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Halogen Derivatives of *m*-Phenylene(carbeno)nitrene: A Switch in Ground-State Multiplicity

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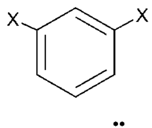
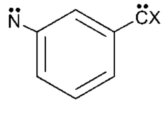
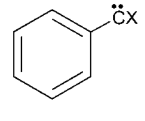
m-Phenylene-coupled carbenonitrenes [(3-nitrenophenyl)methylene (**2-H**), (3-nitrenophenyl)fluoromethylene (**2-F**), (3-nitrenophenyl)chloromethylene (**2-Cl**), (3-nitrenophenyl)bromomethylene (**2-Br**)] have been investigated computationally (with B3LYP, MCSCF, CASPT2, ROMP2, and QCISD(T) methods) and experimentally (with IR, UV, and ESR spectroscopy). For each species, five electronic states were considered. At the highest level of theory explored, the parent compound (**2-H**) has a quintet ground state, but its halogen derivatives (**2-X**, X = F, Cl, and Br) have triplet ground states. A linear relationship between the Q−T energy gap of **2-X** and the T−S gap of the corresponding phenylcarbenes **8-X** is found, which can be helpful in rationalizing and predicting ground-state multiplicities in *m*-phenylene-linked carbenonitrenes and similar species. Precursors for the photochemical generation of **2-X** (X = H, F, Cl, and Br) were synthesized and photolyzed in matrixes (Ar, triacetin) at low temperatures. IR (Ar, 13 K) and ESR (triacetin, 77 K) data are compatible with the generation of triplet halocarbenonitrenes **2-X**, (X = F, Cl, and Br). All four compounds upon further irradiation undergo isomerization to substituted cyclopropenes **5-X** (X = H, F, Cl, and Br), as suggested by their IR spectra.



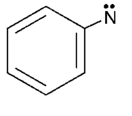
1-CH, X = $\ddot{\mathrm{C}}$H
1-N, X = $\ddot{\mathrm{N}}$
1-CCl, X = $\ddot{\mathrm{C}}$Cl
1-CH$_2$, X = $\dot{\mathrm{C}}$H$_2$



2-H, X = H
2-F, X = F
2-Cl, X = Cl
2-Br, X = Br



8-H, X = H
8-F, X = F
8-Cl, X = Cl
8-Br, X = Br



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In the search for high-spin organic molecules, carbenes and/or nitrenes linked via the *m*-phenylene linker are popular building blocks.[1] This is because *m*-phenylene usually acts as a ferromagnetic coupler between the reactive centers. For example, *m*-phenylene biscarbene (**1-CH**),[2a] *m*-phenylene bisnitrene (**1-N**),[2b] and the corresponding “mixed” carbenonitrene **2-H**[2c] are all known to have quintet ground states. From the study of such systems, the idea has evolved that the meta topology generally leads to high-spin ground states. Such empirical concepts are useful in the design of new compounds, and therefore it is important to gain a deeper insight and understanding of their origins. This is usually achieved by examining and testing model compounds at or close to the limits of the various empirical predictions. Thus, it has been reported that, when the reactive centers are radicals (for example, as with **1-CH$_2$**), the *m*-phenylene linker can be transformed to an antiferromagnetic coupler if the radicals are twisted out of conjugation.[3] This shows the importance of geometrical factors and has been used to explain the low-spin ground states of related *m*-phenylenebis(*tert*-butyl nitroxides).[4] However, this specific type of geometrical distortion is not applicable when the reactive centers are carbenes and/or nitrenes. In this context, it has been argued that the coupling orientation of this linker may be controlled by chemical substitution.[1a] The essence of this idea is that, if the carbene is designed to have a strong intrinsic preference for a singlet ground state, then the tendency of the linker to promote a high-spin ground state may be overridden. In this context, Sheridan reported the formation of what is believed to be *m*-phenylenebischloromethylene (**1-CCl**). On the basis of its reactivity and IR and UV/vis spectra,

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[†] Mie University.

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(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) (a) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (b) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (c) Tukada, H.; Mutai, K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1159.

(3) Fang, S.; Lee, M. S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1995**, *117*, 6727.

(4) (a) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180. (b) Kanno, F.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

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TABLE 1. Relative Energies (kcal/mol) of Various States of 2-X (X = H, F, Cl, and Br) Relative to the $^5A'$ State (Hartree)

species	B3LYP[a]	MCSCF[b]	CASPT2[c]	E_{QCI}[d]
2-H ($^1A''$)		33.4	38.0	
2-H ($^1A'$)		10.1	10.3	
2-H ($^3A''$)	12.3	15.0	18.0	11.9
2-H ($^3A'$)		5.8	5.3	
2-H ($^5A'$)	−324.20098	−322.37862	−323.30523	−323.58826
2-F ($^1A''$)		10.2	14.3	
2-F ($^1A'$)		10.0	9.8	
2-F ($^3A''$)	−8.5	−7.9	−5.3	−11.8
2-F ($^3A'$)		5.9	5.2	
2-F ($^5A'$)	−423.43976	−421.22559	−422.32602	−422.72349
2-Cl ($^1A''$)		21.9	25.3	
2-Cl ($^1A'$)		9.6	9.5	
2-Cl ($^3A''$)	0.4	3.9	5.8	−2.9
2-Cl ($^3A'$)		5.7	5.1	
2-Cl ($^5A'$)	−783.81262	−781.28135	−782.35371	−782.72518
2-Br ($^1A''$)		22.3	25.5	
2-Br ($^1A'$)		9.7	9.5	
2-Br ($^3A''$)	0.4	4.2	5.9	−1.5
2-Br ($^3A'$)		5.7	5.0	
2-Br ($^5A'$)	−2895.32284	−2891.68888	−2892.76209	−2895.56012

[a] Includes zero-point energy corrections using B3LYP/6-31G(d) frequencies scaled by 0.981. [b] Active space includes 10 (11) MOs and 10 (12) electrons for **2-H** (**2-X**, X = F, Cl, and Br). The 6-31G(d) basis set was used. [c] Using the MCSCF wave function described in b. [d] See Computational Procedures.

it was argued that **1-CCl** has a *singlet* ground state (in contrast to the parent **1-CH**).[5] On the other hand, calculations gave conflicting results, with DFT favoring Sheridan's interpretation and MCSCF opposing it.[6] It was concluded that the lowest quintet and singlet states of **1-CCl** are essentially isoenergetic, with the former being slightly favored.[6] The apparent disagreement between theory and experiment in this case is somewhat disturbing. Furthermore, it is desirable to be able to quantify, if possible, the relationship between the intrinsic preference of the carbene subunit for a singlet local configuration and the overall configuration of the *m*-phenylene bis(diradical). In this context, *m*-phenylenecarbenonitrenes **2-X** (X= F, Cl, and Br) seem to be appropriate models for a systematic study of the halogen effect on the carbene center. The ability to generate appropriate photochemical precursors of these compounds makes them attractive experimentally. In addition, the presence of just one carbene subunit implies that halogen substitution introduces only "half" the chemical perturbation introduced by Sheridan's biscarbene, allowing, perhaps, for subtler interactions to be revealed.

Results

For **2-X** (X = H, F, Cl, and Br), five electronic states, one quintet, two triplets (A′ and A″), and two singlets (A′ and A″) were considered. Absolute and relative energies are shown in Table 1 and in Supporting Information (Tables S1 and S2). Optimized geometries were obtained at the MCSCF and DFT levels of theory (Figure 1, Tables S3 and S4). Approximate valence-bond representations of these states are shown in Scheme 4 and discussed in more detail later on.

