

# Substituent Effects on Ring Opening of 2-Furylcarbenes: An ab Initio Study

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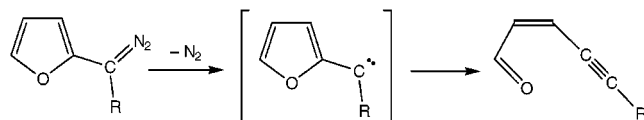
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The ring-opening reactions of a series of substituted 2-furylcarbenes were investigated by G2-(MP2,SVP) theory. The substituents examined include CH<sub>3</sub>, SiH<sub>3</sub>, NH<sub>2</sub>, OH, F, Cl, Br, and CH=CH<sub>2</sub>. The furan ring-opening reaction is predicted to proceed via a six-membered ring transition state, which was described by Herges as a coarctate transition state. The calculated activation barrier depends strongly on the nature of the substituent group, ranging from 8 to 83 kJ mol<sup>-1</sup>. Substituent effects on the carbene reactant and ring-opening transition state were analyzed using isodesmic reactions. Methyl and vinyl substituents stabilize the reactant and transition state to a similar extent. On the other hand, NH<sub>2</sub>, OH, F, Cl, and Br substituents raise the energy barrier due to the greater stabilizing effect on the reactant than the transition state. The predicted aptitude of ring opening in 2-furylcarbenes is in the order SiH<sub>3</sub> > H > CH=CH<sub>2</sub> > CH<sub>3</sub> > Br > Cl > F > NH<sub>2</sub> > OH. This calculated trend is consistent with experimental observations. The amino-, hydroxyl-, and fluoro-substituted 2-furylcarbenes are predicted to be experimentally accessible species in the gas phase. The effects of substitution on furan oxygen of 2-furylcarbene are also reported.

## Introduction

The photochemistry of 2-furyldiazoalkanes and their derivatives has attracted recent interest.<sup>1–3</sup> Early experimental studies by Hoffman and Shechter<sup>1</sup> found that pyrolysis causes 2-furyldiazolalkanes to lose N<sub>2</sub> readily to yield furan ring-opened products. 2-Furylcarbene was proposed to be an intermediate in these reactions.



In the case of alkyl-substituted systems, the ring-opening reaction even dominates over the facile 1,2-H shift reaction. Early attempts to trap the reactive carbenes were not successful. The parent 2-furylcarbene was not observable in low-temperature matrixes.<sup>2a</sup> However, Khasanova and Sheridan have succeeded in detecting 2-furylchlorocarbene in a matrix isolation experiment and they afforded the first IR spectrum of a 2-furylcarbene.<sup>3</sup> Their spectroscopic characterization was supported by density functional calculations. The authors attributed the successful detection of 2-furylchlorocarbene to the stabilization of carbene by chlorine substitution.

To gain further insight into the mechanism of this intriguing furan ring-opening process, in particular the influence of substituents (R) on the carbene center, we have undertaken a systematic theoretical investigation of a series of substituted 2-furylcarbenes, R = H (**1**), CH<sub>3</sub>

(**2**), SiH<sub>3</sub> (**3**), NH<sub>2</sub> (**4**), OH (**5**), F (**6**), Cl (**7**), Br (**8**), and CH=CH<sub>2</sub> (**9**), using G2(MP2,SVP) theory. The effects of substituents on the stabilities of the carbene and transition state were examined using isodesmic reactions. For the parent compound and the chloro-substituted system, the ring opening pathways for both the syn and anti forms of carbenes were calculated and discussed in light of the observed photochemistry.

