6	20.4	64.1
APUMP2	−11.6	28.1	23.4	64.2
RMP4	−34.8	30.2	1.7	82.9
UMP4	−9.9	48.4	18.1	61.7
PMP4	−21.6	35.4	12.8	57.8
APUMP4	−26.5	23.3	15.4	57.7
RCCSD(T)	−28.0	29.7	11.0	−41.5
UCCSD(T)	−22.8	34.0	13.8	58.7
GVB-CI	−28.1[b]	21.0[c]	13.9[c]	

a) Total energies of the ring form were calculated by the RHF-based methods. b) Ref. 38. c) Ref. 39.

From these results, it is concluded that examinations of biradical characters for species under consideration are important for understanding of reliability and convergence behavior of the post HF calculations employed. The RCCSD(T) method is usually reliable if the biradical character does not exceed over 50%, but the use of RMP*n* (*n*=2 and 4) should be careful if the biradical character exceeds over 30%. On the other hand, PMP*n* and APUMP*n* are useful for species with strong biradical characters (>50%), and it is noteworthy that the spin projection for UCCSD(T) is necessary for species in the magnetic region III in Fig. 1. As an example, Figure 5 schematically illustrates a typical energy diagram for nonradical (NR) and biradical (BR) states of OCH_2O (**2**) obtained by both RHF- and UHF-based computational methods. From Fig. 5, it is clear that computations of relative stabilities between NR and BR species are not simple tasks if these MO-theoretical methods are employed. The examination of BR character is at least desirable for confirming reliability of computational results as illustrated in Fig. 2.

Extended Systems Constructed of 1,3-Biradical Units

1. Singlet and Triplet Gaps. Since the UHF-based methods are practically useful in the magnetic region III Figs. 1 and 2, these are applicable to computations of the singlet (S) and triplet (T) energy difference for the 1,3 biradical species. The energy gap is important not only for understanding of biradical reaction mechanisms but also for magnetism. The spin projections for singlet UMP*n* wavefunctions should give substantial improvements for singlet–triplet gaps ΔE_{TS}, since the singlet UMP*n* often is heavily spin contaminated,

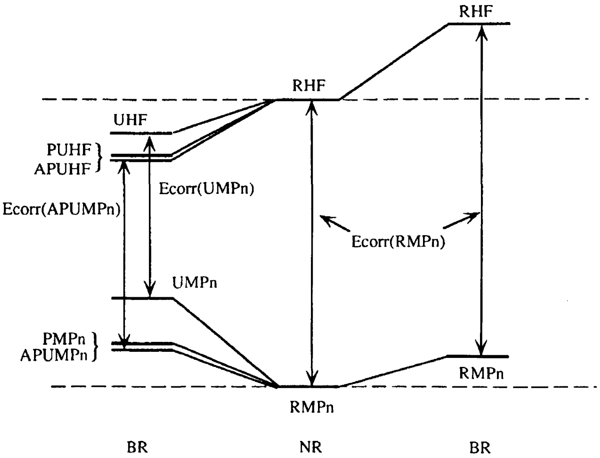


Fig. 5. The energy diagrams for the nonradical (NR) ring form and biradical (BR) open form of OCH_2O (**2**) by the RHF-, UHF-, and APUHF- based methods.

while the triplet UMP*n* is not. The S–T gap is defined by

$$\Delta E_{\mathrm{TS}}(\mathrm{XMP}n) = {}^1E(\mathrm{XMP}n) - {}^3E(\mathrm{UMP}n), \qquad (11)$$

where X denotes U or APU. Table 6 summarizes the S–T gaps for ozone (**1**) and CH_2OO (**4**) at the 6-31G** level. The S–T gaps by the UMP*n* wavefunctions increase approximately by a factor 2 after spin projection. The projected values are in much better agreement with experimental values than the unprojected values. The vertical S–T gaps for **1** are calculated to be 19, 41, and 44 kcal mol^{-1} at the APUHF, APUMP2, and APUMP4 levels. The latter values are consistent with the GVB-CI (37 kcal mol^{-1}) and experimental (39 kcal mol^{-1}) values[38] This clearly show that dynamical correlation correction is necessary for quantitative calculations of S–T gaps. The corresponding vertical S–T gaps for **4** are 31.1, 58.1, and 58.1 kcal mol^{-1}, at MP1, MP2, and MP4 levels, respectively, and the last value is close to that of the GVB-CI value (57.4 kcal mol^{-1}).[39] The method can reproduce the CI results based on GVB, and it provides reasonable S–T gaps, showing that it can be applicable to computation of the high- and low-spin gaps for other 1,3-biradicals and their clusters.[15c]

2. Polyradicals. Recently, 1,3-biradical species without octet stabilization are receiving attention as building blocks for organic ferromagnets[15c] As shown previously,[3a] we have elucidated the mutual relationship between the Heisenberg model and the UHF solutions in the strong correlation regime on the basis of the so-called spin correlation function given by the second-order density matrix.[40] The APUHF method can be applied to systems for which CASCI and CASSCF calculations are impossible because too many active orbitals are required. In fact, Eq. 5 suggests that APUHF can be utilized instead of CASCI for qualitative purposes. For example, a polyradical system is one of such typical examples.[15c]

Table 6. The Singlet and Triplet Energy Gaps (ΔE_{ST}) (kcal mol^{-1}) for Ozone and Methyleneperoxyl by the UMP and APUMP/6-31G** Methods

Methods	O_3 (**1**)	CH_2OO (**4**)
UHF	10.4	18.9
APUHF	19.0	31.1
UNO CASSCF {4,4}	18.1	32.3
UMP2	22.9	32.5
APUMP2	40.8	58.1
UMP4	24.7	32.5
APUMP4	43.9	58.1

Here, in order to show its utility, let us consider the species constructed of trimethylene biradical unit, H–(CH–CH_2)$_{N-1}$ CH–H (*N*=3, 5, and 7) **8** (Chart 8). The highest-spin (HS) and lowest-spin (LS) states of these species were calculated by the UHF/4-31G method. Judging from the spin alignments resulted, these states should be expressed by the spin Hamiltonian, which is given by

$$\boldsymbol{H}(\mathrm{HB}) = -2\sum J_{\mathrm{ab}}\boldsymbol{S}_{\mathrm{a}}\cdot\boldsymbol{S}_{\mathrm{b}}, \qquad (12)$$

where J_{ab} is the effective exchange integral between the nearest spins and $\boldsymbol{S}_{\mathrm{c}}$ is the spin at the site c (=a,b). The spin projection and calculation of J_{ab} were carried out in combination with UHF and the Heisenberg model, as described previously.[15] Table 7 summarizes the total energies of UHF and APUHF of the LS and HS states of **8**. From Table 7, the J_{ab}-value is positive, showing the ferromagnetic ground state.

The APUHF (UHF) method is easily extended to polymers with radical sites by using the cyclic boundary conditions.[15c] Thus, a merit of the APUHF approach is its applicability to ferro- (or antiferro-) magnetic extended systems where the spin polarization (SP) effect is remarkable, while GVB perfect pairing (PP) model[10] does not involve the spin-decoupling (SP) effect.

3. Difference between APUMP*n* and PMP*n*. Schlegel[21] has proposed the Löwdin-type[20] spin projection procedure for the UHF and UMP wavefunctions. His PUHF and PMP methods are usually effective for removal of the spin contamination errors, but the procedures are not size-consistent. Although such an error in PMP is not serious for depicting potential curves for biradical reactions, it might be serious in ab initio calculations of J_{ab} values in the magnetic region. As shown previously,[15c] the descriptions of the LS (singlet) and HS (quintet) states for the dimer of triplet methylene are not balanced in the case of the PUHF method, giving the finite energy difference (the size-inconsistent error) between these states even at the intermolecular distance *R*=10 Å. Here, as an example, let us consider the face-to-face dimer of triplet trimethylene, as illustrated in Fig. 6. The total energies of the singlet and quintet states of the dimer were calculated by PUHF and APUHF/4-31G. The energy

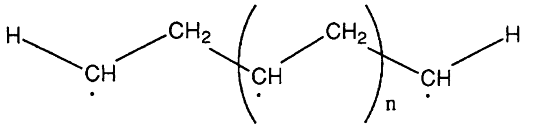


Chart 8.

