2628 *J. Am. Chem. Soc.* **2001,** *123,* 2628−2636

p-Phenylenecarbenonitrene and Its Halogen Derivatives: How Does Resonance Interaction between a Nitrene and a Carbene Center Affect the Overall Electronic Configuration?

Athanassios Nicolaides,*[†] Tomonori Enyo,[§] Daisuke Miura,[§] and Hideo Tomioka*[§]

Contribution from the Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus, and Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507 Japan

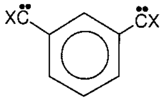
Received October 17, 2000. Revised Manuscript Received December 27, 2000

Abstract: A series of para-conjugatively coupled phenylenecarbenonitrenes {(4-nitrenophenyl)methylene (**3a**), (4-nitrenophenyl)fluoromethylene (**3b**), (4-nitrenophenyl)chloromethylene (**3c**), and (4-nitrenophenyl)bromomethylene (**3d**)} were generated in argon matrix at low temperature (10 or 13 K) and characterized by IR and UV/vis spectroscopy. Density functional theory (B3LYP/6-31G(d)) and ab initio (MCSCF, CASPT2) methods were used to study the ground- and some low-lying excited states of **3a**−**d**. The experimental and computational data suggest that **3a**−**d** have singlet ground states (S$_0$) and can be thought of as quinonoidal biradicals. In all cases, the lowest triplet (T$_1$) and quintet (Q$_1$) states lie about 2 kcal mol^{-1} and 28−29 kcal mol^{-1}, respectively, higher in energy than S$_0$. On the other hand the substituent is found to have a significant effect on the relative energy of the second excited triplet (T$_2$) state. This state tends to become relatively more stable as the ability of the substituent to enforce a closed-shell configuration at the carbene subunit increases. Interestingly, the energy difference between the T$_2$ and S$_0$ states in **3a**−**d** is found to depend linearly on the S−T gap of the corresponding phenylcarbenes **7a**−**d**. This relationship is helpful in predicting when a substituted *p*-phenylenecarbenonitrene may have a triplet ground state instead of a singlet one.

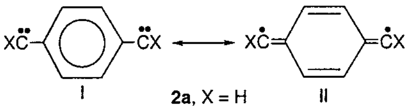
Introduction

Polycarbenes and polynitrenes have received a lot of attention in the search of high-spin organic systems, a search which has been driven in part by the desire for organic molecular magnets.[1] One of the empirical rules that has been developed from this type of research is that the *m*-phenylene linker (meta topology) results in ferromagnetic coupling (i.e., favors high-spin states), whereas the para topology tends to favor low-spin states. Thus, *m*-phenylenebismethylene (**1a**) has been known for a long time to have a quintet ground state,[2] whereas *p*-phenylenebismethylene (**2a**) is believed to have a singlet ground state.[3]

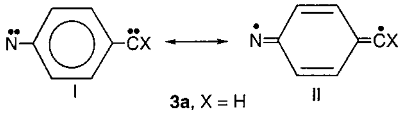
Sheridan has suggested that the nature of the substituent at the carbenic center may play as a significant role as the topology of the system in determining the final electronic configuration.[1a] Thus, there is experimental evidence that substituting the hydrogens at the carbenic centers in **1a** by chlorines (**1b**) results in a singlet ground state.[4] This has been attributed to the preference of the chlorocarbenic subunits for closed-shell (singlet) configurations. Calculations have challenged this conclusion predicting a quintet ground state for **1b**, although the singlet is reported to be essentially isoenergetic.[5]



1a, X = H
1b, X = Cl



2a, X = H
2b, X = F
2c, X = Cl



3a, X = H
3b, X = F
3c, X = Cl
3d, X = Br

In the case of substituted *p*-phenylenecarbenes, the topology would dictate singlet ground states as is true for the parent system **2a**.[3] According to the above hypothesis replacing both carbenic hydrogens with substituents (such as fluorine or chlorine) that favor closed-shell configurations is not expected to change the overall multiplicity of the system, but it is still expected to affect its electronic configuration although in a rather subtle way. Indeed, the elegant experiments by Sheridan et al. have provided strong arguments that both bisfluoromethylene **2b**[6] and bischloromethylene **2c**[7] have singlet ground states, but that the former is better thought of as a $(\sigma^2\sigma^2)$[8] biscarbene (**2b-**

[†] University of Cyprus.

[§] Mie University.

(1) (a) Zuev, P. S.; Sheridan, R. S. *Tetrahedron* **1995**, *51*, 11337. (b) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (c) Dougherty, D. *Acc. Chem. Res.* **1991**, *24*, 88.

(2) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(3) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528.

(4) Zuev, P. S.; Sheridan, R. S. *J. Org. Chem.* **1994**, *59*, 2267.

(5) Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947.

(6) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 9381.

(7) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788.

10.1021/ja003709e CCC: $20.00

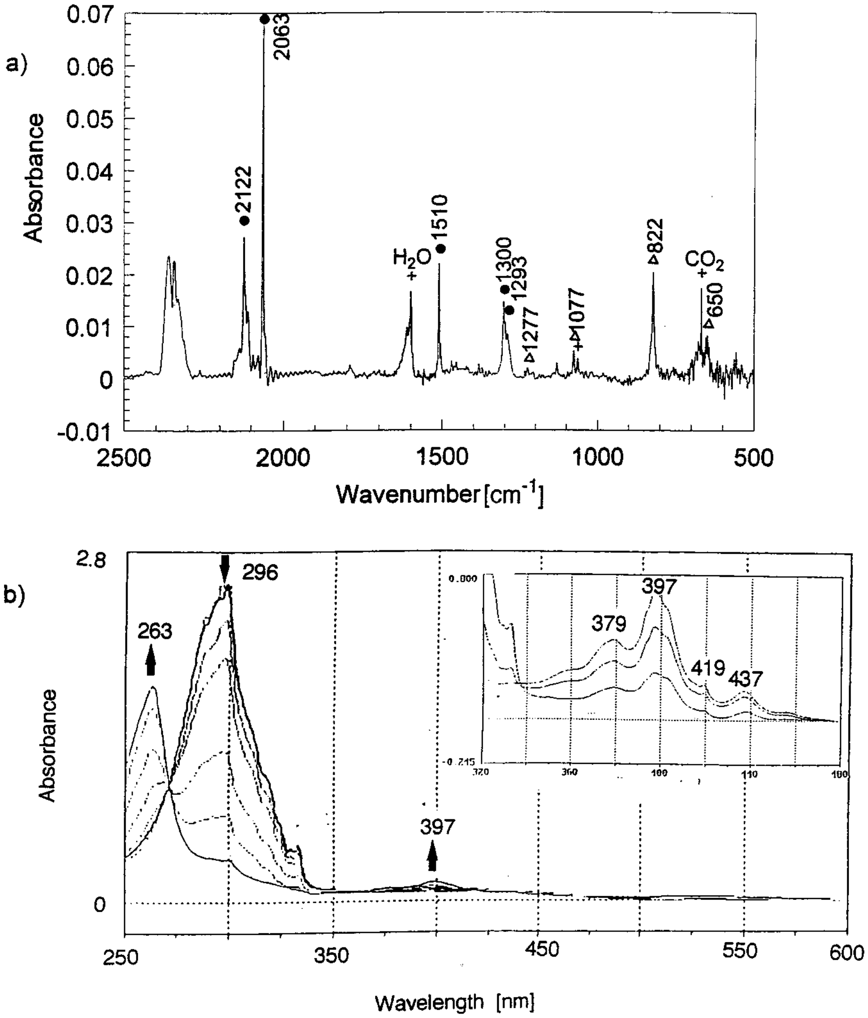


Figure 1. Photolysis (λ > 350 nm) of 4-azidophenyldiazomethane (**4a**) in Ar matrix at 13 K. (a) IR spectrum obtained after 3 min. Bands due to **4a** (●) and those due to the primary photoproduct **A** (△). (b) UV absorptions of **4a** (↓) and **A** (↑).

