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A Determination of the Triplet–Singlet Splitting in Phenylnitrene via Photodetachment Spectroscopy

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Abstract: Photodetachment spectra near threshold have been measured for the phenylnitrene anion. Three onsets are observed and are assigned as transitions to the ground triplet state and the first two singlet states of the phenylnitrene neutral. Theoretical cross sections are calculated and fit to the experimental data in order to assign the wavelength of each onset threshold. From these data, it is found that the first two singlet states of phenylnitrene lie 4.3 ± 0.4 and 8.8 ± 0.5 kcal/mol, respectively, above the ground triplet state. The electron affinity of the triplet phenylnitrene neutral is determined to be 33.7 ± 0.3 kcal/mol.

Molecules possessing unfilled electronic valence levels tend to be very reactive, and thus of much interest to chemists. This is certainly true of the class of compounds known as nitrenes, the nitrogen analogues of carbenes. Like carbenes, nitrenes undergo a variety of addition and insertion reactions and have been implicated as intermediates in a number of chemical reactions.[2]

Due to their high reactivity, it has proven very difficult to obtain spectroscopic information on many nitrene systems. An exception is the simplest nitrene, imidogen (NH), which has been extensively studied by using both experimental and theoretical techniques, and its electronic structure has been fairly well characterized.[3] Information on the electronic structure of other nitrenes, however, is sparse. Most of the current information on substituted nitrenes comes from ESR,[4] absorption,[5-7] and fluorescence[7] studies of nitrenes immobilized in inert matrices at low temperatures. As useful as these approaches have been, they have not been successful in allowing observation of low-lying singlet states of ground-state triplet nitrenes. No measurements of the relative triplet–singlet energy splittings in substituted nitrenes have yet been made at this time.

An alternative method of gaining spectroscopic information on the nitrene systems is through the photodetachment spectrum of the corresponding radical anion of a nitrene (eq 1). For most

$$\text{RN}^- \text{ (doublet)} + h\nu \rightarrow \text{RN (triplet or singlet)} + e^- \quad (1)$$

nitrenes, the first photodetachment onset will correspond to the transition from the doublet state anion to the ground triplet state nitrene. Transitions from the anion to the first and upper singlet states of nitrenes will appear as additional onsets in the photodetachment spectrum. The photon energy difference between these onsets will lead directly to the energy splitting between these different electronic levels. This approach is related quite closely to the previously reported use of negative ion photoelectron spectroscopy to study simple low-valent species such as imidogen[8] (NH) and methylene[9] (CH_2).

In this paper we report the photodetachment spectrum of the gas-phase phenylnitrene radical anion, as measured by using ion cyclotron resonance (ICR) spectrometry and an arc lamp/monochromator light source. The phenylnitrene anion is an attractive species to study for two reasons. First, it is readily formed by low-energy electron impact on phenyl azide (eq 2). This

$$\text{PhN}_3 + e^- \rightarrow \text{PhN}^- + \text{N}_2 \quad (2)$$

process is very efficient, so that extremely low pressures (<5 × 10^{-8} torr) of phenyl azide can be used to form large quantities of the radical anion. This will minimize reactive collisions between the anion and the background azide precursor, leading to long trapping times of the nitrene. Second, the gas-phase ion chemistry of the phenylnitrene anion has been the subject of a number of studies,[10-13] with the observation that the anion does behave like a nitrene radical anion, rather than some rearranged species.

Three low-energy onsets are observed in the phenylnitrene anion photodetachment spectrum reported here, which may be ascribed to transitions from the anion to the lowest energy triplet and to two low-lying singlet states of the phenylnitrene neutral. This is the first direct measurement of the triplet–singlet splitting in a substituted nitrene.

