Are aroylnitrenes species with a singlet ground state?

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The B3LYP calculations of the properties of singlet and triplet benzoylnitrenes and naphthoylnitrenes testify to the stabilization of the $^1A'$ state relative to the $^3A''$ state due to the intermediacy of an NCO structure between nitrene and oxazirene in the $^1A'$ state.

Nitrenes are the key intermediates of azide photolysis and thermolysis. It is well known[1] that alkyl- and arylnitrenes have a triplet ground state. The case with aroylnitrenes[1–4] is more complicated and inconsistent. Taking into account that aroylnitrenes have a singlet ground state, Melvin and Schuster[5] proposed acetyl-substituted aroyl azides as potential photolabeling agents.

Nitrenes, as well as better studied carbenes, have a nontrivial electronic structure with two valence electrons, which are distributed between two nonbonding molecular orbitals (NBMOs). In carbenes, one of the NBMOs is a pure *p*-AO; the second hybridised σ orbital exhibits a considerable 2*s* character and thus a much lower energy. The ground state of the parent carbene CH_2 is a triplet state. The singlet state, in which both of the nonbonding electrons occupy the σ NBMO, is only 38 kJ mol⁻¹ higher in energy. Phenyl[6] and methyl[7] substituents reduce ΔE_{ST} by 20–30 kJ mol⁻¹, and halogens make a singlet state to be the ground state.[8]

Unlike carbenes, in the parent nitrene NH, both of the NBMOs are pure *p*-AOs. Lower Coulomb repulsion in a triplet state cannot be compensated by occupation of the lower MO by two electrons in a singlet state, as in the case of carbene. Therefore, ΔE_{ST} in NH (151 kJ mol⁻¹)[9] is four times higher than that in CH_2. The methyl substituent reduces ΔE_{ST} by 21 kJ mol⁻¹ (ref. 10) (Figure 1) similarly to the case of carbene. However, ΔE_{ST} in phenylnitrene is almost halved (75 kJ mol⁻¹).[11] Calculations[12(a)] demonstrated that the relative energy of the closed-shell singlet ($^1A_1$) in phenylnitrene is reduced slightly (~16 kJ mol⁻¹, Figure 1) as in phenylcarbene. The lowest singlet state of phenylnitrene has the open-shell electronic configuration ($^1A_2$).[12] This state is substantially stabilised due to localization of the unpaired π-electron in the phenyl ring.[12(b)] Nevertheless, of two states of nitrenes with the same open-shell electronic configurations, the triplet state should be lower in energy (Hund's rule) due to lower Coulomb repulsion in this state.†

Knowing the electronic structure of nitrenes and the influence of substituents on ΔE_{ST}, it is difficult to explain why the singlet state of aroylnitrenes could be a ground state. Therefore, this fact was not explained in the literature.[3–5] The goal of this work was to understand whether it is really possible for aroylnitrene to have a singlet ground state and what is the reason for its dramatic stabilization.
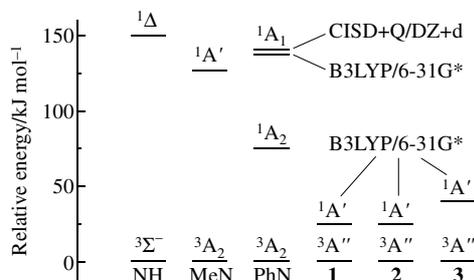
Figure 1 Comparison of relative energies of lowest singlet and triplet states of nitrenes, experimental (NH, MeN, PhN) and calculated by CISD+Q [PhN, ref. 12(a)] and B3LYP/6-31G* (PhN, **1**, **2** and **3**, this work).

† This statement does not concern the situation with *para*-phenylene-dinitrenes, *para*-nitrenophenylcarbenes and related species.[13]
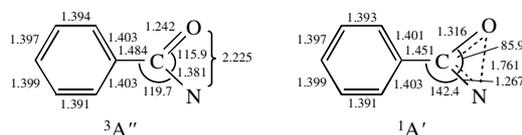
Figure 2 Bond lengths (Å) and bond angles (°) in the singlet $^1A'$ and triplet $^3A''$ states of benzoylnitrene calculated using the B3LYP/6-31G* method.

For this purpose, we calculated the properties of benzoylnitrene **1**, 2-naphthoylnitrene **2** and formylnitrene **3** as a model compound in the lowest singlet and triplet states. The calculations were performed by the standard B3LYP/6-31G* method[14] using the Gaussian-98 program.[15] The DFT calculations with the B3LYP functional were very successful for determining ΔE_{ST} in carbenes.[16–18] In model formylnitrene, the CASSCF(8,8) calculations[19] were also performed.

All structures were found to be the minima on the potential energy surfaces. The zero point energies were calculated using harmonic frequencies, and they were taken into account in the calculations of ΔE_{ST}. The stability of SCF solutions was tested. The instability of the triplet wavefunctions under perturbations was found, and the reoptimization of triplet wavefunctions to lower energy solutions was performed.

