# Hyperconjugative, Secondary Orbital, Electrostatic, and Steric Effects on the Reactivities and *Endo* and *Exo* Stereoselectivities of Cyclopropene Diels−Alder Reactions

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S *Supporting Information*

ABSTRACT: The factors controlling the reactivities and stereoselectivities in the Diels−Alder reactions of substituted cyclopropenes with butadiene were explored with M06-2X density functional theory. Differences in reactivities result from differences in the hyperconjugative aromaticities and anti-aromaticities of the cyclopropenes. When the 3-substituent is a σ-donor, the ground state is destabilized, and the reactivity is enhanced. Acceptors have the opposite effect. Electrostatic, secondary orbital, and steric effects are all found to influence stereoselectivities.

Electrostatic   Orbital   Steric
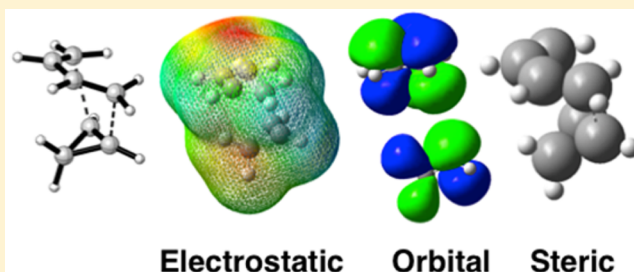
INTRODUCTION

The Diels−Alder reactions of substituted cyclopropenes are of interest in synthetic[1] and bioorthogonal[2] chemistry. While it is widely accepted that the *endo* stereoselectivity in cyclopropene Diels−Alder cycloadditions results from secondary orbital interactions in the *endo* transition state,[3,4] this conclusion has been questioned. Fujimoto studied the Diels−Alder stereoselectivity for a series substituted butadienes with cyclopropene and concluded that both secondary orbital and electrostatic interactions contribute to the stereoselectivity.[5] Garcia and Burnell have questioned the role of secondary orbital interactions and instead favor steric interactions as control elements in the stereoselectivities of Diels−Alder cyclo-additions of cyclopropene and substituted cyclopropenes.[6,7] The influence of secondary orbital, electrostatic, and steric interactions on the stereoselectivity of cyclopropene Diels−Alder reactions is currently an open question.

Scheme 1 shows experimental *endo* and *exo* stereoselectivities for the Diels−Alder reactions of cyclopentadiene with cyclopropene, a cyclopropenone ketal, and 3,3-difluorocyclopropene.[8−10] The Diels−Alder cycloaddition of cyclopenta-

diene with cyclopropene forms the *endo* adduct exclusively. The cyclopropenone ketal gives the *endo* and *exo* adducts in equal amounts. The reaction of cyclopentadiene with 3,3-difluorocyclopropene gives only the *exo* adduct.

The differences between the reactivities of 3-substituted cyclopropenes have previously been described in terms of anomeric effects,[11] frontier molecular orbitals,[2c] and the electronegativity[7] of the substituent. Our lab has shown that the reactivities of 3-substituted cyclopropenes with tetrazine in the inverse electron-demand Diels−Alder reaction correlate with the cyclopropene HOMO energy.[2c] Burnell reported the computed HOMO and LUMO energies for a series of substituted cyclopropenes.[7] The HOMO and LUMO energies range from −9.3 to −11.1 and from 1.0 to 1.2 eV, respectively. The range of LUMO energies is smaller than the HOMO energies, and the frontier molecular orbital interactions cannot explain the reactivity differences of 3-substituted cyclopropenes in the normal electron-demand Diels−Alder reaction. Burnell, and later Poirier, related the reactivities to the electronegativities of the substituents.[7,11] They found that electropositive substituents destabilize the cyclopropene and increase the Diels−Alder reactivity, whereas electronegative substituents have the opposite effect.

Recently, we have shown that the Diels−Alder reactivities of 5-substituted cyclopentadienes are related to the hyperconjugative aromaticity and antiaromaticity of the cyclopentadiene.[12] Schleyer demonstrated that the substituents on the saturated linkage in cyclopropene involve cyclic delocalization of the π electrons via hyperconjugation.[13] To determine if hyperconjugative aromaticity and antiaromaticity determine the Diels−Alder reactivities and stereoselectivities of cyclopro-

