# Full-Optimized Reaction Space MCSCF+MP2 Study on Reactions of Diradical Systems: *o*-$C_6H_4(CH)_2$, *o*-$C_6H_4CHN$, and *o*-$C_6H_4N_2$

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Thermal reactivity of the ortho isomers of the titled compounds has been investigated by using the full-optimized reaction space multiconfiguration self-consistent field (MCSCF) method with the STO-3G and 6-31G(d) basis sets, followed by multireference second-order Moller−Plesset perturbation calculation (MCSCF+MP2). The MCSCF+MP2 calculations lead to the prediction that all the ortho isomers have a singlet ground state but the lowest triplet state lies above the singlet ground state by less than 3 kcal/mol. Fortunately, since the spin−orbit coupling between the two states of interest is small and the singlet ground state is more likely to be produced in the photolysis, the thermal behavior of the isomers has been analyzed on the singlet energy surface. In *o*-phenylenebis(methylene), the *E,E* stereoisomer undergoes ring-closure reaction with no energy barrier to give a bicyclic compound, while the *Z,Z* isomer exhibits a situation of competition between the ring-opening reaction and the CH inversion followed by the ring-closure reaction. In (*o*-nitrenophenyl)methylene, the *E* isomer exhibits a competitive feature between the ring-opening and ring-closure reactions, whereas the *Z* isomer reacts into a linear compound with no energy barrier. In *o*-phenylenebis(nitrene), a spontaneous ring-opening reaction takes place definitely with the formation of a linear compound. These calculated results are in good agreement with the available experimental evidences.

## Introduction

From the designing and synthetic viewpoints of organic magnetic materials, much attention has been drawn to unsaturated molecular systems that might possess a high spin-multiplicity in the ground state.[1−3] Since carbenes and nitrenes are well-known to have a triplet ground state,[4−7] it is probable that the proper combination of carbenes and nitrenes via benzene nuclei could lead to molecular systems whose ground states have a very high spin-multiplicity and, in principle, to polycarbenes and polynitrenes possessing exceptional magnetic properties. The first attempt at the synthesis of such molecular systems would be to investigate the systems constructed by triplet carbene or nitrene centers coupled in a ferromagnetic fashion, frequently with *m*-phenylene linkers. Several research groups have reported experimental evidences that some typical *m*-phenylene linkers have a quintet ground state.[8−11] In a previous study, we have theoretically investigated the stability and reactivity of the geometrical isomers of (nitrenophenyl)methylene ($C_6H_4CHN$) by using the multiconfiguration self-consistent field (MCSCF) method.[12] We have shown that the meta isomer of this molecule has a quintet ground state and that this aspect is well-reflected in the bonding character, which shows no appreciable $\pi$ conjugation between a benzene nucleus and two radical substituents.

In contrast to *m*-phenylene linkers, less is so far known about the stability and reactivity of *o*- and *p*-phenylene linkers.[8,13−16] The present study focuses to investigate the electronic structures and reactivity of typical *o*-phenylene linkers, *o*-phenylenebis(methylene) ($C_6H_4(CH)_2$; CC), (*o*-nitrenophenyl)methylene ($C_6H_4$-CHN; CN), and *o*-phenylenebis(nitrene) ($C_6H_4N_2$; NN) (see Scheme 1). On the basis of our results, we discuss the sharp differences in thermal reactivity among them.

## Methods of Calculation

**Ring-Closure Reactions**. Since static electron correlation strongly affects the relative stability of diradical systems, the full-optimized reaction space (FORS) MCSCF method[17] with the STO-3G basis set proposed by Pople *et al.*[18−19] was employed for the qualitative study on the ring-closure reactions of CC, CN, and NN systems. The MCSCF active spaces include all valence $\pi$ orbitals and a 2p$\sigma$ (lone-pair) orbital of carbene and two 2p$\sigma$ (lone-pair) orbitals of nitrene. Accordingly, the MCSCF active space includes 10 electrons and 10 orbitals for the CC system, 12 electrons and 11 orbitals for the CN system, and 14 electrons and 12 orbitals for the NN system. All geometries were assumed to be planar and optimized at this computational level. The relative energies of the stationary structures were re-estimated by using a larger basis set (6-31G(d))[20−22] and the MCSCF method with the same active space, followed by multireference second-order Moller−Plesset perturbation calculation (MCSCF+MP2).[23]