Experimental Section

Photodetachment experiments were performed by using a modified Varian V-5900 ion cyclotron resonance spectrometer to generate, trap, and detect anions. A home-built capacitance bridge circuit[14] was used for ion detection. A Digital Equipment Corporation MINC-11/23 computer was used to collect ion signal level data from the ICR, as well as to control the monochromator micrometer drive through the use of a stepping motor. Photodetachment data were collected by reading a base line from the ICR with no light incident on the ICR cell and then unblocking the light. The computer stepped the monochromator through a given wavelength range, collecting a signal at each wavelength. From 50 to 100 wavelengths were sampled in a run, with a time base of 2–5s per wavelength. Each wavelength range was measured 2–10 times, depending on the signal to noise of the decreases measured. The relative cross sections measured for each run were then averaged together. The general features of each spectrum thus obtained were confirmed by repeating the entire experiment at least one additional time on a different day.

The light source used in this experiment was a Hanovia 1000-W xenon arc lamp. Wavelength selection was made by passing the lamp output through a Schoeffel $^1/_4$-m grating monochromator. The grating used in the monochromator depended on the wavelength of light desired. A set of matched slits was used to determine the output bandwidth of the light from the monochromator. Typically, the narrowest bandwidth that resulted in a reproducible photodetachment cross section spectrum was used.

For the bandwidths used for the determination of the photodetachment onsets reported here, there is roughly a ±4-nm uncertainty in the absolute wavelength assignment for the points in a data run. This uncertainty

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[1] Current address: Taliq Corporation, Mountain View, CA.

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[4] (a) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220. (b) Wasserman, E.; Murray, R. W.; Trozzolo, A. M.; Smolinsky, G. *Ibid.* **1967**, *89*, 5076.

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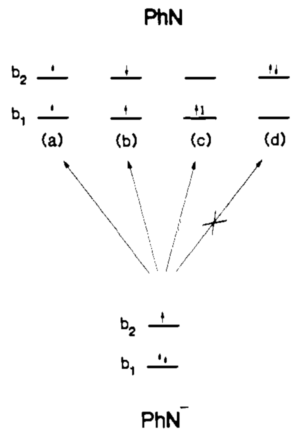

Figure 1. Low-energy transitions for the phenylnitrene anion photodetachment. The relative ordering of the orbitals in the phenylnitrene anion and the phenylnitrene neutral states is taken from SCF 3-21G calculations.[15] Transition d is a two-electron process, and thus it is not expected to be seen in the current set of experiments.

arises from the difficulty in determining the exact center of the band passed by the monochromator. This uncertainty is added to the error limits reported for the assignments of the absolute wavelengths of photodetachment onsets. Since the relative values for a series of onsets in a given run are offset by the same amount, this error does not appear in the values for the energy splittings in phenylnitrene.

The phenylnitrene anion was formed by low-energy (1.0–1.5 V above the trapping plate potential) electron impact of phenyl azide, at phenyl azide pressures of $<5 \times 10^{-8}$ torr. Phenyl azide was obtained from ICN Pharmaceuticals, Inc., as roughly a 30% solution in hexanes. The hexanes were removed by distillation. The phenyl azide was then distilled bulb to bulb on a vacuum line, resulting in a pale yellow solution. This solution was put through several freeze–pump–thaw cycles before being allowed to enter the ICR foreline.

Predicted Photodetachment Transitions Near Threshold

The photodetachment spectrum of the phenylnitrene anion is a rich source of information regarding electronic energy levels in the phenylnitrene system. In order to interpret and assign features in the experimental photodetachment spectrum, it is important to determine which electronic states of the phenylnitrene neutral are accessible from the ground-state anion in a photodetachment process. The electron distribution in the highest occupied molecular orbitals in phenylnitrene is required for the calculation of a theoretical photodetachment cross section, which is used to determine more precisely the threshold energies for the different photodetachment onsets (vide infra).

Electron spin resonance work has shown that the phenylnitrene neutral is probably a ground-state triplet.[4a] From symmetry considerations, the two highest occupied molecular orbitals possess b_1 and b_2 symmetry for the C_{2v} phenylnitrene system, with each orbital containing one electron in the ground-state triplet. In the phenylnitrene anion, one of these orbitals will possess a second electron, leading to a doublet ground state in the anion. The three lowest lying neutral excited states should be singlets, with the b_1 or b_2 orbitals doubly occupied, or both singly occupied; see Figure 1.

