Singlet–Triplet Energy Gaps in Highly Stabilized Nitrenium Ions: Experimental and Theoretical Study of 1,3-Dimethylbenzotriazolium Ion
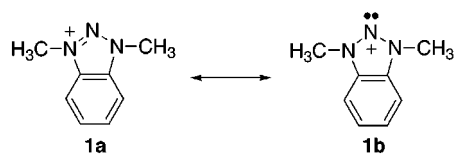
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ABSTRACT

The first experimental determination of a singlet–triplet energy gap (ΔE_{st}) for an organic nitrenium ion was made for 1,3-dimethylbenzotriazolium ion 1. Laser flash photolysis was used to determine ΔE_{st} for this persistent nitrenium ion and a value of -66 ± 3 kcal mol^{-1} was obtained. DFT calculations show excellent agreement with the experiment.

Nitrenium ions and carbenes are intermediates characterized by a hypovalent central nitrogen or carbon atom, which formally possesses a nonbonding electron pair and two nonbonding orbitals of similar energy.[1–5] This situation creates two low-lying electronic states: a singlet state where the nonbonding electrons are paired and a triplet state where they are unpaired and occupy separate orbitals. Accurate assessments of energy gaps (ΔE_{st}) between these two states have preoccupied experimentalists and theoreticians for several decades.[2,6–10] The short lifetimes of these intermediates along with the typically small energy differences between the two states complicates any attempt to measure them directly. For the nitrenium ions the only experimentally derived ΔE_{st} is that for the parent system, NH$_2^+$.[11,12] The latter is a ground-state triplet with $\Delta E_{st} = +30$ kcal mol^{-1}. (A positive sign indicates that the triplet state is lower in energy). This was determined by gas phase mass selective photodetachment spectroscopy. Unfortunately this experiment is very difficult to apply to larger nitrenium ions for a variety of technical reasons. For larger nitrenium ions, only theoretical values for ΔE_{st} are currently available.[6,13,14] It would be useful to have experimental ΔE_{st} values that could be used to evaluate the validity of the various computational

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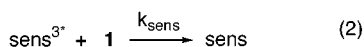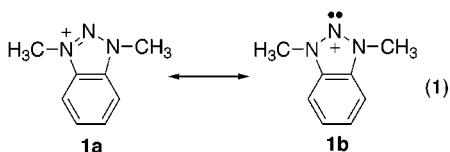(12) Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319–4328.
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methods that are being applied to the more delocalized nitrenium ions. This is especially important considering that highly conjugated arylnitrenium ions are intermediates involved in carcinogenic DNA damage.[15−17]

Recent discoveries of persistent carbenes by Arduengo[18] and persistent nitrenium ions by Boche[19] open the possibility of measuring ΔE_{st} for such species directly using relatively straightforward photophysical methods. 1,2,3-Triazolium salts (e.g., 1,3-dimethylbenzotriazolium perchlorate, $\mathbf{1}^{+}$ ClO_4^{-}) constitute a class of compounds that have been known for several decades[20] and can be considered nitrenium ions on the basis of resonance form **1b** (eq 1), which assigns a

$$H_3C-\overset{+}{N}\overset{N}{\diagdown}N-CH_3 \longleftrightarrow H_3C-\overset{\cdot\cdot}{N}\overset{\overset{\cdot\cdot}{N}}{\underset{+}{\diagdown}}N-CH_3 \qquad (1)$$

$$\mathbf{1a} \qquad\qquad \mathbf{1b}$$

$$\text{sens}^{3*} + \mathbf{1} \xrightarrow{k_{sens}} \text{sens} \qquad (2)$$

positive charge to the central nitrogen.[19,21] Herein we describe a combined experimental and theoretical study aimed at characterizing the ΔE_{st} for nitrenium ion $\mathbf{1}^{+}$. Through a series of laser flash photolysis (LFP) experiments, we have determined the ΔE_{st} for this species to be 66 ± 3 kcal/mol. Theoretical calculations using density functional theory (DFT, BPW91/cc-pVDZ level) are in excellent agreement with the experimental values. As expected such highly stabilized nitrenium ions are ground-state singlets with substantial singlet−triplet energy gaps.

