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# Why Do Two $\pi$-Electron Four-Membered Hückel Rings Pucker?

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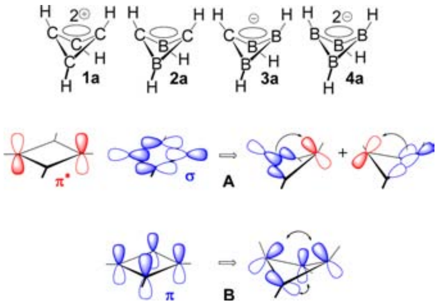
## ABSTRACT



**Notwithstanding their two (i.e., $4n + 2$) $\pi$ electrons, four-membered ring systems, 1–4, favor puckered geometries (1a–4a) despite the reduction in vicinal $\pi$ overlap and in the ring atom bond angles. This nonplanar preference is due to $\sigma \rightarrow \pi^*$ hyperconjugative interactions across the ring (A) rather than to partial 1,3-bonding (B). Electronegative substituents (e.g., F in $C_4F_4^{2+}$) reduce the $\sigma \rightarrow \pi^*$ electron delocalization, and planar geometries result. In contrast, electropositive groups (e.g., $SiH_3$ in $C_4(SiH_3)_4^{2+}$) enhance hyperconjugation and increase the ring inversion barriers substantially.**

Although expected to be planar due to two $\pi$ electron Hückel aromaticity, maximum vicinal $\pi$-overlap, and the decrease in the already small bond angles, four-membered rings (4MRs) such as **1a**–**4a** (see abstract graphic) are puckered.[1] Following Olah's success in preparing, inter alia, the persistent tetramethylcyclobutadiene dication,[1f] theoretical computations predicted that $C_4(CH_3)_4^{2+}$ along with the **1a**,[1b,2a,b] **2a**,[2a,b,c] and **4a**[1a] prototypes favored nonplanar geometries (see abstract graphic). These computations were subsequently verified by comparison of experimental and computed chemical shifts of the $C_4(CH_3)_4^{2+}$,[1c] as well as X-ray structure determinations of **2a**–**4a** derivatives.[3–5]

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Such ring puckering was first attributed to $\sigma$ and $\pi^*$ orbital mixing in lower symmetry; *hyperconjugation* results (see **A** in the abstract graphic).[1b,2a] Increased 1,3 p-orbital overlap and double homoallylic bonding upon folding (see **B**)[2] were proposed as an alternative.[2h,g] This is akin to the homoaromaticity generally invoked for the cyclobutenyl cation (i.e., the homocyclopropenylium ion) and similar systems.[6]

Does hyperconjugation (**A**) or enhanced 1,3-bonding (**B**) stabilize the folded conformers of nonplanar **1a**–**4a**? Does puckering influence the aromaticity of these 4MRs with two quasi "$\pi$" electrons? Irngartinger found no significant experimental support for 1,3-interactions in $(CH)_2(BNR_2)_2$ (R = isopropyl).[3c] Firme et al.'s evidence for increased electron densities at the ring centers of nonplanar derivatives of **1a**[7] is not decisive. As both hyperconjugation and partial 1,3-bonding might delocalize the electron density upon puckering, their relative importance is uncertain.

Other 4MRs with electron-deficient tricoordinate centers, e.g., the cyclobutyl cation and cyclobutylidene, also prefer nonplanar geometries.[8,9] Even $B_4H_4$ (**5a*** and **5a**, Figure 1 top) has a low energy $D_{2d}$ conformer strongly stabilized (by 39 kcal/mol) relative to its planar $D_{4h}$ form. Since the $B_4H_4$ ring has four tricoordinate centers, but no $\pi$-electrons, the puckering preference must be due to changes in the $\sigma$-skeleton. Indeed, correlation of the delocalized Kohn–Sham MOs (Figure 1 top, HOMO-1s: $e_u \rightarrow e$) demonstrates that the B–B $\sigma$-bonding orbitals (analogous to the $\sigma$-orbital depicted in **A** of the abstract graphic) become lower in energy upon puckering. This supports the hyperconjugation argument. NBO localization of the canonical molecular orbitals (CMOs) confirms that ring folding reduces the B–B $\sigma$-bond occupancies of **5a** (by 0.08 electrons) compared to those of **5a***, while the formally empty p-orbitals in **5a*** gain 0.12 electrons each in **5a**, due to $\sigma \rightarrow \pi^*$ hyperconjugation.

