

Stretch Effects Induced by Molecular Strain on Weakening σ -Bonds: Molecular Design of Long-Lived Diradicals (Biradicals)

Manabu Abe,^{*,†,‡,§} Haruka Furunaga,[†] Dongxia Ma,[‡] Laura Gagliardi,[‡] and Graham J. Bodwell^{*,§}

[†]Department of Chemistry, Graduate School of Science, Hiroshima University (HIRODAI), 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan

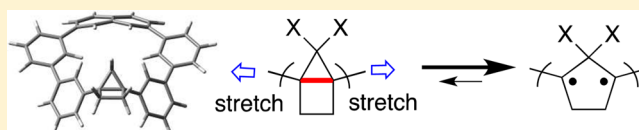
[‡]Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota, United States

[§]Department of Chemistry, Memorial University, St. John's, Newfoundland and Labrador, A1B 3X7, Canada

[#]Institute of Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan

Supporting Information

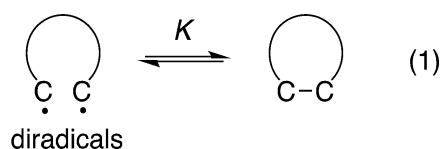
ABSTRACT: Stretch effects induced by two types of molecular strain were examined by quantum chemical calculations at the B3LYP/6-31G(d), B3LYP/cc-PVDZ, CCSD/6-31G(d), and CASPT2/ANO-RCC-VTZP level of theory, to design persistent multiradicals such as localized diradicals and oxyallyls. The cooperative molecular strain (Type-1) induced by the spiro[5.5]-undecane and bicyclo[2.1.0]cyclopentane structures was found to significantly destabilize in energy the ring-closed compounds of the diradicals, leading to small energy differences between the diradicals and the σ -bonded compounds. Another stretch effect (Type-2) induced by macrocyclic systems was also found to energetically destabilize the corresponding ring-closed structures of the 1,3-diradicals. The computational studies predict that the two types of stretch effects are quite effective in lowering the energy barriers of the bond-breaking reaction of the ring-closed compounds and in generating long-lived localized diradicals and oxyallyl derivatives.



INTRODUCTION

The computational calculations described in this paper were conducted with an eye to finding new methods for generating long-lived diradicals (biradicals). The concept of a “stretch effect” induced by two types of molecular strain was proposed and examined. Thus, the principal goal of this study was to provide appropriate molecular designs for long-lived multiradical species.

Open-shell molecules with unpaired electrons are typically highly reactive species, and thus are in general short-lived.¹ The isolation of such highly energetic species is a topic of considerable current research interest. For example, persistent radicals have attracted much attention in the field of novel materials chemistry such as organic magnets,² nonlinear optical materials,³ and radical batteries.⁴ The generation and isolation of such fascinating molecules has been achieved so far using the concepts of kinetic stabilization and thermodynamic stabilization. Kinetic stabilization may be accomplished by the introduction of sterically demanding substituents around the reactive sites, in order to prevent intermolecular reactions. However, kinetic stabilization is not always applicable to



intramolecularly reactive molecules such as diradicals (eq 1). Nevertheless, the effect of steric hindrance was recently used for

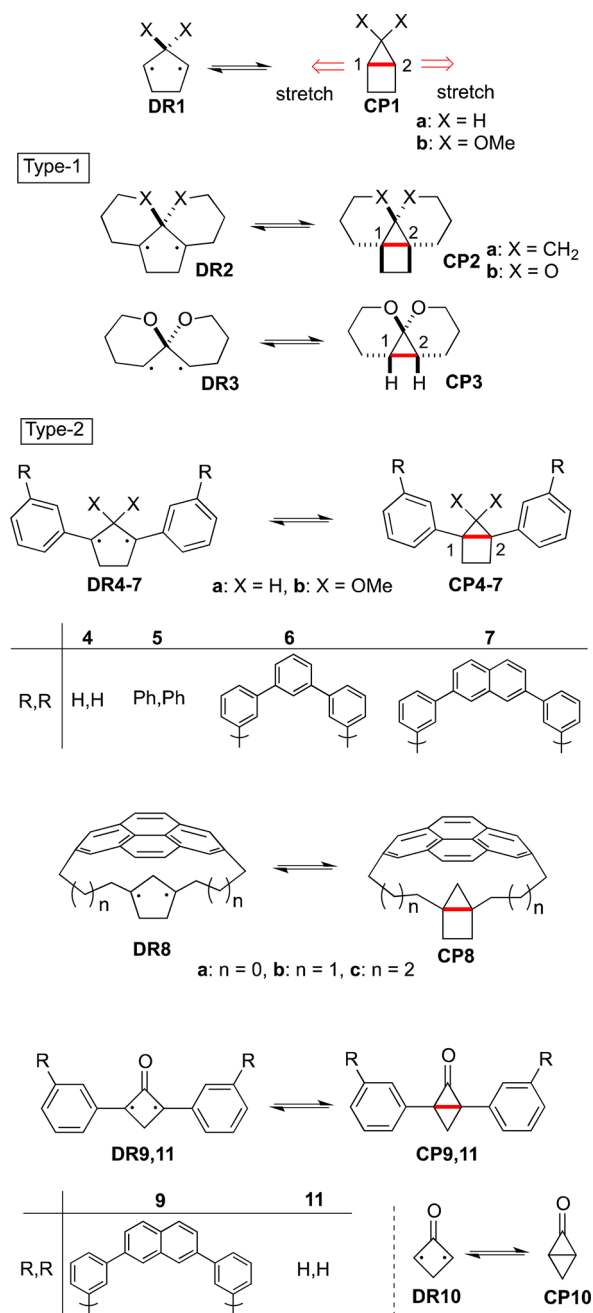
detecting oxyallyl derivatives.⁵ On the other hand, Berson used a strain effect induced by the structure of bicyclo[2.1.0]pentane to generate persistent non-Kekulé molecules (delocalized diradicals), e.g., trimethylenemethanes (TMMs) at low temperature in a rigid matrix.⁶ Electron delocalization, e.g., using π -conjugation, is the essential element of the thermodynamic stabilization-based approach to persistent radicals. In addition to the strategies listed above, which have been successfully applied for isolating or generating persistent reactive intermediates,⁴ a “tension effect” imposed by mechanical force such as ultrasonic irradiation has been recently reported in the field of polymer chemistry to weaken covalent bonds.⁷ Boulatov used cis–trans isomerization of stilbenes to measure force-dependent kinetics of localized reactions.⁸ In the present study, “stretch effects” induced by molecular strain are examined and applied to the design of long-lived diradicals (Chart 1).

