Ab Initio Study of the Solvent Effects on the Singlet−Triplet Gap of Nitrenium Ions and Carbenes

Carlos Gonzalez,*,[†,||] Albeiro Restrepo-Cossio,[‡] Manuel Márquez,[§] Kenneth B. Wiberg,[§] and Michael De Rosa[⊥]

Pittsburgh Supercomputing Center, Carnegie Mellon University, Pittsburgh, Pennsylvania, 15213; Department of Chemistry, Florida Atlantic University, Boca Raton, Florida, 15213; Department of Chemistry, Yale University, New Haven, Connecticut 06520; and Department of Chemistry, Penn State University, Delaware County Campus, Media, Pennsylvania 19063

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Highly correlated ab initio molecular orbital methodologies have been used in the study of substituent effects on the singlet−triplet gaps of a series of nitrenium ions and their corresponding isoelectronic carbenes. Calculations in solution were carried out with the isodensity polarizable continuum models, IPCM. The results show a net stabilization of the singlet species as a result of electronic density donation of the substituents to a vacant p orbital located in the central atom. It is shown that this "π-donor−π-acceptor" dependence of the singlet−triplet gap is more significant in the case of the nitrenium ions, due to the presence of a positive charge. In addition, it was found that the singlet−triplet gaps decrease with the polarity of the solvent, most likely due to stabilizing electrostatic interactions between the solvent and the charge distribution of the singlet.

Introduction

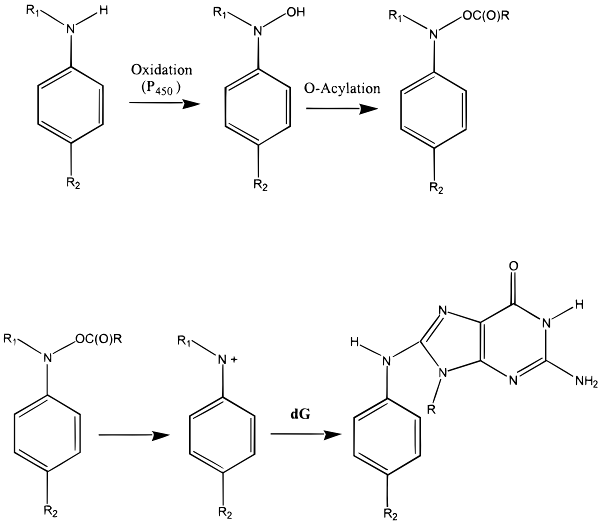
Nitrenium ions are azocations with structure $[R-N-R']^+$ believed to play an important role in carcinogenic processes involving the metabolism of aromatic amines.[1] This carcinogenic power is attributed to their high electrophilicity that allows these species to readily bind to and further modify DNA molecules.[2] Thus, as pointed out in the literature,[3] arylamines are known to readily react with deoxyguanosine, **dG**, via the metabolic pathway given by Scheme 1.

In this mechanism, the amine is metabolically oxidized by the cytochrome P-450-dependent monooxygenase enzyme, and subsequently, *N,O*-acetyltransferase and deacetylase enzymes form the ultimate carcinogen, **UC**, that eventually loses an ester to afford an arylnitrenium ion that attacks the nucleotide bases in DNA (**dG** in Scheme 1), causing severe mutations that ultimately lead to cancer tumors.[4]

Like their isoelectronic carbenes, R−C−R′, they can exist in both the singlet and triplet states, the relative stability of these states being dependent on the substituents bonded to the central atom deficient in electrons. In the singlet state, the nonbonding electrons occupy an sp^2 orbital, leaving an empty p orbital on the central nitrogen, making these species very reactive toward nucleophiles. In the triplet state, the nonbonding electrons have parallel spins and occupy an sp^2 orbital as well as an orbital with large p character, usually behaving as diradicals.

Despite the fact that interesting experimental studies of the spin states of arylnitrenium ions have been recently reported in the literature,[5] relatively little is known about the singlet−triplet, **S−T**, gap of the nitrenium ions in general. In fact, the only experimental value available in the literature is the **S−T** gap for NH_2^+ (30.1 ± 0.2 kcal/mol) obtained by Gibson et al.[6] Results provided by highly correlated ab initio molecular orbital calculations are in excellent agreement with this value.[7] Ford an coworkers[8] have carried out semiempirical and low-level ab initio calculations in order to determine a correlation between the gas-phase **S−T** gaps and the substituent effects in a series of nitrenium ions $[R-N-R']^+$. Recently, more accurate ab initio methodologies as well as density functional theory have been used in the treatment of similar systems.[9]