## Computational Methods

Standard ab initio calculations<sup>4</sup> were carried out using the GAUSSIAN 94 series of programs.<sup>5</sup> The structures and energies of the reactants (substituted 2-furylcarbenes), transition structures, and products were examined by G2(MP2,SVP) theory.<sup>6</sup> This corresponds effectively to the QCISD(T)/6-311+G(3df,2p) level with zero-point vibrational and isogyric corrections. For G2(MP2,SVP) theory, geometry optimization is carried out at the second-order Møller–Plesset perturbation (MP2) level with the split-valence polarized 6-31G\* basis set. Higher-level energy calculation is performed at the QCISD(T)/6-31G\* level, instead of the QCISD/6-311G\*\* level for the standard G2(MP2) theory.<sup>7</sup> Basis-set extension energy contributions are evaluated at the MP2 level using the additivity approximation. Harmonic vibrational frequencies were computed at the HF/6-31G\* level in order to characterize the stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energies (ZPVEs), scaled by

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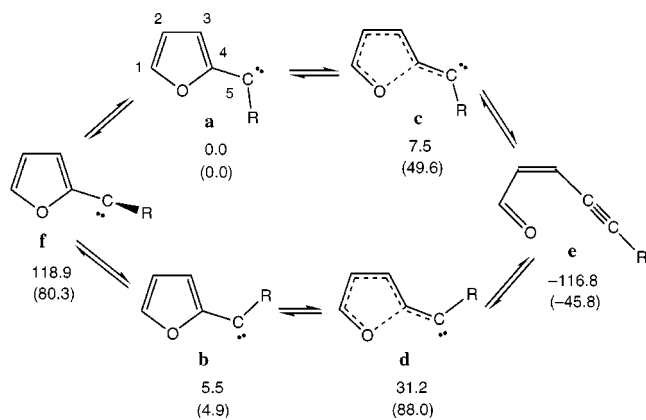
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**Figure 1.** Schematic energy diagram showing the ring opening of syn (**a**) and anti (**b**) conformations of 2-furylcarbene (**1**) and 2-furylchlorocarbene (**7**) [G2(MP2,SVP), kJ mol<sup>-1</sup>]. Calculated relative energies for **7** are in parentheses.

a factor of 0.8929. Unless otherwise noted, all relative energies reported in the text correspond to the G2(MP2,SVP) values and all structural parameters correspond to the MP2/6-31G\* values. CASSCF<sup>8</sup> and MRCI<sup>9</sup> calculations were performed for the singlet and triplet states of the parent 2-furylcarbene using the Molpro 96 programs.<sup>10</sup>

## Results and Discussion

**2-Furylcarbene (1).** We begin our discussion by examining in detail the reaction profile for ring opening of the parent 2-furylcarbene (**1**). The schematic reaction profile and the calculated relative energies are summarized in Figure 1. There are two possible conformations of 2-furylcarbene: syn (**a**) and anti (**b**). The syn conformation corresponds to the cis arrangement of the carbenic lone pair and the C=C double bond of the furan ring, while the anti conformer corresponds to the trans arrangement. The syn conformer (**1a**) is calculated to be the preferred conformation of 2-furylcarbene, while the anti conformer (**1b**) lies 6 kJ mol<sup>-1</sup> higher in energy. The less favorable anti form is readily attributed to the strong lone pair–lone pair repulsion between the furan oxygen and the carbenic carbon.

Ring openings of **1a,b**, via transition structures **1c,d**, respectively, are calculated to be strongly exothermic (117 and 111 kJ mol<sup>-1</sup>, respectively). Both **1a** and **1b** lead to the same ring-opened product: pent-2-en-4-yn-1-al (**1e**). The mechanism of this arrangement was recently described by Herges as a symmetry-allowed, concerted reaction via a coarctate transition state.<sup>11</sup> In particular, he referred to this type of reaction as a “complex reaction” because, during the ring opening of 2-furylcarbene, one  $\pi$  bond and one  $\sigma$  bond are broken and two new  $\pi$  bonds are formed simultaneously at C<sub>4</sub>. The calculated barriers for ring opening of **1a,b** are 8 and 26 kJ mol<sup>-1</sup>, respectively, close to those reported at the DFT level (B3-LYP/6-31G\*).<sup>3</sup> Thus, the syn conformer is predicted to be both kinetically and thermodynamically more favorable toward ring opening than the anti form. With such a small calculated energy barrier, it is unlikely that 2-furylcarbene is experimentally observable. This calculated result

is in excellent accord with the experimental findings of Shechter et al.<sup>1b</sup> and Sander et al.<sup>2a</sup>