**Ring-Opening Reactions.** The MCSCF calculations were also carried out on the ring-opening reactions of the three systems. The MCSCF active spaces include the bonding and antibonding $\sigma$ orbitals of the $C_1−C_6$ bond (see Figure 1) and the bonding and antibonding $\pi$ orbitals of substituents connected with a benzene nucleus, as well as a 2p$\sigma$ (lone-pair) orbital of

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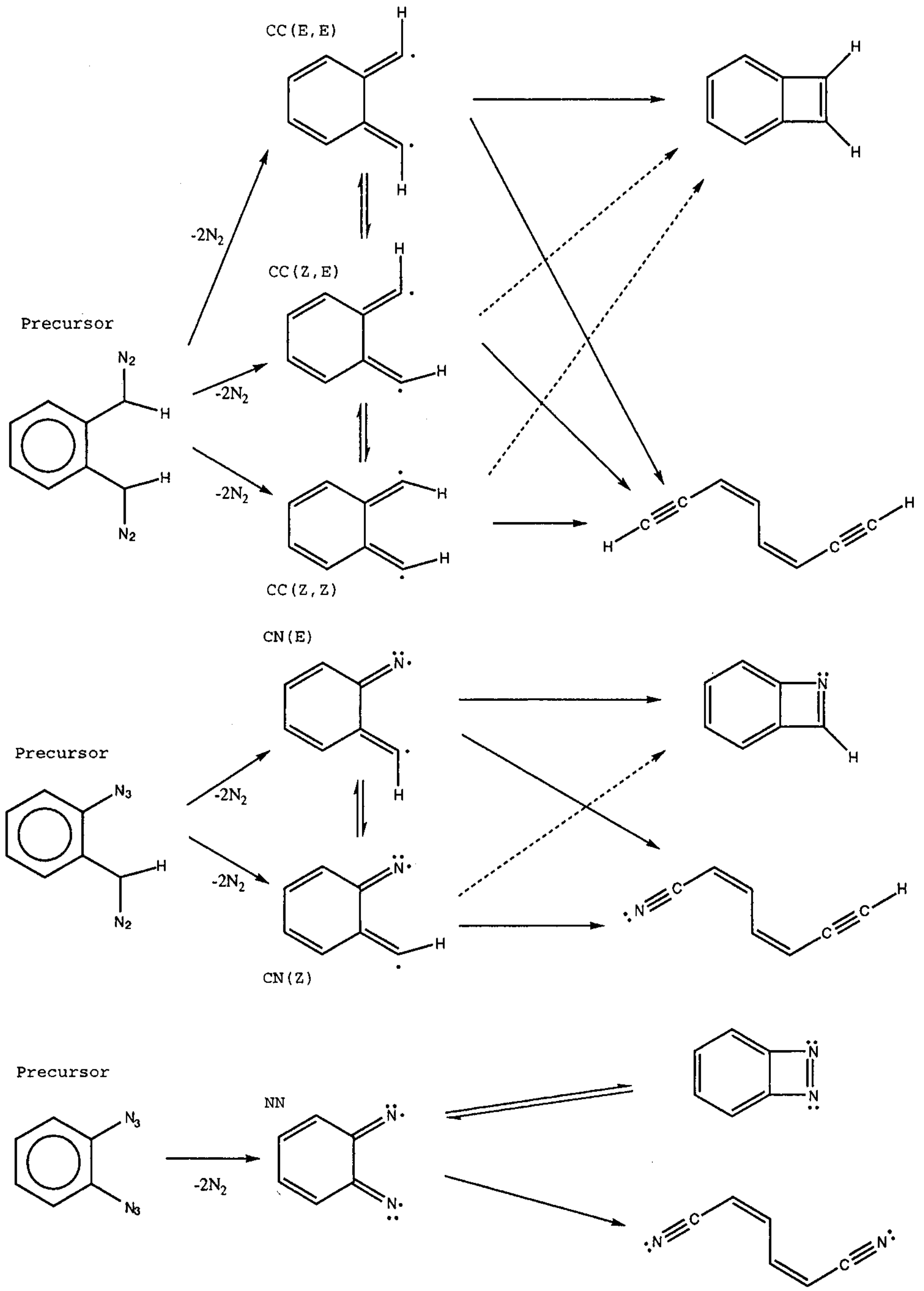
**SCHEME 1**



carbene and two 2p$\sigma$ (lone-pair) orbitals of nitrene. The MCSCF active spaces of these calculations include eight electrons and eight active orbitals in the CC system, 10 electrons and nine active orbitals in the CN system, and 12 electrons and 10 active orbitals in the NN system. The geometry optimizations were carried out by using this MCSCF method, and the vibrational analyses were also performed at every stationary points. We also re-estimated the relative energies of the optimized geometries by using MCSCF/6-31G(d) method with the same active space, also followed by MP2 calculation.[23]