Borden⁹ and our group¹⁰ have so far investigated the substituent (X) effect at the C(2) position on the ground state spin-multiplicity of localized 1,3-diradicals **DRI** and their chemistry (Chart 1). Computational predictions made it possible to experimentally detect singlet cyclopentane-1,3-diyls.¹¹ The species were found to be persistent under rigid matrix conditions at low temperatures. The lifetimes were, however, in the nanosecond (ns) to millisecond (ms) time scale at room temperature, because the ring-closed compounds, σ -bonded structures, are much lower in energy than the corresponding

Received: August 4, 2012

Published: August 9, 2012

Chart 1



open-shell diradicals, i.e., $K \gg 1$. 1,3-Diradicals in four-membered heterocycles were reported as stable molecules at room temperature.¹² The isolation of carbon-centered diradicals is, however, still a challenging subject. When the equilibrium constant (K) between the diradical and the ring-closed compound becomes nearly 1 or less than 1 (eq 1), in principle, the diradical is persistent even at room temperature. However, kinetic stabilization should be needed to prevent intermolecular reactions. There are two strategies to reduce the energy difference between the diradicals and the σ -bonded compounds: (1) the thermodynamic stabilization of diradicals and (2) the energetic destabilization of the σ -bonded compounds.

Diradicals DR and their ring-closed compounds CP computed in this study are listed in Chart 1. In principle, the ring-closed compounds, i.e., σ -bonded species, should be much lower in energy than the open-shell diradicals. As such, the main focus of this work was on examining molecular strain effects on the

destabilization of the σ -bonded compounds. The thermodynamic stabilization of diradicals should be minimized, because the original character of the open-shell molecules may be changed by the π -conjugation. The molecular design was categorized into systems designated as Type 1 and Type 2. In the Type 1 molecules, the molecular strain (stretching) in the ring-closed compounds is induced cooperatively by the spiro-ring junction and the tricyclic structure. In the Type 2 molecules, the molecular strain caused by the macrocyclic ring system is designed to both destabilize the ring-closed compounds and kinetically stabilize the diradicals. The two types of molecular strain serve to “stretch” the fused C(1)–C(2) bond (shown in red) and thus decrease both the energy difference between the diradical and the ring-closed compound, and the energy barrier to generating the corresponding localized diradicals.¹³ The Type 2 molecular design was applied to kinetically stabilize the four-membered oxallyl diradical DR9 and thermodynamically destabilize the corresponding ring-closed compound CP9. By comparison, the parent four-membered ring-closed compound CP10 has been reported to be much lower in energy than the corresponding oxallyl DR10,¹⁴ although the five-membered oxallyl is known to be more stable than the corresponding ring-closed compounds.^{14a} The phenyl-substituted oxallyl DR11 and the ring-closed compound CP11 were also calculated to clarify the Type 2 stretch effect on the energetic destabilization of CP9 (Chart 1). TMM derivatives, which are triplet ground-state molecules, are known to be lower in energy than the corresponding ring-closed compounds.^{14a} Thus, the stretch effect was not examined for non-Kekulé type molecules.

COMPUTATIONAL METHODS

Geometry optimizations were carried out at the B3LYP¹⁵ and/or CCSD¹⁶ level of theory with the 6-31G(d)¹⁷ and/or cc-PVDZ¹⁸ basis set. The broken-symmetry (BS) method¹⁹ (initial guess $\langle S^2 \rangle = 1.00$) was used for the singlet diradicals. The ratio (ψ_S/ψ_A) of occupation number of the two nonbonding molecular orbitals (NBMOs), symmetric ψ_S and antisymmetric ψ_A , in the singlet diradicals was determined using the (6/6)CASSCF²⁰ level of theory, to understand the diradical character. The triplet state of diradicals was calculated with the unrestricted method (initial guess $\langle S^2 \rangle = 2.00$). Excitation energies were computed using time-dependent density functional theory²¹ (TD-B3LYP/cc-PVDZ). The geometries of stationary points and transition states were all located, and vibrational analyses were performed with the Gaussian 03²² suite of programs. The multiconfigurational second-order perturbation theory (CASPT2)²³ calculations were employed with atomic natural orbital (ANO) basis set of VDZP quality,²⁴ after the structural optimization by the DFT method. The MOLCAS 7.7 package²⁵ was used for the calculations. The optimized geometries and their electronic energies are available in the Supporting Information.

RESULTS AND DISCUSSION

Type-1 Molecules. The DFT computed values of $\langle S^2 \rangle$ for the diradicals, the energy differences between CP and DR $\Delta E_{CP-DR} = E_{CP} - E_S$ in kcal mol⁻¹, the spin-corrected singlet–triplet energy spacings in DR $\Delta E_{ST} = E_S - E_T$ in kcal mol⁻¹, the bond lengths in pm of C(1)–C(2), the excitation energies λ_{calc} in nm for the singlet diradicals, and the energy barriers E_a in kcal mol⁻¹ from S-DR to CP are summarized in Table 1. Calculated values for DR1–3 and CP1–3 (Type-1 molecules) are listed in entries 1–11.

The values of $\Delta E_{CP-DR} = -32.2$ kcal mol⁻¹ and $\Delta E_{ST} = +1.4$ kcal mol⁻¹ calculated at the B3LYP/6-31G(d) level for the parent cyclopentane-1,3-diyl (DR1a) and bicyclo[2.1.0]pentane (CP1a) were compared with those reported using the ab initio

Table 1. Computational Results on Localized Diradicals DR1–9,11 and Ring-Closed Compounds CP1–9,11