Scheme 1. *Endo* and *Exo* Stereoselectivities for the Diels−Alder reactions of Cyclopentadiene with Cyclopropene and Substituted Cyclopropenes
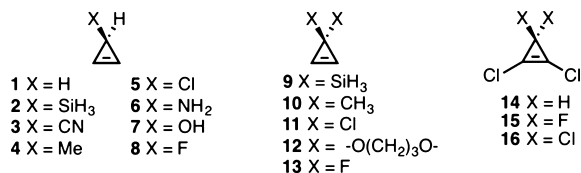

X = H	Yield (*endo* : *exo*)
X = -O(CH₂)₃O-	96% (100 : 0)
X = F	57% (50 : 50)
	41% (0 : 100)
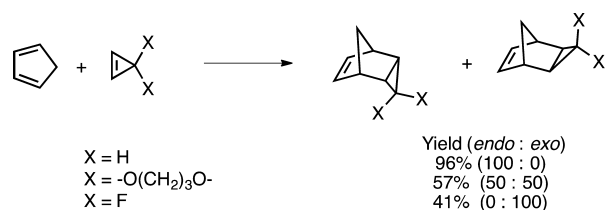
penes, we have studied the origins of reactivity differences and of the *endo* and *exo* stereoselectivities of Diels−Alder cycloadditions of substituted cyclopropenes with butadiene. The structures of theoretically investigated cyclopropenes **1**− **16** are shown in Chart 1.

Chart 1. Cyclopropenes 1−16

1 X = H	**5** X = Cl	**9** X = SiH$_3$
2 X = SiH$_3$	**6** X = NH$_2$	**10** X = CH$_3$
3 X = CN	**7** X = OH	**11** X = Cl
4 X = Me	**8** X = F	**12** X = -O(CH$_2$)$_3$O-
		13 X = F

14 X = H
15 X = F
16 X = Cl

■ **COMPUTATIONAL METHODS**

Computations were performed using *Gaussian 09*, revision D.0.1.[14] Using the M06-2X[15] functional, geometry optimizations were carried out with the 6-31+G(d) basis set. Single-point calculations were performed with the 6-311++G(d,p) basis set. Solvation effects of dichloromethane (DCM) using the conductor polarized continuum model (CPCM)[16] with a standard state of 1 M were included in geometry and single-point calculations. Truhlar's quasiharmonic correction was applied by setting all positive frequencies below 100 cm^{-1} to 100 cm^{-1}.[17] Orbital coefficients and atomic charges were calculated at the HF/6-31G level of theory. The orbital coefficients are obtained from the outer function of the split-valence 6-31G basis set.

■ **RESULTS AND DISCUSSION**

Figure 1 shows the *endo* and *exo* transition structures and Gibbs free energies of activation for the Diels−Alder cycloadditions of
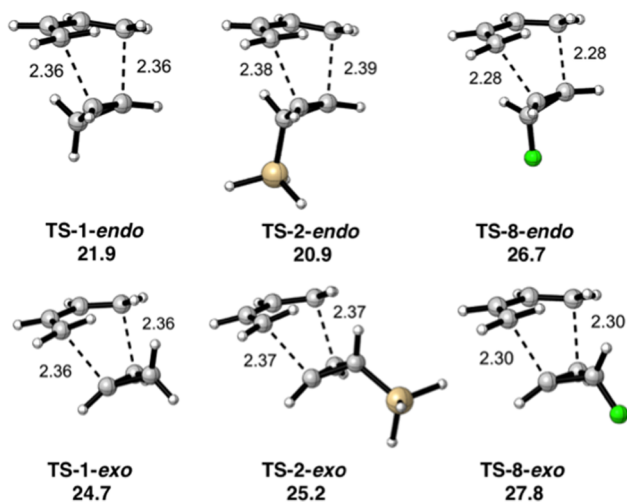

Figure 1. Transition structures and Gibbs free energies of activation ($\Delta G^{\ddagger}$) for the *endo* and *exo* Diels−Alder reactions of cyclopropenes **1**, **2**, and **8** with butadiene. Gibbs free energies of activation are reported in kcal/mol and bond lengths are reported in angstroms.

cyclopropenes **1**, **2**, and **8** with butadiene. The Gibbs free energies of activation for the Diels−Alder reactions of cyclopropenes **1**−**8** with butadiene range from 21 to 27 kcal/ mol and from 25 to 28 kcal/mol in the *endo* and *exo* transition states, respectively. When cyclopropene is substituted, the substituent is preferentially *anti* to butadiene in both the *endo* and *exo* transition states. With cyclopropene the *endo* cycloaddition is favored by 2.8 kcal/mol. The 3-silyl substitution increases the preference for the *endo* cycloaddition

to 4.3 kcal/mol, whereas 3-fluoro substitution decreases the preference to only 1.1 kcal/mol.

