Effect of meta Electron-Donating Groups on the Electronic Structure of Substituted Phenyl Nitrenium Ions

3 AUTHORS, INCLUDING:

Arthur H Winter
Iowa State University
31 PUBLICATIONS **217** CITATIONS

SEE PROFILE

Christopher J Cramer
University of Minnesota Twin Cities
531 PUBLICATIONS **23,395** CITATIONS

SEE PROFILE

Effect of meta Electron-Donating Groups on the Electronic Structure of Substituted Phenyl Nitrenium Ions

Arthur H. Winter,[†] Daniel E. Falvey,*,[†] and Christopher J. Cramer[‡]

*Contribution from the Department of Chemistry and Biochemistry, University of Maryland,
College Park, Maryland 20742-2021, and Department of Chemistry and Supercomputer Institute,
University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431*

Received April 22, 2004; E-mail: falvey@umd.edu

Abstract: Density functional theory (UB3LYP/6-31G(d,p)) was used to determine substituent effects on the singlet–triplet-state energy gap for 21 meta-substituted phenylnitrenium ions. It was found that strongly electron-donating substituents stabilize the triplet state relative to the singlet state. With sufficiently strong meta electron donors (e.g., *m,m′*-diaminophenylnitrenium ion) the triplet is predicted to be the ground state. Analysis of equilibrium geometries, Kohn–Sham orbital distributions, and Mulliken spin densities for the triplet states of this series of nitrenium ions leads to the conclusion that there are two spatially distinct types of low-energy triplet states. Simple arylnitrenium ions such as phenylnitrenium ions as well as those having electron-withdrawing or weakly donating meta substituents have lowest-energy triplet states that are n,π^* in nature. That is, one singly occupied molecular orbital is orthogonal to the plane of the phenyl ring and one is coplanar. These n,π^* triplets are generally characterized by large ArNH bond angles (ca. 130–132°) and an NH bond that is perpendicular to the plane of the phenyl ring. In contrast, meta donor arylnitrenium ions have a lowest-energy triplet state best described as π,π^*. That is, both singly occupied molecular orbitals are orthogonal to the aromatic ring. Such π,π^* states are characterized by NH bonds that are coplanar with the phenyl ring and have ArNH bond angles that are more acute (ca. 110–111°). These triplet nitrenium ions have electronic structures analogous to those of *meta*-benzoquinodimethane derivatives.

Nitrenium ions are reactive intermediates characterized by a dicoordinate, positively charged nitrogen atom.[1-5] The simplest example is NH_2^+. Similar to the isoelectronic carbenes, nitrenium ions have two low-energy electronic configurations, which are depicted schematically in Figure 1. For NH_2^+, the lowest energy state is the np triplet state, with the n^2 singlet state being +29.9 kcal/mol higher in energy.[6-11] The p^2 and np singlets are higher in energy and, as a rule, are not considered to be chemically significant. For substituted nitrenium ions, the singlet–triplet-state energy difference (ΔE_{ST}) has been the subject of numerous
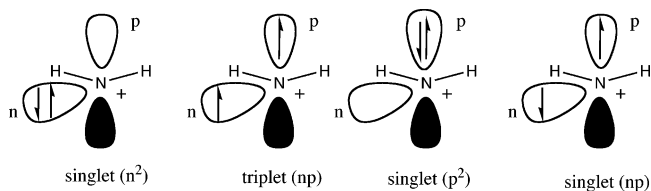

Figure 1. Singlet and triplet NH_2^+.

theoretical[11-21] and experimental studies.[22-29] Aromatic nitrenium ions, in particular, have received the most experimental

[†] University of Maryland.
[‡] University of Minnesota.

(1) Falvey, D. E. *J. Phys. Org. Chem.* **1999**, *12*, 589–596.
(2) Falvey, D. E. In *Organic, Physical, and Materials Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 2000; pp 249–284.
(3) Novak, M.; Rajagopal, S. *Adv. Phys. Org. Chem.* **2001**, *36*, 167–254.
(4) Falvey, D. E. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Maitland Jones, J., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; Vol. 1, pp 593–650.
(5) Abramovitch, R. A.; Jeyaraman, R. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: Orlando, FL, 1984; pp 297–357.
(6) Dunlavey, S. J.; Dyke, J. M.; Jonathan, N.; Morris, A. *Mol. Phys.* **1980**, *39*, 1121–1135.
(7) Barclay, V. J.; Hamilton, I. P.; Jensen, P. *J. Chem. Phys.* **1993**, *99*, 9709–9719.
(8) Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319–4328.
(9) Kabbadj, Y.; Huet, T. R.; Uy, D.; Oka, T. *J. Mol. Spectrosc.* **1996**, *175*, 277–288.
(10) Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1979**, *42*, 167–176.
(11) van Huis, T. J.; Leininger, M. L.; Sherrill, C. D.; Schaefer, H. F., III. *J. Comput. Chem.* **1998**, *63*, 1107–1142.