entry	DR	$\langle S^2 \rangle$, ^e singlet/ triplet	CP	$\Delta E_{\text{CP-DR}}^f$ (kcal mol ⁻¹)	$\Delta E_{\text{ST}}^g = E_S - E_T$ (kcal mol ⁻¹)	C(1)–C(2) in CP ^h (pm)	λ_{calcd}^i (nm)	E_a^j (kcal mol ⁻¹)
1 ^a	DR1a (X = H)	1.01/2.01	CP1a (X = H)	-32.2 ^k (-34.4) ^l	+1.4 ^k (+1.2) ^l	153 ^k	— ^m	+1.3 ^l
2 ^a	DR1b (X = OMe)	0.88/2.01	CP1b (X = OMe)	-30.6	-5.7	156	— ^m	— ^m
3 ^b	DR1b	0.87/2.01	CP1b	-30.2	-5.8	157	552 (0.049)	+1.4
4 ^b	DR2a (X = CH ₂)	1.00/2.01	CP2a (X = CH ₂)	-2.2	+0.59	159	— ^m	+10.6
5 ^c	DR2a	1.02/2.02	CP2a	-5.9	+0.45	157	— ^m	— ^m
6 ^d	DR2a		CP2a	-16.5	+0.21	159	— ^m	— ^m
7 ^b	DR2b (X = O)	0.90/2.01	CP2b (X = O)	+1.6	-4.5	163	662 (0.076)	+9.2
8 ^c	DR2b	1.01/2.01	CP2b	-2.0	-3.8	161	— ^m	— ^m
9 ^d	DR2b		CP2b	-9.3	-5.9	163	— ^m	— ^m
10 ^b	DR3	0.99/2.01	CP3	-15.4	+0.55	155	— ^m	— ^m
11 ^d	DR3		CP3	-25.1	-0.68	155		
12 ^a	DR4a (X = H)	1.05/2.06	CP4a	-7.3	+0.25	157	— ^m	+5.7
13 ^a	DR5a (X = H)	1.05/2.06	CP5a	-7.5	+0.59	158	— ^m	+5.8
14 ^a	DR6a (X = H)	1.01/2.06	CP6a	-5.4	-0.18	162	— ^m	— ^m
15 ^a	DR7a (X = H)	1.05/2.06	CP7a (X = H)	-0.80	+0.55	160	— ^m	+9.2
16 ^a	DR7b (X = OMe)	0.89/2.06	CP7b (X = OMe)	+7.8	-4.8	166	784 (0.30)	— ^m
17 ^a	DR8a (n = 0)	1.01/2.01	CP8a (n = 0)	-1.3	+0.68	161	— ^m	— ^m
18 ^a	DR8b (n = 1)	1.00/2.01	CP8a (n = 1)	-21.0	+0.26	157	— ^m	— ^m
19 ^a	DR8c (n = 2)	1.01/2.01	CP8a (n = 2)	-29.4	+0.50	156	— ^m	— ^m
20 ^a	DR9	0.00/2.06	CP9	— ⁿ	-12.7	— ⁿ	— ^m	— ^m
21 ^a	DR11	0.38/2.06	CP11	-3.6	-7.4	179	— ^m	— ^m

^aAt the (U)B3LYP/6-31G(d) level of theory. ^bAt the (U)B3LYP/cc-PVDZ level of theory. ^cAt the (U)CCSD/6-31G(d) level of theory. ^dAt the CASPT2(6/6)/ANO-RCC-VTZP/(U)B3LYP/cc-PVDZ level of theory. ^eSpin contaminations for the unrestricted singlet and triplet. ^f $\Delta E_{\text{CP-DR}}$ values were calculated as $E_{\text{CP}} - E_{\text{DR}}$, where E_{CP} and E_{DR} are the computed electronic energies of the ring-closed compounds CP and the singlet diradicals S-DR at the optimized geometries. Thus, the negative sign indicates that the ring-closed compounds are energetically more stable than the singlet state of the diradicals. ^g ΔE_{ST} values are the spin-corrected singlet–triplet energy spacing as $E_S - E_T$, where E_S and E_T are the computed electronic energies at the optimized geometries. A negative sign indicates that the singlet state is the ground state. The corrected values were obtained by scaling the singlet electronic energies, to account for the effects of spin contamination, ref 19. ^hAtom distances between C(1)–C(2) at optimized geometries. ⁱAbsorption wavelengths (oscillator strength) for the singlet diradicals were calculated at the B3LYP/cc-PVDZ level of theory. ^jElectronic energy barriers for the ring-closing mode of reactions from the singlet diradical to the corresponding ring-closed compounds. ^kSee ref 27a. ^lSee ref 26. ^mNot determined. ⁿThe singlet diradical DR9 was obtained from the optimization of the compound CP9.

CASPT2/6-31G(d) level;^{26,27} see the values in parentheses in entry 1. The singlet–triplet energy spacing ΔE_{ST} at the DFT method well reproduced the value obtained by the CASPT2 calculation. However, the energy difference between S-DR1a and CP1a, $\Delta E_{\text{CP-DR}}$, at the DFT method was smaller by ca. 2 kcal mol⁻¹ than that obtained using the CASPT2 method. The singlet 2,2-dimethoxycyclopentane-1,3-diyl S-DR1b (X = OMe) with an open-shell character ($S^2 = 0.88$) was also found to be energetically less stable than the ring-closed product CP1b (X = OMe), entries 2 and 3. The energy differences, $\Delta E_{\text{CP-DR}} = -30.6$ kcal mol⁻¹ (entry 2, at the UB3LYP/6-31G(d)) and -30.2 kcal mol⁻¹ (entry 3, at the UB3LYP/cc-PVDZ), were nearly the same as those obtained for the parent compounds DR1a and CP1a. As expected, barrierless processes of the radical–radical coupling reactions were found from DR1 to CP1, $E_a = 1.3$ kcal mol⁻¹ for DR1a (entry 1) and 1.4 kcal mol⁻¹ for DR1b (entry 3). Thus, the strain energy accruing only from the structure of bicyclo[2.1.0]pentane is not enough to make the energy difference $\Delta E_{\text{CP-DR}}$ small. A singlet ground state was found for DR1b with $\Delta E_{\text{ST}} = -5.7$ or -5.8 kcal mol⁻¹ (entries 2 and 3), although DR1a is predicted to be a triplet ground state molecule (entry 1). The alkoxy-group effect (X = OMe) on the singlet ground state was reasonably explained by the hyperconjugative electron delocalization from p- π AOs to the σ^* orbital of the C–O bond in the singlet state.^{9,10} TD-DFT calculations at the B3LYP/cc-PVDZ level of theory revealed that S-DR1b was predicted to absorb light at

$\lambda_{\text{calcd}} = 552$ nm with an oscillator strength of $f = 0.049$. Thus, this species may be detectable by conventional spectroscopic methods such as UV–vis absorption spectroscopy (entry 3).^{11,28}

