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# Why Are Nitrenes More Stable than Carbenes? An Ab Initio Study

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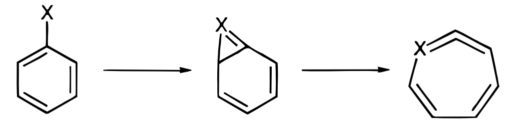
**Abstract:** High level ab initio calculations find that nitrenes are more stable than carbenes, as indicated by the computed enthalpy differences of 25−26 kcal/mol between triplet phenylnitrene and the isomeric triplet pyridylcarbenes. More generally, the greater thermodynamic stability of nitrenes manifests itself in the finding that the N−H bond dissociation energies (BDEs) of aminyl radicals are approximately 20 kcal/mol lower than the C−H BDEs of analogous alkyl radicals. The greater thermodynamic stability of nitrenes, relative to carbenes, is attributed to the large amount of 2s character in the orbital that is occupied by the lone pair of electrons in nitrenes.

Ab initio calculations have found that the ring expansion of singlet phenylcarbene (**PhCH**) to 1,2,4,6-cycloheptatetraene (**CHT**)[1] is much more exothermic than the analogous ring expansion of singlet phenylnitrene (**PhN**) to 1-aza-1,2,4,6-cycloheptatetraene (**ACHT**).[2] The former ring expansion reaction was computed to be exothermic by 16−20 kcal/mol;[1] whereas, the latter was calculated to be nearly thermoneutral.[2]



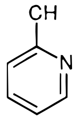
**PhCH**, X = CH
**PhN**, X = N

**CHT**, X = CH
**ACHT**, X = N

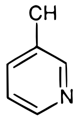
The calculated reversibility of the latter reaction accounts for the experimental finding that 1-aza-1,2,4,6-cycloheptatetraene gives triplet **PhN**,[3] presumably via formation of singlet **PhN**, followed by intersystem crossing.

Evidence was presented that the large difference in the exothermicities of the two ring expansion reactions is primarily due to a large difference in thermodynamic stabilities between singlet **PhCH** and singlet **PhN**.[2] Since the singlet−triplet splitting of 18 kcal/mol in **PhN**[4,5] is considerably greater than $\Delta E_{ST} \approx 5$ kcal/mol in **PhCH**,[1,6,7] the difference between the thermodynamic stabilities of the triplets is ca. 13 kcal/mol larger than that between the singlets. Wentrup and Platz have each suggested that a large difference between the thermodynamic stabilities of the triplets is the origin of the much lower reactivity of triplet **PhN**, compared to triplet **PhCH**.[8] Wentrup and Platz also each proposed that the greater thermodynamic stability of triplet **PhN**, relative to triplet **PhCH**, is mirrored in the relative thermodynamic stabilities of triplet NH versus triplet $CH_2$, as exemplified, for instance, by the lower bond dissociation energy (BDE) for forming triplet NH from $^{\bullet}NH_2$ than for forming triplet $CH_2$ from $^{\bullet}CH_3$.

Since **PhCH** and **PhN** are not isomers, their energies cannot be compared directly. However, pyridylcarbenes (**PyCH**) are isomers of **PhN**, and consistent with the rearrangement of the former to the latter,[9] our calculations found that singlet **PhN** is much lower in energy than both singlet **2-PyCH**[2] and singlet **3-PyCH**.[10] In this paper, we have used **3-PyCH** as a link between **PhCH** and **PhN**,[11] so that we can make meaningful comparisons between the energies of the latter two molecules.



**2-PyCH**



**3-PyCH**

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[10] The lowest singlet state of **3-PyCH** is calculated to be lower in energy than that of **2-PyCH**[2] by 1.0 kcal/mol at (8,8)CASSCF/6-31G* and by 2.0 kcal/mol at (8,8)CASPT2N/6-31G*.