(12) Ford, G. P.; Herman, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3987–3996.
(13) Ford, G. P.; Herman, P. S. *J. Mol. Struct. (THEOCHEM)* **1991**, *236*, 269–282.
(14) Lee, S. T.; Morokuma, K. *J. Am. Chem. Soc.* **1971**, *93*, 6863–6866.
(15) Jordan, F. *J. Phys. Chem.* **1976**, *80*, 76–82.
(16) Wright, T. G.; Miller, T. A. *J. Phys. Chem.* **1996**, *100*, 4408–4412.
(17) Jensen, P.; Bunker, P. R.; McLean, A. D. *Chem. Phys. Lett.* **1987**, *141*, 53–57.
(18) Ford, G. P.; Herman, P. S.; Thompson, J. W. *J. Comput. Chem.* **1999**, *20*, 231–243.
(19) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787–9788.
(20) Gonzales, C.; Restrepo-Cossio, A.; Márquez, M.; Wiberg, K. B.; Rosa, M. D. *J. Phys. Chem. A.* **1998**, *102*, 2732–2738.
(21) Marquez, M.; Marí, F.; Gonzales, C. A. *J. Phys. Chem. A* **1999**, *103*, 6191–6199.
(22) Anderson, G. B.; Yang, L. L.-N.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 7254–7262.
(23) Robbins, R. J.; Falvey, D. E. *Tetrahedron Lett.* **1994**, *35*, 4943–4946.
(24) McClelland, R. A.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1995**, *117*, 4173–4174.
(25) Ren, D.; McClelland, R. A. *Can. J. Chem.* **1998**, *76*, 78–84.
(26) Dicks, A. P.; Ahmad, A.; D'Sa, R.; McClelland, R. A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1–3.
(27) Novak, M.; Lin, J. *J. Org. Chem.* **1999**, *64*, 6032–6040.

attention because of their suspected roles in carcinogenesis[30−35] and in the synthesis of conducting polymers.[36−38]

For substituted nitrenium ions, the prevailing view is that the ΔE_{ST} is determined by both steric and electronic factors. For the parent system (NH_2^+), the singlet state has a bent geometry with a bond angle of 107°, whereas the triplet is quasilinear, having an equilibrium bond angle of 150° and a very low barrier to inversion. Thus, increasing the RNR bond angle with large, sterically demanding substituents is predicted to destabilize the singlet state more than the triplet.[39,40] Nonsymmetric substituents that interact differently with the two nonbonding orbitals will tend to stabilize the singlet state. For example, the filled π-orbitals on an aromatic ring act to raise the energy of the p orbital and thus stabilize the singlet.[19,41,42] In fact, calculations at various levels of theory predict phenylnitreniumion to be a ground-state singlet with $\Delta E_{ST} \approx -20$ kcal/mol (a positive value of ΔE_{ST} indicates a triplet ground state).[19,41,43] Although an experimental measurement of this value is not available, the sum of the indirect evidence on phenylnitrenium ion and similar systems is consistent with this prediction.[3,22,25,44,45]

The trend predicted from this simple picture is supported by a variety of experimental and computational studies. For example, Sullivan et al.[43] calculated ΔE_{ST} values for a series of para-substituted phenylnitrenium ions (**1**). It was found that π-donor substituents (e.g., OCH_3, NH_2, NMe_2) favor the singlet state and that π-acceptor substituents (CHO, NO_2, etc) favor the triplet state. In fact, ΔE_{ST} in this series shows a reasonable Hammett linear free energy correlation with the $\sigma+$ parameter, which represents the resonance electron-withdrawing effect of para substituents. In a related study,[46] it was demonstrated that replacing the benzene ring carbons with nitrogens (e.g., 2-triazolylnitrenium ions **2**) also favors the triplet state. Such heteroaromatic rings are expected to be less effective π-donors because of the electronegative nitrogen atoms.

Organic molecules with stabilized triplet states have attracted interest because of the long-term promise of designing materials with interesting magnetic and electronic properties.[47,48] As a rule, however, paramagnetic organic entities such as free radicals

1   **2**
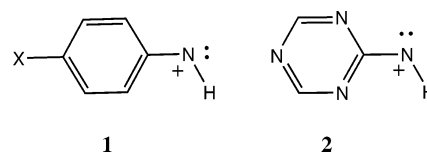
and triplet carbenes are kinetically unstable. Thus, there is interest in identifying novel organic groups that are both paramagnetic and capable of being stabilized through appropriate substitution. To our knowledge, there has been no effort to exploit triplet nitrenium ions to this purpose. This is understandable given the short lifetimes of these species in condensed media[49,50] and that simple structural modifications of NH_2^+ tend to stabilize the singlet in preference to the triplet.

This study was undertaken with the goal of determining how various substitution patterns affected ΔE_{ST} values in phenylnitrenium ions. In particular, we hoped to identify triplet species having sufficient structural complexity that stabilizing elements could be incorporated into the structures without compromising the electronic state. Second, it was hoped that analysis of several such structures would lead to some simple qualitative generalizations that would be useful in guiding future computational and experimental efforts. While the earlier study had addressed the effects of para substitution on ΔE_{ST} for phenylnitrenium ion derivatives, we set out to examine the effects of meta substituents.
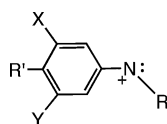
The qualitative picture developed from the previous studies led us to expect only modest effects of meta substituents. Surprisingly, it was found that meta donors dramatically stabilize the triplet states in arylnitrenium ions. It is argued that such nitrenium ions have a triplet state that is not well described by Figure 1. Rather, the meta donor systems have π,π^* orbital character and are better described as *meta*-xylylene analogues.

Results and Discussion

Several earlier studies have demonstrated the utility of density functional theory (DFT) calculations in quantitatively predicting various nitrenium ion properties. For example, McIlroy et al.[51] compared the theoretical and experimental ΔE_{ST} for a stable nitrenium ion **3**. Because this species is stable, it was possible to measure ΔE_{ST} experimentally using standard photophysical techniques. The value derived from BPW91/cc-PVDZ computations (−64.7 kcal/mol) agrees well with the experimentally derived value (−66 ± 3 kcal/mol). Similar DFT computations successfully predict experimental IR frequencies (measured by time-resolved techniques) for diphenylnitrenium ion[52] and N-(4-substituted)phenyl-N-methylnitrenium ions.[45] More recently, Phillips et al.[53−55] successfully computed nitrenium ion Raman frequencies using this approach. Also relevant to this work is