***m*-Phenylene(carbeno)nitrene (2-H).** Selected computed bond lengths and bond angles for **2-H** (anti isomer) are shown in Figure 1.[7] The two computational methods utilized for geometry optimizations (B3LYP and MCSCF) are in reasonable agreement as far as the $^5A'$ and $^3A''$ states of **2-H** are concerned. However, they differ considerably (Figure S2) when it comes to the other states ($^3A'$, $^1A'$, and $^1A''$). The difference is most likely due to the inability of the B3LYP method to properly account for the multiconfigurational character of these states.[8,9] Inspection of the geometries (Figure 1) of the A′ states shows that, independent of the overall multiplicity, the angle at the divalent carbon center is approximately 130°, close to that calculated for triplet phenylcarbene (Figure S3). On the other hand, the A″ geometries are characterized by a narrower bond angle at the carbene center and close to that of singlet phenylcarbene. The C−C bond lengths between the carbene center and the benzene ring follow a similar pattern, i.e., those of the A″ states resemble singlet phenylcarbene and those of the A′ states triplet phenylcarbene (although this is not so clear for the $^1A'$ geometry). The C−N bond length of the A′ and $^3A''$ states is close to that of triplet phenylnitrene ($^3A_2$-**9**, Figure S3), whereas the bond length of $^1A''$ is closer to that of open-shell singlet phenylnitrene ($^1A_2$-**9**). These geometrical similarities between subparts of **2-X** on one hand and the corresponding phenylcarbene (**8-X**) and phenylnitrene on the other are in line with analogies drawn on the basis of the corresponding electronic configurations (vide infra).

As expected, $^5A'$ is predicted (Table 1) to be the ground state of **2-H** at all levels of theory. Three other electronic states lie rather close in energy, while $^1A''$ is predicted to be substantially higher in energy. $^3A''$, which will turn out to be the state of interest for the switching of electronic configurations, lies 15−18 kcal/mol higher in energy than the quintet (MCSCF and CASPT2 methods). However, this energy gap is reduced to about 12 kcal/mol at our highest level of theory (E_{QCI}).[10]

We attempted to generate the desired carbenonitrene by irradiating **3-H** in an Ar matrix at 13 K (Scheme 1, Figures 2 and S1). The process was followed by IR spectroscopy, and the formation of diazonitrene **4-H** at the early stages of the reaction is suggested by the new "diazo" absorption at 2076 cm^{-1}. Continued irradiation of **4-H** resulted in the formation of a new product at the expense of the diazo compound. However, the observed peaks assigned to the final photoproduct were *not* what was calculated for carbenonitrene **2-H**. Instead, an excellent match between experimental and computed vibrational frequencies was found for substituted cyclopropene *Z*-**5-H** (Figure 2a). Irradiation with shorter a wavelength

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[5] Zuev, P. S.; Sheridan, R. S. *J. Org. Chem.* **1994**, *59*, 2267.

[6] Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947.

[7] There are two possible isomers with respect to the orientation of the C−H bond relative to the nitrene center: anti or *E* and syn or *Z*. As expected, their energies, geometries, and vibrationals are essentially the same (Table S1, Figure S4). For simplicity, the anti isomers are referred to throughout the main text for **2-X** (X = H, F, Cl, and Br). Experimentally, both isomers are expected to form.

[8] This inability is reflected also in the high spin-contamination related to these states (Figure S2).

[9] Bally, T.; Borden, W. T. *Rev. Comput. Chem.* **1999**, *13*, 1.

[10] The difference (of approximately 6 kcal/mol) between E_{QCI} and CASPT2 relative energies can be traced mainly to the inclusion of triple excitations and to the larger basis set utilized in the former method (Table S3). Both effects favor the energy of the $^3A''$ state relative to that of $^5A'$.

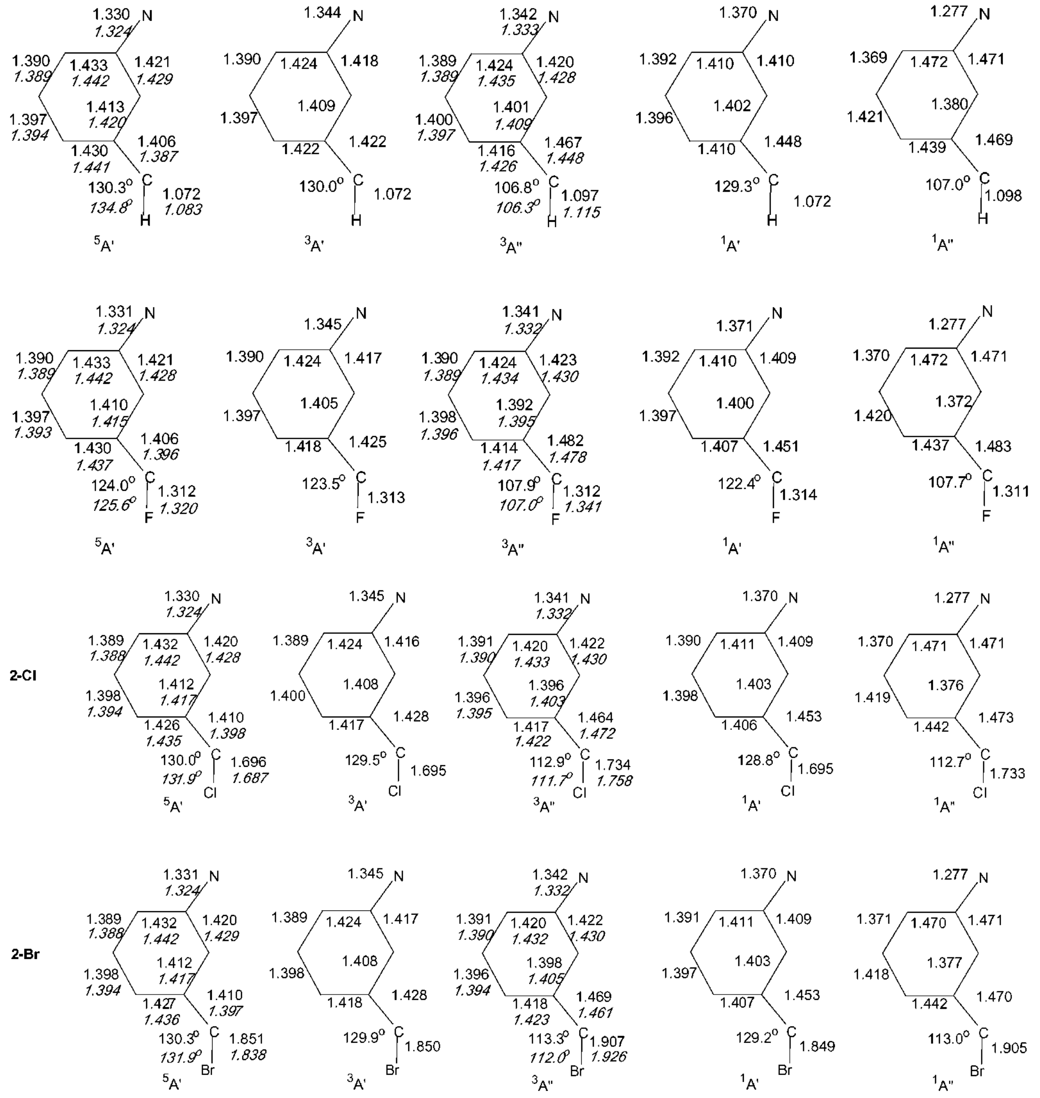
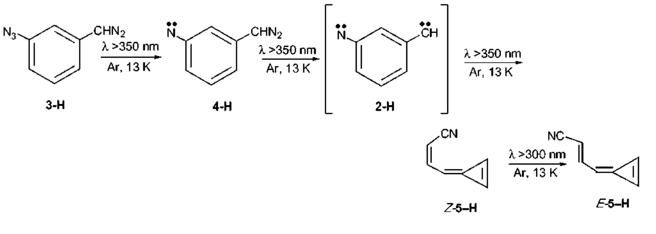


