

Nitrogen Chemistry

Reactivity of Diarylnitrenium Ions

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Abstract: Hydride abstraction from diarylamines with the trityl ion is explored in an attempt to generate a stable diarylnitrenium ion, Ar_2N^+ . Sequential H-atom abstraction reactions ensue. The first H-atom abstraction leads to intensely colored aminium radical cations, $\text{Ar}_2\text{NH}^{+\bullet}$, some of which are quite stable. However, most undergo a second H-atom abstraction leading to ammonium ions, Ar_2NH_2^+ . In the absence of a ready source of H-atoms, a unique self-abstraction reaction occurs when $\text{Ar}=\text{Me}_3\text{C}_6$, leading to a novel iminium radical cation, $\text{Ar}=\text{N}^+\text{Ar}$, which decays via a second self H-atom abstraction reaction to give a stable iminium ion, $\text{Ar}=\text{N}^+\text{HAr}$. These products differ substantially from those derived via photochemically produced diarylnitrenium ions.

Introduction

Nitrenium ions, R_2N^+ , isoelectronic with carbenes, are highly reactive intermediates of dicoordinate positively charged nitrogen having two free electrons.^[1–4] While known as short-lived species, the replacement of C-bonded with N-bonded substituents (R) can greatly stabilize two-coordinate cations,^[5–7] albeit at the loss of nitrenium ion character. There is a single report of room temperature stability and isolation of a C-bonded nitrenium ion.^[8] The substituents are *meso*-porphyrins but in the absence of IR data, which should be diagnostic,^[9] it is difficult to be certain that this apparent nitrenium ion is not instead an amine with a porphyrin π -radical cation substituent.

We are exploring the possible stabilization and potential isolation of nitrenium ions with bulky aryl substituents. This strategy has been successful in the isolation of the first silylium ion,

Mes_3Si^+ ,^[10] and the first borinium ion, Mes_2B^+ .^[11] (Mes = mesityl). We employ carborane anions as counterions in these studies because of their legendary inertness and negligible nucleophilicity.^[12]

Mono-aryl nitrenium ions, ArNH^+ , have been intensively investigated because of their suspected role in carcinogenesis^[13,14] and their arguable role in the formation of conducting polyanilines.^[15] Diaryl nitrenium ions have received much less attention. Diphenyl and di-*p*-halophenyl nitrenium ions,^[16–18] as well as carbazole analogues,^[19,20] have been investigated computationally and experimentally via laser flash photolysis and product trapping. Their lifetimes are short and, based on transient spectra and product analysis, their electronic states are deduced to be singlets. In general, singlets act as Lewis acids adding nucleophiles whereas triplets act as diradicals, sequentially abstracting H-atoms. Herein, we communicate results from attempts to generate bulky diarylnitrenium ions on a synthetic scale.

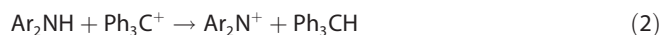
Results and Discussion

Synthesis

Because of the availability of diphenylchloroamine, Ph_2NCl , we utilized halide abstraction by silylium ion-like carboranes^[21] in attempts to generate the diphenyl nitrenium ion (Eq. (1)). The counterion of choice is the undeca-chlorocarborane $\text{CHB}_{11}\text{Cl}_{11}^-$, abbreviated $\{\text{Cl}_{11}^-\}$, and the solvent is weakly nucleophilic *o*-dichlorobenzene (ODCB).



For bulkier diarylamines, where the corresponding chloroamines are unavailable, hydride abstraction using trityl ion is the preferred route (Eq. (2)). The investigated aryl groups (Ar) include mesityl (Mes), pentamethyl (C_6Me_5) and 2,6-di-isopropylphenyl (*i*Pr₂-C₆H₃).