(28) Ramlall, P.; McClelland, R. A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 225−232.
(29) McIlroy, S.; Moran, R. J.; Falvey, D. E. *J. Phys. Chem. A* **2000**, *104*, 11154−11158.
(30) Miller, J. A. *Cancer Res.* **1970**, *30*, 559−576.
(31) Novak, M.; Kahley, M. J.; Eiger, E.; Helmick, J. S.; Peters, H. E. *J. Am. Chem. Soc.* **1993**, *115*, 9453−9460.
(32) Scribner, J. D.; Naimy, N. K. *Cancer Res.* **1975**, *35*, 1416−1421.
(33) Gu, Z.; Gorin, A.; Hingerty, B. E.; Broyde, S.; Patel, D. *Biochemistry* **1999**, *38*, 10855−10870.
(34) McClelland, R. A.; Ahmad, A.; Dicks, A. P.; Licence, V. *J. Am. Chem. Soc.* **1999**, *121*, 3303−3310.
(35) Novak, M.; Kennedy, S. A. *J. Phys. Org. Chem.* **1998**, *11*, 71−76.
(36) Ding, Y.; Padias, A. B.; Hall, H. K., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2569−2579.
(37) Lux, F. *Polym. Rev.* **1995**, *35*, 2915.
(38) Wei, Y.; Tang, X.; Sun, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2385−2396.
(39) Cramer, C. J.; Truhlar, D. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1997**, *119*, 12338−12339.
(40) Cramer, C. J.; Falvey, D. E. *Tetrahedron Lett.* **1997**, *38*, 1515−1518.
(41) Falvey, D. E.; Cramer, C. J. *Tetrahedron Lett.* **1992**, *33*, 1705−1708.
(42) Moran, R. J.; Cramer, C. J.; Falvey, D. E. *J. Org. Chem.* **1996**, *61*, 3195−3199.
(43) Sullivan, M. B.; Brown, K.; Cramer, C. J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 11778−11783.
(44) Chiapperino, D.; Anderson, G. B.; Robbins, R. J.; Falvey, D. E. *J. Org. Chem.* **1996**, *61*, 3195−3199.
(45) Srivastava, S.; Ruane, P. H.; Toscano, J. P.; Sullivan, M. B.; Cramer, C. J.; Chiapperino, D.; Reed, E. C.; Falvey, D. E. *J. Am. Chem. Soc.* **2000**, *122*, 8271−8278.
(46) Sullivan, M. B.; Cramer, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5588−5596.

(47) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.
(48) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.
(49) Srivastava, S.; Falvey, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10186−10193.
(50) Srivastava, S.; Kercher, M.; Falvey, D. E. *J. Org. Chem.* **1999**, *64*, 5853−5857.
(51) McIlroy, S.; Cramer, C. J.; Falvey, D. E. *Org. Lett.* **2000**, *2*, 2451−2454.
(52) Srivastava, S.; Toscano, J. P.; Moran, R. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1997**, *119*, 11552−11553.
(53) Chan, P. Y.; Ong, S. Y.; Zhu, P. Z.; Zhao, C. Y.; Phillips, D. L. *J. Phys. Chem. A* **2003**, *107*, 8067−8074.
(54) Zhu, P.; Ong, S. Y.; Chan, P. Y.; Poon, Y. F.; Leung, K. H.; Phillips, D. L. *Chem.−Eur. J.* **2001**, *7*, 4928−4936.
(55) Zhu, P. Z.; Ong, S. Y.; Chan, P. Y.; Leung, K. H.; Phillips, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 2645−2649.

Table 1. Singlet−Triplet Gaps and Selected Geometric Parameters for Substituted Phenylnitrenium Ions (UB3LYP/6-31G(d,p))

No.	R	R′	X	Y	ΔE_{ST} (kcal/mol)	spin state	θ (deg)	R_1 (ang)	ω (deg)
4	H	H	H	H	−19.2	singlet	112.5	1.294	0.00
						triplet	131.8	1.326	92.63
5	H	H	CH$_3$	H	−18.9	singlet	112.3	1.295	0.00
						triplet	129.8	1.330	92.36
6	H	H	(CH$_3$)$_3$Si	H	−19.2	singlet	112.2	1.294	0.07
						triplet	130.2	1.326	97.31
7	H	H	F	H	−17.1	singlet	112.5	1.295	0.00
						triplet	130.2	1.331	92.81
8	H	H	CN	H	−17.4	singlet	112.8	1.295	0.01
						triplet	132.4	1.327	92.74
9	H	H	OH	H	−13.6	singlet	112.2	1.297	0.00
						triplet	122.7	1.349	91.53
10	H	H	CH=CH$_2$	H	−10.7	singlet	112.2	1.296	0.00
						triplet	110.9	1.339	0.00
11	H	H	PH$_2$	H	−9.8	singlet	112.4	1.295	0.23
						triplet	110.9	1.336	0.48
12	H	H	SH	H	−6.4	singlet	112.3	1.296	0.02
						triplet	111.1	1.336	0.00
13	H	H	OCH$_3$	H	−6.9	singlet	112.1	1.296	0.00
						triplet	111.1	1.335	0.00
14	H	H	NH$_2$	H	+0.4	singlet	112.0	1.298	0.00
						triplet	111.0	1.336	0.00
15	H	H	N=O	H	+2.3	singlet	112.6	1.295	−0.17
						triplet	111.1	1.346	0.00
16	H	H	P(CH$_3$)$_2$	H	+5.7	singlet	112.1	1.294	0.24
						triplet	110.4	1.337	−0.38
17	H	H	NH$_2$	NH$_2$	+7.7	singlet	111.6	1.303	0.00
						triplet	111.0	1.334	0.00
18	H	H	(CH$_3$)$_2$N	(CH$_3$)$_2$N	+11.8	singlet	111.2	1.305	0.00
						triplet	110.6	1.335	0.00
19	H	H	1-azirinyl	H	+11.0	singlet	112.0	1.300	1.03
						triplet	110.4	1.335	−0.27
20	H	H	C$_4$H$_3$	H	+21.2	singlet	111.7	1.310	−0.15
						triplet	110.5	1.343	0.00
21	CH$_3$	H	H	H	−14.3	singlet	124.4	1.310	0.00
						triplet	144.0	1.324	92.39
22	CH$_3$	H	NH$_2$	NH$_2$	+3.0	singlet	123.6	1.317	0.00
						triplet	122.0	1.341	0.00
23	t-Bu	H	NH$_2$	NH$_2$	−4.7	singlet	131.7	1.321	0.00
						triplet	135.6	1.342	93.19
24	H	CH$_3$	Me$_2$N	Me$_2$N	+3.6	singlet	111.4	1.300	−2.15
						triplet	110.7	1.331	−1.10