Table 7. The Lowest Spin (LS) and Highest Spin (HS) Energies (a.u.), Total Spin Angular Momentums (in Parentheses) and J_{ab}-Values for H–(CH–CH_2)$_{N-1}$–CH–H by UHF-Based Methods

N	3	5	7
E_{LS}(APUHF)	−194.14804(0.750)	−348.79226(0.750)	−503.43651(0.750)
E_{LS}(UHF)	−194.14933(1.779)	−348.79491(2.800)	−503.44050(3.820)
E_{HS}(UHF)	−194.15134(3.800)	−348.79952(8.838)	−503.44769(15.875)
J_{ab}(cm^{-1})	218.9	250.3	260.8

gap between these states is given by 6 J_{ab} in the Heisenberg model in Eq. 12. Table 8 summarizes the calculated results.

From Table 8, the J_{ab}-values are negative by both methods, showing that the antiferromagnetic coupling between triplet trimethylenes is more favorable than the ferromagnetic coupling in the stacking mode examined here. The size-inconsistent error remains in the case of PUHF,[21] showing the large negative J_{ab}-value even at the dissociation limit R=6 Å, whereas APUHF does not involve such size-inconsistent errors.

Since the size-inconsistent errors are serious for discussion of magnetism in the case of PUHF by Schlegel,[21] it is interesting to examine whether the MP correction can remove such errors or not. The energy gap (6 J_{ab}) between the singlet and quintet states for the dimer of triplet trimethylene was calculated by APUMP2 and PMP2/4-31G. Table 8 summarizes the calculated results. The J_{ab}-values at the MP2 level are negative, indicating the antiferromagnetic ground state in the face-to-face stacking mode. The values given by PMP2/4-31G are largely negative even at R=6 Å, showing the size-inconsistent error. The MP2 correction does not remedy the error. It is, however, seen in Table 8 that PMP2(est.) estimated by subtraction of error at 6.0 Å is similar to APUMP2. This in turn indicates that APUMP2 does not suffer such errors and is therefore applicable to magnetic interactions between 1,3-biradical species.[15c,15d)]

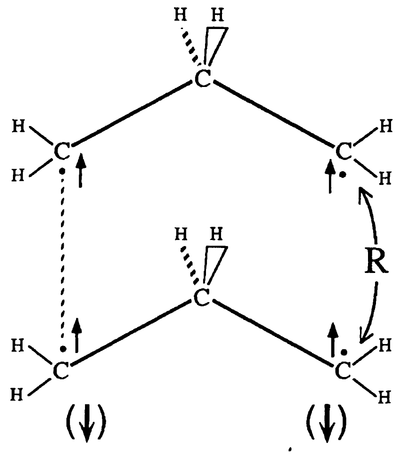


Fig. 6. The stacking structure between triplet trimethylenes. R denotes the intermolecular distance. Allows denote the ferromagnetic and antiferromagnetic (in parentheses) spin couplings in the dimer.

Table 8. Dependencies of J_{ab} Values (cm^{-1}) on Intermolecular Distance (R in Å) in dimer of Triplet Methylenes by Methods of the Spin Projected Wavefunctions

Method	R=3	R=4	R=5	R=6
APUHF	−929.7	−43.3	−0.8	−0.0
PUHF(l=1)[a)]	−40228.4	25309.0	22916.7	22878.1
PUHF(l=2)	−114.7	935.4	984.7	985.4
PUHF(l=3)	−1109.6	−207.7	−166.0	−165.1
PUHF(l=4)	−1067.6	−157.5	−115.3	−114.5
PUHF(l=5)	−1068.5	−158.5	−116.4	−115.6
PUHF(est.)[b)]	−952.9	−42.9	−0.8	0.0
APUMP2	−1209.0	−57.6	−1.1	−0.0
PMP2(l=1)	−40474.9	25234.9	22851.7	22813.3
PMP2(l=2)	−376.8	858.2	917.1	918.0
PMP2(l=3)	−1367.0	−286.6	−235.6	−234.5
PMP2(l=4)	−1325.4	−236.7	−185.2	−184.1
PMP2(est.)	−1141.3	−52.6	−1.1	0.0
APUMP3	−1182.2	−56.3	−1.1	−0.0
PMP3(l=1)	−40493.8	25184.4	22800.0	22761.6
PMP3(l=2)	−416.1	804.9	863.3	864.2
PMP3(l=3)	−1398.7	−341.2	−291.0	−290.0
PMP3(l=4)	−1357.6	−291.5	−240.8	−239.7
PMP3(est.)	−1117.9	−51.8	−1.1	0.0

a) see Ref. 21. b) values estimated by subtraction of error term at 6 Å from the PMP-values.

UNO CI for the Ground and Excited States of 1,3-Biradicals

1. UNO CASCI {2,2} and UNO MR SDCI {2,2} for Biradical States. Although the HF- and DFT-based approach is handy for theoretical treatments of the ground-states at each spin state, it is impossible for excited states in general. However, theoretical treatments of the excited states are particularly important for investigating mechanisms of photochemical reactions of tricentric biradical species. Here, the multireference (MR) configuration interaction (CI) method[6)] is employed for the well-balanced description of the ground and lower-lying excited states of the species, since the present MR CI[18)] is a direct extension of the DODS MO description of the ground biradical state.

Usually the selections of molecular orbitals and configurations are very important for effective MR CI calculations.[17,36,37)] In the present MO-theoretical approach, we use the natural orbitals determined by the corresponding orbital method[4,41)] based on the UHF solutions, which are available even for large molecules. The UHF natural orbitals (UNO) have the following desirable properties: (1) they are symmetry-adapted molecular orbitals, in contradiction to the GVB NOs which are bond orbitals; (2) they are the same before and after the spin symmetry projection,[41b)] allowing a direct extension of the DODS MO description for unstable molecules by the accurate MR CI wavefunctions; (3) the selection of active UNO is easily accomplished by using their occupation numbers as determined by a UHF calculation; (4) the full CI by the use of active UNO (UNO CASCI) gives the ground- and lower-excited wavefunctions which can be used as the references for MR single and double (SD) CI. The present MR CI approach is referred to as UNO MR SDCI because of the use of UHF NO (UNO) and its occupation number for selection of CAS.[18)]

The corresponding orbitals χ_i and η_i (i=0—4) used for MO-theoretical description of 1,3-biradicals are related to the the bonding and antibonding UNOs ϕ_i and $\phi_i{}^*$

$$\chi_i = \cos\theta\phi_i + \sin\theta\phi_i{}^*, \tag{13a}$$

$$\eta_i = \cos\theta\phi_i - \sin\theta\phi_i{}^*, \tag{13b}$$

where θ is the orbital mixing parameter determined by the DODS UHF MO calculation, and the occupation numbers of ϕ_i and $\phi_i{}^*$ are given, respectively, by $1+T_i$ and $1-T_i$ using the orbital overlap $(T_i=\langle\chi_i|\eta_i\rangle)$.[41] Table 9 summarizes the occupation numbers of the occupied and unoccupied UNO for several 1,3-biradical species by the UHF/6-31G** method. The occupation numbers for ozone (**1**) and related species indicate that these species are biradical species in the ground state since only the occupation numbers of LUMO are large. In fact the occupation numbers of the two natural orbitals of **1**, π_A and π_{S2}, are 1.292 and 0.708, respectively, at the UHF optimized geometry. Although the occupation numbers of LUMO+m ($m>0$) are small, these are important for discussions of spin polarization (SP) effects of closed-shell pairs and through-bond effective exchange interactions via the SP mechanism. Because the SP effect is small, three configurations constructed from π_A and π_{S2} are used as the reference configurations for the effective UNO CI calculations of the $^1S_0$-state. Since CASCI[18] arising from two-active UNO two-active electrons {2,2} gives the qualitatively correct description of the $^1S_0$ state of the $\pi\pi$-biradical species,[27] the MR SDCI setting these configurations as the reference should provide the reliable description of both the biradical character and SP effects in the $^1S_0$-state.

