

Hyperconjugative π -Aromaticity: How To Make Cyclopentadiene Aromatic

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Abstract: Cyclopentadienes, when 5,5-disubstituted with electropositive groups, have considerably enhanced cyclic conjugation in comparison with the parent molecule, C₅H₆. According to various aromaticity indices, 5,5-distannylcyclopentadiene is nearly as aromatic as furan. Previous observations on the reactivity were interpreted in the light of the observed aromatic stabilization.

Molecules, aromatic in the classical sense, have delocalized π -electrons.¹ Can a methylene or another saturated group participate effectively in cyclic electron delocalization? A prime example is cyclopentadiene. The antisymmetric σ_{HCH} orbital might serve as a two-electron pseudo- π -donor and complete the aromatic sextet. But is this hyperconjugative interaction² effective? Cyclopentadiene exhibits a somewhat enhanced diamagnetic susceptibility anisotropy,³ but there is no convincing energetic,^{4a–d} geometric,^{4b,c} or NICS (nucleus-independent chemical shift)^{4d} evidence for aromaticity. Hence, the conclusion is ambiguous.⁵ Is it possible to increase the hyperconjugative effect substantially, by placing substituents on the saturated carbon, and achieve an aromatic carbocyclic system with a saturated tetravalent carbon atom?

Silyl-substituted carbons are known to be good π -donors, stabilizing, e.g., carbocations,⁶ carbenes,⁷ and radical cations⁸ which have low-lying empty or half-filled orbitals. We now

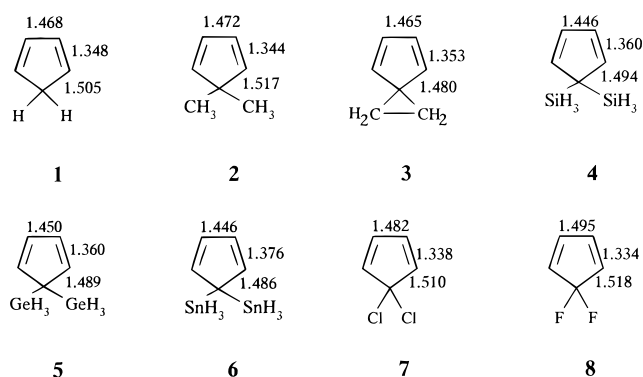


Figure 1. Important bond lengths for cyclopentadienes 1–8.

report that geminal silyl, germyl, and stannyl substituents induce substantial aromaticity in cyclopentadiene, whereas disubstitution by fluorine results in an antiaromatic system.

Figure 1 shows the calculated⁹ bond lengths of cyclopentadiene (1), 5,5-dimethylcyclopentadiene (2), spiro[4.2]heptadiene (3), 5,5-disilylcyclopentadiene (4), 5,5-digermylcyclopentadiene (5), 5,5-distannylcyclopentadiene (6), 5,5-dichlorocyclopentadiene (7), and 5,5-difluorocyclopentadiene (8). The C _{α} C _{β} and the C _{β} C _{β} bond lengths in the cyclopentadiene rings of 1–6 tend more and more to equalize, indicating increased delocalization, e.g., as the substituents involve heavier elements down the period. The effects are enhanced in the spirocyclopropane (3)

(6) This “ β -silyl effect” has been discussed extensively in carbocations; see, e.g.: Sommer, L. H.; Dorfmann, E.; Goldberg, L. M.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 488. Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. Even a stable β -silyl carbocation was reported: Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867 and references therein. Mayr, H.; Basso, N. *Angew. Chem.* **1992**, *104*, 1103. Maerker, C.; Schleyer, P. v. R. Siliconium ions: Quantum Chemical Computations. In *The Chemistry of Organosilicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley: New York, 1998. Apeloig, Y.; Müller, T. In *Theory and Calculations in Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; John Wiley: Chichester, 1997.

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(1) See, e.g.: Minkin, V. I.; Glukhotsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; John Wiley & Sons: New York, 1994. Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

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(5) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559.