There are interesting structural phenomena which warrant discussion. The C–C and C–O and C–H bond lengths in the transition state (**1c**) are of intermediate value between those of the reactant (**1a**) and product (**1e**). For instance, the C<sub>2</sub>–C<sub>3</sub> bond lengths in **1a,c,e** are 1.394, 1.372, and 1.355 Å, respectively (Figure 2). Likewise, the C–H bond length decreases readily from **1a** to **1c** and to **1e**, which readily reflects the change of hybridization from sp<sup>3</sup> to sp<sup>2</sup> and to sp. These structural data suggest that the transition state is stabilized by delocalization of the  $\pi$  electrons. It is of interest to note that the C<sub>1</sub>–C<sub>2</sub> bond is significantly longer than the C<sub>3</sub>–C<sub>4</sub> bond in 2-furylcarbene (**1a**). Accordingly, the C<sub>1</sub>–O bond is longer than C<sub>4</sub>–O bond by 0.094 Å. The weak C<sub>1</sub>–O reflects readily the ease of this system to undergo ring opening.

Khasanova and Sheridan suggested that the *syn*-2-furylcarbene has a stronger anomeric interaction between the carbenic lone pair and the furan C–O  $\sigma^*$  orbital than the anti conformation.<sup>3</sup> This is readily supported by the calculated structural data: the C<sub>1</sub>–O bond is significantly longer (by 0.014 Å) in the syn conformation than in the anti form (Figure 2). Thus, the syn conformation has a relatively weak C–O bond which facilitates ring opening. This stereoelectronic effect may account for the difference in reactivity between the syn and anti conformations of 2-furylcarbenes.

We have also examined the interconversion of the syn (**1a**) and anti (**1b**) conformations of 2-furylcarbene. Rearrangement of **1a** to **1b**, via the rotational transition structure **1f**, is predicted to have a high activation barrier of 119 kJ mol<sup>-1</sup>. In **1f**, the C<sub>5</sub>–H bond is perpendicular to the plane of the furan ring [ $\tau(\text{HC}_5\text{C}_4\text{O}) = 90.0^\circ$ ]. This transition state is described by Herges as Hückel anti-aromatic since the lone pair on the carbenic center is perpendicular to the furan ring and, thus, is expected to have a high barrier.<sup>11</sup>

**Triplet 2-Furylcarbene (1g).** 2-Furylcarbene is calculated to prefer a singlet ground state (**1a**, <sup>1</sup>A') at the G2(MP2,SVP) level. The triplet state (**1g**, <sup>3</sup>A'') lies close in energy, 12 kJ mol<sup>-1</sup>. A previous study on phenylcarbene and methylene have indicated that the stability of singlet carbene is generally overestimated using G2-(MP2,SVP) theory.<sup>12</sup> Multireference configuration interaction (MRCI) calculations employing the 6-311G\*\* basis set, based on active space which includes all the valence  $\pi$  electrons and  $\pi$  orbitals plus the unpaired  $\sigma$ -electron [i.e. CAS(6,6)], lead to a significantly smaller triplet–singlet splitting of just 2 kJ mol<sup>-1</sup>. Thus, we predict that the singlet and triplet states of 2-furylcarbene lie very close in energy. As with the singlet, triplet 2-furylcarbene is predicted to have a planar geometry. The major difference in structures of the two states is the small carbenic angle (108°) found for the singlet state and the large angle (133°) found for the triplet state (Figure 2). For the parent methylene, it has a triplet ground state and a singlet–triplet gap of 38 kJ mol<sup>-1</sup>.<sup>12</sup> The stronger preference of a singlet ground state in 2-furylcarbene may be explained in terms of the orbital interaction between a 2-furyl substituent and a carbene center. In the planar structure of **1a**, the sp<sup>n</sup> orbital of the carbenic carbon (i.e. the lone pair orbital) lies in the nodal plane of the  $\pi$

