Pergamon

Tetrahedron Letters, Vol. 38, No. 9, pp. 1515-1518, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00126-3

Computational Prediction of a Ground-state Triplet Arylnitrenium Ion and a Possible Ground-state Triplet Silylene

Christopher J. Cramer*‡ and Daniel E. Falvey*§

‡ Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, MN 55455.
§ Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.

Abstract: Density functional calculations predict that *bis*-(2,6-di-*t*-butyl)phenylnitrenium has a triplet ground state and that the corresponding silylene has essentially degenerate singlet and triplet states. The steric bulk of the aryl ligand strongly destabilizes the singlets in each case relative to the triplets; the latter can more readily accommodate large valence angles at the nitrogen or silicon atom.

Arylnitrenium ions ($ArNR^+$) and silylenes (ArSiR) are characterized by singlet ground electronic states. These species differ then from isoelectronic arylcarbenes that are typically ground state triplets. For example, the singlet-triplet (S–T) splitting in phenylcarbene favors the triplet state by about 5 kcal/mol,[1] but phenylnitrenium and phenylsilylene each have S–T splittings of about –21 kcal/mol favoring the singlet state (see below). In the nitrenium case, this reversal has been assigned to the much more aggressive π accepting ability of the positively charged nitrogen atom compared to the carbene carbon, i.e., the singlet arylnitrenium may be considered to have significant iminocyclohexadienyl cation character.[2] In the silylene case, on the other hand, the difference can simply be ascribed to the much greater splitting between s and p valence levels for silicon than for carbon, i.e., the p orbital that must be occupied in the silylene triplet lies too high in energy for its single occupation to be balanced by reduced Coulomb repulsion between the two non-bonding electrons.

In the case of nitrenium ions, this difference has biological consequences. Arylnitrenium ions, which can be generated in vivo from aromatic amines, are known to covalently modify genetic material.[3,4] Such reactivity is expected for a singlet state. Spectroscopic data for nitrenium ions in solution are entirely consistent with their having singlet ground states,[5-11] unless they are substituted with strong π-electron withdrawing groups.[12,13] Understanding what controls the magnitude of the S–T splitting in arylnitrenium ions may thus prove useful in understanding aromatic amine carcinogenicity. In the case of silylenes, on the other hand, the quest for a triplet ground state has been motivated primarily by aesthetics.[14]

It has long been recognized in single-center diradicals that the singlet state is destabilized relative to the triplet when the valence angle at the diradical center is forced to become larger.[15,16] In essence, this derives from the reduced ability of the hypovalent atom to provide s character to the singlet lone pair, which is sp^2-like in an ideal representation. Since the sp^2-like orbital is only singly occupied in the triplet, and since the other occupied orbital is the p orbital orthogonal to the plane of the hypovalent atom and its substituents (and thus unaffected by angle bending), the triplet generally has a much shallower potential energy well associated with angle bending. Thus, the quest for triplet silylenes, for example, has largely focused upon silylenes substituted with larger and larger alkyl groups, e.g., *t*-butyl,[14,17] trimethylsilyl,[14] or adamantyl.[18] Much of this work, in addition to a substantial amount of effort aimed at characterizing nitrenium ions,[12,19-24] has been carried out computationally. Recent demonstrations[2,22-24] of the high predictive accuracy of density functional theory (DFT) for S–T gaps in these systems have substantially reduced the computational costs that used to be involved in theoretical studies, these costs being primarily associated with the need for multireference descriptions of the singlets within wave-function-based approaches.[15]

Here we apply DFT to a series of aryl substituted nitrenium ions and silylenes in order to calculate S–T splittings. The bulkiness of the substituents is controlled by substitution at the 2 and 6 positions of the aromatic rings. In particular, we examine the series generated from phenyl, diphenyl, dimesityl, and *bis*(2,6-di-*t*-butyl)phenyl substitution. A key question in such a study relates to the geometries used for evaluation of the electronic energies. For the smaller systems (phenyl and diphenyl) we have compared geometries from lower levels of theory to those derived from full optimization at the DFT level. These methods are then used to optimize the geometries of the larger substituted diradicals and DFT energies are calculated as single points.