SCHEME 1



Nitrenium ions are generally produced in the singlet state, and consequently they must undergo an intersystem crossing to the low-lying triplet state. Gassman[10] has reported intersystem crossing on *N*-chloroazabicyclo[2.2.1]heptane using heavy-atom solvents as catalysts. However, subsequent studies by other researchers using different leaving groups have produced

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[†] Carnegie Mellon University.
[‡] Florida Atlantic University.
[§] Yale University.
[⊥] Penn State University.
[||] Current address: Physical and Chemical Properties Division, Building 221, Room Alll, National Institute of Standards and Technology, Gaithersburg, MD 20899.

negative results. In addition, recent experimental studies[11a] have indicated the possibility of stabilization of the singlet with respect to the triplet as a result of electrostatic interactions with the solvent. Even though a sizable number of theoretical studies have been conducted in order to compute the **S−T** gap of nitrenium ions in the gas phase, the literature is practically void of theoretical computations of **S−T** gaps in solution.[11d] Given the potential role of these species in carcinogenic processes, it is clear that an in-depth understanding of the combined solvent and substituents effects on **S−T** gaps of nitrenium ions is of significant importance.

In the present work, highly correlated ab initio molecular orbital calculations as well as density functional theory, DFT, are used to compute the **S−T** gaps of a series of nitrenium ions $^+$[X−N−H] (with X = H, Cl, F. and CN) in the gas phase as well as in solution. In all cases, solvent effects are computed by means of polarizable continuum model, PCM.[12−14] Due to the availability of theoretical and experimental studies related to gas-phase **S−T** gaps for carbenes,[15] X−C−Y, as well as experimental results describing the effects of the polarity of the solvent on these properties,[16] **S−T** gaps were also computed on the corresponding isoelectronic carbenes X−C−M in both gas phase and solution. The comparison of these data with the results obtained for the nitrenium ions under study provides a useful way of rationalizing the solvent and substituent effects on their **S−T** gaps, especially given the lack of experimental data.

Even though most of the nitrenium ions proposed as ultimate carcinogens are believed to come from larger systems such as aromatic amines, the study of the solvent effects on the **S−T** gaps of the smaller ions considered in this work provides a reasonable model for an understanding of these effects. It should be pointed out from the outset that the purpose of this study is to focus on the electrostatic interactions between the solvent and the solute and that the explicit interaction with the solvent molecules is totally neglected.

Theoretical Method

Full geometry optimizations of all minima were carried out at the MP2 and DFT levels with the 6-311++G** basis set, while gas-phase energy calculations were obtained at QCISD and QCISD(T)[17] with the same basis. The DFT calculations were carried out using the three-parameter hybrid functional B3LYP:[18]

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = (1 - a_0)E_x^{\mathrm{LSDA}} + a_0 E_x^{\mathrm{HF}} + a_x \Delta E^{\mathrm{B88}} + a_c E_c^{\mathrm{LYP}} + (1 - a_c)E_c^{\mathrm{VWN}} \quad (1)$$

where $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$.

In this equation, E_x^{LSDA} is the local Slater exchange energy, E_x^{HF} is the exact exchange energy given by the Hartree−Fock formalism, ΔE^{B88} is Becke's gradient-corrected exchange energy,[19] E_c^{LYP} is the gradient-corrected correlation energy developed by Lee, Yang, and Parr,[20] and E_c^{VWN} is the local correlation energy of Vosko, Wilk, and Nussair.[21] Expression 1 is a variant of Becke's original hybrid functional designed to rectify the failure of conventional DFT in reproducing the exchange-only limit of the adiabatic connection method, ACM.[22]

Analytical second derivatives were used to compute vibrational frequencies and zero-point energy corrections at MP2/6-311++G**. In addition, energies in solution were computed at the B3LYP/6-311++G** and QCISD/6-311++G** level using a recent implementation of the isodensity polarizable continuum model, IPCM, in a local version of the Gaussian ab initio packaged.[23] In the IPCM model, the solute is placed inside a cavity surrounded by a continuous medium (the solvent) with a bulk dielectric constant ϵ. The charge distribution of the solute generates an electric field that in turn induces a dipole density distribution on the solvent. According to this method, the solute Hamiltonian in solution is then given by

$$\mathbf{H} = \mathbf{H} - \sum_i^n \int \frac{\sigma(\mathbf{r_s})\, \mathrm{d}\mathbf{r_s}}{|\mathbf{r}_i - \mathbf{r_s}|} + \sum_A^M Z_A \int \frac{\sigma(\mathbf{r_s})\, \mathrm{d}\mathbf{r_s}}{|\mathbf{R_A} - \mathbf{r_s}|}$$

