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]

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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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(14) Review of electron repulsion in open-shell molecules: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1–72.

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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.

(18) Reviews: (a) Davidson, E. R. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 73–105. (b) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531. For more recent calculations, see: Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* **1987**, *86*, 862.

(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.

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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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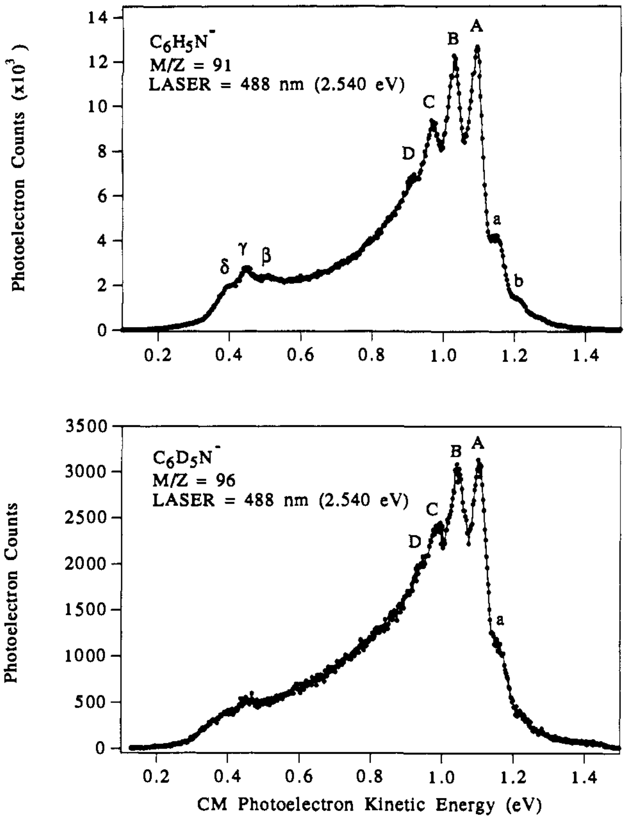


Figure 1. (Top, a) Photoelectron spectrum of $C_6H_5N^-$. The CM kinetic energies (in eV) of the bands are as follows: b, 1.218 ± 0.025; a, 1.154 ± 0.020; A, 1.094 ± 0.012; B, 1.032 ± 0.010; C, 0.974 ± 0.014; D, 0.917 ± 0.020; β, 0.510 ± 0.025; γ, 0.451 ± 0.025; δ, 0.394 ± 0.025. (Bottom, b) Photoelectron spectrum of $C_6D_5N^-$. The CM kinetic energies (in eV) of the bands are as follows: a, 1.161 ± 0.025; A, 1.100 ± 0.012; B, 1.041 ± 0.015; C, 0.985 ± 0.020.

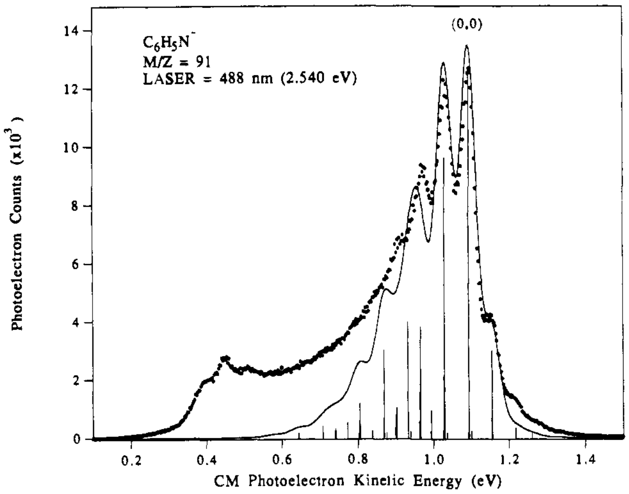


Figure 2. Franck–Condon simulation of the $C_6H_5N^-$ photoelectron spectrum. The points are the data, and the solid line is our fit. The precise constants used in the simulation are combinations of $\omega_1'' = 500$ cm^{-1}, $\omega_1' = 515$ cm^{-1}, $\omega_2'' = 1350$ cm^{-1}, and $\omega_2' = 1300$ cm^{-1}; we estimate an effective vibrational temperature of T_{vib} at approximately 300 °C.

that there is only one state of C_6H_5N present in the region of the A–D features. This is the ground $\tilde{X}$ $^3A_2$ state of phenylnitrene.

