

# Halogen Switching of Azacarbenes $C_2NH$ Ground States at Ab Initio and DFT Levels

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**ABSTRACT:** Relative stabilities and singlet–triplet energy differences are calculated for 24  $C_2NX$  azacarbenes (where  $X$  is H, F, Cl, and Br). Three skeletal arrangements are employed including azacyclopropenylidene, [(imino)methylene]carbene, and cyanocarbene. Halogens appear to alternate the electronic ground states of  $C_2NH$  azacarbenes, from triplet to singlet states, at MP3/6-311++G\*\*, BLYP/6-311++G\*\*, B3LYP/6-311++G\*\*, MP2/6-311++G\*\*, MP4(SDTQ)/6-311++G\*\*, QCISD(T)/6-311++G\*\*, CCSD(T)/6-311++G\*\*, CCSD(T)/cc-pVTZ, G1, and G2 levels of theory. The aromatic characters of singlet cyclic azacyclopropenylidenes are measured using GIAO–NICS calculations. Linear correlations are found between the B3LYP/6-311++G\*\* calculated LUMO–HOMO energy gaps ( $\Delta E_{\text{HOMO-LUMO}}$ ) of the singlet carbenes versus their corresponding singlet–triplet energy separations ( $\Delta E_{\text{s-t}}$ ). Electrophilic characters are found for all singlet azacarbenes in their addition reactions to alkenes with the highest electrophilicity being exhibited for  $X = F$ . © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:377–388, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20442

## INTRODUCTION

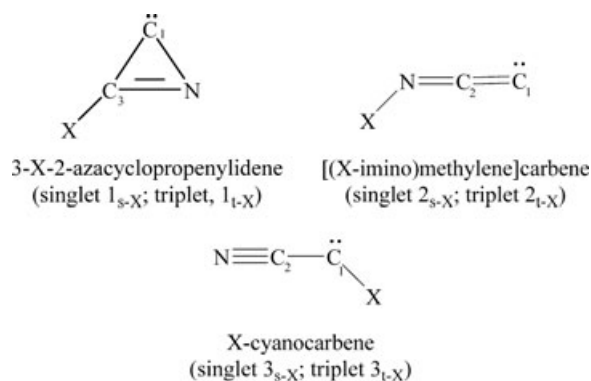
Structures and multiplicities of interstellar carbenic  $C_3H_2$  isomers and their substituted analogues [1] as well as their corresponding nitrogen analogues  $C_2NH$  have become the topic of a large number of theoretical and experimental studies [2,3]. Accordingly, matrix generations of singlet azacyclopropenylidene and singlet bromocyanocarbene (BrCCN) were reported by Maier and coworkers in 1998 [4].

The order of relative stability for the global minima of  $C_3H_2$  isomers at different levels of theory is singlet cyclopropenylidene > triplet propargylene > singlet vinylidencarbene > singlet propargylene [1f,1m]. At the same levels of theory, halogens (X) change this order to singlet cyclopropenylidene > singlet vinylidencarbene > singlet propargylene > triplet propargylene (X = F, Cl, and Br) [1m]. The effect of electron-donating and electron-withdrawing substituents, including amino, cyano, and methoxy groups, on  $C_2NH$  carbenes indicated that only electron-donating substituents switch the multiplicities of their corresponding carbenes [5]. It has been predicted recently that halogens can switch the global minima of  $C_2SiHX$  silylenes [6] and  $C_2GeHX$  germlylenes [7]. However, up to date no attempt has been made to account for how halogens influence the stability and multiplicity of  $C_2NH$  carbenes. Do halogens act like electron-donating, or electron-withdrawing substituents? To answer these questions, in this paper we report the results of our theoretical studies on the singlet (s) and triplet (t) states of 24 different carbenes with  $C_2NX$  formula, where X is H, F, Cl, and Br (Fig. 1).

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**FIGURE 1** Three possible structures considered for each singlet (**s**) and triplet (**t**)  $C_2NX$  carbenes (**1**, **2**, and **3**, where X is H, F, Cl, and Br).

### COMPUTATIONAL DETAILS

Ab initio methodologies, including second-order Møller–Plesset (MP2) [8], third-order Møller–Plesset (MP3) [9], couple-cluster with single and double excitations, and a perturbative treatment of the connected triple excitation [10] and quadratic CI calculations [11] are employed. Density Functional Theory (DFT), with Becke’s hybrid one-parameter and three-parameter functional, using the Lee–Yang–Parr correlation including both local and non-local terms as implemented by Adamo and Barone [12,13], has also been used. Basis sets used for this work are standard 6-311++G\*\* as well as Dunning’s cc-pVTZ correlation consistent [14,15]. To improve the energetic forecasts, the MP2/6-311++G\*\* optimized geometries are submitted for single-point calculations at the MP4(SDTQ)/6-311++G\*\* [16], QCISD(T)/6-311++G\*\*, CCSD(T)/6-311++G\*\*, CCSD(T)/cc-pVTZ, and G1 and G2 levels [17–19]. Singlet states are calculated with spin-restricted wave function, whereas the spin-projected wave functions are employed for triplet states. The harmonic vibrational frequencies and zero-point energies (ZPE) are calculated for the DFT-optimized structures, at the same level used for their optimization. The vibrational frequencies and ZPE data at the B3LYP are scaled by 0.98 [20,21]. The natural bond orbitals (NBO) population analysis is carried out at the B3LYP/6-311++G\*\* [22]. Nucleus independent chemical shifts (NICS) values [23] are calculated by the gauge-independent atomic orbital (GIAO) [24,25] method at the B3LYP/6-311++G\*\*, in which NICS values are measured at the ring center (defined as simple average of Cartesian coordinates for all atoms of a three-member ring) as well as 0.5, 1, 1.5, 2, 2.5 and 3 Å above the plane of

ring. All calculations, in this paper, are performed using the Gaussian 98 program package [26].

### RESULTS AND DISCUSSION

The singlet (**s**) and triplet (**t**) states of 24  $C_2NX$  azacarbenes consist of 3-X-2-azacyclopropenylidene (**1**), [(X-imino)methylene]carbene (**2**), and X-cyanocarbene (**3**) for X=H, F, Cl and Br (Fig. 1 and Tables 1–4). Relative energies of **1–3** are calculated at 10 levels of theory (Tables 1–4). We are intentionally referring to the results obtained using 10 levels of theory, because reporting data at various levels may provide an opportunity to correlate the usefulness of the different levels to the specific molecules. However, examination of the relative energies for **1–3** shows that, in general, energetic results are not very dependent on the computational methods and/or the basis sets employed. Consistency is found among the calculated relative energies at higher levels, QCISD(T), CCSD(T), G1 and G2, with differences between calculated relative energies below 3 kcal/mol. These appear somewhat different from those of MP4(SDTQ), and in contrast to other studies which show CCSD(T)//MP2 relative energies as accurate theoretical predictions [27–30]. Indeed, recent results by Lynch and Truhlar suggest that the location of saddle points using the DFT methods followed by single-point CCSD(T) calculations represents a recipe that can be considered to have an excellent performance-to-cost ratio [31]. Further refined energetic predictions are obtained by using G2 theory as well as by exploiting the important property of Dunning’s correlation-consistent basis sets that exhibit monotonic convergence to an apparent complete basis set (CBS) limit [29]. In addition, it is well known that an important drawback, commonly associated with the use of unrestricted Hartree–Fock wave functions in open-shell calculations, both at the self-consistent field (SCF) and post-Hartree–Fock (MP2, DFT and CCSD-(T)) levels, is the spin-contamination problem [32a]. To overcome this problem, we employed spin-projected MP2 energies corresponding to the appropriate multiplicity [33,34]. The superiority of G2 over other high-level calculation methods, such as QCISD(T) and CCSD(T), partly stems from the so-called higher level correction imposed in G2 theory [32]. Moreover, G2 data appear to be most consistent with those obtained from other rather advanced calculation methods (Tables 1–4). Hence, as “the happy medium,” the G2 energy results emerge and are preferable over other calculation methods used in this work.

In contrast, B3LYP appears quite reliable for computing geometrical parameters [35]. Optimized

**TABLE 1** Comparison of Relative Energies (kcal/mol) for Singlet and Triplet States of C<sub>2</sub>NH Azacarbenes (1–3), at 10 Levels of Theory, Including ZPE Corrections, Along with the B3LYP/6-311++G\*\* Vibrational Zero-Point Energies (VZPE; kcal/mol)

Structure	Relative Energies (kcal/mol)										VZPE (kcal/mol)	
	<sup>a</sup> MP3/ 6-311++G**	B1LYP/ 6-311++G**	B3LYP/ 6-311++G**	<sup>a</sup> MP2/ 6-311++G**	<sup>a</sup> MP4(SDTQ)/ 6-311++G**	<sup>a</sup> QCISD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ cc-pVTZ	G1	G2	B3LYP/ 6-311++G**	
<i>b</i> <sub>1s</sub> -H	10.00	17.00	16.39	40.00	50.00	6.25	5.84	5.26	5.16	5.06	12.84	
<i>1</i> <sub>t</sub> -H	52.54	56.89	56.30	54.53	51.87	53.72	53.66	53.25	53.09	52.09	10.27	
<i>2</i> <sub>s</sub> -H	32.19	41.94	41.09	34.83	29.22	33.75	33.63	32.85	31.49	32.16	11.91	
<i>2</i> <sub>t</sub> -H	30.59	34.29	33.90	33.59	30.65	33.81	33.75	32.68	33.97	33.97	11.62	
<i>3</i> <sub>s</sub> -H	9.91	16.88	16.18	7.28	4.36	9.96	9.83	9.00	7.05	7.61	11.38	
<i>b</i> <sub>3t</sub> -H	0.01	20.00	20.00	4.37	1.03	60.00	70.00	60.00	90.00	100.00	10.85	

<sup>a</sup>ZPE not included.