Hyperconjugative interactions involving the σ-bond of the C$_3$ substituent with the cyclopropene π-system influence the π- delocalization.[13] The hyperconjugative aromatic and antiaromatic stabilization enthalpies (ΔH_{ASE}) of the cyclopropene ground states were calculated using the isodesmic equation shown in Figure 2. The isodesmic equation relates the stability
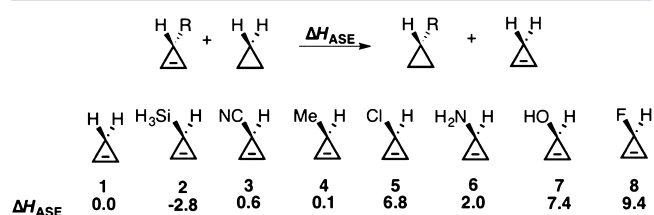

Figure 2. Isodesmic equation and aromatic stabilization enthalpies (ΔH_{ASE}) of cyclopropenes **1**−**8**. Positive values reflect stabilization of the cyclopropene.

of a substituted cyclopropene to the same substituted cyclopropane that does not include the hyperconjugative interactions of the C$_3$−X σ-bond with the cyclopropene π- system. A positive reaction enthalpy in the isodesmic equation means that the hyperconjugative interaction of the substituent with the π system is stabilizing. The calculated reaction enthalpy of 3-fluorocyclopropene is 9.4 kcal/mol. This stabilization is mainly the result of hyperconjugative aromaticity.[13] Hyperconjugation of the C$_3$−F bond gives the cyclopropene ring two-electron aromatic character. For 3- silylcyclopropene the computed reaction enthalpy is −2.8 kcal/ mol. The silyl group is a hyperconjugative donor that destabilizes the cyclopropene ring by giving it four-electron antiaromatic character.

The ground state geometries of cyclopropenes **1**−**8** are shown in Figure 3. The hydrogen atoms in cyclopropene are
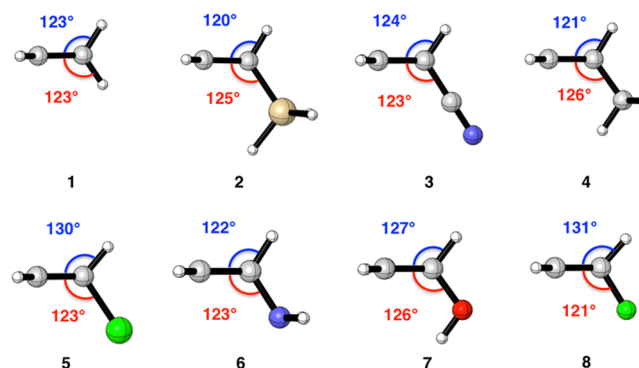

Figure 3. Ground state structures for cyclopropenes **1**−**8** showing the C$_3$−X (red) and C$_3$−H (blue) angles.

positioned 123° from the plane of the cyclopropene. When the C$_3$−X substituent is a σ-acceptor, the p character of the carbon atom increases and the C$_3$−X bond distorts toward the plane of the cyclopropene, although the changes are sometimes small or actually opposite with 3-hydroxycyclopropene **7**. This distortion improves the orbital overlap of the σ^* C$_3$−X orbital with the cyclopropene π-system to maximize the stabilizing effect of the hyperconjugative aromaticity.[12] When C$_3$−X is a σ- donor the distortion is in the opposite direction away from the

cyclopropene and minimizes the destabilizing effects of the hyperconjugative antiaromaticity. In the 3-substituted cyclopropenes **2–8**, the C_3–H bond distorts in the opposite sense from the C_3–X bond. The C_3–X bond distorts toward the cyclopropene ring when X is a σ-acceptor and away from the cyclopropene ring when X is a σ-donor.