Salt $\mathbf{1}^{+}$ ClO_4^{-} [19] has a high-wavelength absorption maximum at 280 nm (CH_3CN) and a fluorescence maximum at 350 nm. An analysis of the fluorescence excitation and emission spectra provides an energy of 92 kcal mol^{-1} for the first excited singlet state. We attempted to detect phosphorescence from $\mathbf{1}^{+}$ both at room temperature and in an ether/2-propanol/ethanol glass at 77 K but were unsuccessful. In situations where it is not possible to detect phosphorescent emission the triplet state energy can be determined by measuring energy transfer rate constants (k_{sen}) from various triplet state donors or sensitizers to the compound in question (eq 2). Generally if the triplet state energy of the sensitizer (E_T) exceeds that of the acceptor (ΔE_{st} in the case of $\mathbf{1}^{+}$) by 3−4 kcal mol^{-1}, then k_{sen} occurs

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Table 1. Rate Constants for Energy Transfer from Various Triplet Sensitizers to **1** (k_{sen} in M^{-1} s^{-1}) and from the Triplet State of **1** to Quenchers **1** (k_q in M^{-1} s^{-1})[23]

sensitizer or quencher	E_T (kcal/mol)	Log(k_{sen})	Log(k_q)
xanthone	74	9.85	
benzophenone	69.2	9.78	
4-methylbenzophenone	69.4	9.78	
thio-9-xanthone	65	8.30	
phthalazine	64	6.82	
quinoxaline	60.8	<5	
2-acetylnaphthalene	59.5	<5	
benzil	54	<5	
biphenyl	65.5		6.57
indene	63		9.65
fumaronitrile	62		9.40
naphthalene	60.9		9.90
quinoxaline	60.7		9.36
E-piperylene	59		9.90
Z-piperylene	57		9.81
E-stilbene	49.3		9.82

at or near the diffusion limit. The value for k_{sen} diminishes rapidly as E_T decreases.

To estimate the triplet energy of $\mathbf{1}^{+}$, we used LFP to determine k_{sen} for the sensitizers listed in Table 1, which have varying values of E_T[22] For example, a solution containing xanthone and **1** ClO_4 was subjected to LFP using 355 nm excitation. (At this wavelength xanthone, but not $\mathbf{1}^{+}$, absorbs the light). Immediately following the laser pulse, we detect the characteristic triplet state spectrum of xanthone (λ_{max} = 635 nm). Addition of $\mathbf{1}^{+}$ ClO_4^{-} quenches (i.e., reduces the lifetime of) this absorption and creates a new transient absorption band attributed to the triplet state of $\mathbf{1}^{+}$ ClO_4^{-} (450 nm). The latter is observed to grow in at the same rate that the xanthone triplet decays. The rate constant for triplet energy transfer from xanthone to $\mathbf{1}^{+}$ was determined to be k_{sen} = 7.1 × 10^9 M^{-1} s^{-1}. The same experiments were carried out with the remaining sensitizers. As illustrated in Figure 1, for sensitizers having E_T > 68 kcal $^{-1}$ mol^{-1},
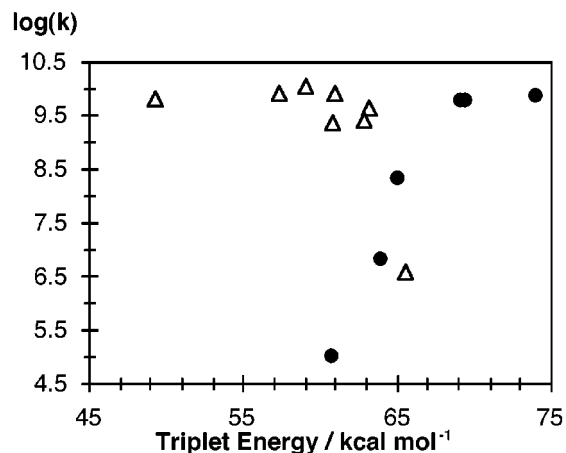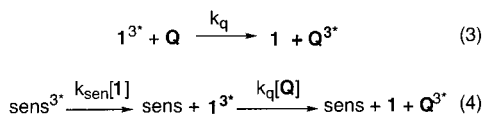