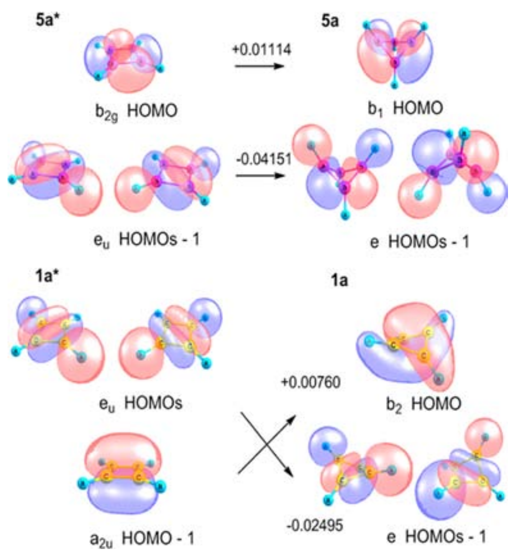

**Figure 1.** B3LYP/6-311+G** changes in orbital energies (au) upon puckering for $B_4H_4$ (**5a*** → **5a**, top) and for $C_4H_4^{2+}$ (**1a*** → **1a**, bottom). The $\sigma$-orbital energies of nonplanar forms are lowered, but the $\pi$ HOMO$-$1 energy of **1a*** is raised. Hence, $\pi$-orbital changes alone cannot be the cause of puckering.

Likewise, the degenerate $\sigma$-MOs (HOMOs, $e_u$) of **1a*** are lowered upon puckering to **1a** (HOMO$-$1s, e) (see Figure 1, bottom), while the $\pi$-orbital energies are raised. This refutes the possibility of any 1,3-bonding being responsible for the nonplanarity of these 4MRs with two quasi "$\pi$" electrons. The corresponding orbital energy changes of **2a**–**4a** are similar. Upon puckering, the stabilizing $2\pi$ electron delocalization in planar **1a*** is reduced to *two* weaker 1,3-$\pi$ orbital interactions in **1a** (see the $b_2$ orbital in Figure 1, bottom and the discussion below). As depicted for **1a** in Figure 2a, the $\sigma$-NBO occupancies of **1a**–**4a** also are lowered (e.g., by 0.03 electrons for each C–C $\sigma$ bond in $C_4H_4^{2+}$), while the p* occupancies of the ring atoms are raised (0.03e for each C p* orbital of $C_4H_4^{2+}$). A second order NBO perturbation analysis of the NBO Fock matrix confirms that hyperconjugative interactions between these orbitals (see Figure 2a) are responsible for this charge transfer. Moreover, the magnitude of the $\sigma \rightarrow$ p* hyperconjugation in **1a**–**4a** increases in the same order as their energetic puckering preferences (see Figure 3).

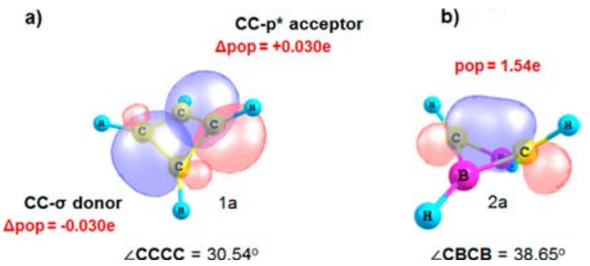

**Figure 2.** (a) Schematic depiction of the $\sigma \rightarrow$ p* cross-ring hyperconjugative interactions responsible for puckering in **1a**. (b) The partly occupied 1,3 C–C NBO for puckered **2a**.

In the NBO formalism, the magnitude of hyperconjugative stabilization between a donor–acceptor localized

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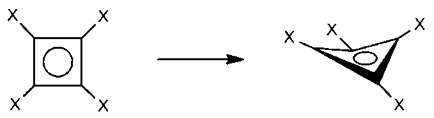
orbital pair (i,j) is proportional to the square of their off-diagonal Fock matrix elements ($F_{ij}$), and inversely proportional to their orbital energy difference ($e_i - e_j$). The $F_{ij}$ term corresponds roughly to the degree of orbital "mixing" and can be related to the overlap of the preorthogonal (i.e., overlap allowed) donor–acceptor orbital pair via a Mulliken-type approximation.[10] This overlap is zero in the planar conformations of **1a**–**4a**, but puckering introduces overlap of the $\sigma$ and p* ring orbitals (see Figure 2a) giving rise to cross-ring hyperconjugative stabilization.