I),[6,9] while the latter as a ($\sigma^2\pi^2$) diradical with a quinonoid structure (**2c-II**)[5,7] like the parent system (**2a-II**). This "switching" of electronic configurations, which is in agreement with recent computational results,[5,9] has been explained qualitatively in terms of fluorine being a more powerful singlet carbene stabilizer than chlorine.[1a]

We reasoned that if Sheridan's hypothesis about substituents enforcing locally closed-shell configurations is correct, then in a suitably substituted system one may be able to observe not only configuration "switching" but a change in the ground-state multiplicity as well. In this respect, compounds **3a**−**d** are suitable candidates for study. In these molecules a nitrene and a carbene center are conjugatively coupled via the *p*-phenylene linker. Both phenylcarbene and phenylnitrene have triplet ground states, but in the former the S−T splitting (around 4 kcal mol^{-1})[10] is much smaller than that in the latter (18 kcal mol^{-1}).[11] Thus, in **3a**−**d**, the nitrene center will have a strong preference for a $\sigma^1\pi^1$ (triplet) configuration, while the "local" electronic configuration at the carbene center can be fine-tuned by changing the substituent. Thus, by analogy to **2b**, it is not unreasonable to expect that in **3b** fluorine will enforce a σ^2 configuration at the carbene center, resulting in an overall ($\sigma^3\pi^1$) ground-state configuration of *triplet* multiplicity.

With the above in mind we decided to generate **3a**−**d** at low temperature and characterize them by IR and UV spectroscopy. In this endeavor, we have used ab initio and DFT calculations to interpret some of our experimental data and also to gain insight (at least in a semiquantitative sense) into the factors that affect electronic configuration "switching" in such systems. *p*-Phenylenenitrenomethylene (**3a**) is not well-known,[12] but it is likely to have a singlet ground state as do both the "parent" **2a**[3a] and *p*-phenylenebisnitrene.[13] To the best of our knowledge compounds **3b**−**d** have not been studied before. In **3b**−**d** the halogen substituents are expected to stabilize the σ^2 configuration at the carbene subunit in varying degrees. In particular

---

[8] See the Computational Procedures section for assignment of electronic configurations in these systems.

[9] Flock, M.; Pierloot, K.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Phys. Chem. A* **2000**, *104*, 4022.

[10] (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022. (c) 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.

[11] (a) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 8699. (b) McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 10857. (c) Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 5349. (d) Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8698. (e) Castell, O.; García, V. M.; Bo, C.; Caballol, R. *J. Comput. Chem.* **1996**, *17*, 42.

[12] For preliminary results, see: Koseki, S.; Tomioka, H.; Toyota, A. *J. Phys. Chem.* **1998**, *120*, 11530.

[13] (a) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526. (b) Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Kaise, M. *Chem. Lett.* 1996, 125. (c) Minato, M.; Lahti, P. *J. Am. Chem. Soc.* **1997**, *119*, 2187. (d) Nicolaides, A.; Tomioka, H.; Murata, S. *J. Am. Chem. Soc.* **1998**, *120*, 11530.

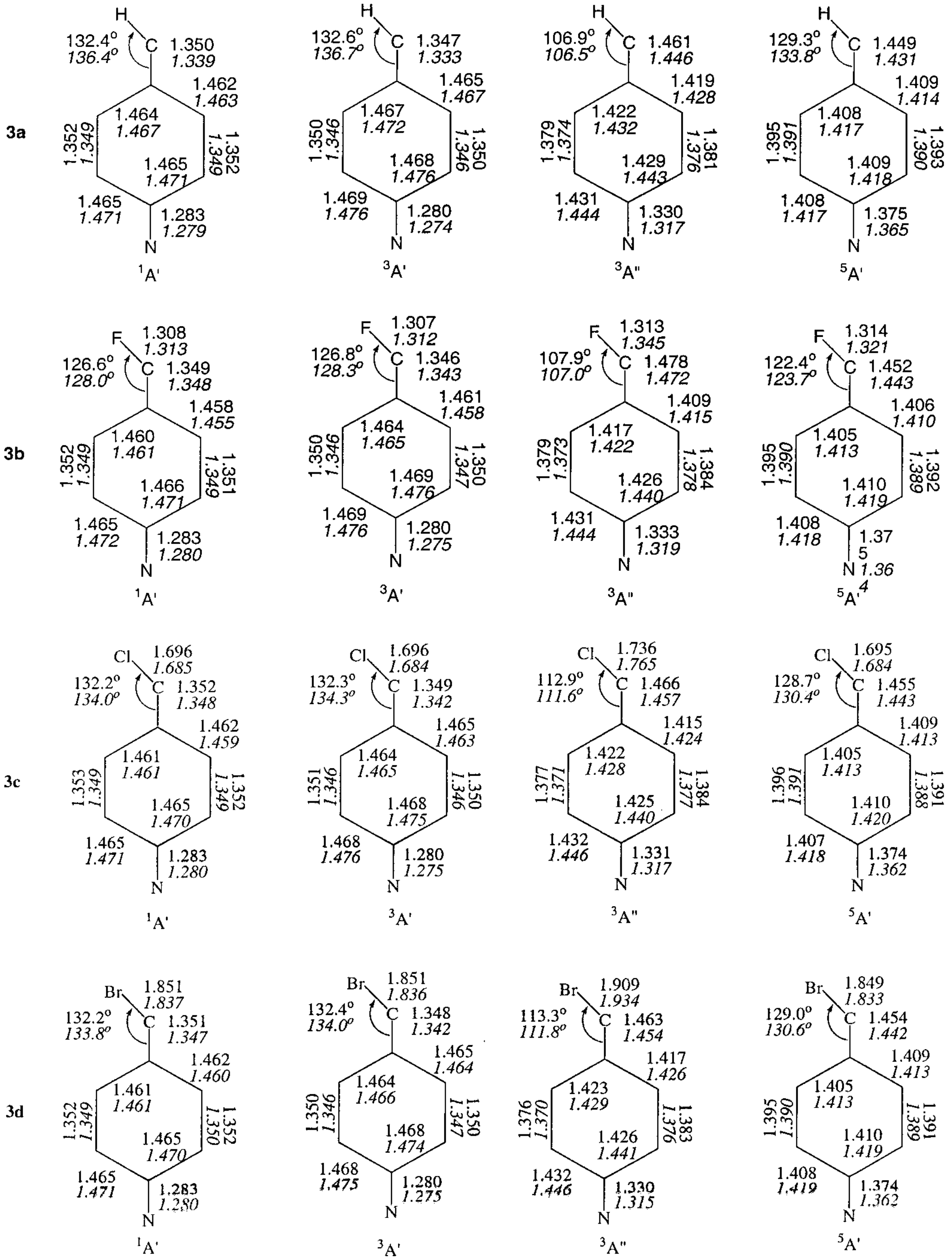
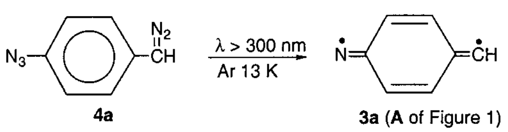


Figure 2. Selected geometrical parameters (distances in Å, angles in degrees) for the ^{1}A′, ^{3}A′, ^{3}A″ and ^{5}A′ states of **3a**−**d** at the MCSCF and UB3LYP levels of theory with the 6-31G(d) basis set.

3b−**c** can be compared directly with the "parent" molecules **2b**−**c**, as far as the factors for configuration "switching" are concerned.

***p*-Phenylenecarbenonitrene (3a).**[13] Along lines similar to those we followed in the preparation of *o*-phenylenecarbenonitrene,[14] 4-azidophenyldiazomethane (**4a**) was deposited in an Ar matrix at 10 K (Scheme 1) and irradiated (λ > 350 nm, 3 min), and the process was monitored by IR spectroscopy. The peaks due to the azido and diazo groups appeared to diminish simultaneously in intensity as new absorptions were observed (Figure 1a, **A**). The observed IR spectrum bears a strong resemblance to that of **2a**[3] and of *p*-phenylenebisnitrene[13d] and is assigned to the desired species **3a** (vide infra).

Scheme 1



3a is quite stable upon further irradiation, and no IR absorptions attributable to cumulenic bonds are observed, suggesting that ring expansion as in the cases of phenylcarbene and phenylnitrene does not take place. This is evidence that the two reactive centers in **3a** do not behave independently. The stability of **3a** is significantly different from that of *p*-phenylenebisnitrene, which was found to be extremely photolabile,[13d] but quite similar to that of *p*-phenylenebiscarbene, which has been reported to be remarkably stable under similar

---

(14) Nicolaides, A.; Nakayama, T.; Yamazaki, K.; Tomioka, H.; Koseki, S.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 10563.

