

## Consistent Aromaticity Evaluations of Methylenecyclopropene Analogues

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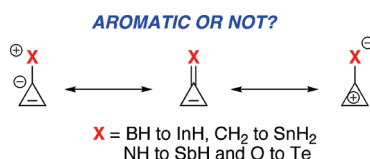
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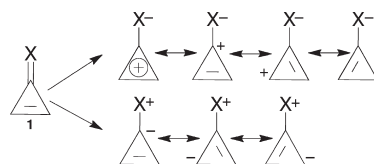
Quantitative evaluations of the aromaticity (antiaromaticity) of neutral exocyclic substituted cyclopropenes (HC)<sub>2</sub>C=X (X = BH to InH (group 13), CH<sub>2</sub> to SnH<sub>2</sub> (group 14), NH to SbH (group 15), O to Te (group 16)) by their computed extra cyclic resonance energies (ECRE, via the block-localized wave function method) and by their aromatic stabilization energies (ASEs, via energy decomposition analyses) correlate satisfactorily ( $R^2 = 0.974$ ). Electronegative X-based substituents increase the aromaticity of the cyclopropene rings, whereas electropositive substituents have the opposite effect. For example, (HC)<sub>2</sub>C=O is the most aromatic (ECRE = 10.3 kcal/mol), and (HC)<sub>2</sub>C=InH is the most antiaromatic (ECRE = -15.0 kcal/mol). The most refined dissected nucleus-independent chemical shift magnetic aromaticity index, NICS(0)<sub>πzz</sub>, also agrees with both energetic indexes ( $R^2 = 0.968$ , for ECRE;  $R^2 = 0.974$ , for ASE), as do anisotropy of the induced current density plots.

### Introduction

To what extent do different exocyclic (C=X) substituents induce aromaticity and antiaromaticity in cyclopropene derivatives, (HC)<sub>2</sub>C=X? Owing to the opposite polarization arising from electronegative (C<sup>-</sup>-X<sup>-</sup>) and electropositive (C<sup>-</sup>-X<sup>+</sup>) substituents, the systems shown in Scheme 1, resembling the cyclopropenyl cation and anion, result. The seminal investigations of R. Breslow revealed the aromatic (2π e) and antiaromatic (4π e) character of such species. Cyclopropenyl cations date from 1957.<sup>1a</sup> Breslow first invoked the “antiaromaticity of cyclopropenyl anions” in 1967.<sup>1b,c</sup> Consistent with the expected high reactivity and instability of 4π electron systems, the parent cyclopropenyl anion<sup>1d</sup> evidently has never been observed, although simple derivatives were generated in the gas phase in 1994.<sup>2a,b</sup> In

contrast, cyclopropenone, (HC)<sub>2</sub>C=O, first synthesized by Breslow in 1967<sup>3</sup> and now known to be an interstellar molecule,<sup>4</sup> was predicted to be aromatic in 1959.<sup>5d</sup>

### SCHEME 1. Resonance Contributors of Polarized Methylenecyclopropene Derivatives<sup>a</sup>



<sup>a</sup>The aromatic 2π electron character is emphasized by the circle notation, in contrast to the anti-aromatic 4π electronic structure.

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Burk et al.<sup>5a</sup> and Bachrach<sup>5b,c</sup> have reviewed the considerable prior literature dating back half a century<sup>5d,e</sup> on the possible aromaticity of cyclopropenone as well as its exocyclic cyclopropene analogues related to methylenecyclopropene. Although a spectrum of views have been expressed,<sup>5c</sup> the consensus opinion suggests that the parent methylenecyclopropene,  $(\text{HC})_2\text{C}=\text{CH}_2$ , the simplest cross-conjugated cyclic hydrocarbon, is nonaromatic on the basis of both experimental observations<sup>6</sup> and theoretical analyses.<sup>7</sup> On the other hand, various criteria agree that cyclopropenone is at least modestly aromatic.<sup>5-7</sup> However, quantitative assessments of the aromaticity of other  $(\text{HC})_2\text{C}=\text{X}$  derivatives have not led to satisfactory agreement.

We now elaborate and extend considerably our two recent, closely related computational studies that show promise in reconciling quantitative aromaticity criteria.<sup>8</sup> The first of these<sup>8a</sup> dealt with the aromaticity (antiaromaticity) assessments of a limited number of electronegative (electropositive) methylenecyclopropene derivatives,  $(\text{HC})_2\text{C}=\text{X}$  ( $\text{X} = \text{CH}_2, \text{NH}, \text{O}, \text{SiH}_2, \text{PH}, \text{S}$ ) based on BLW (block localized wave function) energetic and refined NICS <sub>$\pi$ zz</sub> (nucleus-independent chemical shift) magnetic evaluations; these aromaticity criteria compared well with one another.<sup>8a</sup>