Diphenyl

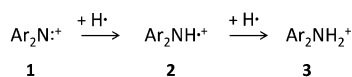
By following ¹H NMR spectra, the product after carrying out reaction (1) is not the diphenylnitrenium ion, rather it is the diphenylammonium ion, **3a**. Colorless crystals of the $\{\text{Cl}_{11}^-\}$ salt were isolated and characterized by IR and X-ray (Supporting Information). This product is consistent with initial formation of a diradical, possibly a triplet diphenylnitrenium ion, followed by successive H-atom abstraction reactions (Scheme 1). It con-

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(a) Ar = Ph (b) Ar = Mes (c) Ar = C₆Me₅ (d) Ar = *i*-Pr₂-C₆H₃

Scheme 1. Sequential H-atom abstraction from a triplet state nitrenium cation forming an aminium radical cation and then an ammonium cation.

firmly that phenyl substituents are unable to stabilize a long-lived nitrenium ion **1 a**, or even its single H-atom abstraction product, the presumed aminium radical cation, Ph₂NH^{•+}, **2 a**. These synthetic scale results contrast with conclusions drawn from photochemically generated diphenylnitrenium ion where spectral data and trapping reactivity are consistent with reactivity from a singlet state.^[16,22] In the absence of trapping agents, the major product from photo-generation was found to be a carbazole, arising from internal cyclization.^[16] In the presence of trapping nucleophiles, the products were those arising from reactivity at *o*- and *p*-positions on the aromatic ring.^[3,13,23] Such products are absent in the present work. The present results, suggesting product origin from a triplet state diphenylnitrenium ion, also contrast with calculations^[18] that predict a singlet ground state with Δ*E*_{ST} > -10 kcal mol⁻¹.

Dimesityl

Carrying out reaction (2) with Ar = mesityl leads to a fairly stable deep-blue solution consistent with the formation of an aminium radical cation [Mes₂NH^{•+}][Cl₁₁⁻], **2 b**, possibly via single H-atom abstraction from solvent by a triplet nitrenium ion. An alternative formation pathway involving electron transfer from the amine with formation of trityl radical is unlikely, if not impossible on the synthetic timescale, because of an unfavorable redox potential difference (554 mV, *E*^o(Ph₃C⁺/Ph₃C) ≪ *E*^o(Mes₂NH^{•+}/Mes₂NH), Supporting Information) and by the absence of observable trityl radical coupling products. Only triphenylmethane is observed (NMR and GC-MS, Supp. Info). Aryl aminium radical cations, **2**, are best known^[24] in the form of "magic blue", (*p*-BrC₆H₄)₃N^{•+}, and their salts are notorious for giving oils rather than crystals. The present case is no

exception, even though we have used a carborane counterion known to aid crystallization. Nevertheless, the deep blue color and the EPR and Mims electron nuclear double resonance (ENDOR) spectra (Figure 1) are characteristic and agree with expectations for this structure. Notably, **2 b** is quite stable and has a sufficiently long electron-spin relaxation time that the Mims ENDOR spectrum can be measured in liquid solution at ambient temperature. Only very slowly does it undergo a further H-atom abstraction reaction to eventually give an ammonium ion, Mes₂NH₂⁺, **3 b**.

Bis-pentamethylphenyl

When reaction (2) was carried out with Ar = pentamethylphenyl substituents, the initially orange solution (color from trityl ion) first became red. Then, over several hours, it turned dark brown and a brown precipitate was obtained upon addition of hexane. ¹H NMR suggested formation of the iminium ion **5** where one phenyl ring has distinct quinoidal character. This was confirmed by X-ray after recrystallization from ODCB (Figure 2).

We understand this reaction to be the result of self H-atom abstraction. The five methyl groups on the phenyl rings apparently prevent the cationic N center from abstracting H-atoms from the solvent and instead, H-atom abstraction occurs from its own most vulnerable site, the *para* methyl group. As indicated in Scheme 2, the first H-atom abstraction would produce equal amounts of aminium radical cation **2 c** and iminium radical cation **4**. A second "self" H-atom abstraction by **4** from the *p*-methyl group of **2 c** leads to a high yield of iminium ion **5** (X-ray) and explains why there is no buildup of color from the required aminium ion intermediate **2 c**.

When the synthetic reaction is carried out in a better H-atom donor solvent, acetonitrile rather than ODCB, a green-colored solution is obtained. This is ascribed to the aminium radical cation **2 c**. We attempted to find the byproducts of H[•] abstraction from solvents (by GC-MS) but their identities are swamped by the preponderance of solvent.