All calculations were carried out by using the quantum chemistry code GAMESS.[24]

## Results and Discussion

**Electronic and Geometrical Structures of Diradical Systems.** The diradical systems, CC, CN, and NN, are considered to be produced by the photolysis of diazo and/or azido groups of the precursors in an argon matrix at very low temperature (see Scheme 1). Further, the resulting CC and CN systems are considered to exist as three and two stereoisomers, respectively.

The MCSCF/STO-3G geometry optimization reveals that a strong $\pi$ interaction occurs between a benzene nucleus and substituents in the lowest singlet and triplet states of all the stereoisomers (Figure 2). This means that $\pi$ bonds are strongly localized in these states. In the lowest quintet state, on the other hand, the optimized geometries exhibit a very weak $\pi$ conjugation between a benzene nucleus and substituents (also see Figure 2). At the MCSCF+MP2/6-31G(d) level of computation, all isomers have a singlet ground state, and the triplet and quintet are calculated to lie above the singlet ground state by less than 3 and by 20−40 kcal/mol, respectively (Table 1). Since the vertical excitation energy from the singlet to the quintet is still larger than 10 kcal/mol even at the optimized geometry of the quintet, no promotion to the quintet is likely to occur thermally.

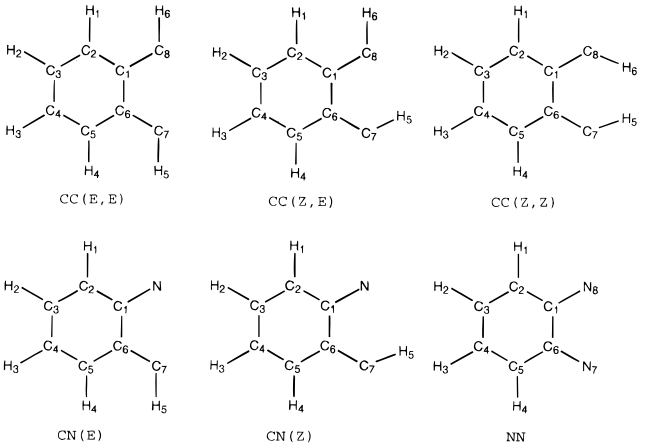


**Figure 1.** Structures of $o$-phenylenebis(methylene) $C_6H_4(CH)_2$, ($o$-nitrenophenyl)methylene $C_6H_4CHN$, and $o$-phenylenebis(nitrene) $C_6H_4N_2$ and numbering of atomic positions.

Accordingly, we can safely rule out the quintet reactant from the scope of the present investigation.

Since the energy difference between the lowest singlet and triplet is very small (Table 1), we first estimated the spin−orbit interaction between these states within one-electron approximation.[25−27] As listed in Table 2, the spin−orbit coupling matrix elements are smaller than 1 $cm^{-1}$ between the singlet ($m_s = 0$) and the triplet substates ($m_s = -1$, or $m_s = 0$) at the geometry optimized for the singlet, so that very slow intersystem crossing would occur from the singlet to the triplet. Therefore, the thermal behavior has been analyzed only on the lowest singlet surfaces of CC, CN, and NN systems in the following sections.

***o*-Phenylenebis(methylene)(CC): *Z,Z*, *Z,E*, and *E,E* Isomers.** At the MCSCF/STO-3G level of computation, three stereoisomers were found to be stationary points on the lowest singlet energy surface of the CC system. The energy differences among these isomers are very small (Table 1). Even if the *Z,Z* isomer is produced by the photolysis, the ring closure would not proceed directly; namely, the CH bond of the carbene groups needs to invert before the ring closure. The energy barrier of the CH inversion is estimated to be about 10 kcal/mol (MCSCF+MP2/6-31G(d)), which is apparently overestimated. On the basis of our calculated results of CH inversion in vinyl radical ($C_2H_3$), this energy barrier would be reduced to *less than 5 kcal/mol* at a higher level of computation. Furthermore, the concerted mechanism of the CH inversion and the ring closure could make an energy barrier smaller along the reaction path from the *Z,Z* isomer to a bicyclic isomer.