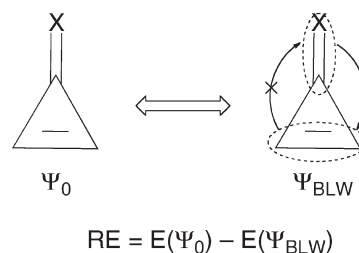
Our second paper<sup>8b</sup> surveyed the aromaticity of the entire set of cyclopropenyl cations based on group 14 elements systematically, from  $\text{C}_3\text{H}_3^+$  through  $\text{E}_3\text{H}_3^+$  ( $\text{E} = \text{C}-\text{Pb}$ ). The results demonstrated that two quite different energetic aromaticity evaluation methods, EDA-ASE and BLW-ECRE, correlated very well with each other. The extra cyclic resonance energy (ECRE) is derived via the block localized wave function method (BLW), while energy decomposition analysis (EDA) gives aromatic stabilization energies (ASEs). Both of these energetic aromaticity criteria were compared to the most refined dissected nucleus-independent chemical shift magnetic index (NICS(0) <sub>$\pi$ zz</sub>).

$(\text{HC})_2\text{C}=\text{X}$  comprising groups 13–16 elements ( $\text{X} = \text{BH}-\text{InH}, \text{CH}_2-\text{SnH}_2, \text{NH}-\text{SbH}, \text{O}-\text{Te}$ ), based on BLW-ECRE (energetic), EDA-ASE (energetic), and NICS (magnetic) analyses. Good correlations among the energetic and magnetic methods for the evaluation of the aromaticity of the extended series of  $(\text{HC})_2\text{C}=\text{X}$  compounds are demonstrated.

## Experimental Section

Resonance energies (REs) and ECREs were computed (B3LYP/def2-TZVPP) using the ab initio valence bond-based

## SCHEME 2. Depiction of the Block-Localized Wavefunction Procedure<sup>a</sup>



<sup>a</sup>RE = adiabatic BLW resonance energy.

block-localized wave function (BLW) method,<sup>9</sup> as implemented in GAMESS (version R5).<sup>10</sup> This method computes RE directly according to the Pauling–Wheland definition, as the energy difference between the fully delocalized, completely optimized molecule ( $E(\Psi_0)$ ) and its most stable resonance contributor ( $E(\Psi_{\text{BLW}})$ ) under the applied BLW constraints (Scheme 2). The wave function of the latter is obtained by separating (localizing) all the electrons and basis functions into several subspaces and then disabling interactions between chosen subspaces. Thus, the BLW procedure does not allow the localized  $\pi$  orbitals of double bonds to interact with one another. When this restriction is removed, the change in energy corresponds to the RE. Vertical BLW computations retain the original  $(\text{HC})_2\text{C}=\text{X}$  geometry, but further geometry optimization under the BLW constraint results in the adiabatic energies, which were employed here to obtain the BLW-REs (Scheme 2). Note that the disadvantages of evaluations requiring model compounds are avoided by this procedure. The molecule itself serves as its own reference. However, REs measure the total resonance stabilization, and comparisons with conjugated but not aromatic standards are necessary in order to evaluate the degree of cyclic electron delocalization, i.e., the “aromaticity”.

The extra cyclic resonance energies (ECRE, Table 1),<sup>11</sup> which measure the extra stabilization or destabilization associated with the aromaticity or antiaromaticity of a molecule, were derived from the difference in adiabatic BLW-REs between the cyclic conjugated compounds,  $(\text{HC})_2\text{C}=\text{X}$ , and the corresponding acyclic polyene reference molecules,  $(\text{H}_2\text{C}=\text{CH})_2\text{C}=\text{X}$  with the same type and number of conjugations. Such BLW-ECREs provide effective aromatic stabilization energy (ASE) evaluations computationally and are comparable to the best ASE estimates based on well-balanced (nearly contamination-free) thermochemical evaluations.<sup>11b,c,12</sup> For example, the ECRE of benzene (29.3 kcal/mol, B3LYP/6-31G\*), obtained from the energy difference between the adiabatic BLW-RE of benzene (61.4 kcal/mol) and that of three *syn* butadienes (10.7 kcal/mol each),<sup>11c</sup> is comparable to the recommended ASE value, 28.8 kcal/mol, based on the equation 3(1,3-cyclohexadiene) + cyclohexane  $\rightarrow$  benzene + 3(cyclohexene) and experimental data.<sup>12</sup>

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


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**TABLE 1.** Computed Adiabatic BLW-REs and ECREs<sup>a</sup> (in kcal/mol, ECRE = RE – RE', B3LYP/def2-TZVPP);  $\Delta E_{\pi}$  and ASEs (in kcal/mol, ASE =  $\Delta E_{\pi} - \Delta E_{\pi}'$ , BP86/TZ2P); NICS(0), NICS(1)<sub>zz</sub>, and NICS(0)<sub>πzz</sub><sup>a</sup> (in ppm, BP86/def2-TZVPP//BP86/TZ2P) for Exocyclic Substituted Cyclopropenes; Computed BLW-RE' and  $\Delta E_{\pi}'$  Values for Acyclic References Are Listed for Comparison