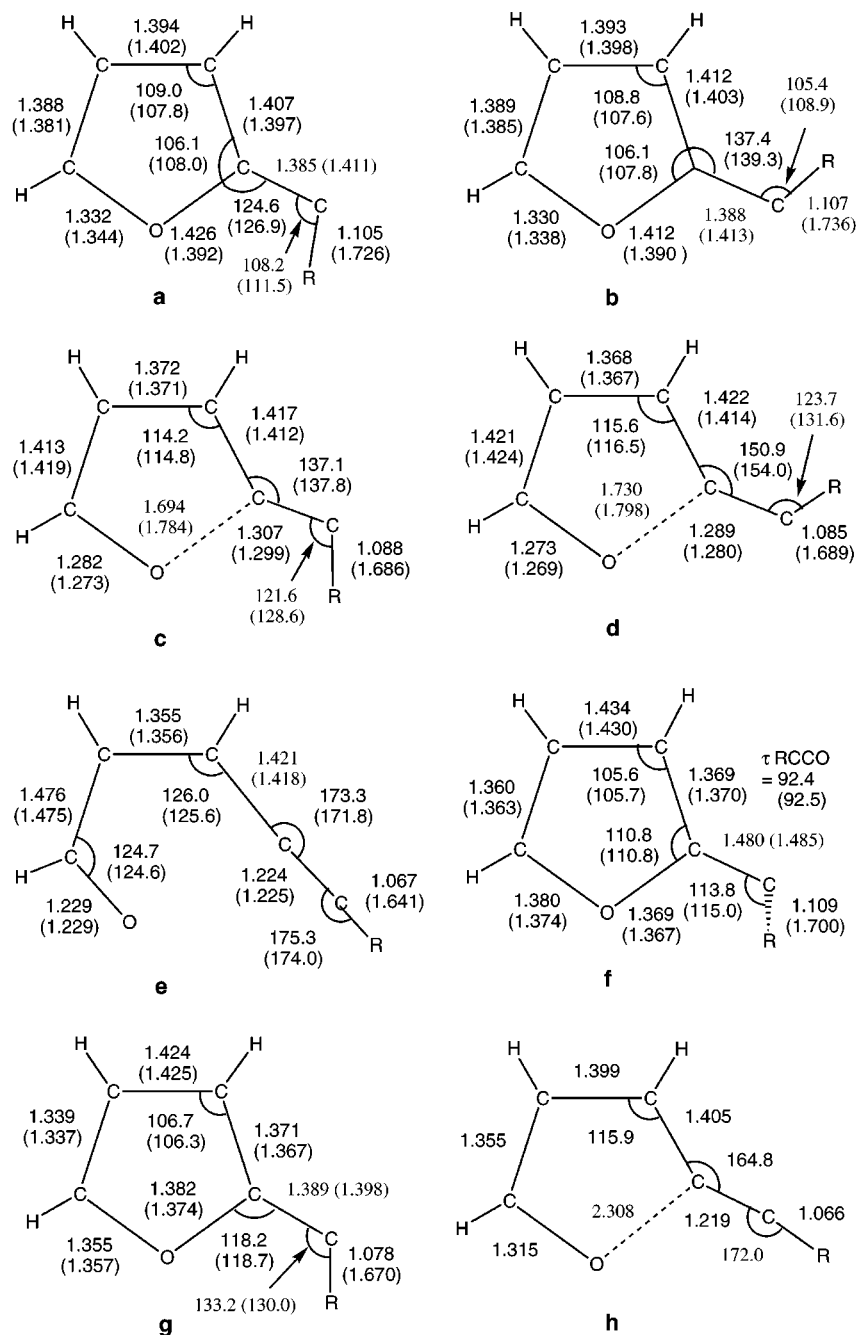
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**Figure 2.** Optimized geometries (MP2/6-31G\*) for the equilibrium and transition structures of 2-furylcarbene (**1**) and 2-furylchlorocarbene (**7**) (bond lengths in Å and angles in deg). Structural parameters for **7** are in parentheses.

