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ARYL- AND ALKYLNITRENIUM IONS: SINGLET-TRIPLET GAPS VIA AB INITIO AND SEMI-EMPIRICAL METHODS

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Abstract: The accuracy of semi-empirically predicted singlet-triplet energy gaps for substituted nitrenium ions is examined by comparison to correlated (CISD), ab initio calculations. Unrealistically low singlet energies are delivered by both the AM1 and MNDO method with the differences being rather random for AM1, but quite consistent for MNDO.

Nitrenium ions ($R\text{-}N\text{-}R'^{+}$) are reactive intermediates which contain a divalent, positively charged nitrogen atom. It has been proposed that nitrenium ions[1] occur as electrophilic intermediates in aryl amine carcinogenesis.[2] Since the singlet and triplet states of these ions will have different lifetimes and reactivities, analysis of their relative energetics is of considerable importance. Unlike their isoelectronic congeners, nitrenes and carbenes, nitrenium ions have seen comparatively little study.[3] This communication describes our recent correlated (CISD) ab initio and semi-empirical calculations on some nitrenium ions. Our objectives were to assess the ability of semi-empirical methods (MNDO, AM1) to predict singlet-triplet gaps in nitrenium ions, and to understand which structural features were important in determining these gaps.

Ford and Scribner (F&S) in 1981 calculated singlet-triplet gaps for a large number of nitrenium ions using semi-empirical methods (MNDO).[4] Limited experimental and ab initio[5] data did not permit an extensive comparison to the semi-empirical results, however, they concluded that arylnitrenium ions were uniformly ground state singlets. Recent experimental results in one of our laboratories (DEF) prompted us to examine this question more closely, especially with respect to a critical evaluation of the ability of semi-empirical methodology to accurately predict singlet-triplet energy gaps. We were especially interested in predicting these energy gaps in conjugated nitrenium ions because of their biological significance. Compounds **1-12** (Figure 1) were studied at the MNDO CI[4,6,7] and AM1 CI[6,7] levels and compared to high level, correlated (CISD) ab initio results for **1-8**,[5a,8,9] These results are summarized in Table 1. While the paucity of experimental data on nitrenium ions allows comparison only to **1**,[10] CI methods have been shown to be quite accurate in the isoelectronic carbenes.[11] Semi-empirical methods have also enjoyed success in predicting carbene S-T gaps.[12]

All structures were characterized at the HF level as local minima by inspection of their respective Hessian matrices, except for C_s singlet **2** and C_{2v} singlet **3**, which are saddle points at the ab initio level (AM1 and MNDO predict local minima). Compounds **11** and **12** have been generated from the corresponding benzisoxazolium salts[13] and AM1 predicts the ring opening to be exothermic by ca. 6 kcal/mol for the ground state singlets. For **4** and **5** while there may be transoid isomers more stable than the cisoid examined here, the latter were chosen as more analogous to the experimentally accessible **11** and **12**. Both **4** and **5** are planar, C_s structures, although in the triplets the ab initio barrier to iminium ion formation is extremely low. AM1 and MNDO generally predict C-N bond lengths considerably longer than those found at the HF level -- up to 0.16 Å for **8**!

F&S proposed MNDO to overestimate relative singlet stability by ca. 9 kcal/mol based on **1**, which was the only compound in their study for which high level ab initio data were available. However, for **1-4**, **6-8**, MNDO CI gives a 16.2±3.7 (one standard deviation) kcal/mol overstabilization of the singlet relative to ab initio CISD. The deviation of **5** from this trend is likely attributable to its unique second row atom. AM1 gives a much less consistent error of 18.8±7.5 kcal/mol. These results are similar to those of Li and Schuster[12] who observed that experimental carbene singlet-triplet gaps correlate with semi-empirical predictions if a constant correction factor is applied. In the same study it was also shown that MNDO correlated better with experiment than AM1. If the trend for **1-4** and **6-8** were to be maintained for **10-12**, the observation of thermally accessible triplet states and products derived therefrom would not be surprising.[13,14]

It must also be pointed out that the CISD results overestimate triplet stabilization by ca. 6 kcal/mole for **1** where an experimental value of 30.1 kcal/mole has been found.[10] However the basis sets used here are more trustworthy for the substituted analogs than they are for the very small **1**, and we expect this error to decrease accordingly.

Analysis of the ab initio geometries and molecular orbitals provides some interesting insights into the singlet-triplet gaps in conjugated nitrenium ions. The two critical orbitals are the in-plane "lone pair" orbital predominantly localized on nitrogen, which is doubly filled in the singlet, and the LUMO of the extended p system, i.e. the aza-allyl nonbonding MO for **4** and the chlorazabutadienyl π_1^* MO for **5**. The C-C bonding, C-N/C-Cl antibonding nature of this latter MO clearly manifests itself in the ab initio geometry of triplet **5**, where it is singly occupied, compared to singlet **5**, where it is empty (Figure 1).