	BH (C <sub>2v</sub> )	CH <sub>2</sub> (C <sub>2v</sub> )	NH (C <sub>s</sub> )	O (C <sub>2v</sub> )	AlH (C <sub>2v</sub> )	SiH <sub>2</sub> (C <sub>2v</sub> )	PH (C <sub>s</sub> )	S (C <sub>2v</sub> )	
	ECRE	-8.10	2.27 (-0.62)	6.89 (5.40)	10.29 (10.53)	-14.37	-4.04 (-2.42)	2.54 (0.16)	7.18 (5.81)
	RE	17.45	24.14	27.11	31.02	20.55	24.44	28.90	34.14
	ASE	-11.8	0.2	4.1	8.0	-22.7	-7.9	-1.6	2.4
	$\Delta E_{\pi}$	23.8	33.4	40.6	44.6	27.2	33.8	41.7	49.4
	NICS(0) <sub>π</sub>	15.31	4.45 (4.41)	-1.85 (-1.86)	-6.18 (-6.13)	24.36	12.84 (8.05) <sup>b</sup>	4.65 (4.93)	-2.14 (-2.05)
	NICS(1) <sub>zz</sub>	-3.34	-10.68	-12.21	-12.50	4.70	-5.74	-11.57	-14.55
	NICS(0)	-23.98	-20.66	-18.10	-14.69	-14.87	-18.83	-18.82	-15.71
	RE'	25.55	21.87	20.22	20.73	34.92	28.48	26.36	26.96
	$\Delta E_{\pi}'$	35.6	33.2	36.5	36.6	49.9	41.7	43.3	47.0
	GeH (C <sub>2v</sub> )	GeH <sub>2</sub> (C <sub>2v</sub> )	AsH (C <sub>s</sub> )	Se (C <sub>2v</sub> )	InH (C <sub>2v</sub> )	SnH <sub>2</sub> (C <sub>2v</sub> )	SbH (C <sub>s</sub> )	Te (C <sub>2v</sub> )	
	ECRE	-13.76	-3.72	2.20	6.44	-15.04	-4.77	1.09	2.27
	RE	21.39	26.09	30.54	35.93	23.04	28.02	32.40	44.56
	ASE	-23.0	-8.9	-3.1	0.5	-26.0	-11.5	-5.1	-1.4
	$\Delta E_{\pi}$	27.1	35.6	43.1	51.5	29.2	37.6	44.8	53.7
	NICS(0) <sub>π</sub>	26.15	14.31	6.24	-0.76	30.42	17.59	8.75	1.54
	NICS(1) <sub>zz</sub>	7.37	-3.66	-10.23	-14.25	37.80	-0.60	-8.50	-13.67
	NICS(0)	-14.22	-17.06	-17.37	-15.37	-10.04	-14.17	-15.24	-14.56
	RE'	35.15	29.81	28.34	29.49	38.08	32.79	31.31	42.29
	$\Delta E_{\pi}'$	50.1	44.5	46.2	51.0	55.2	49.1	49.9	55.1

<sup>a</sup>The B3LYP/6-31G\* ECREs (using two CH<sub>2</sub>=CH–CH=X as reference molecules) and PW91/IGLOIII TZ2P//B3LYP/6-311+G\*\* NICS(0)<sub>πzz</sub> of (HC)<sub>2</sub>C=X (X = CH<sub>2</sub>, NH, O, SiH<sub>2</sub>, PH, S; see ref 8) are shown in parentheses. <sup>b</sup>The C<sub>s</sub> symmetry employed in ref 8 is responsible for the modest discrepancy.

Aromatic stabilization energies (ASEs) were computed via the EDA analyses (at BP86/TZ2P) employing the ADF(2007.01) program.<sup>13</sup> The EDA-ASE estimates were obtained by comparing the computed  $\Delta E_{\pi}$  values (which provide estimates of the  $\pi$ -conjugation/hyperconjugation energies of molecules directly) of the exocyclic substituted cyclopropenes to their acyclic references. This procedure has been applied successfully to compute the ASE values of typical aromatic and antiaromatic organic compounds<sup>14</sup> and also to estimate the aromatic character of metallabenzenes<sup>15</sup> where the application of the very popular magnetic methods for quantifying aromaticity, i.e., NICS and magnetic susceptibility ( $\Delta\chi$ ) exaltations, are complicated because of the anisotropy of the metal center and the effect of the ligands.<sup>16</sup>

The EDA method<sup>17</sup> employs a systematic procedure to evaluate bonding energies. The strategy is to divide the molecule of interest, AB, into fragments, e.g., A and B, which are then recombined in

three separate steps in order to obtain the energies of individual interactions. The last step, which allows the occupied and vacant orbitals of the fragments to mix, lowers the energy and gives the  $\pi$ -REs. Hence, the strategy has similarities to the BLW procedure.