where $\mathbf{H}_0$ is the gas-phase Hamiltonian, the first summation is over electrons, and the second is over nuclei. The virtual charge distribution $\sigma(\mathbf{r_s})$ at point $\mathbf{r_s}$ on the cavity surface is given by the following expression:

$$\sigma(\mathbf{r_s}) = \frac{1-\epsilon}{4\pi\epsilon}\frac{\partial}{\partial\vec{n}}[\Phi_\rho(\mathbf{r_s}) + \Phi_\sigma(\mathbf{r_s})] = \frac{1-\epsilon}{4\pi\epsilon}[\vec{E}_0(\mathbf{r_s}) + \vec{E}_{\mathrm{P}}(\mathbf{r_s})]\cdot\vec{n}(\mathbf{r_s})$$

where $\Phi_{\mathrm{r}}(\mathbf{r_s})$ and $\Phi_{\mathrm{s}}(\mathbf{r_s})$ are the electrostatic potential due to the solute charge distribution and the virtual charges respectively, $E_0(\mathbf{r_s})$ and $E_{\mathrm{P}}(\mathbf{r_s})$ are the electric fields of the solute and the virtual charges, and $\vec{n}(\mathbf{r_s})$ is a unit vector perpendicular to the cavity and pointing in the outward direction. It is well-known that the description of the cavity is central for the performance of the polarizable continuum models. In our IPCM simulations, the volume of the cavity surrounding the solute is computed by an isosurface of electron density obtained from standard quantum chemistry calculations (in this work QCISD and B3LYP).

Results

Validation of the Method. To assess basis sets and correlation effects on the geometry and **S−T** gap in $^+$[NH$_2$], a series of geometry optimizations at MP2 with five different basis sets of increasing flexibility and QCISD with 6-311++G** were carried out. The results shown in Table la indicate that for the singlet, the N−H bond lengths optimized at the MP2 and QCISD levels are cat 0.006−0.014 Å shorter than the value obtained by Cramer et al. using CASSCF calculations with a triplet-ζ plus polarization basis (CASSCF/TZP),[7] while the H−N−H angles are found to be approximately 1.4−2.8° larger than the CASSCF results. The same trend is observed in the case of the triplet (Table lb) where the optimized bond lengths were found to be 0.002−0.008 Å longer than the corresponding values obtained at CASSCF with H−N−H angles 0.1−2.4° larger. It is interesting to notice that there does not seem to be a marked basis sets or a correlation effect on the geometry for these species.

Zero-point energy corrections, ΔZPE, and **S−T** energy gaps calculated at different levels of theory for nitrenium ion are listed in Table 2a,b respectively. The corresponding values obtained by Cramer et al. at the MRCISD(Q)/TZP level[7] as well as the value obtained experimentally are also listed for comparison purposes. As with the optimized geometries, the inclusion of polarization and diffusion functions does not seem to affect the results; however, the inclusion of correlation seems to have a significant effect on the energetics. Thus, fourth-order Moeller−Plesset perturbation theory with spin projection, PMP4,[24] lowers the gap by almost 3 kcal/mol with respect to MP2, while QCISD lowers these values by an extra 3 kcal/mol. In addition, the inclusion of triple corrections in the QCISD treatment decreases the **S−T** gap by an additional 1 kcal/mol. The **S−T** gap obtained at the highest level of theory used in this work (QCISD-

TABLE 1: Optimized Geometry and Absolute Energies for $^1[NH_2]^+$ and $^3[NH_2]^+$

(a) $^1[NH_2]^+$

method	N−H[a]	∠HNH[a]	ex[b]	EMP4[b]	EQCISD(T)[b]
MP2/6-31G*	1.049	108.28	−55.244 19	−55.266 14	−55.271 47
MP2/6-31G**	1.044	108.02	−55.261 32	−55.283 57	−55.288 83
MP2/6-311G**	1.048	107.13	−55.297 74	−55.304 85	−55.310 06
MP2/6-311+G**	1.048	107.09	−55.298 08	−55.305 17	−55.310 68
MP2/6-311++G**	1.048	107.12	−55.298 36	−55.305 43	−55.310 37
QCISD/6-311++G**	1.052	106.98	−55.307 07	−55.310 66	
CASSCF/TZP	1.058	105.50	−55.334 73		