Figure 1. Energy transfer rate constants from triplet $\mathbf{1}^{+}$ to various quenchers (△) and from various triplet sensitizers to $\mathbf{1}^{+}$ (●).

k_{sen} is at or near the diffusion limit. For sensitizers with E_T < 69 kcal mol^{-1}, k_{sen} diminishes rapidly as E_T is decreased. With quinoxaline (E_T = 60.8 kcal mol^{-1}), 2-acetylnaphthalene (E_T = 59.5 kcal mol^{-1}), and benzil (E_T = 54 kcal mol^{-1}) no energy transfer can be detected.

Because the triplet state of 1^+ gives a detectable transient signal, it is possible to characterize the rate of energy transfer from 1^+ to various triplet energy quenchers (eq 3). Laser

$$1^{3*} + Q \xrightarrow{k_q} 1 + Q^{3*} \qquad (3)$$

$$sens^{3*} \xrightarrow{k_{sen}[1]} sens + 1^{3*} \xrightarrow{k_q[Q]} sens + 1 + Q^{3*} \qquad (4)$$

flash photolysis (LFP) of 1^+ ClO$_4^-$ using 266 nm excitation generates a transient absorption signal at 450 nm, which has the same shape and lifetime as the one generated from xanthone sensitization. This signal is quenched by O$_2$ (E_T = 29 kcal mol^{-1}) and the diene quenchers, E-piperylene and Z-piperylene.

Final confirmation of the identity of the 450 nm transient was obtained through an energy relay experiment illustrated in eq 4. For these experiments xanthone was excited at 355 nm in the presence of a high concentration (100 mM) of 1^+. Under these conditions the triplet state of 1^+ is created within the time duration of the laser pulse (Figure 2). When 2.9
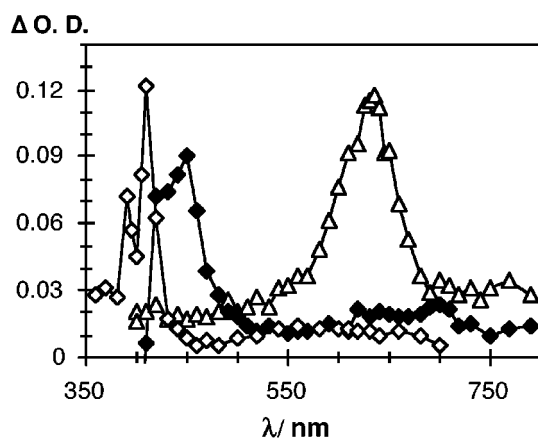

Figure 2. Transient absorption spectra obtained from LFP of xanthone ($\triangle$); xanthone and 5.9 mM 1^+ ClO$_4^-$ ($\blacklozenge$); xanthone, 100 mM 1^+ ClO$_4^-$ and 2.9 mM naphthalene ($\diamondsuit$).

mM naphthalene is added to this solution, the absorption attributed to the triplet state of 1^+ is quenched and is replaced with the characteristic transient absorption bands for the triplet state of naphthalene (λ_{max} = 405, 420 nm). While it is possible for naphthalene to accept triplet energy directly from xanthone, the reported experiments were carried out

under conditions where 1^+ was in such large excess relative to naphthalene that >97% of the xanthone excited states are quenched by 1^+ rather than naphthalene. This successful energy relay experiment rules out the possibility that the 450 nm signal is something other than the triplet state of 1^+. By measuring the decay rate of triplet 1^+ with various concentrations of naphthalene, it is possible to determine the rate constant for energy transfer, k_q. The k_q values for quenchers listed in Table 1 were determined using the same method.