Cross-ring hyperconjugation is also facilitated by the small $e_i - e_j$ energy gaps arising from angle strain. In **1a**–**4a** the $e_i - e_j$ values vary from 0.35 to 0.57 au, i.e., on the low end of the 0.28–1.52 au $e_i - e_j$ range typically observed for donor–acceptor interactions.[11] In addition to its inherent stabilizing character, hyperconjugation also lowers the occupancies of the strained ring $\sigma$-bond orbitals, and thus reduces their mutual interelectronic repulsion. Consequently, the fact that the $\sigma$-HOMO energies of **1a*** lie above its $\pi$-orbital energy indicates high strain (see Figure 1, bottom). The opposite CMO order in **1a** indicates a decrease of this strain upon puckering.[12]

Substituent effects confirm the importance of cross-ring hyperconjugation on the geometries of the **1a**–**4a** analogs. Electronegative groups deactivate $\sigma \rightarrow \pi^*$ hyperconjugation and favor planar geometries (indeed, computations found $C_4F_4^{2+}$ (**1b**) (see Figure 3) to be planar as early as 1978).[1b] The F substituted **2b**–**4b** analogs also prefer planarity considerably. The strong $\sigma$-electron withdrawal by F, evident from Natural Population Analyses (NPA),[13,14] reduces the donor strength of the ring $\sigma$-bonds significantly.



| X = | a (H) | b (F) | c ($SiH_3$) |
|---|---|---|---|
| **1** ($C_4X_4^{2+}$) | -8.37 | +15.03 | -22.72 |
| **2** ($C_2B_2X_4$) | -17.24 | +13.86 | -26.11 |
| **3** ($CB_3X_4^-$) | -11.77 | +11.40 | -19.53 |
| **4** ($B_4X_4^{2-}$) | -12.42 | +10.54 | -21.34 |

**Figure 3.** B3LYP/6-311+G** energy changes (kcal/mol) upon puckering for **1a**–**4a** and their F (**1b**–**4b**) and $SiH_3$ (**1c**–**4c**) substituted derivatives. The X = F estimates were based on partially optimized geometries with ring puckering angles fixed at the corresponding X = H values. (Puckering angles for X = H and X = $SiH_3$ are given in the Supporting Information.)

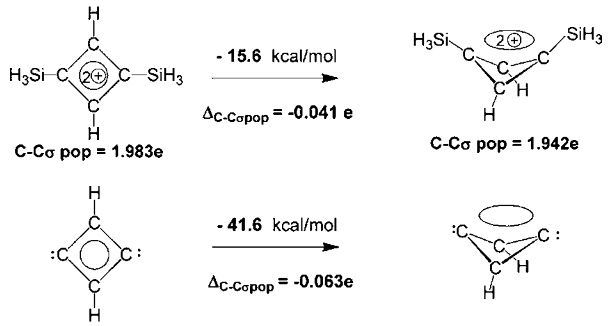


**Figure 4.** B3LYP/6-311+G** inversion barriers and B3LYP/6-31G*//B3LYP/6-311+G** C–C$\sigma$ NBO occupancies for $C_4H_2(SiH_3)_2^{2+}$ and $C_4H_2$. Electron-donating groups enhance cross-ring hyperconjugation, decreasing the occupancy of the strained C–C$\sigma$ bonds.

Electropositive substituents have the opposite effect. The inductive electron donation of $SiH_3$ groups to the ring $\sigma$-bonds[15,16] of **1c**–**4c** enhances $\sigma \rightarrow \pi^*$ hyperconjugation and elevates the inversion barriers substantially (see Figure 3). Carbenic 4MR-2$\pi$ e-aromatic species also may be employed for isoelectronic substitutions of a CH(+) by a singlet C:. Indeed, such carbene species strongly prefer puckered conformations (e.g., by 41.6 kcal/mol for $C_4H_2$; see Figure 4), due to the greatly enhanced cross-ring hyperconjugative interactions and the lowered occupancy of their strained C–C$\sigma$ bonds. Such substituent effects agree with previous structural studies on **1a** derivatives[1b,7] and support the hyperconjugation rationale for the puckering of 4MR-2$\pi$ e-aromatic systems impressively.

A more subtle approach is required to determine the role of partial 1,3 bonding in stabilizing the puckered conformers of **1a**–**4a**. The NBOs of **1a**, **3a**, and **4a** give no indication of 1,3 bonding, but the CMO to NBO localization of **2a** produces a partially filled 1,3 CC bond orbital corresponding to a combination of folded $p_z$ atomic orbitals, as shown in Figure 2b. The short 1.802 Å 1,3 C$\cdots$C distance in **2a** implies a weak bonding interaction not present in the other 2e-aromatic derivatives considered here.

Wiberg Bond Indexes (WBI)[17] are ill-suited for quantifying 1,3 interactions in **1**–**4**. Since puckering enhances the electron density within the rings, 1,3 WBIs increase irrespective of the energetic preferences. Thus, folding increases the 1,3-CC WBIs in both **1a** and **1b** ($C_4F_4^{2+}$) by

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[10] Weinhold, F.; Landis, C. *Valency and Bonding, A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, 2005.

[11] Weinhold, F.; Landis, C. R. *Discovering Chemistry With Natural Bond Orbitals* **2012**, in preparation.