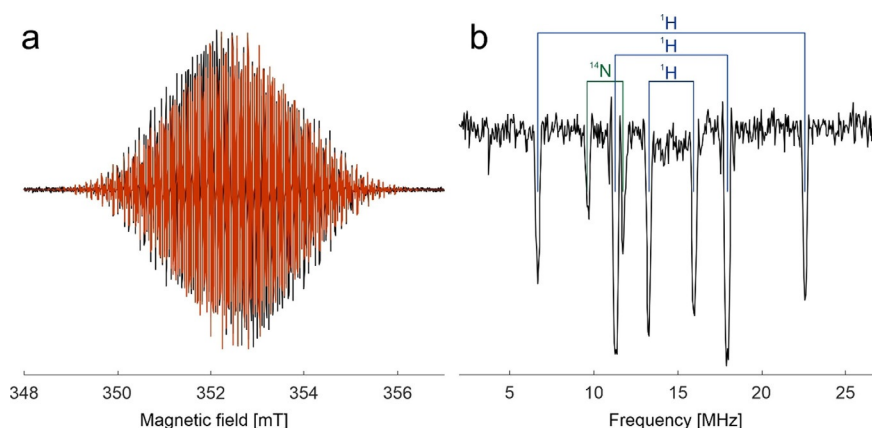


Figure 1. X-band CW EPR experimental (black) and simulated (red) spectrum (a) and Mims ENDOR spectrum (b) of **2 b** at room temperature in ODCB.

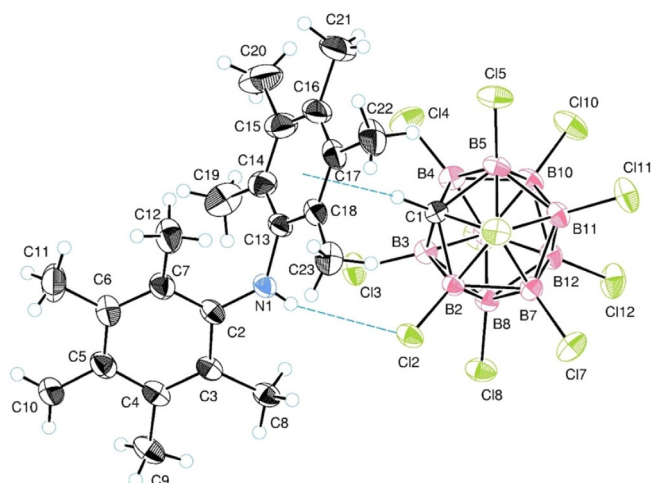
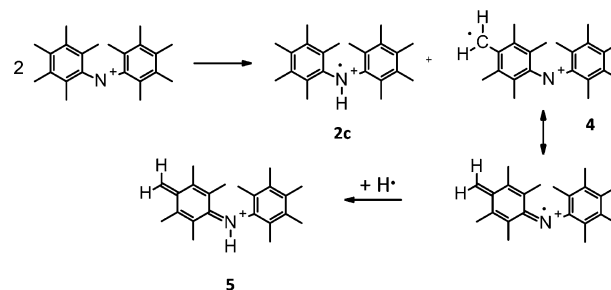


Figure 2. Crystal structure of iminium salt **5**. The C2–N distance is short (1.33 Å), there are alternating single/double C–C bond lengths in the C2–C7 phenyl ring and C5–C10 is a double bond (1.34 Å). The N–Cl distance is long (1.45 Å) and the C–C distances in the C13–C18 phenyl ring are approximately equal (1.38–1.41 Å). Between the cation and anion are hydrogen bonds: NH...Cl and CH...centroid.

Bis(2,6-diisopropylphenyl)

Carrying out reaction (2) with extremely bulky 2,6-diisopropyl groups on the diphenylamine in *o*-difluorobenzene gave a light green-colored solution from which colorless crystals were obtained with hexane. The resolution of a single crystal X-ray study for this material was too low to obtain meaningful metrical data but it can be ascertained that the cation and anion are well separated—too distant for N–H...Cl hydrogen bonding expected of an ammonium ion, **3d**. This implied absence of N–H bonds gave tantalizing evidence for the isolation of a nitrenium ion, **1d**, especially since heating the crystal to 150 °C gave rise to bright green coloration that might be ascribable to radical cation formation, **2c**. However, such optimism was unwarranted. The IR spectrum, obtained on the single crystal used for X-ray, shows clear evidence of N–H bonds with ν_{NH} at 3174 cm^{-1} , indicating the product is the ammonium ion **3d**. Thus, the unexpected separation of anion and cation and the absence of N–H...Cl hydrogen bonding must arise from crystal packing effects engendered by the bulky isopropyl groups.

