# Spin-State Dependent Radical Stabilization in Nitrenes: The Unusually Small Singlet−Triplet Splitting in 2-Furanylnitrene

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**S** *Supporting Information*

**ABSTRACT:** Geometries and energies of the triplet and singlet states of 2-furanylnitrene and 3-furanylnitrene have been calculated by using spin−flip coupled-cluster methods. Calculations with triple-$\zeta$ basis sets predict a singlet−triplet splitting of 10.9 kcal/mol for 2-furanylnitrene, 4.5 kcal/mol smaller than that in phenylnitrene. In contrast, the singlet−triplet splitting in 3-furanylnitrene is computed to be 1.9 kcal/mol larger than that in phenylnitrene. The differences in the singlet−triplet splittings for the furanylnitrenes are attributed to the differences in the radical stabilizing abilities of the 2-furanyl- and 3-furanyl-groups compared to a phenyl ring. Comparison of the singlet−triplet splittings of more than 20 substituted aromatic nitrenes and the radical stabilizing ability of the aromatic systems reveals a high degree of correlation between the singlet−triplet splitting and the radical stabilizing ability, indicating that singlet states of aromatic nitrenes are preferentially stabilized by radical stabilizing substituents. The preferential stabilization of the singlet states is attributed to the decrease in electron pair repulsion resulting from increased delocalization of the radical electron.
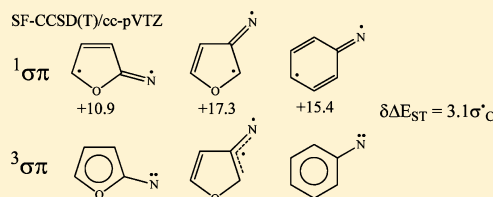
## INTRODUCTION

Nitrenes are well-known intermediates formed in the thermal or photochemical decomposition of aromatic azides. Phenylnitrene (**PhN**), in particular, has been extensively characterized by using time-resolved spectroscopy[1−4] and electronic structure

**PhN**
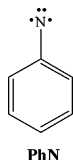
calculations.[1,3,5] Nitrenes, like carbenes, generally have four low-energy electronic states, created by placing two electrons in two similar nonbonding molecular orbitals (NBMOs). In an aromatic nitrene, one NBMO is an in-plane, $\sigma$-like orbital localized on the nitrogen, whereas the other is a benzylic-like $\pi$ orbital. Placing both electrons in a single orbital creates a "closed-shell" singlet state, either $^1\sigma^2$ or $^1\pi^2$. Simple orbital energy considerations, supported by electronic structure calculations,[6−10] predict that occupation of the $\sigma$ orbital will be preferred for the closed-shell state, and the $\sigma^2$ state is lower in energy than the respective $\pi^2$ state. However, the lowest energy singlet states in phenylnitrenes are the open-shell states, $^1\sigma\pi$, which are ca. 15−20 kcal/mol lower in energy than the $\sigma^2$ states.[6−10] The ground state of phenylnitrene, like most nitrenes,[11] is the triplet ($^3\sigma\pi$) state.

The relative energies of the triplet and singlet states of phenylnitrene have been investigated experimentally and computationally. The energy splitting between the triplet and lowest energy (open-shell) singlet state has been measured to be 14.9 kcal/mol by using negative ion photoelectron spectroscopy.[12,13] Relative energies of these states, as well as the closed-shell singlet states, have been calculated in theoretical studies. Proper description of the electron structure, especially that for the open-shell singlet state, requires use of methods capable of describing multiconfigurational wave functions,[7] whereas accurate energetics requires calculations that include dynamic electron correlation.[6,9,10] The highest level calculations (multireference coupled-cluster with complete basis set extrapolations, with zero-point energy corrections)[10] predict a singlet−triplet splitting ($^1\sigma\pi-^3\sigma\pi$) of 15.9 kcal/mol, in very good agreement with the measured value. The $\sigma^2$ state is predicted to be 31.4 kcal/mol higher in energy than the triplet, whereas the energy of the $\pi^2$ state is ca. 55 kcal/mol above the triplet.