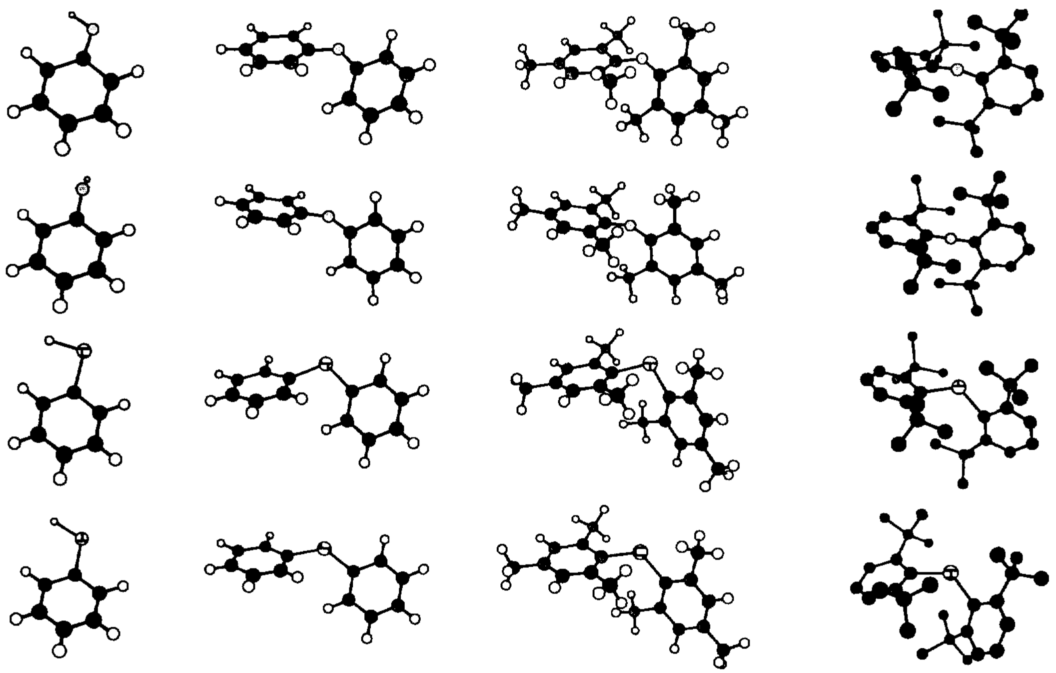

Figure 1. Minimum energy stereostructures for the singlet and triplet states of PhXH, Ph_2X, Mes_2X, and $Bdtbp_2X$ (row 1, singlet, $X=N^+$; row 2, triplet, $X=N^+$; row 3, singlet, X=Si; row 4, triplet, X=Si). For clarity, hydrogens are not shown for $Bdtbp_2X$. Structures were calculated at the following levels: PhXH and Ph_2X, BPW/cc-pVDZ; Mes_2N^+ and $Bdtbp_2N^+$, AM1; Mes_2Si and $Bdtbp_2Si$, RHF/MIDI$^{(*)}$ for singlets and ROHF/MIDI$^{(*)}$ for triplets. See Table 1 for additional data.

Figure 1 presents stereostructures for all compounds as optimized at the highest available level of theory. Table I provides information on two key geometrical features of the molecules, namely the bond distances to and the valence angle at the hypovalent center, as well as energetic information. DFT energies were calculated using the gradient-corrected functionals of Becke[25] (exchange) and Perdew and Wang[26] (correlation) with the correlation-consistent polarized valence-double-ζ basis set (cc-pVDZ) of Dunning.[27] Other DFT functionals give very similar results, as expected;[2,22-24] for brevity those are not included here.

For the nitrenium ions, we found the AM1 level (including a 2x2 CI for the singlet) gave very good geometries by comparison to the DFT level. The average deviation in bond lengths to nitrogen is 0.009 Å; the deviation in the valence angle at nitrogen is 6 to 7 degrees for $PhNH^+$, but this seems to be a problem associated primarily with the hydrogen substituent, since the agreement between the two levels for the valence angles in Ph_2N^+ is much improved. Encouragingly, differences in the predicted S–T gaps for the two sets of geometries are less than 0.5 kcal/mol. Moreover, the *absolute* energies of the various compounds typically drop by only 2 to 3 kcal/mol on reoptimization at the DFT level (1 au = 627.51 kcal/mol). We thus have considerable confidence in the ability of the AM1 method to deliver good geometries for the more hindered nitrenium ions.

Interestingly, the dimesitylnitrenium ions have nitrogen valence angles and C–N bond lengths that are almost identical to those predicted for Ph_2N^+. As illustrated in Figure 1, the additional steric interactions associated with the 2- and 6-methyl substituents are relieved by increasing the torsion angle between the two aromatic planes. Nevertheless, the S–T gap does drop by 6 kcal/mol, suggesting that the torsion angle between the two ring planes also has a differential effect on the two electronic states.