In EDA step 1, the fragments, A and B, with their geometries frozen as in AB are computed individually in appropriately selected spin states (which may not be the ground states) and then are superposed with unrelaxed electron densities at the geometry of AB to give A'B'. This gives the quasiclassical electrostatic interaction,  $\Delta E_{\text{elstat}}$ , as the energy difference between the original AB and A'B', its modified spin state. This superposition usually lowers the energy because the total nuclear–electron attraction in most cases is larger than the sum of the nuclear–nuclear and electron–electron repulsion.<sup>18</sup> However, the resulting product wave function for this modified A'B' species violates the Pauli principle because electrons with same spin may occupy the same spatial region. In step 2, this situation is rectified by antisymmetrization and renormalization of the A'B' wave function thereby removing electron density, particularly from the AB bonding region where the overlap of the frozen densities is large (cf. Figure 3 in ref 17c). This step gives the Pauli repulsion term,  $\Delta E_{\text{Pauli}}$ . In step 3, the molecular orbitals are relaxed in the final step. This allows the occupied and vacant orbitals to mix. The resulting electron delocalization gives the stabilizing orbital interaction term,  $\Delta E_{\text{orb}}$ .

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The total interaction energy,  $\Delta E_{\text{int}}$ , is the sum of the three terms:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

Note that  $\Delta E_{\text{int}}$  is not the same as a bond (or group) dissociation energy, as the additional energy related to the geometric relaxation of the A and B fragments (i.e., the  $\Delta E_{\text{prep}}$  term)<sup>17</sup> is not included.

The  $\Delta E_{\text{orb}}$  term can be dissected into  $\sigma$  ( $\Delta E_{\sigma}$ ) or  $\pi$  ( $\Delta E_{\pi}$ ) orbital contributions. The  $\pi$  term is crucial for the present study, since the  $\Delta E_{\pi}$  contribution provides a direct measure of the strength of  $\pi$ -conjugation and hyperconjugation in a molecule without recourse to external reference systems.<sup>19</sup> Further details regarding the EDA method can be found in the literature.<sup>17</sup>

Our work on the cyclic  $(\text{HC})_2\text{C}=\text{X}$  systems employed unrestricted Kohn–Sham computations of both interacting fragments,  $\text{C}=\text{X}$  and  $\text{HC}=\text{CH}$ , as open-shell singlets each possessing two unpaired electrons. The highest lying singly occupied orbitals are enforced to have different spacial regions but have appropriate spin. This results in one unpaired electron at each carbon atom of  $\text{HC}=\text{CH}$ . The EDA calculations of the acyclic reference systems,  $(\text{H}_2\text{C}=\text{CH})_2\text{C}=\text{X}$ , employed three fragments:  $\text{X}=\text{C}$  as an open-shell singlet having two unpaired electrons and two doublet state  $\text{H}_2\text{C}=\text{CH}$  fragments, computed with opposite spins (see Table S1, Supporting Information).

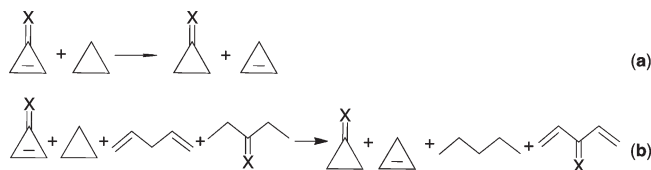
NICS values were computed (BP86/def2-TZVPP) employing the gauge invariant atomic orbital (GIAO) approach<sup>20</sup> and the canonical molecular orbital dissection as implemented in NBO 5.0.<sup>21</sup> The NICS(0)<sub>zzz</sub> values (at ring centers) are based on the out-of-plane (zz) tensor components of the isotropic NICS and only include the contributions of the two  $\pi$  MOs relevant to aromaticity.<sup>21h</sup>

The BLW-REs, BLW-ECREs, EDA-ASEs, and different types of NICS values of the exocyclic substituted cyclopropenes are listed in Table 1. Positive-ECRE/ASE (negative-NICS) values measure the magnitude of aromaticity, whereas negative-ECRE/ASE (positive-NICS) values correspond to antiaromatic systems. Nonaromatic rings have ECRE, ASE, or NICS values close to zero. Note that planar ring symmetries ( $C_{2v}$  or  $C_s$ ) were imposed, as our concern is the effect of the  $\pi$  systems. The number of the BP86/TZ2P//BP86/TZ2P imaginary frequencies (NImag), and the values for  $\Delta E_{\text{int}}$  and its contributing terms of  $(\text{HC})_2\text{C}=\text{X}$  are shown in Table S1 (Supporting Information).