This picture is supported by ab initio SCF calculations at the 3-21G level carried out by Van-Catledge[15] on the phenylnitrene system. In the anion, the two highest orbitals have b_1 and b_2 symmetry, with the b_2 orbital containing the unpaired electron (Figure 1). The b_2 orbital in phenylnitrene may be referred to as a π-orbital,[2] as it consists of p orbitals perpendicular to the plane of the phenyl ring. The b_1 orbital is more like a set of σ orbitals, consisting of in-plane p orbitals also delocalized to some extent into the phenyl ring.

The SCF calculations show that the ground state for the phenylnitrene neutral is a triplet, with the three different singlet states lying higher in energy. These states are diagrammed in Figure 1 and are drawn in order of increasing energy as determined by the SCF calculation.[16] Only states a, b, and c are accessible via a one-electron photodetachment transition; the transition to state d is not accessible, as this is a two-electron process and has low probability.

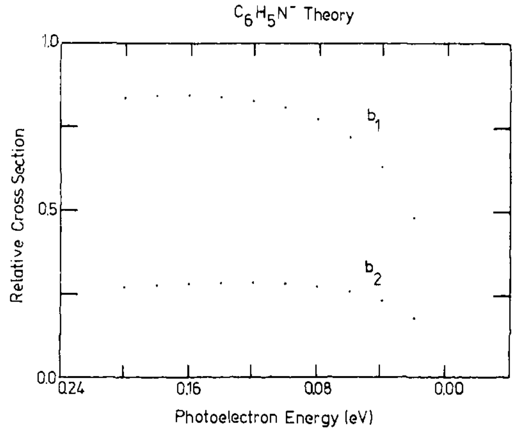

Figure 2. Theoretical cross sections for photodetachment from the b_1 and b_2 orbitals in the phenylnitrene anion.

According to the 3-21G calculation,[15] the transition from the doublet anion to the triplet ground state of the neutral must involve removal of an electron from the b_1 orbital rather than from the b_2 HOMO. This will be generally true provided that no orbital reordering occurs and that the triplet and singlet states lie fairly close in energy.

In order to interpret the photodetachment spectrum of the phenylnitrene anion, it is important to have an idea of what the shape of the photodetachment cross sections from these various orbitals will look like. Theoretical cross sections for photodetachment from phenylnitrene were calculated employing a formalism[17,18]that has shown good agreement with experiment for a number of molecular anions. This formalism treates the photodetachment process as a one-electron, dipole-allowed transition from the anion to produce a neutral plus a continuum electron. The photodetachment cross section is obtained by calculating the matrix element (eq 3), where ψ_i is the initial state of the state of

$$\sigma \propto |\langle \psi_i | \mathbf{r} | \psi_f \rangle|^2 \qquad (3)$$

the anion, **r** the dipole operator, and ψ_f the final state, including the detached electron. It has proven sufficient in the past to treat the continuum electron as a plane wave, and orthogonalize it only to the highest occupied molecular orbital of the anion. The other molecular orbitals are assumed to be unchanged upon photodetachment. The molecular orbital coefficients of the anion may be taken from a semiempirical calculation, such as the INDO method.