Table 4 summarizes the relative energies of the eight biradical states of iminoperoxyl (**7**). Both the APUHF and UNO CASCI {2,2}, the reference function, provide similar energy levels, confirming the relation in Eq. 5. The size of UNO MR SDCI is variable according to the accuracy required for problems under consideration, and the number of configuration state functions (CSF) generated by using the 4-31G basis set is selected by setting the magnitude of the threshold value for configuration selection by the perturbation method.[36] This procedure is practical for tricentric bisdesmiphiles with several substituents, which are actually used as reagents in 1,3-dipolar cycloadditions: it is noteworthy that the number of CSF becomes too large for MR SDCI of these species. The energy levels by UNO MR SDCI {2, 2} are the same as those of APUHF and UNO CASCI {2, 2}. The UNO MR SDCI {2,2} calculations clearly show that the APUHF wavefunction is useful enough for DODS MO description of the ground and lower-lying biradical states of tricentric systems with 1,3-biradical character. This implies that the ground state of 1,3-biradical species can be grasped in terms of the DODS MO's, χ_π and η_π,

$$^1\phi_{\mathrm{APUHF}} = |K\pi_{\mathrm{S1}}^2\chi_\pi\eta_\pi(\alpha\beta-\beta\alpha)|/\sqrt{2}, \tag{14a}$$

which is reduced to the closed-shell RHF MO in nonradical case. The accuracy of the APUHF wavefunction for a 1,3-biradical is almost identical to that of the traditional RHF wavefunction for nonradical closed-shell species. The UNO MR CI wavefunction for both states is therefore rewritten by:

$$^1\phi_{\mathrm{UNO\ MR\ SDCI\ \{2,2\}}} = {}^1\phi_{\mathrm{APUHF}} + {}^1\phi_{\mathrm{corr}}, \tag{14b}$$

where the second term corresponds to the sum of correction terms from the dynamical correlations which are not involved in the HF MO wavefunction.[18] Thus, the MO-type treatment is applicable to the nonradical and lower-lying radical states of tricentric bisdesmiphiles by the aid of the UNO MR SDCI {2,2} starting from the UNO CASCI {2,2} description, which is a general RHF in the sense of Sinanoglu.[33]

2. UNO CASCI {3,4} and UNO MR SDCI {3,4} for Well-Balanced Description of Biradical and Ionic States. The well-balanced description of both the ground and excited states is desirable even for qualitative discussions of photochemical reactions of tricentric bisdesmiphiles. Unfortunately, there is no criterion to check the stability of UNO CI wavefunction for the excited states of these species. However, the UNO MR SDCI starting from the UNO CAS for the ground state usually provides necessary information on lower-excited states. In fact, the UNO MR SDCI {2, 2} result indicates that the method is insufficient for the description of the lower excited singlet states of oxygenated dipoles since the weights of the reference functions for these states are poor as compared with that of the of the ground state. For example, the π_{S1}–π_{S2} excitation contributes considerably to the lower excited state, indicating that the π_{S1}-MO should be included as an "active" orbital for the well-balanced descriptions[17,18] of the ground and excited states of O_3, HNOO, CH_2OO, and CH_2CH_2O. The UNO CASCI {3,4} by the use of these three active UNO and four active electrons corresponds to the full valence π-CI of 1,3-dipolar species, and usually provides qualitatively correct CI descriptions of the ground and lower π-excited states of the species. Figure 7 illustrates the six reference configurations constructed of CAS {3,4}. The UNO MR SDCI {3,4}

Table 9. The Occupation Numbers of UNO for Bisdesmiphiles by the UHF 6-31G**(4-31G) Method

UNO	CH_2OCH_2	CH_2ONH	HNOO (**7**)	O_3 (**1**)	$CH_2CH_2CH_2$ (**3**)
LUMO+4	0.001(0.001)	0.001(0.001)	0.001(0.001)	0.001(0.000)	(0.001)
LUMO+3	0.001(0.001)	0.001(0.001)	0.002(0.001)	0.002(0.001)	(0.001)
LUMO+2	0.003(0.003)	0.003(0.002)	0.002(0.002)	0.002(0.002)	(0.003)
LUMO+1	0.004(0.003)	0.004(0.004)	0.003(0.003)	0.003(0.003)	(0.004)
LUMO	0.645(0.669)	0.723(0.730)	0.741(0.757)	0.708(0.727)	(0.921)
HOMO	1.355(1.331)	1.277(1.270)	1.259(1.243)	1.292(1.273)	(1.079)
HOMO-1	1.996(1.997)	1.996(1.996)	1.997(1.997)	1.997(1.997)	(1.996)
HOMO-2	1.997(1.997)	1.997(1.998)	1.998(1.998)	1.998(1.998)	(1.997)
HOMO-3	1.999(1.999)	1.999(1.999)	1.998(1.999)	1.998(1.999)	(1.999)
HOMO-4	1.999(1.999)	1.999(1.999)	1.999(1.999)	1.999(2.000)	(1.999)

wavefunction involves the important dynamical correlation corrections:

$$ {}^{1}\phi_{\text{UNO MR SDCI}}\{3,4\} = \sum C_i\phi_i(6\times 6) + \sum C_j\phi_j \quad (j\neq i) \qquad (15)$$

where the first term denotes the reference part and C_k ($k=i$ or j) is the CI coefficient. The normalized CASCI coefficients for the reference part {3,4} of UNO MR SDCI are calculated by

$$ {}^{1}\phi_{\text{R}} = \sum b_i\phi_i(6\times 6), \qquad (16)$$

where

$$ b_i = C_i/\sqrt{w}, \quad w = \sum C_i^2 \quad (i = \text{I—VI}). \qquad (17)$$

Table 10 summarizes the excitation energies (ΔE), weights (w) of the reference parts, and renormalized CI coefficients (b_i) obtained for XOO (X=O, NH and CH_2) and CH_2CH_2O.

3. Ground-State Properties by UNO MR SDCI {3,4}. As can be seen from Table 10, the weights (w) of the reference parts in the UNO MR SDCI {3,4} are over 90% for the ground states (${}^1S_0$) of XOO and CH_2CH_2O: The corresponding values are over 82% even for the excited states of the species. This guarantees the well-balanced CI descriptions of both the ground and π-type excited states of the species under consideration. The weights (w_I) of the ground configuration **I** in the UNO CASCI {3,4} reference wavefunctions for the ${}^1S_0$ are 74, 79, and 83%, respectively, for O_3 (**1**), HNOO (**7**), and CH_2OO (**4**), and 61% for CH_2CH_2O (**5**). Therefore, the open-shell (biradical) characters defined by $y=2\ (1-w_I)$, are 52, 42, and 34%, respectively, for **1**, **7**, and **4**, and 77% for **5**. The correction of the APUHF wavefunction for the ${}^1S_0$-state of O_3 is minor. However, the contributions of the configurations **IV** and **V** to the ${}^1S_0$-state of HNOO (**7**) and CH_2OO (**4**) are not negligibly small, compared with that of **II**. This implies that the zwitterionic structures are slightly introduced into the ${}^1S_0$-states of these unsymmetrical oxygenated dipoles in the UNO MR SDCI {3,4} approximation. The DODS MO structures •Y–O–O• (Y=CH_2 and HN) must be slightly modified by the inclusion of the zwitterionic structures: ${}^{+}$Y–O–O^{-} : this situation may be expected for other unsymmetrical oxygenated dipoles (XOY). As shown below, the biradical character of these species by APUHF is slightly reduced indeed after including the ionic term by the UNO CASSCF procedure. On the other hand, contributions of the zwitterionic structures are negligible for the ${}^1S_0$-state of CH_2CH_2O (**5**), although **5** is a strong unsymmetrical tricentric system.