<sup>b</sup>The lowest energy minima are set at 0.00 kcal/mol; the original total energies (hartrees) corresponding to the lowest energy minima at various levels of theory: (1) –131.0381937, (2) –131.402413, (3) –131.4600315, (4) –131.0660802, (5) –131.1052934, (6) –131.1138242, (7) –131.1126264, (8) –131.184034, (9) –131.2017212, (10) –131.2013682.

**TABLE 2** Comparison of Relative Energies (kcal/mol) for Singlet and Triplet States of C<sub>2</sub>NF Azacarbenes (1–3), at 10 Levels of Theory, Including ZPE Corrections, Along with the B3LYP/6-311++G\*\* Vibrational Zero-point Energies (VZPE; kcal/mol)

Structure	Relative Energies (kcal/mol)										VZPE (kcal/mol)	
	<sup>a</sup> MP3/ 6-311++G**	B1LYP/ 6-311++G**	B3LYP/ 6-311++G**	<sup>a</sup> MP2/ 6-311++G**	<sup>a</sup> MP4(SDTQ)/ 6-311++G**	<sup>a</sup> QCISD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ cc-pVTZ	G1	G2	B3LYP/ 6-311++G**	
<i>1</i> <sub>s</sub> -F	5.88	10.66	10.65	8.51	10.88	10.42	10.14	9.12	9.91	9.53	8.68	
<i>1</i> <sub>t</sub> -F	67.54	64.09	63.85	70.71	71.98	69.81	69.77	69.47	71.09	69.90	6.88	
<i>2</i> <sub>s</sub> -F	76.21	72.46	71.37	84.67	77.80	75.70	76.27	76.40	74.69	75.02	7.23	
<i>2</i> <sub>t</sub> -F	100.94	88.23	88.01	111.47	106.73	100.81	101.21	100.70	104.29	103.70	6.86	
<i>b</i> <sub>3s</sub> -F	10.00	20.00	20.00	40.00	50.00	60.00	70.00	60.00	90.00	100.00	7.82	
<i>3</i> <sub>t</sub> -F	14.03	4.96	5.49	19.48	20.26	13.79	13.88	14.13	15.81	15.13	7.99	

<sup>a</sup>ZPE not included.

<sup>b</sup>The lowest energy minimum is set at 0.00 kcal/mol; the total energies (hartrees) corresponding to the lowest energy minimum *3*<sub>s-F</sub> at various levels of theory: (1) –230.0544994, (2) –230.6410538, (3) –230.7169123, (4) –230.1546678, (5) –230.2010162, (6) –230.1964128, (7) –230.1948702, (8) –230.3200509, (9) –230.3631656, (10) –230.3612768.

**TABLE 3** Comparison of Relative Energies (kcal/mol) for Singlet and Triplet States of C<sub>2</sub>NCl Azacarbenes (1–3), at 10 Levels of Theory, Including ZPE Corrections, Along with the B3LYP/6-311++G\*\* Vibrational Zero Point Energies (VZPE; kcal/mol)

Structure	Relative Energies (kcal/mol)										VZPE (kcal/mol)	
	<sup>a</sup> MP3/ 6-311++G**	B1LYP/ 6-311++G**	B3LYP/ 6-311++G**	<sup>a</sup> MP2/ 6-311++G**	<sup>a</sup> MP4(SDTQ)/ 6-311++G**	<sup>a</sup> QCISD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ cc-pVTZ	G1	G2	B3LYP/ 6-311++G**	
1 <sub>s</sub> -Cl	1.01	13.05	12.57	5.12	7.69	7.67	7.30	7.26	8.30	7.55	7.68	
1 <sub>t</sub> -Cl	21.05	58.78	58.17	30.38	30.25	25.54	25.48	26.07	30.02	28.62	5.85	
2 <sub>s</sub> -Cl	56.54	58.20	56.79	65.00	59.85	57.80	58.14	56.46	55.91	56.55	6.68	
2 <sub>t</sub> -Cl	67.00	63.80	63.35	77.23	74.52	70.28	70.40	68.43	71.46	70.95	6.58	
b <sub>3s</sub> -Cl	10.00	3.98	3.24	40.00	50.00	60.00	70.00	80.00	90.00	100.00	7.22	
b <sub>3t</sub> -Cl	3.18	20.00	30.00	11.45	11.09	3.76	3.80	4.16	6.69	5.60	7.23	

<sup>a</sup>ZPE not included.

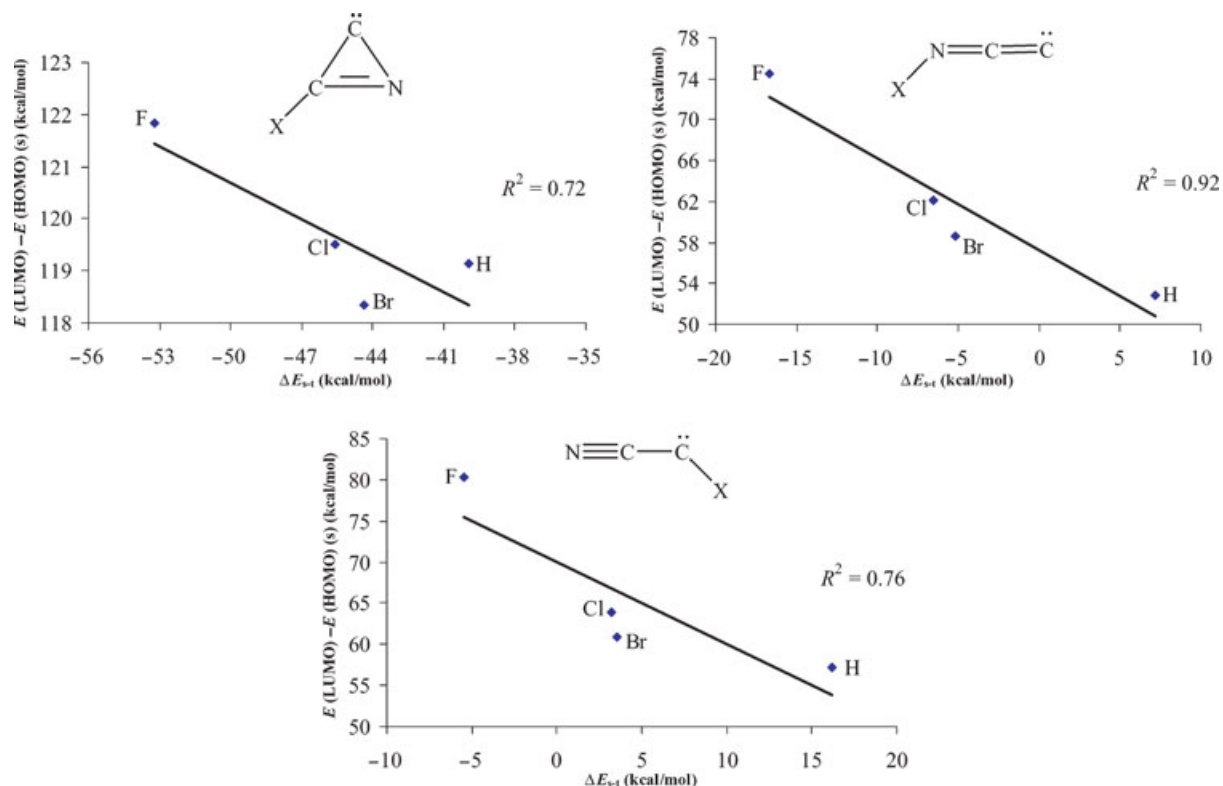
<sup>b</sup>The lowest energy minima are set at 0.00 kcal/mol; the original total energies (hartrees) for the lowest energy minima at various levels of theory: (1) –590.0678768, (2) –591.00965659, (3) –591.0796877, (4) –590.132001, (5) –590.1869125, (6) –590.1843901, (7) –590.182984, (8) –590.3218257, (9) –590.3614087, (10) –590.3581698.