The calculated energies of the lowest singlet and triplet states of aroylnitrenes **1** and **2** and formylnitrene **3** are displayed in Figure 1, which demonstrates a dramatic (100–130 kJ mol⁻¹) reduction of ΔE_{ST} for these nitrenes as compared with NH, MeN and PhN. The reason for this wonderful stabilization of a singlet state can be understood from the calculated geometry of singlet species. The bond lengths and bond angles of the CNO fragment in the same spin states of nitrenes **1–3** are very similar (differences are less than 0.01 Å and 1°). As an example, Figure 2 displays the calculated geometry for nitrene **1**. In the triplet nitrene, the C=O bond length (1.242 Å) has a typical value, and the C–N bond length (1.381 Å) is intermediate between those of ^3PhN (1.34 Å)[12(b)] and ^3MeN (1.42 Å).[20]

In the singlet $^1A'$ state (Figure 2), the CO bond (1.316 Å) is much longer than that in the triplet state and close to the single bond length. The CN bond length (1.267 Å) is substantially shorter than that in the triplet state and close to the CN double bond length. The NCO bond angle is very small (~86°). There is no alteration in C–C bond lengths in the phenyl rings of both triplet and singlet aroylnitrenes (Figure 2). The highest doubly occupied Kohn–Sham orbital in the singlet $^1A'$ state is the π-type orbital delocalised in the CON fragment. The CON fragment in the $^1A'$ state exhibits the structure of cyclic oxazirene; however, the N–O distance (1.761 Å) is longer than the normal ordinary N–O single bond (about 1.4 Å or ~1.5 Å in strained cycles).[21]

Note that the singlet formylmethylene (^1FM) has a similar unusual geometry.[22] The CCO bond angle is also small (~91°), and the CO distance (1.87 Å) is somewhat longer than the NO distance in ^{1}**1**. Oxirene (Ox) is a very flat minimum on the potential energy surface, and the activation energy of its rearrangement to ^1FM is as low as 0.3 kcal mol⁻¹.[22]

Unlike HC(O)CH, the singlet potential energy surface of R-C(O)N has only one minimum, *i.e.*, the species in the $^1A'$

^{1}FM   Ox
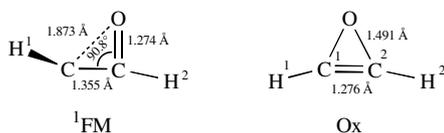
with the structure superimposed of nitrene and oxazirene. The formation of this singlet species can be responsible for the unusual properties of aroylnitrenes.[3–5]

According to the B3LYP/6-31G* calculations, the energy differences between these species (^{1}A′) and triplet nitrenes (^{3}A″) are small, but the triplet states (^{3}**1**–^{3}**3**) are lower in energy (Figure 1). The results of our CASSCF(8,8)/cc-pVTZ calculations for model formylnitrene are very similar to those obtained by the B3LYP method (Figure 1). The singlet species in the ^{1}A′ state has a structure superimposed of nitrene and oxazirene, and its energy is 10.2 kJ mol^{-1} higher than that of ^{3}**3** (34.1 kJ mol^{-1} in DFT calculations). Shapley and Bacskay[23] performed high-level calculations of a potential-energy surface associated with the dissociation of the formaldiminoxy radical CH$_2$NO. Along with other products and intermediates, they calculated the structures and energies of triplet formylnitrene (^{3}A″) and 'cyclic'-C(H)NO (^{1}A′). The structures of these intermediates calculated using the MP2/6-31G* and CASSCF(11,11)/cc-pVDZ methods are very similar to those calculated in this work. The ΔE_{ST} values calculated from published data[23] are 14.9 kJ mol^{-1} and 3.1 kJ mol^{-1} at the CASPT2(11,11) and QCISD(T) levels of the theory with the cc-pVTZ basis set, respectively. Using the G2 method,[23] ΔE_{ST} was calculated to be –10.6 kJ mol^{-1}.

Therefore, the standard B3LYP/6-31G* calculations (Figure 1) overestimated ΔE_{ST} by 20–40 kJ mol^{-1}. Taking into account this overestimation, we can predict that the ΔE_{ST} values for aroylnitrenes **1** and **2** will be close to or, most probably, lower than zero. The B3LYP calculations using the PCM model[24] for solvation showed the further reduction of ΔE_{ST} for all nitrenes **1**–**3** by 5–6 kJ mol^{-1} in heptane and by 9–10 kJ mol^{-1} in acetonitrile.

Therefore, the calculations revealed that, in the case of aroylnitrenes, the singlet ^{1}A′ state should be lower in energy than the triplet ^{3}A″ state. However, the species in the ^{1}A′ state has a structure superimposed of the nitrene and oxazirene.

If the ^{1}A′ state is the lowest energy minimum, it is easy to explain why the EPR spectra of triplet aroylnitrenes were not detected upon photolysis of aroyl azides.[3,4] The direct measurement of spectra should be performed and the reaction kinetics of intermediates should be studied to prove that the singlet species with the structure superimposed of nitrene and oxazirene is really the reactive intermediate of aroyl azide photolysis.

To predict the electronic absorption spectra of these intermediates, the time-dependent DFT calculations[25] at the B3LYP/6-31+G* level were performed. The near-UV and visible spectrum of the species in the ^{1}A′ state has transitions at 532 ($f = 0$) and 306 nm ($f = 6\times10^{-3}$) in the case of benzoylnitrene. The spectrum of naphthoylnitrene has two transitions with non-zero intensities at 319 ($f = 3.4\times10^{-3}$) and 313 nm ($f = 1.5\times10^{-2}$). This is in agreement with the fact that no intermediates with absorption in the region 350–600 nm were observed upon photolysis of benzoyl and naphthoyl azides.[3,5]

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