FIGURE 1. Selected geometrical parameters (distances in Å, angles in deg) for the $^5A'$, $^3A'$, $^3A''$, $^1A'$, and $^1A''$ states of **2-X** (X = H, F, Cl, and Br) at the MCSCF and UB3LYP (in italics) levels of theory with the 6-31G(d) basis set.

SCHEME 1



(λ > 300 nm) caused further changes in the IR spectrum, and the calculations suggest that this is due to a *Z* to *E* isomerization of the cyano substituent (Scheme 1, Figure 2b,c).

***m*-Phenylene(fluorocarbeno)nitrene.** As with the parent carbenonitrene (**2-H**), the geometrical characteristics of the A′ and A″ states at the divalent carbon center are similar to those of triplet and singlet phenylcarbene, respectively (Figure 1). The bond angles at the carbene center of the A′ states are systematically narrower (by about 7°) in **2-F** than those in **2-H**. This can be attributed to the higher electronegativity of F, which is expected to decrease the s character of the carbon orbitals that participate in the C−F bond. The C−N bond lengths in **2-F** are similar to that in triplet phenylnitrene, except for $^1A''$-**2-F**, which resembles $^1A_2$-**9** in this respect.

The different computational methods all predict that **2-F** has a triplet ($^3A''$) ground state *in contrast* to the parent **2-H** (Table 1). The energy difference between the $^3A''$ and $^5A'$ states (which corresponds to the first excited state) is 11.8 kcal/mol. As in the case of **2-H**, MCSCF and CASPT2 methods overestimate the relative stability of the $^5A'$ state and the predicted $^5A'-^3A''$ energy gap is found to be smaller (in absolute value) by a similar amount. In addition, the $^1A'$ and $^3A'$ states are higher in energy than the $^5A'$ state by amounts that are essentially the same in **2-F** as in **2-H**.

The initial photoproduct (Figure S5) of the irradiation of **6-F** is assigned to its diazo isomer **4-F** on the basis of the observed peak at 2029 cm^{-1} and in agreement with our previous experience (Scheme 2, Figures 3 and S5).[11] Further irradiation leads to a compound that shows no azido or diazo absorptions in the IR and for which the

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[11] Under similar experimental conditions, the para isomer of **4-F** also isomerizes to its corresponding diazo isomer.[12]

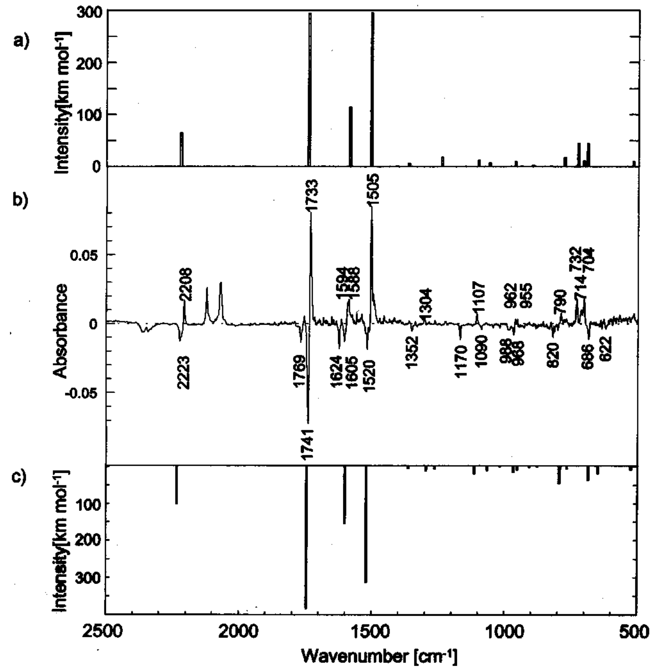
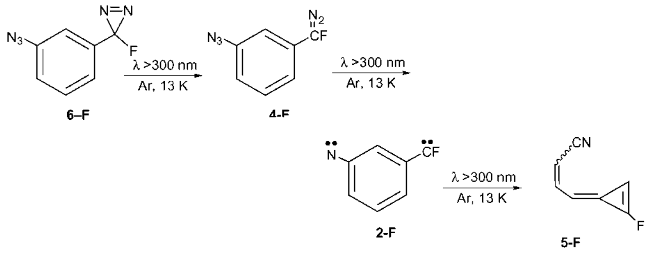


FIGURE 2. (a) Calculated (B3LYP/6-31G(d)) spectrum for *Z*-**5-H**. (b) Difference spectrum between the photoproduct formed after 505 min of irradiation with $\lambda > 350$ nm (*Z*-**5-H**, upper part) and final photoproduct formed after an additional 215 min of irradiation with $\lambda > 300$ nm (*E*-**5-H**, lower part). (c) Calculated (B3LYP/6-31G(d)) spectrum for *E*-**5-H**.

SCHEME 2



targeted carbenonitrene structure **2-F** is proposed on the basis of the good agreement with the computed spectra. Actually, the computations suggest that the observed IR spectrum should be assigned to the $^3A''$ state of **2-F** rather than the $^5A'$ state implying a triplet ground state (Figure S5d,e).

UV spectra of the secondary photoproduct (**2-F**), taken under the same experimental conditions, show a strong absorption at 245 nm and a very weak and broad one at 420 nm. Although **2-F** is observable, it decays upon continued irradiation giving rise to new peaks in the IR and UV spectra (Figure 3d,f). By comparison with computed vibrational frequencies (Figure 3e), the structure **5-F** is assigned to the final photoproduct.

Finally, irradiation of **6-F** in a triacetin matrix at 77 K gave UV spectra similar to those obtained in the Ar matrix. The peaks observed in triacetin that are attributed to **2-F** (Figure S5) are shifted by about 10 nm with respect to the UV spectra taken in the Ar matrix. At the same time, ESR signals attributable to a triplet nitrene species were detected (Figure 3g), but no evidence for the presence of a quintet species was found.