the application of DFT methods to the study of ΔE_{ST} values in arylcarbenes.[19,39,56−61]
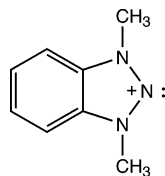
3

Structures for all of the nitrenium ions in the present study were determined using DFT at the UB3LYP/6-31G(d,p) level.

(56) Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2000**, *65*, 8348−8356.
(57) Wang, Y.; Hadad, C. M.; Toscano, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 1761−1767.
(58) Hill, B. T.; Zhu, Z.; Boeder, A.; Hadad, C. M.; Platz, M. S. *J. Phys. Chem. A* **2002**, *106*, 4970−4979.
(59) Trindle, C. *J. Org. Chem.* **2003**, *68*, 9669−9677.
(60) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F., III. *J. Org. Chem.* **1996**, *61*, 7030−7039.
(61) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535−1542.

Both the geometry optimizations and the vibrational modes were calculated at this level. Energy differences (ΔE_{ST}) include zero-point vibrational energy corrections, which were unscaled. All singlet and triplet states were found to be local minima with no imaginary vibrational frequencies. As discussed in a subsequent section, several alternative basis sets were examined. The trends described below are robust, irrespective of the size of the basis set or the absence or presence of polarization functions.

Table 1 lists all of the substituted phenylnitrenium ions examined along with their corresponding ΔE_{ST} values. Also included in that table are some key geometric data, including the ArN bond length (R_1), the ArNR bond angle (θ), and the torsional angle (ω) between the N−R bond and the phenyl ring. The first two examples, phenylnitrenium ion **4** and *N*-methyl-*N*-phenylnitrenium ion **21**, have been studied previously. These are computed at the present level of theory to be ground-state singlets by −19.2 and −14.3 kcal/mol, respectively. The smaller ΔE_{ST} value predicted for the *N*-methyl system has been attributed to the steric effect of the *N*-methyl group, where the
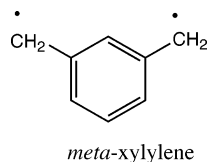
Figure 2. Rotational isomers of substituted phenylnitrenium ions.

methyl group forces a wider bond angle preferred by the triplet state. We note that for the triplet states of these two nitrenium ions, the N−R bond (R=H, Me) is approximately perpendicular to the phenyl ring. This was also predicted by the previous study.[19,40,62]

For several of the monosubstituted systems (**5**−**16**, **19**, **20**), there exists the possibility for two rotational isomers. The first isomer, which we label "anti", has the nitrenium center NH bond directed away from the substituent. The second isomer, which we label "syn", has the NH bond directed toward the substituent. Likewise, some substituents themselves can isomerize through rotation about their bond to the phenyl ring. For the monosubstituted systems, this results in four isomers for each state: anti−anti′, anti−syn′, syn−anti′, and syn−syn′. These are shown in Figure 2. The relative stabilities of these isomers were compared at the semiempirical level (AM1). In most cases, the anti−anti′ isomers were found to be the more stable. The differences were not large, in most cases being less than 1 kcal/mol within a given spin state. Therefore, the detailed DFT calculations were carried out only for the anti and the anti−anti′ isomers.

Extrapolation of the earlier Hammett correlation[43] predicts that meta substituents will have only a very modest effect on ΔE_{ST}. Indeed, calculations on the systems with *m*-Me (**5**), *m*-SiMe$_3$ (**6**), *m*-F (**7**), and *m*-CN (**8**) support this prediction. None of these substituents alters ΔE_{ST} by more than 2.1 kcal/mol relative to the unsubstituted system **4**. It is also noteworthy that these arylnitrenium ions show singlet and triplet geometries that are not greatly altered from PhNH$^+$. That is, the singlets all have ArNR bond angles in the range of 112−113°, and the N−H bond is essentially coplanar with the ring ($\omega \approx 0°$). In the case of the triplets, the NH bonds are perpendicular to the plane of the phenyl ring ($\omega \approx 90$) and the ArNH bond angles fall in the range of 129−132°.

Substitution with meta donor substituents, however, dramatically alters the nature of the triplet state. First, *m*-NH$_2$ **14**, *m,m′*-diNH$_2$ (**17**), *m,m′*-diNMe$_2$ (**18**), *m*-PMe$_2$ (**16**), *m*-cyclobutadienyl (**20**), *m*-azirinyl (**19**), and *m*-nitroso groups (**15**) substantially alter ΔE_{ST}, increasing it by more than 19 kcal/mol. In fact, all of these derivatives are predicted to be ground-state triplets. Second, in each case, the triplets show planar geometries ($\omega \approx 0°$). Third, and more remarkably, the triplet states of these derivatives all have ArNR bond angles (θ) that are ca. 20° smaller than the bond angle for the triplet states of the non meta donor systems (**5**−**8**). Indeed, the meta donor triplets all have bond angles that are smaller than the corresponding singlets. Finally, the C−N bond lengths (where C refers to the ipso carbon in the phenyl ring) are ca. 0.005 Å longer than the non meta donor triplets. Figure 3 shows the geometries of the 3-amino-phenylnitrenium ion and the 3-fluoro-phenylnitrenium

(62) Cramer, C. J.; Worthington, S. E. *J. Phys. Chem.* **1995**, *99*, 1492.

