Inverted Bond and Its Effect on the Strains of [1.1.1]Propellane Frameworks

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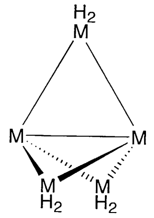
The delocalization of σ electrons from a normal bond to a geminal "inverted" bond was shown to be strongly bonding due to the orbital phase property. The bonding property of the geminal delocalization was predicted to increase with the bond inversion. The central bond between the bridgehead atoms in the [1.1.1]propellane frameworks (**1**) is inverted to relax the ring strains as the row of the elements is high in the periodical table. The strain decreases in the order of **1a** (M=C) > **1b** (M=Si) > **1c** (M=Ge) > **1d** (M=Sn).

[1.1.1]Propellane and its congeners (**1**) have been investigated extensively.[1-5] Interestingly, pentasila[1.1.1]propellane (**1b**)[2] was reported to be less strained than [1.1.1]propellane (**1a**)[3] while the component monocyclic three-membered ring cyclotrisilane[6] is more strained than cyclopropane.[7] The low strain of **1b** relative to **1a** was interpreted in terms of the stretching of the central Si-Si bond between the bridgehead atoms, which converts the three-membered rings into the less strained four-membered rings.[2a,b] The intuitive explanation is not convincing. The strain energies calculated from the homodesmotic reactions,[8]

$$M_5H_6 + 7\ MH_3MH_3 \longrightarrow 2\ M(MH_3)_4 + 3\ MH_3MH_2MH_3,$$

includes the bond energies. The bond stretching itself destabilizes the bonds and does not decrease but increases the strain. The low strain of **1b** suggested that the destabilization by the bond stretching should be overcome by the stabilization by some other mechanism.



1 **a**: M=C
b: M=Si
c: M=Ge
d: M=Sn

The central bond between the bridgehead atoms in **1** is an "inverted" bond where the hybrid orbitals are directed away from each other.[4] Here, we theoretically show that the bond inversion generally increases the bonding property of the geminal delocalization of σ electrons from a normal bond to an inverted bond. From the inversion of the central bond we predict that the strain decreases in the order of **1a** (M=C) > **1b** (M=Si) > **1c** (M=Ge) > **1d** (M=Sn).

The geminal delocalization between the normal bonds (Figure 1a) was previously[9-11] shown to be less bonding than usually or antibonding ($h_{\sigma\sigma^*}-s_{\sigma\sigma^*}h_{\sigma\sigma}>0$ for $s_{\sigma\sigma^*}>0$ since $|h_{\sigma\sigma^*}|<|s_{\sigma\sigma^*}h_{\sigma\sigma}|$ where $h_{\sigma\sigma^*}$, $s_{\sigma\sigma^*}$ and $h_{\sigma\sigma}$ denote the resonance and overlap integrals between the σ and σ* orbitals involved in the geminal delocalization and the σ orbital energy, respectively). The geminal hybrid orbital interaction or the resonance integral h_{13} between the hybrid orbital χ_1 and χ_3 reduces $|h_{\sigma\sigma^*}|$ due to the phase relation between χ_1 and χ_3 opposite to that between χ_2 and χ_4 (Figure 1a), while $|s_{\sigma\sigma^*}h_{\sigma\sigma}|$ remains unchanged on the inclusion of $s_{13}(=0)$. The antibonding property of the geminal delocalization is reduced with the decrease in $|h_{13}|$. The strain of the three-membered ring composed of normal bonds is relaxed with the decrease in $|h_{13}|$ or with the *decreasing* s-character of χ_1 and χ_3. As the bond is inverted (Figure 1b), the lobe of χ_3 preferentially interacting with χ_1 changes from the front side to the back side. The phase relations turns identical between χ_1 and χ_3 and between χ_2 and χ_4. The inclusion of $|h_{13}|$ increases $|h_{\sigma\sigma^*}|$, leading to $|h_{\sigma\sigma^*}|>|s_{\sigma\sigma^*}h_{\sigma\sigma}|$ or to $h_{\sigma\sigma^*}-s_{\sigma\sigma^*}h_{\sigma\sigma}<0$ for $s_{\sigma\sigma^*}>0$. The geminal delocalization turns bonding. The bonding property increases with $|h_{13}|$ or with the *increasing* s-character of χ_3. The relaxation ring strain increases with the bond inversion.