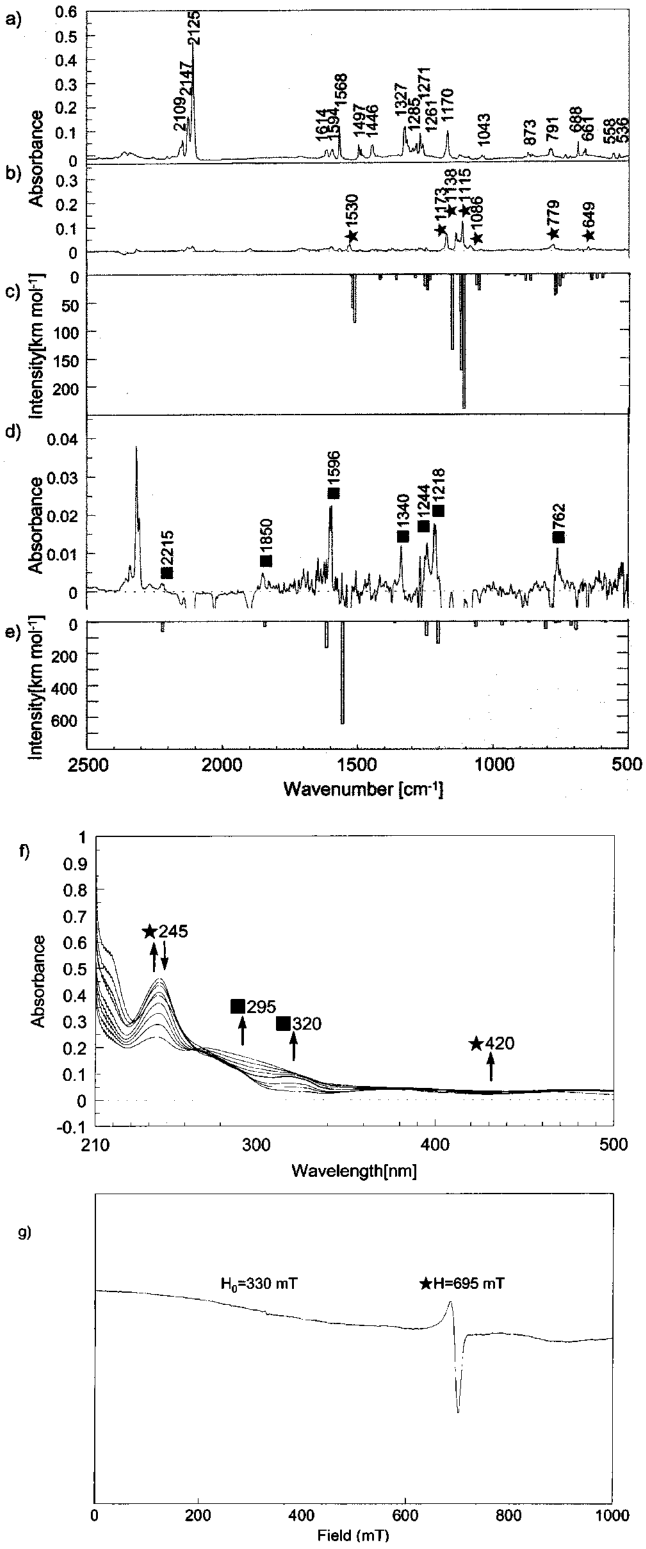
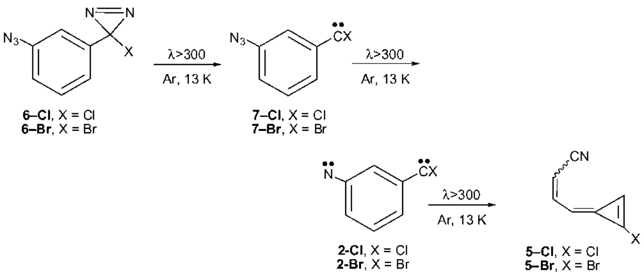


FIGURE 3. Photolysis ($\lambda > 300$ nm) of **6-F** in an Ar matrix at 13 K. (a) Total IR spectrum of **6-F** before irradiation. (b) Total IR spectrum obtained after 6 min of irradiation. Bands due to the secondary photoproduct (**2-F**) are marked "★". (c) Calculated (B3LYP/6-31G(d)) spectrum of triplet ($^3A''$) **2-F**. (d) Difference spectrum of F2 (lower part) and the photoproduct formed after 105 min of irradiation (**5-F**, "■"). (e) Calculated (B3LYP/6-31G(d)) spectrum of **5-F**. (f) UV spectra obtained from 15 s to 23 min of irradiation time. (g) ESR spectra obtained after 16 min of irradiation of **6-F** in triacetin at 77 K.

SCHEME 3



m-Phenylene(chlorocarbeno)nitrene and m-Phenylene(bromocarbeno)nitrene. The calculated geometries of the various states of **2-Cl** and **2-Br** show general characteristics similar to those discussed above for **2-H** and **2-F**. Relative MCSCF and CASPT2 energies predict that $^5A'$ should be the ground state for **2-Cl** and **2-Br** and not $^3A''$ as suggested by the IR spectra. B3LYP finds that the two states are essentially isoenergetic. At our best level of theory (E_{QCI}), both species have $^3A''$ groundstates, with the quintet state lying about 2−3 kcal/mol higher in energy. As above, DFT and MCSCF methods tend to overestimate the relative stability of the quintet. The difference between E_{QCI} and CASPT2 for the Q−T(A″) gap in **2-Cl** and **2-Br** is around 8 kcal/mol, similar to the case of **2-H**.

Irradiation of **6-Cl** and **6-Br** (Scheme 3, Figures 4, 5, S6, and S7) gives initially the corresponding azidocarbenes **7-X** (X = Cl and Br) as judged by the new azido peaks observed in the IR. It seems, then, that the first nitrogen molecule comes off from the diazirine ring and not from the azido group. As before, the reaction proceeds via the loss of a second N_2 to give the targeted carbenonitrenes **2-X** (X = Cl and Br). As with the fluorine derivative, the computed vibrational frequencies suggest that the $^3A''$ states of the carbenonitrenes are observed.

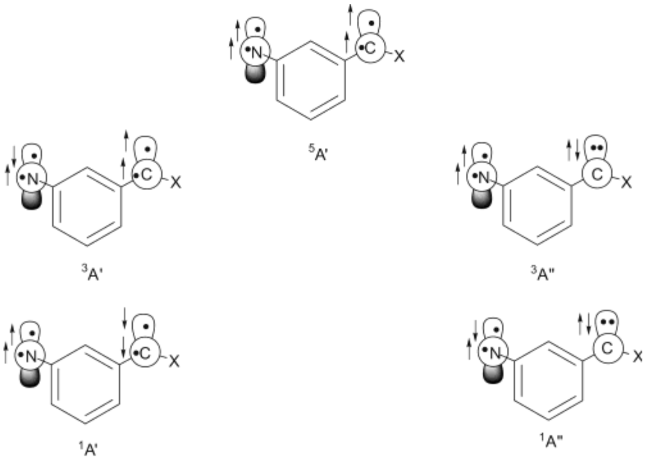
Further irradiation causes both **2-Cl** and **2-Br** to isomerize to substituted cyclopropenes (**5-Cl** and **5-Br**, respectively). As in the case of **2-F**, formation of the carbenonitrenes **2-Cl** and **2-Br** is associated with the observation of strong UV absorptions (257 nm for **2-Cl** and 241 and 262 nm for **2-Br**) and very weak and broad absorptions at long wavelengths (395 and 404 nm, respectively).

When **6-Cl** and **6-Br** were irradiated in triacetin at 77 K, the UV spectra were similar to those obtained in the Ar matrix. The triacetin spectra are red-shifted by about 10 nm with respect to the Ar ones. This shift is similar in magnitude but opposite in direction compared to that in **2-F**. ESR spectra obtained under these conditions (Figures 4g and 5g) showed the presence of triplet nitrene species (assigned to **2-Cl** and **2-Br**, respectively) and the absence of significant amounts of quintet species.