This cross-section calculation was performed for photodetachment from both the b_2 and b_1 orbitals of the phenylnitrene anion. The molecular orbital coefficients were obtained from an INDO calculation[19] and are as follows:

$$\psi_{b_2} = -0.722\mathrm{N}(p_z) - 0.0538\mathrm{C}_1(p_z) - 0.3906\mathrm{C}_2(p_z) + 0.0274\mathrm{C}_3(p_z) + 0.4109\mathrm{C}_4(p_z) + 0.0274\mathrm{C}_5(p_z) - 0.3906\mathrm{C}_6(p_z)$$

$$\psi_{b_1} = -0.8573\mathrm{N}(p_x) + 0.2103\mathrm{C}_1(p_x) + 0.1383\mathrm{C}_2(s) - 0.2057\mathrm{C}_2(p_x) + 0.1410\mathrm{C}_2(p_y) - 0.0449\mathrm{C}_3(s) + 0.455\mathrm{C}_3(p_x) - 0.0483\mathrm{C}_3(p_y) - 0.0659\mathrm{C}_4(p_x) + 0.0449\mathrm{C}_5(s) + 0.0455\mathrm{C}_5(p_x) + 0.0483\mathrm{C}_5(p_y) - 0.1383\mathrm{C}_6(s) - 0.2057\mathrm{C}_6(p_x) - 0.1410\mathrm{C}_6(p_y) - 0.0877\mathrm{H}_2(s) + 0.1134\mathrm{H}_3(s) - 0.1134\mathrm{H}_5(s) + 0.0877\mathrm{H}_6(s)$$

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(15) Van-Catledge, F. A. (Du Pont), personal communication.

(16) In contrast, INDO calculations (Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970) place the unpaired electron in the phenylnitrene anion in the b_1 orbital and predict state c in Figure 1 to be the lowest singlet in the neutral phenylnitrene. The triplet state a is predicted by INDO to be the ground state in agreement with the 3-21G calculation.

(17) Reed, K. J.; Zimmerman, A. H.; Andersen, H. C.; Brauman, J. I. *J. Chem. Phys.* **1976**, *64*, 1368.

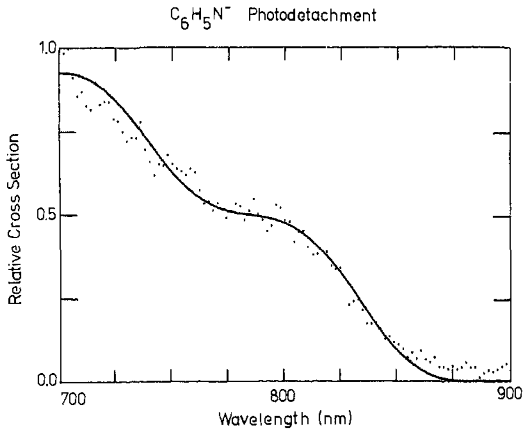

Figure 3. Experimental (•) and theoretical (–) photodetachment cross sections for the phenylnitrene anion from 700 to 900 nm. The experimental bandwidth is 40 nm at fwhm. Onsets for the theoretical curve were chosen at 848 and 752 nm.

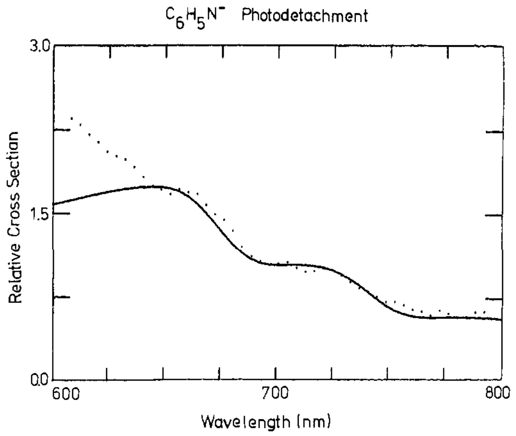

Figure 4. Experimental (•) and theoretical (–) photodetachment cross sections for the phenylnitrene anion from 600 to 800 nm. The experimental bandwidth is 23 nm at fwhm. Onsets for the theoretical curve were chosen at 752 and 672 nm.

This numbering scheme labels the carbon attached to the nitrogen as C_1, and then advances around the ring.