The stretch effect induced by the combination of the bicyclo[2.1.0]pentane system and the spiro[5.5]undecane system was examined in the equilibrium between S-DR2a (X = CH₂) and CP2a (X = CH₂) (entries 4–6). The diradical was optimized in C₂ symmetry. The ring-closed compound was calculated in C₁ symmetry. The energy difference $\Delta E_{\text{CP-DR}} = -2.2$ kcal mol⁻¹ was found to be much smaller (by ~ 30 kcal mol⁻¹) than that calculated for DR1a and CP1a at the UB3LYP/cc-PVDZ level of theory (entry 4). The (U)B3LYP method overestimated the stability of the singlet diradical, because the obtained $\Delta E_{\text{CP-DR}}$ values at the (U)CCSD/6-31G(d) and the (6/6)CASPT2/ANO-RCC-VTZP were -5.9 and -16.5 kcal mol⁻¹, respectively (entries 5 and 6). Thus, the combination of the two strained bonding systems was found to significantly make the energy difference small in comparison with the parent system of 1a. A triplet ground state was computed for DR2a with $\Delta E_{\text{ST}} \sim +0.5$ kcal mol⁻¹ (entries 4–6). The triplet diradical would be detected by conventional spectroscopic analysis such as EPR. The bond length of C(1)–C(2) in CP2a (~ 159 pm), as expected, was found to be significantly longer than that in CP1a (153 pm). Indeed, the stretch effect was found to increase the energy barrier (E_a) from the singlet diradical S-DR2a to the ring-closed compound CP2a. Thus, for DR2a, the energy barrier was

calculated to be $10.6 \text{ kcal mol}^{-1}$ (entry 4 in Table 1, **TS2a** in Figure 1), which was much higher than that for **DR1a**, $1.3 \text{ kcal mol}^{-1}$

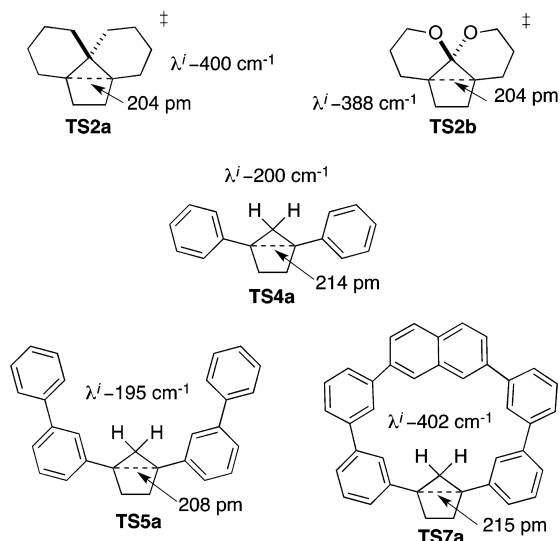


Figure 1. Transition state structures for the ring-closing reaction of the singlet diradicals **DR2a**, **DR2b**, **DR4a**, **DR5a**, and **DR7a**.

(entry 1). Thus, the equilibration between the two compounds are expected to be very slow at low-temperature matrix conditions and be fast at room temperature.

To gain further insight into the strain effects on $\Delta E_{\text{CP-DR}}$, the strain energy (SE) of **CP2a** was calculated and found to be $81.5 \text{ kcal mol}^{-1}$ at the B3LYP/6-311+G(d) level of theory, which is a standard level of theory for the calculations of strain energy.²⁹ The strain energy of **CP2a** was 24 kcal mol^{-1} higher than the sum of the strain energies of bicyclo[2.1.0]pentane (SE = 54 kcal mol^{-1}) and spiro[5.5]undecane (SE = $3.5 \text{ kcal mol}^{-1}$).²⁹ Thus, the notable destabilization of **CP2** in energy was explained by the cooperative molecular strain induced by the structure of the bicyclo[2.1.0]pentane and the spiro[5.5]undecane systems. The trans-fused bicyclic ring in **CP2a** would be the main reason for the cooperativity.

The combined strain effects, which serve to stretch the fused bond of the ring-closed compounds, also came into play with diradical **DR2b** (X = O) (entries 7–9). In this case, the singlet diradical **S-DR2b** in C_2 symmetry was computed to be more stable in energy than the ring-closed compound **CP2b** and the triplet state **T-DR2b** by 1.6 and $4.5 \text{ kcal mol}^{-1}$, respectively, at the UB3LYP/cc-PVDZ level of theory (entry 7). However, whereas **S-DR2b** was found to be lower in energy than **CP2b** by $1.6 \text{ kcal mol}^{-1}$ at the DFT level, the ring-closed compound **CP2b** was found to be more stable in energy than **S-DR2b** by 2.0 and $9.3 \text{ kcal mol}^{-1}$ at the CCSD/6-31G(d) and CASPT2/ANO-RCC-VTZP levels of theory, respectively (entries 8 and 9). A smaller energy difference in **2b** (X = O, $\Delta E_{\text{CP-DR}} = -9.3 \text{ kcal mol}^{-1}$, entry 9) than that in **2a** was found (X = CH_2 , $\Delta E_{\text{CP-DR}} = -16.5 \text{ kcal mol}^{-1}$, entry 6). The energy difference of $|\Delta \Delta E_{\text{CP-DR}}| = 7.2 \text{ kcal mol}^{-1}$ was nearly the same as the energy difference of the singlet–triplet energy gap between **DR2a** and **DR2b**, i.e., $|\Delta \Delta E_{\text{ST}}| = 6.1 \text{ kcal mol}^{-1}$. The singlet ground state was found for **DR2b** with $\Delta E_{\text{ST}} = -5.9 \text{ kcal mol}^{-1}$ (entry 9), whereas the triplet state was the ground state for **DR2a** with $\Delta E_{\text{ST}} = +0.21$ (entry 6). The singlet–triplet energy spacing calculated by DFT ($\Delta E_{\text{ST}} = -4.5 \text{ kcal mol}^{-1}$) was found to be nearly the same as that obtained by the ab initio calculations for **DR2b**. To probe the

character of the singlet diradical **S-DR2b**, the ratio of the occupation number in the singlet diradical **S-DR2b** was

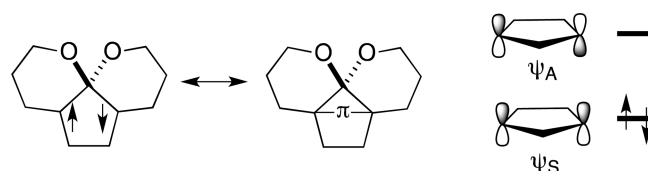
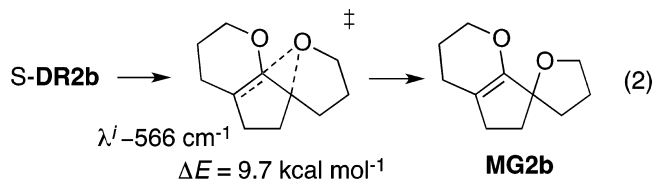


Figure 2. The most stable electronic configuration of **S-DR2a** and its π -single-bonded character.

calculated at the (6/6)CASSCF/ANO-RCC-VTZP level of theory and found to be $\psi_S/\psi_A = 1.33/0.67 = 2.0$ (Figure 2). Thus, the singlet diradical possesses some π single-bonding character between the two radical sites.¹⁰ The bond-order between the two radical sites for the diradical **DR1** (X = OH) was found to be 0.58.^{10b}