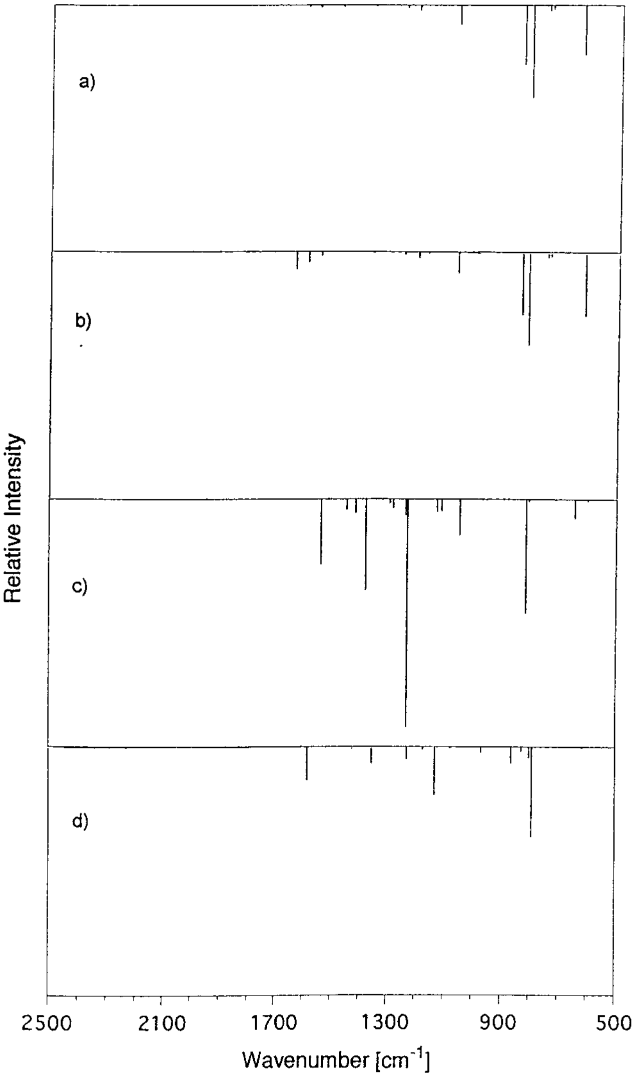


Figure 3. Calculated IR spectra (UB3LYP/6-31G(d)) for $^1A'$ (a), $^3A'$ (b), $^3A''$ (c), and $^5A'$ (d) states of **3a**.

conditions.[3] The UV spectrum of **3a** shows long-wavength absorptions in the area of 375−440 nm (Figure 1b). This is quite similar to the spectrum of the "parent" **2a**, which also shows absorptions in the area 365−460 nm.[3]

Important geometrical characteristics calculated at the UB3LYP/6-31G(d) and MCSCF/6-31G(d) levels of theory for the ground state of **3a** ($^1A'$), and some of its excited states are shown in Figure 2. In agreement with our previous experience UB3LYP and MCSCF methods give similar results.[14] The geometry of the quintet state of **3a** ($^5A'$-**3a**) displays little bond alternation in the benzene ring (the ring C−C bonds differ by less than 0.02 Å) in contrast to the geometries of $^1A'$- and $^3A'$-**3a** which exhibit considerable bond localization. Thus, the quintet state has a benzenoid geometry and can be thought of as being constructed from two local triplet subunits (a carbene and a nitrene) linked via the *p*-phenylene unit as resonance structure **3a-I** implies. On the other hand, both $^1A'$-**3a** and $^3A'$-**3a** are better thought of as *p*-quinomethideimine diradicals (**3a-II**). In all three states the angle at the divalent carbon is around 130°, close to that expected of a triplet carbene or of a vinyl radical.

The angle of the carbene subunit of the second excited triplet ($^3A''$-**3a**) is approximately 107° and corresponds to that expected of a singlet carbene. This state exhibits also a benzenoid geometry quite similar to that of the quintet state. Thus, by analogy, $^3A''$-**3a** can be thought of as an entity made of a singlet carbene and a triplet nitrene (**3a-I**, with the spins on the carbon coupled in a singlet fashion).

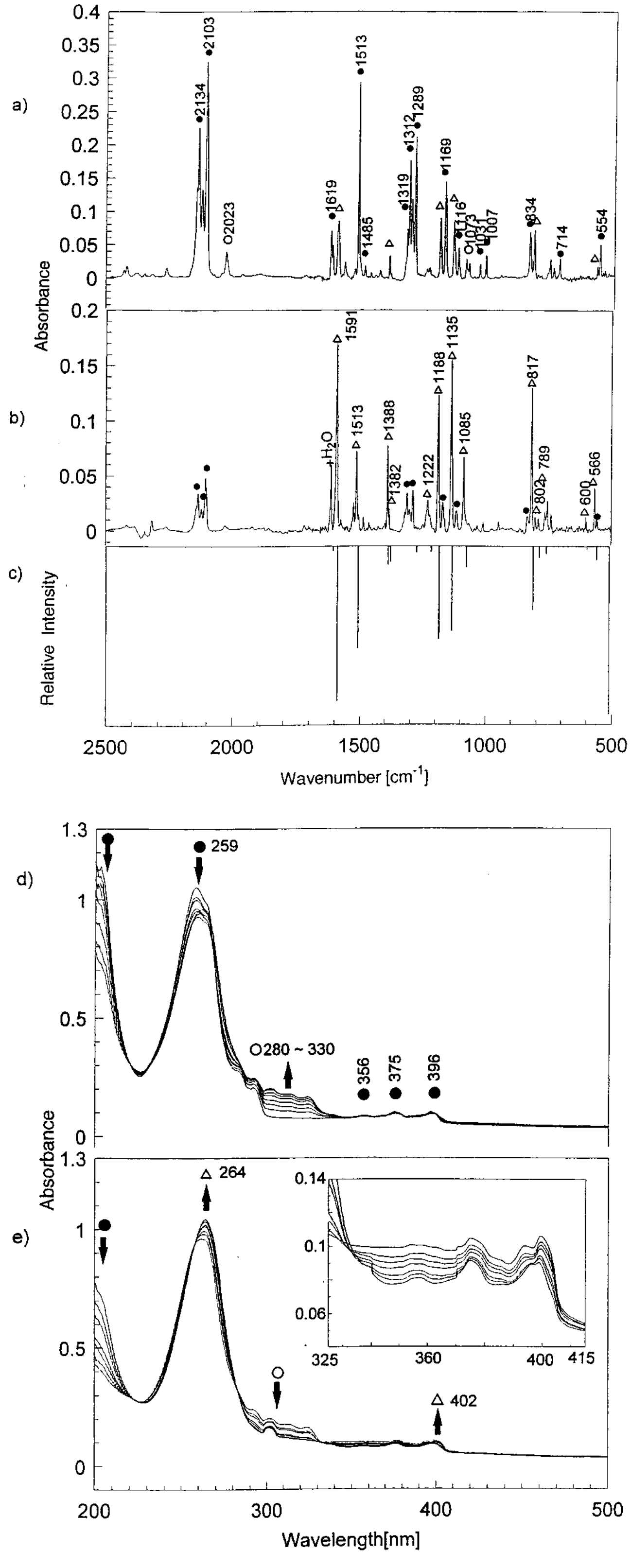


Figure 4. Photolysis ($\lambda >$ 300 nm) of 3-(4-azidophenyl)-3-fluorodiazirine (**4b**) in Ar matrix at 13 K. (a) IR spectrum obtained after 1 min. Bands due to **4b** (●), those due to the primary photoproduct B (○), and those of the final photoproduct C (△). (b) IR spectrum obtained after 9 min irradiation under the same conditions. (c) Calculated IR spectrum for singlet ^{1}**3b**. (d) UV spectrum obtained after 75 s of irradiation. (e) UV spectrum obtained after 330 s of irradiation.

