hydrogenation of the double bond with PtO_2/H_2 takes place exclusively from the sterically least hindered side and gave the *cis*-pyrrolizidinone **10**.[16] Reduction of **10** with $LiAlH_4$ afforded (±)-heliotridane (**1a**) in 54% overall yield from **7**. The preparation of pyrrolizidinone **9** also constitutes a formal total synthesis of (±)-supinidine (**1b**) since **9** has previously been converted into **1b**.[17]

Acknowledgment. Financial support from the Swedish Natural Science Research Council and the Swedish Board of Technical Development is gratefully acknowledged.

Supplementary Material Available: Description of general procedure for the palladium-catalyzed tandem cyclization reaction and listings of spectral data for **3b**, **4a,b**, and **8** (2 pages). Ordering information is given on any current masthead page.

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(17) This transformation involves one step. See ref 16.

Ab Initio Calculations of the Singlet–Triplet Energy Difference in Phenylnitrene

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Depending on the conditions under which phenylnitrene (PhN) is generated, chemistry can be observed from either the singlet or the triplet state.[1] EPR studies by Wasserman and co-workers established that the triplet is the ground state.[2] Photodetachment measurements of phenylnitrene radical anion were interpreted by Drzaic and Brauman in terms of energy differences of 4.3 and 8.8 kcal/mol between the triplet and the two low-lying singlet states.[3] These values, when compared to the energy difference of 36.0 kcal/mol measured between the $^3\Sigma^-$ ground state and the degenerate $^1\Delta$ state of HN,[4] indicate a tremendous stabilization of both singlet states, relative to the triplet, by the phenyl group in PhN.

In order to understand how a phenyl substituent exerts such a large stabilizing effect on both singlet states, we have performed ab initio MCSCF and CI calculations on PhN. Our calculations find that only one of the two degenerate singlet states of HN is significantly stabilized, relative to the triplet, by the phenyl group in PhN. Moreover, the selective stabilization of this singlet is computed to be considerably less than the 32 kcal/mol indicated by the original interpretation of the radical anion photodetachment spectrum.[3]

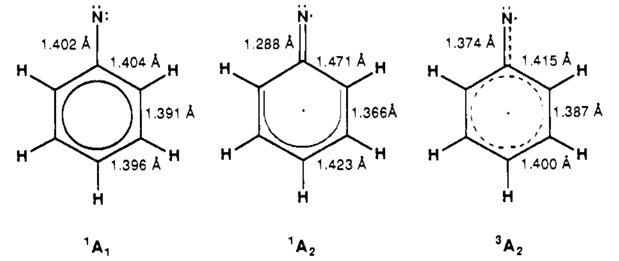

Figure 1. (8/8) MCSCF/3-21G bond lengths in the three lowest states of phenylnitrene.

Table I. Triplet Energies (hartrees) and Singlet–Triplet Energy Differences (kcal/mol) for PhN at (8/8) MCSCF/3-21G Optimized Geometries and for HN at ROHF/3-21G Optimized Geometries

state	(8/8) MCSCF/3-21G	(8/8) CI/6-31G*	π-SDCI/6-31G*	σ-S, π-SDCI/6-31G*
$^3A_2$	−283.0106	−284.5734	−284.6070	−284.7959
$^1A_2$	21.5	17.3	19.5	18.3
$^1A_1$	43.3	39.0	39.8	38.7
$^3\Sigma^-$	−54.6550[a]	−54.9517[a]		−55.0778[b]
$^1\Delta$	44.6	43.2		42.7

[a] ROHF calculation on HN. [b] SDCI calculation on HN.

The geometries of the $^3A_2$, $^1A_2$, and $^1A_1$ states of PhN were optimized with the 3-21G basis set,[5] using an MCSCF wave function that included all configurations in which the six benzene π electrons and the two, highest energy, nonbonding nitrogen electrons were distributed among seven π orbitals and the σ–p orbital that is largely localized on nitrogen.[6] The optimized C–C bond lengths in each state are shown in Figure 1.[7] Vibrational analyses showed the optimized geometries to be minima.[8]

Using the 6-31G* basis set,[9] 8-electron/8-orbital full CI calculations[10] were performed with K orbitals[11] at the 3-21G optimized geometries. The (8/8) MCSCF and CI energies with both basis sets are given in Table I. In order to assess the effect of additional configurations containing all the virtual π orbitals, π-SDCI calculations were performed, using one reference configuration for the two A_2 states and two for $^1A_1$.[10] Correlation between σ and π electrons was also provided by addition of all single σ excitations (σ-S, π-SDCI). The CI results are also given in Table I. For comparison, the results of comparable calculations on HN are also given in Table I.[12]