Table 1. B3LYP/6-311+G**^a Magnetic (NICS, NICS(π),^b Diamagnetic Susceptibility Exaltation), Energetic (ASE in kcal/mol), and Geometric (Bird Index (BI), Julg Index (A), Julg Index Calculated from the C α C β and C β C β Bonds Only (A3), and Bond Shortening Index (BDSHRT)) Aromaticity Measures of the Investigated Ring Systems (the Values in Parentheses Are Obtained at the B3LYP/3-21G(*) Level)

	NICS	NICS(π)	$\Delta\chi$	ASE	BI	A/A3	BDSHRT
1	-3.1 (-4.2)	-16.0	-3.5	2.60 (2.19)	29 (30)	0.43/0.63	45 (46)
2	-2.2 (-3.3)		-2.4	0.85 (-1.23)	22 (27)	0.32/0.57	44 (45)
3	-3.4		-3.2	3.74	41	0.60/0.68	49
4	-7.8 (-7.8)	-19.4	-7.1	9.87 (10.31)	48 (47)	0.60/0.81	49 (49)
5	-7.5 (-7.4)	-	-8.1 (-4.9)	9.25 (9.64)	45 (47)	0.62/0.79	48 (48)
6^a	-9.6 (-8.5)	-	(-4.7)	13.76 (13.60)	56 (54)	0.73/0.87	51 (49)
7	+0.5 (-1.2)		-1.3	-5.13(-4.43)	21	0.30/0.55	45
8	+3.2 (+2.1)		+3.5	-9.53 (-7.44)	14	0.18/0.33	44
C ₄ H ₄ O	-12.3	-20.3	-5.2	15.80 (15.43)	49	-/0.81	51
C ₄ H ₄ S	-13.2	-20.3	-9.5	19.07(19.31)	68	-/0.90	57
C ₄ H ₅ N	-14.7	-20.5	-10.4	21.40(23.24)	73	-/0.94	55
C ₅ H ₅ ⁻	-14.2	-22.5	-15.0	20.32	100	1.0/1.0	52

^a For the distannyl derivative (**6**), the LANL2DZ basis with polarization functions has been used; see note 14. ^b The NICS(π) values are obtained by using the BIII basis; see note 9.

(due to the Walsh orbitals in the three-membered rings) relative to **2**.¹⁰ In contrast, the bond length alternation is even larger in the dichloro- (**7**) and the difluoro-substituted (**8**) rings than in the parent cyclopentadiene. The geometric aromaticity indices (the Bird index, BI,¹¹ the Julg parameter, A;¹² the modified Julg parameter calculated from the C α C β and C β C β bonds only, A3; and the bond-shortening index, BDSHRT¹³ in Table 1) indicate sizable changes in aromaticity. Are the changes in the bond lengths' equalization indeed due to variation in the aromatic character of the ring?

Magnetic and energetic measures of aromaticity are also collected in Table 1 for the 5,5-disubstituted cyclopentadienes.

(9) Calculations were performed with the Gaussian 94 program package (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995). Geometries were optimized at the B3LYP/6-311+G** (see also note 15) and B3LYP/3-21G(*) levels, resulting in similar structures. The NMR shielding tensors (in ppm) were calculated by the GIAO scheme; diamagnetic susceptibilities (in ppm) were calculated by the IGAIM method with the 6-311+G** basis at the B3LYP/6-311+G** optimized geometries and with the 3-21G(*) basis at the B3LYP/3-21G(*) geometries. Second derivatives were calculated at the optimized structures at both B3LYP/3-21G(*) and the B3LYP/6-311+G** levels. SOS-DFT routines (Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80) of the DeMon program package (Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898) were used with the BIII basis set (Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Princ. Prog.* **1990**, *23*, 190) to compute the individual localized molecular orbital contributions to the NICS value by employing the Pipek-Mezey localization (Pipek, J.; Mezey, P. G. *Chem. Phys.* **1989**, *90*, 4916), which separates σ - and π -components of the double bonds; see also ref 18. Diamagnetic susceptibilities, calculated NMR chemical shifts on the β carbon atom, and total energies are given as Supporting Information.

(10) Sieber et al. (Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987) have shown that the three-membered ring has considerable hyperconjugative participation in the phenonium ion 6 π aromatic system.