Given the interest in the electronic structure of phenylnitrene, many studies have been carried out to investigate how it is affected by substitution of hydrogen atoms on the aromatic ring and subsequently how that affects the reactivity of the nitrene. For example, experimental studies have examined the effect of substitution on the rates of intersystem crossing (ISC) from the initially formed singlet to the triplet state,[14,15] whereas computational studies have investigated the effect on the singlet−triplet energy splitting.[9] Although there is some variation in the ISC rates and singlet−triplet splittings, the effects are, in general, not large and do not followany clear trends. The most significant exception to this is found for the *p*-dimethylamino-substituted phenylnitrene, for which the ISC rate is 3 orders of magnitude faster than in the unsubstituted nitrene and ca. 500 times faster than other para-substituted

1a     1b     1c

2a     2b     2c

**Scheme 1**



2c
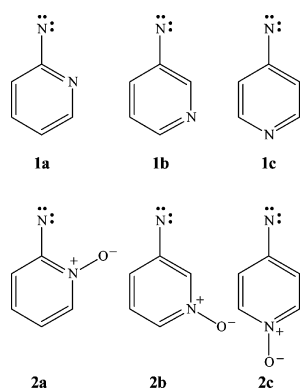
systems.[2,3] The dramatic jump in ISC rates suggests a fundamental difference in electronic structure, but the difference has not been found computationally, as the lowest energy singlet is still the open-shell state, and the closed-shell singlet is still more than 25 kcal/mol higher in energy than the triplet.[9]

Systematic studies of nitrenes substituted by aromatic heterocycles have focused on pyridine derivatives, **1a**−**c**. The 2-pyridinylnitrene, **1a**, was generated initially via decomposition of tetrazolo[1,5-a]pyridine, eq 1.[16,17] Matrix isolated triplet **1a**,



(1)

1a
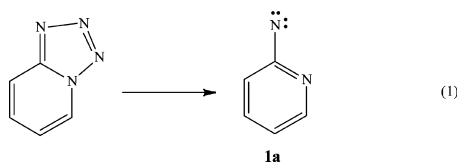
generated eitherfrom thermal decomposition of the tetrazole or upon photolysis of the corresponding azide, has been observed by EPR.[18] The singlet–triplet splitting of **1a** is calculated to be 18.6 kcal/mol at the MCSCF level of theory.[18] The computed singlet–triplet splitting is similar to that obtained for phenylnitrene at the same level of theory,[7] indicating that the pyridine ring does not significantly affect the term energies of the aromatic nitrene. Similarly, photolysis of matrix-isolated 3-azidopyridine leads to formation of **1b**, and the triplet nitrene can be detected by IR and UV spectroscopy.[19] Upon extended photolysis, it undergoes ring-opening, similar to what is observed for **1a**. The chemistry of **1c** has not been characterized experimentally, but DFT calculations predict that the singlet–triplet splitting in **1c** is about 1 kcal/mol higher than that in phenylnitrene.[20]

Poole and co-workers have carried out laser flash photolysis and matrix isolation studies of pyridinyl N-oxide nitrenes, **2a**−**c**.[21] Unlike most aromatic nitrenes, 4-pyrdinyl-n-oxide nitrene, **2c**, does not undergo a rapid ring expansion reaction. The 3-isomer, **2b**, does, however, undergo ring expansion, consistent with the predictions that the nitrene in the meta position is not significantly different from phenylnitrene. Indeed, the singlet–triplet splitting in **2b** is calculated to be similar to that in **PhN**.[22]

Density functional calculations predict the singlet–triplet splitting in **2c**[20,21] to be 6 kcal/mol smaller than that in phenylnitrene. The EPR studies carried out by Poole and co-workers provide insight into the origins of the smaller singlet–triplet splitting.[21] As shown in Scheme 1, it would be expected that the radical can be stabilized by delocalization onto the oxygen, essentially creating a nitroxyl radical, which is generally considered a highly stable free radical. The zero field splittings measured for **2c** are much smaller than those found for **2b**,[21] indicating that the $\pi$ spin density in **2c** is more delocalized than
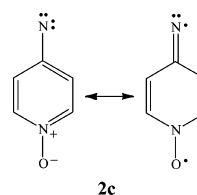
that in **2b**, consistent with the simple resonance predictions. However, the extent of delocalization in the triplet state of **2c** is likely less than it would be in the singlet state, where separating the spins provides additional energy stabilization beyond just delocalization.[23] Similarly, the open-shell singlet state in the pyridine N-oxide derivative of m-xylylene is also calculated to be preferentially stabilized relative to the triplet and closed-shell singlet states.[24]

The 4-pyridinyl N-oxide group is an example of a "super radical stabilizer". Creary[25] has described a version of a radical substituent parameter, $\sigma^{\bullet}_C$, determined from the relative rates of the methylenecyclopropane rearrangements of aryl-substituted methylenecyclopropanes. Although other radical substituent scales are known, the Creary parameter has the advantage of being available for a large range of substituents. In particular, Creary has used this approach to identify groups that have a very large stabilizing effect on the radical formed in the methylenecyclopropane rearrangement. Whereas most of the substituents that have been examined have $\sigma^{\bullet}_C$ values less than ca. 1,[26] those for "super radical stabilizers" are greater than 1.5. Other examples of super radical stabilizers provided by Creary include bridged [10]annulenyl-, 2-thienyl-, and 2-furanyl-groups.