**TABLE 4** Comparison of Relative Energies (kcal/mol) for Singlet and Triplet States of C<sub>2</sub>NBr Azacarbenes (1–3), at 10 Levels of Theory, Including ZPE Corrections, Along with the B3LYP/6-311++G\*\* Vibrational Zero Point Energies (VZPE; kcal/mol)

Structure	Relative Energies (kcal/mol)										VZPE (kcal/mol)	
	<sup>a</sup> MP3/ 6-311++G**	B1LYP/ 6-311++G**	B3LYP/ 6-311++G**	<sup>a</sup> MP2/ 6-311++G**	<sup>a</sup> MP4(SDTQ)/ 6-311++G**	<sup>a</sup> QCISD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ 6-311++G**	<sup>a</sup> CCSD(T)/ cc-pVTZ	G1	G2	B3LYP/ 6-311++G**	
b <sub>1s</sub> -Br	10.00	14.40	13.92	5.55	8.51	8.48	8.01	7.65	9.02	8.22	7.31	
1 <sub>t</sub> -Br	55.11	58.88	58.31	65.25	64.95	59.89	59.79	59.19	61.86	60.26	5.55	
2 <sub>s</sub> -Br	51.60	53.08	51.59	58.48	53.96	51.78	52.09	51.27	50.27	50.90	6.49	
2 <sub>t</sub> -Br	81.95	57.15	56.73	68.80	66.80	62.70	62.72	61.07	68.90	68.60	6.31	
b <sub>3s</sub> -Br	1.05	4.38	3.53	40.00	50.00	60.00	70.00	80.00	90.00	100.00	6.97	
b <sub>3t</sub> -Br	2.92	20.00	30.00	11.03	10.68	2.91	2.89	3.13	6.03	5.13	6.94	

<sup>a</sup>ZPE not included.

<sup>b</sup>The lowest energy minima are set at 0.00 kcal/mol; the original total energies (hartrees) for the lowest energy minima at various levels of theory: (1) –2700.469428, (2) –2704.928583, (3) –2705.003327, (4) –2702.979898, (5) –2703.033729, (6) –2703.030921, (7) –2703.029361, (8) –2703.296069, (9) –2703.188526, (10) –2703.193563.



**FIGURE 2** Correlations between the LUMO–HOMO energy gaps (kcal/mol) of the singlet (**s**) C<sub>2</sub>NX azacarbenes (**1**<sub>s-X</sub>, **1**<sub>t-X</sub>; **2**<sub>s-X</sub>, **2**<sub>t-X</sub>, and **3**<sub>s-X</sub>, **3**<sub>t-X</sub>) and their corresponding singlet–triplet energy separations ( $\Delta E_{s-t,X}$ ) (kcal/mol), calculated at B3LYP/6-311++G\*\* for X = H, F, Cl, and Br ( $R^2$  = correlation coefficient).

geometrical parameters of **1** through **3** are reported, using B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels of theory. All optimizations are performed with no imposed constraints, making the starting structures free to transform through optimizations. Discrepancies in bond lengths and bond angles, computed using different methods, and/or basis sets, are in general small. All the optimized structures appear planar with C<sub>s</sub> symmetry. For both singlet structures of C<sub>2</sub>NX, the energies of HOMO and LUMO orbitals are obtained via NBO population analysis at B3LYP/6-311++G\*\* [22]. Linear correlations are found between the LUMO–HOMO energy gaps of the singlet carbenes with their corresponding  $\Delta E_{s-t,X}$  calculated at B3LYP/6-311++G\*\* level of theory (Fig. 2). Evidently, halogens increase the magnitude of LUMO–HOMO energy gaps. The order of LUMO–HOMO energy gaps as a function of X follows the electronegativity: F > Cl > Br > H. The linearity trend appears as **2**<sub>s-X</sub> ( $R^2 = 0.92$ ) > **3**<sub>s-X</sub> ( $R^2 = 0.76$ ) > **1**<sub>s-X</sub> ( $R^2 = 0.72$ ), where  $R^2$  is a correlation coefficient.

The NBO-calculated atomic charges, bond orders, and hybridizations, at B3LYP/6-311++G\*\* level are presented for three C<sub>2</sub>NX azacarbenic structures (Tables 5 and 6). Force constant calculations show imaginary frequencies for cyclic triplet car-

benes **1**<sub>t-H</sub>, **1**<sub>t-Cl</sub>, and **1**<sub>t-Br</sub>, counting them as an unreal isomer (transition state). For the sake of brevity, calculated harmonic frequencies are omitted but are available upon request. Bending potential energy curves for acyclic **3**<sub>s-X</sub> and **3**<sub>t-X</sub> species are calculated at B3LYP/6-311++G\*\* (Fig. 3). Finally, the total NICS values (ppm) for singlet cyclic azacarbenes are calculated at different distances above the plane of rings (Table 7).

**TABLE 5** The B3LYP/6-311++G\*\* NBO Calculated Hybridizations of Singlet (**1**<sub>s-X</sub> and **3**<sub>s-X</sub>) and Triplet States (**1**<sub>t-X</sub> and **3**<sub>t-X</sub>) of C<sub>2</sub>NX Azacarbenes

Structure	Bond		Structure	Bond	
	$\sigma_{C_1-N}$	$\sigma_{C_1-C_3}$		$\sigma_{C_1-X}$	$\sigma_{C_1-C_2}$
<b>1</b> <sub>s-H</sub>	s <sup>1</sup> p <sup>5.84</sup>	s <sup>1</sup> p <sup>4.30</sup>	<b>3</b> <sub>s-H</sub>	s <sup>1</sup> p <sup>3.69</sup>	s <sup>1</sup> p <sup>2.32</sup>
<b>1</b> <sub>t-H</sub>	s <sup>1</sup> p <sup>2.75</sup>	s <sup>1</sup> p <sup>2.73</sup>	<b>3</b> <sub>t-H</sub>	s <sup>1</sup> p <sup>1.33</sup>	s <sup>1</sup> p <sup>1.17</sup>
<b>1</b> <sub>s-F</sub>	s <sup>1</sup> p <sup>6.52</sup>	s <sup>1</sup> p <sup>4.58</sup>	<b>3</b> <sub>s-F</sub>	s <sup>1</sup> p <sup>4.51</sup>	s <sup>1</sup> p <sup>3.16</sup>
<b>1</b> <sub>t-F</sub>	s <sup>1</sup> p <sup>4.24</sup>	s <sup>1</sup> p <sup>2.37</sup>	<b>3</b> <sub>t-F</sub>	s <sup>1</sup> p <sup>3.25</sup>	s <sup>1</sup> p <sup>1.53</sup>
<b>1</b> <sub>s-Cl</sub>	s <sup>1</sup> p <sup>6.19</sup>	s <sup>1</sup> p <sup>4.31</sup>	<b>3</b> <sub>s-Cl</sub>	s <sup>1</sup> p <sup>4.79</sup>	s <sup>1</sup> p <sup>2.52</sup>
<b>1</b> <sub>t-Cl</sub>	s <sup>1</sup> p <sup>2.92</sup>	s <sup>1</sup> p <sup>2.64</sup>	<b>3</b> <sub>t-Cl</sub>	s <sup>1</sup> p <sup>2.54</sup>	s <sup>1</sup> p <sup>1.35</sup>
<b>1</b> <sub>s-Br</sub>	s <sup>1</sup> p <sup>6.11</sup>	s <sup>1</sup> p <sup>4.24</sup>	<b>3</b> <sub>s-Br</sub>	s <sup>1</sup> p <sup>5.83</sup>	s <sup>1</sup> p <sup>2.52</sup>
<b>1</b> <sub>t-Br</sub>	s <sup>1</sup> p <sup>2.82</sup>	s <sup>1</sup> p <sup>2.65</sup>	<b>3</b> <sub>t-Br</sub>	s <sup>1</sup> p <sup>2.74</sup>	s <sup>1</sup> p <sup>1.73</sup>

The insignificant *d* orbital hybridizations are not included.

**TABLE 6** NBO Analyses Including Atomic Charges and Bond Orders of C<sub>2</sub>NX Azacarbenes **1–3**, Calculated at B3LYP/6-311++G\*\* (where X is H, F, Cl, and Br)

Structure	Species	Atomic Charge				Bond Order			
		C <sub>1</sub>	C <sub>3</sub>	N	X	C <sub>1</sub> –C <sub>3</sub>	C <sub>1</sub> –N	C <sub>3</sub> –N	C <sub>3</sub> –X
<b>1</b>	<b>1<sub>s</sub>-H</b>	0.08	0.02	–0.31	0.22	1.17	1.29	1.65	0.98
	<b>1<sub>t</sub>-H</b>	–0.12	–0.51	–0.50	0.14	–	–	–	–
	<b>1<sub>s</sub>-F</b>	0.09	0.51	–0.33	–0.27	1.15	1.26	1.62	0.89
	<b>1<sub>t</sub>-F</b>	0.13	0.48	–0.36	–0.25	1.79	1.39	1.21	0.92
	<b>1<sub>s</sub>-Cl</b>	0.12	0.06	–0.32	0.14	1.17	1.26	1.67	1.30
	<b>1<sub>t</sub>-Cl</b>	–0.12	–0.41	–0.53	0.05	–	–	–	–
	<b>1<sub>s</sub>-Br</b>	0.12	0.00	–0.33	0.21	1.17	1.27	1.67	1.34
	<b>1<sub>t</sub>-Br</b>	0.17	–0.15	–0.32	0.29	–	–	–	–
<b>2</b>	<b>2<sub>s</sub>-H</b>	0.07	–0.02	–0.42	0.36	1.95	1.81	0.82	
	<b>2<sub>t</sub>-H</b>	–0.03	0.11	–0.50	0.42	1.87	1.86	0.76	
	<b>2<sub>s</sub>-F</b>	0.21	–0.15	0.15	–0.22	1.89	1.75	1.17	
	<b>2<sub>t</sub>-F</b>	0.09	0.01	0.08	–0.18	1.88	1.78	1.17	
	<b>2<sub>s</sub>-Cl</b>	0.17	–0.09	–0.23	0.15	1.87	1.75	1.29	
	<b>2<sub>t</sub>-Cl</b>	0.03	0.06	–0.34	0.25	1.86	1.80	1.29	
	<b>2<sub>s</sub>-Br</b>	0.17	–0.09	–0.28	0.19	1.85	1.77	1.26	
	<b>2<sub>t</sub>-Br</b>	0.03	0.05	–0.40	0.31	1.84	1.82	1.22	
<b>3</b>	<b>3<sub>s</sub>-H</b>	–0.03	0.05	–0.18	0.15	1.47	0.95	2.30	
	<b>3<sub>t</sub>-H</b>	–0.05	0.03	–0.19	0.21	1.86	1.00	2.10	
	<b>3<sub>s</sub>-F</b>	0.41	0.06	–0.18	–0.29	1.15	1.05	2.41	
	<b>3<sub>t</sub>-F</b>	0.48	0.01	–0.21	–0.28	1.53	1.08	2.29	
	<b>3<sub>s</sub>-Cl</b>	–0.04	0.09	–0.19	0.14	1.27	1.48	2.38	
	<b>3<sub>t</sub>-Cl</b>	–0.01	0.06	–0.21	0.16	1.62	1.51	2.25	
	<b>3<sub>s</sub>-Br</b>	–0.12	0.08	–0.18	0.23	1.29	1.53	2.37	
	<b>3<sub>t</sub>-Br</b>	–0.10	0.06	–0.21	0.25	1.62	1.55	2.25	