Figure 4 shows a plot of the activation enthalpy against the hyperconjugative aromatic stabilization enthalpy for the *endo*
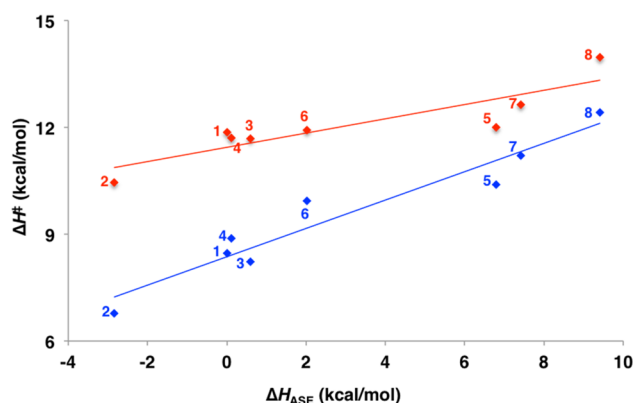

Figure 4. Plot of the activation enthalpy ($\Delta H^{\ddagger}$) against the hyperconjugative aromatic stabilization enthalpy (ΔH_{ASE}) for the *endo* (blue) and *exo* (red) Diels−Alder reactions of butadiene with cyclopropenes **1–8**. $\Delta H^{\ddagger}_{endo} = 0.40\ \Delta H_{ASE} + 8.4$, $r^2 = 0.93$. $\Delta H^{\ddagger}_{exo} = 0.20\ \Delta H_{ASE} + 11.4$, $r^2 = 0.77$.

and *exo* Diels−Alder reactions of cyclopropenes **1–8** with butadiene. The LUMO energies of the cyclopropenes are similar, ranging from 2.5 to 2.9 eV. The modest linear correlations suggest that differences in the Diels−Alder reactivities of the cyclopropenes result from the differences in the hyperconjugative aromaticities of the cyclopropenes. The *endo* selectivity diminishes as the C_3−X substituent becomes a stronger σ-acceptor.

To understand the origins of the *endo* and *exo* stereoselectivity in the Diels−Alder reactions of cyclopropenes, we have analyzed the transition states of cyclopropenes **1–8** with the distortion/interaction[18] (or Activation Strain)[19] model.[20] Activation energies ($\Delta E^{\ddagger}$), not the Gibbs free energies of activation ($\Delta G^{\ddagger}$), are used in this analysis. The distortion energy ($\Delta E^{\ddagger}_d$) is the energy required to deform the ground states of the reactants into their transition state geometries. The interaction energy ($\Delta E^{\ddagger}_i$) results from the stabilizing interactions between these distorted transition structures. The results from the distortion/interaction analysis are summarized in Table 1. The distortion energies of the *endo* and *exo* transition states of cyclopropenes **1–8** with butadiene are nearly identical, differing by 0.9 kcal/mol at most. The interaction energies always favor the *endo* transition state by 2−3 kcal/mol.

Figure 5 shows a plot of the *endo* and *exo* stereoselectivity (measured by $\Delta\Delta E^{\ddagger}$) versus the difference between the interaction energies in the *endo* and *exo* transition states. There is a linear correlation: the stereoselectivities result from the differences between the interaction energies of the *endo* and *exo* transition states. The interaction energies may include charge transfer interactions, related to filled-vacant orbital interactions, closed-shell repulsion between occupied orbitals (steric effects), electrostatic effects, and dispersive interactions.

Table 1. Distortion/Interaction Analysis for the Diels−Alder Reactions of Cyclopropenes 1−8 with Butadiene[a]

TS	$\Delta\Delta E^{\ddagger}$	$\Delta\Delta E^{\ddagger}_d$	$\Delta\Delta E^{\ddagger}_i$
1	−3.2	−0.5	−2.7
2	−3.9	−0.9	−3.0
3	−3.5	−0.5	−3.0
4	−2.8	−0.2	−2.6
5	−1.7	0.6	−2.3
6	−2.0	0.3	−2.3
7	−1.4	0.6	−2.0
8	−1.5	0.8	−2.2

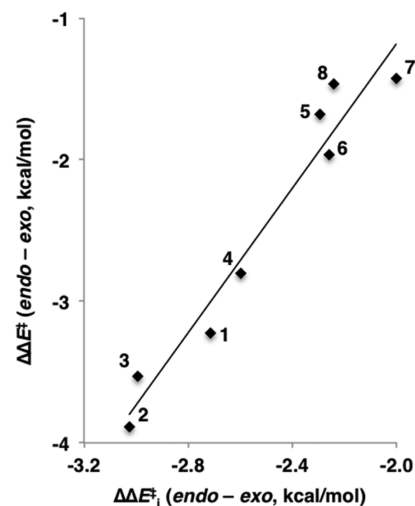[a]Energy differences ($E_{endo} - E_{exo}$) are given in kcal/mol.