The identification of the 2-furanyl substituent as a super radical stabilizer has potential implications in nitrene chemistry. Whereas phenyl azides are well-known to undergo slow decomposition, more rapid decomposition is found to occur for azide-substituted heterocycles, such as pyrazoles, thiophenes, and furans.[27−29] The decomposition of the heterocyclic azides involves loss of nitrogen, and so nitrene intermediates are often proposed. Although concerted processes can be envisioned to avoid formation of the high-energy nitrene,[27] the observations suggest that intermediates like the 2-furanylnitrene are readily accessed and highly reactive.

This work describes a computational study of the structures and energetics of the 2- and 3-furanyl nitrenes, **2FN** and **3FN**, to investigate whether the radical stabilizing ability of the 2-furanyl affects the singlet–triplet splitting in the nitrene to an extent observed for the other super stabilizer, 4-pyridinyl N-oxide. Calculations at the coupled-cluster level, with large basis sets, show that indeed, 2-furanylnitrene has a significantly smaller singlet–triplet splitting than that in phenylnitrene. In contrast, there is little difference between the energetics for phenyl- and 3-furanylnitrenes. Finally, a comparison of nitrene singlet–triplet splittings calculated in this work and those reported previously with the $\sigma^{\bullet}_C$ values reported by Creary shows that the singlet–triplet splittings of aromatic nitrenes can be predicted very accurately from the radical stabilizing ability of the aromatic substituents.

## ■ COMPUTATIONAL METHODS

The furanylnitrenes were investigated computationally by using the spin–flip approach.[30] Calculations of open-shell systems like nitrenes are very challenging because they require multireference wave

functions. Moreover, simple multiconfigurational SCF calculations are not sufficient, and dynamic electron correlation is also required. The spin−flip (SF) method, developed by Krylov and co-workers,[30−33] is well-suited for these types of calculations, especially for the calculation of the open-shell singlet.

The SF method calculates the energy of the electronic state as an excitation accompanied by "flipping" the spin of one of the electrons from a high-spin reference state. For example, an "open-shell" singlet configuration can be created by flipping one of the unpaired electrons in the $m_s = 1$ triplet state (eq 2a). However, because there are two
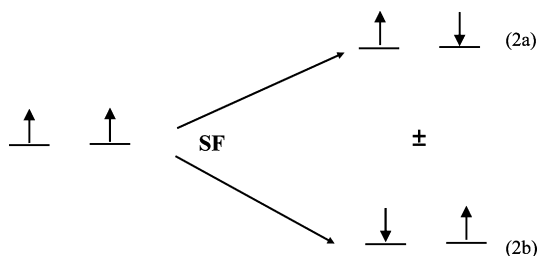


unpaired electrons in the triplet state, there are two configurations that can be formed by a spin flip (eq 2a,b). Linear combination of these two configurations gives rise toeither the open-shell singlet state (by taking the difference) or the $m_s = 0$ triplet (by using the sum). Multireference, closed-shell wave functions can be similarly created by having an orbital change accompanying the spin−flip, as shown in eq 3.
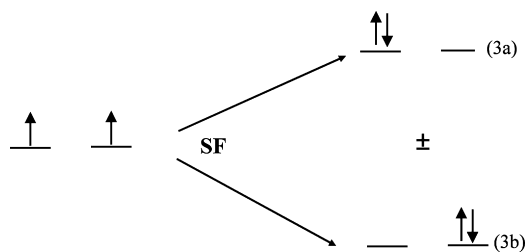


Spin−flip calculations are carried out using the equation-of-motion coupled-cluster approach.[30] Because calculations can be carried out within coupled-cluster theory, they include dynamic correlation. In this work, we use coupled-cluster theory with all single and double excitations (CCSD) and with perturbative treatment of triple excitations.

Geometries of the triplet nitrenes were optimized at the UCCSD/6-31G* level of theory, whereas the geometries of the singlet states of the nitrenes ($\sigma\pi, \sigma^2, \pi^2$) were optimized at the SF-CCSD/6-31G* level of theory, using the triplet nitrene as the reference state. In the geometry optimizations of open-shell states, the unrestricted Hartree−Fock (UHF) orbitals were used as the basis for the CCSD calculation. Although the UHF calculation for the triplet nitrene suffers from some spin contamination ($\langle s^2 \rangle \approx 2.7$), it is not expected to have a large effect on relative geometries of the singlets and triplet states.[34,35] However, spin contamination does affect the vertical state energies, and therefore, single point coupled-cluster energies were carried out using the Kohn−Sham orbitals from B3LYP as the orbital basis in order to minimize its effect, as we have done previously.[36,37] Non-Hartree−Fock orbitals are often used in coupled-cluster calculations involving especially problematic systems,[38] and previous studies have shown that coupled-cluster calculations with DFT orbitals with CCSD(T) calculations can give results similar to what is obtained for open-shell systems using orbitals that minimize spin contamination, such as coupled-cluster optimized orbitals.[39] Although restricted open-shell HF orbitals could also be used to this end, it was found that B3LYP orbitals were easier to converge for these systems, especially with the large basis sets. Whereas the minimization of the effects of spin contamination in the reference wave function is critical for obtaining accurate energetics for the aromatic nitrenes, using DFT orbitals can lead to errors for systems