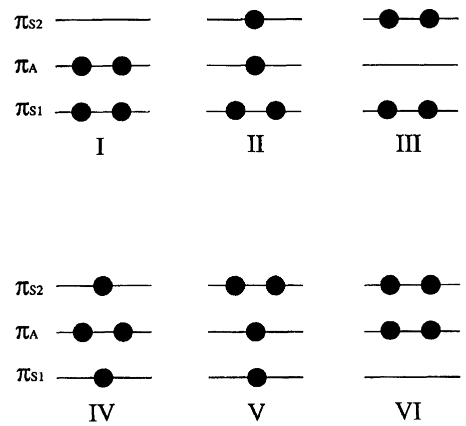


Fig. 7. The six orbital configurations **I**—**VI** constructed of the three-active delocalized UNO and four-active electrons for 1,3-dipolar species.

4. Excited State Properties by UNO MR SDCI {3, 4}. The excitation energy calculated for the first π-type excited (${}^1S_1$) state (Hartree band) of O_3 by UNO MR SDCI {3,4} is 5.73 eV, in excellent agreement with the observed excitation energy (5.6 eV),[42] and the GVB CI value by Hay and Dunning, Jr.[38] The excitation energy for the ${}^1S_1$-state of CH_2OO is 4.55 eV, which is almost identical to the GVB CI value for Wadt and Goddard.[10b] The corresponding value for HNOO is 5.01 eV. Therefore, the first excitation energy for XOO decreases with the decrease of symmetry: O<NH<CH_2. On the other hand, the tendency for XOO is reversed for the second π-type excitation energy.

Table 10. Excitation Enegies, CI Coefficients, and Weights of the References for XOO (X=O, CH_2, NH) and CH_2CH_2O by the UNO MR SDCI Method

Compounds	State	ΔE	b_I*						W
		eV	I	II	III	IV	V	VI	%
O_3	${}^1S_0$	0.0	0.86	−0.48	−0.04	0.0	−0.14	0.0	91
	${}^1S_1$	5.726	0.0	0.0	0.0	−0.75	0.0	−0.66	83
	${}^1S_2$	7.608	0.27	0.74	0.07	0.0	−0.62	0.0	82
CH_2OO	${}^1S_0$	0.0	0.91	−0.33	−0.05	0.15	0.16	−0.09	91
	${}^1S_1$	4.553	0.01	−0.60	0.03	−0.68	−0.26	0.33	87
	${}^1S_2$	10.00	−0.21	−0.55	0.10	0.50	−0.52	−0.37	89
HNOO	${}^1S_0$	0.0	0.89	−0.41	−0.04	−0.08	−0.17	−0.07	90
	${}^1S_1$	5.013	−0.04	−0.50	0.03	0.68	0.27	0.46	83
	${}^1S_2$	7.935	−0.21	−0.60	0.08	−0.42	−0.53	−0.35	84
CH_2CH_2O	${}^1S_0$	0.0	0.78	−0.62	−0.01	0.04	−0.04	−0.03	94
	${}^1S_1$	4.561	0.38	0.57	−0.02	0.68	−0.18	0.19	86
	${}^1S_2$	10.326	−0.39	−0.47	0.04	0.59	0.35	0.40	90

These results show that the UNO MR SDCI is reliable for MO-theoretical analysis of the excited states of these species. From Table 10, the UNO CASCI {3,4} reference wavefunctions for the excited state are written by the linear combinations of the three or four configurations constructed of the delocalized UNO. Since the reference part is the full CI wavefunction within the valence π-orbitals, it is invariant under the unitary transformation of the basis π-orbitals. This guarantees the transformation of the present MO CI wavefunctions into the VB-CI type wavefunctions. To this end, we define the localized natural orbitals (LNO) as the corresponding orbitals at the dissociation limit: θ=45° in Eq. 12.[30] where $\chi_{HO}=\phi_l$, $\eta_{HO}=\phi_r$ and $\pi_{HO-1}=\phi_c$. The LNO (ϕ_l, ϕ_c, ϕ_r) obtained are mainly localized on the left, central, and right atoms of the A–B–C system, respectively. For a symmetric A–B–A system such as ozone, the in- and out-of phase combinations of zwitterionic structures are resulted from this transformation as show in Fig. 8, whereas the remaining VB-structures are the covalent and dication–dianion (DCA) pair. For an unsymmetrical system, there are one covalent, four zwitterionic and one DCA structures obtained. It is noteworthy that these VB structures are defined by LNO instead of atomic orbitals in the true VB CI theory.

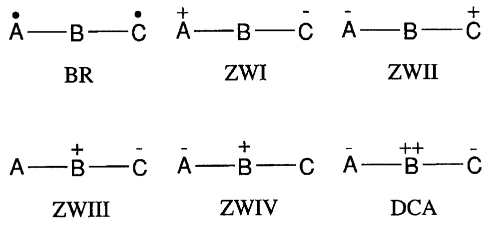


Fig. 8. Biradical (BR), zwitterionic (ZW), and dication–dianion (DCA) configurations given by the localized UNO (LNO).

As is apparent form Table 10, the first ($^1S_1$)- and second ($^1S_2$)-excited states O_3 are expressed by the linear combination of the out- and in-phase zwitterionic structures, respectively. The situations are similar for the $^1S_3$- and $^1S_4$-excited states of O_3. Therefore, the four lower π-excited states of O_3 are ionic. The same situation is expected for other tricentric systems. As an example of unsymmetrical systems, the MO- and VB-CI type coefficients for the 6×6 CI of CH_2CH_2O are shown in Table 11. From Table 11, the following relations are recognized:

$$\phi(^1S_0) = BR, \phi(^1S_5) = DCA, \tag{18a}$$

$$\phi(^1S_1) = d_1 ZW\ I - d_2 ZW\ II, \tag{18b}$$

$$\phi(^1S_2) = d_3 ZW\ III - d_4 ZW\ IV, \tag{18c}$$

$$\phi(^1S_3) = d_2 ZW\ I + d_1 ZW\ II, \tag{18d}$$

$$\phi(^1S_4) = d_4 ZW\ III + d_3 ZW\ IV, \tag{18e}$$

where the coefficients (d_i) correspond to those of the VB CI based on LNO. The four lower π-excited states are expressed by the linear combinations of two zwitterionic structures in the VB-CI sense, respectively. The ground- and highest-excited states are described as covalent and dication–dianion pair respectively. These results are not changed by UNO MR SDCI {3,4} as can be recognized from the CI coefficients in Table 10. The similar relations are recognized for CH_2OO and HNOO although the contributions of the covalent structure to excited states of these species are not negligible. The ratio $\gamma_1=d_1/d_2$ decreases with the decrease of the unsymmetry: $CH_2CH_2O > CH_2OO >$ HNOO. On the other hand, the ratio $\gamma_2=d_3/d_4$ is almost constant (1.0) for these species. Apparently, the VB-CI type expressions of the CAS or MR CI wavefunctions based on the localized UNO (LNO) are useful for qualitative explanations of the excited states of XOO and CH_2CH_2O as illustrated in Fig. 2.