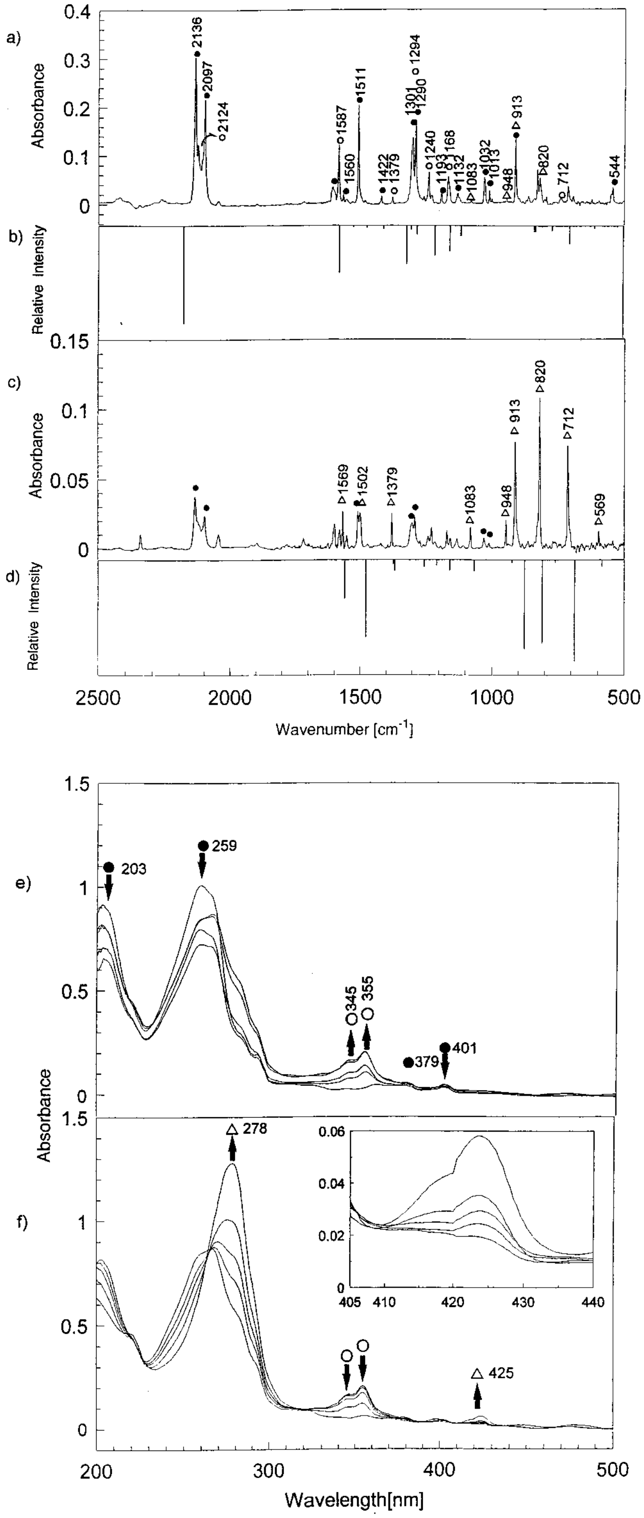


Figure 5. Photolysis (λ > 350 nm) of 3-(4-azidophenyl)-3-chlorodiazirine (**4c**) in Ar matrix at 13 K. (a) IR spectrum obtained after 1 min. Bands due to **4c** (●), those due to the primary photoproduct **D** (○), and those of the final photoproduct **E** (△). (b) Calculated IR spectrum for **6-Cl**. (c) IR spectrum obtained after 15 min irradiation under the same conditions. (d) Calculated IR spectrum for ^{1}**3c**. (e) UV spectrum obtained after 35 s of irradiation. (f) UV spectrum obtained after 210 s of irradiation.

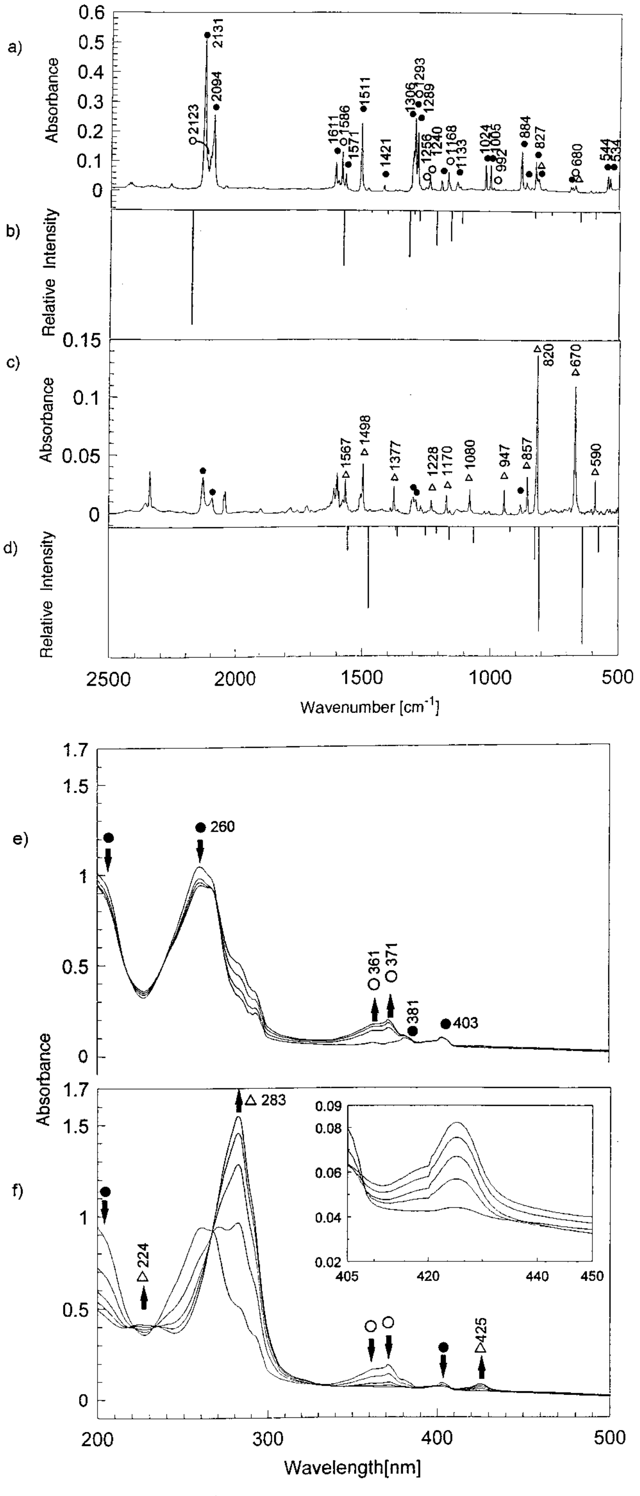


Figure 6. Photolysis (λ > 350 nm) of 3-(4-azidophenyl)-3-bromodiazirine (**4d**) in Ar matrix at 13 K. (a) IR spectrum obtained after 20 s. Bands due to **4d** (●), those due to the primary photoproduct **F** (○), and those of the final photoproduct **G** (△). (b) Calculated IR spectrum for **6-Br**. (c) IR spectrum obtained after 10 min irradiation under the same conditions. (d) Calculated IR spectrum for ^{1}**3d**. (e) UV spectrum obtained after 20 s of irradiation. (f) UV spectrum obtained after 310 s of irradiation.