that are not well-suited for DFT, such as those involving long-range van der Waals interactions.[40] SF-CCSD(T) single point energies were calculated using cc-VDZ and cc-VTZ basis sets and were carried out for the $\sigma\pi$, $\sigma^2$, and $\pi^2$ singlet and the triplet states at all of the optimized singlet and triplet geometries. The triplet energies used for singlet−triplet energy comparisons are those obtained for the $m_s = 0$ state in the SF calculation, as recommended by Krylov and co-workers.[31,33] Calculations for other closed-shell species were carried out by using the same approach, including using B3LYP orbitals, but with the restricted wave function. All calculations were carried out using the QCHEM program.[41]

## ■ RESULTS AND DISCUSSION

The electronic structures of the furylnitrenes are similar to that of phenylnitrene. Each has two electrons that occupy a set of $\sigma$ and $\pi$ NBMOs. Schematic depictions of the $\pi$ NBMOs **2**- and **3FN** are shown in Scheme 2. Occupation of these orbitals by two electrons results in four possible electronic states.

**Scheme 2**
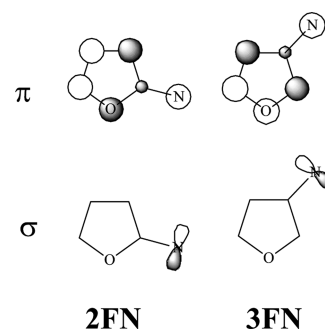


Geometries and energies have been calculated for the $^3\sigma\pi$, $^1\sigma\pi$, $^1\sigma^2$, and $^1\pi^2$ states of **3FN** and the $^3\sigma\pi$, $^1\sigma\pi$, and $^1\pi^2$ states of **2FN** at the SF-CCSD/cc-pVDZ level of theory. Optimization of the $\sigma^2$ state of **2FN** did not result in a nitrene but instead led directly to the ring-opened cyano-substituted acrolein (eq 4), which is ca. 2 eV lower in energy than the
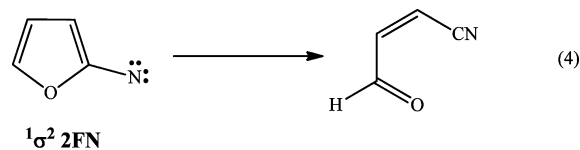


triplet nitrene. Optimized bond lengths and bond angles for **2FN** and **3FN** are shown in Tables 1 and 2. The atom numbers refer to those shown in Scheme 3.

Valence bond representations of the geometries of the furylnitrenes, reflecting the calculated bond lengths, are shown in Figure 1. As with phenylnitrene, the differences in the geometries between the triplet and open-shell singlet states result from differences in spatial distributions of the electrons. More bond localization occurs in the open-shell singlet state because it spatially separates the electrons, thereby reducing electron pair repulsion.[7] Similarly, the preference for having an occupied $\sigma$ orbital and unoccupied $\pi$ orbital makes the $\sigma^2$ singlet lower in energy than the $\pi^2$ state.

The geometries of the $\pi^2$ states are similar for the two isomers. The C−N bond lengths are more consistent with single bonds, and the bond lengths within the ring are similar to those in furan. The polar structure for the $\sigma^2$ state of **2FN** has been proposed as an intermediate in the decomposition of

**Table 1. Optimized Bond Lengths and Geometries for Electronic States of 2-Furylnitrene**

| state | $^3\sigma\pi$ | $^1\sigma\pi$ | $^1\pi^2$ |
|---|---|---|---|
| bond lengths, Å | | | |
| O−C2 | 1.387 | 1.403 | 1.362 |
| C2−C3 | 1.420 | 1.471 | 1.354 |
| C3−C4 | 1.410 | 1.382 | 1.452 |
| C4−C5 | 1.370 | 1.381 | 1.342 |
| C5−O | 1.366 | 1.369 | 1.387 |
| C2−N | 1.306 | 1.257 | 1.374 |
| bond angles | | | |
| O−C2−C3 | 108.8 | 107.3 | 112.7 |
| C2−C3−C4 | 106.4 | 106.5 | 104.2 |
| C3−C4−C5 | 106.8 | 107.7 | 107.5 |
| C4−C5−O | 111.6 | 112.0 | 110.3 |
| C5−O−C2 | 106.5 | 106.5 | 105.4 |
| O−C2−N | 120.3 | 121.8 | 113.7 |