## Results and Discussion

Exocyclic substituents have substantial effects on the aromaticity/antiaromaticity of methylene cyclopropene derivatives,  $(\text{HC})_2\text{C}=\text{X}$ . More electronegative substituents, e.g.,  $\text{X}=\text{O}$ , polarize the exocyclic double bond away from the three-membered ring (3MR), which then resembles the (aromatic)  $2\pi$  electron cyclopropenyl cation (see Scheme 1). More electropositive substituents, e.g.,  $\text{X} = \text{InH}$ , behave in the

## SCHEME 3. Isodesmic Equations Proposed for Evaluating the REs of Exocyclic Substituted Cyclopropenes



opposite way and polarize the exocyclic double bond toward the 3MR, which then resembles the (antiaromatic)  $4\pi$  electron cyclopropenyl anion (Scheme 1). Thus, the ECREs for  $\text{X} = \text{BH}$  to  $\text{InH}$  (group 13),  $\text{CH}_2$  to  $\text{SnH}_2$  (group 14),  $\text{NH}$  to  $\text{SbH}$  (group 15), and  $\text{O}$  to  $\text{Te}$  (group 16) range from  $-15$  to  $10$  kcal/mol, their ASEs range from  $-26$  to  $8$  kcal/mol, and their NICS(0)<sub>zzz</sub> values vary from  $+30$  to  $-6$  ppm. These three independent estimations demonstrate that the aromaticity of the cyclopropene derivatives is extremely sensitive to the substituent effects.

**Resonance Energies and Extra Cyclic Resonance Energies.** The REs of the exocyclic cyclopropene derivatives  $(\text{HC})_2\text{C}=\text{CH}_2$  and  $(\text{HC})_2\text{C}=\text{O}$  have often been evaluated by employing isodesmic equation a in Scheme 3.<sup>22</sup>

However, such evaluations are seriously marred by hybridization and other imbalances on both sides of the equation. Both species on the right side are stabilized by hyperconjugation, and there is no compensation on the left side. The assumption of balanced ring strain is highly dubious when the 3MRs have different numbers of  $\text{sp}^2$  centers. Bachrach's proposed improvement via a group equivalent reaction, i.e., equation b (Scheme 3),<sup>23</sup> is unsatisfactory; it does not correct these problems, introduces additional contaminations, and actually evaluates the ASE rather than the RE. Neither equation performs well. The B3LYP/def2-TZVPP values for  $(\text{HC})_2\text{C}=\text{CH}_2$  (eq a:  $9.6$  kcal/mol; eq b:  $4.5$  kcal/mol) and for  $(\text{HC})_2\text{C}=\text{O}$  (eq a:  $23.0$  kcal/mol; eq b:  $18.8$  kcal/mol) do not agree with our definitive BLW (ECRE) and ASE results (Table 1). Thus, at the same theoretical level, the BLW-REs and ECREs (kcal/mol) are  $24.1$  and  $2.3$  for  $(\text{HC})_2\text{C}=\text{CH}_2$  and  $31.0$  and  $10.5$  for  $(\text{HC})_2\text{C}=\text{O}$ , respectively. As has been amply demonstrated,<sup>24</sup> the BLW method computes REs effectively using the molecule itself as its own reference. Hence, the BLW method does not suffer from the contaminating effects of reference molecules.

Table 1 lists the computed BLW-REs and ECREs of the various methylenecyclopropene derivatives. The ECRE order of the 3MRs corresponds to the BLW-REs: group 16 > group 15 > group 14 > group 13. Specifically,  $(\text{HC})_2\text{C}=\text{O}$  is the most aromatic, and  $(\text{HC})_2\text{C}=\text{InH}$  is the least so. Species with more electronegative exocyclic X substituents have positive ECREs, as the  $\text{C}=\text{X}$  bonds are polarized away from the pseudo  $2\pi$  aromatic 3MRs (resembling the aromatic cyclopropenyl cation). In contrast, those with electropositive X have negative ECREs, since the  $\text{C}=\text{X}$  bonds are polarized toward the carbon centers, resulting in a pseudo  $4\pi$  antiaromatic system (like the cyclopropenyl anion). The ECREs of the exocyclic substituted

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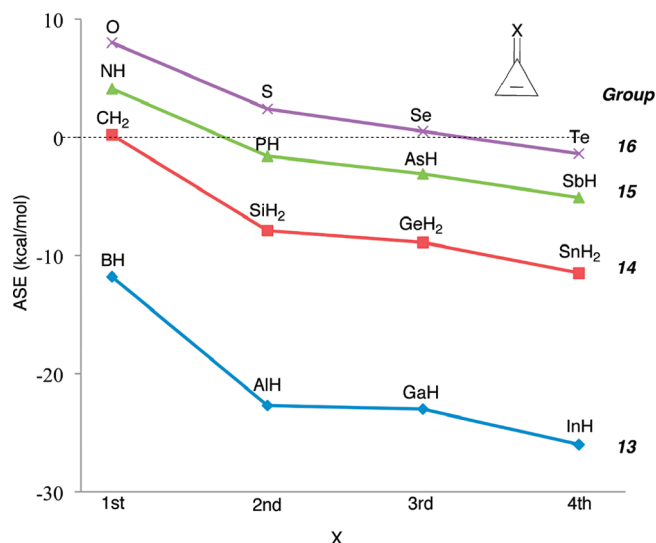
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**FIGURE 1.** Computed EDA-ASE values for  $(\text{HC})_2\text{C}=\text{X}$  ( $\text{X} = \text{BH}$  to  $\text{InH}$  (group 13),  $\text{CH}_2$  to  $\text{SnH}_2$  (group 14),  $\text{NH}$  to  $\text{SbH}$  (group 15), and  $\text{O}$  to  $\text{Te}$  (group 16)).