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**Table 1.** Relative Energies and Enthalpies at CASSCF/6-31G* Optimized Geometries of Triplet **3-PyCH**, Triplet **PhN**, and Pairs of Molecules Formed from Them by Addition of Hydrogen Atoms[a]

| calculation | **3-PyCH$_3$**[b] | **PhNH$_2$** | **3-PyCH$_2$**[b] | **PhNH** | **3-PyCH**[b,c] | **PhN** |
|---|---|---|---|---|---|---|
| | $^1A'$ | $^1A'$ | $^2A''$ | $^2A''$ | $^3A''$ | $^3A_2$ |
| ZPE | 77.0 | +0.5[d] | 67.6 | +0.8[d] | 59.6 | +0.5[d] |
| $C_v \times 298$ K | 6.3 | +0.3[d] | 6.3 | −0.2[d] | 6.1 | −0.2[d] |
| CASSCF/6-31G* | −285.80990 | +5.7[e] | −285.19124 | −1.9[e] | −284.55070 | −27.8[e] |
| CASPT2N/6-31G* | −286.68371 | +1.9[e] | −286.04787 | −1.5[e] | −285.38350 | −26.4[e] |
| BVWN5/cc-pVDZ | −289.02535 | −0.9[e] | −288.35937 | −2.2[e] | −287.65819 | −25.5[e] |
| BVWN5/AUG-cc-pVTZ | −289.12245 | −3.2[e] | −288.45363 | −3.3[e] | −287.74861 | −25.3[e] |

[a] The electrons correlated in the CASSCF calculations consisted of the $\pi$ plus the unpaired $\sigma$ electrons. [b] Absolute energies in hartrees, unscaled CASSCF/6-31G* zero-point energies (ZPEs) and heat capacities in kcal/mol. [c] Energies and enthalpies are for the syn conformer. [d] Relative energy in kcal/mol. [e] Relative energy has been converted to an enthalpy difference by correcting for $\Delta$ZPE and $\Delta C_v \times 298$ K.

Comparing the lowest singlet states of **PhCH** and **PhN** is complicated by the fact that they have different orbital occupancies. In $^1A'$ **PhCH,** two electrons occupy the hybridized, $\sigma$, nonbonding orbital on carbon;[1,7] whereas, in $^1A_2$ **PhN**, only one electron occupies the pure 2p, $\sigma$, nonbonding orbital on nitrogen.[2,5] However, the lowest triplet states ($^3A''$ in **PhCH** and $^3A_2$ in **PhN**) each have one unpaired electron in a nonbonding $\sigma$ orbital and one in a nonbonding $\pi$ MO. This makes comparison of the triplet ground states of **PhCH** and **PhN** much easier, both conceptually and computationally,[12] than comparison of their singlet states.

The results of our calculations on triplet **PhCH** and triplet **PhN** support the conjecture[8] that the latter is less reactive than the former because the N−H BDE in anilinyl radical (**PhNH**) is much smaller than the C−H BDE in benzyl radical (**PhCH$_2$**). Our calculations also provide an explanation for this large difference in BDEs.

## Computational Methods

Geometry optimizations were performed using complete active space (CAS) SCF calculations with the 6-31G* basis set.[13] In each case, the electrons correlated in the CASSCF calculations consisted of all of the $\pi$ plus the unpaired $\sigma$ electrons. CASSCF/6-31G* frequency calculations confirmed that the stationary points found were minima, and the calculations also provided unscaled, zero-point energy (ZPE) corrections.

Only real vibrational frequencies were found for all molecules, except for the $D_{3h}$ methyl radical. At the ROHF level of theory, it showed one imaginary frequency, correspondng to an out-of-plane distortion; an ROHF geometry reoptimization provided an energy minimum with $C_{3v}$ symmetry and an energy 0.03 kcal/mol lower than that at the $D_{3h}$ geometry. However, the $C_{3v}$ geometry was found to be higher in energy than the $D_{3h}$ geometry at correlated levels of theory; thus, we have reported single-point energies at the $D_{3h}$ geometry. The zero-point vibrational energy for $D_{3h}$ methyl radical was taken from UHF/6-31G* calculations, which find this geometry to be an energy minimum.

Second-order Møller−Plesset theory was used to provide dynamic correlation beyond the CASSCF level via CASPT2N[14] calculations, which were performed at the CASSCF/6-31G*-optimized geometries. For species lacking the large phenyl and pyridyl substituents, G2 enthalpies[15] were also computed.