The combined results of the sensitization and quenching experiments are shown in Figure 1. Triplet sensitizers with energies in excess of 69 kcal/mol are quenched at the diffusion limit by 1^+. Likewise quenchers with triplet energies under 63 kcal/mol quench the triplet state of 1^+ at or near the diffusion limit. Therefore it is clear that the ΔE_{st} must lie between these two values. In fact at intermediate values some energy transfer is observed, but in each case it occurs several orders of magnitude below the diffusion limit. On the basis of these measurements we determine ΔE_{st} = −66 ± 3 kcal mol^{-1} for nitrenium ion 1^+.

Computations[24] on the singlet and triplet state of 1^+ were carried out using DFT. In particular, we used the gradient-corrected functionals of Becke[25] for exchange and of Perdew and Wang[26] for correlation (BPW91) with the correlation-consistent polarized valence double-ζ[27] (cc-pVDZ) basis set. Calculations employing gradient-corrected functionals and analogous basis sets have been demonstrated to predict S-T splittings accurate to within about 2 kcal/mol, as compared to either experiment or well converged electronic structure calculations at alternative levels of theory, for a variety of nitrenium ions.[28] Analytic frequency calculations were performed to verify the singlet (C_{2v}, $^1A_1$ state) and triplet (C_2, ^3B state) structures as minima.

At the BPW91/cc-pVDZ level, the predicted gas-phase ΔE_{st} is −64.7 kcal/mol, in excellent agreement with the experimental measurement. Standard-state solvation free energies ΔG^o_S in CH$_3$CN were calculated using the SM5.42R/BPW91/6-31G* model.[29] Solvation is predicted to favor the triplet, but by only 0.6 kcal/mol, leaving the net state-energy splitting within the experimental uncertainty.[30]

To gain additional insight into the nature of the triplet excited state, we analyzed the multiconfigurational wave function of the triplet at the CAS(12,10)/cc-pVDZ level of theory (the active space is comprised of the 10 π electrons

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(30) Thermal contributions to the enthalpies and free energies of the two spin states can be derived from the frequency calculations using standard statistical mechanical approximations. At 298 K these favor the triplet by about 3 kcal/mol. However, since measured rates of triplet energy transfer are not obviously tied to the fully equilibrated free energy difference between the singlet and triplet states of the nitrenium ion (i.e., there may be vertical character to the energy transfer and/or exciplexes may be involved), it is not obvious that inclusion of thermal contributions is more physical

and the nitrenium nitrogen lone pair distributed among the 9 π orbitals and the in-plane nonbonding orbital of the nitrenium nitrogen). At the DFT geometry, the triplet state is well described as a $\pi \rightarrow \pi^*$ excited state having essentially no $n \rightarrow \pi^*$ character (the occupation number of the in-plane nitrenium nitrogen lone pair is predicted to be 1.983). This contrasts with many less stable nitrenium ions, where triplets are typically dominated by $n \rightarrow \pi^*$ character. The difference can be ascribed to a combination of the electron-rich nature of the triazole π system and the geometric constraints of having the nitrenium nitrogen atom incorporated in a five-membered ring ($n \rightarrow \pi^*$ triplets tend to prefer large valence bond angles at nitrogen to decrease s character to the half-occupied orbital).

These results represent the first experimental determination of the ΔE_{st} for any organic nitrenium ion. In contrast to the parent system, NH_2^+, nitrenium ion $\mathbf{1}^+$ has a singlet ground state that is highly stabilized by an electron-rich π-system. The excellent quantitative agreement between DFT and experiment for these very different cases implies that this method can reliably predict ΔE_{st} values for $PhNH^+$ and its derivatives which are likely to show π-stabilization that is intermediate between $\mathbf{1}^+$ and NH_2^+.