[12] As is well known, hyperconjugation with exocyclic acceptor substituent $\pi^*$- or p-orbitals decreases the strain of cyclopropane: Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907. Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Chem. Soc.* **1984**, *106*, 4412. Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69 and references therein.

[13] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

[14] The sum of the occupancies of the 2s, $2p_x$, and 2p orbitals, comprising the $\sigma$-framework of **1b**–**4b**, are decreased relative to **1a**–**4a**, e.g., by −0.716 e for planar **1b** vs puckered **1a**.

[15] For example, the sum of NPA changes in the 2s, $2p_x$, and $2p_y$ orbitals of each carbon is +0.188 greater in **1c** than in **1a**.

[16] Hehre, W. J.; Radom, L.; P. v. R. Schleyer, Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: 1986.

[17] Wiberg, K. B. *Tetrahedron* **1968**, *1968*, 1083.

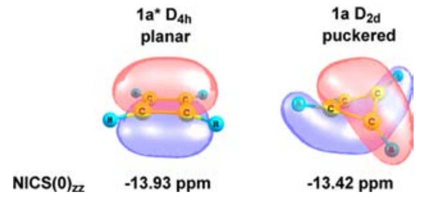

**Figure 5.** Dissected NICS(0)$_{\pi zz}$ values for **1a*** ($D_{4h}$) and **1a** ($D_{2d}$) comprising only the NICS(0)$_{zz}$ contributions of the $\pi$ (and "quasi" $\pi$) MOs.

about 0.038, despite the large destabilization of $C_4F_4^{2+}$ relative to its planar minimum (Figure 3).[18]

Partial 1,3 bonding is not responsible for the puckering of 2$\pi$ aromatic 4MRs. This is demonstrated definitively by optimizations of partially folded **1a**–**4a** in the absence of cross-ring hyperconjugation. While the usual unrestricted optimizations result in the fully puckered conformers of **1a**–**4a**, restricted optimizations, in which the $F_{ij}$ terms corresponding to NBO mixing between the ring $\sigma$ and p* orbitals are set to zero, lead in each case to the planar conformers (corresponding to the respective planar transition states on the *delocalized* PES). Thus, even though they are still potentially operative under such constraints, the 1,3-bonding interactions are ineffective. Instead, cross-ring hyperconjugation clearly is responsible for the puckering of 4MR-2$\pi$ e aromatics.

Although 1,3-$\pi$ overlap is present, in **1a**–**4a** as well as in puckered homoaromatics systems (e.g., the cyclobutenyl cation),[6] it is not the cause of ring puckering in these 4MR systems. These weak 1,3 interactions in **1a**–**4a** have quasi "$\pi$" character (see Figure 1, bottom, HOMO $b_2$ and Figure 2b) and are the residual effects of the 2$\pi$ electron delocalization stabilization in *planar* **1a**–**4a** upon puckering. Indeed, both planar and puckered **1a** are $\pi$-aromatic.[1e,6] Dissected nucleus independent chemical shifts (NICS, at GIAO-PW91/IGLOIII),[19] NICS(0)$_{\pi zz}$, computed at the heavy atom ring centers of planar (−13.9 ppm) and puckered (−13.4 ppm) **1a** are nearly the same (see Figure 5). This is roughly one-third of the NICS(0)$_{\pi zz}$ value for benzene (−35.6 ppm), computed at the same level. For comparison, the NICS(0)$_{\pi zz}$ of the antiaromatic $C_4H_4$ ($D_{2h}$) is +58.2 ppm. NICS$_{\pi zz}$ is the most refined NICS index for evaluating $\pi$-aromaticity, as it extracts only the out-of-plane (*zz*) tensor component of the relevant $\pi$ MOs (or the quasi $\pi$ HOMO, $b_2$, for puckered **1a**) involved in aromaticity.

Hückel 4MR-2$\pi$ electron aromatics have only one occupied $\pi$ MO and no strong preference for planarity. The decrease in vicinal p-$\pi$ overlap on puckering counteracts any gain in double cross-ring 1,3 p-overlap. Such p-$\pi$ effects are not responsible for the puckering of **1a**–**4a**. Instead, the considerable $\sigma$–$\pi$* mixing (i.e., hyperconjugation across the ring) is responsible for the lower energy of the puckered conformers **1a**–**4a**. Cross-ring hyperconjugation favors nonplanar 4MR geometries generally, even for saturated rings (e.g., cyclobutane[20]).

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**Supporting Information Available.** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] The 1,3 C···C bond indices of planar vs puckered $C_4H_4^{2+}$ are 0.262 and 0.300 respectively, while those of $C_4F_4^{2+}$ are 0.208 and 0.171. F subsitution decreases the electron density in the ring center, and smaller absolute bond indices of $C_4F_4^{2+}$ relative to $C_4H_4^{2+}$ result.

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The authors declare no competing financial interest.