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o-Phenylene Halocarbenonitrenes and *o*-Phenylene Chlorocarbenocarbene: A Combined Experimental and Computational Approach

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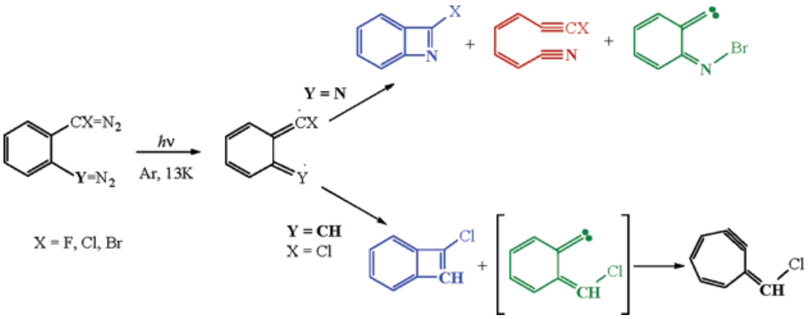

Computations find that *o*-phenylene(halo)carbenonitrenes **2-XN**, X = F, Cl, Br, have quinoidal singlet biradical ground states such as the parent *o*-phenylenecarbenonitrene (**2-HN**). Compared to the parent **2-HN**, halogen substitution stabilizes the A″ states relative to the A′ ones. Halogen substitution also affects the barrier and exothermicity of the ring-opening reaction (to form unsaturated nitriles **4-XN**, X = F, Cl, Br), but it has a smaller effect on the ring-closing reaction (to form benzo(aza)cyclobutadiene **3-XN**, X = F, Cl, Br). Attempts to generate and observe the *o*-phenylene(halo)carbenonitrenes **2-XN**, X = F, Cl, Br, using matrix isolation spectroscopy under conditions similar to those of the successful observation of **2-HN** failed. Instead, the observed photoproducts were a mixture of **3-XN** and **4-XN**. In each case, the major product of the mixture appears to be the thermodynamically more stable one. In the case of X = Br, the observed mixture contains an additional component that is postulated to be *Z*-**6-BrN**. *o*-Phenylenechlorocarbenocarbene is also computed to have a quinoidal singlet biradical ground state and relatively stabilized A″ excited states. Attempts to generate the biscarbene under matrix isolation conditions led to the detection of benzochlorocyclobutadiene (**3-ClC**), small amounts of the ring-open product (dienediyne **4-ClC**), and cycloalkyne **5-ClC**. Computations suggest that the formation of **5-ClC** implies the generation of *Z*-**6-ClC**, which is analogous to the formation of *Z*-**6-BrN** from **2-BrN**.

Introduction

Intermediates with more than one "reactive" site can exhibit properties that are not the simple "sum" of the constituent parts. Thus, the chemistry of biradicals[1] and biscarbenes[2] is substantially richer and more complicated than that of the corresponding "monomeric" species. For example, treating a carbene as a diradical (i.e., as a two-electron-in-two-orbitals problem) gives rise to six electronic configurations,[3] which can be grouped in four states (one triplet and three singlets). In the case of a biscarbene (or a bisdiradical in general), there are 70 configurations that break down to 20 singlets, 15 triplets, and one quintet.[4] While many of these 36 states are expected to be of high energy, there are several left that can be accessible, and understanding the factors that determine their relative energetics is important in controlling their spin properties. One of the important factors is the so-called "linker", which is the part of the molecule that connects the two reactive centers. Since it was discovered that biscarbenes linked with the *m*-phenylene

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[†] Mie University.
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(1) Borden, W. T., Ed. *Diradicals*; Wiley: New York, 1982.
(2) Zuev, P. S.; Sheridan, R. S. *Tetrahedron* **1995**, *51*, 11337.
(3) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69.
(4) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

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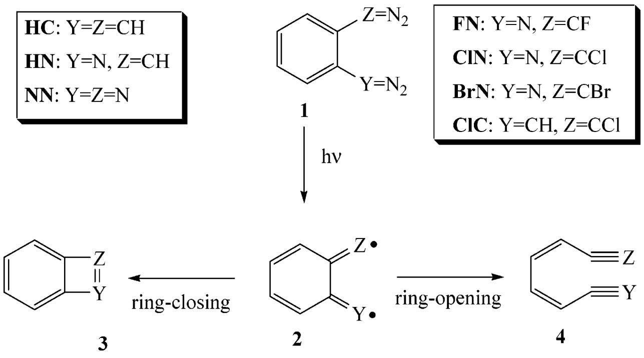
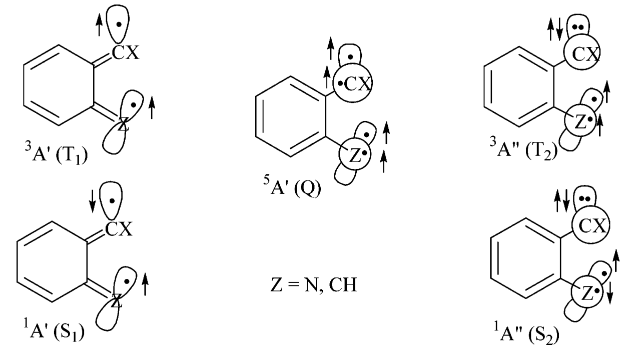
SCHEME 1



SCHEME 2



linker have quintet ground states,[5] research activities on poly(diradical) species have focused to a large extent on this linker for generating high-spin organic molecules.[6] In marked contrast, the *o*- and *p*-phenylene linkers have been much less explored, since the conjugative interaction between the diradical centers is expected to promote antiferromagnetic coupling leading to singlet ground states[2] and, therefore, are not attractive in terms of technological application.