The weak features in our photoelectron spectrum at low kinetic energy (β, γ, and δ) are associated with a second electronic state of phenylnitrene. A preliminary spectrum[5] with an Ar III laser ($\hbar\omega_{351\text{nm}}$) has clearly revealed the entire second electronic state of C_6H_5N. The weak features in our 488-nm spectrum (β, γ, and δ in Figure 1) correspond to detachment from hot bands of the ion [($\tilde{a}$ $^1A_2$) $C_6H_5N(v'=0)$ ← ($\tilde{X}$ $^2B_2$) $C_6H_5N^-(v''=1,2,3)$]; scattered electrons from the (0,0) band for the ($\tilde{a}$ $^1A_2$) C_6H_5N ← ($\tilde{X}$ $^2B_2$) $C_6H_5N^-$ transition would appear at 0.29 eV, which is just outside the transmission energy of our hemispheric analyzer. This electronic state corresponds to the first singlet state of phenylnitrene ($\tilde{a}$ $^1A_2$) that has an approximate[6] ΔE_{ST} of 18 kcal/mol.

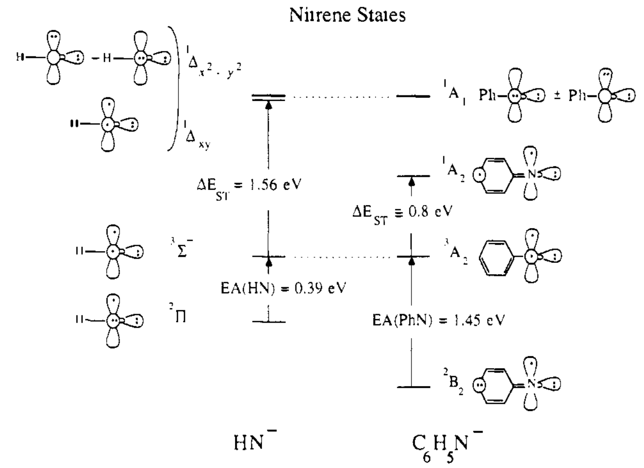
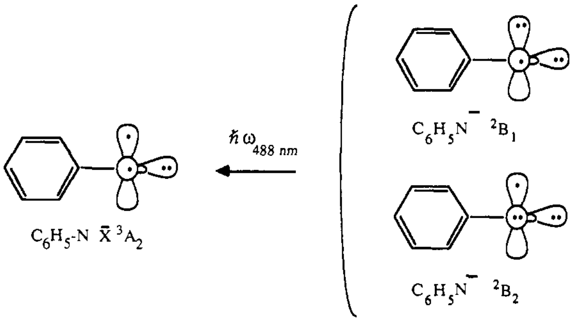


Figure 3. A symbolic comparison of the electronic states of NH with C_6H_5N. Delocalization of the charge in $C_6H_5N^-$ results in an increase in the electron affinity relative to NH^-; delocalization[6] of the radical in the $\tilde{a}$ $^1A_2$ state of C_6H_5N lowers the exchange integral, $K_{\sigma\pi}$, leading to a diminished $\Delta E_{ST}(C_6H_5N)$.

The ground states of several nitrenes have been studied by EPR spectroscopy, and all but aminonitrenes are known to be triplets.[7] Phenylnitrene can be written as a localized diradical with a (p_x,p_y) pair of electrons triplet-coupled. Consequently the ground state of C_6H_5N is $\tilde{X}$ $^3A_2$, and we can represent our negative ion photodetachment experiment as



(2)

Equation 2 suggests that we need to consider two different states for the $C_6H_5N^-$ ion. One of these, $^2B_2$, is a ($\sigma\pi^2$) species while the $^2B_1$ state is a ($\sigma^2\pi$) ion. The extensive Franck–Condon envelope in Figures 1 and 2 is a clear indication[8] that the ground state of the $C_6H_5N^-$ ion has a substantially different geometry than C_6H_5N. This is to be contrasted with the simplest nitrene, HN. The photodetachment spectrum[9] of the localized ion HN^-

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[5] Gilles, M. K.; Cowles, D. C.; Travers, M. J.; Ellison, G. B.; Lineberger, W. C. Unpublished results. Complete Ar III photoelectron spectra of $C_6H_5N^-$ and $C_6D_5N^-$ will be published in a later, full paper.

[6] Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.*, preceding paper in this issue. See also the CISD ab initio study by Kim et al.: Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1992**, *114*, 5349.

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[8] The charge delocalization onto the phenyl ring in $C_6H_5N^-$ is completely analogous to that previously found in the benzyl and phenoxide anions. For example, detachment of the $C_6H_5O^-$ ion is accompanied by excitation of ring breathing modes of the phenyl ring. See: Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes*, in press.

[9] Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1412.

($^2\Pi$) is a pair of vertical transitions, one to the ground state of NH ($^3\Sigma^-$) and the other to the excited singlet state, $^1\Delta$. The extended Franck–Condon contour in our photodetachment spectra with excitation of ring-breathing modes implies that the ground state of the $C_6H_5N^-$ ion is $\tilde{X}\,^2B_2$ and that much of the charge is delocalized from the N atom onto the phenyl ring. This contrasts with the $\tilde{A}\,^2B_1$ ion which localizes the extra electron in the b_2, nonbonding orbital, on the N atom. Preliminary UHF calculations[10] on both states of the $C_6H_5N^-$ ion in a 6-311++G** basis lead to the $^2B_2$ state being stabilized by about 10 kcal/mol below the $^2B_1$ state. Figure 3 is a symbolic drawing which contrasts the electronic states of NH with those of C_6H_5N.