On the other hand, the ring-closure reaction in the *E,E* isomer can occur straightforwardly to produce a bicyclic isomer. Because the energy barrier is estimated to be less than 1 kcal/mol by using the MCSCF/STO-3G method and this small barrier disappears at the MCSCF+MP2/6-31G(d) level of computation (Table 3), we conclude that the ring-closure reaction in the *E,E* isomer occurs with no energy barrier.

The MCSCF+MP2/6-31G(d) calculations give an energy barrier of 4.0 kcal/mol to the ring-opening reaction in the *Z,Z* isomer (Table 3; zero-point energy (ZPE) correction reduces it to 2.0 kcal/mol). *Z,E* and *E,E* isomers also can react into a linear isomer, but their energy barriers are relatively large (8.5 (= 9.8 − 1.3) and 17.6 (= 18.5 − 0.9) kcal/mol after the inclusion of ZPE correction; see Table 3). The differences in the energy barrier will be ascribed mostly to the repulsive interaction between the nonbonded H atoms of the carbene groups. This is because upon the ring-opening reaction a reduction of the nuclear repulsion is larger for the *Z,Z* isomer than for *Z,E* and *E,E* isomers in view of the spatial arrangement of the carbene groups (Figure 2). The transition state structures of these ring-opening reactions are illustrated in Figure 3. These structures have only one imaginary frequency at the MCSCF/STO-3G level of computation. Thus, if the *E,E* isomer is produced upon the photolysis, a bicyclic isomer would be an end product. Meanwhile, in the *Z,Z* isomer, the ring opening would be in competition with the concerted reaction of the CH inversion and the ring closure. Additionally, the energy difference between the bicyclic and linear isomers is remarkably