In the last 10 years systematic studies employing matrix isolation spectroscopic techniques in combination with computational chemistry have begun to unfold properties and structures of species linked in *p*-phenylene systems.[7,8] The parent *p*-phenylenebiscarbene has been characterized and shown to have a singlet quinoidal biradical ground state,[7a] and the same is true for the isoelectronic *p*-phenylenebisnitrene.[8b] Some of these studies[7b,c,8b,c] have examined how substitution at the diradical center affects its "local" electronic configuration, which in turn can have a significant influence on the electronic structure of the species and its chemical and spectroscopic properties. In contrast, very little is known about their isomeric *o*-phenylene-linked bisdiradicals.[9] While the electronic effects of *p*- and *o*-phenylene systems are expected to be very similar, the proximity of the reactive centers in the latter case allows for the possibility of (thermal) reaction. This extra possible complication makes the study of the *o*-isomers more difficult and challenging.

According to a previous study,[9] the *o*-phenylene-bis(diradicals) **2-NN**, **2-HN**, and **2-HC** when generated in an inert matrix at low temperature may undergo either a ring-opening reaction to give dienediyne derivatives **4** or a ring-closing one to form benzocyclobutadiene derivatives **3** (Scheme 1). The selectivity for ring opening versus closure is highly dependent upon the nature of the local diradical subunits. Thus, calculations predict that biscarbene **2-HC** prefers the ring-closure path while both theory and experiment agree that the nitrenes **2-NN** and **2-HN** prefer the ring-opening one. However, due to lack of an appropriate precursor, the computational prediction for **2-HC** has not been tested yet. Herein we wish to report our efforts to analyze the photoproducts from 3-halo-3-(2-azidophenyl)diazirines (**1-XN**, X = F, Cl, Br) and 3-chloro-3-(2-diazomethylphenyl)diazirine (**1-ClC**) by using matrix isolation spectroscopy and computational methods. With the first three precursors, we attempt to understand further how the nature of the diradical affects the reactivity of the parent **2-HN** by perturbing electronically the carbene moiety. With **2-ClC**, we attempt to test the previous computational prediction for *ortho*-phenylene-linked biscarbenes.

Results and Discussion

Carbenonitrenes 2-XN. (a) Computational Considerations. Selected optimized geometrical parameters of the desired carbenonitrenes (**2-XN**, X = H, F, Cl, Br) are displayed in Figure S1 of the Supporting Information. The relative energies of the different states are listed in Table S1, and approximate valence bond depictions are shown in Scheme 2.

In agreement with previous findings,[8b,c,9] the lowest singlet ($^1A'$) and triplet states ($^3A'$) have *o*-quinoid geometries (Figure S1). On the other hand, the C−C bond lengths of the benzene rings of the quintet states can be considered as benzenoid. Between the two "extremes" lie the geometries of the A″ states. The geometries of the A″ states are characterized by a relatively small bond angle at the carbene center (106°−109° for X = H, F and 113°−116° for X = Cl, Br). This suggests a "local" σ^2-electronic configuration or, in other words, a "local" closed-shell configuration state for the carbene subunit.[10] The C−N bond length (1.274−1.275 Å) of the singlet A″ states is essentially the same as that computed for the $^1A_2$ phenylnitrene, and by analogy, the nitrene in **2-XN**, X = H, F, Cl, Br, may be thought of as having a "local" open-shell singlet ($\sigma^1\pi^1$) configuration, with its π-electron delocalized in the benzene ring.[11] Overall the geometries are compatible with the approximate valence bond depic-

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(5) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(6) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

(7) (a) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528. (b) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788. (c) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem.* Soc. **1994**, *116*, 9381.

(8) (a) Tomioka, H.; Komatsu, K.; Nakayama, T.; Shimizu, M. *Chem. Lett.* **1993**, 1291. (b) Nicolaides, A.; Tomioka, H.; Murata, S. *J. Am. Chem. Soc.* **1998**, *120*, 11530. (c) Nicolaides, A.; Enyo, T.; Miura, D.; Tomioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 2628.

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

(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.; Borden, W. T.; Hamilton, T. P., Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030. (d) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787.

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

tions of Scheme 2. The singlet and triplet A′ states are *o*-quinoidal biradicals, which are expected to have a low T−S splitting due to the rather large distance (~3 Å) between the radical centers. The quintet state is approximated as the high-spin coupling of a triplet nitrene and a triplet carbene, whereas the A″ states contain a closed-shell singlet carbene and a $\sigma^1\pi^1$ nitrene, with the multiplicity of the latter determining the multiplicity of the whole molecule.