Diradical ^{1}A′-**3a** is calculated to be the ground state, with ^{3}A′-**3a** lying slightly higher (2.0 kcal mol^{-1} at the CASPT2 level of theory) in energy, in agreement with expectations.[15] The quintet state lies approximately 30 kcal mol^{-1} above the ground state. The second excited triplet (^{3}A″-**3a**) lies energetically close to the quintet state, and depending on the computational method used, it is found to be slightly lower (UB3LYP)

---

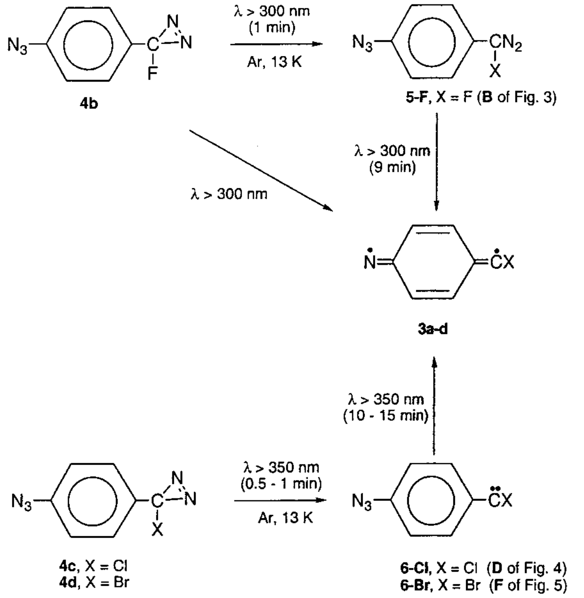
[15] For example, the calculated S−T gaps of the ortho isomer of **3a**[14] and of *p*-phenylenebisnitrene[13d] are 2.7 and 1.9 kcal mol^{-1}, respectively.

Table 1. Total (hartree) and Relative (kcal mol^{-1}) Energies of 4-Nitrenophenylcarbenes (**3a**) and 4-Nitrenophenyl(halocarbenes) (**3b**−**3d**) at the B3LYP, MCSCF, and CASPT2 Levels of Theory and Calculated (B3LYP) Spin-Squared Expectation Values ($\langle S^2\rangle$)[a]

	B3LYP[b]	$\langle S^2\rangle$[c]	MCSCF[d]	CASPT2[d]
^{3}A″-**3a**	26.8	2.058	34.6	34.0
^{5}A-**3a**	29.5	6.016	30.6	29.3
^{3}A′-**3a**	1.4	2.016	1.5	2.0
^{1}A′-**3a**	−324.22765	1.136	−322.32006	−323.24217
^{3}A″-**3b**	6.7	2.056	12.1	11.2
^{5}A′-**3b**	29.6	6.015	30.6	29.0
^{3}A′-**3b**	1.3	2.016	1.5	1.9
^{1}A′-**3b**	−423.46701	1.132	−421.17332	−422.26914
^{3}A″-**3c**	14.2	2.057	22.9	21.1
^{5}A′-**3c**	28.3	6.018	29.8	28.1
^{3}A′-**3c**	1.4	2.016	1.5	2.0
^{1}A′-**3c**	−783.83870	1.136	−781.22967	−782.29734
^{3}A″-**3d**	14.0	2.057	23.3	21.1
^{5}A′-**3d**	28.3	6.019	29.9	28.2
^{3}A′-**3d**	1.3	2.016	1.5	2.1
^{1}A′-**3d**	−2895.34898	1.133	−2891.63784	−2892.70637

[a] With the 6-31G(d) basis set and including ZPE corrections based on the UB3LYP frequencies scaled by 0.981.[32] [b] At the UB3LYP/6-31G(d) optimized geometries. [c] The $\langle S^2\rangle$ value for pure singlet, triplet, and quintet is 0.0, 2.0, and 6.0, respectively. [d] At the MCSCF/6-31G(d) optimized geometries.

Scheme 2



or somewhat higher (CASPT2) in energy (Table 1). We note that there is a rather large difference of around 8 kcal mol^{-1} between UB3LYP and MCSCF methods in determining the relative energy of this state, while there is satisfactory agreement between the two methods as far as the relative energies of the other excited states are concerned.

In Figure 3 the calculated IR spectra for **3a** are displayed graphically. It is seen that there are significant differences between the spectra for states ^{1}A′ and ^{3}A′ on one hand and ^{3}A″ and ^{5}A′ on the other. However, the differences between the theoretical spectra for ^{1}A′ and ^{3}A′ are not so large as to allow unambiguous determination of the multiplicity simply by comparing computed and experimental IR data. In both cases the agreement with the experiment is reasonable, supporting the quinonoid structure of the observed species. The assignment of **A** (the photoproduct of the irradiation of **4a**) as ^{1}A′-**3a** is mainly based on the computational finding that the singlet is the ground state. In the "parent" system **2a** the singlet state is believed to be the ground state for similar reasons. In *p*-phenylenebisnitrene, apart from the theoretical data, ESR experiments also support a singlet ground state. [13b,c]

4-Nitrenophenyl(halocarbenes). 3-(4-Azidophenyl)-3-fluorodiazirine (**4b**), -3-chlorodiazirine (**4c**), and -3-bromodiazirine (**4d**) were used as the precursors for the generation of the target carbenonitrenes. In the fluoro case at the early stages of the irradiation of **4b**, an intermediate (**B**) is observed during the formation of the final photoproduct (**C**) (Figure 4a,b, Scheme 2). While the IR data of **B** are limited, the absorption at 2023 cm^{-1} suggests that it is **5-F**, the azidodiazo isomer of **4b**. On the other hand, in the chloro and bromo cases the generation of primary photoproducts (**D** and **F**, in Figures 5a and 6a, respectively) is more clear (Scheme 2).[16] The observation of new azido peaks associated with the appearance of **D** and **F** suggests that these are **6-Cl** and **6-Br**, respectively, in agreement with the computational data (Figures 5b and 6b) for the other observed peaks. Further irradiation of **D** and **F** results in the formation of the final photoproducts **E** and **G**, which are assigned as the carbenonitrenes **3c** and **3d**, respectively.

Azidocarbene **6-Cl** shows absorptions at 345 and 355 nm nm (Figure 5e) in an area where other arylchlorocarbenes are known to absorb.[17] The UV spectrum of **6-Br** (Figure 6e) shows a bathochromic shift of 16 nm compared to that of **6-Cl**. On the other hand, the final photoproducts (diradicals **3c** and **3d**) show the same long-wavelegth absorptions (Figures 5f and 6f). In the case of **4b**, at the beginning of the irradiation new peaks appear in the area 280−330 nm (Figure 4d). In this area 4-azidophenyldiazomethane also absorbs (Figure 1b), providing some further evidence for the formation of **5-F**. Finally the UV spectrum assigned to **3b** shows a weak absorption at 402 nm (Figure 4e).

Important geometrical parameters for the ^{1}A′, ^{3}A′, ^{3}A″, and ^{5}A′ states of **3b**−**d** are shown in Figure 2. It is seen that substitution of the carbenic hydrogen by a halogen does not have a significant effect on the calculated geometry. Thus, following the same arguments as before, one can classify the ^{1}A′ and ^{3}A′ states of **3b**−**d** as quinonoidal diradicals (**3-II**), and their quintet and ^{3}A″ states as "localized" carbenonitrenes (**3-I**).[20]As is also seen in Table 1, substitution at the divalent carbon by halogen hardly affects the relative energies of the symmetric (A′) states. As in the case of **3a** B3LYP relative energies are close to the CASPT2 ones, except for the relative energy of the antisymmetric state (^{3}A″), where a difference of 5−7 kcal mol^{-1} between the two methods is found.

Discussion

All four nitrogenous precursors (**4a**−**d**) when irradiated in an argon matrix at low temperature give final products that result from double nitrogen elimination, resulting in the formation of biradical quinonoid compounds (**3a**−**d**). In the cases of the chloro and bromo precursors a stepwise elimination of nitrogen molecules takes place, since the corresponding azidocarbenes (**6-Cl** and **6-Br**) are obseved. It is quite possible that azidocar-

---

(16) Weak peaks at 2045 cm^{-1} (Figure 5a) and 2048 cm^{-1} (Figure 6a) suggest that small amounts of diazo compounds **5-Cl** and **5-Br** are also formed.

(17) For example, phenylchlorocarbene has two rather broad absorptions at 285 and 308 nm.[18] 3-(4-Chloromethylenephenyl)-3-chlorodiazirine is reported to show absorptions at 342, 359, 368, 374, 380 nm.[19]

(18) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

(19) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788.

(20) In the quintet state both reactive centers are (locally) high spin (triplet), whereas in ^{3}A″ the carbene center is low spin, and the nitrene center high spin.