### Singlet–Triplet Energy Gaps versus Structures

Cyclic singlet 3-X-2-azacyclopropenylienes (**1<sub>s-x</sub>**), appear more stable than their corresponding triplet states (**1<sub>t-x</sub>**), mostly due to the aromatic character of the former and angle strains involved in the latter (X=H, F, Cl, and Br; Tables 1–4). These results appear consistent with those of C<sub>3</sub>HX carbenes, C<sub>2</sub>SiHX silylenes, and C<sub>2</sub>GeHX germylenes [1m,6,7]. The **1<sub>s-x</sub>** species with a nitrogen atom attached to a divalent carbon and with expected aromatic character is close to the first isolated carbenes, with imidazol-2-ylidene structure, reported by Arduengo and coworker [36]. The G2 calculated order of singlet–triplet energy gaps ( $\Delta E_{s-t,x}$ ) between **1<sub>s-x</sub>** and **1<sub>t-x</sub>** is  $\Delta E_{s-t,F}$  (60.37 kcal/mol) >  $\Delta E_{s-t,Br}$  (52.04 kcal/mol) >  $\Delta E_{s-t,H}$  (47.03 kcal/mol) >  $\Delta E_{s-t,Cl}$  (21.07 kcal/mol) (Tables 1–4). In this trend, fluorine apparently increases the stability of the singlet state more than the other halogens. Except for **1<sub>t-cl</sub>**, cyclic triplet states (**1<sub>t-x</sub>**) are exclusively possible for X=H, F, and Br. All divalent angles  $\angle C_3C_1N$  of the singlet

states (**1<sub>s-x</sub>**) are smaller than those of their corresponding triplet states, **1<sub>t-x</sub>**. This is consistent with the analogues cyclic carbenes, while is in contrast to the analogues cyclic silylenes and/or germylenes [1m,6,7]. This phenomenon can be rationalized by considering the electronic structures and hybridizations of the atoms attached to the divalent centers [7]. For instance, in the cyclic structures **1<sub>s-x</sub>** and **1<sub>t-x</sub>**, as well as the acyclic structures **3<sub>s-x</sub>** and **3<sub>t-x</sub>**, the strictly localized NBO of the  $\sigma$  molecular orbitals have significant p character for the divalent centers (C<sub>1</sub>). The significance of p orbitals of divalent C<sub>1</sub> in the  $\sigma_{C_1-N}$  bond is more than the  $\sigma_{C_1-C_3}$ , for **1<sub>s-x</sub>** and **1<sub>t-x</sub>**. However, the p characters of divalent atoms in singlet states (**1<sub>s-x</sub>** and **3<sub>s-x</sub>**) are higher than their corresponding triplet states (**1<sub>t-x</sub>** and **3<sub>t-x</sub>**) (Table 5). This may be the cause for decrease in the divalent angle in singlet states **1<sub>s-x</sub>** and **3<sub>s-x</sub>** compared with their corresponding triplet states **1<sub>t-x</sub>** and **3<sub>t-x</sub>**. The C<sub>1</sub>–N bond lengths in singlet **1<sub>s-x</sub>** increases if H is replaced with the halogens.

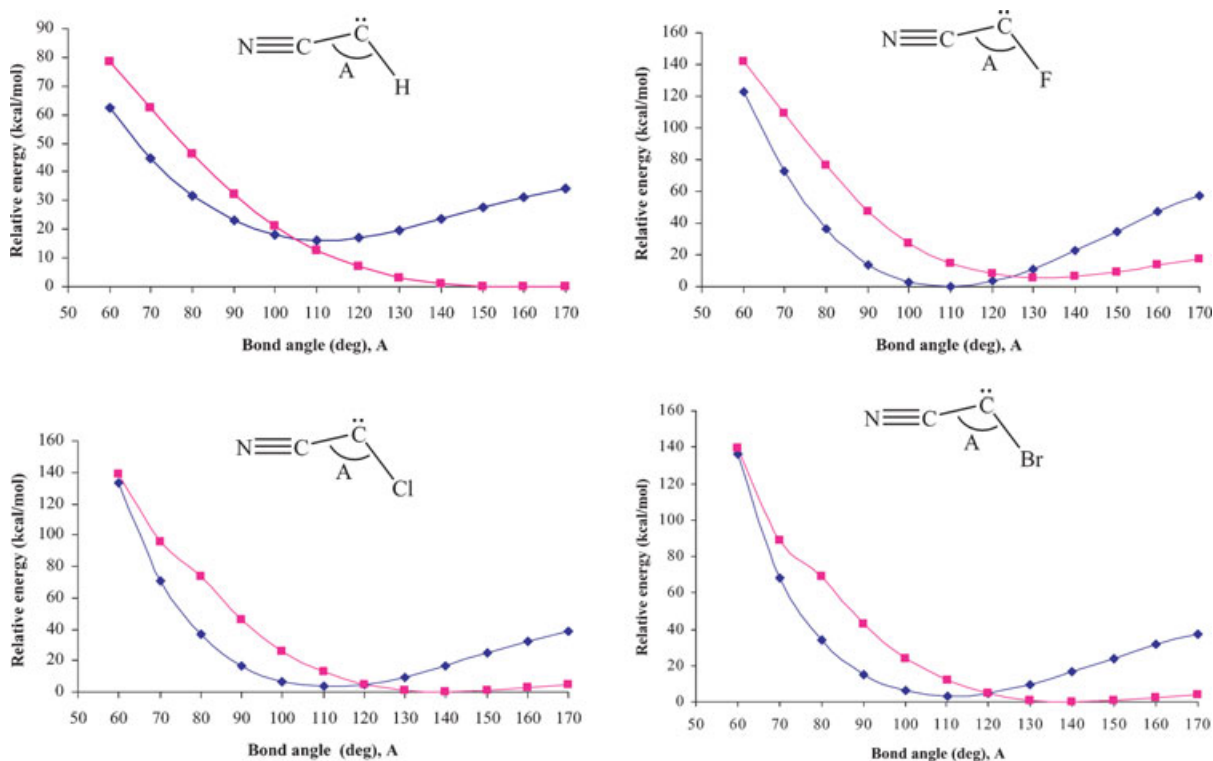


FIGURE 3 B3LYP/6-311++G\*\* calculated relative energies (kcal/mol) for the singlet (**s**,  $\blacktriangle$ ) and triplet (**t**,  $\blacksquare$ ) states of X-cyanocarbenes **3**<sub>s-X</sub> and **3**<sub>t-X</sub>, plotted as a function of the corresponding divalent bond angles (XC<sub>1</sub>C<sub>2</sub>, A (deg), where X is H, F, Cl, and Br.

Acyclic [(X-imino)methylene]carbenes (**2**) are more sensitive to halogens than the cyclic carbenes **1**. This may be due to the higher linearity of the former, which enhances the direct resonance effects of halogens to the divalent center (Fig. 1). Higher significance of the resonance in the singlet states makes **2**<sub>s-X</sub> species more stable than their corresponding triplet states **2**<sub>t-X</sub>, where X is H, F, Cl, and Br (Tables 1–4). The C<sub>1</sub>=C<sub>2</sub> bond lengths in **2**<sub>s-H</sub> and **2**<sub>t-H</sub> are longer than those of the halogenated **2**<sub>s-X</sub> and **2**<sub>t-X</sub>. However, C–N bond lengths in the halogenated **2**<sub>s-X</sub> and **2**<sub>t-X</sub> are nearly similar. Every  $\angle$ XNC<sub>2</sub> angle in **2**<sub>s-X</sub> isomers is greatly smaller than that in **2**<sub>t-X</sub>. All the  $\angle$ C<sub>1</sub>C<sub>2</sub>N in **2**<sub>s-X</sub> and **2**<sub>t-X</sub> are somewhat bent. The linearity of C<sub>1</sub>=C<sub>2</sub>=N moiety in **2**<sub>t-X</sub> is more than that in **2**<sub>s-X</sub>. The G2 calculated order of singlet–triplet energy gaps ( $\Delta E_{s-t,X}$ ) between **2**<sub>s-X</sub> and **2**<sub>t-X</sub> is  $\Delta E_{s-t,F}$  (28.68 kcal/mol) >  $\Delta E_{s-t,Br}$  (17.70 kcal/mol) >  $\Delta E_{s-t,Cl}$  (14.40 kcal/mol) >  $\Delta E_{s-t,H}$  (1.81 kcal/mol) (Tables 1–4). Apparently, halogens stabilize singlet states **2**<sub>s-X</sub>.