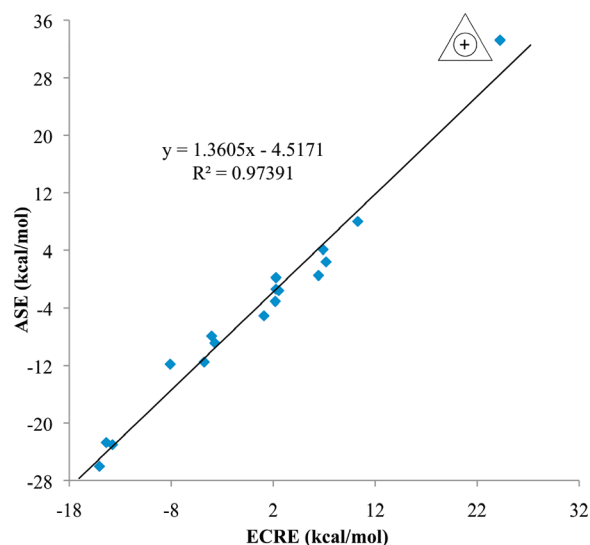
cyclopropenes were derived by comparing their BLW-REs to those of their acyclic references,  $(\text{H}_2\text{C}=\text{CH})_2\text{C}=\text{X}$ , which retain the point group as well as the numbers and types of conjugation. Note that the T-shape arrangement of the double bonds in  $(\text{HC})_2\text{C}=\text{X}$  results in two formal conjugations.

The nice consistency of  $(\text{HC})_2\text{C}=\text{X}$  ( $\text{X} = \text{CH}_2$ ,  $\text{NH}$ ,  $\text{O}$ ,  $\text{SiH}_2$ ,  $\text{PH}$ ,  $\text{S}$ ) between the previous (computed at B3LYP/6-31G\*, using two  $\text{CH}_2=\text{CH}-\text{CH}=\text{X}$  as reference molecules)<sup>24</sup> and current ECRE values reveals that the energetic ECRE criterion is essentially independent of the computational level and employed reference molecules.

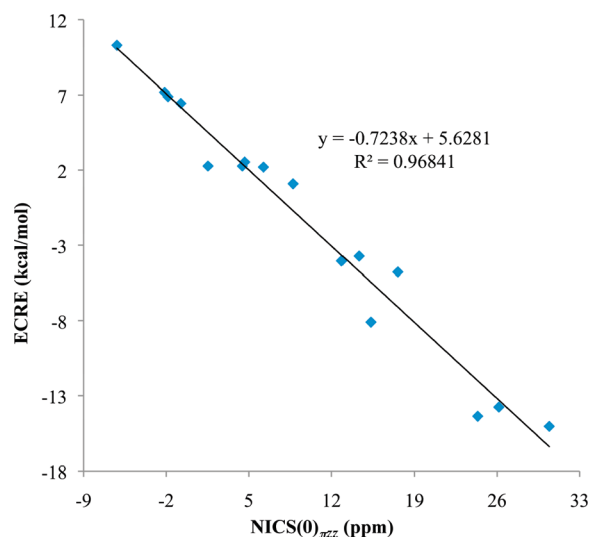
**Aromatic Stabilization Energies.** Within each period, 3MRs with exocyclic group 16 substituents have more positive (or less negative) EDA-ASE values and are more aromatic. Those with group 13 substituents have more negative EDA-ASE values and are generally antiaromatic. The values for  $\Delta E_\pi$  of  $(\text{HC})_2\text{C}=\text{X}$  behave similarly (Table 1). Additionally, the ASE interval of the 3MRs is roughly equal among those having substituents from group 14 to group 15 to group 16, but those having group 13 substituents have much smaller ASEs, probably ascribing to the relatively larger  $\sigma_{\text{CH}}$  or  $\sigma_{\text{CC}} \rightarrow \text{p}_X$  (vacant) hyperconjugations in the acyclic reference molecules. The trend of the ASE values for the 3MRs is displayed in Figure 1. There is a steady decrease of the ASE values within a group and within each row when the atom becomes less electronegative.