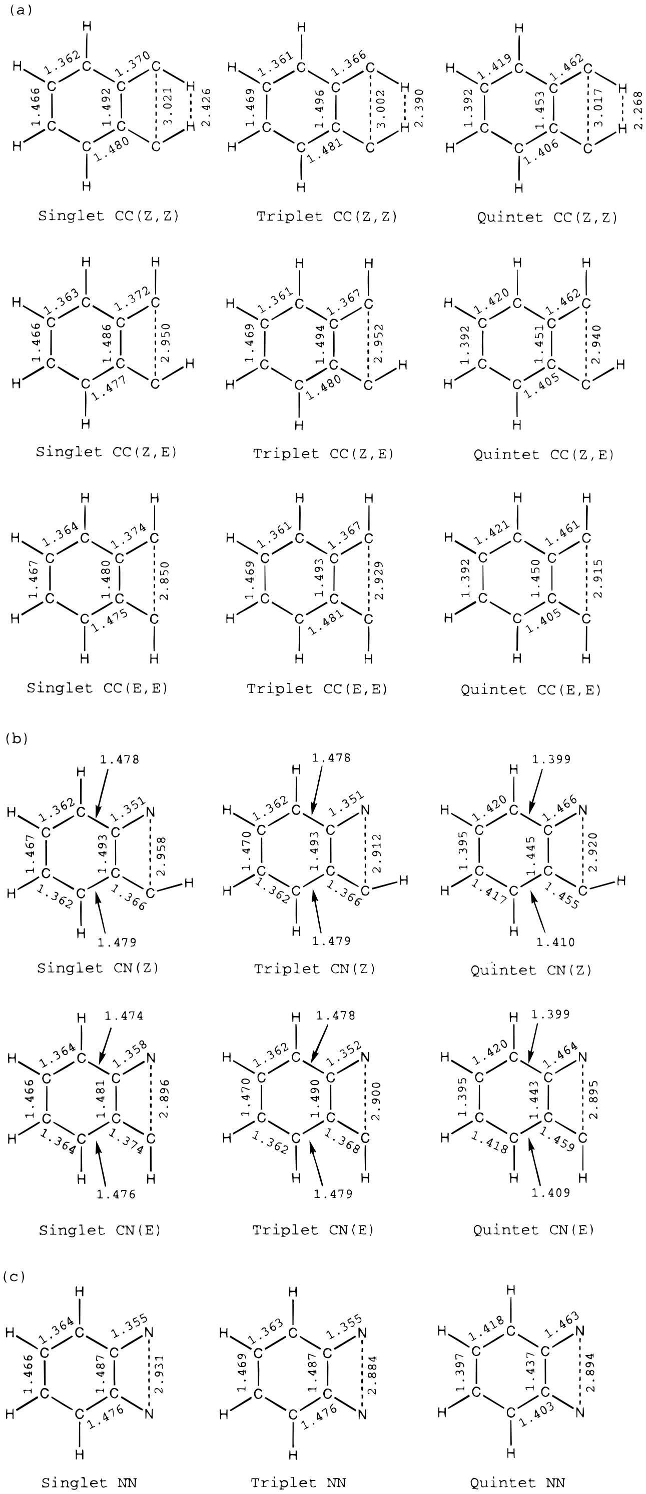


**Figure 2.** C−C and C−N bond lengths (Å) in the lowest singlet, triplet, and quintet states of reactants: (a) CC system, (b) CN system, and (c) NN system.

**TABLE 1: Total Energies (Hartree) and Relative Energies (kcal/mol) of the Reactants Calculated by Using the MCSCF+MP2/6-31G(d)//MCSCF/STO-3G Method**

| | CC (*Z*,*Z*) | CC (*Z*,*E*) | CC (*E*,*E*) | CN (*Z*) | CN (*E*) | NN |
|---|---|---|---|---|---|---|
| | $^1A_1$ | $^1A'$ | $^1A_1$ | $^1A'$ | $^1A'$ | $^1A_1$ |
| MSCSF | 0.0 | −0.7 | −2.2 | 0.0 | +1.2 | 0.0 |
| +MP2[a] | 0.0 | −0.7 | −2.5 | 0.0 | +2.9 | 0.0 |
| +ZPE[b] | 0.0 | −0.6 | −2.4 | 0.0 | +2.9 | 0.0 |
| | $^3B_2$ | $^3A'$ | $^3B_2$ | $^3A'$ | $^3A'$ | $^3B_2$ |
| MSCSF | +1.8 | +1.4 | +1.8 | +1.4 | +2.9 | +1.4 |
| +MP2[a] | +1.4 | +1.0 | +1.5 | +1.2 | +4.8 | +1.3[c] |
| +ZPE[b] | +1.4 | +1.0 | +1.4 | +1.5 | +4.9 | +1.3 |
| | $^5A_1$ | $^5A'$ | $^5A_1$ | $^5A'$ | $^5A'$ | $^5A_1$ |
| MSCSF | +22.0 | +21.2 | +21.4 | +28.0 | +28.6 | +31.6 |
| +MP2[a] | +22.9 | +22.0 | +22.3 | +29.4 | +33.1 | +42.3[c] |
| +ZPE[b] | +21.5 | +20.8 | +21.1 | +28.4 | +32.1 | +42.3 |

[a] Reference 19. [b] Zero-point energies are obtained by using MSCSF/STO-3G hessians. [c] Energies are estimated by the results obtained by using a smaller MSCSF active space.

**TABLE 2: Vertical Excitation Energies (Δ*E*, kcal/mol) and One-Electron Spin−Orbit Coupling Constants ($|H_{so}|$, cm$^{-1}$) Calculated by Using the Geometries and Orbitals Optimized for the Lowest Singlet**

| | CC (*Z*,*Z*) | CC (*Z*,*E*) | CC (*E*,*E*) | CN (*E*) | CN (*Z*) | NN |
|---|---|---|---|---|---|---|
| Δ*E* | 2.7 | 2.6 | 3.5 | 3.0 | 2.6 | 3.0 |
| $\|H_{so}\|$ | 0.0301<br>type 1[a] | 0.0178<br>type 2[a] | 0.0595<br>type 1 | 0.1154<br>type 2 | 0.0127<br>type 2 | 0.1250<br>type 1 |

[a] Type 1: $|H_{so}| = |\langle {}^1A_1(m_s{=}0)\ |H_{so}|\ {}^3B_2(m_2{=}1)\rangle|$. Type 2: $|H_{so}| = |\langle {}^1A'(m_s{=}0)\ |H_{so}|\ {}^3A'(m_s{=}0)\rangle|$.