**Table 2. Optimized Bond Lengths and Geometries for Electronic States of 3-Furylnitrene**

| state | $^3\sigma\pi$ | $^1\sigma\pi$ | $^1\sigma^2$ | $^1\pi^2$ |
|---|---|---|---|---|
| bond lengths, Å | | | | |
| O−C2 | 1.359 | 1.363 | 1.308 | 1.373 |
| C2−C3 | 1.398 | 1.447 | 1.402 | 1.364 |
| C3−C4 | 1.464 | 1.489 | 1.488 | 1.471 |
| C4−C5 | 1.346 | 1.334 | 1.334 | 1.350 |
| C5−O | 1.376 | 1.386 | 1.418 | 1.349 |
| C3−N | 1.331 | 1.271 | 1.309 | 1.336 |
| bond angles | | | | |
| O−C2−C3 | 110.6 | 110.7 | 113.0 | 110.5 |
| C2−C3−C4 | 104.8 | 103.2 | 102.8 | 105.3 |
| C3−C4−C5 | 106.0 | 106.4 | 107.0 | 105.2 |
| C4−C5−O | 111.9 | 113.5 | 110.2 | 112.1 |
| C5−O−C2 | 106.7 | 106.3 | 107.0 | 106.9 |
| C2−C3−N | 127.3 | 128.9 | 124.3 | 133.3 |

**Scheme 3**
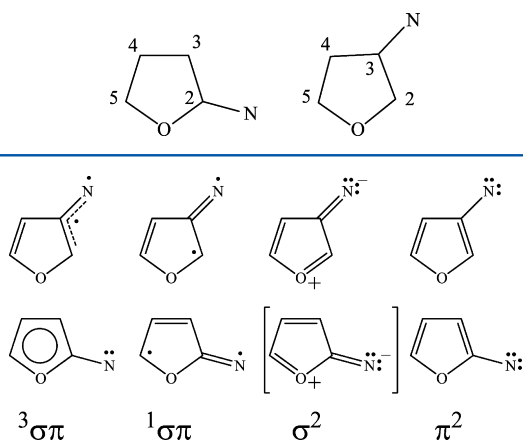


**Figure 1.** Valence bond structures that reflect the bond alternation in the optimized geometries. The structure of the $\sigma^2$ state of **2FN** is projected on the basis of correlation with the optimized structure, cis-cyanoacrolein (eq 4).

2-azidofuran.[27−29] However, as noted above, the optimized geometry for that electronic state corresponds to the stable, ring-opened cyanoacrolein. Ring-opening of the $\sigma^2$ state upon geometry optimization was also observed when using MP2

calculations.[42] The fact that a non-ring-opened structure has not been found for the $\sigma^2$ state of **2FN** in either study suggests that it is not a stable species, although that would need to be confirmed by using a transition state optimization, which is outside the scope of this work.

Both **2FN** and **3FN** are predicted to be ground state triplets. The relative energies of the singlet states, computed at the SF-CCSD(T)/cc-pVTZ level of theory using the CCSD/cc-pVDZ geometries are shown in Table 3. The energies of the

**Table 3. Relative Energies (kcal/mol) of Electronic States in 2FN, 3FN, and Phenylnitrene[a]**

| state | 2FN | 3FN | PhN |
|---|---|---|---|
| $^3\sigma\pi$ | 0.0 | 0.0 | 0.0 |
| $^1\sigma\pi$ | 10.9 | 17.3 | 15.4 |
| | | | 14.9[b] |
| $^1\sigma^2$ | 13.4[c] | 22.1 | 30.1 |
| $^1\pi^2$ | 67.5 | 54.9 | 50.3 |

[a]SF-CCSD(T)/cc-pVTZ single point electronic energies calculated using the SF-CCSD/cc-pVDZ geometries do not include ZPE. [b]Experimental value (ref 12 and 13). [c]Calculated at the geometry of the $^1\sigma\pi$ state

corresponding states in phenylnitrene (**PhN**) are also shown in Table 3, for comparison. Because the $\sigma^2$ state ring-opens during geometry optimization, the energy of that state in Table 3 corresponds to the energy at the open-shell singlet geometry of the nitrene.