The differences in the energies of the *E*- and *Z*-isomers are about 2 kcal/mol or less, with the exception of the A′ singlets where it can become up to 4 kcal/mol (Table S1). Interestingly, it is the *Z*-isomer that seems to be preferred energetically. In all cases the singlet biradical (S_1) is predicted to be the ground state with T_1 lying a couple of kilocalories per mole higher in energy in formal violation of Hund's rule but as expected from spin-polarization arguments.[12,13] The quintet states lie about 26−27 kcal/mol above the ground states, although in the case of the parent compound (**2-HN**) this gap is somewhat lower (23 kcal/mol). In a qualitative sense, the Q−S splitting can be attributed to the extra π-bond present in the ground state.[14]

The energy difference between the two A″ states is around 16−17 kcal/mol and close to the ΔE_{S-T} of phenylnitrene (18 kcal/mol).[15] This is what is expected according to Scheme 2 where the singlet and triplet A″ states of **2-XN** differ in the "local" configuration of the nitrene center (singlet or triplet, respectively).

Despite some variations, the relative energies of states belonging to the same symmetry are not affected significantly by the halogen substitution. But, halogen substitution seems to have an important effect on the relative energies of the A″ states with respect to the A′ ones. This can be understood in terms of Scheme 2, which suggests that the carbene has a $\sigma^1\pi^1$ configuration in the A′ states but σ^2 in the A″ ones. Halogen substitution is known to stabilize the singlet state of carbenes (relative to the triplet).[16] Thus, the valence bond depictions of Scheme 2 predict that the halogen should stabilize selectively the A″ states.

Considering the quintet and the A″ triplet states, their energy difference $\Delta E(Q - T_2)$ can be approximated with the difference between the triplet state of the carbene subunit and its closed-shell singlet, which in turn should be equal to the T−S splitting of the corresponding phenylcarbene. A linear relationship is found between $\Delta E(Q - T_2)$ of **2-XN** and $\Delta E(T - S)$ of PhCX.[17] Since the $Q{-}S_1$ splitting of **2-XN** remains roughly constant throughout the examined series, a linear relationship between the $T_2{-}S_1$ splitting of **2-XN** and the T−S splitting of PhCX is also found (Figure 1). At the CASPT2 level, the linear best fit has a slope of −0.78, an intercept of 29.2 kcal/mol, and a squared regression coefficient of 0.9984.[18] This in turn implies that if the "intrinsic" preference of the carbene subunit for a σ^2 "local" configuration is more than 37 kcal/mol (33 kcal/mol at the MCSCF level of theory) then the carbenonitrene would have a triplet (A″) ground state.[19] Thus, the expected halogen effect on the relative energies of the A″ states is fulfilled, and it is strongest for the fluorine.

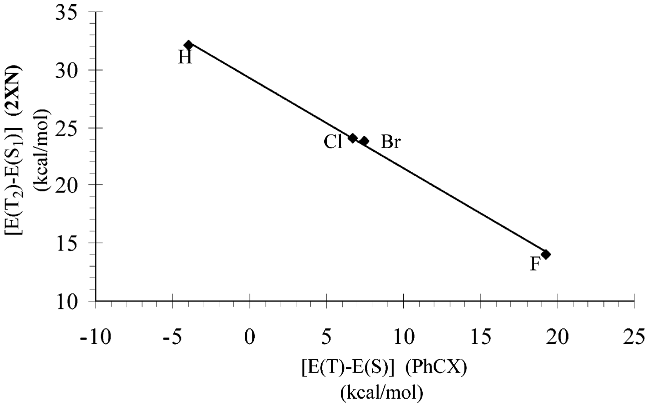

FIGURE 1. Least-squares fit between the $^3A''{-}^1A'$ splitting of **2-XN** and that of PhCX at the CASPT2 level of theory.

The above results are comparable to those obtained for the para isomers of **2-XN**, X = H, F, Cl, Br. Thus, the para isomers were also found to be singlet biradical ground states, with small $T_1{-}S_1$ gaps and a $Q{-}S_1$ splitting of about 29 kcal/mol. The A″ states of the para isomers are also stabilized with respect to the A′ ones, but the crossover point between S_1 and T_2 was predicted to happen when the T−S splitting of the carbene subunit is ~30 kcal/mol, which is 3−7 kcal/mol smaller than that in the case of **2-XN**. These similarities between ortho and para isomers are compatible with the notion that the conjugative nature of the two topologies gives rise to similar, but not identical, electronic effects.

(b) Photolysis Study. Photolysis of 1-XN. We have reported previously the generation and observation of **2-HN**[9] under matrix isolation conditions as well as that of *p*-phenylenecarbenonitrene and its halogen derivatives.[8c] It seemed reasonable to follow similar procedures for the matrix isolation of carbenonitrenes **2-XN**, X = F, Cl, Br.

3-Chloro- (**1-ClN**) and 3-bromo-3-(2-azidomethylphenyl)diazirines (**1-BrN**), potential precursors of **2-ClN** and **2-BrN**, respectively, were prepared according to the procedures outlined in Scheme 3. The fluoro derivative (**1-FN**) was prepared by substitution reaction of the corresponding bromo derivative **1-BrN** with tetrabutylammonium fluoride. All the diazirines were rather stable and could be purified by silica gel chromatography.

The diazirines thus obtained were deposited in an Ar matrix at 20 K and irradiated (λ > 350 nm) at 13 K. IR

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[12] Hund, F. *Z. Phys.* **1928**, *51*, 759.