(b) $^3[HN_2]^+$

method	N−H[a]	∠HNH[a]	ex[b]	EMP4[b]	EPMP4[b]	EQCISD(T)[b]
MP2/6-31G*	1.033	151.17	−55.306 57	−55.322 68	−55.324 63	−55.324 61
MP2/6-31G**	1.029	149.98	−55.323 01	−55.339 27	−55.341 10	−55.341 06
MP2/6-311G**	1.031	149.84	−55.358 83	−55.359 80	−55.361 71	−55.361 67
MP2/6-311+G**	1.031	149.95	−55.359 08	−55.360 03	−55.361 94	−55.361 91
MP2/6-311++G**	1.031	149.95	−55.359 35	−55.360 28	−55.362 19	−55.362 16
QCISD/6-311++G**	1.035	151.39	−55.360 22	−55.362 21		
CASSCF/TZP	1.037	149.70	−55.382 67			

[a] N−H bond lengths in angstroms and angles ∠HNH in degrees. [b] Energies in au.

TABLE 2: $[NH_2]^+$ ZPE and S−T Gaps at Different Levels of Theory[a]

(a) $[NH_2]^+$ ZPE

method	singlet	triplet	AZPE
MP2/6-31G*	11.66	11.04	0.62
MP2/6-31G**	11.74	11.22	0.52
MP2/6-311G**	11.51	11.08	0.43
MP2/6-311+G**	11.51	11.06	0.45
MP2/6-311++G**	11.51	11.06	0.45
QCISD/6-311++G**	11.35	10.85	0.50
B3LYP/6-311++G**	11.10	10.50	0.60

(b) $[NH_2]^+$ S−T Gaps[b]

method	ΔE_x	ΔEMP4	ΔEPMP4	ΔEQCISD(T)
MP2/6-31G*	39.77	36.10	37.32	33.96
MP2/6-31G**	39.23	35.47	36.62	33.40
MP2/6-311G**	38.77	34.92	36.11	32.81
MP2/6-311+G**	38.73	34.88	36.08	32.60
MP2/6-311++G**	38.72	34.87	36.07	32.95
QCISD/6-311++G**	33.85	32.85		
B3LYP/6-311++G**	33.57			
MRCISD(Q)/TZP[c]	30.08			
experimental[c]	30.10			

[a] Energies in kcal/mol. [b] Relative energies in kcal/mol. [c] Cramer, C. J.; Dulles, F. J.; Storer, J. W.; Worthington, S. *Chem. Phys. Lett.* **1994**, *218*, 387. [d] Berkowitz, J.; Cho, H. *J. Chem. Phys.* **1989**, *90*, 1.

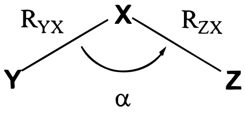
(T)/6311++G**//QCISD/6-311++G**) overestimates the experimental value by ca. 2.8 kcal/mol (see Table 2b).

On the basis of these results, we have adopted MP2/6-311++G** geometry optimizations and zero-point energy corrections, ZPE, followed by QCISD(T)/6311++G** single-point calculations as the method of choice to compute the **S−T** gaps of the rest of the molecules under study. This combination provides a good compromise between accuracy and computational expense and seems like a very reasonable approach to examine substituent effects on the **S−T** gaps of nitrenium ions.

Gas-Phase Geometries and Energetics. Table 3 lists the fully optimized equilibrium geometries at the MP2/6311++G** level for all the singlet and triplet nitrenium ions as well as the carbenes considered in this study. The corresponding results obtained at B3LYP/6-311++G** are shown in Table 4. In the case of the carbenes, the optimized geometries are in excellent agreement with previous theoretical and experimental results.[15] The optimized geometries for the nitrenium ions are in very good agreement with the results obtained by Gobbi and Frenking, using MP2/6-31G(d).[9h]

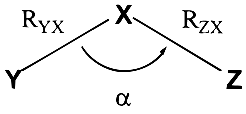
TABLE 3: Optimized Geometries (MP2/6-311++G) for Singlet and Triplet Nitrenium Ions and Carbenes**

(a) Singlet



X	Y	Z	R_{YX}	R_{ZX}	α
N	H	H	1.048	1.048	107.12
C	H	H	1.100	1.100	101.80
N	Cl	H	1.542	1.041	108.49
C	C1	H	1.686	1.108	102.76
N	F	H	1.223	1.055	105.10
C	F	H	1.310	1.118	102.16
N	CN	H	1.263	1.040	116.92
C	CN	H	1.406	1.102	108.00

(b) Triplet

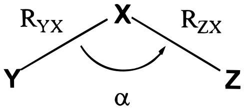


X	Y	Z	R_{YX}	R_{ZX}	α
N	H	H	1.031	1.031	149.95
C	H	H	1.080	1.080	132.70
N	C1	H	1.518	1.032	134.42
C	C1	H	1.668	1.082	125.97
N	F	H	1.225	1.052	126.38
C	F	H	1.317	1.085	121.34
N	CN	H	1.130	1.016	180.0
C	CN	H	1.378	1.076	135.08