The results contained in Table I clearly show that the phenyl group provides the most stabilization for $^1A_2$, the state in which one nonbonding nitrogen electron occupies a σ–p orbital and another occupies a π orbital. On going from HN to PhN, this singlet state is stabilized by about 25 kcal/mol, relative to the triplet ground state, resulting in a predicted energy difference between $^1A_2$ and $^3A_2$ in PhN of 18.3 kcal/mol at the σ-S, π-SDCI level. In contrast, $^1A_1$, which consists of two dominant configurations in which the σ–p orbital is either doubly occupied or empty,[13] is stabilized, relative to the triplet, by only about 4 kcal/mol on going from HN to PhN.

The origin of the selective stabilization of $^1A_2$ is indicated by the C–C bond lengths shown in Figure 1. Unlike the case in either $^3A_2$ or $^1A_1$, in $^1A_2$ there is a strong π bond formed between nitrogen and the phenyl group; and an open-shell π electron, which is localized on nitrogen in HN, is highly delocalized into the phenyl

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(7) A complete listing of optimized geometries is available as supplementary material.

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(12) Previous CI calculations with better basis sets have given $^1\Delta$–$^3\Sigma^-$ energy separations of 41.2 kcal/mol (Fueno, T.; Bonacic-Koutecky, V.; Koutecky, J. *J. Am. Chem. Soc.* **1983**, *105*, 5547) and 40.6 kcal/mol (Alexander, M. H.; Werner, H.-J.; Dagdigian, P. J. *J. Chem. Phys.* **1988**, *89*, 1388).

(13) The configuration in which the σ–p orbital is filled is favored in all our calculations, but decreasingly so with more highly correlated wave functions.

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group in this state of PhN. This delocalization is favorable energetically because in $^1A_2$ the nonbonding σ and π electrons have opposite spins, so that the motions of these two electrons are not correlated by the Pauli exclusion principle. Hence, in the $^1\Delta$ state of HN these two nonbonding electrons have a large Coulombic repulsion energy.[14] However, in PhN, delocalization of the π electron into the phenyl group allows these two electrons to occupy different regions of space, thus minimizing their Coulombic repulsion energy.[14,15] In carbenes, too, an adjacent π bond provides selective stabilization for the open-shell singlet state ($^1A''$).[16,17]

Despite the selective stabilization of $^1A_2$ in PhN, we still compute it to lie about 18 kcal/mol above the $^3A_2$ ground state. As shown in Table I, neither this calculated energy difference nor that between the $^1\Delta$ and $^3\Sigma^-$ states of NH shows much sensitivity to the amount of electron correlation provided.

As is the case in calculations on methylene,[18] the results of our calculations and previous[12] calculations on HN suggest that *very large* basis sets appear to be necessary to correlate the two electrons of opposite spin in the lowest singlet, since both are localized on nitrogen. However, in the $^1A_2$ state of PhN the delocalization of the π electron into the phenyl group should allow a modest basis set, like 6-31G*, to provide a much more accurate value than in HN for the energy difference between this singlet and the triplet ground state.[19] It is probably for this reason that our calculated value of 18 kcal/mol for the energy difference between $^1A_2$ and $^3A_2$ in PhN[20] is in excellent agreement with two very recent measurements of this energy separation,[21] both of which came to our attention after our study was completed, and with a reinterpretation,[22] based on our computational results, of the photodetachment spectrum obtained by Drzaic and Brauman.[3]

Acknowledgment. We thank the National Science Foundation for support of this research and for a grant that allowed purchase of the Convex C-210 computer, on which some of these calculations were performed. We also thank the San Diego Supercomputer Center for a generous allocation of computer time, Professor Matthew S. Platz for conversations that stimulated this computational study, Professor G. Barney Ellison for agreeing to simultaneous publication, and Professor Richard N. McDonald for communicating his results to us in advance of publication.

Registry No. HN, 13774-92-0; PhN, 2655-25-6.

Supplementary Material Available: Optimized (8/8) MCSCF/3-21G geometries for the three lowest states of PhN (1 page). Ordering information is given on any current masthead page.

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[17] Our unpublished π-SDCI/6-31G*//(8/8)MCSCF/3-21G calculations on phenylmethylene find that the phenyl group stabilizes the closed-shell singlet ($^1A'$), relative to the triplet, by about 5 kcal/mol; but the open-shell singlet ($^1A''$) is stabilized by four times as much.