[13] 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. *Acc. Chem. Res.* **1994**, *27*, 109.

[14] The weakness of this π-bond is presumably due to the loss of the aromaticity of the benzene ring in the ground states.

[15] As measured by photoelectron spectroscopy. (a) Travers, M. J.; Cowles, D. D.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 1699. (b) McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 10857.

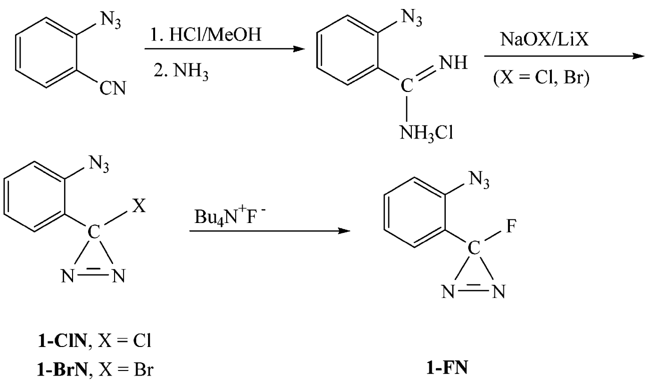
[16] Mueller, P. M.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049.

[17] The best linear fit has a slope of 0.97 (1.00), an intercept of −4.4 kcal/mol (−3.0 kcal/mol), and a squared-regression coefficient of 0.9965 at the CASPT2 (MCSCF) level of theory.

[18] At the MCSCF level, the values are −0.90, 29.6 kcal/mol, and 0.9968, respectively.

[19] This can be realized with a substituent that is a stronger π-donor than F, as for example with an amino or even perhaps with a hydroxy one. Feller, D.; Borden, W. T.; Davidson, E. R. *Chem. Phys. Lett.* **1980**, *71*, 22.

SCHEME 3



monitoring of the irradiation of chlorodiazirine **1-ClN** indicated that the peaks due to the azide and diazirine groups appeared to diminish simultaneously in intensity as new absorption bands were observed. After irradiation for 375 min, almost all the bands due to **1-ClN** were converted to product peaks. Some of the product bands changed upon subsequent irradiation, suggesting that at least two species (A and B) were formed (Figures 2a and S2b). Neither of the observed peaks assigned to the photoproducts A and B coincided with what was calculated for either isomer (*Z* or *E*) of carbenonitrene **2-ClN** (Figure 2d). Instead, an excellent match of the experimental vibrational frequencies observed for A with the computed ones for benzo(aza)cyclobutadiene **3-ClN** (Figure 2b) was found. On the other hand, the presence of a rather strong band at 2231 cm^{-1} of B indicated the presence of a nitrile group. Actually, the vibrational frequencies calculated for *Z*,*Z*-cyano-hexadienyne **4-ClN** (Figure 2c) are in good agreement with the observed ones for B.[20] Support for this assignment is lent by the observation that further irradiation of the product mixture with a shorter wavelength light (λ > 300 nm) resulted in change of the bands due to B to new absorption bands at 2220 and 2205 cm^{-1}, while the bands due to A (**3-ClN**) changed very little. The calculations suggest that this is due to a *Z* to *E* isomerization of the cyano substituent in B (*Z*,*Z*-**4-ClN** to *E*,*Z*-**4-ClN**) (Figure S2). All attempts to detect bands ascribable to carbenonitrene **2-ClN** by changing the wavelength of irradiating light and/or irradiation times were unsuccessful.

When the photolysis was monitored by UV/vis spectroscopy, a broad absorption band with apparent maximum at 278 nm appeared as the original band of **1-ClN** was depleted upon irradiation (λ > 350 nm) (Figure 2e). The new band stopped growing after 430 min of irradiation but started to disappear to form stronger bands with maxima at 268 and 279 nm when the irradiation was carried out with shorter wavelength light (λ > 300 nm) (Figure 2f). In combination with the IR data, the initially observed band with maximum at 278 nm is assigned to *Z*,*Z*-**4-ClN**, while the bands formed from the initial photoproduct are attributed to the corresponding *E*,*Z*-isomer. Absorption bands ascribable to benzo(aza)chlorocyclobutadiene (**3-ClN**) could not be observed under these conditions. It may be that these bands are very weak compared to those of polyenynes.