(11) Bird, C. W. *Tetrahedron* **1985**, *41*, 1409. The Gordy equation was used (Gordy, W. J. *Chem. Phys.* **1947**, *15*, 305) to calculate the bond orders. The Gordy constants were calculated from the bond lengths of ethylene and ethane obtained at the same level of the theory (B3LYP/3-21G(*) or B3LYP/6-311+G**) as the optimized structure of the ring. To give the bond orders at the saturated carbon atom substituted with (EH₃)₂ groups (E = C, Si, Ge, Sn), the Gordy constants were obtained from the CC bond lengths of CH₃CH(EH₃)₂ and CH₂C(EH₃)₂.

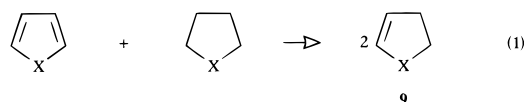
(12) Julg, A.; Francois, P. *Theor. Chim. Acta* **1967**, *8*, 249. Only the C α C β and the C β C β bond lengths were considered for A3.

(13) BDSHRT (see ref 4c) was obtained as an average of the Gordy bond orders minus 1, and multiplied by 100.

These data, obtained at the B3LYP/3-21G(*) and B3LYP/6-311+G** levels of density functional theory,¹⁴ are very similar for the C-, Si-, and Ge-containing systems, e.g., **1**–**5**. Like the geometries, the NICS values are not sensitive to the basis set. Hence, the B3LYP/3-21G(*) geometries and NICS values also should be reliable for the tin compound. The good structural and energetic agreement between the B3LYP/3-21G(*) and the B3LYP/LANL2DZ*¹⁴ results for **6** (Table 1) supports this conclusion.

While the methyl groups in **2** only result in small changes in the properties, the effects of the silyl, the germyl, and the stannyl groups are quite large according to all the aromaticity measures (Table 1). The values approach those for the common five-membered heteroaromatics, furan, thiophene, and pyrrole. Substitution by electronegative substituents such as chlorine or fluorine results in a decrease of the aromatic character of the ring.

Energetic Measures. Reaction 1 (X = CR₂, O, S, NH; R₂ = Me₂, CH₂CH₂, (SiH₃)₂, (GeH₃)₂, (SnH₃)₂, Cl₂, and F₂), is based on conjugated systems and compensates for ring strain.^{4b}



While the aromatic stabilization energies (ASE), measured by reaction 1, for cyclopentadiene (**1**) and its 5,5-dimethyl derivative (**2**) are quite small, the stabilization energy is about 10 kcal/mol for the disilyl (**4**) and the digermyl (**5**) derivatives. The spirocyclopropane (**3**) shows the expected¹⁰ enhancement. The largest value (13 kcal/mol) is found for the distannyl derivative (**6**). The stabilization of furan, thiophene, and pyrrole is only somewhat larger (15–21 kcal/mol) at the same level of theory.^{4b,d,5} The destabilization of the dichloro (5.1 kcal/mol) and especially the difluoro (9.5 kcal/mol) derivatives in reaction 1 indicates the antiaromaticity of **7** and **8**.¹⁶ The effects in conjugated systems, e.g., **9**, are much less. Thus the stabilization by the β -silyl groups in eq 2 is only 2.2 kcal/mol. The rotational

(14) For **6**, the LANL2DZ pseudopotential was used for tin and the D95 basis for the other atoms instead of 6-311+G** basis. d polarization functions (0.8 at carbon and 0.183 at tin) were added.

(15) Le Serre, S.; Guillemin, J.-C.; Kárpáti, T.; Soós, L.; Nyulászi, L.; Veszprémi, T. *J. Org. Chem.* **1998**, *63*, 59.

(16) Wiberg and Marquez (Wiberg, K. B.; Marquez, M. *J. Am. Chem. Soc.* **1998**, *120*, 2932) have discussed recently the effect of F substitution in small rings, noting the preference of F substitution on C atoms with enhanced p character.