orbitals of the 2-furyl substituent. Thus, the  $sp^n$  orbital is unperturbed by the 2-furyl substituent. On the other hand, the 2p (i.e.  $2p_z$ ) orbital of the carbene is raised in energy by the 2-furyl substituent due to the favorable overlap between the carbene vacant 2p orbital and the furan  $\pi$  orbital. This conjugation effect is reflected in the shorter  $C_4-C_5$  bond length (1.385 Å) in **1a** (Figure 2). As a consequence, the separation of the 2p and  $sp^n$  orbitals is increased and the triplet state is destabilized. Ring opening of the triplet state, via transition structure **1h**, is predicted to have a substantially higher barrier (118  $\text{kJ mol}^{-1}$ ) than the singlet state.

**2-Furylchlorocarbene (7).** Next, we examine the reaction profile of 2-furylchlorocarbene (**7**), of which experimental characterization by matrix IR and density functional calculations (B3-LYP/6-31G\*) have been re-

ported by Khasanova and Sheridan.<sup>3</sup> The calculated schematic potential energy profile for ring opening of the chloro-substituted system is summarized in Figure 1. As with the parent compound (**1**), the syn conformation of carbene (**7a**) is the preferred structure of carbene. The calculated enthalpy for ring opening of **7a** ( $-46 \text{ kJ mol}^{-1}$ ) is significantly smaller than the parent analogue. Accordingly, the calculated energy barrier of **7a** is significantly higher (50  $\text{kJ mol}^{-1}$ ). The higher activation barrier is consistent with the observation of 2-furylchlorocarbene in a matrix.<sup>3</sup> Interestingly, the interconversion of the syn (**7a**) and anti (**7b**) conformers, via transition structure **7f**, is calculated to have a smaller barrier of 80  $\text{kJ mol}^{-1}$ . Nevertheless, this barrier height is sufficiently high that the syn and anti conformers will not interconvert at low temperatures. As with the parent compound, the anti

**Table 1. Calculated Total Energies (hartrees) and Relative Energies (kJ mol<sup>-1</sup>) of 2-Furylcarbenes and Related Systems<sup>a</sup>**

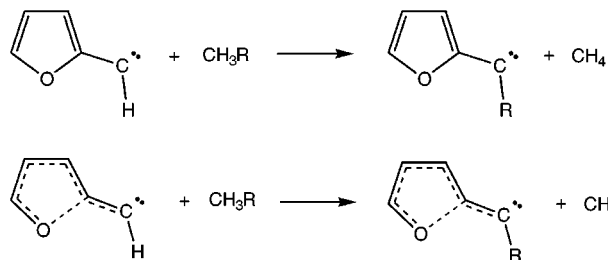
species	tot. energy	barrier <sup>b</sup>	enthalpy <sup>b</sup>	anti/syn <sup>c</sup>
H (1)	-267.554 63	7.5	-116.8	5.5
CH <sub>3</sub> (2)	-306.787 12	12.9	-113.5	7.8
SiH <sub>3</sub> (3)	-557.806 92	-4.6	-141.4	-3.5
NH <sub>2</sub> (4)	-322.881 02	81.2	21.5	16.4
OH (5)	-342.730 22	82.5	9.3	26.1
F (6)	-366.726 41	78.2	1.6	3.9
Cl (7)	-726.719 18	49.6	-45.8	4.9
Br (8)	-2839.553 37	44.0	-48.3	4.9
CH=CH <sub>2</sub> (9)	-344.810 24	16.3	-96.4	7.2
CH <sub>2</sub> analogue (10) <sup>d</sup>	-231.620 89	6.1	-142.1	-1.7
NH analogue (11) <sup>d</sup>	-247.704 91	53.2	-44.5	-10.4
S analogue (12) <sup>d</sup>	-590.173 57	22.3	-66.3	16.4

<sup>a</sup> G2(MP2,SVP) level. <sup>b</sup> Ring opening of the syn conformer. <sup>c</sup> Energy difference between the anti and syn forms. <sup>d</sup> Substitution on furan oxygen of 2-furylcarbene.

conformer is predicted to have a higher barrier than the syn form. This may account for the different photochemistry observed for the two conformers of 2-furylchlorocarbene.<sup>3</sup> As one might have expected, chlorine substitution stabilizes singlet carbene. Thus, the triplet state (7g) is significantly higher in energy (by 51 kJ mol<sup>-1</sup>) than the singlet ground state (7a).