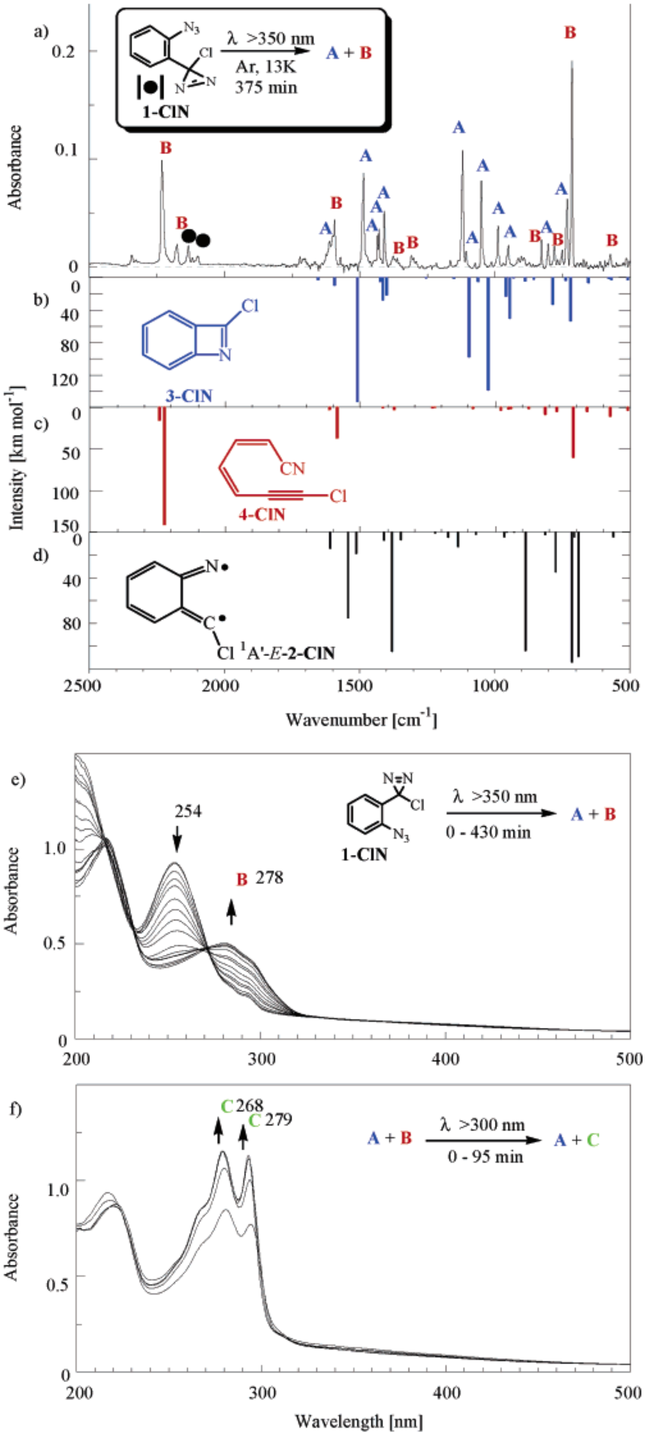


FIGURE 2. Photolysis of **1-ClN** in an Ar matrix at 13 K. (a) Total IR spectrum obtained after 375 min of irradiation (λ > 350 nm) of **1-ClN**. Calculated (B3LYP/6-31G(d)) spectra of (b) benzo(aza)chlorocyclobutadiene (**3-ClN**), (c) *Z*,*Z*-cyanohexadienyne **4-ClN**, and (d) singlet quinoidal diradical (^{1}A′-*E*-**2-ClN**). (e) UV spectrum obtained by irradiating **1-ClN** from 0 to 430 min at λ > 350 nm. (f) UV spectrum obtained by additional irradiation for 95 min at λ > 300 nm.

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[20] There is an apparent conflict between the observed peaks at 2231 and 716 cm^{-1} of **4-ClN** and the intensities of the corresponding computed peaks (at 2224 and 713 cm^{-1}, respectively). However, as mentioned later in the text, computed intensities relate to the area of the absorbance peaks rather than to their height. The line width of the observed peak at 2231 cm^{-1} is visibly larger than that of the 716 cm^{-1} peak. Indeed, the ratio of the areas of the two peaks is about 1.4, which compares favorably to the 3:1 ratio of corresponding computed intensities.

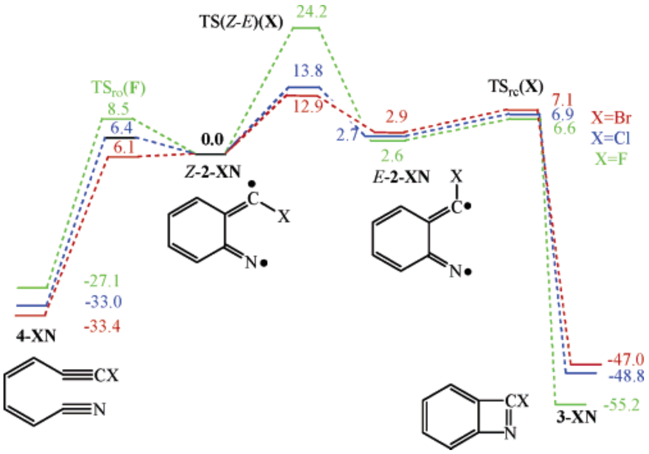

FIGURE 3. B3LYP/6-31G(d) relative energies (kcal/mol) for the ring-closure and ring-opening reactions of **2-XN**. X = F (green), X = Cl (blue), and X = Br (red).

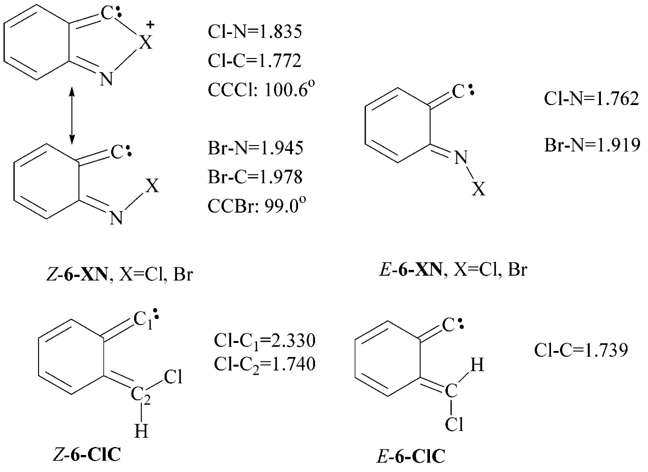

FIGURE 4. Selected bond lengths (Å) and bond angles (deg) for compounds **6** computed at the B3LYP/6-31G(d) level of theory.