Single-point density functional theory (DFT) calculations were carried out at CASSCF/6-31G* optimized geometries, using Becke's 1988 exchange functional[16] and Vosko, Wilk, and Nusair's correlation functional V.[17] This method is designated as BVWN5. Recent calculations by Squires and co-workers have found that BVWN5 energies are in good agreement with experimental measures of both $\Delta E_{ST}$ and "carbene stabilization energy" for phenylcarbene.[18] Two different correlation-consistent basis sets[19] were used in the DFT calculations, a polarized valence double-$\zeta$ basis set and a polarized valence triple-$\zeta$ basis set that was augmented with diffuse functions (s, p, and d on hydrogen; s, p, d, and f on carbon and nitrogen). These basis sets are designated as cc-pVDZ and AUG-cc-pVTZ, respectively.

CASPT2N calculations were performed using MOLCAS-3.[20] All other calculations were carried out using Gaussian 94.[21] Optimized geometries and single-point energies are available as Supporting Information.

## Results and Discussion

As shown in Table 1, triplet **PhN** is calculated to be 25−26 kcal/mol lower in enthalpy than triplet **3-PyCH**[22] at the CASPT2N/6-31G* and BVWN5/AUG-cc-pVTZ levels of theory. Table 1 also shows that the corresponding radicals, **PhNH** and **3-PyCH$_2$**, differ in enthalpy by only 1−3 kcal/mol. Therefore, the large enthalpy difference between **PhN** and **3-PyCH** must reflect an intrinsic enthalpy difference between arylnitrenes and arylcarbenes, rather than a difference between the abilities of the phenyl and pyridyl groups to stabilize an unpaired $\pi$ electron. In fact, our calculations find that the rotation barriers for the

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(11) **3-PyCH** was chosen over **2-PyCH** for detailed study because the interaction between the ring nitrogen and the divalent carbon atom is smaller in the former carbene than in the latter. For example, whereas, at the CASPT2N level, the syn and anti geometries differ in energy by only 0.3 kcal/mol in singlet **3-PyCH**, they differ by 3.6 kcal/mol in singlet **2-PyCH**. The greater similarity in energies of the syn and anti conformers of **3-PyCH**, compared to **2-PyCH**, thus makes **3-PyCH** a better model for **PhCH**, for which the analogous conformers are degenerate.

(12) For example, CASPT2N/6-31G* calculations give a singlet−triplet splitting that is too large by almost 10 kcal/mol for **PhCH**,[1c] but that is very close to experiment for **PhN**.[2,4] These findings indicate that CASPT2N gives much more accurate results for electronic states with the same type of orbital occupancy (e.g., the $^1A_2$ and $^3A_2$ states of **PhN**) than with different orbital occupancies (e.g., the $^1A'$ and $^3A''$ states of **PhCH**).

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(15) The G2 method gives energies that are effectively equivalent to QCISD(T)/6-311+G(3df, 2p)//Full-MP2/6-31G* calculations, which are then corrected with scaled HF/6-31G* zero-point and thermal corrections to obtain enthalpies at 298 K. [Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.]

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(22) Since the energy of *syn*-**3-PyCH** is lower than that of the *anti*-**3-PyCH** in both the lowest singlet and triplet states, the energies computed for the syn stereoisomer are those that are reported in Table 1.

**Table 2.** BDE ($DH_{298}$ in kcal/mol) of $RNH_2$, Relative to $R'CH_3$, [$\Delta H(1)$] at CASSCF/6-31G* Optimized Geometries[a]

| substituents/calculation | $\Delta H(1)$ |
|---|---|
| R = R′ = H[b] | |
| ΔZPE | +0.3 |
| $\Delta C_v \times 298$ K | −0.5 |
| R(O)HF[c]/6-31G* | −6.2 |
| CASPT2N[d]/6-31G* | −1.3 |
| BVWN5/cc-pVDZ | −1.1 |
| BVWN5/AUG-cc-pVTZ | 1.4 |
| G2 | 2.1 |
| exptl $\Delta DH_{298}$[e] | 3.7 |
| R = R′ = Ph[f] | |
| ΔZPE | +0.2 |
| $\Delta C_v \times 298$ K | −0.5 |
| CASSCF/6-31G* | −7.3 |
| CASPT2N/6-31G* | −3.0 |
| BVWN5/cc-pVDZ | −1.0 |
| BVWN5/AUG-cc-pVTZ | 0.3 |
| R = Ph, R′ = 3-Py[f] | |
| ΔZPE | +0.3 |
| $\Delta C_v \times 298$ K | −0.5 |
| CASSCF/6-31G* | −7.6 |
| CASPT2N/6-31G* | −3.4 |
| BVWN5/cc-pVDZ | −1.3 |
| BVWN5/AUG-cc-pVTZ | −0.1 |