The bond length of C(1)–C(2) of **CP2b** was calculated to be 163 pm at the B3LYP/cc-PVDZ level of theory (entry 7) and 161 pm at the CCSD/6-31G(d) level of theory (entry 8), which are much longer than that in **CP1b**, 156 pm (entry 2). An energy barrier of $E_a = 9.2 \text{ kcal mol}^{-1}$ was found for the disrotatory ring-closing mode of reaction from **S-DR2b** to **CP2b** at the UB3LYP/cc-PVDZ level of theory (entry 6, **TS2b** in Figure 1). An alternative reaction pathway of **S-DR2b**,³⁰ which produces the migration product **MG2b**, was also found (eq 2). The activation



energy of this process was calculated to be $E_a = 9.7 \text{ kcal mol}^{-1}$, which was slightly larger than that for the ring-closing reaction of **S-DR2b**. The TD-DFT calculation at the B3LYP/cc-PVDZ level of theory revealed that **S-DR2b** was predicted to absorb light at $\lambda_{\text{calcd}} 662 \text{ nm}$ with a high oscillator strength ($f = 0.076$). Thus, this species could be detected by conventional spectroscopic methods such as UV–vis absorption spectroscopy.

A larger energy difference of $|\Delta E_{\text{CP-DR}}| \sim 15 \text{ kcal mol}^{-1}$ was calculated for the equilibrium reaction of **DR3** with **CP3** at the B3LYP/cc-PVDZ level of theory (entry 10), in which only the spiro[5.5]undecane structure is involved in the ring-closed structure, than that for **DR2b** and **CP2b**. The energy spacing was found to be $-25.1 \text{ kcal mol}^{-1}$ at the (6/6)CASPT2/ANO-RCC-VTZP level of theory (entry 11). Thus, the cooperative effect of the two types of molecular strain is necessary to sufficiently destabilize the ring-closed compounds. It should be noted that the triplet ground state was calculated for the 2,2-dialkoxy-1,3-diradical **DR3** at the UB3LYP/cc-PVDZ level of theory, $\Delta E_{\text{ST}} = +0.55 \text{ kcal mol}^{-1}$ (entry 10). The singlet preference with a small singlet–triplet energy spacing of $\Delta E_{\text{ST}} = -0.68 \text{ kcal mol}^{-1}$ was found at the (6/6)CASPT2/ANO-RCC-VTZP level of theory (entry 11), although a much larger singlet preference was calculated for 2,2-dialkoxycyclopentane-1,3-diols such as **DR1b** ($\Delta E_{\text{ST}} = -5.7 \text{ kcal mol}^{-1}$, entry 3) and **DR2b** ($\Delta E_{\text{ST}} = -5.9 \text{ kcal mol}^{-1}$, entry 9). This noteworthy difference may be attributed to the twisted conformation of **DR3**, which is evident in the structure obtained from optimization in C_2 symmetry (Figure 3). The two

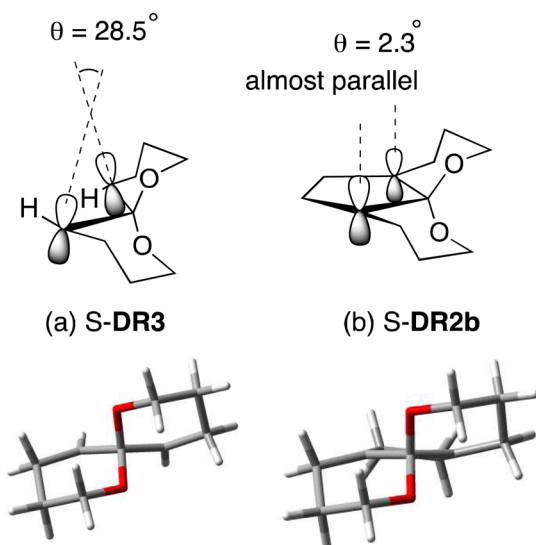


Figure 3. Optimized structures of the singlet state diradical (a) DR3 and (b) DR2b.

p-orbitals in the singlet state of DR3 form a twist angle (θ) of 28.5° . In contrast, a nearly parallel orientation of the two p-orbitals was calculated for DR2b ($\theta = 2.3^\circ$), for which the optimization was also performed in C_2 symmetry. Thus, the through-space interaction between the two p-orbitals and the pseudo π interaction in DR3 are smaller than those in DR2b.^{9,10} This leads to a smaller energy gap between the two NBMOs (ψ_S and ψ_A) and a smaller energetic preference for the singlet state in DR3 than those in DR2b. Indeed, the energy gaps between the two NBMOs were found to be 4.2×10^{-4} eV for the triplet state of DR3 and 2.2×10^{-2} eV for the triplet state of DR2b at the UB3LYP/cc-PVDZ level of theory. The occupation number of $\psi_S/\psi_A = 1.3$ was calculated for S-DR3, which was significantly smaller than that of S-DR2b (Figure 2).

Type-2 Molecules. The Type-2 molecules DR6–8, in which the radical moiety is embedded in a macrocyclic system, were designed to be long-lived multiradical species (entries 14–19). To evaluate the effect of the strain energy induced by the

macrocyclic ring, first of all, the energy difference between the diradicals DR4a,5a (R,R = H,H, X = H; R,R = Ph,Ph, X = H) and the corresponding ring-closed compounds CP4a,5a was calculated at the (U)B3LYP/6-31G(d) level of theory (entries 12 and 13). The phenyl substitution at the radical sites thermodynamically stabilizes the diradical compound DR4a. Thus, the energy difference of $\Delta E_{CP-DR} = -7.3$ kcal mol⁻¹ was found to be much smaller than that between DR1a and CP1a ($\Delta E_{CP-DR} = -32.2$ kcal mol⁻¹, entry 1). Indeed, the C(1)–C(2) bond length of CP4a was found to be 157 pm, which is longer than that of CP1a (153 pm, entry 1). The energy barrier for the ring-closing reaction was found to be 5.7 kcal mol⁻¹ at the (U)B3LYP/6-31G(d) level of theory (TS4a in Figure 1). Thus, the energy barrier from CP4a to DR4a was calculated to be 13.0 ($= E_a + |\Delta E_{CP-DR}|$) kcal mol⁻¹, which is consistent with the experimental value determined by Dougherty et al., $\Delta H^\ddagger = 12.2 \pm 0.6$ kcal mol⁻¹ and $\Delta S^\ddagger = -16.4 \pm 1.5$ eu.³¹ Thus, the UB3LYP/6-31G(d) level of theory reproduced the experimental observation very well.³² Nearly the same values were obtained for the biphenyl-substituted DR5a and CP5a (entry 13). A similar transition state structure TS5a was found between S-DR5a and CP5a (TS5a in Figure 1). Connecting the two ends of CP5 with an arylene unit results in the formation of a strained macrocyclic system, in which the strain has the effect of pulling C(1) and C(2) away from one another and thus stretching the C(1)–C(2) bond. When a *m*-phenylene unit was introduced to form a macrocyclic system, the energy difference between S-DR6a (X = H) and CP6a (X = H) decreased to 5.4 kcal mol⁻¹ (entry 14). A substantial increase in the bond length of the fused C(1)–C(2) bond (162 pm) in CP6a was also found. When a larger aromatic system, a 2,7-naphthylene unit, was embedded in the macrocyclic system, it was expected that the stretch effect on the C(1)–C(2) bond would increase. Indeed, a long C(1)–C(2) bond distance of 160 pm was also calculated for CP7a (entry 15). The energy difference of ΔE_{CP-DR} was found to be just -0.8 kcal mol⁻¹. The triplet was calculated to be the ground state spin-multiplicity with $\Delta E_{ST} = +0.55$ kcal mol⁻¹ for DR7a. The energy barrier for the ring-closing reaction of the singlet diradical was found to be 9.2 kcal mol⁻¹ (TS7a in Figure 1). Thus, the high-spin diradical T-DR7a was predicted to be detectable at room temperature.