Irradiation of 3-fluoro- (**1-FN**) and 3-bromo-3-(2-azidomethylphenyl)diazirine (**1-BrN**) under similar conditions gave essentially the same results, as indicated in Figures S3 and S4, respectively. Thus, photolysis ($\lambda >$ 350 nm) of **1-XN** (X = F, Br) in Ar at 13 K resulted in the formation of two products, which are assigned to benzo(aza)cyclobutadiene **3-XN** (X = F, Br) (Figures S3b and S4b, respectively) and cyanohexadienyne **4-XN** (X = F, Br) (Figures S3c and S4d, respectively) by comparing the observed IR spectra with the computed ones. Upon further irradiation with shorter wavelength light ($\lambda >$ 300 nm), *Z* to *E* isomerization of the cyano substituent in **4-XN** (X = F, Br) was again observed (Figure S5). In neither case were any absorption bands ascribable to carbenonitrenes **2-XN** (X = F, Br) detected.

The agreement between the experimental and the computed data is less good for **3-BrN** (compare Figures S4a with S4b and S4d) than for **3-FN** (compare Figures S3a with S3b and S3c) and **3-ClN** (compare Figure 3a with 3b and 3c). Thus, in the 1400–1600 cm^{-1} area, calculations predict (Figure S4b) a strong absorption at 1498 cm^{-1} (150 km/mol), with weak absorptions at 1403 (31 km/mol) and 1416 cm^{-1} (23 km/mol) for **3-BrN**.[21] In contrast, the experimental spectrum shows five absorptions at 1600, 1476, 1432, 1427, and 1405 cm^{-1} (Figure S4a) of strong and medium intensity and a weaker one at 1445 cm^{-1}. This could indicate some deficiency of the computational method, but in such a case it is not clear why the same methodology was successful in the study of the halogenated *p*-isomers of **2-XN**.[8c] An alternative explanation is that peaks identified as "A" in Figure S4a belong to two distinct components, even though these peaks appear to grow with the same rate during the experiment. Of the several structures screened computationally,[22] the presence of *Z*-**6-BrN** (Figure 5) increases the match between experimental and computational data (Figure S4c) and seems as a possible candidate for some of the peaks "A" of Figure S4a. According to this hypothesis, the observed peaks at 1476 cm^{-1} and the partially overlapping ones at 1432 and 1427 cm^{-1} are likely to belong to **3-BrN**, but the ones at 1600, 1445, and 1405 cm^{-1} are likely to belong to *Z*-**6-BrN**. A more detailed discussion of *Z*-**6-BrN** is given in a later section.

(c) Reactivities of 1-XN. Although the halocarbenonitrenes (**2-XN**, X = F, Cl, Br) themselves were not observed, the detected photoproducts are compatible with their formation in these experiments. The successful observation of the *p*-isomers of **2-XN**, X = F, Cl, Br,[8c] and of the parent **2-HN**[9] also lends support to the hypothesis that halocarbenonitrenes **2-XN** are intermediates in the above-described photochemical processes.

However, the overall observed reactivity pattern for the halogenated azo-precursors (**1-XN**, X = F, Cl, Br) differs from that of the parent **1-HN**. In the halogen-substituted cases, the formation of both ring-opened and ring-closed products is observed, whereas for the parent system, only ring-opened products were formed. Previous computations[9] on the potential energy surface of **2-HN** have found that the ring-closed product **3-HN** is formed from the *E*-isomer of **2-HN** and requires a barrier of 6.8 kcal/mol. On the other hand, the ring-opened one (**4-HN**) is formed from the *Z*-isomer of **2-HN** requiring a lower barrier (3.3 kcal/mol). Since the barrier for the *E* to *Z* isomerization of **2-HN** (3.5 kcal/mol) is lower than that for the ring-closing reaction, it is expected that the *E*-isomer will preferentially give its *Z*-isomer, which will eventually lead to the ring-opened product **4-HN**. Thus, at low temperature, the exclusive formation of **4-HN** is expected in agreement with the experimental results.

In the cases of the halogen derivatives **2-XN**, X = F, Cl, Br, the barrier for the *E*–*Z* isomerization of the halocarbenonitrenes is higher than the barrier for either the ring-opening or ring-closing reaction (Figure 3, Table S2). Thus, for **2-FN**, the barrier for the *E*–*Z* isomerization is 17.6 and 15.7 kcal/mol higher than the barriers

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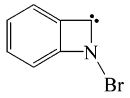
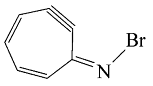
(21) Although three more absorptions at 1427, 1591, and 1656 cm^{-1} are also predicted, these are very weak (7, 7, and 2 km/mol, respectively) and not likely to be observable under our experimental conditions.