Figure 5. Plot of the differences in the electronic activation energies ($\Delta\Delta E^{\ddagger} = \Delta E^{\ddagger}_{endo} - \Delta E^{\ddagger}_{exo}$) versus the differences in the interaction energies ($\Delta\Delta E^{\ddagger}_i = \Delta E^{\ddagger}_{i\ endo} - \Delta E^{\ddagger}_{i\ exo}$) between the *endo* and *exo* transition states for the Diels−Alder reactions of cyclopropenes **1–8** with butadiene. $\Delta\Delta E^{\ddagger} = 2.6\ \Delta\Delta E^{\ddagger}_i + 3.9$, $r^2 = 0.95$.

To determine the contribution of the secondary orbital and electrostatic interactions in the *endo* transition states to the stereoselectivity, we have evaluated quantities that we assume are the major stabilizing interactions. These quantities are reported in Table 2 and include the s-orbital coefficients in the HOMO of the cyclopropene ground state, the natural bond order (NBO) charges for the *syn* hydrogen of cyclopropenes **1–8**, the sum of charges at C_2 and C_3 of butadiene, and the

Table 2. S-Orbital Coefficients in the HOMO for the *Syn* Hydrogen Computed in the Ground State, NBO Charges at the *Syn* Hydrogen of the Cyclopropene, the Sum of Charges at C_2 and C_3 of Butadiene, and CH/π Distances in the *Endo* Transition States of Cyclopropenes 1−8

TS	H s-orbital coefficient (HOMO)	Charge *syn* H (Cyclopropene)	C_2C_3 charge (Butadiene)	CH/π distance (Å)
1	0.19	0.21	−0.57	2.37
2	0.19	0.24	−0.57	2.32
3	0.17	0.27	−0.56	2.34
4	0.19	0.22	−0.57	2.36
5	0.16	0.26	−0.56	2.46
6	0.21	0.22	−0.57	2.43
7	0.16	0.22	−0.56	2.47
8	0.17	0.21	−0.56	2.51

distance between the *syn* hydrogen and the forming π-bond in the *endo* transition state. The s-orbital HOMO coefficients of the *syn* hydrogen atoms are similar, ranging from 0.16 to 0.21 in the ground states. The forming π-bond in the *endo* transition state of butadiene is electron-rich with the sum of charges across C_2 and C_3 of butadiene ranging from −0.56 to −0.57. The *syn* hydrogen atoms are positively charged and range from 0.21 to 0.27 in the *endo* transition states. Although the orbital coefficients and charges are similar in magnitude across the cyclopropene series, the strength of the secondary orbital and electrostatic interactions is also distance dependent. The distance between the *syn* hydrogen atom and the forming π-bond, measured as the distance between the *syn* hydrogen and the center of the C_2C_3 bond in butadiene, as shown in Figure 6,
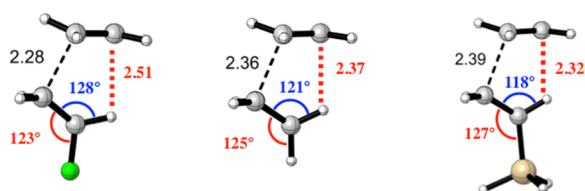

Figure 6. CH/π interactions in the *endo* transition states of cyclopropenes **1**, **2**, and **8**. The angle that the *syn* hydrogen atom is distorted from the plane of the cyclopropene ring is shown in blue. Bond lengths are reported in angstroms.

ranges from 2.32 to 2.51 Å in the *endo* transition states of cyclopropenes **1−8**. A closer distance increases the favorable secondary orbital overlap and attractive electrostatic interaction, further stabilizing the *endo* transition state.

The CH/π distance is related to the position of the transition state and the angle by which the *syn* hydrogen atom is distorted from the plane of the cyclopropene. The angle ranges from 118° to 128° in the *endo* transition states of cyclopropenes **1−8** and is linked to the hyperconjugative aromaticity of the cyclopropene. When the C_3 substituent is a σ-acceptor, the C_3−H bond is distorted away from the cyclopropene ring resulting in a further CH/π distance in the *endo* transition state. In addition, a later transition state results in greater pyramidilization of the carbons involved in bonding. Figure 7 shows a plot of the differences in the interaction energies between the *endo*
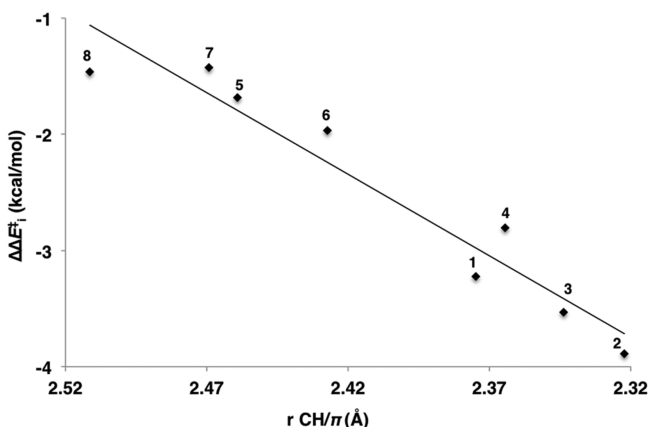