**Substituent Effects on the Carbene Center.** To investigate the effects of substituents on the activation barrier for ring opening of 2-furylcarbene (1), we have considered a series of substituents on the carbenic center, including CH<sub>3</sub> (2), SiH<sub>3</sub> (3), NH<sub>2</sub> (4), OH (5), F (6), Cl (7), Br (8), and CH=CH<sub>2</sub> (9). All substituted 2-furylcarbenes, except for the silyl substituent, favor the syn conformation (Table 1). Thus, from now on we focus only on the ring opening of the syn conformer. As evident in Table 1, the calculated barrier height is strongly dependent on the nature of substituent, ranging for -5 to 83 kJ mol<sup>-1</sup>. Methyl and vinyl substitutions have a small effect on the calculated ring-opening barrier. On the other hand, a significantly higher barrier is predicted for the NH<sub>2</sub>, OH, F, Cl, and Br substitutions. Interestingly, the silyl substitution leads to a negative energy barrier (-5 kJ mol<sup>-1</sup>). This suggests that 2-furylsilylcarbene (3a) may not exist at higher levels of theory.

How does one account for this trend of calculated barriers? The magnitude of the ring-opening barrier in 2-furylcarbenes depends on the relative stabilization effect of a particular substituent (R) on the reactant and transition state. To assess the substituent effects independently, we have employed two isodesmic stabilization reactions,<sup>4</sup> one for the carbene reactant (eq 1) and one for the ring-opening transition state (eq 2). Schlegel et



al. have recently employed the approach of isodesmic reaction to examine the effects of substituents on transition state.<sup>14</sup> The calculated stabilization energies based on eqs 1 and 2 enable us to assess the relative importance

**Table 2. Calculated Stabilization Energies (kJ mol<sup>-1</sup>) of 2-Furylcarbenes<sup>a</sup>**

R	reactant	transition state
H (1)	0	0
CH <sub>3</sub> (2)	37.0	31.5
SiH <sub>3</sub> (3)	26.2	38.3
NH <sub>2</sub> (4)	187.2	113.5
OH (5)	139.3	64.4
F (6)	79.5	8.9
Cl (7)	74.0	31.9
Br (8)	67.4	30.9
CH=CH <sub>2</sub> (9)	58.4	49.5

<sup>a</sup> G2(MP2,SVP) level.

of conjugative, hyperconjugative, and inductive effects by the various substituents. A positive value of stabilization energy (SE) indicates stabilization of a particular substituent group (R) with respect to the parent compound (1). The two sets of isodesmic reactions were computed at the G2(MP2,SVP) level (Table 2). By comparing the stabilization energies of each carbene and its corresponding transition state, one can readily explain the substituent effects on the activation barrier. First, we note that all the substituent groups considered here lead to stabilization in both the reactant and transition state. However, the extent of stabilization can be significantly different. For instance, chlorine substitution (7) stabilizes the carbene by 78 kJ mol<sup>-1</sup> while it stabilizes the transition state by a much smaller amount of 30 kJ mol<sup>-1</sup>. This differential stabilization effect leads to a net increase of the activation barrier in 2-furylchlorocarbene (7a) compared to the parent compound (1a). For the methyl substituent (2), the calculated stabilization energies of the reactant and transition state are roughly the same, which gives a small change in barrier height.