Finally, the steric interactions between the two aromatic rings in $Bdtbp_2N^+$ are severe enough to significantly increase the valence angle at nitrogen—in the triplet the angle becomes linear! Some shortening of the C–N bonds occurs, consistent with increased nitrogen s character in these bonds as a result of angle widening. Increased torsion between the aromatic ring planes is also observed, as illustrated in Figure 1. The net

Table I. Energetic and Selected Geometrical Data for PhXH, Ph_2X, Mes_2X, and $Bdtbp_2X$.

Molecule	Electronic State	Geometry	rXC, Å	∠CXC, deg[a]	*E*(DFT), au[b]	S–T gap, kcal/mol[c]
$PhNH^+$ (X=N)	$^1A'$	AM1-CI(2,2)	1.298	117.6	–286.649 57	
		BPW91/cc-pVDZ	1.308	111.2	–286.653 30	
	$^3A''$	AM1	1.334	138.9	–286.617 28	–20.3
		BPW91/cc-pVDZ	1.330	131.8	–286.620 18	–20.8
Ph_2N^+ (X=N)	^1A	AM1-CI(2,2)	1.348	128.2	–517.730 90	
		BPW91/cc-pVDZ	1.351	125.0	–517.734 29	
	^3B	AM1	1.308	149.7	–517.713 07	–11.2
		BPW91/cc-pVDZ	1.328	147.9	–517.715 78	–11.6
Mes_2N^+ (X=N)	^1A	AM1-CI(2,2)	1.348	128.2	–753.603 01	
	^3B	AM1	1.309	148.9	–753.593 68	–5.8
$Bdtbp_2N^+$ (X=N)	^1A	AM1-CI(2,2)	1.338	141.0	–1146.543 35	
	$^3B_{1u}$	AM1	1.292	180.0	–1146.555 04	7.3
PhSiH (X=Si)	$^1A'$	RHF/MIDI$^{(*)}$	1.909	96.5	–521.661 01	
		BPW91/cc-pVDZ	1.908	94.5	–521.665 56	
	$^3A''$	ROHF/MIDI$^{(*)}$	1.905	117.3	–521.627 31	–21.1
		BPW91/cc-pVDZ	1.875	117.9	–521.632 19	–20.9
Ph_2Si (X=Si)	^1A	RHF/MIDI$^{(*)}$	1.922	104.0	–752.704 11	
		BPW91/cc-pVDZ	1.921	102.6	–752.713 08	
	^3B	ROHF/MIDI$^{(*)}$	1.906	118.0	–752.669 10	–22.0
		BPW91/cc-pVDZ	1.880	122.0	–752.678 95	–21.4
Mes_2Si (X=Si)	^1A	RHF/MIDI$^{(*)}$	1.939	105.5	–988.544 72	
	^3B	ROHF/MIDI$^{(*)}$	1.914	122.3	–988.520 26	–15.4
$Bdtbp_2Si$ (X=Si)	^1A	RHF/MIDI$^{(*)}$	1.973	121.9	–1381.490 24	
	^3B	ROHF/MIDI$^{(*)}$	1.939	124.7	–1381.487 67	–1.6

a) CXH angle for $PhNH^+$ and PhSiH. b) BPW91/cc-pVDZ level of theory. c) Calculated from DFT energies for geometries at consistent theoretical levels.

consequence of these geometric distortions is to reverse the sign of the S–T gap, *making the triplet the lower energy state by 7.3 kcal/mol*, an amount large enough that possible errors in the theory would not be expected to reverse the state ordering. It is interesting to further speculate that if this molecule can be made, it might be expected to have a significant lifetime, given that sterically hindered triplet aryl*carbenes* have been generated with lifetimes on the order of minutes.[28]

For the silylenes, semiempirical methods proved extremely inaccurate for geometries. We found small-basis-set Hartree-Fock calculations to be reasonably effective, however. For the triplets, restricted open-shell methods were required because of the severe spin contamination of unrestricted wave functions (a flaw from which unrestricted DFT methods do not suffer[2]). We employed the MIDI basis set[29] with d functions on Si, denoted here as MIDI$^{(*)}$; this basis set with appropriately chosen d functions has been noted for giving good geometries (and partial atomic charges) in compounds containing second- and third-row atoms.[30] The largest discrepancy between HF and DFT geometries occurs in the triplets, where the ROHF method predicts C–Si bond lengths to be shorter by about 0.03 Å. However, this does not seem to have much effect on the computed S–T splittings. Interestingly, the *absolute* energies of the molecules drop quite a bit more in the silylene series than was the case for the nitrenium series, but this appears to be a phenomenon associated with the phenyl rings (about 3 kcal/mol per ring) that cancels out in the calculation of the S–T splitting.