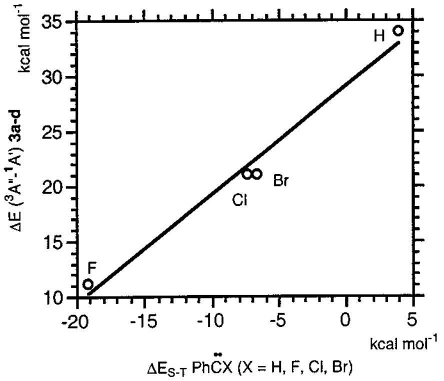


Figure 7. Energies of ^{3}A″ states relative to ^{1}A′ (ΔE (^{3}A″ − ^{1}A′), kcal mol^{-1}) in **3a**−**d** plotted against the singlet−triplet splittings (ΔE_{S-T}, kcal mol^{-1}) of the corresponding phenylcarbenes.

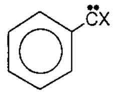
Table 2. Corrected Singlet−Triplet Splittings (kcal mol^{-1}) in Phenylcarbenes PhCX at the B3LYP, MCSCF, and CASPT2 Levels of Theory[a,b]

X	B3LYP[c]	MCSCF[d]	CASPT2[d]
H	4.0	4.0	4.0
F	−16.3	−18.3	−19.2
Cl	−7.6	−6.8	−6.7
Br	−7.8	−6.5	−7.4

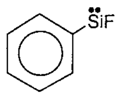
[a] The best calculated value for the S−T gap in phenylcarbene is 4 ± 1 kcal mol^{-1}.[10] The reported S−T gaps have been corrected on the basis of this value and using the equation: ΔE_{S-T}(X)(corrected) = 4 + (ΔE_{S-T}(PhCX) − ΔE_{S-T}(PhCH)), where the units are kcal mol^{-1}. Negative signs indicate singlet ground states. [b] With the 6-31G(d) basis set and including ZPE corrections based on the UB3LYP frequencies scaled by 0.981.[32] [c] At the UB3LYP/6-31G(d) optimized geometries. [d] At the MCSCF/6-31G(d) optimized geometries.

benes are formed also during the irradiation of **4a** and **4b**,[21] but either they are more photolabile under our experimental conditions, or they are formed at vibrationally excited states and proceed to the final photoproducts before a sufficient amount for their detection accumulates. All species **3a**−**3d** are predicted to have singlet ground states (^{1}A′) and be ($\sigma^2\pi^2$) diradicals, thus constituting formal violations of Hund's rule as applied to molecules.[22−24] The lowest S−T and S−Q calculated splittings are essentially the same in all cases (Table 1). However, the relative energy of the ^{3}A″ state depends strongly on the nature of the substituent and in a manner compatible with the notion that these states are made of a singlet carbene and a triplet nitrene subunit. Thus, the energy of the ^{3}A″ state relative to the ground state is the highest for the parent compound **3a** and the lowest for the fluoro compound as one would expect on the basis of the strong tendency of fluorine to stabilize singlet carbenes. This implies that there should be a correlation between the S−T gap of the carbene subunit and the S_0−T_2 gap (i.e., the energy difference of ^{1}A′ and ^{3}A″ states) in systems such as **3**. Indeed if the S−T gap of the "local" carbenes in compounds **3** is modeled by the S−T gaps of the corresponding phenylcarbenes **7** and the latter are plotted against the ^{1}A′−^{3}A″ splittings in compounds **3**, a linear relationship is found (Figure 7). By extrapolating to an S_0−T_2 splitting of zero, one estimates that if the S−T gap of the "local" carbene is less than that of phenylcarbene by approximately 34 kcal/mol^{-1},[25] then the corresponding phenylenenitrenocarbene should have a triplet (^{3}A″) ground state.

Preliminary calculations support this semiquantitative expectation. Thus, phenyl fluorosilylene (**8**) is predicted to have a singlet ground state with an S−T splitting 56.6 kcal mol^{-1} smaller than that of phenylcarbene.[26] According to the above, 4-nitrenophenylene fluorosilylene, the silicon analogue of **3b**, should have a triplet (^{3}A″) ground state lying approximately 20.8 kcal mol^{-1} below the corresponding ^{1}A′ state. In qualitative agreement with this, MCSCF calculations find that 4-nitrenophenylene fluorosilylene has a ^{3}A″ ground state, lying 32.4 kcal mol^{-1} lower in energy than the ^{1}A′ state.



7a, X = H
7b, X = F
7c, X = Cl
7d, X = Br



8

A possible way to justify the above requirement is to note that the quintet states of **3a**−**d** lie about 30 kcal mol^{-1} higher in energy than the corresponding ^{1}A′ states. On the basis of resonance structures **3-I** and **3-II** one may argue that formally there is one less (π) bond in the quintet states as compared to the ground states, and to a first approximation the energetic value of this "extra" bond should be equal to the S−Q splitting. One can then discern two main factors in determining the ground-state electronic configuration in systems such as **2** and **3**. One factor tries to maximize the bonding by forming the extra π bond. This requires that both reactive centers offer one π electron, implying that "locally" the reactive centers are in a triplet state ($\sigma^1\pi^1$). The other factor has to do with the inherent tendency of the reactive center for a "local" singlet (closed-shell, σ^2) or triplet (open-shell, $\sigma^1\pi^1$) configuration. If the two factors act in the same direction, then the ^{1}A′ states should be the lowest in energy. But if the two factors oppose each other, then the preference for a local closed-shell configuration should be at least as large as the magnitude (i.e. around 30 kcal mol^{-1}) of the extra bond that is sacrificed for ^{3}A″ to compete energetically with ^{1}A′. It is of interest to note that the above are compatible with Sheridan's arguments concerning the electronic configurations in **2a**−**c**. Thus, in **2a**, the two methylene subunits are inherently ground-state triplets ($\sigma^1\pi^1$), and therefore both factors drive the system into a $\sigma^2\pi^2$ biradical configuration. On the other hand, in **2b**, the local carbene units prefer closed-shell configurations, and their combined S−T splittings are −38.4 kcal mol^{-1} (Table 2). This is predicted to be enough to override the energetic benefit from the formation of the extra π bond, and the system is better described as **2b**−**I**. Finally, in **2c**, the chlorocarbenic centers also have an inherent preference for singlet ground states, but their combined effect

---

(21) When **4b** was irradiated with $\lambda > 350$ nm, IR abosrptions due to cumulenic bonds were observed. It is likely that under these conditions cycloheptatetraene-type of compounds are formed (at least to some extent), presumably via the corresponding azidocarbene.

(22) On the basis of Hund's rule[23] one may have expected that the triplet A′ states would be lower in energy than the singlet A′ ones.[24]

(23) Hund, F. *Z. Phys.* **1928**, *51*, 759.

(24) For violations of Hund's rule in organic molecules see, for example: (a) Hrovat, D. A.; Borden, W. T. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*, 211. (b) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

(25) At the CASPT2 and MCSCF levels of theory. This corresponds to a "corrected" S−T gap of −30 kcal mol^{-1} (Table 2, footnote a). At the B3LYP level of theory the break-even point is estimated at 26 kcal mol^{-1} below the S−T gap of phenyl carbene (i.e., for a "corrected" S−T splitting of −22 kcal mol^{-1}). This discrepancy between the two methods can be traced back to the underestimation of the relative energy of the ^{3}A″ state with the B3LYP method as compared with the MCSCF and CASPT2 methods.

(26) The S−T spliting of **8** is 54.8 and 52.0 kcal mol^{-1} smaller than the S−T of phenylcarbene at the MCSCF and B3LYP levels of theory, respectively.

(−13.4 kcal mol^{-1}) is not enough to establish a $\sigma^2\sigma^2$ ground electronic state, and **2c** is better described as **2c-II**. In the particular case of compounds **3**, since phenylnitrene has a triplet ground state, the only way to induce a switching of electronic configuration and multiplicity in the ground state is by coupling with a carbene center that has an inherently large preference for a closed-shell configuration. We are currently investigating such possibilities.

