

Experimental Confirmation of the Iminocyclohexadienyl Cation-like Structure of Arylnitrenium Ions: Time-Resolved IR Studies of Diphenylnitrenium Ion

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Nitrenium ions (R_2N^+)¹ are reactive intermediates involved in a variety of organic reactions² and have also been implicated as carcinogens produced from aromatic amine metabolism.³ Because of this relevance, the chemistry of nitrenium ions has recently received increasing attention. Nevertheless, when compared with their isoelectronic counterparts, carbenes ($R_2C:$) and carbenium ions (R_2CH^+), very little of our understanding of nitrenium ions comes from direct spectroscopic methods. For example, although diphenylcarbene⁴ and diphenylcarbenium ion⁵ have been the subject of variety of spectroscopic investigations over the past 20 years, diphenylnitrenium ion has only very recently been detected by transient absorption spectroscopy.⁶

On the basis of both experiment and theory, aryl nitrenium ions have been proposed to possess significant iminocyclohexadienyl cation character (Figure 1). Nucleophiles react with singlet nitrenium ions not at nitrogen, but by attacking the aromatic ring to give ultimately *ortho*- and *para*-substituted amines (Scheme 1).⁷ McClelland and co-workers have demonstrated that the basicities of 4-biphenyl- and 2-fluorenylnitrenium ions are consistent with those expected for an imine

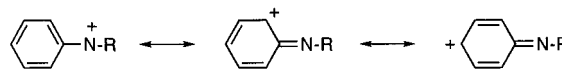
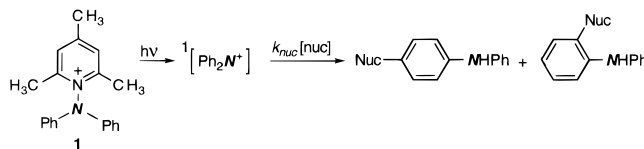


Figure 1. Important resonance contributors for aryl nitrenium ions.

Scheme 1



with a nearby positive charge.⁸ They have also pointed out the close similarity of the absorption spectra of *N*-H and *N*-acetyl aryl nitrenium ions,⁸ again consistent with the chromophore having substantial cyclohexadienyl cation character. Recent calculations are also in agreement with such a structure.⁹ Thus, singlet phenyl- and diphenylnitrenium ion have been calculated to have significantly shortened C–N bonds and alternating C–C bond lengths due to resonance delocalization. In order to provide spectroscopic confirmation of this structure, we are pleased to report herein a time-resolved infrared (TRIR) study of diphenylnitrenium ion (Ph_2N^+). This work represents the first vibrational characterization of an aryl nitrenium ion.

TRIR experiments were performed following the method of Hamaguchi and co-workers.¹⁰ This method allows access to the entire mid-IR spectrum ($4000\text{--}800\text{ cm}^{-1}$) with high sensitivity and sufficient time (*ca.* 50 ns) and frequency ($4\text{--}16\text{ cm}^{-1}$) resolution to probe a wide range of transient intermediates in solution. Briefly, the broad-band output of a newly developed MoSi₂ infrared source (JASCO) is crossed with excitation pulses (266 nm, 10 ns, 0.4 mJ) from a Continuum HPO-300 diode-pumped Nd:YAG laser. Changes in infrared intensity are monitored by a MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1), amplified, and digitized with a Tektronix TDS520A oscilloscope. The experiment is conducted in the dispersive mode with a JASCO TRIR-1000 spectrometer. In order to obtain spectra with sufficient sensitivity, several thousand laser shots are typically signal averaged at each IR frequency of interest. Since data are collected at 200 Hz, a flow cell is necessary to prevent excessive sample decomposition. A reservoir of *ca.* 15 mL solution is continually circulated between two calcium fluoride salt plates.