Much as in the nitrenium series, the effect of dimesityl substitution on the geometries differs from diphenyl substitution only in the extent to which the aromatic rings rotate to avoid one another. And, as in the nitrenium case, the energetic consequence of this distortion is to reduce the S–T splitting by 6 kcal/mol.

For the case of Bdtbp$_2$Si, on the other hand, the geometries of the singlet and triplet states are quite different from the corresponding nitrenium ions. Presumably because of the significantly longer Si–C bonds (compared to N–C), the steric interactions between the aromatic rings are reduced sufficiently that the C–Si–C angles are only 121.9 and 124.7 deg in the singlet and triplet, respectively. Coincidentally, however, the energetic effect of this angle widening is to reduce the S–T splitting by a similar margin to that found for the nitrenium series. In the silylene case, it becomes only 1.6 kcal/mol favoring the singlet. Given the approximations in the geometries and the likely accuracy of the DFT calculations, the magnitude of this splitting is too small to be certain that it is of the correct sign, i.e., Bdtbp$_2$Si could have either a singlet or a triplet ground state. Experimental studies directed along these lines might be rewarding.

In conclusion, we have benchmarked low levels of theory that accurately predict molecular geometries for arylnitrenium ions and -silylenes. Higher-level single-point calculations with density functional theory predict unambiguously that the *bis*(2,6-di-*t*-butyl)phenylnitrenium ion has a triplet ground state; these calculations also predict that the singlet and triplet states of *bis*(2,6-di-*t*-butyl)phenylsilylene are very close to one another in energy.

Acknowledgments. Both CJC and DEF thank the NSF for funding and are grateful for high-performance vector and parallel computing resources made available by the Minnesota Supercomputer Institute and the University of Minnesota-IBM Shared Research Project, respectively.

References and Notes

1. Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.
2. Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787.
3. Scribner, J. D.; Naimy, N. *Cancer Res.* **1975**, *35*, 1416.
4. Stadler, W. M. *Int. J. Oncol.* **1993**, *3*, 549.
5. Novak, M.; Kahley, M. J.; Eiger, E.; Helmick, J. S.; Peters, H. E. *J. Am. Chem. Soc.* **1993**, *115*, 9453.
6. Anderson, G. B.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 9870.
7. Anderson, G. B.; Yang, L. L. N.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 7254.
8. Robbins, R. J.; Falvey, D. E. *Tetrahedron Lett.* **1994**, *35*, 4943.
9. Davidse, P. A.; Kahley, M. J.; McClelland, R. A.; Novak, M. *J. Am. Chem. Soc.* **1994**, *116*, 4513.
10. McClelland, R. A.; Kahley, M. J.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1996**, *118*, 4794.
11. Moran, R. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1996**, *118*, 8965.
12. Falvey, D. E.; Cramer, C. J. *Tetrahedron Lett.* **1992**, *33*, 1705.
13. Srivastava, S.; Falvey, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10186.
14. Grev, R. S.; Schaefer, H. F., III; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638.
15. Davidson, E. R. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p. 73.
16. Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348.
17. Gordon, M. S.; Schmidt, M. W. *Chem. Phys. Lett.* **1986**, *132*, 294.
18. Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.
19. Ford, G. P.; Scribner, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 4281.
20. Ford, G. P.; Herman, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3987.
21. Glover, S. A.; Scott, A. P. *Tetrahedron* **1989**, *45*, 1763.
22. Cramer, C. J.; Dulles, F. J.; Storer, J. W.; Worthington, S. E. *Chem. Phys. Lett.* **1994**, *218*, 387.
23. Cramer, C. J.; Worthington, S. E. *J. Phys. Chem.* **1995**, *99*, 1462.
24. Lim, M. H.; Worthington, S. E.; Dulles, F. J.; Cramer, C. J. *ACS Symp. Ser.* **1996**, *629*, 402.
25. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
26. Perdew, J.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
27. Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
28. Tomioka, H.; Hattori, M.; Hirai, K.; Murata, S. *J. Am. Chem. Soc.* **1996**, *118*, 8723.
29. Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. In *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.
30. Easton, R. E.; Giesen, D. J.; Welch, A.; Cramer, C. J.; Truhlar, D. G. *Theor. Chim. Acta* **1996**, *93*, 281.

(*Received in USA* 1 *November* 1996; *revised* 15 *January* 1997; *accepted* 16 *January* 1997)