Since singlet 2-furylcarbene possesses a vacant 2p orbital as well as an orthogonal lone pair orbital, the carbene center can be stabilized by inductive, conjugative, and hyperconjugative effects. As evident in Table 2, the calculated stabilization effect is particularly strong for  $\pi$ -donors with an unshared pair of electrons. An electron lone pair stabilizes a carbene center by its interaction with the vacant 2p orbital. The importance of this conjugative effect is reflected in the calculated C-R bond lengths. For example, the C-N bond length in 4a (1.322 Å) is substantially shorter than that of a typical C-N single bond length. The calculated stabilization energies for amino (4a) and hydroxyl (5a) substituents are the highest in the series (186 and 113 kJ mol<sup>-1</sup>, respectively). In accordance with the  $\pi$ -donating ability, the stabilization energy increases in the order F < OH < NH<sub>2</sub>. For the halogen series, F (6), Cl (7), and Br (8), the calculated stabilization energies are similar. However, in this case, inductive stabilization effect of the carbenic lone pair by these electron-withdrawing substituents may also be important.

In the transition state for ring opening (c), the "vacant" 2p orbital of the carbenic center is used to form a new  $\pi$  bond with the carbon atom C<sub>4</sub>. The calculated C<sub>4</sub>-C<sub>5</sub> bond lengths in carbene 7a (1.411 Å) and transition state 7c (1.299 Å) clearly indicate that there is a substantial increase in the double-bond character in the transition state. Thus, the carbene center in the transition state is less effective than the reactant as a  $\pi$ -acceptor. As a

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result, the transition state is less influenced by substituent effects than the carbene reactant, leading to an increase of barrier height for the series of substituted carbenes (**4**–**8**). This is readily confirmed by the calculated stabilization energies (Table 2). The differential stabilization effect between the reactant and transition state is particularly large for the hydroxyl substituent (**4**), which gives a high energy barrier of 83 kJ mol<sup>-1</sup>.

Both methyl (**2**) and silyl (**3**) substitutions stabilize the carbene and transition state by hyperconjugation, which is a weaker effect than by conjugation. For methyl substitution, there is an overall slight increase of energy barrier. In contrast, the silyl substituent (**3**) stabilizes the reactant less than the transition state, which gives an almost barrier-free ring-opening reaction. We have examined the 1,2-H migration process of 2-furylmethylcarbene (**2a**). The computed 1,2-H shift barrier is 53 kJ mol<sup>-1</sup> (G2(MP2,SVP) level), significantly higher than the barrier for furan ring opening (13 kJ mol<sup>-1</sup>). Hence, our calculation confirms the experimental finding that ring opening is more favorable than the 1,2-H shift in alkyl-substituted 2-furylcarbenes.<sup>1</sup>

A vinyl substituent (**9**) stabilizes the carbene by  $\pi$  donation. Since a  $\pi$  orbital is a less effective donor than a lone pair, the calculated stabilization effect for vinyl substitution is smaller than those substituents with a lone pair for both the carbene reactant and transition state (Table 2). Thus, there is only a slight increase in the ring-opening barrier for **9a**, compared to the parent compound.

It is worth noting that an electron-rich substituent strongly destabilizes the alkyne product. Thus, for NH<sub>2</sub>-, OH-, and F-substituted carbenes, the ring-opening reactions are calculated to be slightly endothermic (Table 1), in sharp contrast to the parent compound.

Since the fluoro (**6**), hydroxy (**5**), and amino (**4**) substitutions lead to a higher barrier than that of 2-furylchlorocarbene (**7**) which has been observed experimentally,<sup>3</sup> carbenes **4a**, **5a**, and **6a** are predicted to be experimentally observable. For carbenes **1a**, **2a**, **3a**, and **9a**, the ring-opening barriers are very small. Therefore, they are unlikely to be experimentally accessible in the gas phase. To facilitate future characterization of carbenes **4a**, **5a**, **6a**, and **8a** and their ring-opened products **4e**, **5e**, **6e**, and **8e**, vibrational frequencies and infrared intensities were reported at the B3-LYP/6-31G\* level (Table 3, Supporting Information). The calculated vibrational frequencies are scaled by 0.9613 to account for the overestimation of vibrational frequencies at this level of theory.<sup>15</sup> For 2-furylchlorocarbene (**7a**), the agreement between theory and experiment is very good. The vibrations of **7a** most prominent for comparison are 1542, 1432, 1401, 1311, and 1184 cm<sup>-1</sup>.<sup>3</sup> The corresponding calculated values are 1530, 1411, 1400, 1292, and 1177 cm<sup>-1</sup>, respectively. For the ring-opened products (both *Z*- and *E*-isomers) of 2-furylchlorocarbene, B3-LYP/6-31G\* calculations reproduce readily the experimental IR spectra.<sup>3</sup>