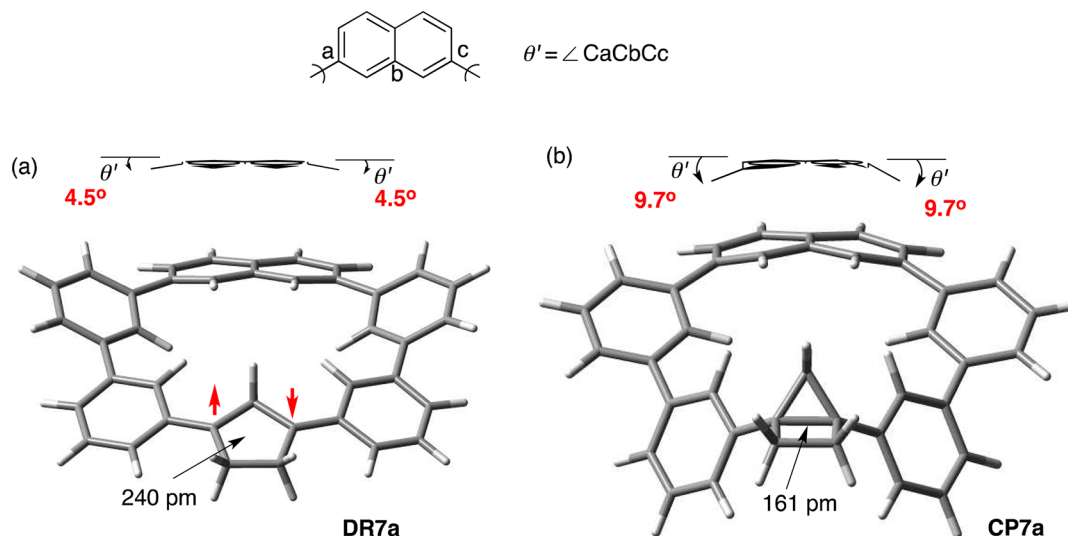


Figure 4. Optimized structures of (a) the singlet state diradical DR7a and (b) the ring-closed compound CP7a.

The molecular strain in the ring-closed compound **CP7a** is apparent from the bent structure of the naphthalene-2,7-diyl system (Figure 4b). Thus, the bend angle was calculated to be $2\theta' = 2\alpha < \text{CaCbCc} = 19.4^\circ$. By comparison, this angle was found to be 9.0° for singlet diradical **DR7a** (Figure 4a). The stretch effect induced by the macrocyclic system was also applied successfully to the design of persistent singlet diradicals. For example, the singlet diradical **S-DR7b** ($X = \text{OMe}$) was calculated to be considerably more stable than the ring-closed compound **CP7b**, $\Delta E_{\text{CP-DR}} = +7.8$ (entry 16). As found for **S-DR1b**, **S-DR7b** was calculated (B3LYP/6-31G(d) level of theory) to absorb light at an easily detectable wavelength, 784 nm ($f = 0.30$).

Relatively simple [n]cyclophane structures are also interesting to see whether the stretch effect on the kinetic stabilization of the multiradical species is possible or not. In such systems, the aromatic system is held in a bent conformation by the bridge. However, at the same time, the bent aromatic system stretches the bridge as it attempts to become planar. Among the numerous conceivable cyclophane structures,³³ (2,7)pyrenophane derivatives **DR8** and **CP8** were chosen for this study (entries 17–19), because a variety of (2,7)pyrenophanes has been synthesized.³⁴ The energy difference $|\Delta E_{\text{CP-DR}}|$ between the singlet diradical **S-DR8** and the corresponding ring-closed compound **CP8** was found to increase with increasing the carbon chain length. Thus, a negligible energy difference, $\Delta E_{\text{CP-DR}} = -1.3 \text{ kcal mol}^{-1}$, was calculated for the smallest bridge size of the cyclophane of **DR8a** ($n = 0$) and **CP8a** ($n = 0$) (entry 17). The energy differences for **DR8b/CP8b** ($n = 1$) and **DR8c/CP8c** ($n = 2$) were found to be -21.0 and $-29.4 \text{ kcal mol}^{-1}$, respectively (entries 18,19). As expected, the degree of bend in the pyrene system decreased dramatically as the length of the bridge became progressively larger. The bend angles ($2\theta''$)^{34d} calculated at the B3LYP/6-31G(d) level of theory were 120° , 82° , and 51° for **CP8a**, **CP8b**, and **CP8c**, respectively. The pyrene system in **CP8a** is severely distorted (Figure 5). Indeed, it is predicted to be on the upper end of what would be synthetically accessible.^{34c,d}

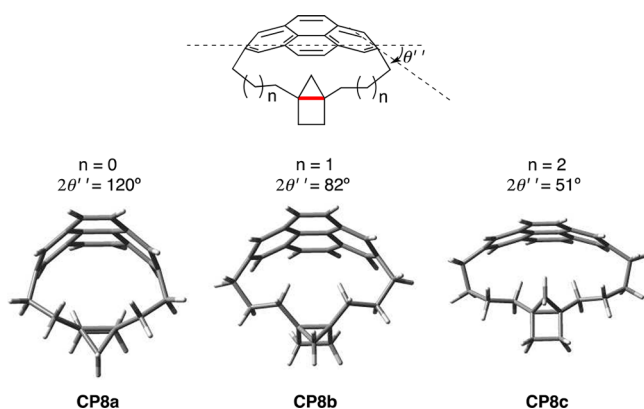


Figure 5. The bent structure of **CP8a–c** induced by the (2,7)-pyrenophane macrocycle.