Discussion

The electronic configurations of the five electronic states of **2-X** considered can be approximated by the valence pictures shown in Scheme 4. Support for these descriptions comes from the geometrical characteristics discussed in the previous section and also from inspection of the leading configurations of the MCSCF wave functions. Using these simplistic pictures allows a conceptually transparent partition of the molecules in diradical subunits (carbene or nitrene sites) and the linker (m-phenylene). With the further approximation that the “intrinsic” T−S splitting of a diradical site in **2-X** is modeled reasonably well by the appropriate T−S gap of phenylcarbene **8-X** or phenylnitrene (**9**), the relative energies shown in Table 1 can be understood and the preference of m-phenylene for high-spin states can be quantified.

SCHEME 4



The $^5A'$ states can be thought of as the high-spin coupling of the triplet states of the two reactive centers, while the $^1A'$ states can be thought of as the low-spin coupling. Interestingly, the difference in energy between these two states is about 10 kcal/mol *independent* of the nature of X. This is the same amount by which singlet **1-CH₂** (antiferromagnetic coupling of the radical centers) lies higher in energy than triplet **1-CH₂**.[3] It seems, then, that 10 kcal/mol is the energy required to impose a low-spin coupling in the π space of the m-phenylene linker in order to overcome its preference for ferromagnetic coupling.

Both A″ states of **2-X** can be thought of as containing a singlet carbene subunit. Their difference is that the $^3A''$ states have a triplet nitrene subunit, but the $^1A''$ states have a singlet (open-shell) nitrene site. As is known,[13] the lowest singlet phenylnitrene ($^1A_2$) has open-shell character and is approximately described as a biradical with one odd electron localized in the σ orbital of the nitrene and the other in the π space. Thus, the energy difference $^1A''-^3A''$ in **2-X** should be approximately equal to the singlet−triplet splitting of phenylnitrene (18−19 kcal/mol) and this is easily derived from the data in Table 1.

The $^3A'$ states lie about 5 kcal/mol higher in energy than the corresponding quintet states. One may approximate the $^3A'$ states as the combination of a triplet carbene with a nitrene in which its σ and π electrons have opposite spins. It is tempting to identify the latter configuration as being analogous to the lowest singlet state of phenylnitrene (open-shell singlet, $^1A_2$). However, if that were the case, then the $^3A'$ state should be higher

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(12) Nicolaides, A.; Enyo, T.; Miura, D.; Tomioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 2628.

(13) Hrovat, D. A.; Waali, E. E.; Borden, W. T *J. Am. Chem. Soc.* **1992**, *114*, 8698.

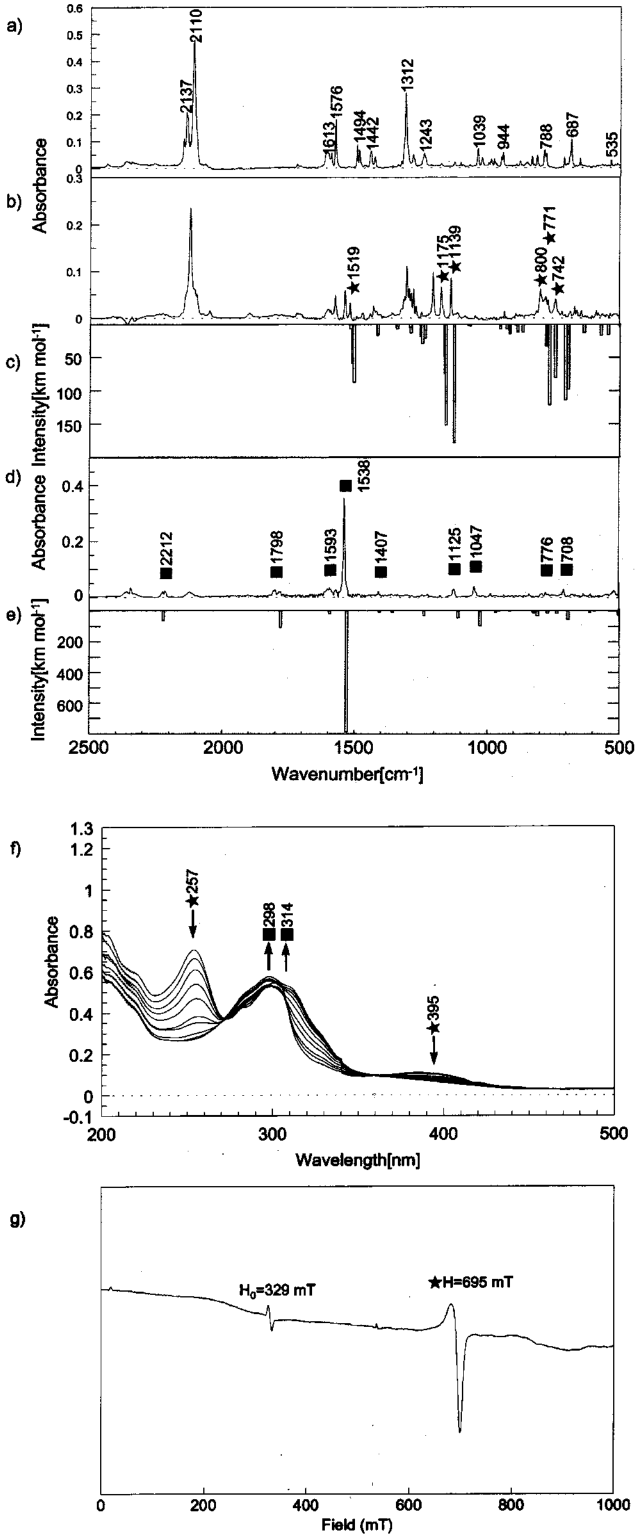

FIGURE 4. Photolysis ($\lambda > 350$ nm) of **6-Cl** in an Ar matrix at 13 K. (a) Total IR spectrum of **6-Cl** before irradiation. (b) Total IR spectrum obtained after 10 min of irradiation. Bands due to the secondary photoproduct (**2-Cl**) are marked "★". (c) Calculated (B3LYP/6-31G(d)) spectrum of triplet ($^3A''$) **2-Cl**. (d) Total IR spectrum obtained after 220 min of irradiation. Bands due to the final photoproduct (**5-Cl**) are marked "■". (e) Calculated (B3LYP/6-31G(d)) spectrum of **5-Cl**. (f) UV spectra obtained from 4 to 90 min of irradiation time. (g) ESR spectra obtained after 10 min of irradiation of **6-Cl** in triacetin at 77 K.