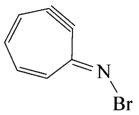
(22) Apart from *Z*- and *E*-**6-BrN** the following aminocarbene and two cycloalkynes were screened computationally, but it is unlikely that they were formed.



7-BrN



Z-**5-BrN**



E-**5-BrN**

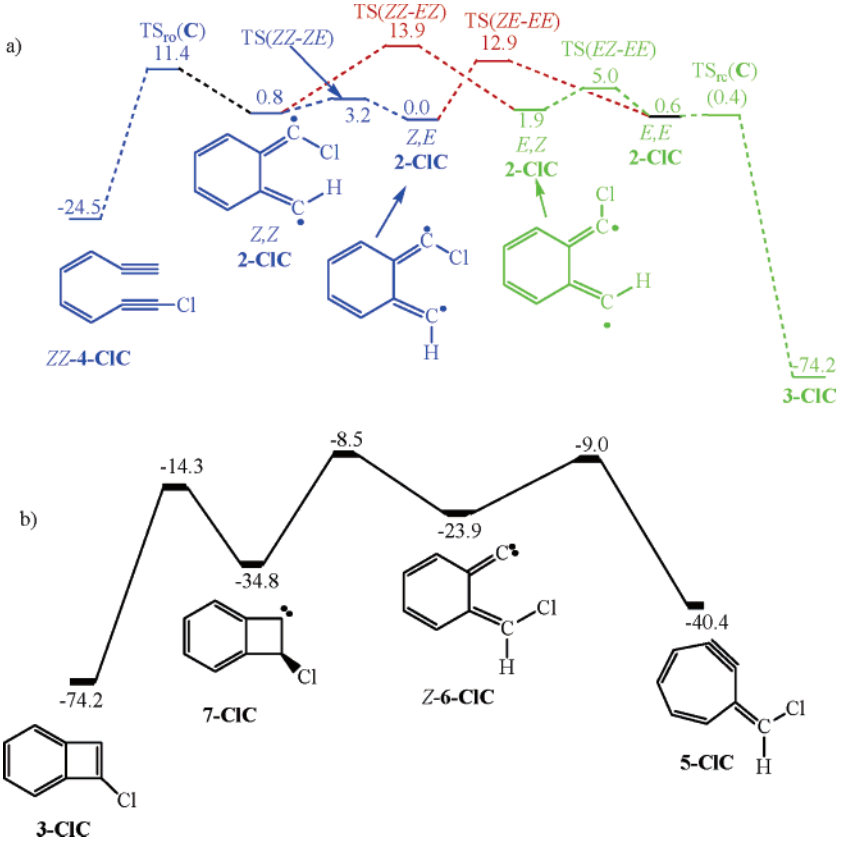


FIGURE 5. B3LYP/6-31G(d) energies (kcal/mol) relative to *Z*,*E*-**2-ClC** for (a) the ring-closure and ring-opening reactions of **2-ClC** and for (b) isomerization pathways of *Z*-**6-ClC**.

for the formation of **3-FN** (from *E*-**2-FN**) and **4-FN** (from *Z*-**2-FN**), respectively. At low temperatures, no equilibration between *E*- and *Z*-isomers is expected, even though their energies are quite similar (within 3−4 kcal/mol, Table S1). The *E*-isomer is calculated to give the ring-closed product (**3-XN**), and *Z*-isomer the ring-opened one (**4-XN**) in qualitative agreement with the experimental data that a mixture is formed.

Although a mixture of ring-closed and ring-opened products is observed, the experimental data seem to suggest that their ratio is not the same for the three halogens. In Figure S3a, the peak observed at 2316 cm^{-1} is assigned to the C−C(F) triple-bond stretch (computed at 2335 cm^{-1}), and if the computed intensities are realistic then this should be the dominant peak if the mixture of ring-closed and ring-opened products was equimolar. Instead, the 1594 cm^{-1} is the dominant one, which, according to calculations, should be the second most intense peak for **3-FN** and is assigned to the C═N stretch. It follows that the ratio [**3-FN**]/[**4-FN**] is higher than unity.[23]

The objection may be raised that the computed intensities are far from perfect and that they are not directly related to absorbances but rather to intensities, that is, to the area of the IR peaks.[24] Since the shape of peaks of different vibrations may not be the same, a direct relation between computed intensities and observed spectra is not possible. However, a second piece of evidence, involving the C═N stretch of **3-XN** and the nitrile stretch of **4-XN**, suggests that the previous analysis may be qualitatively correct, and this comes by comparing Figure S3a with Figures 3a and S4a. The C═N stretches of the ring-closed products **3-FN**, **3-ClN**, and **3-BrN** appear (are computed) at 1593 (1589), 1486 (1509), and 1476 (1498) cm^{-1}, respectively. The computed intensities for these stretches are 158, 153, and 150 km/mol, respectively, strongly suggesting that they are essentially independent of the nature of the halogen. In the case of the ring-opened products, the CN group is far enough from the halogen that its influence on the frequency and intensity of the CN stretch should not be significant. Indeed, the nitrile stretch for **4-ClN** and **4-BrN** is observed (computed) at 2231 (2245) and 2227 (2245) cm^{-1}, respectively. The computed intensities for these two stretches are 15 and 11 km/mol, respectively. For **4-FN** this stretch was not detected but it is computed to be at 2242 cm^{-1} and have an intensity of 12 km/mol.[25] Assuming that the shapes of the peak for the nitrile stretch and of the C═N double bond stretch are independent of the nature of the

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[23] The UV/vis spectra also provide some evidence for this, since the band due to the initial photoproduct was notably weaker in the photolysis of **1-FN** as opposed to that in photolysis of **1-ClN** and **1-BrN**.