**TABLE 3: Total Energies (Hartree) and Relative Energies (kcal/mol) of Stationary Structures Calculated by Using the MCSCF+MP2/6-31G(d)//MCSCF/STO-3G Method**

| | CC (*Z*,*Z*) | CC (*Z*,*E*) | CC (*E*,*E*) | CN (*Z*) | CN (*E*) | NN |
|---|---|---|---|---|---|---|
| Ring-Closure Reaction | | | | | | |
| reactant | | | | | | |
| MCSCF | 0.0 | −0.7 | −2.2 | 0.0 | +1.2 | 0.0 |
| +MP2[a] | 0.0 | −0.7 | −2.5 | 0.0 | +2.9 | 0.0 |
| +ZPE[b] | 0.0 | −0.6 | −2.4 | 0.0 | +2.9 | 0.0 |
| transition state | | | | | | |
| MCSCF | | | −3.9 | | +2.3 | +10.6 |
| +MP2[a] | | | −4.9 | | +0.9 | +8.4[c] |
| +ZPE[b] | | | −5.1 | | +0.7 | +8.2 |
| product | | | | | | |
| MCSCF | | | −70.7 | | −42.6 | −1.4 |
| +MP2[a] | | | −75.8 | | −41.5 | −2.6[c] |
| +ZPE[b] | | | −71.8 | | −39.1 | −0.3 |
| Ring-Opening Reaction | | | | | | |
| reactant | | | | | | |
| MCSCF | 0.0 | +0.6 | +0.2 | 0.0 | +2.4 | 0.0 |
| +MP2[a] | 0.0 | +1.2 | +0.8 | 0.0 | +2.2 | 0.0 |
| +ZPE[b] | 0.0 | +1.3 | +0.9 | 0.0 | +2.3 | 0.0 |
| transition state | | | | | | |
| MCSCF | +4.9 | +13.3 | +22.1 | −1.8 | +7.2 | −6.0 |
| +MP2[a] | +4.0 | +12.4 | +21.5 | −3.9 | +5.0 | −8.1 |
| +ZPE[b] | +2.0 | +9.8 | +18.5 | −5.3 | +3.0 | −9.1 |
| product | | | | | | |
| MCSCF | −51.0 | −51.0 | −51.0 | −67.6 | −67.6 | −85.9 |
| +MP2[a] | −43.4 | −43.4 | −43.4 | −61.5 | −61.5 | −80.7 |
| +ZPE[b] | −44.9 | −44.9 | −44.9 | −62.2 | −62.2 | −80.9 |

[a] Reference 19. [b] Zero-point energies are obtained by using MCSCF/STO-3G hessians. [c] Energies are estimated by the results obtained by using a smaller MCSCF active space.

reduced by the extension of the basis set from STO-3G (39.3 kcal/mol) to 6-31G(d) (19.7 (= 70.7 − 51.0) kcal/mol). However, the inclusion of the dynamic correlation effect makes the difference larger again (32.4 (= 75.8 − 43.4) kcal/mol). Therefore, it can be concluded that the bicyclic isomer is more stable than the linear one, though the difference is somewhat reduced by ZPE correction.

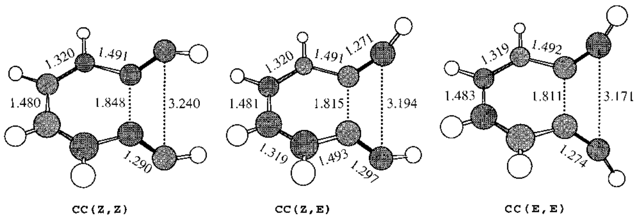


**Figure 3.** C−C bond lengths (Å) in the transition state geometries of the ring-opening reactions of *o*-phenylenebis(methylene) isomers.

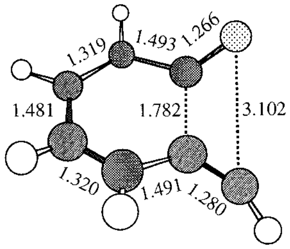


**Figure 4.** C−C and C−N bond lengths (Å) in the transition state geometry of the ring-opening reaction of (*o*-nitrophenyl)methylene *E* isomer CN(*E*).