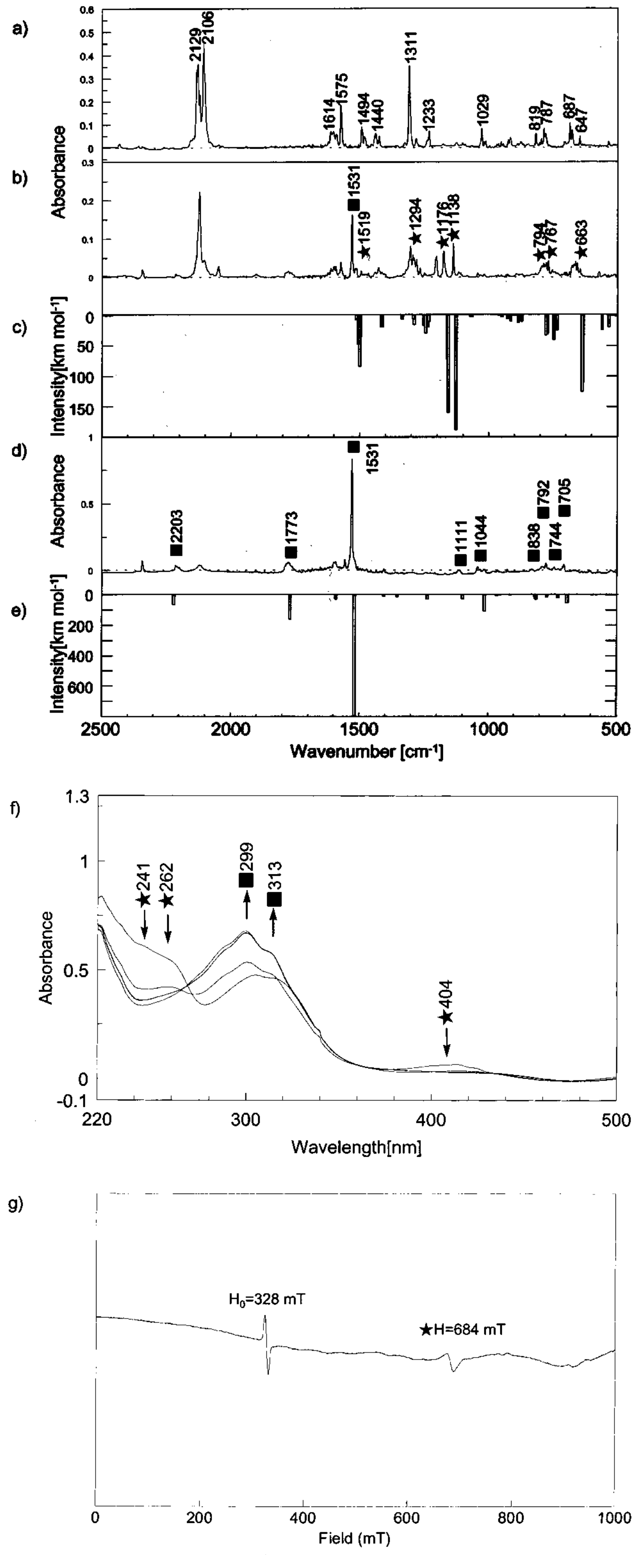

FIGURE 5. Photolysis ($\lambda > 350$ nm) of **6-Br** in an Ar matrix at 13 K. (a) Total IR spectrum of **6-Br** before irradiation. (b) Total IR spectrum obtained after 9 min of irradiation. Bands due to the secondary photoproduct (**2-Br**) are marked "★". Bands due to the final photoproduct (B3) are marked "■". (c) Calculated (B3LYP/6-31G(d)) spectrum of triplet ($^3A''$) **2-Br**. (d) Total IR spectrum obtained after 310 min of irradiation. Bands due to the final photoproduct (**5-Br**) are marked "■". (e) Calculated (B3LYP/6-31G(d)) spectrum of **5-Br**. (f) UV spectra obtained from 10 to 210 min of irradiation time. (g) ESR spectrum obtained after 10 min of irradiation of **6-Br** in triacetin at 77 K.

TABLE 2. Relative Energies (kcal/mol) of $^1A'$ and $^1A''$ States of 8-X (X = H, F, Cl, and Br) and $^1A_1$ and $^1A_2$ States of 9 Relative to the $^3A''$ and $^3A_2$ States, Respectively

species	B3LYP[a]	MCSCF[b]	CASPT2[c]	E_{QCI}[d]
8-H ($^1A''$)		23.2	22.1	
8-H ($^1A'$)	7.3	10.6	14.1	4.4
8-H ($^3A''$)	−270.12902	−268.55494	−269.36123	−269.60053
8-F ($^1A''$)		24.6	23.2	
8-F ($^1A'$)	−13.0	−11.8	−9.1	−17.0
8-F ($^3A''$)	−369.36822	−367.40263	−368.38390	−368.73644
8-Cl ($^1A''$)		24.1	22.2	
8-Cl ($^1A'$)	−4.3	−0.2	3.5	−8.2
8-Cl ($^3A''$)	−729.74144	−727.45881	−728.41184	−728.73818
8-Br ($^1A''$)		23.7	22.0	
8-Br ($^1A'$)	−4.4	0.0	2.7	−6.9
8-Br ($^3A''$)	−2841.25159	−2837.86628	−2838.81882	−2841.5731
9 ($^1A_1$)	33.7	41.9	36.9	
9 ($^1A_2$)		17.8	19.4	
9 ($^3A_2$)	−286.21818	−284.59560	−285.42619	

[a] Includes zero-point energy corrections using B3LYP/6-31G(d) frequencies scaled by 0.981. [b] Active space includes 8 (9) MOs and 8 (10) electrons for **2-H** and **9** (**2-X**, X = F, Cl, and Br). The 6-31G(d) basis set was used. [c] Using the MCSCF wave function described in b. [d] See Computational Procedures.

in energy than the corresponding $^5A'$ state by the same amount that $^1A''$ is higher in energy than $^3A''$ (18−19 kcal/mol, vide supra). To resolve the issue, we propose that, although the σ and π electrons on the nitrene center have opposite spins, the overall configuration is somewhat different than that of an open-shell singlet ($^1A_2$) phenylnitrene. In the latter molecule, the nitrene center can be described (qualitatively) by two determinants: $|...\pi_N(\alpha)\sigma_N(\beta)| - |...\sigma_N(\alpha)\pi_N(\beta)|$, whereas, in the former case, only the first determinant would be important because the *m*-phenylene linker promotes the ferromagnetic coupling between the nitrene and carbene subunits. In other words, in the $^3A'$ states of **2-X**, if the carbene is locally in a triplet configuration ($|...\pi_C(\alpha)\sigma_C(\alpha)|$), a reasonably good qualitative description of these states is $|...\pi_C(\alpha)\sigma_C(\alpha)\pi_N(\alpha)\sigma_N(\beta)|$, whereas the contribution of $|...\pi_C(\alpha)\sigma_C(\alpha)\sigma_N(\alpha)\pi_N(\beta)|$ is not as important. This is also supported by examining the leading configurations of the $^5A'$ MCSCF wave functions, which show that two π electrons are triplet coupled.

It can be shown that, for two electrons, a determinant of the type $|\pi(\alpha)\sigma(\beta)|$ corresponds to neither a pure singlet nor a pure triplet wave function. It represents rather a "mixed" wave function made of 50% singlet and 50% triplet character.[14] By extending this analogy to the $^3A'$ states of **2-X**, the "local" nitrene subunit is expected to lie energetically "halfway" between triplet and (open-shell) singlet phenylnitrene. This means that these states should be roughly 9 kcal/mol (i.e., half of the gap in phenylnitrene) higher in energy than the corresponding $^5A'$ states. If one takes into account our simplistic assumptions, this expectation is essentially fulfilled by the computationally derived $^5A'-^3A'$ gap of 5 kcal/mol. Thus, one may argue that the *m*-phenylene linker, by promoting ferromagnetic coupling in its π space, allows for favorable electron correlation at the nitrene center, reducing the energy of the $^3A'$ state.