Acyclic X-cyanocarbenes (**3**) are also more affected by halogen substitutions than cyclic carbenes **1**, due to the direct attachment of the halogens to their divalent centers (Fig. 1). Triplet **3**<sub>t-H</sub> appears more stable than its corresponding singlet **3**<sub>s-H</sub>. This is in agreement with that of its C<sub>3</sub>H<sub>2</sub> ana-

logues [1m]. In contrast, singlet states **3**<sub>s-X</sub> (X = F, Cl, and Br) are more stable than their corresponding triplets **3**<sub>t-X</sub>, due to the stabilization of the singlet states by electronegative halogens. Among all the halogenated C<sub>2</sub>NX azacarbenes, the lowest energy minima appear to be singlet **3**<sub>s-X</sub>, whereas for C<sub>2</sub>NH analogues the lowest energy minimum is triplet **3**<sub>t-H</sub>. These results are in clear contrast to the C<sub>3</sub>HX, C<sub>2</sub>SiHX, and C<sub>2</sub>GeHX, where singlet cyclic aromatic **1**<sub>s-H</sub> was more stable than its corresponding triplet **3**<sub>t-H</sub> [1m,6,7]. Resonance-stabilizing effects of the cyano group (CN) along with inductive and/or resonance effects of halogens in both singlet and triplet states of structure **3** can justify this trend of stability (Fig. 1). In C<sub>2</sub>NH isomers (where X is H), the aromaticity in the cyclic **1**<sub>s-H</sub> causes stability yet less than conjugation of C<sub>1</sub> with the CN group encountered in the cyanocarbene **3** (Table 7 and Fig. 1). Singlet–triplet energy gaps between **3**<sub>s-X</sub> and **3**<sub>t-X</sub> ( $\Delta E_{s-t,X}$ ) calculated at the G2 level is  $\Delta E_{s-t,F}$  (15.13 kcal/mol) >  $\Delta E_{s-t,H}$  (–7.61 kcal/mol) >  $\Delta E_{s-t,Cl}$  (5.60 kcal/mol) >  $\Delta E_{s-t,Br}$  (5.13 kcal/mol) (Tables 1–4). Since the difference between  $\Delta E_{s-t,Cl}$  and  $\Delta E_{s-t,Br}$  is small, one can conclude that resonance effects of halogens may also act as an stabilizing effect for divalent centers. MP2 and B3LYP calculations suggest

**TABLE 7** The NICS (Total) Values (ppm) at the Ring Centers, NICS(0), and 0.5, 1, 1.5, 2, 2.5, and 3 Å Above the Plane of the Rings (NICS(0.5), NICS(1), NICS(1.5), NICS(2), NICS(2.5), and NICS(3), Respectively), for Singlet (**s**) States of C<sub>2</sub>NX (**1<sub>s-X</sub>**, X = H, F, Cl, and Br) Azacarbenes As Well As the Cyclopropenyl Cation, Cyclopropenyl Anion, Cyclopropenyl Radical and Cyclopropenylidene (Singlet), Calculated at GIAO–B3LYP/6-311++G\*\*// B3LYP/6-311++G\*\* Level

Structure	NICS(0)	NICS(0.5)	NICS(1)	NICS(1.5)	NICS(2)	NICS(2.5)	NICS(3)
<b>1<sub>s-H</sub></b>	−10.4	−27.4	−18.0	−8.4	−4.2	−2.4	−1.5
<b>1<sub>s-F</sub></b>	−17.6	−27.8	−15.4	−6.5	−3.1	−1.7	−1.1
<b>1<sub>s-Cl</sub></b>	−13.4	−26.9	−16.2	−7.2	−3.5	−2.0	−1.3
<b>1<sub>s-Br</sub></b>	−11.8	−26.2	−16.0	−7.2	−3.5	−2.0	−1.3
Cyclopropenyl cation	−22.8	−28.5	−14.7	−6.1	−2.9	−1.6	−1.0
Cyclopropenyl anion	4.2	15.0	16.6	9.8	4.9	2.3	0.9
Cyclopropenyl radical	−9.5	−0.5	5.2	3.2	1.5	0.6	0.2
Cyclopropenylidene (singlet)	−16.7	−27.5	−17.1	−7.8	−3.8	−2.1	−1.3

that C<sub>1</sub>–C<sub>2</sub> bond lengths of both **3<sub>s-X</sub>** and **3<sub>t-X</sub>** are longer than those in **3<sub>s-H</sub>** and **3<sub>t-H</sub>**, similarly the C≡N bond orders in **3<sub>s-X</sub>** and **3<sub>t-X</sub>** are higher than those in **3<sub>s-H</sub>** and **3<sub>t-H</sub>**. The change in C<sub>1</sub>–C<sub>2</sub> bond lengths in **3<sub>s-X</sub>** as a function of X follows the electronegativity: F (1.45 Å) > Cl (1.41 Å) > Br (1.40 Å) > H (1.37 Å), indicating that in the presence of halogens, the involvement of the cyano group for the stabilization of divalent center decreases. On the other hand, ∠C<sub>2</sub>C<sub>1</sub>X of all singlet states **3<sub>s-X</sub>** are smaller than their corresponding triplet states **3<sub>t-X</sub>**. The linearity of N≡C<sub>2</sub>–C<sub>1</sub> moiety in triplet states **3<sub>t-X</sub>** is higher than their corresponding singlet states **3<sub>s-X</sub>**. One significant parameter affecting the Δ*E*<sub>s-t</sub> and determining the electronic ground state of carbenes is the magnitude of the divalent bond angle. Therefore, bending potential energy curves or relative energies as a function of divalent bond angles ∠XC<sub>1</sub>C<sub>2</sub> are calculated at B3LYP/6-311++G\*\* for **3<sub>s-X</sub>** and **3<sub>t-X</sub>** (Fig. 3). Stabilizing the singlet states, the halogens employed increase the angle of singlet and triplet states crossing, in accordance with their electronegativity: F (125°) > Cl (120°) > Br (118°) > H (114°).

### Relative Energies

The G2 calculated order of relative stability for the C<sub>2</sub>NH carbenes is **3<sub>t-H</sub>** (0.00 kcal/mol) > **1<sub>s-H</sub>** (5.06 kcal/mol) > **3<sub>s-H</sub>** (7.61 kcal/mol) > **2<sub>s-H</sub>** (32.16 kcal/mol) > **2<sub>t-H</sub>** (33.97 kcal/mol) > **1<sub>t-H</sub>** (52.09 kcal/mol) (Table 1). Hence, the global minimum for azacarbene C<sub>2</sub>NH emerges as triplet cyanocarbene **3<sub>t-H</sub>**. This is in contrast to the C<sub>3</sub>H<sub>2</sub> carbenes, where the cyclic structure **1<sub>s-H</sub>** is the global minimum [1m]. Again, **1<sub>s-H</sub>** has a great stabilization of σ<sup>2</sup> center that enables it to show an aromatic character. We employed NICS which is a computational method that provides an indirect theoretical probe of ring currents to serve as an aromaticity criterion [23]. NICS(1) (i.e., at points 1 Å

above the ring center) is suggested to be a better measure of the π electron delocalization, compared with NICS(0) (i.e., at the ring center) [37]. Our calculated NICS values indicate that all singlet cyclic carbenes (**1<sub>s-X</sub>**) show high aromatic character, for having large ring negative NICS values (Table 7). Such an aromaticity is anticipated for these cyclic, planar, continuously conjugated 2π-containing species. Even, the aromatic characters of **1<sub>s-H</sub>** (NICS(1) = −17.99 ppm) are higher than those of the singlet cyclopropenylidene (NICS(1) = −17.07 ppm), cyclopropenyl cation (NICS(1) = −14.69 ppm), and benzene ring (NICS(1) = −10.6 ppm) (Table 7) [23,38]. Halogens appear to somewhat decrease the aromaticity of singlet carbenes, possibly due to the cross-conjugation.

The cyano group (CN) shows stabilizing effects on its adjacent carbenic center, for both singlet and triplet states. **2<sub>s-H</sub>** is less stable than **3<sub>s-H</sub>**, due to the lack of such CN group stabilization. Because of the angle strain associated with the nonaromatic three-membered rings, **1<sub>t-H</sub>** is the lowest stable triplet isomer among the C<sub>2</sub>NH series.