Figure 7. Plot of the difference in the interaction energies of *endo* and *exo* transition states ($\Delta\Delta E^{\ddagger}_i = \Delta E^{\ddagger}_{i\ endo} - \Delta E^{\ddagger}_{i\ exo}$) versus the CH/$\pi$ distance in the *endo* transition states of cyclopropenes **1−8**. $\Delta\Delta E^{\ddagger}_i = 14.0\ r - 36.3$, $r^2 = 0.93$.

and *exo* transition states versus the CH/π distance. The interaction energies favor *endo* as the CH/π distance decreases because of the increase in the secondary orbital overlap of the *syn* hydrogen s-orbital in the HOMO of the cyclopropene with the C_2C_3 π-orbitals of the butadiene LUMO and the increase in the strength of the stabilizing electrostatic interactions of the partial positively charged *syn* hydrogen with the electron-rich forming π bond in butadiene as the CH/π distance decreases.

Figure 8 shows the *endo* and *exo* transition states for the Diels−Alder reaction of 3,3-difluorocyclopropene with buta-
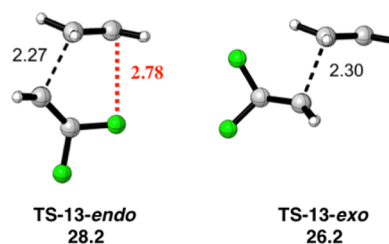

Figure 8. *Endo* and *exo* transition structures for the Diels−Alder reactions of 3,3-difluorocyclopropene with butadiene. Gibbs free energies of activation ($\Delta G^{\ddagger}$) are reported in kcal/mol and bond lengths are reported in angstroms.

diene. The *exo* cycloaddition is favored by 2.0 kcal/mol, consistent with experiments.[10] In the *endo* transition state, the fluorine atom bears a partial negative charge of −0.43 and is 2.78 Å away from the forming π-bond. The CF/π electrostatic interaction in the *endo* transition state is destabilizing, and *exo* stereoselectivity is favored.[21]

To calculate the total contribution of the secondary orbital interactions and electrostatic interactions to the stereo-selectivity we have compared the strength of the orbital and electrostatic interactions along the intrinsic reaction coordinate (IRC) for the *endo* and *exo* transition states of butadiene with cyclopropene and 3,3-difluorocyclopropene. The analysis was performed with the Amsterdam Density Functional (ADF) program developed by Baerends et al.[22,23] Figure 9 shows a plot of the orbital and electrostatic interactions along the IRC for the *endo* and *exo* reactions of cyclopropene, 3-fluorocyclo-propene, and 3,3-difluorocyclopropene, from forming C−C bond distances of 2.7 Å to the transition state. For the Diels−Alder reaction of cyclopropene with butadiene, both the secondary orbital and the CH/π electrostatic interactions favor the *endo* transition state, resulting in *endo* stereoselectivity. For the 3-fluorocyclopropene, the smaller preference for *endo* results from the diminished strength of the secondary orbital and electrostatic interactions along the reaction coordinate in the *endo* transition state. In the reaction of 3,3-difluorocyclo-propene with butadiene, the orbital interactions are nearly identical along the reaction coordinate, and the electrostatic CF/π interaction, which is destabilizing in the *endo* transition state, and all along the reaction coordinate, results in *exo* stereoselectivity.