The results of this calculation are shown in Figure 2. As observed, the shapes of the cross sections for the b_1 and b_2 orbitals are very similar, rising sharply at the threshold. This is not surprising, as the slope at the threshold is determining by the angular momentum of the orbital from which the electron is being detached.[17] Since both the b_1 and b_2 orbitals possess a large component of a p orbital on the nitrogen, the resulting cross sections will look very much like s waves, with sharply rising values near threshold. Both cross sections flatten out at a small energy above threshold and remain relatively constant. The magnitude of the cross section for photodetachment from the b_1 orbital is predicted to be somewhat larger than that from the b_2 orbital. However, the accuracy of the relative magnitudes of calculated cross sections has not been tested, so we do not attach any importance to that particular difference. Aside from the difference in magnitude, the cross-section shapes are virtually identical for the b_1 and b_2 orbitals, so that it is not possible in this case to differentiate the onsets to the b_1 and b_2 orbitals on the basis of cross-section shapes.

In order to fit the theoretical curves to the experimental cross section, it is also necessary to compensate for the bandwidth of the monochromator used to select the wavelength of the incident light in the photodetachment experiment. This was accomplished by convoluting the predicted cross sections with a triangular slit function over the bandwidth of the light used in the experiment. The different onsets were added together to form a composite spectrum before the convolution was performed. One result of the convolution is to smooth out any structure smaller than the instrumental bandwidth.

Experimental Cross Section for the Phenylnitrene Anion

The photodetachment spectrum of the phenylnitrene anion from 900 to 700 nm is shown in Figure 3. This spectrum was measured with a 40-nm monochromator bandwidth. There are two onsets near 850 and 750 nm which rise rather sharply and then turn over and flatten out. This structure may be modeled by using the theoretical cross section calculated for phenylnitrene anion. The solid curve in Figure 3 shows the result of convoluting two onsets of equal intensity, one at 848 nm and the other at 752 nm; there is good agreement between the experimental and theoretical curves in this region.

Figure 4 shows the photodetachment spectrum for the phenylnitrene anion from 800 to 600 nm, employing a 23-nm bandwidth for the monochromator. Aside from the onset already seen at 752 nm, another onset appears at roughly 680 nm. This region was modeled as before, with one onset taken at 752 nm and another onset at 672 nm. The 672-nm onset was given an intensity 1.5 times that of the 752-nm onset. There is again good agreement between the experimental and calculated cross sections for the observed onsets, although the experimental cross section deviates from the calculated cross section below 650 nm.

At approximately 650 nm the photodetachment cross section again rises sharply (Figure 4). None of the structure below 650 nm could be modeled by using the theoretical cross section, in contrast to the threshold region. As will be discussed in a separate paper,[20] this and other, lower wavelength structure evident in the phenylnitrene anion spectrum can be assigned to transitions to electronically excited states of the anion. This structure appears very similar to the short-wavelength photodetachment spectra of the anilide and benzyl anions.[20]

Assignment of Onsets in the Phenylnitrene Anion Photodetachment Spectrum

The ability of the theoretical model to fit the first three onsets observed in the phenylnitrene anion photodetachment spectrum indicates that these are direct photodetachment transitions to different final states of the phenylnitrene neutral. For phenylnitrene, these transitions may be to one of the different electronic states previously mentioned or to an excited vibrational level of one of these electronic states.

It is unlikel that any of these transitions involve excited vibrational levels, however, considering the intensity and energy spacing of the different onsets. Transitions to different vibrational levels of a given electronic state are governed by the Franck–Condon factors for that transition, and these depend strongly on the relative geometries of the anion and the neutral product. For the phenylnitrene anion, removal of an electron would not be expected to alter the structure of the phenyl ring to any great extent, although it might affect the bonding between the nitrogen substituent and the ring. This possibility was checked by performing a series of INDO calculations on the phenylnitrene system, optimizing the carbon–nitrogen bond length and angle for the anion, neutral triplet, and neutral singlet (b_2) systems. These calculations show that there is very little difference (<0.02 Å) in the optimum C–N bond length for the phenylnitrene anion and the neutral systems. The optimum bond angle in each system places the nitrogen in the place of the phenyl ring and on the C_2 axis.