The energy orderings of the electronic states of the three nitrenes are computed to be the same, with the open-shell states being the lowest energy singlets. For all three nitrenes, the $\pi^2$ states are the highest energy states, and they will not be considered further. The relative energies of the $\sigma^2$ states of the furanylnitrenes are lower than that in phenylnitrene, which can likely be attributed to the stability of the polar structures shown in Figure 1 and particularly the stability of the oxonium ion.

Contrasting results are obtained for the relative energies of the open-shell singlet states of the isomeric furylnitrenes. Whereas the singlet−triplet splitting in **3FN** is slightly larger than that in **PhN**, the singlet−triplet splitting in **2FN** is significantly smaller. In fact, both of the differences in the singlet−triplet splittings with that in **PhN** are outside of the range of what has been predicted for typical substituent effects. For example, Johnson et al. calculated the singlet−triplet splittings of ca. 30 substituted phenylnitrenes.[9] The largest effect they found was for the *para*-methylamino-substituted nitrene, which had a singlet−triplet splitting that was 2.6 kcal/mol smaller than that in **PhN**. The largest *destabilizing* effect on a singlet was found for the *m*-OCH$_3$ group, which increased the singlet−triplet splitting by 0.7 kcal/mol compared to that of **PhN**. In contrast, the singlet−triplet splitting in **2FN** is calculated to be 4.5 kcal/mol smaller than that in **PhN**, whereas that in **3FN** is 1.9 kcal/mol larger. Some of the difference could be attributable to the use of the spin−flip approach as opposed to MCSCF methods, but the deviations also correlate with the radical stabilizing effects of the 2- and 3-furanyl groups. In particular, as described above, the 2-furanyl substituent has a large radical stabilizing effect. The $\sigma^\bullet_C$ value for the 2-furanyl group is 1.64, indicating that it is a super radical stabilizer. Interestingly, the $\sigma^\bullet_C$ value for the 2-furanyl group is slightly smaller than that for the 4-pyridinyl *N*-oxide, which has $\sigma^\bullet_C$ = 1.88, whereas the computed singlet−triplet splitting in **2c** is

6 kcal/mol lower than that in **PhN**,[20] slightly larger than the difference for **2FN**.

Similarly, the $\sigma^{\bullet}_C$ for the 3-furanyl group is −0.11, indicating that it is a radical destabilizing group. Other radical destabilizing groups, such as p-F, m-CN, m-NO$_2$, m-CF$_3$, m-Cl, m-F, and m-OCH$_3$, which have $\sigma^{\bullet}_C$ = −0.06, −0.13, −0.11, −0.08, −0.03, −0.02, and −0.02, respectively, are all calculated by Johnson and Cramer[9] to have singlet−triplet splittings larger than that in **PhN**. Although all of the phenylnitrenes with these radical destabilizing substituents ($\sigma^{\bullet}_C$ < 0) were calculated to have singlet−triplet splittings larger than that of **PhN**, the differences were all smaller than that found for **3FN**.

The effects of substituents on the singlet−triplet splittings for the super radical stabilizers and the radical destabilizers suggests that there is a relationship between radical stabilizing ability and singlet−triplet splitting. The extent of the relationship is evident in Figure 2, which is a plot of the calculated singlet−
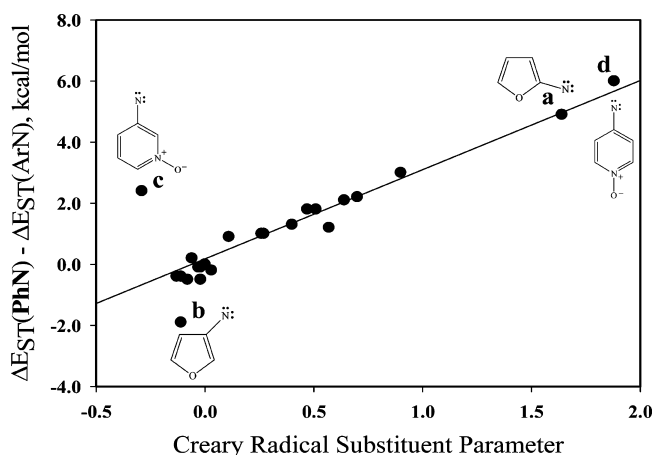


**Figure 2.** A plot of the relative singlet−triplet splittings of aromatic nitrenes vs the Creary radical substituent parameter, $\sigma^{\bullet}_C$. The solid line is a linear regression with a slope of 3.1 kcal/mol. The points labeled a (**2FN**) and b (**3FN**) are from this work. Points c and d are 3- and 4-pyridinyl N-oxide nitrenes, from ref 22 and 21, respectively. The singlet−triplet splittings for the unlabeled points are from ref 9. Radical substituent parameters are all from ref 25. A complete listing of the specific nitrenes and all the values are provided in the Supporting Information.

triplet splitting difference (from that in **PhN**)[9,22] versus $\sigma^{\bullet}_C$.[25] The correlation does not just occur at the end of the ranges and is essentially linear over almost all substituents. The most notable exception to the trend is the 3-pyridinyl N-oxide nitrene (point c in Figure 2), which is calculated[22] to have a singlet−triplet splitting that is 2.4 kcal/mol smaller than that in **PhN**, despite a negative $\sigma^{\bullet}_C$ parameter.[25,43] Similarly, **3FN** is noticeably off the line in the other direction. With those two exceptions, the correlation is very high ($R^2$ = 0.97) with a slope of 3.1 kcal/mol.