**(*o*-Nitrenophenyl)methylene (CN): *Z* and *E* Isomers.** Both *Z* and *E* isomers are predicted to be stationary points on the MCSCF/STO-3G energy surface. According to the MCSCF+MP2/6-31G(d) results, the *Z* isomer is somewhat lower in energy than the *E* isomer because of the attractive interaction between the H atom of carbene and the N atom. No energy barrier exists in the ring-opening reaction of the *Z* isomer, while a small energy barrier is found in that of the *E* isomer (2.8 (= 5.0 − 2.2) kcal/mol, which is reduced to only 0.7 (= 3.0 − 2.3) kcal/mol by ZPE correction; Table 3). The structure of the transition state in the latter reaction is depicted in Figure 4.

At the MCSCF+MP2/6-31G(d) level of computation, the MCSCF energy barrier of the ring closure in the *E* isomer disappears by the inclusion of the dynamic correlation effect (Table 3), while the *Z* isomer needs to undergo CH inversion with an energy barrier of about 11 kcal/mol before the ring closure. Though the energy barrier of the CH inversion is overestimated as mentioned in the previous section, the *E* isomer would undergo the ring closure, rather than the CH inversion to the *Z* isomer. Accordingly, if the *E* isomer is produced by the photolysis, then the product would be a bicyclic compound. On the other hand, if the *Z* isomer is a reactant, the ring opening is preferable to the CH inversion followed by the ring closure. The experimental evidences show that the end product has a linear structure,[10] suggesting that the *Z* isomer is a major product of the photolysis in an argon matrix and the ring-opening reaction occurs.

***o*-Phenylenebis(nitrene)(NN).** The NN system can react directly into bicyclic and linear isomers. At the MCSCF/STO-3G level of computation, the energy barriers of the ring-closure and ring-opening reactions are estimated to be 11.1 and 2.4 kcal/mol, respectively. However, the MCSCF+MP2/6-31G(d) energy calculations at the MCSCF/STO-3G geometries show that the transition state for the ring-closure reaction (Figure 5) lies high above the reactant by 8.4 kcal/mol (8.2 with ZPE correction; Table 3) and that there is no energy barrier for the ring opening. Note that, since the bicyclic isomer is approximately as stable as the reactant (Table 3), the reverse reaction of the ring closure is likely to occur easily. Thus, we

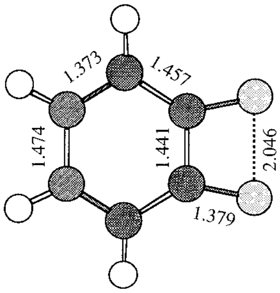


**Figure 5.** Bond lengths (Å) in the transition state geometry of the ring-closure reaction of *o*-phenylenebis(nitrene).

can conclude that the end product of the NN system is a linear compound in good agreement with the experimental evidence.[10]

## Summary

From this theoretical investigation, we can draw the following conclusions regarding reactivity of the diradical systems examined. In *o*-phenylenebis(methylene), if the *Z*,*Z* isomer is produced by the photolysis, the ring-opening reaction is in competition with the concerted reaction of the CH inversion and the ring closure. But if the *E*,*E* isomer is a reactant, a bicyclic compound is produced by the ring-closure reaction with no energy barrier. In (*o*-nitrophenyl)methylene, the *E* isomer exhibits a competitive feature between the ring-opening and ring-closure reactions, whereas the *Z* isomer reacts into a linear compound with no energy barrier. In *o*-phenylenebis(nitrene), the ring-opening reaction takes place spontaneously with the formation of a linear compound.

In this connection, recent experiments reveal that the ring opening is the main reaction for (*o*-nitrenophenyl)methylene, suggesting that the *Z* isomer is generated upon photolysis. By reference to such experimental evidence, it can be predicted that the *Z*,*Z* isomer of *o*-phenylenebis(methylene) is mainly generated upon the photolysis of the precursor, exhibiting a competitive feature between the ring-opening and ring-closure reactions. Furthermore, it is suggested that the introduction of nitrene groups to the ortho position of a certain aromatic ring results in a cleavage of the ring where nitrene groups are attached, while the introduction of carbene groups leads to the formation of a new four-membered ring. Such a difference in reactivity seems to arise from the stability of C−C and N−N double bonds.

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**Supporting Information Available:** Listing of Cartesian coordinates of the stationary structures optimized by using MCSCF/STO-3G method (13 pages). Ordering information is given on any current masthead page.

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