These optimization calculations indicate that the phenylnitrene anion and the resulting neutral product from photodetachment should possess similar geometries. This makes it unlikely that the Franck–Condon factors for transitions to excited vibrational

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(18) Engelking, P. C. *Phys. Rev. A* **1982**, *26*, 740.

(19) Although the INDO calculation gives an incorrect ordering of energy levels (relative to 3-21G), the wave functions are likely to be acceptable for calculation of the photodetachment cross sections, as only the atomic orbital coefficients of HOMO enter into the calculation. This is supported by the agreement between the calculated and experimental cross sections.

(20) Drzaic, P. S.; Brauman, J. I., submitted for publication.

Table I. Absolute and Relative Energies for Electronic Levels in phenylnitrene

state	onset, nm	absolute energy, kcal/mol	rel energy, kcal/mol
T_0	848 ± 8	33.7 ± 0.3	0
S_0	752 ± 8	38.0 ± 0.4	4.3 ± 0.4
S_1	672 ± 8	42.5 ± 0.5	8.8 ± 0.5

levels of phenylnitrene are as large as the diagonal, 0–0 transition. Any transitions to excited vibrational levels of the neutral will probably exhibit a much smaller intensity than the transition between the same vibrational level in the anion and neutral. As seen, the first two onsets observed in the photodetachment spectrum (Figures 3 and 4) of phenylnitrene are of roughly the same intensity, indicating that they do not belong to transitions to different vibrational levels of the same excited state. Additionally, since the third onset is much larger than either of the first two, it is improbable that it belongs to a transition to an excited vibrational level of the same electronic state of one of the lower energy onsets.

It is also necessary to consider whether the first or second onsets observed in this spectrum are due to hot band transitions from excited vibrational levels of the anion to lower levels, of the neutral. This is a distinct possibility, since the exothermicity of the electron capture process producing phenylnitrene can be estimated as roughly 30 kcal/mol.[21] Although collisional and radiative processes will tend to thermalize ions trapped for hundreds of milliseconds in the ICR (as in this case), an internal energy level of 30 kcal/mol makes it possible for a significant fraction of the phenylnitrene anions to populate a 4.4-kcal/mol oscillator (1500 cm^{-1}; the energy gap between the two closest onsets).

It is very improbable, however, that at these levels of internal excitation only one mode would contribute to hot band structure. Many other high- and low-frequency modes in the anion would also be populated, and onsets of different intensities should appear for these oscillators. The resulting spectrum would then appear as a number of closely spaced onsets, which would be flattened and smoothed by the bandwidth of the light used in this experiment. This "composite" cross section would not look like a single onset but would be much broader and shallower in slope. Since the spectrum measured here is so successfully fit by three widely spaced onsets, it is probable that the ions are more or less thermalized, and hot bands make only a small contribution to the observed cross section.

The first three onsets in the phenylnitrene photodetachment spectrum and thus assigned as transitions to the three lowest electronic states of the phenylnitrene neutral. On the basis of ESR work[4a] the first transition is assigned to the triplet ground state and corresponds to the electron affinity of ground-state phenylnitrene. The second and third transitions involve transitions to singlet states of the nitrene. The absolute energies and the error limits were determined by fitting the theoretical cross section at different onset energies to the measured spectrum for each of the three onsets. These energies, as well as the relative splitting between the states, are given in Table I. These values represent the first measured splitting between triplet and singlet states in a substituted nitrene.

These experiments cannot place the relative ordering of orbitals in either the phenylnitrene anion or neutral, since the photodetachment cross section for the removal of an electron from either the b_2 or b_1 orbitals is calculated to have the same shape (vide supra). The experimental cross sections all show roughly the same shape, although it is interesting that the first two onsets have approximately the same magnitude, while the third onset is much larger. It is not possible, however, to use this difference in cross-section magnitude to assign the onsets to specific transitions.