Probably the situations are similar for π–π* excited states of other A–B–C species. The UNO CI procedures presented above are equally applicable to other (σσ, σπ, πσ) biradical states. As an example, Table 4 summarizes the calculated results for iminoperoxyl HNOO. In conclusion, the UNO

Table 11. Excitation Enegies, CI Coefficients for the Ring-Opend Oxirane (CH_2CH_2O) by the UNO CASCI {3,4}/4-31G Method

States	ΔE		CI coefficients					
	eV		C_1	C_2	C_3	C_4	C_5	C_6
$^1S_0$	0.0	MO	0.746	−0.666	−0.007	−0.001	0.004	−0.003
		VB	0.998	0.039	0.041	0.005	0.001	−0.007
$^1S_1$	8.826	MO	0.428	0.476	−0.030	0.673	−0.242	0.279
		VB	−0.034	0.928	0.024	−0.368	0.026	−0.030
$^1S_2$	11.745	MO	−0.344	−0.386	0.059	0.461	0.502	0.515
		VB	0.030	−0.039	−0.691	0.009	0.719	0.059
$^1S_3$	15.331	MO	0.167	0.193	0.041	0.267	0.671	−0.642
		VB	−0.018	−0.369	0.009	−0.928	0.021	0.041
$^1S_4$	18.672	MO	0.338	0.379	0.022	−0.513	0.483	0.495
		VB	−0.029	0.004	0.721	−0.008	0.692	0.022
$^1S_5$	32.047	MO	0.024	0.016	0.997	−0.007	−0.075	−0.007
		VB	0.006	0.015	0.025	0.048	−0.058	0.997

a) MO: C_1=I, C_2=II, C_3=III, C_4=IV, C_5=V, C_6=VI; VB: C_1=BR, C_2=ZWI, C_3=ZWII, C_4=ZWIII, C_5=ZWIV, C_6=DCA.

CASCI and UNO MR SDCI provide semi-quantitative descriptions of both the ground and lower-excited states of tricentric bisdesmiphiles from the MO-theoretical view point. The VB explanations of these CI results for biradical species are feasible using the localized UNO (LNO) (see Fig. 2). The reduction of UNO MR SDCI to the second-order perturbation scheme starting from UNO CASCI and UNO first-order (FO) CI schemes were discussed in Ref. 18c. It is noteworthy that our MR MP2 based on UNO CASCI and UNO FOCI is a direct extension of the PMP2 and APUMP2 for the ground state and it reduces to CIS MP2[16)] in the case of closed-shell species for which CIS=UNO FOCI.

CASSCF Calculations of Tricentric Bisdesmiphiles

1. UNO CASSCF Calculations. The preceding MO description by the best Hartree-Fock solution without instabilities followed by the MP perturbation and UNO CI corrections can be utilized for semi-quantitative discussions of relative stabilities of both stable and unstable tricentric bisdesmiphiles in the ground and excited states.[6,18)] However, for more quantitative investigations of relative stabilities of their nonradical and biradical states, more rigorous treatments are necessary. There are two different approaches for further refinements of the *R*(UMP) and UNO CI wavefunctions: one is to incorporate the higher-order excitations from the *R*(UHF) reference state by the use of the coupled-cluster (CC) type approximation:[18)] the single (S), double (D), and higher excitation operators are necessary when the HF single determinant is used as a starting point. The other is the multireference (MR) CC approach where the multideterminants are used for the reference in order to limit the excitation operators at the S and D levels. In our MR CC approach,[18)] the zero-order wavefunction is taken as UNO CAS CI one. Therefore, the MR CC single (S) wavefunction is nothing but the UNO CASSCF wavefunction as shown previously.[18)] The detailed analysis of the UNO CASCI or MR

$$\Phi_{\mathrm{UNOCASSCF}} = \Phi_{\mathrm{MRCC}} = \exp\{T_1\}\,\Phi_{\mathrm{UNOCASCI}}. \qquad (19)$$

SDCI results[18)] showed that UNO and its occupation number should be useful for constructing effective trials for full valence MCSCF or CASSCF[23—25)] wavefunctions. In fact, Pulay's group[25)] has clarified the rapid convergence behaviors of the CASSCF calculations starting from the trial vectors given by UNO CASCI. We have also shown that the UNO CASSCF procedure was successfully applied to medium-size polyradicals, as shown previously.[18)]

In order to confirm the APUHF and UNO CASCI $\{2,2\}$ results, we first carried out the UNO CASSCF $\{m,m\}$ calculations of the ground state of ozone (**1**) varying the CAS space from $m=2$ to $m=8$ in conformity with the occupation numbers given in Table 9. The correlation corrections obtained by these computations are summarized in Tables 1 and 2. The nondynamical correlation correction for **1** by UNO CASSCF $\{2,2\}$ is almost equal to that of APUHF in all the basis sets examined here. The situation is the same for other 1,3-biradical species (**2**, **4**, **5**, **6**) as shown in Table 2. Similarly, the nondynamical correlation energies of trimethylene (**3**) were 87 and 93 kcal mol^{-1}, respectively, by UNO CASSCF $\{2,2\}$ and $\{4,4\}$/6-31G*, in agreement with that 92 kcal mol^{-1} of APUHF. The dynamical correlation corrections obtained by UNO CASSCF ($m>2$) are larger than those of UNO CASCI ($m>2$), indicating that UNO's except for biradical pairs of **1** are significantly improved by the CASSCF procedure. However, the occupation numbers of LUMO+1 and LUMO+2 by UNO CASSCF $\{6,6\}$/6-31G* are only 0.048 and 0.037, which are about one-tenth of the occupation number of LUMO, indicating that the biradical characters of the π_{S1}- and OO σ-bonds are only 10 and 8 (%), respectively. This in turn indicates that ozone (**1**) and related tricentric bisdesmiphiles are essentially biradicals in nature even at the CASSCF level, since the occupation numbers of LUMO+m ($m\neq 0$) except for LUMO are negligible.

2. Full Geometry Optimizations by UNO CASSCF. The biradical characters of tricentric bisdesmiphiles are dependent on the geometries employed. As shown previously,[6)] the energy gradient method based on UHF and UMP solution was conveniently used for full geometry optimizations of biradical intermediates. This technique was certainly useful for qualitative studies of geometrical structures of the species, but it often suffered from spin contamination errors, particularly in the case of singlet biradicals. On the other hand, the UNO CASSCF energy gradient technique has no limitation for locations of transition structures of biradical reactions and full geometry optimizations of biradical intermediates As an extention of previous works,[5,6)] it was applied to the full geometry optimizations of tricentric bisdesmiphiles.

The optimized O–O bond lengths of ozone (**1**) are 1.351 and 1.561 Å, respectively, by UNO CASSCF $\{2,2\}$ and $\{6,6\}$ with the 4-31G basis set. The corresponding values for HNOO (**7**) are 1.336 and 1.483 Å, respectively. The present and other results[38)] show that the 4-31G basis set is insufficient for depicting the potential curves of the O–O bond dissociation in oxygenated dipoles. At least the 6-31G** and more flexible basis sets are crucial for the geometry optimizations. Table 12 summarizes the optimized geometrical parameters of several tricentric bisdesmiphiles by UNO CASSCF/6-31G** method.