[a] The electrons correlated in the CASSCF calculations consisted of the $\pi$ plus the unpaired $\sigma$ electrons. [b] Enthalpies for eq 1 include differences in zero-point energies (ΔZPE) and heat capacities at 298 K ($\Delta C_v \times 298$ K), obtained from calculations at the R(O)HF/6-31G* level of theory. [c] RHF for $RNH_2$ and $R'CH_3$; ROHF for RNH and $R'CH_2$. [d] Using R(O)HF reference wave functions. [e] Values are averages in kcal/mol from ref 26. [f] Enthalpies for eq 1 include differences in zero-point energies (ΔZPE) and heat capacities at 298 K ($\Delta C_v \times 298$ K), obtained from calculations at the CASSCF/6-31G* level of theory.

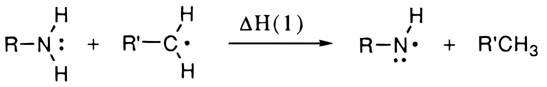
**Table 3.** BDE ($DH_{298}$ in kcal/mol) of RNH, Relative to $R'CH_2$, [$\Delta H(2)$] at CASSCF/6-31G* Optimized Geometries[a]

| substituents/calculation | $\Delta H(2)$ |
|---|---|
| R = R′ = H[b] | |
| ΔZPE | −0.1 |
| $\Delta C_v \times 298$ K | +0.2 |
| ROHF/6-31G* | −23.2 |
| CASPT2N[c]/6-31G* | −21.9 |
| BVWN5/cc-pVDZ | −19.3 |
| BVWN5/AUG-cc-pVTZ | −17.5 |
| G2 | −18.4 |
| exptl $\Delta DH_{298}$[d] | −18.7 |
| R = R′ = Ph[e] | |
| ΔZPE | −0.2 |
| $\Delta C_v$ x 298 K | +0.1 |
| CASSCF/6-31G* | −25.6 |
| CASPT2N/6-31G* | −24.7 |
| BVWN5/cc-pVDZ | −23.7 |
| BVWN5/AUG-cc-pVTZ | −22.5 |
| R = Ph, R′ = 3-Py[e] | |
| ΔZPE | −0.2 |
| $\Delta C_v$ x 298 K | +0.1 |
| CASSCF/6-31G* | −25.8 |
| CASPT2N/6-31G* | −24.8 |
| BVWN5/cc-pVDZ | −23.2 |
| BVWN5/AUG-cc-pVTZ | −21.9 |

[a] The electrons correlated in the CASSCF calculations consisted of the $\pi$ plus the unpaired $\sigma$ electrons. [b] Enthalpies for eq 2 include differences in zero-point energies (ΔZPE) and heat capacities at 298 K ($\Delta C_v \times 298$ K), obtained from calculations at the ROHF/6-31G* level of theory. [c] Using ROHF reference wave functions. [d] Values are averages in kcal/mol from ref 26. [e] Enthalpies for eq 2 include differences in zero-point energies (ΔZPE) and heat capacities at 298 K ($\Delta C_v \times 298$ K), obtained from calculations at the CASSCF/6-31G* level of theory.

methylene groups in **$PhCH_2$** and **3-$PyCH_2$** differ by only 0.3 kcal/mol at the CASSCF/6-31G* level of theory, confirming that phenyl and 3-pyridyl do, indeed, provide comparable stabilization for an unpaired $\pi$ electron.

Since our calculations find that, like **PhNH** and **3-$PyCH_2$**, **$PhNH_2$** and **3-$PyCH_3$** have very similar enthalpies, the data in Table 1 imply that the N−H BDE of **$PhNH_2$** and C−H BDE of **3-$PyCH_3$** are quite similar. The reaction in eq 1 can be used to demonstrate that this is, in fact, the case not only for R = Ph and R′ = 3-Py but also for R = R′ = Ph and for R = R′ = H. The enthalpies calculated for this reaction at different levels of theory are given in Table 2.