Finally, the $^3A''$ states result from the combination of triplet nitrene and a closed-shell singlet carbene. These are the states expected to be mostly affected by the halogen substitution and are relevant for achieving configuration switching. The implicit assumption is that halogen substitution at the carbene center of **2-X** stabilizes the $^3A''$ states compared to the $^5A'$ ones, in a similar way that the (closed-shell) singlet of the phenylcarbene **8-X** is stabilized with respect to the triplet state (Table 2). In other words, it is expected that the Q−T(A″) splitting in **2-X** ($\Delta E(^3A''-^5A')$) is proportional to the T−S splitting in **8-X** ($\Delta E(^1A'-^3A'')$). Exactly this is found when the computational data are plotted (Figure 6). From the linear fitting of the E_{QCI} energies (regression coefficient = 0.998), the following equation linking the two quantities (in kcal/mol) is found:

$$\Delta E(^3A''-^5A') = 6.6 + 1.1 \times \Delta E(^1A'-^3A'') \qquad (1)$$

On the basis of these values, configuration switching is expected to take place when $\Delta E(^1A'-^3A'')$ is −6 kcal/mol or less.

Linear relationships were found with the other computational methods as well.[15] Thus, all four methods predict that the stabilization effect of the halogen in **2-X** is linearly related to that in **8-X**. On the other hand, there is little agreement as far as the Q−T(A″) splitting of **2-X** is concerned. While it is encouraging that the differences between the methods appear to be systematic, this splitting is important in establishing the ground-state multiplicity of **2-Cl** and **2-Br**.

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(14) See, for example: Szabo, A.; Ostlund, N. In *Modern Quantum Chemistry*; Dover Publications, Inc.: Mineola, NY, 1996; p 102.

(15) The following equations were obtained for the other methods (regression coefficients in parentheses): $\Delta E(^3A''-^5A') = 4.8 + 1.0 \times \Delta E(^1A'-^3A'')$ B3LYP (1.000); $\Delta E(^3A''-^5A') = 4.2 + 1.0 \times \Delta E(^1A'-^3A'')$ MCSCF (1.000); $\Delta E(^3A''-^5A') = 3.3 + 1.0 \times \Delta E(^1A'-^3A'')$ CASPT2 (0.997).

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(18) The intensity of the strongest absorption of **3-H** is computed to be ca. 820 km/mol, while that of quintet **2-H** is about 32 km/mol (Figure S1h). Since, in the former case, the strongest measured absorbance was 1.45, those of **2-H** should be around 0.06(well within the limits of experimental detection). This approximation assumes that the **3-H** → **2-H** transformation is completed *before* the latter starts reacting further. However, this is not the case, since **5-H** appears during the early stages of the irradiation, when about 10% of **3-H** has reacted. Thus, the strongest absorbances of $^5A'$-**2-H** are an order of magnitude less than "normally" expected, and we expect the corresponding signals to lie within the noise level of our instrument.

(19) Using the strongest observed peak for the $^3A''$ state of **2-F** (1115 cm^{-1}, absorbance 0.126) and computed peaks (1111 cm^{-1} (240 km/mol) for the $^3A''$ state and 1380 cm^{-1} (105 km/mol) for the $^5A'$) and assuming a threshold absorbance of 0.005 finds the maximum possible amount of quintet present to be less than 10% of the triplet A″ state.

(20) Assuming a threshold absorbance of 0.005, the estimation is based on the observed peak at 1139 cm^{-1} (absorbance = 0.081) and the computed peaks at 1126 cm^{-1} (178 km/mol) for $^3A''$-**2-Cl** and at 837 cm^{-1} (71 km/mol) for $^5A'$-**2-Cl**.

(21) From the observed peak at 1138 cm^{-1} (absorbance = 0.145) and the computed peaks at 1128 cm^{-1} (188 km/mol) for $^3A''$-**2-Br** and at 803 cm^{-1} (19 km/mol) for $^5A'$-**2-Br**, the maximum possible amount of quintet present is about 35% of that of the observed triplet. A smaller percentage (15%) is found if the peak at 655 cm^{-1} (42 km/mol) is used. However, if these peaks overlap with those observed for the triplet (794 and 663 m^{-1}, respectively), then the presence of larger amounts of quintet could be masked. Estimations based on ratios of computed intensities show that, depending on the peaks chosen, the presence of the quintet could vary between 10% and 110% of the triplet.

(22) One can think of several possible isomers depending on the positions of the halogen and CN substituents and the relative conformation of the two exocyclic double bonds. It is not possible to discriminate among all the possibilities only from the IR data, and further studies are required before the exact structures are assigned unambiguously.

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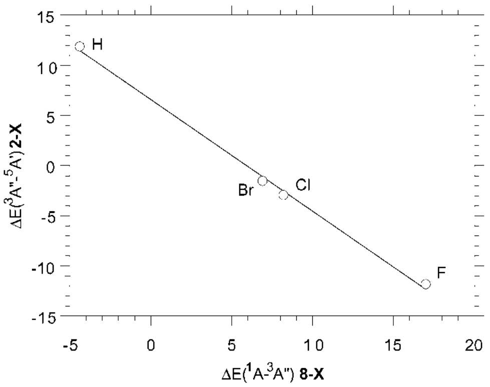

FIGURE 6. E_{QCI} relative energies of $^3A''$ and $^5A'$ states ($\Delta E(^3A''-^5A')$, kcal/mol) of **2-X** (X = H, F, Cl, Br) plotted against the E_{QCI} singlet−triplet splittings ($\Delta E(^1A'-^3A'')$, kcal/mol) of the corresponding phenylcarbenes (**8-X**).

Computing relative energies of entities of different multiplicities is a very difficult task, and in this respect, the E_{QCI} energies are the best computational results reported thus far in the study of such bis(diradicals). These results are unlikely to be changed significantly by higher-level calculations and can be used as benchmarks for B3LYP- and MCSCF-based methods. According to this method, all three halocarbenes **2-X** (X = F, Cl, and Br) are predicted to have triplet ground states. From Tables 1 and 2, B3LYP tends to overestimate the stability of the high-spin state (Q in the case of **2-X**, T in the case of **8-X**) compared to the low-spin state (T(A″) and S, respectively) on average by about 3 kcal/mol. At the MCSCF and CASPT2 levels, the overestimation is about 6 and 8 kcal/mol, respectively. It should be noted that the B3LYP values (the least expensive computationally) are in better agreement with the E_{QCI} results than are the MCSCF and CASPT2 values.

To the extent that the differences in the methods are systematic, the above overestimations are likely to be transferable. If this is correct, then in the case of **1-CCl**, where the quintet and singlet states were found to be nearly isoenergetic at the MCSCF level of theory,[6] in reality the singlet is likely to be the ground state. On the basis of the previous approximation and taking into account that there are two Cl substituents in **1-CCl**, the singlet is expected to be about 12 kcal/mol more stable than the quintet. In agreement with this expectation, the E_{QCI} level of theory predicts a splitting of −11.5 kcal/mol, supporting Sheridan's interpretation. [6]

The above shows that special caution is needed when estimating relative energies of different electronic states in these kinds of systems. At the same time, it shows the importance of generating these species experimentally, since small energy differences, even when computed at high levels of theory, can be sources of ambiguity and controversy.