Overall, the results shown in Table 3 indicate that optimized bond lengths between the substituents and the central atom for the singlet and the triplet nitrenium ions are approximately 0.05−0.25 Å too short when compared to the equivalent bond lengths in their isoelectronic carbenes. In addition, larger bond angles are also observed in the case of the nitrenium ions. This trend is not surprising given the stronger bonding existing in the nitrenium ions as a result of the positive charge. It is interesting to notice, however, that in the case of the substituent CN, the triplet [NC−C−H] exhibits a bond angle of ca. 135°, while in the triplet $[NC-N-H]^+$ this angle is exactly 180°, leading to a linear structure. This difference can be attributed

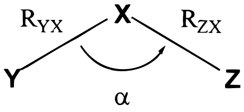
TABLE 4: Optimized Geometries (B3LYP/6-311++G) for Singlet and Triplet Nitrenium Ions and Carbenes**

(a) Singlet



X	Y	Z	R_{YX}	R_{ZX}	α
N	H	H	1.057	1.057	107.07
C	H	H	1.114	1.114	101.51
N	C1	H	1.566	1.047	108.70
C	C1	H	1.717	1.112	101.67
N	F	H	1.235	1.066	105.10
C	F	H	1.316	1.124	101.88
N	CN	H	1.238	1.039	120.41
C	CN	H	1.372	1.099	111.50

(b) Triplet



X	Y	Z	R_{YX}	R_{ZX}	α
N	H	H	1.038	1.038	154.76
C	H	H	1.080	1.080	135.42
N	C1	H	1.545	1.037	133.73
C	C1	H	1.676	1.086	126.24
N	F	H	1.236	1.061	125.70
C	F	H	1.317	1.090	121.54
N	CN	H	1.170	1.021	180.00
C	CN	H	1.295	1.067	159.44

to a stronger interaction in the ion between one of the π bonds on the cyano group and one of the unpaired electrons on the central nitrogen leading to the formation of two adjacent N−C double bonds, which forces the structure to be linear. In this case, each nitrogen ends up with an unpaired electron with parallel spins.

Further analysis of the data presented in these tables indicate that for the nitrenium ions as well as the carbenes the bond angles in the singlet are considerably smaller than in the triplet, while the bond lengths are very similar in both states. In the case of the carbenes (singlet and triplet) and the singlet nitrenium ions, the bond lengths follow the order X−H < X−F < X−CN < X−CT, with X = N, C. In the case of the triplet nitreniurn ions, the order is N−H < N−CN < N−F < N−Cl, which is a direct consequence of the interaction between the π bond on the cyano and the unpaired electron on the central N as previously discussed.

Tables 3 and 4 show excellent agreement between the equilibrium geometries at B3LYP and the ones obtained at MP2. This result is very encouraging given that B3LYP is considerably less computationally demanding[25] and suggests the possibility of employing this method for geometry optimizations of even larger nitrenium ions.

Table 5 lists the **S**−**T** gaps in gas phase for all the species studied in this work computed at the QCISD(T)/6-311++G**/ /MP2/6-311+G** level and B3LYP/6-311++G**. As in the case of the optimized geometries, the **S**−**T** gaps for the different carbenes reported in this work are in very good agreement with previous theoretical and experimental work.[15] The results show that, the **S**−**T** gaps for the substituted nitrenium ions are larger than their isoelectronic carbene counterparts in the cases where the substituents are either H or CN. In the case of fluorine and chlorine, the singlet species are more stable than the triplet and the **S**−**T** gaps become negative. The magnitude of this "gap inversion" is predicted to be larger in the carbenes (see Table 5). This trend was also found by calculations carried out by Gobbi and Frenking[9h] at the MP4/6-311G(2df)//MP2/6-31G(d) level of theory.

TABLE 5: S−T Gaps[a] and Dipole Moment Changes[b] in the Gas Phase for Nitrenium Ions and Carbenes

species	Δ*E*[QCISD(T)]	Δ*E*[B3LYP]	Δμ[QCISD]	Δμ[B3LYP]
$[NH_2]^+$	32.85	33.57	1.35	1.52
$[NCNH]^+$	21.99	27.47	−0.31	−0.63
$[ClNH]^+$	−1.22	5.02	−0.28	−0.16
$[FNH]^+$	−4.69	−0.29	−0.68	−0.53
CH_2	11.68	11.76	1.51	1.37
NCCH	9.37	16.20	−0.52	−0.92
C1CH	−4.16	−3.46	0.90	0.86
FCH	−13.20	−11.56	0.61	0.39

[a] Gaps in kcal/mol. [b] $\Delta\mu = (\mu_s - \mu_t)$ in debye.

