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Ab Initio Characterization of Phenylnitrenium and Phenylcarbene: Remarkably Different Properties for Isoelectronic Species

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Nitrenium ions ($R–N–R'^+$) are reactive intermediates implicated as carcinogenic products from aromatic amine catabolism.[1–7] Metabolic activation is postulated to proceed via formation of the corresponding arylhydroxylamine esters,[1–9] which then generate the reactive species upon heterolysis of the N–O bond. The divalent nitrenium ions, which are isoelectronic to carbenes, go on to covalently modify DNA. Bimolecular nucleophilic substitution at nitrogen has alternatively been proposed in some instances.[10,11]

Carbenes[12] and nitrenium ions[6,13–17] have been extensively characterized experimentally. However, experimentally measured singlet–triplet (S–T) gaps are available only for NH_2^+ itself among nitrenium ions (30.1 ± 0.2 kcal/mol, where a positive sign indicates the triplet to be the more stable multiplicity),[18] and for a handful of small carbenes,[19,20] including CH_2 (9.00 ± 0.01 kcal/mol).[21] In the particular case of phenyl substitution, phenylcarbene, **1**, has been observed to be a ground-state triplet with a postulated gap of 1–5 kcal/mol.[22–24] Theoretical calculations have been attempted only for relatively low levels of theory and, in general, show a strong preference for the triplet.[25–29] Phenylnitrenium, **2**, has not yet been spectroscopically characterized; theoretical calculations at semiempirical[30–32] and ab initio[32,33] levels uniformly predict the singlet to be considerably lower in energy than the triplet. Although the theoretical S–T gaps are far from converged, it is clear that phenyl substitution stabilizes the singlet[19] dramatically more for the nitrenium ion case (40+ kcal/mol) than for the carbene case (approximately 5 kcal/mol).

We report here large basis set[34] Hartree–Fock (HF), post-HF, and density functional theory (DFT) calculations,[35] the latter levels taking extensive account of correlation. Solutions from the spin-polarized DFT (Kohn–Sham) self-consistent field equations have been shown in general to suffer from minimal spin contamination;[36] in contrast, *very* high spin contamination plagues the UHF triplet wave functions for both **1** and **2**.[37] In addition, we have found DFT to compare remarkably well (±0–2 kcal/mol) with multireference configuration interaction calculations for the prediction of S–T gaps in several small molecules, including CH_2 and NH_2^+.[38,39]

The following discussion refers only to calculations at the BVWN5/cc-pVTZ//BVWN5/cc-pVDZ level of theory (294 basis functions), which we regard as best on the basis of negligible spin contamination, convergence with respect to basis set size, and its good agreement with sophisticated post-HF methods both here (computational details for several levels of theory are provided in the supplementary material) and elsewhere.[38,39] Our key results are as follows: (i) The predicted S–T gaps for **1** and **2**, including zero-point corrections, are 4.3 and −21.2 kcal/mol, respectively. (ii) Triplet **1** is a planar species (ip) with a predicted barrier to rotation about the exocyclic bond[28] of 2.7 kcal/mol; however, *the corresponding structure for triplet **2** is a rotational transition state (TS) structure. The global minimum instead has the N–H bond perpendicular to the plane of the aromatic ring (oop).* and the rotational barrier is 1.8 kcal/mol. Prior calculations have not compared the two possibilities[30,32,33] and/or have been misled

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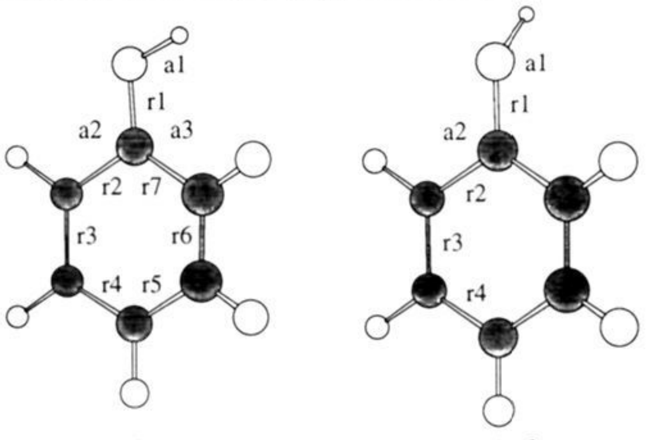
Table 1. Heavy Atom Bond Lengths (Å) and Selected Bond Angles (deg) for **1** and **2**[a]