The hyperconjugative interactions are related to the electronic nature of the cyclopropene substituents, which can be represented by the charge at C_3. Figure 10 shows a plot of the *endo* and *exo* stereoselectivity versus the charge at C_3 in the *endo* transition state for the Diels−Alder reactions of cyclopropenes **1−16** with butadiene. There is a linear correlation between the *endo* and *exo* stereoselectivity and the charge at C_3. The stereoselectivity for the Diels−Alder
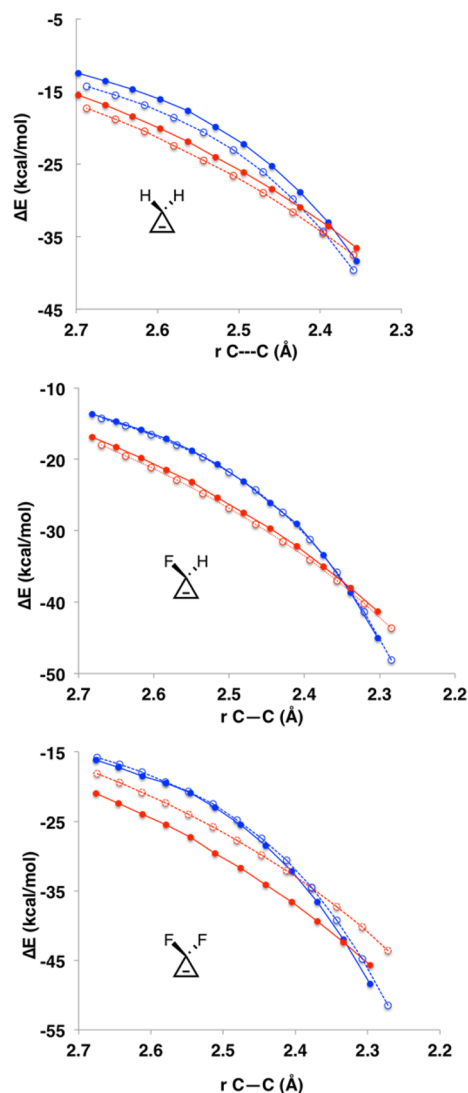
Figure 9. Plot of the electrostatic (red) and orbital (blue) interactions along the intrinsic reaction coordinates for the *endo* (dashed) and *exo* (solid) Diels−Alder reactions of butadiene with cyclopropene (top), 3-fluorocyclopropene (middle), and 3,3-difluorocyclopropene (bottom). The plots end at the transition state geometries.
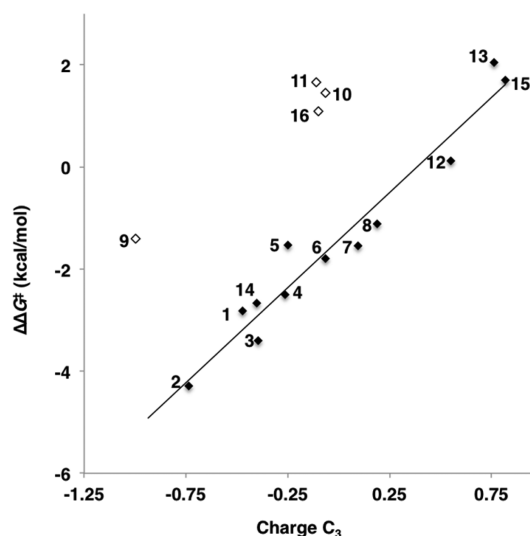
Figure 10. Plot of the differences in the activation free energies ($\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_{endo} - \Delta G^{\ddagger}_{exo}$) versus the charge at the C_3 carbon for the Diels−Alder reactions of cyclopropenes **1−16** with butadiene. $\Delta\Delta G^{\ddagger} = 3.73\ C_3 - 1.43$, $r^2 = 0.95$.

CONCLUSION

The Diels−Alder reactivity and *endo* selectivity increases when the C_3 substituent is a σ-donor. σ-Donors destabilize the cyclopropene ring by giving it four-electron antiaromatic character. In the ground state the C_3−X bond distorts away from the plane of the cyclopropene ring minimizing the antiaromatic character. This distortion results in a more favorable geometry for the secondary orbital and the CH/π electrostatic interactions in the *endo* transition state. An acceptor substituent stabilizes and bends toward the three-membered ring. The charge at C_3 is an indicator of the substituent electronic effects and is useful as a simple predictive property in determining the reactivity and *endo* and *exo* stereoselectivity of cyclopropene Diels−Alder cycloadditions in the absence of steric interactions, which decrease the reactivity and *endo* stereoselectivity.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10463.