As a result of the higher electronegativities of  $\text{O}$  (3.50 on the Allred-Rochow scale) and  $\text{N}$  (3.07),  $(\text{HC})_2\text{C}=\text{O}$  and  $(\text{HC})_2\text{C}=\text{NH}$  are aromatic.  $(\text{HC})_2\text{C}=\text{S}$  also is aromatic. Although  $\text{C}$  (2.50) and  $\text{Si}$  (2.44) have similar electronegativities,  $\text{S}$  is a good  $\pi$  acceptor and can accommodate additional  $\pi$  electron density, also due to its relatively large size compared to the first row atoms. Thus, Wiberg et al. found that the  $\pi$  density of the  $\text{C}=\text{X}$  bond in  $(\text{HC})_2\text{C}=\text{S}$  resembles that of  $(\text{HC})_2\text{C}=\text{O}$ .<sup>25</sup>

Figure 2 displays the satisfactory correlation ( $R^2 = 0.974$ ) between the ADE-ASEs and BLW-ECREs. The more



**FIGURE 2.** ASE versus ECRE plot for the methylenecyclopropenes and the cyclopropenyl cation.

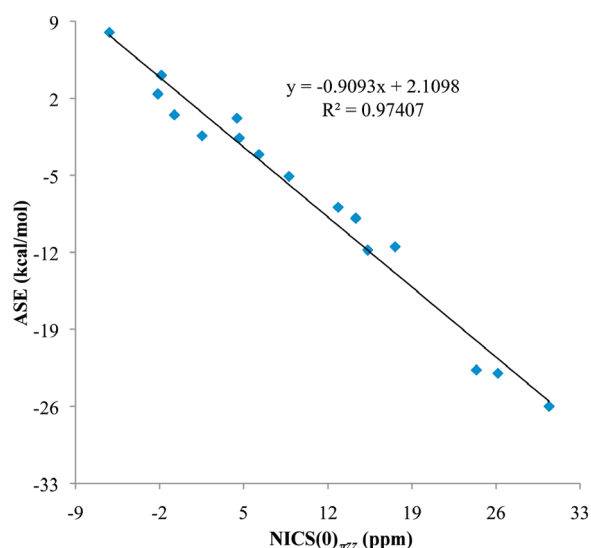


**FIGURE 3.** ECRE versus  $\text{NICS}(0)_{\pi_{zz}}$  plot for the methylenecyclopropenes.

electron-withdrawing group 16 substituents (e.g.,  $\text{O}$ ) induce  $\text{C}^+\text{X}^-$  type bond polarization and thus enhance the  $2-\pi$  3MR aromaticity. In contrast, the more electropositive group 13 substituents (e.g.,  $\text{BH}$ ) induce  $\text{C}^-\text{X}^+$  polarization, which increases the  $4\pi$  antiaromatic character of the 3MRs. Note that the ECREs (Figure 2) are somewhat more positive than the EDA-ASEs (slope = 1.36). The 33.2 (ASE) and 24.2 kcal/mol (ECRE) point for the cyclopropenyl cation was added for comparison (but did not change  $R^2$ ).

**Nucleus-Independent Chemical Shifts.** The deficiencies of the original isotropic NICS for three-membered ring applications were apparent in the original work,<sup>21a</sup> and the reasons were appreciated very early.<sup>21b</sup> The general trend of  $\text{NICS}(0)_{\pi_{zz}}$  (Table 1) values<sup>21h</sup> for the exocyclic substituted cyclopropenes follows the same expectations. Those with more electronegative substituents have negative  $\text{NICS}(0)_{\pi_{zz}}$  values (aromatic), and those with electropositive substituents have positive  $\text{NICS}(0)_{\pi_{zz}}$  values (antiaromatic).

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**FIGURE 4.** ASE versus  $\text{NICS}(0)_{\pi_{zz}}$  plot for the methylenecyclopropenes.

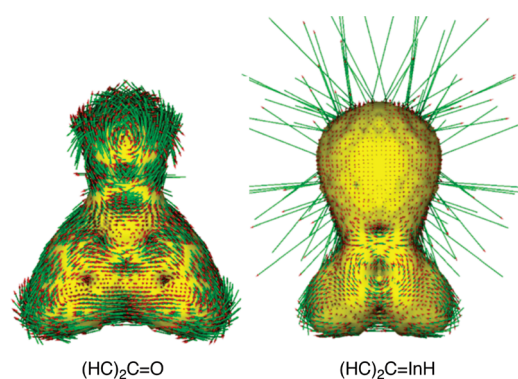
The  $\text{NICS}(0)_{\pi_{zz}}$  analyses correlate quite well with the ECRE ( $R^2 = 0.968$ ; Figure 3) and the ASE ( $R^2 = 0.974$ ; Figure 4) data.

As has long been recognized,<sup>21b</sup> unrefined NICS computations of 3MRs suffer from severe contaminations coming from the  $\sigma$  orbital contributions as well as the in-plane tensor components, not related to aromaticity.<sup>21</sup> Isotropic NICS(0) values in 3MR ring centers are especially unreliable; they give misleading conclusions and should not be employed. The proper remedy, the  $\text{NICS}(0)_{\pi_{zz}}$  refinement,<sup>21h</sup> overcomes the problems and, as we demonstrate here again (see Figures 3 and 4), performs very well.