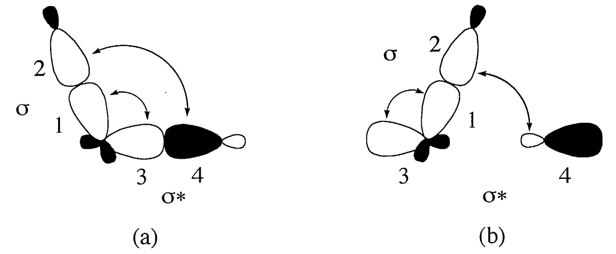


Figure 1. Orbital phase control of the antibonding and bonding properties of geminal delocalizations (a) between normal bonds and (b) from a normal bond to an inverted bond, respectively.

The bond orbitals of **1a** and **1b** or the hybrid orbitals used to express the bonds, were optimized.[9-11] The central bond between the bridgeheads was found to be only a little inverted in **1a** ($-sp^{69.8}$) and significantly inverted in **1b** ($-sp^{4.3}$)[12,13] (the minus sign denotes the bond inversion). The bond inversions lead to the bonding properties of the geminal delocalization, which were confirmed by the positive values of the calculated interbond populations $IBP_{\sigma\sigma^*}$[9-11] ($=2P_{\sigma\sigma^*}S_{\sigma\sigma^*}$; 0.035 for **1a**[14] and 0.034 for **1b**).[12,13] Comparison with the antibonding properties in cyclopropane (-0.003) and cyclotrisilane (-0.021) suggests that the ring strain of **1a** and **1b** should be relaxed by the geminal delocalization. It is preferable to use the energy rather than the population when the molecules composed of different elements are compared with one another. We defined the interbond energy between the bond orbitals ϕ_i and ϕ_j as $IBE_{ij}=P_{ij}(F_{ij}+H_{ij})$ where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonian matrices, respectively. The calculated interbond energies showed that the geminal delocalization relaxes the ring strain of **1b** ($\mathrm{IBE}_{\sigma\sigma^*}$=-0.290 au) more than **1a** ($\mathrm{IBE}_{\sigma\sigma^*}$=-0.228 au).[12,13] This makes remarkable contrast with the positive interbond energies of the monocyclic three-membered rings ($\mathrm{IBE}_{\sigma\sigma^*}$=0.113 au for cyclotrisilane and 0.011 au for cyclopropane). We understood in terms of the geminal delocalization that **1b** is less strained than **1a** while cyclotrisilane is more strained than cyclopropane.[10]

From the geminal delocalization the strain of **1** was predicted to be relaxed as the row of the ring elements is high in the periodic table. The interbond population showed that the bonding property of the geminal delocalization increases in the order of **1b** (0.041) < **1c** (0.052) < **1d** (0.063).[12,15] The interbond energy (au) showed that the stabilization by the geminal delocalization increases in the same order (**1b**: -0.125; **1c**: -0.159; **1d**: -0.175).[12,15] The ordering of the bonding property and the stabilization by the geminal delocalization are in accordance with the inversion of the central bond (**1b**: -sp$^{9.9}$; **1c**: -sp$^{7.3}$; **1d**: -sp$^{4.3}$). The strain energies calculated from the homodesmotic reactions at the RHF/3-21G* level confirmed the prediction of the strain relaxation. The strain energies (kcal/mol) decrease in the order of **1a** (110.6) > **1b** (79.0) > **1c** (68.9) > **1d** (64.3). The inclusion of electron correlation by the single point calculations (MP2/3-21G*//RHF/3-21G*) confirmed the sequence of the strain energies (kcal/mol) [**1a:** 109.6; **1b:** 64.6; **1c:** 59.5; **1d:** 52.6]. The MP2/LanL1DZ calculations gave a clearer sequence (kcal/mol): **1b** (73.4) > **1c** (52.8) > **1d** (39.4).

The geminal delocalization theory for ring strain relaxation previously contributed to understanding and predicting interesting properties of monocyclic[9-11] and bicyclic[16] strained molecules. The successful application to [1.1.1]propellane and its congeners in the present work further confirmed the significance of the geminal delocalization of σ-electrons in molecular properties and supported the usefulness of the classical bond model for small ring molecules containing even an inverted bond.

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