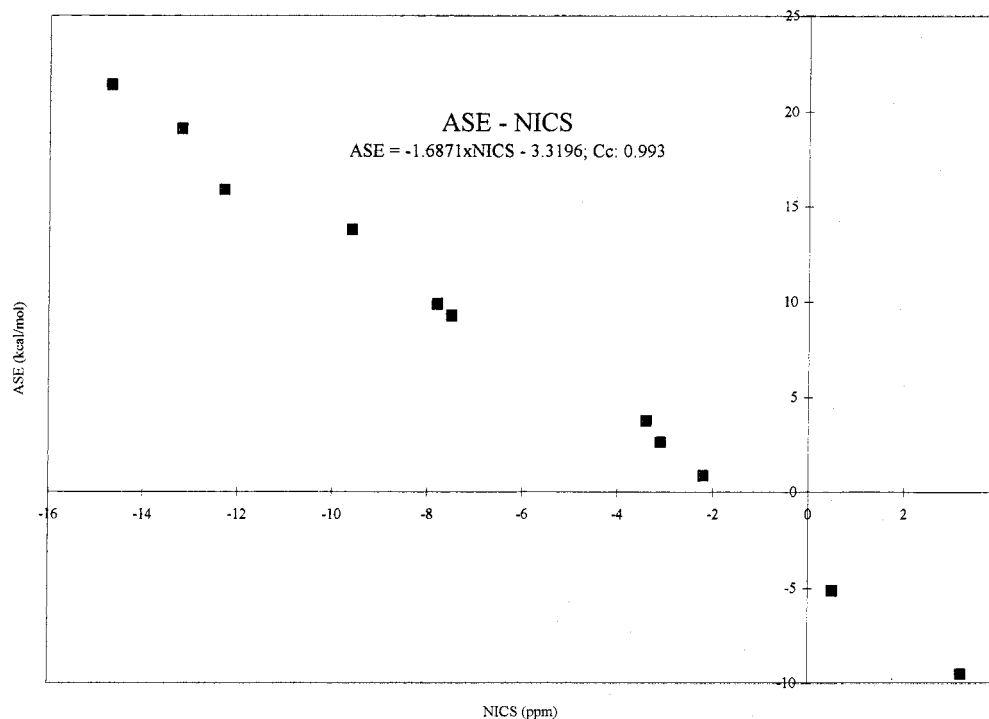
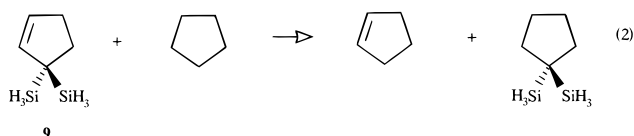


Figure 2. Correlation of the NICS values of **1–8** as well as furan, thiophene, and pyrrole with the ASEs calculated by eq 1.

barrier about the CC single bond in allyl-silane is 3.7 kcal/mol¹⁵ (MP2/6-31G*), partly due to the stabilizing effect of the β -silyl group.



Magnetic Measures. The NICS values¹⁷ of **4–6** are significantly larger than in cyclopentadiene (**1**) and in its 5,5-dimethyl derivative (**2**). However, these values are smaller to those for furan, thiophene, or pyrrole (see Table 1). Figure 2 shows the excellent correlation of the NICS values of **1–8** as well as furan, thiophene, and pyrrole with the ASEs calculated by eq 1. The NICS value for **7** is near 0, while for **8** it is positive (+3.2), in accord with the antiaromaticity of the ring. The σ framework contributions are paratropic and act to reduce the negative NICS values computed at the ring centers. The dissected NICS(π)¹⁸ value of the 5,5-disilacyclopentadiene (–19.4) is quite close to the NICS(π) value of furan, thiophene, or pyrrole. The contributions of each of the localized π -MOs increase from –6.1 (cyclopentadiene, **1**) to –7.3 (5,5-disilacyclopentadiene **4**). Each C–Si bond contributes –2.4 ppm (in **4**) compared to the –1.9 ppm contribution of the hyperconjugated CH bonds in cyclopentadiene **1**.