Following the recently reported laser flash photolysis (LFP) study,⁶ Ph_2N^+ was produced by photolysis of 1-(*N,N*-diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate (**1**, Scheme 1). This method of nitrenium ion production has been developed by Takeuchi¹¹ and by Abramovitch.¹² Figure 2 shows the TRIR difference spectra observed from 1700 to 1200 cm^{-1} over the first 0.5 μs following photolysis of pyridinium ion **1a** and its ¹⁵N-labeled analogue **1b** (8 mM) in argon-saturated acetonitrile-*d*₃. (Only the nitrogen shown in italics in Scheme 1 is labeled.) A fresh reservoir of solution was used for each 100 cm^{-1} segment of the data set. Acetonitrile-*d*₃ was used as the solvent in order to shift a strong acetonitrile IR band at 1430 cm^{-1} out of the spectral region of interest. (The detection of transient species is more problematic in regions with strong solvent bands due to the low transmission of IR light.¹⁰)

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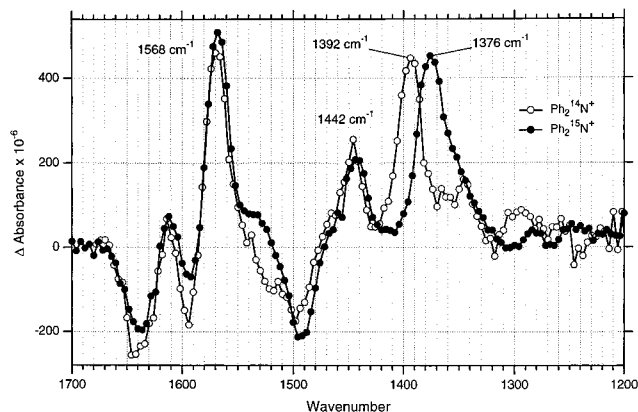


Figure 2. TRIR difference spectra observed over the first 0.5 μ s following photolysis (266 nm, 10 ns, 0.4 mJ) of pyridinium ion **1a** and its ^{15}N -labeled analogue **1b** (8 mM) in argon-saturated acetonitrile- d_3 .

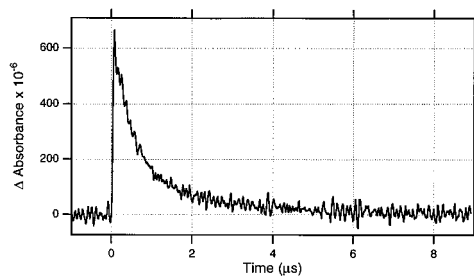


Figure 3. Kinetic trace observed at 1392 cm^{-1} following 266 nm photolysis of **1a** (8 mM) in argon-saturated acetonitrile- d_3 . The lifetime of Ph_2N^+ under these conditions is $0.97\ \mu\text{s}$.

The negative bands observed in Figure 2 are due to depletion of pyridinium ion **1**. The positive bands at 1568 , 1442 , and 1392 (1376) cm^{-1} are assigned to singlet Ph_2N^+ on the basis of the following: (1) The observed rate of decay for each of these signals (e.g., Figure 3) indicates that the lifetime of Ph_2N^+ under the conditions of the TRIR experiment is *ca.* $1\ \mu\text{s}$, consistent with the previous LFP study.^{6,13} (2) These decay rates are unaffected by oxygen. (3) Each of the signals is quenched by nucleophiles such as Cl^- , I^- , and MeOH. The rate constants for decay at 1392 cm^{-1} (k_{obsd}) were measured as a function of nucleophile concentration and analyzed according to the pseudo-first-order equation $k_{\text{obsd}} = k_0 + k_{\text{nuc}}[\text{nucleophile}]$, where k_{nuc} is the second-order rate constant for reaction of Ph_2N^+ with nucleophiles and k_0 is the rate of decay of Ph_2N^+ in the absence of nucleophiles. Values for k_{nuc} (Table 1) are consistent with previous work and confirm that halide ions react significantly faster than alcohol.^{6,14} (4) At longer times, additional IR bands appear that we attribute to the diphenylamine radical and radical cation, intermediates detected in previous photochemical studies of pyridinium ions.⁶ The vibrational characteristics of these species will be addressed in a future publication.