Figure 3. Geometries of the singlet (triplet) states of nitrenium ions **7** and **14** (bond lengths in angstroms).

Figure 4. Geometry of 4-methyl-3,3′bis(dimethylamino)phenylnitrenium ion **24** in the triplet state (left) and the singlet state (right).

ion, which are typical examples of the non meta donor and meta donor series.

In contrast, meta donor substitution seems to have only a modest effect on the singlet states of the corresponding nitrenium ions. The singlet ArNH bond angles are relatively insensitive to the presence of meta donor substituents. Likewise, the singlets in every case we examined are planar ($\omega \approx 0°$). The only parameter showing any significant effect is the Ar−N bond distance R_1. This is consistently shorter in the meta donor systems than it is in the non meta donor derivatives.

The significance of the conjugation by the meta donor groups is further emphasized by nitrenium ion **24**, shown in Figure 4. In this species, the two dimethylamino groups flank an additional *para*-methyl substituent. The steric effect of this methyl group requires that the dimethylamino groups rotate out of the phenyl ring plane by 58° in the singlet and 23° in the triplet. This appears to destabilize the triplet more significantly than the singlet as ΔE_{ST} decreases by over 8 kcal/mol compared with **18**, where this group is not present.

The meta π-donor systems also differ in how ΔE_{ST} responds to N-alkylation. The current study (see structures **1** and **2**), as well as previous reports, indicates that N-alkylation of phenylnitrenium ions destabilizes the singlet relative to the triplet state. This is generally attributed to a steric effect wherein the singlet state, preferring the smaller ArNR bond angle, is destabilized more than the triplet. By our computations, N-methylation of phenylnitrenium ion shifts ΔE_{ST} by ca. 5 kcal/mol in favor of the triplet. In contrast, consider structures **22** and **23**. Here the methyl and *tert*-butyl group shifts ΔE_{ST} in favor of the *singlet* by 5 and 9 kcal/mol, respectively. Of special note is that the *tert*-butyl group in the triplet of **23** is actually out of plane in the same way that the N−R bonds in the meta non π-donor triplets. As might be expected, N-alkylation increases the bond angle for both the singlet and the triplet state.

Nitrenium ions **14**−**20** all differ in rather substantial ways from phenylnitrenium ion and its simple para derivatives. First, these species all have triplet, rather than singlet, ground states. Second, they respond in the opposite way to N-alkylation. Finally, the triplet-state geometries of these species are qualitatively different from the geometries of the parent system.

meta-xylylene

Figure 5. The non-Kekulé diradical *meta*-xylylene.

Figure 6. Models of the electronic states of meta-substituted phenylnitrenium ion.

These rather substantial differences suggest that the effect of the meta donors goes beyond a simple quantitative perturbation of the electronic structure depicted in Figure 1.

The diradical, *meta*-xylylene (also known as *meta*-benzoquinodimethane or MBQDM), shown in Figure 5, has a triplet ground state with $^3A'$ state symmetry and ΔE_{ST} of +9.6 kcal/mol.[63–69] This species has been the subject of numerous computational and experimental studies, as have many of its simple derivatives. In contrast to the carbenes and simple nitrenium ions, where the two SOMOs are orthogonal, *meta*-xylylene's triplet ground state is attributed to degenerate but nondisjoint SOMOs.[70–72]

We considered the possibility that the meta donor phenylnitrenium ions might adopt an electronic structure analogous to *meta*-xylylene. This can be visualized in a schematic way by starting with the arylnitrenium ion's singlet state, and then transferring an electron from a nonbonding orbital on the donor substituent(s) to the out-of-plane nonbonding orbital on the nitrenium ion center. This would create a species that would have aminyl radical character at the original nitrenium ion center and a cation radical site on the meta substituent(s).

Figure 6 illustrates simple models for the lowest electronic states of meta donor-substituted nitrenium ions. The lowest singlet state is designated "n^2", referring to the occupancy of the HOMO. The lowest triplet state typical of non meta donor arylnitrenium ions is designated "n,π^*". This state is derived from promotion of an electron from the n orbital on the nitrenium center to a π^* orbital, which results from the mixing of the nonbonding orbital on the N and the π^* orbitals of the phenyl ring. Finally, the lowest triplet state of the meta π-donors is designated "π,π^*", indicating that this state is derived from promotion of an electron on a substituent nonbonding orbital of π-symmetry to the π^* level.

One potential source of confusion in Figure 6 is the nature of the nonbonding orbitals. In our studies, every n,π^* triplet has the N—R bond nearly perpendicular ($\omega = 90°$) to the plane of the aromatic ring. Thus, the relevant N-localized nonbonding orbital that is antisymmetric with respect to the plane of the phenyl ring is approximately sp^2 hybridized. Likewise, the N-localized nonbonding orbital that is symmetric with respect to the phenyl ring plane is unhybridized. In contrast, the n^2 singlet and π,π^* triplet both have an unhybridized p nonbonding