Like the aromatic stabilization energies, the diamagnetic susceptibility exaltations (obtained from reaction 1) are appreciable only for the silyl- (**4**) and germynyl-substituted (**5**) derivatives; these are even larger than those for furan.

Electronic Structure of 5,5-Disilylcyclopentadiene (4). The occupied π -MOs of **4** (Figure 3) show the typical MO patterns

(17) The nucleus-independent chemical shift (NICS) is defined as a negative of the NMR shielding computed, e.g., in the ring center; see refs 4d and 9.

(18) The NICS(π) values describe the π -contributions to the total NICS values (Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkin, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669).

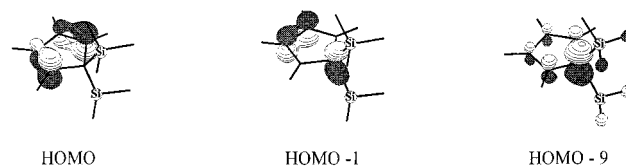


Figure 3. HF/3-21G*/B3LYP/3-21G* π -type MOs of 5,5-disilacyclopentadiene (**4**) as plotted by the MOLDEEN program.¹⁹

for a five-membered heteroaromatic π -system.²⁰ Along with HOMO-9, the b_1 symmetry HOMO-1 Si–Si orbital mixes strongly with the dienic π -system. This hyperconjugative electron donation by the substituents results in a partially anionic ring (the B3LYP/6-311+G** NPA charge sum of the C₅H₄ ring moiety is –0.94 and –0.86 for **4** and **5**, respectively, compared to –0.12 for **2**).

Concluding Remarks

The tuning of the character of cyclopentadiene by varying the substituents at the 5 position is remarkably effective.²¹ While, e.g., cyclopentadienyl–Li and –Na ion pairs have long been known to be aromatic, the unexpectedly strong influence of less electropositive elements has not been recognized before. 5,5-Difluorocyclopentadiene (**8**) is antiaromatic, whereas 5,5-disilyl- (**4**) 5,5-digermynyl- (**5**), and 5,5-distannylcyclopentadienes (**6**) are aromatic. The magnitude of the pronounced effect in **4–6** even approaches that of furan. This influences the chemistry.

(19) Schaftenaar, G. *MOLDEEN 2.5*; Caos/CAMM Center: Nijmegen, The Netherlands, 1994.

(20) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*. Academic Press: New York 1973

(21) With more electropositive groups than Si, the conventional structures are not minima. E.g., for Li, the substituents occupy a bridging position on the top of the ring while increasing the aromaticity further (Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997**, *16*, 1543). We found a similar effect for BeH. In the case of diboro substitution, one of the BH₂ groups forms a bridging bond above the C–C bond of the ring. These systems will be discussed elsewhere.

Consistent with the increased aromatic stabilization of the distannylated ring, 5,5-bis(trimethylstannyl)cyclopentadiene is the only monomeric product observed upon metallating and subsequently stannylating bicyclopentadiene.²² The aromatic stabilization affects the relative stability of the isomers, too. 1,4-Disilylcyclopentadiene and 1,5-disilylcyclopentadiene by 4.7 and 1.7 kcal/mol, respectively, are *less* stable than 5,5-disilacyclopentadiene (**4**) (at the B3LYP/6-311+G** level). The relative stability of 1,4-distanylcyclopentadiene (**6**) with respect to 1,4-distanylcyclopentadiene and 1,5-distanylcyclopentadiene is even larger: 6.2 and 3.2 kcal/mol, respectively (B3LYP/LANL2DZ* level). In contrast, 1,4- and 1,5-dimethylcyclopentadienes are 6.9 and 3.7 kcal/mol, respectively, *more* stable than the 5,5-isomer (**2**).

(22) Blümel, J.; Köhler, F. H. *J. Organomet. Chem.* **1988**, 340, 303.

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Supporting Information Available: HF/6-311+G**//B3LYP/6-311+G** diamagnetic susceptibility exaltation (χ in cgs) and HF/6-311+G**//B3LYP/6-311+G** NMR shifts of β carbon atoms of the cyclopentadiene ring, as well as B3LYP/6-311+G** total energies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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