The G2 calculated order of relative stability for C<sub>2</sub>NF isomers is **3<sub>s-F</sub>** (0.00 kcal/mol) > **1<sub>s-F</sub>** (9.53 kcal/mol) > **3<sub>t-F</sub>** (15.13 kcal/mol) > **1<sub>t-F</sub>** (69.90 kcal/mol) > **2<sub>s-F</sub>** (75.02 kcal/mol) > **2<sub>t-F</sub>** (103.70 kcal/mol) (Table 2). Clearly, the stability order of C<sub>2</sub>NF appears different from the above stability trend for C<sub>2</sub>NH. Moreover, the range of relative energies for the former is considerably larger than the latter. Again the global minimum for the set of C<sub>2</sub>NF azacarbenes appears to be singlet cyanocarbene, **3<sub>s-F</sub>**. This structure is highly stabilized by fluorine attached to the divalent center, along with the resonance stabilization by the CN group (Fig. 1). Such a phenomenon possibly has more stabilizing effect than the aromaticity predicted in **1<sub>s-F</sub>** (Table 7). This result is consistent with the results of analogues C<sub>2</sub>SiHF silylenes and/or C<sub>2</sub>GeHF germylenes and is different from those of the C<sub>3</sub>H<sub>2</sub> carbenes [1m,6,7].



Nevertheless, aromaticity justifies the higher stability of **1**<sub>s-F</sub> over **3**<sub>t-F</sub>. Higher electronegativity of fluorine causes stabilization of all singlet-state azacarbenes over their corresponding triplet state. In contrast to the transition state **1**<sub>t-H</sub>, the minimum **1**<sub>t-F</sub> is remarkably more stable than the acyclic **2**<sub>s-F</sub> and/or **2**<sub>t-F</sub>. One may conclude from this finding that fluorine destabilizes the canonical form which nonbonding lone-pair of nitrogen delocalizes to the carbenic center, making a nitrogen atom possesses the positive charge. This conclusion can also be reached by the consideration of the respective atomic charges and bond orders (Table 6). The N–C bond order of **2**<sub>s-X</sub> is the highest when X=H and decreases for halogens. The negative charges on N atom change little as a function of halogens (Table 6).

The G2 calculated order of relative stability for C<sub>2</sub>NCl isomers is **3**<sub>s-Cl</sub> (0.00 kcal/mol) > **3**<sub>t-Cl</sub> (5.60 kcal/mol) > **1**<sub>s-Cl</sub> (7.55 kcal/mol) > **1**<sub>t-Cl</sub> (28.63 kcal/mol) > **2**<sub>s-Cl</sub> (56.55 kcal/mol) > **2**<sub>t-Cl</sub> (70.95 kcal/mol) (Table 3). Also, the G2 calculated order of relative stability for C<sub>2</sub>NBr structures is **3**<sub>s-Br</sub> (0.00 kcal/mol) > **3**<sub>t-Br</sub> (5.13 kcal/mol) > **1**<sub>s-Br</sub> (8.22 kcal/mol) > **2**<sub>s-Br</sub> (50.90 kcal/mol) > **1**<sub>t-Br</sub> (60.26 kcal/mol) > **2**<sub>t-Br</sub> (68.60 kcal/mol) (Table 4). Comparison between the above stability trends for singlet (**s**) and triplet (**t**) states of **1**<sub>X</sub>, **2**<sub>X</sub>, and **3**<sub>X</sub> shows some similarity on the one hand, and differences on the other hand (Tables 2–4). For instance, every singlet state structure is more stable than its corresponding triplet state structure. Also, regardless of the employed X, the most stable species are singlet states of a similar structure: **3**<sub>s-F</sub>, **3**<sub>t-Cl</sub>, and **3**<sub>s-Br</sub>, while the least stable species are singlet states of another analogous structure: **2**<sub>t-F</sub>, **2**<sub>t-Cl</sub>, and **2**<sub>s-Br</sub>. However, the second most stable structures for X=Cl or Br is **3**<sub>t-Cl</sub> and **3**<sub>t-Br</sub>, respectively, which are different from

X=F, where the second highest stable structure is **1**<sub>s-F</sub>. This can be attributed to the higher electronegativity of F (than Cl or Br), where a wider energy gaps ( $\Delta E_{s-t}$ ) between **3**<sub>s-F</sub> and **3**<sub>t-F</sub> is anticipated [39].

Generally in discussing the halogen effects, our results are in well agreement with the theoretical report of Dixon et al. [40]. In fact, all halogens stabilize the singlet states over the triplet states for the studied carbenes. However, it is remarkable that the halogens show different electron-withdrawing and/or resonance effects depending on where they are bonded. Also, resonance effects of halogens differ depending on the halogens per se and the structural characters.

### Philicity

A principal feature of the carbene–alkene addition reaction is the carbene’s “philicity,” that is the electronic character of its selectivity or response to the alkene’s substituents [41,42]. Singlet carbenes are characterized as electrophilic, ambiphilic, or nucleophilic on the basis of their selectivities toward electron-rich and electron-poor alkenes. These characters can be predicted by calculation of the differential orbital energies, HOMO and LUMO of carbenes and alkenes, given by Eqs. (1) and (2).

$$\Delta\varepsilon_E = \varepsilon_{\text{carbene}}^{\text{LUMO}} - \varepsilon_{\text{alkene}}^{\text{HOMO}} = p - \pi \quad (1)$$

$$\Delta\varepsilon_N = \varepsilon_{\text{alkene}}^{\text{LUMO}} - \varepsilon_{\text{carbene}}^{\text{HOMO}} = \pi^* - \sigma \quad (2)$$

$\Delta\varepsilon_E$  and  $\Delta\varepsilon_N$  are the differential orbital energies corresponding to the electrophilic and nucleophilic interactions, respectively (Fig. 4). Alkenes Me<sub>2</sub>C=CMe<sub>2</sub>, Me<sub>2</sub>C=CHMe, and Me<sub>2</sub>C=CH<sub>2</sub> are considered as electron-rich alkenes. Alkenes H<sub>2</sub>C=COOMe and H<sub>2</sub>C=CN are considered as

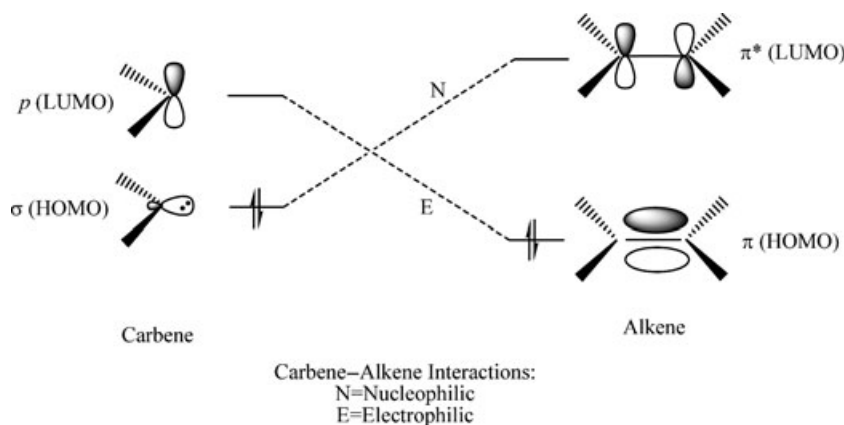


FIGURE 4 Schematic illustrations of frontier molecular orbital interactions, showing the definitions of “ $\pi$  molecular electronegativity” and the electrophilic and nucleophilic interaction terms.

TABLE 8 Differential Orbital Energies (kcal/mol) for Azacarbene ( $1_{s-X}$ )–Alkene Additions<sup>a</sup>

Alkene	$1_{s-H}^b$		$1_{s-F}^b$		$1_{s-Cl}^b$		$1_{s-Br}^b$	
	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	83.6	166.9	75.5	177.6	80.3	170.5	81.0	168.7
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>3</sub>	90.0	168.4	82.0	179.1	86.7	172.1	87.4	170.2
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	98.4	168.9	90.3	179.7	95.1	172.6	95.8	170.7
<i>trans</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub>	97.6	172.0	89.6	182.7	94.3	175.6	95.0	173.8
CH <sub>2</sub> =CHCOOCH <sub>3</sub>	126.7	134.3	118.6	145.0	123.4	137.9	124.1	136.1
CH <sub>2</sub> =CHCN	134.5	127.8	126.5	138.5	131.2	131.4	131.9	129.6

<sup>a</sup>See Eqs. (1) and (2). Orbital energies calculated at B3LYP/6-311++G\*\* level.<sup>b</sup>The subscript E in  $\varepsilon_E$  = electrophilic. The subscript N in  $\varepsilon_N$  = nucleophilic.TABLE 9 Differential Orbital Energies (kcal/mol) for Azacarbene ( $2_{s-X}$ )–Alkene Additions<sup>a</sup>

Alkene	$2_{s-H}^b$		$2_{s-F}^b$		$2_{s-Cl}^b$		$2_{s-Br}^b$	
	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	19.2	164.9	3.9	201.9	9.7	183.8	11.3	178.6
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>3</sub>	25.7	166.4	10.3	203.4	16.1	185.3	17.7	180.1
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	34.0	166.9	18.6	203.9	24.5	185.8	26.1	180.6
<i>trans</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub>	33.3	169.9	17.9	207.0	23.7	188.9	25.4	183.7
CH <sub>2</sub> =CHCOOCH <sub>3</sub>	62.3	132.2	46.9	169.3	52.8	151.2	54.4	146.0
CH <sub>2</sub> =CHCN	70.2	125.7	54.8	162.8	60.6	144.7	62.2	139.5