In both, the nitrenium ions as well as the carbenes, the **S**−**T** gap decreases following the trend H−X−H > H−X−CN > M−X−Cl > H−X−F with X = N, C. This result can be attributed to the stabilization of the singlet as a result of the "π-donor" character of the substituents whereby the substituent donates electronic density to the deficient p orbital on the central atom. This stabilization is less important in the triplet species where there are not vacant orbitals. In the case of strong π donors such as chlorine and fluorine, this interaction seems to be so large that the singlet becomes more stable than the triplet, inverting the **S**−**T** gap (see Table 5).

Given that as a result of computational convenience it would be desirable to study solvent effects on the **S**−**T** gaps of these species using the IPCM model at the B3LYP/6-311++G** level, it is necessary to determine whether gas-phase gaps as well as dipole moment differences, Δμ, between the singlet and the triplet compare well with the values obtained with the more accurate QCISD methodology. The results shown on Table 5 indicate a very good agreement between the Δμ values obtained at B3LYP and the QCISD results. In addition, with the exception of $[ClNH]^+$ and $[FNH]^+$, the **S**−**T** gaps obtained at B3LYP are in reasonable agreement with the QCISD(T) values. However, B3LYP seems to overestimate the **S**−**T** gap for $[ClNH]^+$ to the point that it predicts the triplet to be more stable than the singlet, contrary to the QCISD(T) results (Table 5). This is particularly disturbing since as explained before, due to the relatively strong "π-donor" character of chlorine, the **S**−**T** gap for $[C1NH]^+$ is expected to be smaller. Given this marked discrepancy between B3LYP and QCISD(T) and the lack of experimental data available in the literature, full geometry optimizations using the multireference CASSCF[26] method with Dunning's correlation consistent basis set TZP (including f functions)[27] were performed on the singlet and triplet states of $[C1NH]^+$ and $[FNH]^+$. In all cases, a total of 12 electrons and 9 orbitals were considered in the active space (full valence). Single-point energies were computed at the MRCI/TZP[28] level using the previous CASSCF wave function as reference. All calculations were carried out with the MOLPRO 96.4 software.[29] Although not shown here, the optimized geometrical parameters obtained at CASSCFF/TZP level are in very good agreement with the results previously obtained with B3LYP and QCISD. **S**−**T** gaps of −0.36 and −7.97 kcal/mol[30] were obtained at the MRCI/TZP//CASSCF/TZP level for $[ClNH]^+$ and $[FNH]^+$, respectively. Comparison of the corresponding **S**−**T** gaps obtained at B3LYP and QCISD(T) (Table 5) with these results leads to the conclusion that QCISD(T) correctly predicts $^1[ClNH]^+$ to lie lower than $^3[C1NH]^+$, contrary to the results given by B3LYP. Work is currently under way leading to a

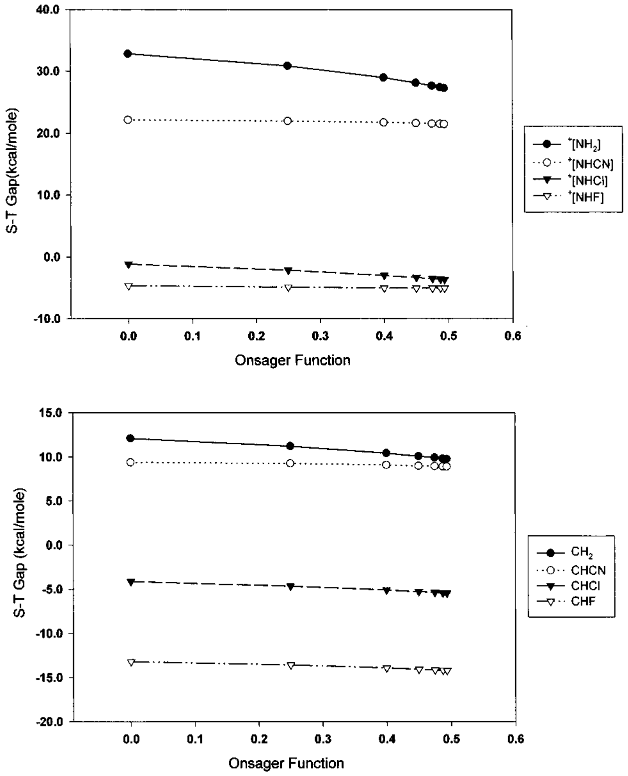


Figure 1. (a, top) **S**−**T** gap (in kcal/mol) vs Onsager function for substituted nitrenium ions computed at QCISD(T)/6-311++G**//MP2/6-31G++**. (b, bottom) **S**−**T** gap (in kcal/mol) vs Onsager function for substituted carbenes computed at QCISD(T)/6-311++G**//MP2/6-31G++* *.