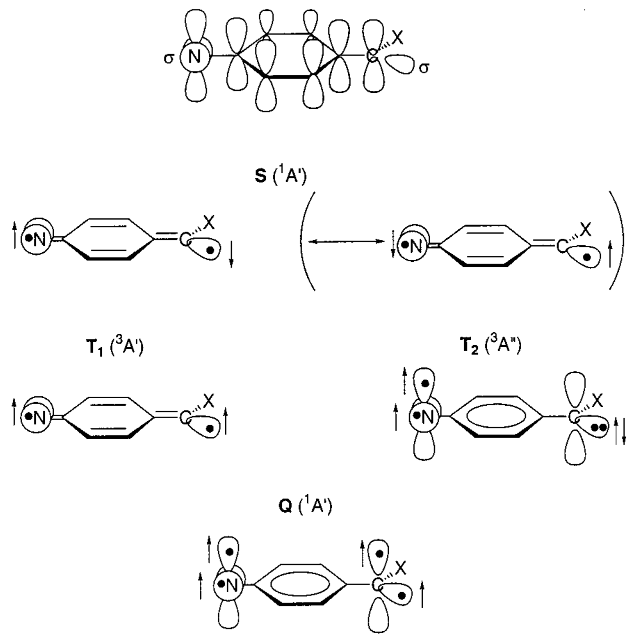
Conclusions

In concluding we have prepared and characterized in an Ar matrix a family of reactive intermediates in which a nitrene and a carbene center are coupled via the para phenylene linker. While all of these species are predicted to be ground-state singlet biradicals, the systematic effect of the halogen substituent on the carbenic center reveals that the energy of an excited triplet state becomes increasingly favored as the preference of the carbene subunit for closed-shell electronic configuration increases.

Computational Procedures

Ab initio molecular orbital calculations[27] were carried out using the GAUSSIAN 94,[28] GAMESS,[29] and MOLCAS[30] programs. Optimized geometries were obtained at the B3LYP/6-31G(d)[28,31] and MCSCF/6-31G(d) levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.[32] For the DFT calculations UB3LYP wave functions were used to describe the open-shell singlet diradicals (^{1}A′-**3a**−**d**). The so-calculated wave functions do not correspond to "pure" singlet states but rather to mixtures of singlet and triplet states. However, in this type of systems it seems that this is a reasonable approximation.[14,33] For **3a** the active space used in the MCSCF calculations comprised of 10 electrons in 10 MOs (four π and four π^* (of symmetry A″) MOs plus two σ ones (of symmetry A′)) denoted as MCSCF(10,10). For **3b**−**d** the active space was expanded to include the π lone pair (A″) of the halogen substituent (MCSCF(12,11)). At the top of Scheme 3 the relevant atomic orbitals are shown for **3a** (X = H), where also the two σ orbitals have been marked. Also in Scheme 3 are shown approximate valence bond representation of the states considered. States with even number of electrons in the π system are described by wave functions of A′ symmetry (S, T$_1$, and Q in Scheme 3), whereas T$_2$ with an odd number of π electrons is classsified as A″.

Scheme 3



Concentrating only on the four electrons of the reactive centers the three A′ states can be also described as having $\sigma^2\pi^2$ configurations, since each reactive center contributes a σ and a π electron. On the other hand the triplet A" state can be described as a $\sigma^3\pi^1$ state.

For phenylcarbene the active space included the six π MOs related to the carbons of the benzene ring and the one σ and the one π of the carbene subunit (MCSCF(8,8)). In the halogen-substituted phenylcarbenes the active space included, in addition, the π lone pair (A″) of the halogen (MCSCF(10,9)).

CASPT2/6-31G(d)[30] calculations were carried out at the corresponding MCSCF/6-31G(d) optimized geometries.

Experimental Section

Materials and General Methods. ^{1}H- and ^{13}C NMR spectra were recorded on a JEOL JNML-AL-300 spectrometer using $CDCl_3$ as a solvent. IR spectra were taken on a JASCO FT-IR410 spectrometer. UV−vis spectra were taken on a JASCO CT-560 UV−vis spectrometer. Melting points were measured with a Yanaco MP500D apparatus. Gel permeation chromatography was carried out on a Shodex GPCH-2001P column using a JASCO HLC-01 instrument equipped with a UVIDEC-100-II UV−vis detector.

4-Azidobenzonitrile was prepared following the literature procedure.[34] A mixture of 4-aminobenzonitrile (800 mg, 6.8 mmol), water (19 mL), and concentrated hydrochloric acid (19 mL) was stirred at 0−5 °C. The amine hydrochloride was deazotized by adding dropwise a solution of sodium nitrite (570 mg) in water (8 mL). To the stirred solution was added a solution of sodium azide (880 mg, 13 mmol) in water (8 mL) at 0−5 °C. After the reaction mixture was stirred for an additional hour, the resulting solution was extracted with CH_2Cl_2. The organic phase was washed (H_2O), dried (Na_2SO_4), filtered, evaporated, and dried in vacuo to give 4-azidobenzonitrile (975 mg, 96%) as a light yellow solid: mp 62−64 °C; ^{1}H NMR ($CDCl_3$) δ 7.11 (d, J = 8.82 Hz, 2H), 7.64 (d, J = 8.82 Hz, 2H); IR (KBr disk) ν 2222 (m), 2154 (m), 2111 (s), 1600 (m), 1506 (m), 1317 (m), 1276 (w), 1177 (m), 1127 (w), 836 (m), 598 (w), 547 (m) cm^{-1}.

4-Azidophenylimidate hydrochloride was prepared following the literature procedure.[35] Dry hydrogen chloride was passed into a solution of 4-azidobenzonitrile (500 mg, 3.5 mmol) in absolute ethanol (0.21 mL, 3.5 mmol) and absolute $CHCl_3$ (1.2 mL) for 2 h. Then the flask

---

(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(29) Schmidt, M. W.; Baldridge, K. K.; Boats, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347.

(30) Andersson, K.; Blomberg, M. R.A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS*, version 4; Lund University: Sweden 1997.

(31) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(33) For a review on calculations for open-shell species, see: Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipowitz, K. B., Boyd, D. B., Eds.; Wiley: New York, 1999; Vol. 13, p 1.

(34) Smith, P. A. S.; Boyer J. H. *Organic Syntheses;* Wiley & Sons: New York, 1963; Collect. Vol. IV, p 75.

was tightly stoppered and allowed to stand in a freezer. After 4 days, absolute Et_2O was added to the mixture and stirred. The precipitate was filtered, washed (Et_2O), and dried in vacuo to give 4-azidophenylimidate hydrochloride (700 mg, 89%) as a white solid: mp 118 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.62 (t, $J = 6.80$ Hz, 3H), 4.92 (q, $J = 6.80$ Hz, 2H), 7.18 (d, $J = 8.82$ Hz, 2H), 8.43 (d, $J = 8.82$ Hz, 2H); IR (KBr disk) ν 3200−2600 (br. s), 2119 (s), 1707 (w), 1603 (s), 1512 (w), 1463 (m), 1444 (m), 1392 (w), 1362 (w), 1303 (m), 1287 (m), 1194 (m), 1132 (w), 1065 (m), 1000 (w), 850 (w), 836 (w), 776 (w), 747 (w) 673 (w) cm^{-1}.

4-Azidophenylamidine hydrochloride was prepared following the literature procedure.[35] To a solution of ethanol saturated with ammonia was added 4-azidophenylimidate hydrochloride (680 mg, 3.0 mmol). After stirring for 4 h, the resulting solution was filtered to remove ammonium chloride. Removal of the solvent and drying of the solid in vacuo afforded 4-azidophenylamidine hydrochloride (530 mg, 86%) as a white solid: mp 194 °C (dec); IR (KBr disk) 3450−3000 (br. m), 2113 (s), 1673 (s), 1605 (s), 1491 (m), 1314 (m), 1297 (m), 1202 (w), 1133(w), 837 (w), 736 (w), 712 (w), 658 (w), 534 (w) cm^{-1}.