(63) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409–5424.
(64) Havlas, Z.; Michl, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2299–2303.
(65) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400–7404.
(66) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354–1359.
(67) West, A. P.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452–1463.
(68) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628–630.
(69) Zhang, G. B.; Liu, S. H.; Jiang, Y. S. *J. Phys. Chem. A* **2003**, *107*, 5573–5582.
(70) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 195–258.
(71) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109–116.
(72) Berson, J. A. In *Magnetic Properties of Organic Materials*; Lahti, P., Ed.; Marcel Dekker: New York, 1999; pp 7–26.
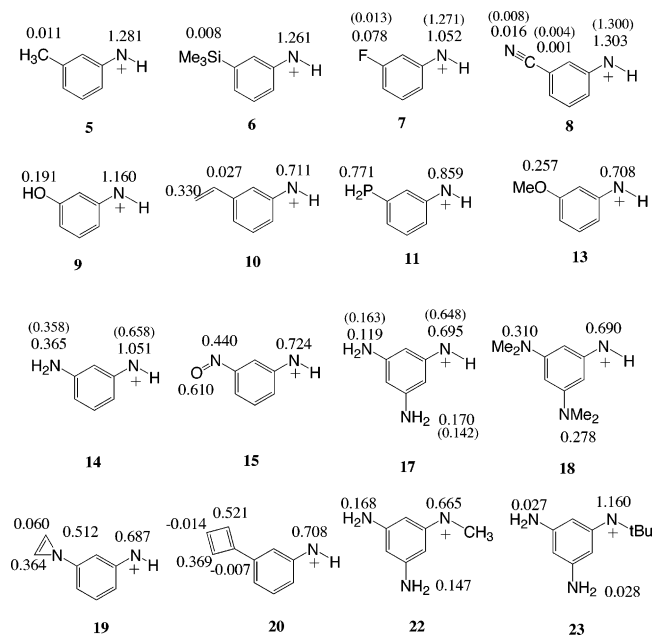

Figure 7. SOMO densities (top and side views) for the UB3LYP computed triplet states of nitrenium ions **7** (bottom) and **17** (top).

orbital, which interacts with the phenyl π-orbitals, and an sp^2-like orbital that is designated "n".

This qualitative picture leads to three specific predictions. (1) The two SOMOs in the π,π^* triplet state should have π-symmetry. That is, they should both have a nodal plane that coincides with the phenyl ring's plane. (2) Such a π,π^* triplet state should exhibit substantial spin delocalization onto the substituent(s). (3) The nitrenium ion center, having a doubly occupied n orbital, should be approximately sp^2 hybridized and thus have geometric characteristics similar to that of the anilino radical (PhNH•). More specifically, the doubly occupied n-type orbital on nitrogen should lead to a sp^2-like geometry and a CNH angle <120° because of the in-plane lone pair.

The first prediction, regarding the nodal properties of the SOMOs, is illustrated in Figure 7, which shows visualizations of the Kohn–Sham SOMOs derived from the DFT calculations for triplet *m*-fluorophenylnitrenium ion **7** along with the those calculated for *m,m'*-bis(diamino)phenylnitrenium ion **17**. The former is representative of the non meta donor series, and the latter is representative of the meta donors.

As the simple model predicts, the triplet state of ion **7** has the characteristics of a n,π^* state. One SOMO is symmetric and the other is antisymmetric with respect to the phenyl ring's plane. Similar SOMOs are observed for **4**–**6**, **8**, and **9** (data not shown). In contrast, the triplet state of ion **17** has the characteristics of a π,π^* state. The two SOMOs are antisymmetric with respect to the phenyl ring plane. Similar pictures are derived from the triplet states of the other meta π-donor

Figure 8. Mulliken (NPA) spin densities on substituent heavy atoms on meta-substituted triplet phenylnitrenium ions derived from UB3LYP/6-31G-(d,p) calculations.

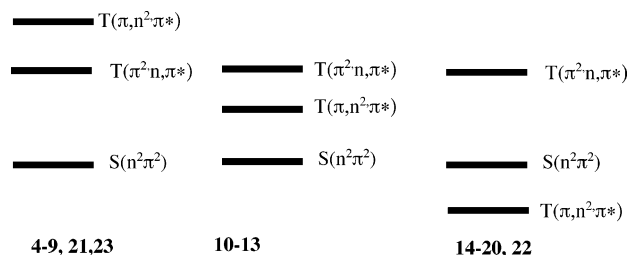**Figure 9.** Proposed qualitative state orderings for substituted phenylnitrenium ions, illustrating the effect of increasingly effective meta π-donation from left to right.
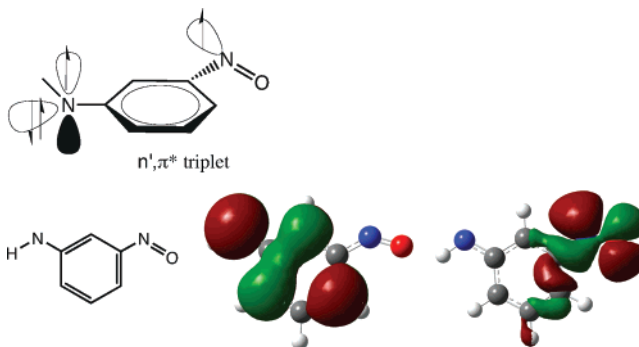

Figure 10. Geometry and SOMO densities for nitrenium ion **15**.

systems: **10−14** and **16−20**. The meta nitroso derivative, **15**, is considered below.

The second prediction is illustrated by the Mulliken spin densities shown in Figure 8. The numbers in the figure represent the Mulliken spin densities on the non-hydrogen atoms in the substituent. It is clear that the non meta donor systems (e.g., **5−8**) show very little (<0.08) spin delocalization onto the meta substituents. In contrast, the meta donor species (**11−20**) all show significant (>0.3) spin density on the substituents. There are several alternative schemes for assigning electron density to individual atoms. Spin densities were also calculated for the triplet states of **7**, **8**, **14**, and **17** using natural population analysis (NPA). This method gives results that are qualitatively similar to the Mulliken analysis: structures **7** and **8** show minimal spin delocalization onto the substituents, whereas **14** and **17** show significant delocalization. Structures **22** and **23** are interesting because, as noted above, N-alkylation actually acts to destabilize the π,π^* triplet state relative to the singlet and the n,π^* triplet. This is seen in the reduced spin delocalization in these structures. In the case of the *N-tert*-butyl derivative (**23**), the perpendicular (i.e., $\omega \approx 90°$) geometry of N-substituent and the nodal properties of the SOMO indicate that the lowest triplet for this species is n,π^*.