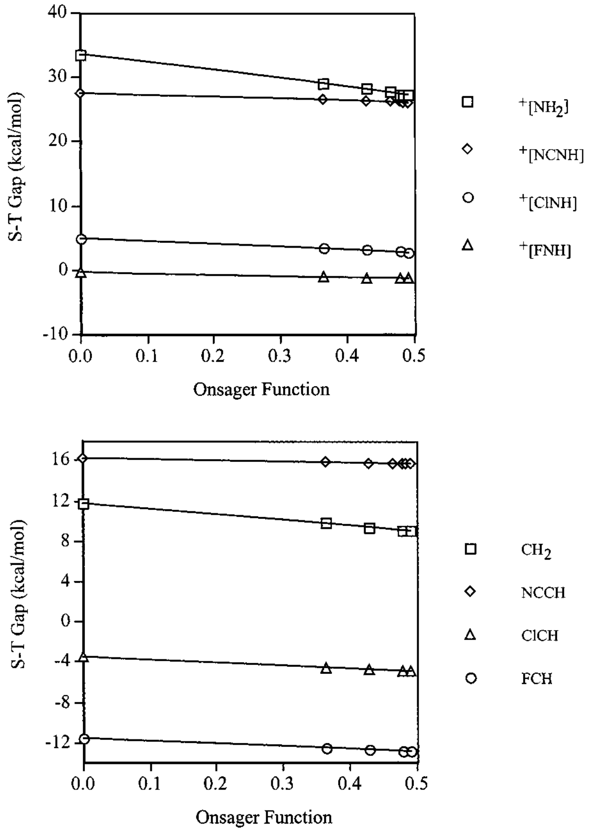


Figure 2. (a, top) **S**−**T** gap (in kcal/mol) vs Onsager function for substituted nitrenium ions computed at B3LYP/6-311++G**. (b, bottom) **S**−**T** gap (in kcal/mol) vs Onsager function for substituted carbenes computed B3LYP/6-31G++**.

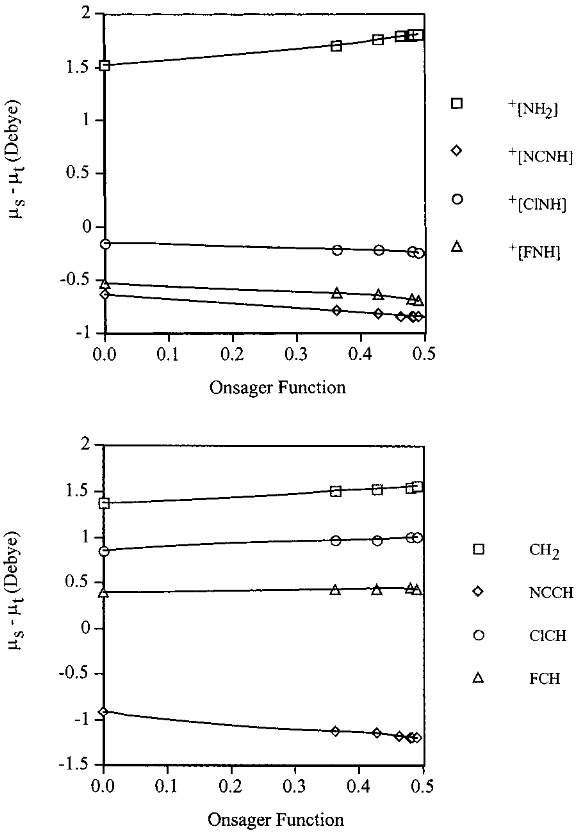


Figure 3. (a, top) $\Delta\mu$ (in debye) vs Onsager function for substituted nitrenium ions. (b, bottom) $\Delta\mu$ (in debye) vs Onsager function for substituted carbenes.

systematic study to understand the nature of these and related problems DFT seems to have in the proper treatment of singlet and triplet species of molecular cations and systems where strong "π-donor−π-acceptor" interactions are important.