The O–O length of **1** by the use of CAS $\{2,2\}$ and $\{6,6\}$ are 1.256 and 1.296 Å, respectively: these are shorter and longer by 0.02 Å than the experimental value (1,278 Å). The inclusion of the antibonding O–O σ-bond (LUMO+2 in Table 9) at UNO CASSCF $\{6,6\}$/6-31G** gives rise to the overestimation of the O–O length. However, the O–O length by CASSCF $\{6,6\}$ is close to that 1.299 Å of GVB CI. This in turn suggests that more larger CAS ($m>6$) and extended basis sets are desirable for rigorous investigations of the geometrical structures and potential curves of **1** and related species. Although such rigorous treatments are crucial for reaction dynamics simulations, these problems are out of our present purpose of classification and characterization of 1,3-dipolar species, in relation to their theoretical descriptions by Huisgen,[7)] Firestone,[11)] Goddard,[10)] and ours.[1—5)] In fact, several MO-theoretical techniques examined here are

Table 12. The Optimized Bond Length and Angles of Bisdesmiphiles by the UNO CASSCF/6-31G** Method

Systems	UNO CASSCF {2,2}		UNO CASSCF {6,6}	
	$R_{A-B}$$(_{B-C})$	∠ABC	$R_{A-B}$$(_{B-C})$	∠ABC
CH_2NHNH	1.323(1.297)	126.8	1.340(1.301)	126.7
CH_2NHO	1.304(1.241)	127.9	1.319(1.247)	127.9
NHNHNH	1.273(1.280)	127.8	1.269(1.284)	127.7
NHNHO	1.256(1.222)	129.1	1.278(1.226)	129.2
ONHO	1.203	127.4	1.216	127.6
OOO (**1**)	1.256	115.2	1.296[a)]	114.2[a)]
HNOO (**7**)	1.298(1.258)	115.5	1.327(1.303)	114.4
CH_2OCH_2	1.313	127.5	1.311	127.9
CH_2ONH	1.310(1.307)	120.3	1.305(1.307)	120.7
OCH_2O (**2**)	1.359	117.7	1.386	117.6
CH_2CH_2NH			1.495(1.450)	112.8
$NHCH_2NH$	1.438	122.5	1.441	122.3

a) Experimental values are 1.278 Å and 116.8°, respectively.

useful for characteristics of these species as shown in Fig. 2.

The O–O bond length of **7** by UNO CASSCF {2,2} and {6,6}/6-31G* are 1.258 and 1.303 Å, respectively. Judging from the results for **1**, the intermediate bond length (R(O–O)={1.258+1.303}/2=1.280 Å) seems reasonable for **7**. The C–O, C–N, and O–N bond lengths for other 1,3-biradicals in Table 12 are not so dependent on the magnitude of CAS. The A–B–C angles are also insensitive to the size of CAS. The optimized C–N and N–O lengths of CH_2NHO by UNO CASSCF {6,6}/6-31G* are 1.319 and 1.247 Å, respectively. These are close to the experimental values (R(C–N)=1.296—1.327 and R(N–O)=1.274—1.300 Å).[5)] Although experimental results are not available for other 1,3-biradical species, the optimized bond lengths and angles by UNO CASSCF in Table 12 should be reliable for semiqunatitative discussions of the ground state geometries of tricentric bisdesmiphiles.

3. Biradical Characters by UNO CASSCF. The biradical character at UNO CASSCF {*m*,*m*} is defined as twice the occupation numbers of the LUMO, as an extension of its APUHF definition (Eq. 3). Table 13 summarizes the biradical characters calculated by UNO CASSCF {*m*,*m*} (*m*=2 or 6) at each optimized geometry. The biradical character of **1** is calculated to be abnormally large at the optimized geometry by UNO CASSCF {2,2}/4-31G because the O–O bond is largely broken at this computational level. The situation is similar in the case of **4**. On the other hand, the biradical character of oxygenated dipoles XOY (X,Y=CH_2, NH) are about 38—40%, by UNO CASSCF {2,2} and {6, 6}/6-31G*, whereas those of APUHF are 40—55%. The APUHF overestimates the biradical character. However, the biradical characters by both methods are quite reasonable in comparison with those of other methods.[38)] The biradical characters of azomethyne betaines XNHY (X, Y=CH_2, NH, and O) by UNO CASSCF are in the range; 10—20%, showing weak biradical characters. The biradical characters of 1,3-biradicals XCH_2Y without the octet stabilization are over 80%. Judging from the numerical values in Table 13, APUHF becomes a good approximation to UNO CASSCF for species in the so-called magnetic regime.[18b)]

Table 13. Biradical Characters (%) of Bisdesmiphiles by the APUHF and UNO CASSCF Methods[a)]

Molecules	4-31G			6-31G*		
	APUHF	CAS1	CAS2	APUHF	CAS1	CAS2
CH_2NHNH	18	23		15	19	17
CH_2NHO	10	17	14	6	14	12
NHNHNH	19	23	21	15	18	16
NHNHO	14	20	17	9	14	13
ONHO	16	22	19	5	14	13
O_3 (**1**)	49	62	84	46	40	37
HNOO (**7**)	55	50	54	53	39	36
CH_2OCH_2	40	38	37	37	36	34
CH_2ONH	50	41	41	49	35	32
NHO_2	54	55	68	52	38	35
OCH_2O (**2**)	80	84	83	80	80	78
CH_2CH_2NH	80	90	90			90
$NHCH_2NH$	77	82	81	78	81	82

a) CAS1=UNO CASSCF {2,2} and CAS2=UNO CASSCF {6, 6}.

CASSCF MP2 Calculations of Tricentric Bisdesmiphiles

Judging from the UNO CASSCF(=UNO MR CC S) results, the double excitation (D) operator in Eq. 9 is desirable for more quantitative purpose, leading to the MR CC SD approach. However, the MR CC SD calculations are time-consuming for larger systems, and therefore MR CC SD is truncated at the second-order perturbation (MP2) level, providing the UNO CASSCF MP2 (CASMP2) approximation for dynamical correlation corrections if virtual orbitals are appropriately improved. The preceding UNO MR SDCI {3,4} results show that at least the average CASSCF {3, 4} is necessary for well-balanced descriptions of both the ground biradical and lower excited ionic states of tricentric bisdesmiphiles and for effective computations of the correlation energies at the second-order (MP2) level. However, the UNO MR SDCI {2,2} results indicates that UNO CAS {2,2} is sufficient in the ground state for the state-specific multireference (MR) MP2. As an example, let us consider the dynamical correlation corrections for ozone (**1**) by the MP2 method based on the UNO CASSCF {2,2}. The results are given in Table 1. From Table 1, the correlation energy by UNO CASMP2 {2,2} by GAUSSIAN94[16)] is close to those of UNO MR SDCI {2,2} and APUMP2, whereas UNO CASMP2 {2,2} by HONDO95[26)] provides a correlation correction similar to those of UNO MR SDCI {2,2} with Davidson's correction[37)] and APUMP4. These results in turn indicates that the reference space {2,2} is appropriate, showing that both the perturbation and variation methods based on {2,2} provide quite similar MO descriptions of ozone (**1**).

In order to confirm the above tendency, the CASMP2 calculations were carried out for typical 1,3-biradical species by using the CASMP2 scheme implemented in GAUSSIAN94.[16)] Table 2 summarizes the calculated results. From Table 2, the magnitude of the correlation corrections for each 1,3-biradical species examined here decrease in the order: APUMP4 > UNO CASMP2 {2,2} > APUMP2. The APUMPn (n=2 or 4) can reproduce qualitatively the UNO CASMP2 {2,2} results. This in turn indicates that the UNO CASSCF coupled-cluster (CC) SD(T) (CASCC SD(T))[18] is necessary for refinements of the RCCSD(T), UCCSD(T), and APUCCSD(T) results for **1**, **2**, **4** etc. Probably, these tendencies are not changed for other 1,3-biradical species. Thus, the present ab initio computations reveal that a systematic MO-theoretical description of tricentric bisdesmiphiles is feasible by using several computational techniques examined here: Their selections are generally dependent on purposes and systems under consideration, as illustrated in Fig. 2.