Creary and co-workers have similarly found[44] a linear relationship between the radical substituent parameter and the benzylic radical stabilization energy, which was simply calculated as the difference between the bond dissociation energy in the methyl-substituted aromatic system and toluene (eq 5).

$$\text{PhCH}_3 + \text{ArCH}_2 \rightarrow \text{PhCH}_2 + \text{ArCH}_3 \qquad (5)$$
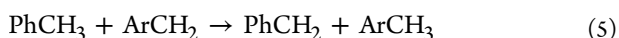
Although excellent correlation was observed, the slope of the plot of $\sigma^{\bullet}_C$ vs the radical stabilization energy was found to be 0.7 mol/kcal. Assuming that the plot goes through the point for H ($\sigma^{\bullet}_C$ = 0, resonance stabilization energy = 0), then the inverse plot would have a slope of ca. 1.4−1.5 kcal/mol, about half of that found for the plot shown in Figure 2. The difference in slopes indicates that the singlet−triplet splittings in nitrenes are more sensitive to radical stabilization effects than are benzylic-like BDEs.[45]

Additional insight into the differences in the substituent effects for the triplet and singlet states of the nitrenes can be obtained by considering the effects on the energies for nitrene formation from the corresponding amine, by using the reaction shown in eq 6 where **FN** is the furanylnitrene and FNH$_2$ is the corresponding aminofuran.

$$\text{PhNH}_2 + \text{FN} \rightarrow \text{PhN} + \text{FNH}_2 \qquad (6)$$

The reaction energies for the triplet and singlet states of the nitrenes are shown in Table 4. Positive values indicate that the

**Table 4. Calculated Energies for H$_2$ Transfer Between Nitrenes**[a]

|  | 2-furanylnitrene | 3-furanylnitrene |
|---|---|---|
| triplet state |  |  |
| (U)CCSD/cc-pVTZ | 2.9 | 2.2 |
| (U)CCSD(T)/cc-VTZ | 3.8 | 2.7 |
| singlet state[b] |  |  |
| CCSD/cc-pVTZ | 8.4 | 1.0 |
| CCSD(T)/cc-pVTZ | 8.2 | 0.8 |

[a]The calculated energies for hydrogen transfer between aniline and the furanylnitrene, as shown in eq 6. [b]Calculated by using the reaction energies for the triplet states, corrected by the spin−flip singlet−triplet splittings shown in Table 3.

hydrogen (H$_2$) transfer from aniline to the furanylnitrene is unfavorable, such that the furanylnitrene is more energetically favorable than phenylnitrene. As indicated in the table, the reaction energies for the triplets were obtained directly by using the unrestricted coupled-cluster approach (with B3LYP orbitals) for the open-shell states. Reaction energies for the singlet states were obtained by combining those for the triplets with the singlet−triplet splittings calculated using the spin−flip approach. This approach has been utilized previously for calculating absolute energies of the benzynes.[46]

Considering that 2-furanyl is known to be a better radical stabilizing group than phenyl,[25] it is not surprising that the triplet state of **2FN** is more stable than that for **PhN**. In contrast, the fact that triplet **3FN** is more stable than triplet **PhN** is inconsistent with the radical destabilizing property of 3-furanyl.[25] However, this can be attributed to a destabilizing interaction between the amino group and aromatic ring in 3-aminofuran (**3FNH$_2$**) as opposed to stability of the radical. The instability of 3-aminofuran compared to aniline is illustrated by the deviation from bond additivity in the energy of the 3-aminofuran.

$$\text{PhNH}_2 + \text{furan} \rightarrow \text{benzene} + \text{3FNH}_2 \qquad (7)$$
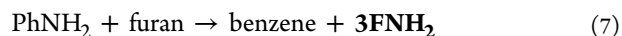
The energy for the reaction shown in eq 7 is calculated (CCSD(T)/cc-pVTZ) to be +4.6 kcal/mol, indicating that the aminofuran is destabilized by that amount. In contrast, the energy for a similar calculation using 2-aminofuran is only +0.4 kcal/mol, indicating that the interaction between the NH$_2$

group and the furan ring is essentially the same as that between the $NH_2$ and aromatic ring in aniline.