Compounds **3-H** and **4-X** (X = F, Cl, and Br) were synthesized as precursors for the computed *m*-phenylene-linked carbenonitrenes. In all cases, the final photoproducts are substituted cyclopropenes (**5-X**, X = H, F, Cl, and Br). In the case of the halogen derivatives, the intermediate formation of the corresponding carbenonitrenes **2-X** was also observed. On the other hand, we were not able to detect **2-H**. A possible explanation for this failure is that **4-H** transforms directly to *Z*-**5-H**, without the intermediate formation of **2-H**. Indeed, it has been demonstrated that the photochemical decomposition of diazo compounds often leads directly to products derived from rearrangements of the nitrogen-containing precursors themselves.[16,17] However, in the particular case of **4-H**, it seems less likely that this may be the case, since the concomitant elimination of two nitrogen molecules is required. An alternative explanation is that **2-H** is formed but its concentration remains below the threshold required for its detection under our experimental conditions. This can happen if **2-H** is formed vibrationally excited and/or is photosensitive under the irradiation conditions. We favor this explanation, since **2-H** has been detected by ESR[2c] under similar conditions and since we are able to observe its halogen analogues by IR.[18]

In the case of **2-F**, the computed $^5A'-^3A''$ gap is sufficiently large that the quintet state is not expected to be thermally populated. In addition, the strongest IR absorption of the quintet state is predicted to be well separated from peaks attributable to $^3A''$ **2-F** and therefore should have been observed if present in significant amounts.[19]

In the case of **2-Cl**, the quintet state can be present in up to about 20% of the amount of the observed triplet (A″) and still evade detection under our experimental conditions.[20] The strongest peaks of the quintet state of **2-Br** are predicted to be close to absorptions of its triplet state. Possible overlap between the peaks of the two states could result in masking of significant amounts of quintet.[21]

The ESR spectra, although obtained under different conditions (triacetin matrix, 77 K), support the results of the IR experiments. This is particularly important for **2-Br** (and to a lesser extent for **2-Cl** and **2-F**). Compound **2-Br** has the smallest predicted Q−T(A″) splitting among the three halocarbenes and is the one for which IR has the greatest uncertainty as far as the presence of the quintet state is observed. Thus, the observation of ESR signals attributable to triplet nitrene species under conditions where UV spectroscopy suggests the presence of $^3A''$-**2-Br** provides strong evidence that this is the observed species. The absence of signals attributable to quintet **2-Br** strongly suggests that if this state is present, then its concentration must be significantly less than that of the observed triplet.

Overall the experimental data suggest that the observed halocarbenes **2-X** (X= F, Cl, and Br) are mainly (if not totally) in their triplet states. Taking into account the high-level computational results, the best interpretation seems to be that these are the ground states of the species under consideration.

Under our experimental conditions, the carbenonitrenes **2-X** (X = F, Cl, and Br), although observable by IR (in contrast to **2-H**), react photochemically giving rise to new compounds as monitored both by IR and UV spectroscopy. The computational data strongly suggest that the final photoproducts are substituted cyclopropenes **5-X** (X = F, Cl, and Br).[22] This remarkable bond reorganization reaction, while surprising at first, is reminiscent of the photoreactivity of *p*-phenylenebisnitrene, which also isomerizes to a cyclopropene derivative.[23] The formation of a strong carbon−nitrogen triple bond seems to be part of the driving force behind this transformation.

On the other hand, the para isomers of **2-X** are reasonably inert under similar irradiation conditions.[12] This difference in reactivity between meta and para topologies is difficult to explain without a knowledge of the mechanism. While this is under investigation, a plausible explanation can be found by looking at the geometries and electronic structures of the two kinds of species. In the para isomers of **2-X**, there is strong conjugative coupling between the reactive centers, transforming them to vinyl and iminyl moieties, and the whole molecule is better described as a biradical.[12] On the other hand, in the meta carbenonitrenes **2-X** (X = H, F, Cl, and Br), the two reactive centers retain much of their carbenic and nitrenic identities and the whole molecule can be thought of as resulting from a rather weak coupling of a local (triplet) phenylnitrene and a local phenylcarbene (triplet for X = H or singlet for X = F, Cl, and Br). Since phenylnitrene and phenylcarbene are known to be photoreactive, the higher reactivity of the meta compounds may be understood at least in this qualitative manner.

In conclusion, **3-H** and **4-X** (X = F, Cl, and Br) react photochemically to give, as final photoproducts, substituted cyclopropenes. Our computational and experimental data support the existence of the corresponding carbenonitrenes **2-X** (X = H, F, Cl, and Br) as intermediates. The ground-state electronic configuration in **2-X** depends on the intrinsic preference of the carbene subunit for the singlet or triplet state (approximated as the T−S gap of the corresponding phenylcarbene **8-X**) and on the preference of the *m*-phenylene linker to promote high-spin coupling in its π space (estimated at 6−10 kcal/mol). On the basis of this simple model, the quintet ground state of the parent **2-H** and the triplet (A″) state of **2-F** on one hand and the small Q−T(A″) splitting of **2-Cl** and **2-Br** on the other are easily rationalized. The finding that **2-Cl** has a ^{3}A″ ground state instead of a ^{5}A′ one supports Sheridan's assignment of **1-CCl** as having a singlet ground state.[5] It further suggests that just one Cl substituent at a carbene center suffices to cause configuration switching in *m*-phenylene-linked bis(diradicals) of this type.

Our data justify the hypothesis that chemical substitution at the carbene center can cause switching from a high-spin ground state to a lower multiplicity and also provide quantitative insight as to when such switching is likely to take place.

All four carbenonitrenes are photolabile *irrespective* of their ground-state multiplicity isomerizing to substituted cyclopropenes upon continued irradiation.

Computational Procedures

B3LYP/6-31G(d)[24]-optimized geometries and vibrational frequencies were obtained with GAUSSIAN 98;[25] MCSCF/6-31G(d) geometry optimizations were carried out with GAMESS,[26] and single-point CASPT2 energies (at MCSCF/6-31G(d)-optimized geometries) were computed with MOLCAS.[27] Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.[28] Better relative energies were obtained at a modified G2(MP2,SVP)[29] level (denoted by E_{QCI}) of theory. More specifically, the MP2 calculations for the open-shell species were carried out on ROHF wave functions[25] to avoid problems arising from spin contamination.[30a] The MCSCF-optimized geometries were used for the required QCISD(T) and MP2 single-point calculations. These modifications and omitting the so-called higher-level correction allowed a T−S gap of 4.4 kcal/mol (Table 2) to be predicted for phenylcarbene (**8-H**) in very good agreement with the available experimental and computational data.[30]

The active space of the MCSCF wave functions consisted of 10 (**2-H**) or 12 (**2-X**, X = F, Cl, Br) electrons and 10 or 11 molecular orbitals, respectively. The active MOs were the six MOs contributed by the *m*-phenylene linker (three π and three π^*), one σ (A′), and one π (A″) per reactive center and (for the halogen derivatives) a MO corresponding to the A″ lone pair of the halogen. In total, five different electronic states were considered for each carbenonitrene **2-X**; one quintet (^{5}A′), two triplets (^{3}A′ and ^{3}A″), and two singlets (^{1}A′ and ^{1}A″).

For phenylcarbene and phenylnitrene, the active space included the six π MOs related to the carbons of the benzene ring and one σ MO and one π MO of the active center (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)).

Experimental Section

Material and General Methods. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent. ESR spectra were measured on a spectrometer with an X-band microwave unit and 100 kHz field modulation.

Synthetic procedures and spectroscopic data are given in Supporting Information.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques[31,32] using a 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

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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 quartz outer window were used. The temperature of the matrix was controlled by a gold vs chromel thermocouple.

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

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Supporting Information Available: Details of experimental methods and data, total energies and geometries of **2-X**, and IR, UV, and ESR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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