Finally, the geometry of the anilino radical (PhNH•) was computed using the same methodology as was applied to the nitrenium ions. This species shows an NH bond that is coplanar with the phenyl ring and has an equilibrium PHNH bond angle of 111.0°. This small bond angle is readily attributed to a filled n orbital on the nitrogen that is in the plane of the ring. This bond angle resembles the triplet meta donor nitrenium ion bond angles (110−111°) far more than the non meta donor arylnitrenium ions, whose bond angles are >130°.

Nitrenium ions **10−13** having vinyl, phosphino, sulfhydryl, and methoxy substituents illustrate intermediate cases. Each of these species is predicted to be a ground-state singlet. However, their lowest triplet states are apparently π,π^*. All of these have

CNH bond angles closer to the ideal of the anilino radical, in the range of 110−111°. Visualization of the SOMOs also verifies that these are π,π^* in nature. Apparently, these substituents interact sufficiently with the phenyl π-system to make π,π^* the lowest triplet state, but not so sufficiently as to make that state more stable than the singlet. Thus, we concluded that meta substituents have their strongest effect on the π,π^* triplet states. This is illustrated in Figure 9.[73] In some cases, the computations identified two geometrically and energetically distinct triplet states. For example, initial calculations on **7** showed a π,π^* triplet state, with $\omega = 0.02°$, 3.84 kcal/mol higher in energy than the n,π^* triplet ($\omega = 92.8°$) reported in Table 1. We hope to undertake a more systematic study of these higher energy triplet states in the future.

The nitroso derivative **15** is an interesting exception to the trends described above. This ion is predicted be a ground-state triplet, and its triplet state has the small bond angle characteristic of the π,π^* states. However, calculations constrained to C_s symmetry show that the triplet state has $^3A''$ orbital symmetry. Visualization of the Kohn−Sham SOMOs for the triplet is given in Figure 10. Note the conspicuous *lack* of n-SOMO density on the formal nitrenium center. It is clear that this triplet state can be approximated as being derived from promotion of an electron from the *nitroso* lone pair to the π^* orbital. Thus, we term **15** and similar systems n′,π^* triplets. Here the prime indicates that the electron is derived from an orbital primarily on the substituent, rather than the formal nitrenium ion center. A similar, albeit less pronounced, effect has been proposed for the triplet states of certain heteroarylnitrenium ions.[46]

Computational Methods

All geometry optimizations and vibrational frequency calculations were carried out using the Gaussian03 suite of programs.[74] The values

(73) Preliminary analysis of TD-DFT calculations on triplets 7 and 14 seem to support this picture. Thus, the first excited state of triplet **7** can be represented as a $\pi−\pi^*$. Likewise the first excited state of triplet 14 can be well described as n,π^*.

Table 2. Effect of Basis Set on Predicted Singlet−Triplet Gaps ΔE_{ST} (kilocalories per mole) and Various Geometric Parameters of Selected meta-Substituted Phenylnitrenium Ions

nitrenium ion	basis set	ΔE_{ST}	θ (deg) singlet−triplet	R_1 (Å) singlet−triplet	ω triplet
4	6-31G	−15.4	115.4/139.4	1.306/1.330	92.4
	6-311G	−15.5	115.2/139.7	1.305/1.330	92.2
	6-31G (d,p)	−19.2	112.5/131.8	1.294/1.326	92.6
7	6-31G	−13.5	115.6/139.1	1.306/1.332	92.1
	6-311G	−13.7	115.3/139.5	1.306/1.332	92.6
	6-31G (d,p)	−17.1	112.5/130.2	1.295/1.331	92.8
		$(−17.1)^a$			
	cc-pVDZ	−17.6	112.3/129.4	1.297/1.337	93.3
	cc-pVTZ	$−17.3^b$	112.9/130.4	1.289/1.325	92.0
14	6-31G	+1.3	114.9/113.5	1.310/1.351	0.0
	6-311G	−1.2	114.6/113.2	1.310/1.353	0.0
	6-31G (d,p)	+0.4	112.0/111.0	1.336/1.335	0.0
		$(−1.4)^a$			
	cc-pVDZ	−1.4	111.6/110.8	1.303/1.339	0.0
	cc-pVTZ	$−0.1^b$	112.3/111.5	1.293/1.331	0.0
		$(−1.9)^a$			
17	6-31G	+8.8	114.4/113.4	1.315/1.350	0.0
	6-311G	+8.7	114.1/113.2	1.315/1.351	0.0
	6-31G (d,p)	+7.7	111.6/111.0	1.303/1.334	0.0
		$(+4.6)^a$			
	cc-pVDZ	+7.7	111.2/110.6	1.304/1.335	0.0

C$_4$H$_3$ = ⬦ ; azirinyl = ▷N—
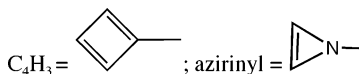
[a] Numbers in parentheses derived from broken-symmetry calculations. Geometry reoptimization lowers the energy by less than 0.1 kcal/mol, and thus different geometric data for the broken-symmetry solution are not reported. [b] Zero-point vibrational corrections added from cc-pVDZ calculations.

in Table 1 were calculated using density functional theory and, in particular, the hybrid B3LYP functional, comprising Becke's B3 three-parameter gradient-corrected exchange functional[75,76] with the LYP correlation functional of Lee, Yang, and Parr[77] as originally described by Stevens et al.[78] For these calculations, the 6-31G(d,p) basis set [79] was employed. We note that $\langle S^2 \rangle$ for all triplet states was computed to range from 2.0002 to 2.0021, implying negligible spin contamination.