4-Azidophenyldiazomethane (**4a**) was prepared according to a modified procedure of Rees.[36] Thus, a mixture of 4-azidobenzaldehyde (500 mg, 3.4 mmol) and *p*-tosylhydrazine (633 mg, 3.4 mmol) in anhydrous tetrahydrofuran (30 mL) was stirred overnight at room temperature in the dark. After evaporation of the solvent, 4-azidobenzaldehyde tosylhydrazone was obtained as a yellowish solid, which was used for the next step without further purification. To a stirred suspension of sodium hydride (60% oil supension, 254 mg, 6.35 mmol) in anhydrous tetrahydrofuran (10 mL) was added the hydrazone (2.0 g, 6.35 mmol), and the mixture was stirred for 15 min at room temperature. The precipitate was collected by filtration and washed thoroughly with anhydrous ether to give sodium 4-azidobenzaldehyde tosylhydrozonate as a yellowish solid (2.1 g, 98%). The sodium salt (50 mg, 0.15 mmol) was placed in a micro sublimation apparatus and heated at 120 °C under 5×10^{-4} Torr. The diazo azido was collected from a coldfinger as a rather unstable red liquid (18 mg, 75%) and was immediately used for the matrix photolysis experiments: ^{1}H NMR ($CDCl_3$) δ 4.94 (s, 1H), 6.91 (d, $J = 2.30$ Hz, 2H), 6.96 (d, $J = 2.30$ Hz, 2H); IR (Ar, 10 K) ν 2122 (m), 2063 (vs), 1510 (m), 1384 (w), 1300 (m), 1293 (m), 824 (w), 558 (vw) cm^{-1}; UV (Ar, 10 K) λ_{max} 296, 333 nm.

3-(4-Azidophenyl)-3-fluorodiazirine (4b) was prepared following the literature procedure.[37] A mixture of **4d** (200 mg, 0.84 mmol), *n*-$Bu_4N^+F^-$ (700 mg, 2.7 mmol), and absolute acetonitrile (1 mL) was stirred at 25 °C in the dark for 4 h. The reaction was quenched with water (5 mL), and the resulting solution was extracted with *n*-hexane (3 × 10 mL). The combined hexane extracts were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by gel permeation chromatography to give **4b** (60 mg, 40%) as a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.02 (d, $J = 8.82$ Hz, 2H), 7.07 (d, $J = 9.00$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 71 ($J_{C-F} = 262.8$ Hz), 119, 126 ($J_{C-F} = 4.36$ Hz), 128 ($J_{C-F} = 30.5$ Hz), 142; IR (Ar, 13 K) ν 2142 (m), 2134 (s), 2118 (m), 2103 (vs), 1619 (m), 1588 (w), 1564 (w), 1513 (s), 1485 (w), 1425 (w), 1319 (m), 1312 (m), 1302 (m), 1289 (s), 1189 (m), 1169 (m), 1134 (w), 1116 (w), 1031 (w), 1007 (w), 834 (m), 714 (w), 554 (w) cm^{-1}; UV (Ar, 13 K) λ_{max} 396, 375, 356, 292 sh, 283 sh, 264 sh, 258 nm.

3-(4-Azidophenyl)-3-chlorodiazirine (4c) was prepared following the literature procedure.[38] A mixture of 4-azidophenylamidine hydrochloride (200 mg, 1.0 mmol), dimethyl sulfoxide (3.5 mL), LiCl (230 mg), and *n*-hexane (3 mL) was stirred at ∼5 °C. A hypochlorite solution (8.0 mL) containing NaCl (1.4 g) was added rapidly to the stirred solution. After the reaction mixture was stirred for an additional hour, the resulting mixture was extracted with *n*-hexane (3 × 10 mL). The combined hexane portions were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by gel permeation chromatography to give **4c** (83 mg, 43%) as a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.02 (d, $J = 8.64$ Hz, 2H), 7.09 (d, $J = 8.64$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 43, 119, 127, 132, 141; IR (Ar, 13 K) ν 2136 (vs), 2097 (s), 1609 (w), 1590 (w), 1569 (vw), 1560 (vw), 1511 (s), 1422 (vw), 1301 (m), 1290 (m), 1193 (w), 1132 (w), 1032 (w), 1013 (w), 914 (m), 828 (w), 816 (vw), 550 (vw), 544 (w) cm^{-1}; UV (Ar, 13 K) λ_{max} 401, 379, 362, 293 sh, 259, 203 nm.

3-(4-Azidophenyl)-3-bromodiazirine (4d) was prepared following the literature procedure.[37] A mixture of 4-azidophenylamidine hydrochloride (440 mg, 2.2 mmol) dimethyl sulfoxide (9.5 mL), $LiBr \cdot H_2O$ (1.1 g), and *n*-hexane (5 mL) was stirred at ∼5 °C. A fresh solution of NaOBr, prepared by the slow addition of bromine (1.1 mL) to a stirred and cooled (−10 °C) solution of NaOH (2.2 g) and NaBr (6.9 g) in water (16 mL), was added rapidly to the stirred solution, and the whole was stirred for an additional hour. The resulting mixture was extracted with *n*-hexane (4 × 10 mL). The combined hexane portions were dried (Na_2SO_4), filtered, and evaporated. The residue was purified by gel permeation chromatography to give **4d** (420 mg, 79%) as a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.01 (d, $J = 8.82$ Hz, 2H), 7.12 (d, $J = 9.00$); IR (Ar, 13 K) ν 2131 (vs), 2094 (s), 1611 (m), 1586 (w), 1571 (w), 1511 (s), 1482 (w), 1421 (w), 1306 (m), 1298 (m), 1288 (m), 1194 (w), 1134 (w), 1122 (w), 1024 (m), 1005 (m), 884 (m), 863 (w), 827 (m), 814 (w), 689 (w), 544 (w), 534 (w) cm^{-1}; UV (Ar, 13 K) 402, 381, 361, 293 sh, 259 nm.

4-Nitrenophenylcarbene (3a): IR (Ar, 10 K) ν 1277, 1077, 822, 650 cm^{-1}; UV (Ar, 10K) λ_{max} 263, 379, 397, 419, 437 nm.

4-Nitrenophenylfluorocarbene (3b): IR (Ar, 13 K) ν 1591, 1513, 1388, 1382, 1222, 1188, 1135, 1085, 817, 802, 789, 600, 566 cm^{-1}; UV (Ar, 13 K) λ_{max} 264, 402 nm

4-Nitrenophenylchlorocarbene (3c): IR (Ar, 13 K) ν 1569, 1502, 1379, 1083, 948, 913, 820, 712, 569 cm^{-1}; UV (Ar, 13 K) λ_{max} 278, 425 nm.

4-Nitrenophenylbromocarbene (3d): IR (Ar, 13 K) ν 1567, 1498, 1377, 1228, 1170, 1080, 947, 857, 820, 670, 590 cm^{-1}; UV (Ar, 13 K) λ_{max} 224, 283, 425 nm.

4-Azidophenylchlorocarbene (6-Cl): IR (Ar, 13 K) ν 2124, 1587, 1379, 1294, 1240, 1168, 712 cm^{-1}; UV (Ar, 13 K) λ_{max} 345, 355 nm.

4-Azidophenylbromocarbene (6-Br): IR (Ar, 13 K) ν 2123, 1586, 1293, 1256, 1168, 992, 680 cm^{-1}; UV (Ar, 13 K) λ_{max} 361, 371 nm.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques[39,40] using an Iwatani Cryo Mini closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fit with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and a quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 controller (gold vs chromel thermocouple).

Irradiations were carried out with a Wacom 500 W xenon high-pressure arc lamp. For broad-band irradiation Toshiba cutoff filters were used (50% transmittance at the specified wavelength).

Supporting Information Available: Total energies (B3LYP, MCSCF, CASPT2) of **3a−d**, **7a−d**, and **8** (Tables S1 and S2), Gaussian archive entries for **3a−d**, **6-Cl**, **6-Br**, **7a−d**, and **8** (Table S3), Cartesian coordinates of MCSCF geometries for **3a−d**, **7a−d**, and **8** (Table S4), and plots of UB3LYP frequencies for **3a−d** (Figure S1) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003709E

---

(35) Dox, A. W. *Organic Syntheses;* Wiley & Sons: New York, 1945; Collect. Vol. I, p 5.

(36) Adger, B. M.; Bradbury, S.; Keating, M.; Rees, C. W.; Storr, R. C.; Williams, M. T. *J. Chem. Soc., Perkin Trans. 1* **1975**, 31.

(37) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denny, D. Z.; Krogh-Jesperson, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

(38) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(39) Tomioka, H.; Ichikawa, N.; Komatsu, K. *J. Am. Chem. Soc.* **1992**, *114*, 6045.

(40) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.