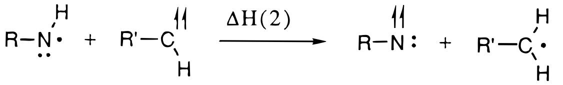


$$\mathrm{R{-}\ddot{N}H_2} + \mathrm{R'{-}\dot{C}H_2} \xrightarrow{\Delta H(1)} \mathrm{R{-}\underset{\cdot\cdot}{\dot{N}}H} + \mathrm{R'CH_3} \qquad (1)$$

As shown in Table 2, the computed differences [$\Delta H(1)$ in eq 1] between the BDEs ($DH_{298}$) depend somewhat on the level of theory used. However, for R = R′ = H, BVWN5/AUG-cc-pVTZ gives essentially the same value for $\Delta H(1)$ as the G2 calculations, and the G2 enthalpy for the reaction in eq 1 is within 2 kcal/mol of the experimental difference between the BDEs of $NH_3$ and $CH_4$. For all three sets of R and R′, CASPT2N/6-31G* gives values for $\Delta H(1)$ that are ca. 3 kcal/mol lower than those computed with BVWN5/AUG-cc-pVTZ.

The computed differences between the BDEs also depend somewhat on the substituents, R and R′. For example, with R = R′ = Ph, $\Delta H(1)$ is calculated to be up to 2 kcal/mol smaller than that for R = R′ = H. Nevertheless, regardless of the set of substituents or of the level of theory used, the results in Table 2 show that *the N−H BDEs of primary amines are nearly the same as the C−H BDEs of the analogous primary alkanes*, despite the greater electronegativity of nitrogen compared to carbon.

In contrast, the much lower enthalpy computed for triplet **PhN**, compared to triplet **3-PyCH**, implies that the N−H BDE of **PhNH** radical is much reduced from the C−H BDE of **3-$PyCH_2$** radical. The reaction in eq 2 can be used to demonstrate that the N−H BDE of RNH is lower than the C−H BDE of $R'CH_2$, not only for R = Ph and R′ = 3-Py but also for R = R′ = Ph and for R = R′ = H. The enthalpies calculated



$$\mathrm{R{-}\underset{\cdot\cdot}{\dot{N}}H} + \mathrm{R'{-}\overset{\uparrow\uparrow}{C}H} \xrightarrow{\Delta H(2)} \mathrm{R{-}\overset{\uparrow\uparrow}{N}{:}} + \mathrm{R'{-}\dot{C}H_2} \qquad (2)$$

for this reaction are given in Table 3. They indicate that triplet nitrenes are, in general, much more thermodynamically stable than the analogous triplet carbenes.

The enthalpies in Table 3 for the reaction in eq 2 show small variations with levels of theory and substituents, R and R′, which are very similar to those seen in Table 2 for the reaction in eq 1. For R = R′ = H, the BVWN5/AUG-cc-pVTZ and G2 values for $\Delta H(2)$ are, like those for $\Delta H(1)$, within 1 kcal/mol of each other, and these enthalpy changes are essentially the same as the differences between the experimental heats of formation of the molecules in eq 2. For all three sets of substituents, CASPT2N/6-31G* gives values of $\Delta H(2)$ that are again ca. 3 kcal/mol lower than those computed with BVWN5/AUG-cc-pVTZ, and like $\Delta H(1)$, $\Delta H(2)$ is calculated to be 2−5 kcal/mol more negative for R = R′ = Ph than for R = R′ = H.

Despite these small variations with the substituents, R and R′, and with the level of theory used, the results in Table 3 show that the N−H BDE of an aminyl radical to form a triplet nitrene is much lower than the C−H BDE of a comparable primary alkyl radical to form a triplet carbene. Since the much lower N−H BDE of **PhNH**, compared to the C−H BDE of **3-PyCH$_2$**, can be rigorously attributed to the much lower enthalpy of the triplet nitrene, relative to the triplet carbene, the results in Table 3 establish that, *in general, triplet nitrenes are ca. 20 kcal/mol more thermodynamically stable than comparably substituted triplet carbenes*.