For the singlet spin states, the values in Table 1 were computed using restricted DFT. We examined in several instances whether the restricted Kohn−Sham solutions were stable with respect to symmetry breaking, since broken-symmetry solutions more accurately account for nondynamical correlation effects that are often present in singlet biradicals.[80−82] In the case of **7**, which is a typical member of the set of nitrenium ions having the singlet state much more stable than the triplet, the restricted solution was found to be stable. In the case of **15**, the restricted singlet was also found to be stable. In the case of **14**, on the other hand, symmetry-breaking was found to lower the energy of the singlet state by 1.9 kcal/mol (thereby inverting the ordering of the

singlet and triplet states). Finally, for **17**, symmetry breaking also was observed to lower the energy of the singlet state by 3.1 kcal/mol, which was therefore not enough to invert the state ordering in this system. Because we were concerned here more with the qualitatively novel aspects of meta substitution than we were with obtaining quantitatively accurate gas-phase predictions, we did not examine the propensity to break symmetry in additional cases, judging that **7**, **14**, **15**, and **17** were sufficiently representative.

Although the 6-31G(d,p) basis set was chosen on the basis of size and balance, it is conceivable that one might wish to employ more economical (but less well balanced) basis sets in much larger systems. To evaluate the likely success of such an approach, Table 2 compares the performance of other basis sets for several examples from this series, including phenylnitrenium ion **4** and *m*-fluorophenylnitrenium ion **7**. These species are taken to be representative of the nitrenium ions that show no meta donor effect. Likewise, 3-aminophenylnitrenium ion **14** and 3,3′-diamino-phenylnitrenium ion **17** were also studied. These latter two species were taken to be representative of species that show the meta donor effect.

Several generalizations can be made. All of the methods predicted very similar geometries. For example, the triplet states of **4** and **7** were predicted to give out-of-plane NH bonds ($\omega \approx 90°$) regardless of the basis set or method applied. In contrast, the triplet states of **14** and **17** were predicted to have in-plane NH bonds ($\omega \approx 0°$). Likewise, the singlets were all predicted to have in-plane NH bonds ($\omega = 0°$) with much more acute bond angles. Arylnitrenium geometries were well-converged with the unpolarized 6-31G basis set.

For the meta π-donor systems (**14** and **17**), discrepancies in ΔE_{ST} values were small, being <2 kcal/mol when 6-31G was compared with 6-311G and 6-31G(d,p). On the other hand, the H-atom polarized basis sets showed systematically smaller ArNH bond angles, differing by <4° for the singlets and as much as 9° for the triplets. Likewise, the polarized basis sets showed smaller Ar−N bond distances for the singlets by 0.011 Å. Thus, for these systems, we conclude that 6-31G was overall adequate for calculating ΔE_{ST} and predicting general trends in this value as the structures were modified.

In contrast, ΔE_{ST} values in the non meta donor systems **4** and **7** showed a much stronger dependence on the inclusion of H-atom polarization functions. In both cases, use of the 6-311G and 6-31G

(74) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.
(75) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(76) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(77) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785−789.
(78) Stevens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11632−11627.
(79) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(80) Polo, V.; Kraka, E.; Cremer, D. *Theor. Chim. Acta* **2002**, *107*, 291−303.
(81) Cramer, C. J. *J. Am. Chem. Soc.* **1998**, *120*, 6261−6269.
(82) Kraka, E.; Cremer, D.; Bucher, G.; Wandel, H.; Sander, W. *Chem. Phys. Lett.* **1997**, *268*, 313.

basis sets consistently overestimated the stability of the triplet state by 3−6 kcal/mol compared to the polarized, cc-pVDZ and 6-31G(d,p) basis sets.

Finally, to gauge how well converged ΔE_{ST} values may be considered to be with the 6-31G(d,p) basis set, we carried out calculations with the cc-pVTZ basis set of Dunning [83] for **7** and **14**. As can be seen in Table 2, the significant increase in basis set size had fairly little effect on the predicted splittings and geometrical parameters. The most noteworthy effect was the systematic shortening of the CN bonds in both states with the larger basis set. As noted above, when symmetry breaking was allowed for the singlet state of **14** with the larger basis set, the energy lowering effect was small and reoptimization of the restricted geometry afforded less than 0.1 kcal/mol additional energy lowering.

Conclusions

These computations identify a novel class of triplet organic species: arylnitrenium ions having electron-donating meta substituents. Analysis of the structures of these species suggests that the effect of these substituents is to stabilize a π,π^* triplet state that is qualitatively similar to the well-characterized non-Kekulé *meta*-xylylene diradicals. The generalizations derived from this study suggest that triplet diradical ions of this nature are not confined to the phenylnitrenium ion series. Any species with a strong electron acceptor and a strong donor that are conjugated with nondisjoint π-orbitals could, in principle, have a triplet ground state. While this generalization has been appreciated for many years with respect to neutral diradicals, to our knowledge there have been few, if any, studies of ionic species having this connectivity. We note that preliminary calculations on *m,m′*-bis(dimethylamino)benzyl cation suggest that this species is also a ground-state triplet with $\Delta E_{ST} = +2.0$ kcal/mol (in contrast to unsubstituted benzyl cation, which is predicted to have $\Delta E_{ST} = -39.7$ kcal/mol (B3LYP/6-31+G-(d,p)). We are currently attempting to generate and characterize these triplet nitrenium ions and carbenium ions experimentally.

Supporting Information Available: Tables of Cartesian coordinates and energies for the singlet and triplet states of **4**−**24** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(83) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

JA047677X