The major IR bands in the spectral region $1700\text{--}1200\text{ cm}^{-1}$ for Ph_2N^+ are compared with those of diphenylamine (Ph_2NH)

(13) The rate of decay of Ph_2N^+ is weakly dependent on the initial concentration of pyridinium ion **1**. Lifetimes determined by LFP and TRIR spectroscopy are equivalent provided the starting concentrations of pyridinium ion **1** are comparable. (For $[\text{1}] = 8\text{ mM}$, the lifetime of Ph_2N^+ is $0.97\ \mu\text{s}$.)

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Table 1. Second-Order Rate Constants Observed in Acetonitrile (LFP) or Acetonitrile- d_3 (TRIR) for the Reaction of Ph_2N^+ with Nucleophiles

nucleophile	$k_{\text{nuc}}\ (\text{M}^{-1}\ \text{s}^{-1})$	
	by LFP ^a	by TRIR ^b
I^-	1.0×10^{10}	$(1.1 \pm 0.1) \times 10^{10}$
Cl^-	1.0×10^{10}	$(0.9 \pm 0.1) \times 10^{10}$
MeOH	5.2×10^6	$(7.0 \pm 0.5) \times 10^6$

^a Reference 6. ^b This work.

Table 2. Major IR Bands of Ph_2N^+ and Ph_2NH Observed from 1700 to 1200 cm^{-1}

	C–N stretch (cm^{-1})	C–C stretch (cm^{-1})
$\text{Ph}_2^{14}\text{N}^+$ ($\text{Ph}_2^{15}\text{N}^+$)	1392 (1376); $\Delta\nu = 16$	1442 (1440), 1568 (1568)
$\text{Ph}_2^{14}\text{NH}$ ($\text{Ph}_2^{15}\text{NH}$)	1320 (1304); $\Delta\nu = 16$	1495 (1493), 1597 (1594)

in Table 2. Bands for Ph_2N^+ were assigned on the basis of this comparison, and the outcome of ^{15}N -labeling shown in Figure 2. The only Ph_2N^+ IR band shifted upon ^{15}N -labeling is that observed at 1392 cm^{-1} . Thus, this band is assigned to a C–N stretch, whereas those observed at 1568 and 1442 cm^{-1} are assigned to C–C stretches. Preliminary density functional calculations show good agreement with the values for the experimentally observed IR bands.¹⁵ The detailed nature of these modes, however, appears to be more complex than simple localized C–N or C–C vibrations and will be quantitatively addressed in future work.

The importance of iminocyclohexadienyl cation-like resonance structures for Ph_2N^+ (Figure 1) is reflected in the observed IR bands. For example, when compared with the corresponding band in Ph_2NH (Table 2), the C–N stretching vibration in Ph_2N^+ shows more double bond character. Density functional calculations^{9b} indicate that the two C–N bonds in Ph_2N^+ are equivalent and shortened to $1.351\ \text{\AA}$ from $1.40\ \text{\AA}$ in Ph_2NH .¹⁶ The C–N bond is calculated to be shortened even further to $1.308\ \text{\AA}$ in phenylnitrenium ion (PhNH^+), since delocalization is limited to one phenyl ring.^{9b} On the basis of these calculations and our results for Ph_2N^+ , the C–N bond in PhNH^+ is expected to be shifted to a frequency even higher than 1392 cm^{-1} . In future TRIR studies a series of *para*-substituted phenylnitrenium ions will be examined to determine how electronic factors influence structure and ultimately reactivity.

In summary, we report the first vibrational characterization of an aryl nitrenium ion by TRIR spectroscopy. This study provides direct experimental confirmation of the iminocyclohexadienyl cation-like structure of aryl nitrenium ions inferred from previous experimental and theoretical work. In addition, these results demonstrate the potential of TRIR spectroscopy to establish important structure/reactivity relationships for short-lived reactive intermediates.

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