These computational results confirm the suggestions of Wentrup and Platz that (a) the relative lack of reactivity and the greater selectivity found for triplet **PhN**, compared to triplet **PhCH**, has a thermodynamic origin and (b) this difference between the thermodynamic stabilities of **PhN** and **PhCH** is but one example of a more general difference between the thermodynamic stabilities of nitrenes and carbenes, which is also seen in the difference between the N−H BDE in $^{\bullet}NH_2$ and the C−H BDE in $^{\bullet}CH_3$.[8]

Despite the ca. 13 kcal/mol larger value of $\Delta E_{ST}$ in **PhN**[2,4,5] than in **PhCH**,[1,6,7] the even larger difference between the thermodynamic stabilities of triplet **PhN** and triplet **PhCH** results in singlet **PhN** also being predicted to be considerably more thermodynamically stable than singlet **PhCH**.[23] The greater thermodynamic stability of **PhN** accounts for the calculated differences between the overall energetics of the ring expansions of singlet **PhN** and **PhCH**.[2] Whereas ring expansion of singlet **PhCH** to **CHT** is computed to be very exothermic,[1] that of singlet **PhN** to **ACHT** is calculated to be nearly thermoneutral.[2,24] As noted in the Introduction, experimental evidence indicates that ring expansion of singlet **PhN** is, in fact, reversible.[3]

The explanation of why nitrenes are thermodynamically more stable than carbenes must be the same as the reason the N−H BDE in RNH is much smaller than the C−H BDE in RCH$_2$. Part of the reason for this difference in BDEs could be the difference in hybridization of the X−H bonds that are broken in the two radicals. For example, for R = R′ = H, the CISD/6-311G(2d,p)-optimized bond angle in $^{\bullet}NH_2$ is 102.6°; whereas, the H−C−H bond angles in $^{\bullet}CH_3$ are 120.0°. Comparison of these bond angles indicates that the N−H bonds in $^{\bullet}NH_2$ have less 2s character than the C−H bonds in $^{\bullet}CH_3$, and this difference in hybridization could account for at least some of the difference between the BDEs in these two radicals.

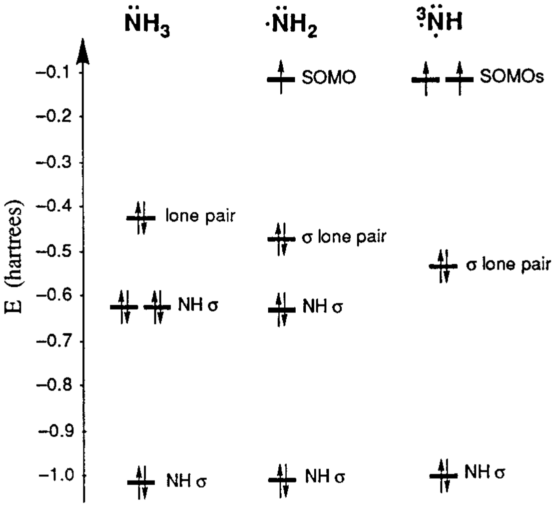
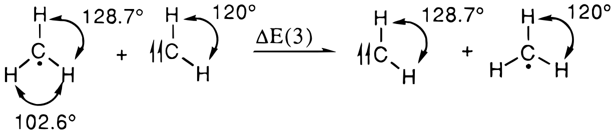


**Figure 1.** R(O)HF/6-311G(2d,p) MO energies (hartrees) for NH$_3$, $^{\bullet}NH_2$, and triplet NH.

An estimate of the size of this effect was obtained by constraining one of the H−C−H bond angles in $^{\bullet}CH_3$ to the H−N−H bond angle of 102.6° in $^{\bullet}NH_2$ and comparing the BDE of one of the C−H bonds, thus constrained, to that of one of the unconstrained C−H bonds in $^{\bullet}CH_3$. To maintain as closely as possible the same hybridization in each of the two triplet methylenes as in the methyl radical from which it was formed, the H−C−H bond angle was frozen at a value of 128.7° in one triplet methylene and at 120.0° in the other. The resulting isodesmic reaction, which probes the effect of hybridization on the BDE of methyl radical, is given in eq 3.