Table I. Calculated Singlet-Triplet Energy Gaps and Bond Angles for Nitrenium Ions **1-12**.

	E (S$_0$) -E (T$_1$), kcal/mol				R-N-R' Angle, Degrees Singlet (Triplet)		
Ion	MNDO^a	AM1 CI^a	CISD I^b	CISD II^c	MNDO^a	AM1^a	UHF/6-31G*
1	16.7	24.9	36.1	36.3	110.4 (147.6)	115.8 (155.4)	110.0 (150.8)
2	1.6	1.9	20.9^d	20.8^d	117.3 (150.8)	119.9 (152.5)	112.8^d (151.1)
3	1.2	-4.7	22.3^d	22.2^d	127.0 (157.6)	124.4 (153.5)	120.5^d (150.4)
4	-1.6	-7.4	9.7	10.0	128.3 (163.8)	121.6 (159.4)	126.3 (152.7)
5	-5.3	-7.0	-1.7	---	128.9 (165.7)	126.5 (160.3)	126.7 (153.9)
6	-10.6	-21.8	4.3	---	112.3 (125.9)	110.9 (122.4)	109.4 (121.4)
7	-4.6	-14.2	9.6	---	124.7 (140.0)	122.6 (135.1)	121.6 (135.7)
8	-33.5	-28.0	-20.5	---	120.3 (153.1)	120.3 (156.8)	114.3 (147.1)
9	-28.7	-20.7	---	---	140.2 (165.8)	132.2 (155.0)	---
10	-19.6	-21.8	---	---	140.2 (164.9)	132.0 (156.8)	---
11	-14.5	-15.3	---	---	138.0 (157.4)	130.9 (160.3)	---
12	-13.7	-14.7	---	---	137.9 (157.4)	130.9 (160.3)	---

a) See reference 6. b) UCISD/6-31G*//UHF/6-31G* level. c) UCISD/6-311G*//UHF/6-31G* level. d) Singlet is a saddle point; rearrangement to the iminium ion appears to be spontaneous on the ab initio hypersurface.

When the gap between these two orbitals is small, Coulomb repulsion relief and exchange energy are sufficient to favor a triplet ground state. Thus, electron deficient π systems, like **4**, will generally favor the triplet while electron rich π systems, like **8**, will favor the singlet. Small S-T gaps will be observed for ions intermediate between these two extremes, like **5**. Semi-empirical methods mirror this trend, and predict that it will continue with the larger aryl nitreniums. Thus, the electron-withdrawing acetyl group in **11** and **12** shifts the energy gap in favor of the triplet when compared with **9** and **10**.