> Additional computational results, Cartesian coordinates, and energies of all stationary points (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

reactions of 3,3-disubstituted cyclopropenes **9−11** and **16** deviate further toward *exo* selectivity from the established correlation with the NBO charge at C_3 as the size of the substituent increases (SiH$_3$ > Cl > Me ≫ OR, F, H). The deviation is a consequence of a steric interaction between butadiene and the C_3−X substituent *syn* to butadiene that results in an unfavorable distortion of the C_3−X bond from the plane of the cyclopropene in the *endo* transition state. For 3,3-difluorocyclopropene **13** and the cyclopropeneketal **12**, this steric interaction is weak, and the predicted stereoselectivities correlate well with the NBO charge at C_3. In the *endo* transition states of butadiene with cyclopropenes **9**, **10**, and **11** the steric interaction results in a 3.7, 3.1, and 3.5 kcal/mol deviation toward the *exo* transition state, respectively. The stereoselectivity of the 1,2-dichloro substituted analogs **14−16** is similar to that of cyclopropenes **1**, **11**, and **13**. Chlorine substitution across the double bond of a cyclopropene does not significantly influence the stereoselectivity.

the optimized structures, and Sofware for Chemistry & Materials for use of the ADF modeling suite.

■ REFERENCES

(1) (a) Rubin, M.; Rubina, M.; Gevorgyan, V. *Synthesis* **2006**, *2006*, 1221. (b) Marek, I.; Simaan, S.; Masarwa, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7364. (c) Zhu, Z.-B.; Wei, Y.; Shi, M. *Chem. Soc. Rev.* **2011**, *40*, 5534. (d) Shi, Y.; Wilmot, J. T.; Nordstrøm, L. U.; Tan, D. S.; Gin, D. Y. *J. Am. Chem. Soc.* **2013**, *135*, 14313. (e) Oblak, E. Z.; VanHeyst, M. D.; Li, J.; Wiemer, A. J.; Wright, D. L. *J. Am. Chem. Soc.* **2014**, *136*, 4309.

(2) (a) Liang, Y.; Mackey, J. L.; Lopez, S. A.; Liu, F.; Houk, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 17904. (b) Kamber, D. N.; Nazarova, L. A.; Liang, Y.; Lopez, S. A.; Patterson, D. M.; Shih, H.-W.; Houk, K. N.; Prescher, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 13680. (c) Yang, J.; Liang, Y.; Šečkute, J.; Houk, K. N.; Devaraj, N. K. *Chem. - Eur. J.* **2014**, *20*, 3365.

(3) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4388.

(4) (a) Matzner, E.; Apeloig, Y. *J. Am. Chem. Soc.* **1995**, *117*, 5375. (b) Jursic, B. S. *J. Org. Chem.* **1997**, *62*, 3046. (c) Wannere, C. S.; Paul, A.; Herges, R.; Houk, K. N.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Comput. Chem.* **2007**, *28*, 344.

(5) Imade, M.; Hirao, H.; Omoto, K.; Fujimoto, H. *J. Org. Chem.* **1999**, *64*, 6697.

(6) García, J. I.; Mayoral, J. A.; Salvatella, L. *Acc. Chem. Res.* **2000**, *33*, 658.

(7) Xidos, J. D.; Gosse, T. L.; Burke, E. D.; Poirier, R. A.; Burnell, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 5482.

(8) Wiberg, K. B.; Bartley, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 6375.

(9) Boger, D. L.; Brotherton, C. E. *Tetrahedron* **1986**, *42*, 2777.

(10) Battiste, M. A.; Posey, R. G. J. *J. Fluorine Chem.* **2000**, *102*, 285.

(11) Gosse, T. L.; Poirier, R. A. *Can. J. Chem.* **2004**, *82*, 1589.

(12) This distortion is also observed in the C_5-X bonds of cyclopentadiene, but in the opposite direction for donors and acceptors. Levandowski, B. J.; Zou, L.; Houk, K. N. *J. Comput. Chem.* **2016**, *37*, 117.

(13) Fernandez, I.; Wu, J. I.; Schleyer, P. v. R. *Org. Lett.* **2013**, *15*, 2990.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

(15) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(16) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.

(17) Zhao, Y.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813.

(18) (a) Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 10646. (b) Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 10187.

(19) (a) van Zeist, W.-J.; Bickelhaupt, F. M. *Org. Biomol. Chem.* **2010**, *8*, 3118. (b) Fernandez, I.; Bickelhaupt, F. M. *Chem. Soc. Rev.* **2014**, *43*, 4953.

(20) Levandowski, B. J.; Houk, K. N. *J. Org. Chem.* **2015**, *80*, 3530.

(21) Kawahara, S.; Tsuzuki, S.; Uchimaru, T. J. *J. Phys. Chem. A* **2004**, *108*, 6744.

(22) (a) ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. (b) Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. (c) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(23) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(24) Legault, C. Y. *CYLview*, 1.0b; Université de Sherbrooke: Sherbrooke, QC, Canada, 2009. Available at: http://www.cylview.org.