(3)

The geometry constraints in eq 3 make $^{\bullet}CH_3$ and triplet CH$_2$ each higher in energy on the left-hand side of this equation than on the right. Nevertheless, the CISD/6-311G(2d,p) energy of $\Delta E(3) = -4.5$ kcal/mol is 16.3 kcal/mol smaller in size than that of $\Delta E = -20.8$ kcal/mol for the reaction in eq 2 at the same level of theory for R = R′ = H. Therefore, the difference in hybridization between $^{\bullet}NH_2$ and $^{\bullet}CH_3$ probably accounts for less than a quarter of the difference between the BDEs in eq 2 for R = R′ = H.

If the difference in hybridization of the bonds being broken accounts for only a small fraction of the difference between the BDEs of $^{\bullet}NH_2$ and $^{\bullet}CH_3$, the major contributor to the difference between these BDEs must reside in the *changes* in hybridization that accompany formation of triplet NH and triplet CH$_2$.[25] Loss of H$^{\bullet}$ from both $^{\bullet}NH_2$ and $^{\bullet}CH_3$ allows the 2s character in the remaining doubly occupied $\sigma$ orbitals to increase. These increases are evident in (a) the loss of all 2s character from the $\sigma$ orbital that becomes singly occupied on going from $^{\bullet}NH_2$ to triplet NH and (b) the opening of the H−C−H angle on going from $^{\bullet}CH_3$ (H−C−H = 120°) to triplet CH$_2$ (H−C−H = 132.5° at the CISD/6-311G(2d,p) level of theory). However, the electrons in the lone pair orbital of triplet NH benefit from rehybridization more than those in the C−H bonding orbitals of triplet CH$_2$ (or in the N−H bonding orbital of triplet NH), because the lone pair of electrons in NH is localized almost entirely on N; whereas, the pair of electrons in each C−H bond of CH$_2$ is shared between carbon and hydrogen.

Figure 1 gives the R(O)HF/6-311G(2d,p) orbital energies for NH$_3$, $^{\bullet}NH_2$, and triplet NH. It shows graphically the decrease

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(23) The values of 23−25 kcal/mol for the difference between the N−H and C−H BDEs in forming triplet **PhN** from **PhNH** and triplet **PhCH** from **PhCH$_2$** are 10−12 kcal/mol larger than the ca. 13 kcal/mol difference between $\Delta E_{ST}$ in **PhN** and **PhCH**.[1,4−7] Therefore, 10−12 kcal/mol less energy is required to form singlet **PhN** from **PhNH** than to form singlet **PhCH** from **PhCH$_2$**.

(24) Ring expansion of singlet **2-PyCH** to **ACHT** is computed to be exothermic by ca. 26 kcal/mol at the CASPT2N/6-31G* level of theory. The large difference between the energies of the ring expansion reactions of singlet **2-PyCH** and singlet **PhN** to the same molecule (**ACHT**) obviously must be due to the higher energy of singlet **2-PyCH**, relative to singlet **PhN**. It should be noted, however, that CASPT2N/6-31G* overestimates the size of the energy difference between singlet **2-PyCH** and singlet **PhN** by ca. 10 kcal/mol, because the CASPT2N value for $\Delta E_{ST}$ in arylcarbenes is too large by about this amount, but the CASPT2N value for $\Delta E_{ST}$ in **PhN** is in excellent agreement with experiment.[12]

(25) Rehybridization results in both unpaired electrons occupying pure 2p orbitals in triplet NH; whereas, in triplet CH$_2$ one unpaired electron occupies an orbital with substantial amounts of 2s character. A simplistic argument, based on this difference in hybridization, predicts that a C−H bond formed by triplet CH$_2$ should indeed be stronger than an N−H bond formed by triplet NH.

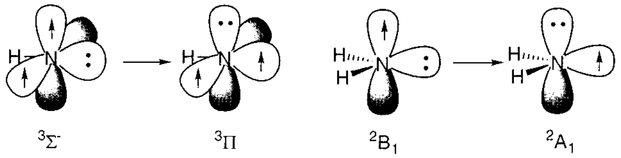

**Figure 2.** Schematic depiction of the $^3\Sigma^- \rightarrow {}^3\Pi$ excitation in NH and the $^2B_1 \rightarrow {}^2A_1$ excitation in $^{\bullet}NH_2$.

in the energy of the lone pair orbital on going from $^{\bullet}NH_2$ to triplet NH. The energy of the lone pair orbital drops by 38 kcal/mol.