<sup>a</sup>See Eqs. (1) and (2). Orbital energies calculated at B3LYP/6-311++G\*\* level.<sup>b</sup>The Subscript E in  $\varepsilon_E$  = electrophilic. The subscript N in  $\varepsilon_N$  = nucleophilic.TABLE 10 Differential Orbital Energies (kcal/mol) for Azacarbene ( $3_{s-X}$ )–Alkene Additions<sup>a</sup>

Alkene	$3_{s-H}^b$		$3_{s-F}^b$		$3_{s-Cl}^b$		$3_{s-Br}^b$	
	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$	$\Delta\varepsilon_E$	$\Delta\varepsilon_N$
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> ) <sub>2</sub>	17.6	170.9	27.5	184.1	23.8	171.5	23.5	168.7
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>3</sub>	24.1	172.4	33.9	185.6	30.2	173.0	29.9	170.2
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	32.4	173.0	42.3	186.1	38.6	173.5	38.3	170.8
<i>trans</i> -CH <sub>3</sub> CH=CHCH <sub>3</sub>	31.7	176.0	41.5	189.2	37.9	176.5	37.5	173.8
CH <sub>2</sub> =CHCOOCH <sub>3</sub>	60.7	138.3	70.6	151.5	66.9	138.8	66.6	136.1
CH <sub>2</sub> =CHCN	68.6	131.8	78.4	145.0	74.7	132.3	74.4	129.6

<sup>a</sup>See Eqs. (1) and (2). Orbital energies calculated at B3LYP/6-311++G\*\* level.<sup>b</sup>The subscript E in  $\varepsilon_E$  = electrophilic. The subscript N in  $\varepsilon_N$  = nucleophilic.

electron-poor alkenes. *trans*-2-Butene is designated as a standard alkene [43]. According to frontier molecular orbital (MO) theory [43], the stabilization energy of a cycloaddition transition state depends inversely on the differential energies of the interacting “frontier” MOs. Where neglecting overlaps, the smaller  $\Delta\varepsilon$  implies the greater stabilization, the lower activation energy, and the higher rate constant. If the  $\Delta\varepsilon_E$  values of a carbene for the given set of alkenes are smaller than the  $\Delta\varepsilon_N$  values, this carbene exhibits electrophilic character in the addition reaction to alkenes. If the  $\Delta\varepsilon_N$  values of a carbene for the given set of alkenes are smaller than the  $\Delta\varepsilon_E$  values, this carbene exhibits nucleophilic character in the addition reaction to alkenes. If the  $\Delta\varepsilon_E$  values

of a carbene for the electron-rich alkenes is smaller than the  $\Delta\varepsilon_N$  values, and for the electron-poor alkenes is higher than  $\Delta\varepsilon_N$ , this carbene exhibits the ambiphilic character in the addition reaction to alkenes.

For the singlet structures of C<sub>2</sub>NX and alkenes, the energies of HOMO and LUMO orbitals are obtained using NBO population analysis at B3LYP/6-311++G\*\* level, and then the  $\Delta\varepsilon_E$  and  $\Delta\varepsilon_N$  values are calculated for the singlet C<sub>2</sub>NX azacarbenes (Tables 8–10). Our calculation indicates that all singlet azacarbenes have electrophilic character in the alkene addition reactions. The  $2_{s-X}$  species exhibit interestingly more electrophilic character than other species in the addition reaction to alkenes, and in

the **1–3** species electrophilic character appears the highest for X = F.

## CONCLUSION

Singlet–triplet energy separations ( $\Delta E_{s-t,X}$ ), relative stabilities, and structures of several new carbenic reactive intermediates C<sub>2</sub>NX are compared and contrasted at 10 ab initio and DFT levels, for X = H, F, Cl, and Br. Three possible structures are anticipated for each singlet (**s**) and/or triplet (**t**) C<sub>2</sub>NX azacarbenes: 3-X-2-azacyclopropenyldiene (**1**), [(X-imino)methylene]carbene (**2**), and X-cyanocarbene (**3**). The magnitude of  $\Delta E_{s-t,X}$  is the highest for fluorinated C<sub>2</sub>NF carbenes. All the optimized structures are planar with the C<sub>s</sub> point groups. For the six species with X = H, the stability order is **3<sub>t-H</sub>** > **1<sub>s-H</sub>** > **3<sub>s-H</sub>** > **2<sub>s-H</sub>** > **2<sub>t-H</sub>** > **1<sub>t-H</sub>**. The stability order for isomers with X = F is **3<sub>s-F</sub>** > **1<sub>s-F</sub>** > **3<sub>t-F</sub>** > **1<sub>t-F</sub>** > **2<sub>s-F</sub>** > **2<sub>t-F</sub>**. Likewise, the order of stability for six C<sub>2</sub>NCl carbenes is **3<sub>s-Cl</sub>** > **3<sub>t-Cl</sub>** > **1<sub>s-Cl</sub>** > **1<sub>t-Cl</sub>** > **2<sub>s-Cl</sub>** > **2<sub>t-Cl</sub>**. Finally, the order of stability for six isomers of C<sub>2</sub>NBr is **3<sub>s-Br</sub>** > **1<sub>s-Br</sub>** > **2<sub>s-Br</sub>** > **3<sub>t-Br</sub>** > **1<sub>t-Br</sub>** > **2<sub>t-Br</sub>**. The aromaticities of the singlet cyclic structures (**1<sub>s-X</sub>**) are measured by the GIAO–NICS method. Linear correlations are found between the LUMO–HOMO energy gaps of the singlet carbenes and their corresponding  $\Delta E_{s-t,X}$ , calculated at B3LYP/6-311++G\*\*. Besides the electronegativity, resonance effects of halogens are also important in the stabilization of singlet-state carbenes. Electrophilic characters are found for all singlet azacarbenes in their addition reactions to alkenes with the highest electrophilicity being exhibited for X = F. Even though, G2 appears as the method of choice, a conspicuous consistency is observed between the relative energies calculated at the various levels employed.

## SUPPLEMENTARY INFORMATION

Data on bond lengths and bond angles for singlet (**s**) and triplet (**t**) of 3-X-2-aza-1-cyclopropenyldiene (**1<sub>s-X</sub>** and **1<sub>t-X</sub>**), [(X-imino)methylene]carbene (**2<sub>s-X</sub>** and **2<sub>t-X</sub>**), and cyanocarbene (**3<sub>s-X</sub>** and **3<sub>t-X</sub>**) at two levels of theory (B3LYP/6-311++G\*\* and MP2/6-311++G\*\*) are available from the corresponding author on request.