In summary, ring opening of 2-furylcarbenes is a facile reaction. The low barrier is attributed to the stabilization of the coarctate transition state. The ring-opening barrier can be raised by a  $\pi$ -donating substituent. In particular, for substituents with an unshared pair of electrons, the carbene is sufficiently stable to be observed in the gas phase.

**Substituent Effects on Furan Ring.** Finally, we consider the effects of substitution on the furan oxygen of 2-furylcarbene (X = O). We have examined the CH<sub>2</sub> (**10**), NH (**11**), and S (**12**) analogues of **1**. Their calculated barriers and reaction enthalpies for ring opening are collected in Table 1. Both S and NH analogues are predicted to have a higher activation barrier, while CH<sub>2</sub> substitution has little effect. The calculated higher barrier for 2-thienylcarbene (**12a**) is consistent with the experimental finding that its ring opening is more difficult than 2-furylcarbene.<sup>1b</sup> There is a strong correlation ( $R^2 = 0.97$ ) between the calculated barriers and heats of reaction, which indicates that enthalpy is the major factor influencing the ring-opening reactions. The large variation of reaction enthalpies can be understood in terms of the relative stability of the reactant and product. The stability of the products is governed mainly by the strength of the C=X bond, which is in the order C=C > C=N > C=O > C=S. For the carbene reactants, their stability is strongly determined by the aromaticity of the five-membered ring. One simple way to determine the relative aromaticity of this series of carbenes is to compute the nucleus-independent chemical shifts (NICS).<sup>16</sup> The calculated NICS values (HF/6-31+G\*//MP2/6-31G\*) for **10a**, **11a**, **1a**, and **12a** are 2.6, -8.7, -6.8, and -6.9, respectively, which suggest the aromaticity is in the order **11a** > **12a**  $\approx$  **1a**  $\gg$  **10a**. Thus, one may conclude the stability of the carbene reactant is in the order NH > S  $\approx$  O  $\gg$  CH<sub>2</sub>. It is not surprising that **10a** is calculated to be antiaromatic (positive NICS value) as no  $\pi$  type orbital of the X atom is available for delocalization of the  $\pi$  electrons in the ring. The differential stabilization effect on the reactant and product leads to the calculated trend of enthalpies. It is worth noting that, for the CH<sub>2</sub> and NH analogues, where there is no lone pair in the five-membered ring, the preferred conformation is the anti form (Table 1).

## Conclusions

We have presented an ab initio study of ring opening of 2-furylcarbenes. The calculated result shows pronounced substituent effects on the activation barrier. The effects of substituents on the carbene reactant and transition state were analyzed using isodesmic reactions. The furan ring-opening reaction is calculated to be a facile process. However, for electron-rich substituents (those with an unshared pair of electrons), the stabilization effect on the reactant is greater than the transition state, leading to a significantly higher energy barrier. Therefore, 2-furylcarbene with NH<sub>2</sub>, OH, or F substituent is predicted to be an experimentally accessible species in the gas phase. The calculated aptitude of ring opening is consistent with the experimental observations.

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**Supporting Information Available:** Calculated B3-LYP/6-31G\* infrared spectral data for **4a**, **5a**, **6a**, **7a**, **8a**, **4e**, **5e**, **6e**, **7e**, and **8e**. This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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