Solvent Effects on the Energetics. Given the problems B3LYP seems to have in reproducing the relative stability of the gas-phase singlet with respect to the triplet in the case of $^+$[NHCl], it was decided to compute the solvent effects using the IPCM method at the QCISD/6311++G** level of theory instead. Figure la,b show plots of the **S**−**T** gap vs the Onsager function[31] for $[XNH]^+$ and [CHX], respectively. In general, it is observed that the **S**−**T** gap decreases with the dielectric constant, ϵ (Figure l) indicating a net stabilization of the singlet species with respect to the triplet as result of the interaction with the solvent. These findings are in good agreement with recent experimental results obtained by Garcia-Garibay and collaborators[16e−g] on a series of carbenes in solution. This effect seems to be stronger in the case of the nitrenium ions (Figure l) where larger negative slopes are observed in the **S**−**T** gap vs Onsager function plots. For comparison purposes, the same kind of simulations in solution were carried out at the B3LYP/6-311++G** level (Figure 2). Despite the overestimation of the instability of the gas phase singlet with respect to the triplet in the cases of $[C1NH]^+$ and $[FNH]^+$ by B3LYP, it is surprising to see how well it reproduces the overall trend found with the more accurate method QCISD.

Figure 3 depicts plots of the dipole moment difference, $\Delta\mu = \mu_s - \mu_t$, between the singlet and triplet for all the molecules studied in this work as a function of the dielectric constant of the solvent, given by the Onsager function. The results indicate larger positive $\Delta\mu$ changes in the case of $[NH_2]^+$ when compared to the substituted nitrenium ions. The fact that the dipole moment of the singlet becomes larger with ϵ is an indication of stronger electrostatic interactions with the solvent leading to a net stabilization of the singlet with respect to the triplet. This effect is less marked in the substituted species where $\Delta\mu$ does not change so rapidly with ϵ and consequently the corresponding **S−T** gap decreases more slowly. This seems particularly true for the strong π donors F and Cl, where $\Delta\mu$ (already negative in gas phase) remains almost constant throughout the whole dielectric constant range (see Figure 3a). Similar behavior is observed in the case of the carbenes (see Figure 3b). However, in contrast to their isoelectronic nitrenium ions, the dipole moment difference for [CHCl] and [CHF] remains positive. This is not surprising given that in these cases, the π-donor−π-acceptor interaction is not as strong as in the nitrenium ions where a positive charge exits.

Conclusions

The results obtained in this work show how the **S−T** gap of nitrenium ions as well as their isoelectronic carbenes decreases with the π-donor character of the ligands attached to the central atom. This effect seems to bet more important in the case of nitrenium ions (when compared to their corresponding carbenes) probably due to the presence of a positive charge that makes the "π-donor−π-acceptor" interaction somewhat stronger. **S−T** gap calculations in solution indicate that the polarity of the solvent tends to increase the stability of the singlet with respect to the triplet. These results can be attributed to a stronger interaction of the solvent with the singlet (as indicated by larger dipole moments of the singlets) leading to its net stabilization.

In the case of the carbenes studied in this work, the gas-phase **S−T** gaps agree with previous experimental and theoretical work. In addition, the trends experimentally observed for solvent effects on **S−T** gaps agree with the trend obtained by our calculations. On the basis of these observations, it seems reasonable to expect that the theoretical results obtained in the case of the nitrenium ions provide a reasonable accurate description of the electrostatics of these systems, despite the fact that direct experimental observations of **S−T** gaps of these species in the gas phase and solution are not available.

Even though the results obtained in this study are encouraging, they are based on a model that neglects the explicit treatment of the interactions of the solvent molecules with the nitrenium ions. Accounting for these interactions is critical in order to get a more realistic view of the behavior of these species in solution. Consequently, care should be excercised when interpreting the results reported in this work.

Finally, the hybrid three-parameter DFT functional B3LYP incorrectly predicts the singlet $[ClNH]^+$ to lie above the triplet, contrary to results obtained at QCISD(T) and MRCI levels. A better understanding of this and similar problems of DFT is central for the application of this computational efficient method in the treatment of larger and more realistic systems such as aryl nitrenium ions in solution. Work is currently underway leading to the development of new hybrid functionals able to accurately predict **S−T** gaps as well energetics of nitrenium ions in both the gas phase and in solution.

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(30) It is interesting to notice that the results obtained by Gobbi and Frenking at the MP4/6-311G(2df)//MP2/6-31g(d) for $^{+}$[NHC1] and $^{+}$[NHF] are in better agreement with these MRCI results than the corresponding gaps obtained with the higher correlated method QCISD(T)/6-311++G**/ /MP2/6-311++G** used in the present work.

(31) The Onsager function, OF, is related to the bulk dielectric constant, ϵ, by the expression $OF = (\epsilon - 1)/2\epsilon$.