Theoretical Classifications of 1,3-Dipoles

1. Relations to Huisgen's Classification of 1,3-Dipoles. (A) DODS MO Description. In this section, we examine qualitative ideas for theoretical descriptions of reaction intermediates from present computational results. As shown in Fig. 2, Huisgen[7] classified tricentric bisdesmiphiles into four groups; (1) type A: diazonium betaines, (2) type B: azomethinium betaines and carbonyl betaines, (3) type C: nitrilium betaines, and (4) type D: 1,3-dipoles without octet stabilization The present MO description is consistent with this classification. The DODS MO description reduces to a traditional closed-shell MO description for the type A and C species such as diazomethane and related diazonium betaines. Experimental data for 1,3-dipolar cycloadditions of type A and C species have been rationalized by frontier orbital theory on the closed-shell RHF approximation.[7] In fact, the reactions of diazonium and nitrilium betaines are all characteristic of closed-shell species, as summarized in the review article.[5]

On the other hand, the present MO descriptions for the ground states of carbonyl betaines: ozone (**1**), methyleneperoxyl (**4**), and iminoperoxyl (**7**) are DODS type, showing the moderate biradical character: The y-values by APUHF/6-31G* are 46,40, and 52% for **1**, **4**, and **7**, respectively. On the other hand, the biradical character is very strong for 1,3-dipoles without octet stabilization: methylenebis(oxyl) (**2**), trimethylene (**3**) and ethyleneoxyl (**5**): The biradical characters are 80, 84, and 82% for **2**, **3**, and **5**, respectively. The DODS MO descriptions[1—6] of these species are close to those afforded by the generalized VB (GVB) method[10] as illustrated in Fig. 3. The present DODS MO descriptions are wholly compatible with Huisgen's classifications of 1,3-dipolar species on the ground of experimental data.[5,7]

(B) UNO CASSCF Description. Experimental results for 1,3-dipolar species and 1,3-dipolar cycloadditions[7] can be understood on the basis of the UNO CASSCF results by using the occupation numbers of natural orbitals. The azomethinium betaines (type B) have weak biradical character: 10—20% at the UNO CASSCF {2,2} and {6,6} level. Judging from these small values, the reactions of the species should be closed-shell type, in accord with Huisgen's experimental results.[7] On the other hand, the biradical character is 36—40% for carbonyl betaines (or oxygenated dipoles), so that none of them have a stable C–O double bond, in accord with small rotational barriers. The reactions of oxygenated dipoles should be complex because they belong to the intermediate correlation regime: Both biradical and concerted reactions are feasible, depending on the environmental effects such as solvent, temperature and other reaction conditions. In fact, experimental results for oxygenated dipoles are rather complex.[5] Judging from the large biradical character of 1,3-dipoles without octet stabilization, these species are actually the 1,3-diradicals instead of 1,3-dipoles, exhibiting the biradical type reactions. Thus, the biradical characters based on UNO CASSCF are wholly consistent with Huisgen's classifications of 1,3-dipolar species and various experimental data on 1,3-dipolar cycloadditions.

2. Relations to Firestone's Arguments on Biradical Character. Firestone[11] has utilized the VB descriptions of 1,3-dipolar species presented by Linnett[12] to explain the mechanism of 1,3-dipolar cycloaddition. Since the Linnett's wavefunctions are written as the VB CI forms by use of atomic orbitals, these should be transformed into the CI expressions based on the natural orbitals (NO) defined by Löwdin,[20] providing a unique criterion describing the biradical character. As an example, the NO's and their occupation numbers of ozone and allyl anion were calculated by diagonalizing the first order density matrices derived from the RHF, full VB CI simple VB, extended Hartree–Fock (EHF) and spin optimized (SO) SCF wavefunctions presented by Linnett et.al.[12] The NO's of O_3 and allyl anion are C_{2v}-symmetry adapted in all the cases like those of the RHF, UHF, and CASSCF solutions. However, the occupation number of the NOs are different among the computational methods. The BR characters (y) of ozone are estimated by the occupation numbers of the LUMO (S_2). They are 32% by the full VB CI, 68% by the simple VB, and 50% by the EHF, respectively. The last value is close to the GVB CI and present UNO CI values. While, the full CI value is compatible with the UNO CASSCF value and the value redefined by using the VB CI wavefunction of Hiberty and Leforestier.[29] Thus the BR character of ozone is at most 50%, even if the Linnett's VB and VB-CI wavefunctions are used. On the other hand, the BR character of allyl anion is 12% by the full VB CI, although the VB-type wavefunctions overestimate its BR character. The present MO theory indicates no BR character for allyl anion since APUHF reduces to RHF. There is no significant discrepancy between the MO CI and VB CI descriptions of ozone and allyl anion if the natural orbitals (NO) and their occupation numbers are employed as the common basis for their comparisons. Thus, at least in our definition, there is no serious discrepancy among Huisgen,[7] Firestone,[11] and Goddard[10] arguments on biradical characters of 1,3-dipolar species. It should be noted again that the present MO-theoretical results are consistent with Huisgen's experimental results.[7]

3. Relations to Hiberty–Leforstier Arguments on Biradical Character. Further theoretical aspects of description of the biradical and zwitterionic characters are briefly discussed in relation to Hiberty–Leforstier discussions on biradical character. For the nonradical ground state of H_2 molecule by the simple MO theory, the weights of the covalent and ionic VB structures are 50 and 50%, respectively, indicating that stable H_2 molecule has 50% biradical character if the covalent structure (°H···H°) in the simple VB structure is regarded as a biradical (BR) structure responsible for biradical type reactions. Similarly, the ground MO configuration $G=|K\pi_{S1}^2\pi_A^2\pi_{S2}^0|$ for oxygenated dipoles (XOY) involves about 25% biradical character, if the covalent structure °X–O–Y° in the simple VB theory is defined as the BR structure for the species. Hiberty and Leforstier (HL) have performed the transformations of the MO and MO CI wavefunctions for XOY species into the simple VB CI wavefunctions defined by atomic orbital bases.29) Their results indicate that the ground MO configuration of XOY involves about 20% covalent structure in the simple VB theory. However, the MO and simple VB treatments of biradical character are different for the XOY species, just as they are in the case of the H_2 molecule.

Hiberty and Leforstier (HL)29) explained the biradical properties of XOY species by the weights of the covalent structures in the simple VB theory. The weights of the covalent structures °X–O–X° in the simple VB theory increase after the configuration mixing between the ground and the doubly excited (D) configurations in the MO CI and the contributions of the ionic structures $^+$X–O–Y$^-$ and $^-$X–O–Y$^+$ in the simple VB theory decrease as in the case of the CI for H_2 molecule. In fact, the corresponding increases of the covalent VB structures by the HL's CI are 34, 33, and 38%, respectively, for CH_2OCH_2, CH_2OO, and O_3. These increments by the VB CI are approximately equal to the biradical character defined for these species in the present MO-description. The simple VB CI and MO pictures for XOY species are compatible. Under this definition, the biradical character of diazomethane is calculated to be 12% by HL's CI result. In fact, any closed-shell MO pair has about 10% biradical character in the VB-type formulation, although it is relation to the biradical reactivity. On the other hand, diazomethane and diazonium betaines are nonradical in the MO theory, as shown in Table 14, since the DODS UHF solution reduces to the RHF solution.

The HL-type expansion29) is feasible for any wave function of a XOY species constructed of the minimum basis set. The simple VB CI type expansions are certainly useful for the explanations of excited states of both symmetrical and unsymmetrical A–B–C systems such as O_3 and CH_2OO. Unfortunately, the HL formulations become impractical if 1, 3-dipoles with substituents are investigated, although the VB CI concepts are still useful for the qualitative explanations of these species. On the other hand, the present transformation of the UNO CASCI wavefunction into the VB-CI type wavefunction based on localized NO (LNO) is always possible for any molecules, since it is based on the transformation of basis MO's instead of basis AO's.