The extent to which rehybridization stabilizes the lone pair orbital in triplet NH can be independently assessed by comparing the vertical $^3\Sigma^- \rightarrow {}^3\Pi$ excitation energy in NH with the vertical $^2B_1 \rightarrow {}^2A_1$ excitation energy in $^{\bullet}NH_2$. As shown schematically in Figure 2, in both of these electronic transitions one electron is excited from a lone pair orbital into a 2p $\pi$ orbital. At the geometry of the $^3\Sigma^-$ state of NH, CISD/6-311G(2d,p) calculations place $^3\Pi$ 89 kcal/mol higher in energy than $^3\Sigma^-$; whereas, at the geometry of the $^2B_1$ state of $^{\bullet}NH_2$, $^2A_1$ is calculated to lie only 52 kcal/mol above $^2B_1$. The CISD/6-311G(2d,p) difference of 37 kcal/mol between this pair of excitation energies is very close to the ROHF/6-311G(2d,p) difference of 38 kcal/mol between the energies of the lone pair orbitals in $^{\bullet}NH_2$ and in triplet NH.

Figure 1 shows that the increase in 2s character, due to rehybridization, also stabilizes the lone pair orbital on formation of $^{\bullet}NH_2$ from $NH_3$. The lowering of the energy of the MO that is occupied by the lone pair of electrons in $^{\bullet}NH_2$ acts to stabilize $^{\bullet}NH_2$, relative to $^{\bullet}CH_3$, since, like triplet $CH_2$, $^{\bullet}CH_3$ lacks a lone pair of electrons. The greater stabilization provided by rehybridization in $^{\bullet}NH_2$, compared to $^{\bullet}CH_3$, provides an explanation for why the BDEs[26] of $CH_4$ (105 kcal/mol) and $NH_3$ (109 kcal/mol) are very similar, despite the greater electronegativity of N versus C.[27]

The increase in BDE between $CH_4$ and $NH_3$ is much smaller than the increases between $NH_3$, $H_2O$ (119 kcal/mol), and HF (136 kcal/mol). Unlike $CH_4$, the latter three molecules each have a lone pair of electrons that is stabilized by rehybridization in the radical formed by loss of a hydrogen atom.[28] Therefore, substantial differences in radical rehybridization energies do not act to reduce the effect of the electronegativity of the central atom on the BDEs of $NH_3$, $H_2O$, and HF.[27]

## Conclusions

Our computational results demonstrate that triplet nitrenes are generally more thermodynamically stable than comparable triplet carbenes, as evidenced by comparison of the relative enthalpies of nitrenes and carbenes that are isomers (e.g., **PhN** and **3-PyCH**) and by comparison of the X−H BDEs of RNH and $RCH_2$ radicals. The greater thermodynamic stability of triplet **PhN**, compared to triplet **PhCH**, accounts for the much lower reactivity of the former.[8]

Despite the fact that the energy differences between the lowest singlet states of arylnitrenes and arylcarbenes are smaller than those between the triplet ground states, the energy differences between the singlets are still large enough to explain why (a) the ring expansion of singlet **PhN** is reversible,[2,3] whereas that of singlet **PhCH** is quite exothermic,[1,2] and (b) why singlet pyridyl carbenes (e.g., **2-PyCH** and **3-PyCH**) rearrange to **PhN**.[9] We attribute the greater thermodynamic stability of nitrenes, relative to carbenes, to the presence in the former of a lone pair of electrons which occupies an orbital that is rich in 2s character.

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**Supporting Information Available:** Geometries and energies for molecules discussed in this paper (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(27) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1948.

(28) In the second row of the periodic table, the Si−H BDE in $SiH_4$ is also larger than one would expect on the basis of electronegativity; in fact, it is actually larger than the P−H BDE in $PH_3$. Again, it is the lone pair in $PH_3$ that causes the P−H BDE to be lower than the Si−H BDE of $SiH_4$, but *not* because of rehybridization of $^{\bullet}PH_2$. Rather, the very large amount of 3s character already in the lone pair orbital of $PH_3$ results in the P−H bonds having much less 3s character and, hence, being weaker than the Si−H bonds in $SiH_4$. [Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275].