The ESR study[4a] of the phenylnitrene neutral leads to a fairly secure assignment of the first photodetachment onset as a transition to the ground-state triplet, with the next two onsets belonging to higher energy singlet states of the phenylnitrene neutral. The precise identity of the higher energy singlet levels in the phenylnitrene neutral cannot yet be assigned experimentally. The ordering of the b_1 vs. b_2 orbitals in the phenylnitrene anion and triplet and the various singlet states of the phenylnitrene neutral are taken from a SCF 3-21G calculation[15] (Figure 1).

The relative position and energy differences between these levels differs greatly from that observed in the simplest nitrene, imidogen. The highest occupied orbitals in NH are a pair of degenerate p orbitals on the nitrogen, with the lowest level being the $^3\Sigma^-$ state. The next two higher energy states are the $^1\Delta$ and $^1\Sigma^+$ levels, respectively. In NH there are large contributions from the electron–electron Coulomb and exchange integrals. The contribution from the exchange integral[22] is very large in NH, as evidenced by the large splitting[23] between the $^3\Sigma^-$ and $^1\Sigma^+$ levels (2.63 eV). Although the $^1\Delta$ state will be destabilized relative to the $^1\Sigma^+$ state by the increased Coulombic repulsion of having two electrons in the same orbital, the $^1\Delta$ state is still much lower in energy than the $^1\Sigma^+$ state[21] (1.07 eV) due to the unfavorable exchange interaction present in the $^1\Sigma^+$ state.[22]

The exchange interaction in the phenylnitrene system, however, seems to be much less important than that in imidogen. One reason for this effect is that the two highest orbitals in phenylnitrene are no longer degenerate, but are split in energy due to different interactions with the phenyl substituent. These two orbitals are also separated in space and more diffuse than in NH. This leads to lessened contributions from the exchange and Coulomb interactions due to reduced spatial overlap of the orbitals. This reduced overlap is reflected by the 4–5-kcal/mol splitting between the various levels in phenylnitrene, compared to the 20–30-kcal/mol splitting between levels in NH. Coulombic interactions, as well as the energy splitting between the b_1 and b_2 levels, are likely as important in phenylnitrene as the exchange interactions.

Summary

The photodetachment spectrum of the phenylnitrene anion has led to a direct determination of the energy splittings between the ground triplet state and two upper singlet states of the phenylnitrene neutral. The precision of these determinations was improved by fitting theoretical photodetachment cross sections to the experimental data in order to determine the threshold wavelength for each onset. The splittings between these levels are much smaller than the energy splittings between corresponding states in imidogen, NH. This is due to the greater diffuseness and spatial separation of the molecular orbitals in the phenylnitrene compared to imidogen.

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Registry No. Phenylnitrene radical anion, 74586-02-0.

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(21) This value is determined by using the heats of formation for the species involved in the reaction $PhN_3 + e^- \rightarrow PhN^- + N_2$. (a) $\Delta H_f°(PhN_3)$ = 92 kcal/mol (est): Shaw, R. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed., Wiley: New York, 1978; Part 1. (b) $\Delta H_f°(PhN^-)$ = 60 ± 2 kcal/mol: ref 11. (c) $\Delta H_f°(e^-) = 0$; $\Delta H_f°(N_2) = 0$.

(22) To a first approximation, the energy of the $^3\Sigma^-$ state in NH may be given as $E_{core} + J_{12} - K_{12}$, while the $^1\Sigma^+$ state has energy $E_{core} + J_{12} + K_{12}$. J_{12} and K_{12} are the Coulomb and exchange interactions, respectively, between the degenerate highest occupied p orbitals in NH. The $^1\Sigma^+$ state, in comparison, has energy $E_{core} + J_{11}$, where J_{11} is the Coulombic repulsion between the two electrons in the same orbital.

(23) Okabe, H. "Photochemistry of Small Molecules"; Wiley-Interscience: New York, 1978; pp 193–195.