## REFERENCES

- [1] (a) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys J* 1985, 299, L63; (b) Reisenauer, H. P.; Maier, G.; Reimann, A.; Hoffmann, R. W. *Angew Chem, Int Ed* 1984, 96, 596; (c) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vrtilek, J. M. *Astrophys J* 1991, 368, L39; (d) Maier, G.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Spirko, V.; Hess, B. A.; Schaad, L. J. *J Chem Phys* 1989, 91, 4763; (e) Vrtilek, J. M.; Gottlieb, C. A.; Gottlieb, E. W.; Killian, T. C.; Thaddeus, P. *Astrophys J* 1990, 364, L53; (f) Jonas, V.; Bohme, M.; Frenking, G. *J Phys Chem* 1992, 96, 1640; (g) Heher, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J Am Chem Soc* 1976, 98, 4378; (h) DeFrees, D. J.; McLean, A. D. *Astrophys J* 1986, 308, L31; (i) Cooper, D. L.; Murphy, S. C. *Astrophys J* 1988, 333, 482; (j) Fan, Q.; Pfeiffer, G. V. *Chem Phys Lett* 1989, 162, 472; (k) Redondo, J. R.; Redondo, P.; Largo, A. *J Mol Struct (Theochem)* 2003, 621, 59; (l) Redondo, P.; Redondo, J. R.; Largo, A. *J Mol Struct (Theochem)* 2000, 505, 221; (m) Kassae, M. Z.; Haerizade, B. N.; Arshadi, S. *J Mol Struct (Theochem)* 2003, 639, 187; (n) Bogey, M.; Demuyneck, C.; Destombes, J. L. *Chem Phys Lett* 1986, 125, 569; (o) Bogey, M.; Destombes, J. L. *Astron Astrophys* 1986, 159, L8; (p) Bogey, M.; Demuyneck, C.; Destombes, J. L.; Dubus, H. *J Mol Spectrosc* 1987, 122, 1987; (q) Gottlieb, C. A.; Killian, T. C.; Thaddeus, P.; Botschwina, P.; Flügge, J.; Oswald, M. *J Chem Phys* 1992, 98, 4478; (r) Mollaaghababa, R.; Gottlieb, C. A.; Vrtilek, J. M.; Thaddeus, P. *J Chem Phys* 1993, 99, 890; (s) Hirahara, Y.; Masuda, A.; Kawaguchi, K. *J Chem Phys* 1991, 95, 3975; (t) Clauberg, H.; Minsek, D. W.; Chen, P. *J Am Chem Soc* 1992, 114, 99; (u) Huang, J. W.; Graham, W. R. *J Chem Phys* 1990, 93, 1583; (v) Seburg, R. A.; DePinto, J. T.; Patterson, E. V.; McMahon, R. J. *J Am Chem Soc* 1995, 117, 835; (w) Ionescu, E.; Reid, S. A. *J Mol Struct (Theochem)* 2005, 725, 45.
- [2] (a) Bernheim, R. A.; Kempf, R. J.; Humer, P. W.; Skell, P. S. *J Chem Phys* 1964, 41, 1156; (b) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J Chem Phys* 1965, 43, 196; (c) Bernheim, R. A.; Kempf, R. J.; Reichenberger, E. F. *J Magn Reson* 1970, 3, 5; (d) Wasserman, E.; Yager, W. A.; Kuck, J. *Chem Phys Lett* 1970, 7, 409; (f) Merer, A. J.; Travis, D. N. *Can J Phys* 1965, 43, 1795; (g) Merer, A. J.; Travis, D. N. *Can J Phys* 1966, 44, 353; (h) Dendramis, A.; Leroi, G. E. *J Chem Phys* 1977, 66, 4334; (i) Saito, S.; Endo, Y.; Hirota, E. *J Chem Phys* 1984, 80, 1427; (j) Brown, F. X.; Saito, S.; Yamamoto, S. *J Mol Spectrosc* 1990, 143, 203; (k) Endo, Y.; Ohshima, Y. *J Chem Phys* 1993, 98, 6618; (l) Miller, C. E.; Eckhoff, W. C.; Curl, R. F. *J Mol Struct* 1995, 352, 435; (m) McCarthy, M. C.; Gottlieb, C. A.; Cooksy, A. L.; Thaddeus, P. *J Chem Phys* 1995, 103, 7779; (n) Sun, F.; Kosterev, A.; Scott, G.; Litosh, V.; Curl, R. F. *J Chem Phys* 1998, 109, 8851; (o) Han, J.; Hung, P. Y.; Desain, J.; Jones, W. E.; Curl, R. F. *J Mol Spectrosc* 1999, 198, 421; (p) Hung, P. Y.; Sun, F.; Hunt, N. T.; Burns, L. A.; Curl, R. F. *J Chem Phys* 2001, 115, 9331; (q) Allen, M. D.; Evenson, K. M.; Brown, J. M. *J Mol Spectrosc* 2001, 209, 143; (r) Nimlos, M. R.; Davico, G.; Geise, C. M.; Wenthold, P. G.; Lineberger, W. C.; Blanksby, S. J.; Hadad, C. M.; Petersson, G. A.; Ellison, G. B. *J Chem Phys* 2002, 117, 4323; (s) Poutsma, J. C.; Upshaw, S. D.; Squires, R. R.; Wenthold, P. G. *J Phys Chem A* 2002, 106, 1067; (t) Harrison, J. F.; Dendramis, A.; Leroi, G. E. *J Am Chem Soc* 1978, 100, 4352; (u) Zandler, M. E.; Goddard, J. D.;

- Schaefer, H. F., III. *J Am Chem Soc* 1977, 101, 1072; (v) Kim, K. S.; Schaefer, H. F., III; Radom, L.; Pople, J. A.; Binkley, J. S. *J Am Chem Soc* 1983, 105, 4148; (w) Rice, J. E.; Schaefer, H. F., III. *J Chem Phys* 1987, 86, 7051; (x) Malmquist, M. A.; Lindh, R.; Roos, B. O.; Roos, S. *Theor Chim Acta* 1988, 73, 155; (y) Seidl, E. T.; Schaefer, H. F., III. *J Chem Phys* 1992, 96, 4449; (z) Aoki, K.; Ikuta, S.; Nomura, O. *J Chem Phys* 1993, 99, 3809.
- [3] (a) Kellogg, C. B.; Galbraith, J. M.; Fowler, J. E.; Schaefer, H. F., III. *J Chem Phys* 1994, 101, 430; (b) Goldberg, N.; Fiedler, A.; Schwartz, H. *J Phys Chem* 1995, 99, 15327; (c) Koput, J. *J Phys Chem A* 2002, 106, 6183.
- [4] (a) Maier, G.; Reisenauer, H. P.; Rademacher, K. *Chem Eur J* 1998, 4, 1957; (b) Maier, G.; Bothur, A.; Eckwert, J.; Reisenauer, H. P. *Chem Eur J* 1998, 4, 1964.
- [5] Kassae, M. Z.; Musavi, S. M.; Buazar, F. *J Mol Struct (Theochem)* 2005, 728, 15.
- [6] Kassae, M. Z.; Musavi, S. M.; Buazar, F.; Ghambarian, M. *J Mol Struct (Theochem)* 2005, 722, 151.
- [7] Kassae, M. Z.; Musavi, S. M.; Ghambarian, M.; Khalili-Zanjani, M. R. *J Organomet Chem* 2006, 691, 2933.
- [8] Saebo, S.; Almlof, J. *Chem Phys Lett* 1989, 154, 83.
- [9] Pople, J. A.; Binkley, J. S.; Seeger, R. *Int J Quant Chem Symp* 1976, 10, 1.
- [10] Scuseria, G. E.; Schaefer, H. F. III. *J Chem Phys* 1989, 90, 3700.
- [11] Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J Chem Phys* 1987, 87, 5968.
- [12] Becke, A. D. *J Chem Phys* 1996, 104, 1040.
- [13] Adamo, C.; Barone, V. *Chem Phys Lett* 1997, 274, 242.
- [14] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J Chem Phys* 1980, 72, 650.
- [15] Woon, D. E.; Dunning, T. H., Jr. *J Chem Phys* 1993, 98, 1358.
- [16] Pople, J. A.; Krishnan, R. *Int J Quant Chem* 1978, 14, 91.
- [17] Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J Chem Phys* 1989, 90, 5622.
- [18] Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J Chem Phys* 1990, 93, 2537.
- [19] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J Chem Phys* 1991, 94, 7221.
- [20] Hout, R. F.; Levi, B. A.; Heher, W. J. *J Comput Chem* 1985, 82, 234.
- [21] Defrees, D. J.; McLean, A. D. *J Chem Phys* 1985, 82, 333.
- [22] Carpenter, J. E.; Weinhold, F. *J Mol Struct (Theochem)* 1988, 41, 169.
- [23] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J Am Chem Soc* 1996, 118, 6317.
- [24] Chesnut, D. B.; Moore, K. D. *J Comput Chem* 1985, 10, 648.
- [25] Wolinski, K.; Hinton, J. F.; Pulay, P. *J Am Chem Soc* 1990, 112, 8251.
- [26] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G., Jr.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomnelly, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98, Revision A.7*; Gaussian Inc.; Pittsburgh, PA, 1998.
- [27] Feller, D.; Sordo, J. A. *J Chem Phys* 2000, 112, 5604.
- [28] Feller, D.; Sordo, J. A. *J Chem Phys* 2000, 113, 485.
- [29] Sordo, J. A. *J Chem Phys* 2001, 114, 1974.
- [30] Dunning, T. H., Jr. *J Phys Chem A* 2000, 104, 9062.
- [31] Lynch, B. J.; Truhlar, D. G. *J Phys Chem A* 2001, 105, 2936.
- [32] (a) Menéndez, B.; Rayn, V. M.; Sordo, J. A.; Cimas, A.; Barrientos, C.; Largo, A. *J Phys Chem A* 2001, 105, 9917; (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J Chem Phys* 1991, 94, 7221.
- [33] Schlegel, H. B. *J Chem Phys* 1986, 84, 4530.
- [34] Stanton, J. F. *J Chem Phys* 1994, 101, 371.
- [35] Barrientos, C.; Cimas, A.; Largo, A. *J Phys Chem A* 2001, 105, 6724.
- [36] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J Am Chem Soc* 1991, 113, 36.
- [37] Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org Lett* 2001, 3, 2465.
- [38] Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J Phys Chem* 1996, 100, 17801.
- [39] Gaspar, P. P.; Xiao, M.; Pae, D. H.; Berger, D. J.; Haile, T.; Chen, T.; Lei, D.; Winchester, W. R.; Jiang, P. *J Organomet Chem* 2002, 646, 68.
- [40] Dixon, D. A.; Arduengo, A. J. III. *J Phys Chem A* 2006, 110, 1968.
- [41] Moss, R. A. *Acc Chem Res* 1980, 13, 58.
- [42] Moss, R. A. *Acc Chem Res* 1989, 22, 15.
- [43] (a) Hoffmann, R. *J Am Chem Soc* 1968, 90, 1475; (b) Sustmann, R. *Tetrahedron Lett* 1971, 2717, 2721; (c) Houk, K. N. *Acc Chem Res* 1975, 8, 361; (d) Mayor, C.; Wentrup, C. *J Am Chem Soc* 1975, 97, 7467; (e) Jones, W. M.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J Am Chem Soc* 1977, 99, 6379; (f) Schoeller, W. W. *Tetrahedron Lett* 1980, 21, 1505, 1509; (g) Fleming, I.; *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.