Whereas the triplet state of **2FN** is slightly stabilized compared to triplet state of PhN, the effect on the singlet state is much larger. This also reflects that the 2-furanyl group preferentially stabilizes the singlet state of the nitrene. Similarly, the 3-furanyl group also has different effects on the singlet and triplet state, although the sizes of the effects are smaller. After accounting for the instability of the aminofuran, both the singlet and triplet states of **3FN** are destabilized compared to the corresponding states in **PhN**.

The preferential stabilization of the singlet state in **2FN** likely results from the extensive delocalization, as reflected in the structures in Figure 1. Borden and Davidson[23] have proposed that singlet states of diradicals (including nitrenes) are destabilized by Coulombic repulsion when the unpaired electrons are in the same region of space. Consequently, Hrovat et al.[7] have shown that the geometry of the singlet state of phenylnitrene separates the unpaired electrons, resulting in lower electron pair repulsion than would be present in the triplet geometry, where the unpaired electrons are more localized on the nitrogen. A similar mechanism stabilizes the singlet state of **2c**,[21] as illustrated in Scheme 1.

Presumably, the reason the 2-furanyl-group is a "super radical stabilizer" (compared to phenyl) is because it is able to delocalize the radical without a large cost of aromatic stabilization energy.[47] In the nitrene, the delocalization of the $\pi$-radical electron preferentially stabilizes the singlet state because it decreases the extent of electron pair repulsion. As shown in Figure 1, the calculated bond lengths for the singlet state are consistent with having the radical delocalized to the 4-position of the nitrene, especially compared to the geometry of the triplet state.

The stabilization of singlet states by delocalization accounts for the correlation between singlet−triplet splitting and radical stabilization parameter shown in Figure 2. Because the low-lying triplet and singlet states in aromatic nitrenes are open-shell states with benzylic-like $\pi$ radicals, it is not surprising that they are stabilized by radical stabilizing substituents. However, as described above, because the mechanism of radical stabilization is generally delocalization, the stabilization of the singlet states goes beyond that of typically radical stabilization and also includes the stabilization due to decrease in electron pair repulsion, which does not occur for the triplet states.[48] That the preferential stabilization of the singlet states should be linear with $\sigma^{\bullet}_C$ is not necessary, although approximately found to be the case empirically.

## CONCLUSIONS

The triplet and open-shell singlet states of aromatic nitrenes both have benzyl-like $\pi$ radicals, but are affected very differently by the addition of radical stabilizing substituents, particularly those that stabilize via electron delocalization. Comparison of computed singlet−triplet splittings in substituted aromatic nitrenes indicates that singlet states are affected more significantly than triplet states by radical stabilizing substituents, which can be attributed to differences in electron repulsion inherent in singlet and triplet states. The effects of the differential stabilization are very pronounced in systems such as 4-pyridinyl N-oxide nitrene or 2-furanylnitrene, the subject of this work, because the 4-pyridinyl N-oxide and 2-furanyl moieties are examples of "super radical stabilizers". In this work, high-level electronic structure calculations predict the singlet−

triplet splitting of 2-furanylnitrene to be 10−11 kcal/mol, much smaller than that in phenylnitrene, which can be attributed to the radical delocalizing ability of the 2-furanyl-group. The enhanced stabilization of the singlet does not occur in 3-furanylnitrene because the 3-furanyl-group is not a good radical stabilizer.

The results for the 4-pyridinyl N-oxide and 2-furanylnitrenes suggest that even larger effects could be obtained by combining the two motifs, as in the 5-isoxazolyl-n-oxide nitrene, **5ION** (Scheme 4). In that system, the delocalization to form the

**Scheme 4**



**5ION**
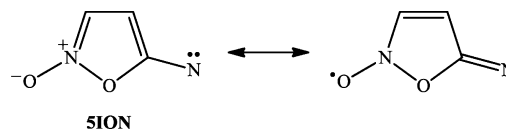
nitroxyl radical can occur, as in the pyridinyl N-oxide nitrene, but only with the cost of the furan aromatic stabilization energy. If an N-oxide moiety has the same effect on the furanylnitrene singlet−triplet splitting as it does on that in phenylnitrene ($\delta\Delta E_{ST} \approx 6$ kcal/mol), the resulting singlet−triplet splitting in **5ION** would be ca. 5 kcal/mol! A computational study of **5ION** is currently underway.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Relative and absolute energies of **2FN**, **3FN**, **2b**, **2c**, and **PhN** (as in Table 3) at lower levels of theory, geometries and energies of species in eqs 6 and 7, and the radical substituent parameters and singlet−triplet splitting values used in Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENTS

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