Finally, to test the stretch effect on destabilization of the ring-closed diradicals derived from delocalized diradicals, the oxyallyl **DR9** and the corresponding **CP9** were calculated at the (U)B3LYP/6-31G(d) level of theory (entry 20). As reported for the parent four-membered oxyallyl **DR10** (Chart 1), the singlet ground state was calculated to be the

ground state spin-multiplicity. It should be noted that during the optimization of the ring-closed compound **CP9** the singlet diradical structure of **S-DR9** was obtained. This strongly suggests that the ring-opening process from **CP9** to **S-DR9** is barrierless. At the UB3LYP/6-31G(d) level of theory, the $\langle S^2 \rangle$ value was found to be 0.00 (entry 20), indicating that the diradical **S-DR9** is not the open-shell molecules, but the closed-shell compound. To evaluate accurately the diradical character of **S-DR9**, the occupation number in the two nonbonding molecular orbital was calculated at the CASSCF-(2/2)/6-31G(d) level of theory. Thus, the occupation number was found to be 1.90/0.10 = 19, suggesting that **S-DR9** has a small diradical character.

To clarify the stretch effect of Type-2, the phenyl-substituted diradical **DR11** ($R = \text{H}$) and its ring-closed counterpart **CP11** ($R = \text{H}$) were computed (entry 21). In contrast to the macrocyclic system of **DR9** and **CP9**, the ring-closed compound **CP11** was found to be more stable by 3.6 kcal mol⁻¹ at the (U)B3LYP/6-31G(d) level of theory. The energy difference between the parent **DR10** and **CP10** was reported to be 28.9^{14c} and 25.0^{14d} kcal mol⁻¹ at the CASPT2/6-31G(d) and UB3LYP/6-31G(d) levels of theory, respectively. Thus, the diphenyl substitution is responsible for the much smaller energy difference between **DR11** and **CP11**. The stretch effect was found to be effective also for the kinetic stabilization of oxyallyl diradicals.

SUMMARY

In the present study, “stretch” effects induced by molecular strain on weakening σ -bonds were investigated computationally to design long-lived localized diradicals and oxyallyls. The molecular strain derived from the combination of the spiro[5.5]-undecane and bicyclo[2.1.0]cyclopentane systems was found to energetically destabilize the ring-closed compound, leading to small, or even negligible, energy differences with the corresponding singlet diradicals. Thus, the stretch effect caused by the Type-1 molecular strain was found to be useful for the generation of long-lived localized diradicals with a low energy barrier from the ring-closed compounds. Another stretch effect derived from the macrocyclic system, which is the Type-2 molecular strain, was also found to significantly destabilize the ring-closed structures of the corresponding 1,3-diradicals. The stretch effect was successfully applied for other multiradical species such as oxyallyls. These findings should stimulate further calculations and experiments on these fascinating molecules. Experimental studies based on these computational findings are now underway.

ASSOCIATED CONTENT

Supporting Information

Computational details including optimized geometries and energies of **DR1–9,11** and **CP1–9,11** and full citation for ref 22. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mabe@hiroshima-u.ac.jp; gbodwell@mun.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Grant-in-Aid for Scientific Research on Innovative Areas "Stimuli-responsive Chemical Species" (24109008) (M.A.), " π -Space" (No. 21108516) (M.A.), the Scientific Research (No. 19350021) (M.A.), Tokuyama Science Foundation (M.A.), Mazda Foundation (M.A.), and the Natural Sciences and Engineering Research Council (NSERC) of Canada (G.J.B.).

DEDICATION

This paper is dedicated to Professor Dr. Waldemar Adam on the occasion of his 75th birthday.