We note that good old-fashioned IR spectroscopy provides an excellent way of distinguishing the various species containing N–H bonds (Figure 3). Neutral amines have N–H stretches in the range 3400–3450 cm^{-1} while in aminium radical cations they appear at 3300–3400 cm^{-1} , with distinctive overtones 3560–3570 cm^{-1} and near 3640 cm^{-1} . Ammonium cations that are H-bonded by weakly basic anions,^[25] show two bands in the range 3100–3200 cm^{-1} . The iminium ion **5** has a unique sharp N–H band at 3330 cm^{-1} . IR spectra were not reported for the pro-



Scheme 2. Self H-atom abstraction leading to iminium ion **5** (X-ray).

posed stable bis-porphyrin nitrenium ion^[8] so it is difficult to be sure that N–H bonds are absent.

Conclusions

We conclude that no matter how bulky and numerous the substituents on the phenyl rings are, there is no evidence for a stable diarylnitrenium ion on the synthetic timescale. Our product outcomes differ unexpectedly from those of photochemically produced diarylnitrenium ions, raising interesting

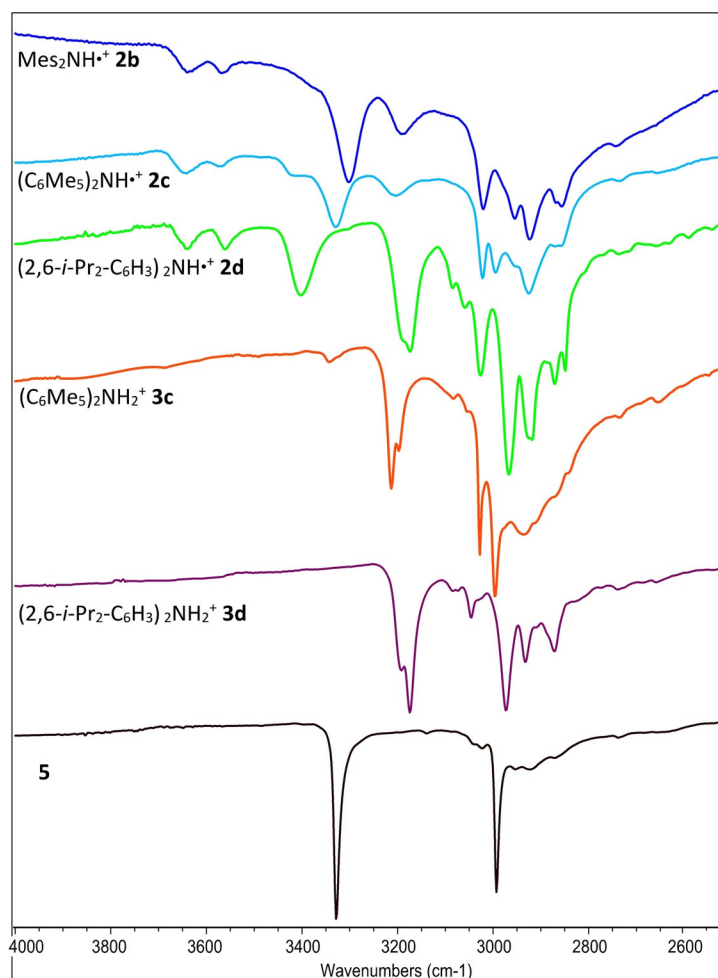


Figure 3. IR spectra (4000–2500 cm^{-1}) of selected compounds.

questions about the nature of the synthetically generated intermediate. We are exploring these questions via calculation. One possibility includes the existence of an n,p open-shell singlet nitrenium ion, for which there is suggestive evidence.^[20]

In attempting to prepare stable diarylnitrenium ions we have expanded the scope of H-atom abstraction chemistry to produce new amine radical cations whose tendency towards subsequent H-atom abstraction is shown to vary with the nature of the o,p substituents. A new, self H-atom abstraction reaction has been uncovered that ultimately leads to formation of a stable iminium ion.

The prospects for isolating stable diarylnitrenium ions analogous to silylium and borenium ions appear slim, making the one report of a stable nitrenium^[8] all the more remarkable, or doubtful.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aminium radical cation • bulky substituents • iminium radical cations • nitrenium ion • triplet

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