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[19] Since in the $^1A_1$ state both nonbonding electrons remain largely localized on nitrogen, it is likely that calculations with 6-31G* overestimate its energy, relative to that of $^3A_2$, by about the same amount as in HN.

[20] CI calculations by Kim et al. (Kim, S.-J.; Hamilton, T. P.; Shaefer, H. F., III. *J. Am. Chem. Soc.* **1992**, *114*, 5349), which appeared after this communication was submitted, obtained essentially the same results as those reported here.

[21] Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.*, following paper in this issue. McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.*, submitted for publication.

[22] An onset, observed around 530 nm, which "in the absence of theoretical guidance, ... was suggested to be an excited state of the anion..., gives a singlet–triplet splitting of about 20 kcal/mol." Brauman, J. I. Private communication.

Photoelectron Spectroscopy of the Phenylnitrene Anion

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This communication is concerned with the spectroscopy of the most famous organic nitrene, phenylnitrene.[1] Our approach to the study of C_6H_5N is to scrutinize the photoelectron spectrum of the radical anion, $C_6H_5N^-$. The negative ion photoelectron spectra furnish us with a measure of the electron affinity of phenylnitrene: EA(C_6H_5N) is 1.45 ± 0.02 eV, and EA(C_6D_5N) is 1.44 ± 0.02 eV. The photoelectron spectrum of $C_6H_5N^-$ is composed of an extensive Franck–Condon envelope, which suggests that the electric charge is strongly delocalized over the radical anion. Besides detachment of the $C_6H_5N^-$ ion to the ground state of phenylnitrene, $\tilde{X}\ ^3A_2$, our spectra also contain bands which we attribute to the singlet state of C_6H_5N, $\tilde{a}\ ^1A_2$. The approximate ΔE_{ST} is 18 ± 2 kcal/mol.

Using phenylazide as a precursor, we prepared negative ions in a hot cathode ion source and extracted the negative ions to form an ion beam with an energy of 700 eV. The $C_6H_5N_3$ was synthesized in roughly 10 g quantities from phenylhydrazine and sodium azide,[2] the deuterated isomer requiring preparation of phenylhydrazine-d_5 from aniline-d_5. The $C_6H_5N^-$ sample was prepared by leaking a mixture of $C_6H_5N_3$ and N_2O gases into the plasma source with a 0.015 in. W filament at a pressure of 0.1 Torr; ion beams of 1–3 nA are commonly achieved. We use the 488-nm (2.540 eV) line of an Ar II laser in an intracavity configuration to study the photoelectron spectrum of the phenylnitrene anion.[3]

$$C_6H_5N^-(v'',J'') + \hbar\omega_{488\,\mathrm{nm}} \rightarrow C_6H_5N(v',J') + e^-(\mathrm{KE}) \quad (1)$$

Photodetached electrons are energy analyzed in a hemispherical electrostatic analyzer with a resolution of about 10 meV (FWHM) as measured by photodetachment of a calibration ion, O^-.

The photodetachment of $C_6H_5N^-$ has been studied in an ICR spectrometer,[4] and the detachment threshold for the phenylnitrene ion was observed at $\lambda_{\mathrm{thresh}}$ = 848 ± 8 nm, which corresponds to an EA(C_6H_5N) of 1.46 ± 0.01 eV. The electron affinity determined in this experiment is completely in accord with both threshold electron affinities. Figure 1 depicts the photoelectron spectra of the $C_6H_5N^-$ and $C_6D_5N^-$ ions. The origin of these spectra is feature A; assignment of the (0,0) band leads to raw electron affinities of the nitrenes. Proper consideration of the rotational, spin–orbit, sequence band shift and scale compression corrections provides us with our final electron affinities: EA(C_6H_5N) is 1.45 ± 0.02 eV, and EA(C_6D_5N) is 1.44 ± 0.02 eV. The ions in Figure 1 are rotationally hot, and this results in extensive congestion of the photoelectron spectra; we estimate T_{rot} to be roughly 1200 °C. Figure 2 shows a Franck–Condon fit to the first band system in the $C_6H_5N^-$ spectrum; this simulation ignores features near the β, γ, and δ bands. The active modes in our simulation are a phenyl ring/C–N distortion at 1300 cm^{-1} and a ring-breathing vibration at 515 cm^{-1}. While we only have an approximate fit to the Franck–Condon profile, it seems certain

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