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Registry No. $C_6H_5N_3$, 622-37-7; $C_6D_5N_3$, 85770-99-6; $C_6H_5N^-$, 74586-02-0; $C_6D_5N^-$, 143332-33-6; C_6H_5N, 2655-25-6; C_6D_5N, 143332-34-7.

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[10] GAUSSIAN 90, Revision J: M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1990.

Total Synthesis of the NodRm-IV Factors, the Rhizobium Nodulation Signals

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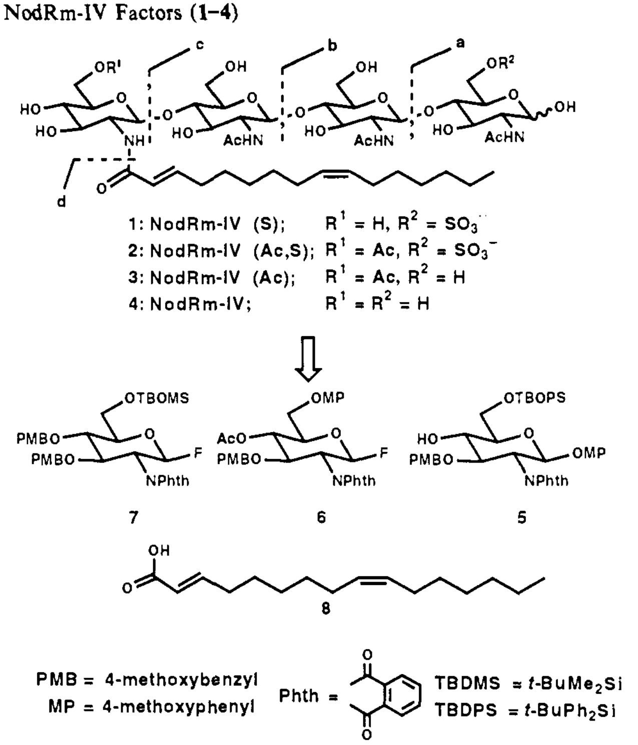
NodRm-IV (S) (**1**) and NodRm-IV (Ac,S) (**2**) are sulfated lipooligosaccharides of *N*-acetyl-D-glucosamine secreted by the microorganism *Rhizobium meliloti*.[1-6] These remarkably specific compounds play a crucial role in the Rhizobium–legume symbiosis by eliciting the formation of nitrogen-fixing root nodules and root hair deformation on alfalfa but not on vetch. Interestingly, the non-sulfated compounds NodRm-IV (Ac) (**3**) and NodRm-IV (**4**) elicit the same organogenesis and root morphology on vetch but not on alfalfa.[5,6] Experiments with mutant strains of *R. meliloti* identified the genes responsible for the sulfation of these lipooligosaccharides.[7] The important actions of these molecules coupled with their fascinating specificity, natural scarcity, and challenging molecular structures prompted us to target them for chemical synthesis. Herein we report the first total synthesis of these substances (**1–4**) in their naturally occurring forms.

Scheme I. Structures and Retrosynthetic Disconnections of NodRm-IV Factors (**1–4**)



Despite their repetitive nature in glucosamine units, the structures of NodRm-IV factors (**1–4**) are synthetically quite challenging due to the presence of unsaturation, nitrogen, and sulfur. This variety of functional groups required a carefully designed and executed strategy. Scheme I presents the retrosynthetic analysis on which the synthesis was based. Thus, disconnections at the indicated bonds led to key building blocks **5–8**. The projected construction called for an a, b, c, d sequence of coupling reactions and selective deblocking of hydroxyl groups.

Coupling of glucosamine derivative **5** with glycosyl fluoride **6** under the Mukaiyama–Suzuki[8] conditions led to disaccharide **9** with a β-glycoside linkage as expected from the directing effect of the *N*-phthalimido group (Scheme II). Liberation of the 4′-OH group followed by attachment of a second glucosamine unit **6** as above resulted in the stereospecific formation of trisaccharide **11**. Having performed their function as activating and β-directing groups, the phthalimide moieties were removed with hydrazine, leading to the triamine **12**, which was acetylated to afford the triacetamide **13**. Introduction of the final glucosamine unit was accomplished using derivative **7** and the above mentioned conditions, furnishing tetrasaccharide **14** stereoselectively. Generation of the free amine functionality from **14** as described above allowed the incorporation of the unsaturated fatty acid chain **8** through intermediate **15** and the action of 2-chloro-1-methylpyridinium

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