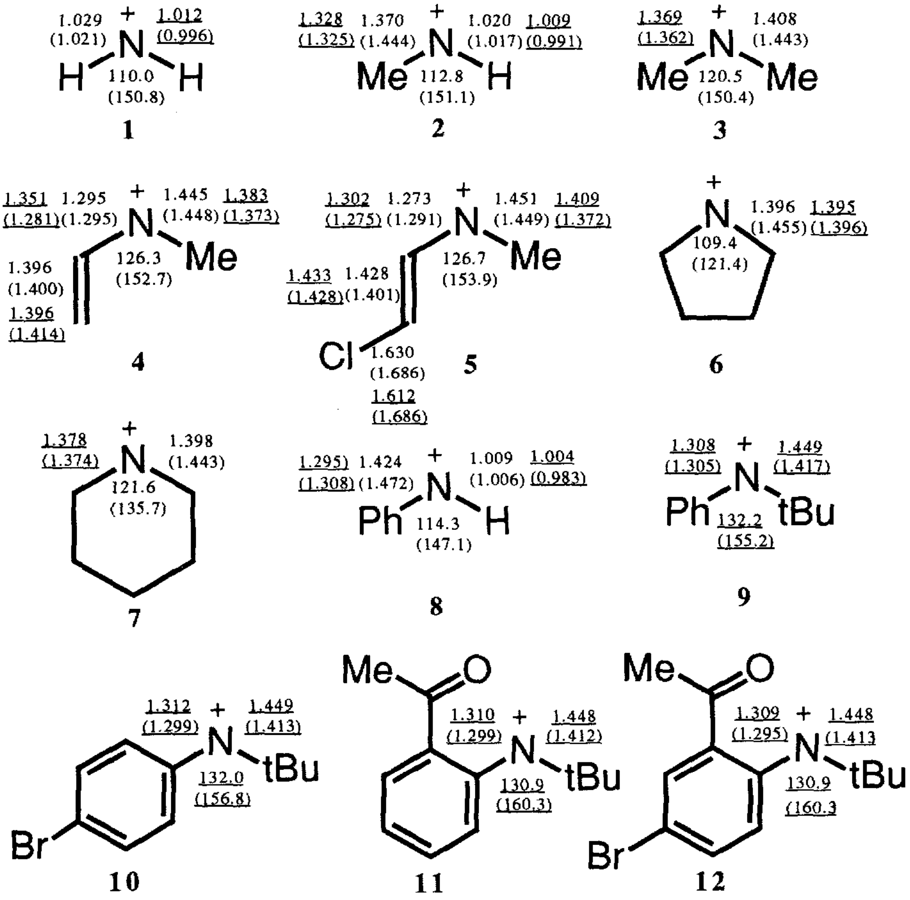

Figure 1. Selected UHF /6-31G* and AM1 CI geometrical data for singlet and (triplet) nitrenium ions. Bond angles are in degrees and bond lengths are in Ångstroms.

Geometric constraints on the R-N-R' bond angle also have a significant effect on the S-T gap. Unconstrained triplets have bond angles of 150-160° while the singlet angles are typically 110-130°. Placing the nitrogen in a small ring will destabilize the triplet state by preventing it from opening to its preferred bond angle. Conversely, adding bulky substituents to acyclic nitrenium ions is predicted to destabilize the singlet state by preventing closure to more favorable angles. The ab initio calculations on **3**, **6**, and **7** provide an interesting example of this effect. As the bond angle is held more acute by substitution in a 6-membered (**7**) and a 5-membered ring (**6**), the energy gaps shift increasingly to favor the singlet state. This trend is predicted at all levels by the corresponding calculations. Additionally, the semi-empirical calculations predict that bulky substituents will destabilize the singlet. Thus, substitution of a large *tert*-butyl group in **9** for the hydrogen atom in **8** is shown to shift the energy gap by ca. 5 kcal/mol in favor of the triplet.

Semi-empirical methods predict structural effects on singlet-triplet energy gaps in nitrenium ions in a way that is consistent with ab initio predictions and intuitive expectations. Thus electron-rich π-systems favor the singlet and electron deficient π-systems favor the triplet. Bulky substituents on the nitrogen will also favor the triplet by increasing the R-N-R' bond angle. Caution should be exercised when interpreting the absolute magnitude of S-T gaps derived from semi-empirical calculations: in general these calculations will overestimate the stability of the singlet state.

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6. Calculations employed the ROHF methodology with a 2x2 CI included in both full geometry optimizations and energies. For all but **1**-**3** the *semi-empirical* CI contribution was less than 0.1 kcal/mol. Software: Stewart, J. J. P. MOPAC v5.0, QCPE #455.
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8. Although UHF methodology was used throughout for consistency, no separation of α and β orbitals was observed in the singlets. Absolute energies (au) of triplets at UCISD/6-311G*//UHF/6-31G* (II) and UCISD/6-31G*//UHF/6-31G* (I): **1**, II, -55.34178, I -55.32080; **2**, II, -94.59954, I,-94.52698; **3**, II, -133.75658, I, -133.71323; **4**, II, -171.72920, I -171.67847; **5**, I, -630.67139; **6**, I, -210.82633; **7**, I, -249.97081, **8**, I, -285.56224. Singlet energies may be deduced from these and Table 1. In general, the *ab initio* CI contribution to the singlet exceeded that to the triplet by 17-20 kcal/mol. Software: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S; Gonzalez, C; DeFrees, D. J; Fox, D. J; Whiteside, R. A; Seeger, R.; Melius, C. F; Baker, J; Martin, R. L; Kahn, L. R; Stewart, J. J. P; Fluder, E. M; Topiol S.; Pople, J. A.; *Gaussian 88*, Gaussian Inc., Pittsburgh PA.
9. Additionally, alkylnitrenium ions **2**,**7**, and **8** have been examined at ab initio levels employing an unprojected Møller-Plesset (MP) perturbational treatment of correlation (see reference 5b). However, even after projecting out the largest component of spin contamination (PMP), we observe unsatisfactory convergence with this approach for vinylnitrenium ions **4** and **5**. For example, compound **4**, using the 6-311G* basis set gave singlet-triplet gaps of: MP2, -4.7; MP3(SDT), 2.2; MP4(SDTQ), -2.6; PMP2, 3.8;PMP3(SDT), 8.4; PMP4(SDTQ), 3.6 (kcal/mole). We expect this discrepancy between CI and MP treatments to become more profound with increasing conjugation. See: Nobes, R.H.; Pople, J.A.; Radom, L.; Handy, N.C.; Knowles, P.J. *Chem. Phys. Lett.* **1987**, *138*, 481.
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