The in-plane ( $xx$ ,  $yy$ ) shielding tensor components of the isotropic NICS can be large, especially for the small 3MRs.<sup>21f</sup> For example, the large negative NICS(0) values for all of the 3MR species listed in Table 1 are dominated by large negative  $xx$  and  $yy$  in-plane tensor components, unrelated to the  $\pi$  aromaticity. This is not the only problem, since the “second best”  $\text{NICS}(1)_{zz}$  index<sup>21h</sup> does not perform satisfactorily either (see Table 1), due to the  $zz$  tensor contaminations from the  $\sigma$  orbitals. For similar reasons, diamagnetic magnetic susceptibilities, which often depend on the molecular ring size, also are not suitable for probing the aromaticity of small rings. Dissected  $\text{NICS}(0)_{\pi_{zz}}$  values, which include only the out of plane tensor components of the  $\pi$  MO contributions, are far superior.<sup>21h</sup>

Like the ECREs, the  $\text{NICS}(0)_{\pi_{zz}}$  values for  $(\text{HC})_2\text{C}=\text{X}$  ( $\text{X} = \text{CH}_2, \text{NH}, \text{O}, \text{SiH}_2, \text{PH}, \text{S}$ ) in Table 1 agree well with those reported previously (at PW91/IGLOIII TZ2P//B3LYP/6-311+G\*\*).<sup>5</sup> This documents the essential insensitivity of  $\text{NICS}(0)_{\pi_{zz}}$  to the computational level.

**Anisotropy of the Induced Current Density (ACID).** The ACID (anisotropy of the induced current densities) plots in Figure 5 display the aromatic/antiaromatic nature of the exocyclic substituted cyclopropenes impressively. The ACID method, developed by Herges and co-workers,<sup>26</sup> was applied to the most aromatic,  $(\text{HC})_2\text{C}=\text{O}$ , and most antiaromatic,  $(\text{HC})_2\text{C}=\text{InH}$ , as confirmed by the BLW-ECRE, EDA-ASE, and  $\text{NICS}(0)_{\pi_{zz}}$  analyses. The ACID method nicely



**FIGURE 5.** Contrasting ACID plots for aromatic  $(\text{HC})_2\text{C}=\text{O}$  and antiaromatic  $(\text{HC})_2\text{C}=\text{InH}$  (0.04 au isosurface values).

agrees with this description. Strong diatropic (anticlockwise) induced current vectors are shown clearly for the aromatic  $(\text{HC})_2\text{C}=\text{O}$ , whereas paratropic current (clockwise vectors) characterize the antiaromatic  $(\text{HC})_2\text{C}=\text{InH}$ .

## Conclusions

Based on the various measures, from EDA-ASE to BLW-ECRE and to the most refined  $\text{NICS}(0)_{\pi_{zz}}$ , the aromaticity of exocyclic substituted cyclopropenes  $(\text{HC})_2\text{C}=\text{X}$  is extremely sensitive to the substituents ( $\text{X} = \text{BH}-\text{InH}, \text{CH}_2-\text{SnH}_2, \text{NH}-\text{SbH}, \text{O}-\text{Te}$ ). It is clear that the ECRE, ASE, and  $\text{NICS}(0)_{\pi_{zz}}$  results correlate well with one another (see Figures 2–4). The ACID plots agree nicely with the conclusions given by the above three criteria. Exocyclic substituted cyclopropenes with electron-withdrawing (electronegative) substituents have positive ECRE/ASE (negative  $\text{NICS}(0)_{\pi_{zz}}$ ) values and are aromatic (resembling the  $2\pi$  electron cyclopropenium cation). Exocyclic substituted cyclopropenes with electron-donating (electropositive) substituents<sup>27</sup> have negative ECRE/ASE (positive  $\text{NICS}(0)_{\pi_{zz}}$ ) values and are antiaromatic (resembling the  $4\pi$  electron cyclopropenium anion). Specifically,  $(\text{HC})_2\text{C}=\text{O}$  and  $(\text{HC})_2\text{C}=\text{InH}$  are the most aromatic and most antiaromatic species in our set. However, the calibrating point for the parent cyclopropenium ion in Figure 2 shows that the neutral  $(\text{HC})_2\text{C}=\text{O}$  is far from having the maximum possible 3MR aromaticity. This can be enhanced by protonation<sup>5a</sup> or Lewis acid complexation.

**Acknowledgment.** We dedicate this paper to Ronald Breslow for his seminal investigations of 3MR aromaticity and antiaromaticity. This work was supported by the Deutsche Forschungsgemeinschaft in Germany and by the NSF Grant CHE-0716718 in the United States. We thank the China Scholarship Council (CSC) for a study fellowship for Y.W. at the University of Georgia as well as Yirong Mo for his methodological developments and advice. I.F. is a Ramón y Cajal fellow.

**Supporting Information Available:** BP86/TZ2P, Cartesian coordinates, and EDA results for exocyclic-substituted cyclopropenes and the reference molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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