in-plane *out-of-plane*

structure	r1	r2	r3	r4	r5	r6	r7	a1	a2	a3
in plane										
$^1A'$-**1**	1.455	1.436	1.402	1.412	1.414	1.400	1.439	105.9	117.3	125.4
$^3A''$-**1**	1.400	1.444	1.397	1.415	1.414	1.398	1.448	135.4	121.4	121.4
$^1A'$-**2**	1.311	1.479	1.384	1.426	1.433	1.381	1.479	111.7	116.0	125.0
$^3A''$-**2**	1.307	1.462	1.385	1.423	1.423	1.385	1.475	145.6	120.9	119.5
out of plane										
$^1A'$-**1**	1.447	1.431	1.404	1.408				108.7	120.8	
$^3A''$-**1**	1.414	1.441	1.400	1.413				144.7	121.4	
$^1A_1$-**2**	1.288	1.488	1.386	1.432				180.0	118.8	
$^3A''$-**2**	1.338	1.460	1.386	1.426				129.9	119.8	

[a] BVWN5/cc-pVDZ optimized geometries.

by high spin contamination,[31] which causes the UHF Hessian matrix to have no negative eigenvalues for the planar structure. Post-HF methods all agree that the perpendicular isomer is lower in energy than the planar, as does DFT, which moreover predicts a single imaginary frequency for the latter and none for the former. (iii) Singlet **1** is a planar species with a predicted barrier to rotation about the exocyclic bond[28] of 11.0 kcal/mol; however, we find that singlet **2** does not rotate about this bond, but instead inverts through nitrogen, resulting in a high-energy C_{2v} linear TS structure; the inversion barrier is 26.0 kcal/mol.[31]

The much larger singlet stabilization by phenyl substitution for nitrenium compared to carbene[19] derives from the considerably enhanced π-acceptor characteristics of a positively charged nitrogen compared to a neutral carbon; this differential π-accepting ability is more manifest in the singlets, where an empty p orbital serves as acceptor, than it is in the triplets. Geometrical analysis, provided in Table 1, shows singlet ip-**2** to resemble an imine-substituted cyclohexadienyl cation—the C–N bond is quite short at 1.311 Å, and the ring bond alternation is consistent with such a description.[40] Excitation out of the in-plane lone-pair-like highest occupied molecular orbital (HOMO) into the π-type lowest unoccupied molecular orbital (LUMO) opens the C–N–H bond angle considerably (thereby removing s character from the now only singly occupied molecular orbital (SOMO) in plane) but does not otherwise have much effect on the iminocyclohexadienyl structure. The π SOMO is weakly antibonding between C and N; the low rotational barrier about this bond is consistent with a loss of all double-bond character. The C–N bond does shorten, however, both because of decreased steric interactions between H(N) and the ring and because of the increased s character of the nitrogen bonding orbital. The preference for the oop isomer in triplet **2** presumably derives from either or both of two effects: (i) the oop π-acceptor orbital on nitrogen, which includes some N–H antibonding character, is a better acceptor than a singly-occupied p orbital, and (ii) in the oop structure there is reduced repulsion between the (bent away) sp^2-like unpaired electron on nitrogen and the π system by comparison to the p-like unpaired electron in the ip structure. Many of these same effects are present for the weakly electron-deficient carbene,[19] but to a much lesser degree. One measure of this is that while singlet **2** prefers to isomerize by inverting (like an imine), singlet **1** rotates out of plane.

Although the singlet is the lower energy spin state for **2**, substitution of the aromatic ring with groups which function as π acids and/or σ donors decreases the gap between the two SOMOs of the triplet (by stabilizing the π LUMO relative to the σ HOMO of the singlet) and can make this spin state accessible.[16,29,30,32,41] It is noteworthy that an oop triplet arylnitrenium would moreover apparently allow very bulky *N*-substituents to minimize unfavorable steric interactions with the ring, an option not available to the ip singlet. We will report further on ground-state arylnitrenium triplets in due course.

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Supplementary Material Available: Table of UHF, ROHF, MP4, BLYP, BPL, and CISD energies for different basis sets and geometries and Gaussian 92 archive files for all calculations (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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