Table 14. The Orbital Overlaps (T_{HO}) and Biradical Characters (y_i) by the DODS MO, UNO CASCI, and GVB Methods

Compounds	GVB		DODS MO		UNO CAS CI
	T_{HO}	y_i	T_{HO}	y_i	y_i
$CH_2CH_2CH_2$(**3**)	0.1	80	0.074	85(80)	80
CH_2CH_2O(**5**)				77	77
O_3 (**1**)	0.28	48	0.252	53(50)	54
HNCO (**7**)			0.278	49	42
CH_2OO (**4**)	0.346	38	0.317	42	34
CH_2NHCH_2 (**6**)			0.539	22	
$CH_2N{=}N$	0.600	12	1.000	0	
$CH_2C{=}O$	0.696	6	1.000	0	
$CH_2{=}O$	0.628	10	1.000	0	
$NH_2CH{=}O$	0.689	7	1.000	0	
$CH_2{=}CH_2$(MB)	0.578	13			
(DZ)	0.631	10			
(POL)	0.644	9			
$CH_2NHO(H_2O)_n$			1.000	0	
$CH_2OO(H_2O)_n$			1.000	0	
CH_2CH_2CO(M^+ ion)			1.000	0	

4. Comparison between GVB and DODS MO Descriptions. The expression of the biradical character is the same between the GVB and DODS MO theories.13) Both theories provide similar orbital overlaps T_{HO} between the biradical orbitals χ_π and η_π for tricentric systems with moderate 50% and strong 80% biradical properties, as shown in Table 14. Similar biradical characters for these species are also obtained from the extensive MR CI results as shown in Table 14. Therefore the biradical characters for the species are common: independent on the computational methods used.

The biradical characters (y) of ozone (**1**) and methyleneperoxyl (**4**) have been stressed in relation to ozonolysis reactions of olefins in gas phase by Goddard and his collaborators from the GVB theoretical viewpoints.10) The y-values of **1** and **4** are calculated to be 48 and 38%, respectively, using the orbital overlaps (T_{HO}) determined by the GVB theory. This in turn indicates that the ground states of **1** and **4** are far different from the pure covalent structures in the simple VB theory, even if the ab initio VB-type method is employed. In this sense, the GVB orbitals of **1** and **4** are regarded as the "DODS" orbitals determined by the ab initio VB techniques, which are essentially the limited MCSCF procedures.24)

It is, however, noted that the GVB and DODS MO descriptions are apparently different for stable closed-shell species. For example, the orbital overlap T_{HO} between χ_π and η_π by the APUHF method becomes 1.0 for formaldehyde, formamide, and ethylene: The APUHF solutions reduce to the traditional RHF solutions. Similarly the transition from APUHF to RHF occurs in the course of clusterings of waters to methyleneperoxyl, in accord with the transition from its biradical to zwitterionic state by solvation. Therefore these species and solvated methyleneperoxyls are closed-shell species in the MO theory. On the other hand, the T_{HO}-values by the GVB method are much smaller than 1.0 even for these species, as shown in Table 14.43) Therefore, these species have 6—12% biradical characters in the GVB theory.

However, these values are not responsible for radical reactivities of the complexes. Similarly, diazomethane has 12% biradical character: according to Walch and Goddard, it is a biradical.[39] Since the GVB wavefunction involves partly an intrapair dynamical correlation correction, the orbital overlap between the up- and down-spin orbitals should be always smaller than 1.0 for any bond of a molecule: indeed the GVB orbitals are always "biradicaloid" orbitals because of intrapair dynamical correlation. Thus, the VB-type theory used by Linnett,[12] Firestone,[11] and Goddard[10] overestimates the biradical character because of inclusion of dynamical electron correlation, compared with the DODS MO theory discussed here.

5. Extention of MO-Theoretical Description. The biradical character is almost the same for GVB,[10] VB-CI,[29] UNO MR SDCI, UNO CASSCF, and UNO CASMP2, although the zero-order starting wavefunctions are different among them: The biradical character related to the dynamical correlation is always recognized for any bond in a molecule, and this biradical character is not responsible or BR-type chemical behaviors (for example non-stereospecificity and small rotational barriers discussed in the succeeding paper[44]) of reaction intermediates and activated complexes. Although a choice of the zero-order starting point wavefunction, i.e., VB and MO, is more or less a matter of taste and training in quantum chemistry (see comments in Ref. 45), we use the MO-type wavefunction as a starting point. The well-established MO concepts and rules for concerted[46] and zwitterionic reactions[7,47] are not changed by this choice. The VB-type explanations[10,29] for tricentric biradicals are also obtained from the DODS MO determined by the ab initio HF and post HF techniques,[1—6,15,18] which are applicable to large molecules and molecular clusters in a size-consistent manner. Furthermore, general spin orbital (GSO) description including the spin-orbit interaction will be necessary for MO-theoretical characterization of several catalytic systems involving heavy atoms, although it is untouched here.[18] The present MO-theoretical description hold equally in the case of the density function theory (DFT).[31,32] Thus, a systematic MO-theoretical description of ionic, homolytic biradical and charge-transfer biradical intermediates is feasible in order to explore electronic mechanisms of chemical reactions.[1—6]

Concluding Remarks

From the present computational results, a systematic MO-theoretical description of tricentric bisdesmiphiles in the ground and excited states is feasible, as illustrated in Fig. 2: The DODS MO description is similar to the GVB description for tricentric species with a moderate or strong biradical character, whereas it reduces to the traditional MO (RHF) description for a zwitterion and a closed-shell species with a weak biradical character. Several methods for inclusion of dynamical correlation corrections starting from stable HF solutions were investigated in detail. The present MO-theoretical calculations elucidated that diazonium and nitrilium betaines are nonradical closed-shell species, whereas azomethinium betaines have weak biradical character. The reactions of these species classified into types A and C by Huisgen[7] should be closed-shell type, in compatible with many experimental data available.[5] The extended Hückel MO theory is reliable enough for rationalization of the reaction mechanisms of these species.[46] On the other hand, carbonyl betaines (oxygenated dipoles) have moderate biradical character, suggesting complex behaviors of the chemical reactions of these species with various substrates. Since electronic structures of these species belong to the intermediate correlation regime, several post HF methods should be applied to explore the nature of the π-bond. The 1,3-dipoles without octet stabilization are essentially 1,3-biradicals, for which radical reactions are plausible, in compatible with various experiments.[5] The reactions of these species are therefore rationalized by using a simple VB-type model. The species of 1,3-biradicals have receiving current interest as building blocks of organic magnetic materials. The effective exchange integrals in the Heisenberg model for clusters of these species were calculated by using the several ab initio techniques.

The computational results are summarized as follows: (1) The MO-theoretical description (best HF MO plus succeeding UNO CASCI and UNO CASSCF) can be applicable to unstable tricentric biradical species; (2) there is no need to change the well-established and familiar classic MO pictures for nonradical tricentric systems; (3) the DODS MO for oxygenated dipoles and 1,3-dipoles without octet stabilization are close to those of GVB; (4) the transformations of the UNO CAS CI wavefunctions into the VB CI wavefunctions based on localized NO (LNO) are useful for qualitative VB explanations of excited states of tricentric biradicals; (5) the UNO CASCI vector is a good trial for the UNO CASSCF calculation; (6) the energy gradient technique based on UNO CASSCF is efficient for the full geometry optimization of tricentric bisdesmiphiles; (7) the dynamical correlation by the UNO MR SDCI and CASMP2 does not change qualitative MO pictures for the ground state properties by UNO CASCI, although it is crucial for quantitative estimates of binding energies and constructions of potential curves; (8) the approximately spin-projected (AP) but size-consistent UMP (APUMP) method provides similar correlation corrections for tricentric systems by UNO MR SDCI and CASMP2; (9) the size-consistency of APUMP*n* guarantees its applicability to clusters of 1,3-biradical species.

The present MO-theoretical description of unstable intermediates and the related computational procedures will be applied to explore the electronic mechanisms of organic reactions in the intermediate correlation regime (region II in Figs. 1 and 2) where the post HF treatments are crucial:[44] Several types of oxygenation reactions and related phenomena are typical examples where reaction mechanisms are highly dependent on geometrical structures, environmental effects, spin states, etc. These complex behaviors are theoretically conceivable since the electronic structures of the oxygenated dipoles belong to this regime where the biradical character changes sharply. Therefore, reaction modes of these species should be controlled by several internal parameters (substituents etc.) and external parameters (hydrogen bonding, solvent, temperature, etc). Judging from the wholly compatible theoretical and experimental results on 1,3-dipolar species,[1—5)] the basic concepts and ab initio computational procedures examined here should be useful for theoretical studies of these complex reactions.

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