REFERENCES

- (1) *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; John Wiley & Sons: Hoboken, NJ, 2004.
- (2) (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) Ratera, I.; Veciana, J. *Chem. Soc. Rev.* **2012**, *41*, 303.
- (3) Nakano, M.; Minami, T.; Yoneda, K.; Muhammad, S.; Kishi, R.; Shigeta, Y.; Kubo, T.; Rougier, L.; Champagne, B.; Kamada, K.; Ohta, K. *J. Phys. Chem. Lett.* **2011**, *2*, 1094.
- (4) *Stable Radicals*; Hicks, R. G., Ed.; John Wiley & Sons: Southern Gate, Chichester, 2010.
- (5) Kuzmanich, G.; Spanig, F.; Tsai, C.-K.; Um, J. M.; Hoekstra, R. M.; Houk, K. N.; Guldi, D.; Garcia-Garibay, M. *J. Am. Chem. Soc.* **2011**, *133*, 2342.
- (6) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.
- (7) (a) Beyer, M. K.; Clausen-Schaumann, H. *Chem. Rev.* **2005**, *105*, 2922. (b) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. *Nature* **2007**, *446*, 423. (c) Park, I.; Sheiko, S. S.; Nese, A.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 1805. (d) Lenhardt, J. M.; Black, A. L.; Craig, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 10818. (e) Wu, D.; Lenhardt, J. M.; Black, A. L.; Akhremitchev, B. B.; Craig, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 15936. (f) Lenhardt, J. M.; Ong, M. T.; Choe, R.; Evenhuis, C. R.; Martinez, T. J.; Craig, S. L. *Science* **2010**, *329*, 1057. (g) Lenhardt, J. M.; Ogle, J. W.; Ong, M. T.; Choe, R.; Martinez, T. J.; Craig, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 3222. (h) Klukovich, H. M.; Kean, Z. S.; Iacono, S. T.; Craig, S. L. *J. Am. Chem. Soc.* **2011**, *133*, 17882. (i) Black, A. L.; Lenhardt, J. M.; Craig, S. L. *J. Mater. Chem.* **2011**, *21*, 1655. (j) Akbulatov, S.; Tian, Y.; Boulatov, R. *J. Am. Chem. Soc.* **2012**, *134*, 7620. (k) Klukovich, H. M.; Kean, Z. S.; Black Ramirez, A. L.; Lenhardt, J. M.; Lin, J.; Hu, X.; Sraig, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 9577.
- (8) (a) Akbulatov, S.; Tian, Y.; Boulatov, R. *J. Am. Chem. Soc.* **2012**, *134*, 7620. (b) Huang, Z.; Boulatov, R. *Chem. Soc. Rev.* **2011**, *40*, 2359. (c) Yang, Q.-Z.; Huang, Z.; Kucharski, T. J.; Khvostichenko, D.; Chen, J.; Boulatov, R. *Nat. Nanotechnol.* **2009**, *4*, 302.
- (9) Borden, W. T. *Chem. Commun.* **1998**, 1919.
- (10) (a) Abe, M.; Ye, J.; Mishima, M. *Chem. Soc. Rev.* **2012**, *41*, 3808. (b) Abe, M.; Adam, W.; Hara, M.; Hattori, M.; Majima, T.; Nojima, M.; Tachibana, K.; Tojo, S. *J. Am. Chem. Soc.* **2002**, *124*, 6540.
- (11) (a) Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Jeubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593. (b) Abe, M.; Adam, W.; Heidenfelder, T.; Nau, W. M.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 2019. (c) Abe, M.; Kubo, E.; Nozaki, K.; Matsuo, T.; Hayashi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7828.
- (12) For isolated examples of singlet diradicals in heterocycles, see; (a) Niecke, E.; Fuchs, A.; Nieger, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3028. (b) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880. (c) Cui, C.; Brynda, M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 6510. (d) Cox, H.; Hitchcock, P. B.; Lappert, M. F.; Peirssens, L. J.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4500. (e) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2011**, *133*, 12478. (f) Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. *Angew. Chem. Int. Ed.* **1995**, *34*, 555. (g) Schoeller, W. W.; Rozhenko, A.; Bourissou, D.; Bertrand, G. *Chem.–Eur. J.* **2003**, *9*, 3611. (h) Schoeller, W. W.; Niecke, E. *Phys. Chem. Chem. Phys.* **2012**, *14*, 2015.
- (13) For long C–C single bonds, see; (a) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 1757. (b) Kawai, H.; Takeda, T.; Fujiwara, K.; Inabe, T.; Suzuki, T. *Cryst. Growth Des.* **2005**, *5*, 2256. (c) Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature* **2011**, *477*, 308. (d) Lemal, D. M. *J. Org. Chem.* **2009**, *74*, 2413. (e) Lemal, D. M. *J. Org. Chem.* **2010**, *75*, 6411.
- (14) (a) Ichimura, A. S.; Lahti, P. M.; Matlin, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2868. (b) Powell, H. K.; Borden, W. T. *J. Org. Chem.* **1995**, *60*, 2654. (c) Hrovat, D. A.; Rauk, A.; Sorensen, T. S.; Powell, H. K.; Borden, W. T. *J. Am. Chem. Soc.* **1996**, *118*, 4159. (d) Hess, B. A., Jr.; Smentek, L. *Eur. J. Org. Chem.* **1999**, 3363.
- (15) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.
- (16) (a) Cizek, T. In *Advances in Chemical Physics*; Hariharan, P. C., Ed.; Wiley Interscience: New York, 1969; Vol. 14, p 35. (b) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (c) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 7382. (d) Scuseria, G. E.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, *90*, 3700.
- (17) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- (18) Dunning, T. H. *J. Phys. Chem.* **1989**, *90*, 1007.
- (19) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537.
- (20) Eade, R. H. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362.
- (21) (a) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218. (b) Casida, M. E.; Jamorksi, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439–4449.
- (22) Frisch, M. J. et al, *Gaussian 03*, Revision C.02; Gaussian Inc.: Wallingford, CT, 2004. See the Supporting Information for full citation.
- (23) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
- (24) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *108*, 2851.
- (25) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P. O.; Cossi, M.; Schimmelpennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222.
- (26) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425.
- (27) (a) Abe, M.; Ishihara, C.; Takegami, A. *J. Org. Chem.* **2004**, *69*, 7250. (b) Nakamura, T.; Gagliardi, L.; Abe, M. *J. Phys. Org. Chem.* **2010**, *23*, 300.
- (28) Abe, M.; Adam, W.; Borden, W. T.; Hattori, M.; Hrovat, D. A.; Nojima, M.; Nozaki, K.; Wirz, J. *J. Am. Chem. Soc.* **2004**, *126*, 574.
- (29) Wiberg, K. B. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; John Wiley & Sons: Hoboken, NJ, 2004; p 717.
- (30) Abe, M.; Hattori, M.; Takegami, A.; Masuyama, A.; Hayashi, T.; Seki, S.; Tagawa, S. *J. Am. Chem. Soc.* **2006**, *128*, 8008.
- (31) Combs, D. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 6894.
- (32) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *J. Mol. Struct.: THEOCHEM* **1997**, 398.
- (33) Smith, B. H. *Bridged Aromatic Compounds*; Academic Press: New York, 1964. (b) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vols. 1 and 2. (c) *Top. Curr. Chem.* **1983**, *113*; *Top. Curr. Chem.* **1983**, *115*. (d) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: London, U.K., 1991. (e) Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, 1993. (f) *Top. Curr. Chem.* **1994**, *172*. (g) Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994**, *50*, 4575–4622. (h) Bodwell, G. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2085–2088. (i) de Meijere, A.; König, B. *Synlett* **1997**, 1221–1232.

(j) Bodwell, G. J.; Satou, T. *Angew. Chem.* **2002**, *114*, 4175–4178; *Angew. Chem., Int. Ed.* **2002**, *41*, 4003. (k) Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000. (l) *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004.

(34) (a) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1320. (b) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. *Chem.—Eur. J.* **1999**, *5*, 1823. (c) Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2000**, *65*, 5360. (d) Bodwell, G. J.; Fleming, J. J.; Miller, D. O. *Tetrahedron* **2001**, *57*, 3577. (e) Bodwell, G. J.; Miller, D. O.; Vermeij, R. J. *Org. Lett.* **2001**, *3*, 2093. (f) Lai, R. Y.; Fleming, J. J.; Merner, B. L.; Vermeij, R. J.; Bodwell, G. J.; Bard, A. J. *J. Phys. Chem. A* **2004**, *108*, 376. (g) Aprahamian, I.; Bodwell, G. J.; Fleming, J. J.; Manning, G. P.; Mannion, M. R.; Merner, B. L.; Sheradsky, T.; Vermeij, R. J.; Rabinovitz, M. *J. Am. Chem. Soc.* **2004**, *126*, 6765. (h) Zhang, B.; Manning, G. P.; Dobrowolski, M. A.; Cyrański, M. K.; Bodwell, G. J. *Org. Lett.* **2008**, *10*, 273. (i) Dobrowolski, M. A.; Cyrański, M. K.; Merner, B. L.; Bodwell, G. J.; Wu, J.; Schleyer, P. v. R. *J. Org. Chem.* **2008**, *73*, 8001. (j) Vermeij, R. J.; Miller, D. O.; Dawe, L. N.; Aprahamian, I.; Sheradsky, T.; Rabinovitz, M.; Bodwell, G. J. *Aust. J. Chem.* **2010**, *63*, 1703.