[24] (a) Pugh, L. A.; Narahari Rao, K. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic Press: New York, 1976; Vol. II, pp 165−227. (b) For an interesting case of comparing computed and experimental IR spectra, see: Friderichsen, A. V.; Radziszewski, J. G.; Nimlos, M. R.; Winter, P. R.; Dayton, D. C.; David, D. E.; Ellison, G. B. *J. Am. Chem. Soc.* **2001**, *123*, 1977.

[25] The computed frequencies (intensities) for the nitrile stretch are for the *s*-cis isomers, which are nonplanar. For the planar *s*-trans isomers, the predictions are 2242 cm^{-1} (41 km/mol), 2242 cm^{-1} (23 km/mol), and 2242 cm^{-1} (32 km/mol) for **4-FN**, **4-ClN**, and **4-BrN**, respectively.

halogen, the observed relative absorbances of the nitrile versus C=N stretch can be used as a (qualitative) measure for the relative ratios of **3-XN** versus **4-XN**. Thus, the fact that the CN triple bond stretch of **4-FN** was not detected provides the second piece of evidence that, in the case of F, the ratio [**3-XN**]/[**4-XN**] is higher than that in the cases of Cl and Br.

Although the computational results agree with the experimental results that a mixture of **3-XN** and **4-XN** should be obtained, the above analysis suggests that the actual photochemistry may be more complicated than what Figure 3 implies.[26] According to Figure 3, if there is no equilibration between *E*- and *Z*-isomers, then the former should give exclusively **3-XN** and the latter **4-XN**, making the [**3-XN**]/[**4-XN**] ratio equal to the ratio [*E*-**2-XN**]/[*Z*-**2-XN**]. One possible explanation for the observed results is that, in the case of X = F, formation of the *E*-isomer is for some reason relatively preferred, even though it is energetically less stable than its *Z* counterpart. While this is attractive, it shifts the problem to explaining why the nature of the halogen affects the *E*/*Z* ratio of **2-XN**. Another possibility is that *E*- and *Z*-isomers are in a photoequilibrium and that in the case of X = F the *Z* to *E* isomerization is relatively more efficient than the *E* to *Z* one, compared to the cases of X = Cl and Br. Finally, it is of interest to note that **3-FN** is 28 kcal/mol more stable than **4-FN**, while in the cases of X = Cl and Br **3-XN** is only 15−16 kcal/mol more stable than **4-XN**. Thus, phenomenologically the higher [**3-XN**]/[**4-XN**] ratio in the case of X = F correlates with a relatively higher stability of **3-FN** compared to **4-FN**. Whatever the case may be, the reason for the dependence of the [**3-XN**]/[**4-XN**] ratio on the nature of the halogen remains currently unresolved.

(d) Other Intermediates. As mentioned above, the formation of *Z*-**6-BrN** during the photolysis of **1-BrN**, although not definitive, seems possible. Careful analysis of the IR spectrum of the photoproduct from **1-ClN** (Figure 3a) failed to reveal any detectable amounts of *Z*-**6-ClN**. This is compatible with the finding that *Z*-**6-BrN** lies 2.7 kcal/mol lower in energy than the *Z*-isomer of ^{1}A′-**2-BrN**, but *Z*-**6-ClN** lies 4.7 kcal/mol higher in energy than its isomer *Z*-^{1}A′-**2-ClN**.

Species *Z*-**6-XN**, X = Cl, Br, are closed shell, unlike **2-XN**, X = Cl, Br. Their geometric isomers, *E*-**6-XN**, may be thought of as quinoidal imine vinylidene compounds. However, these are significantly less stable than their *Z* counterparts by 19.7 and 23.0 kcal/mol for X = Cl, Br, respectively. Comparison of the geometrical parameters between *E*- and *Z*-isomers of **6-XN**, X = Cl, Br (Figure 4)- and of the computed charges of their halogens[27] suggests that the *Z*-**6-XN**, X = Cl, Br, may be thought of as cyclic internal ylides[29] that result from the internal trapping of the nitrenocarbene diradical. In contrast, *Z*-**6-ClC** (vide infra) is better viewed as a vinylidene.

The *Z*-**6-XN**, X = Cl, Br, isomers are intriguing since they are formally derived from their ^{1}A′-**2-XN** isomers by a geometric distortion of the CCX bond angle. On the other hand, their charge distributions are quite different, and they should be described by different wave functions. This isomerization can be visualized as a transfer of a Br atom from the carbene center to the nitrene. This bond-breaking bond-forming process would leave behind an excited vinylidene (with the two unpaired electrons occupying different orbitals), which after electronic reorganization would have the electronic distribution of *Z*-**6-BrN**. We speculate that this transformation involves a conical intersection, but due to the size of the active space involved we have not been able to locate it. Thus, it is not surprising that our DFT efforts to find the transition structure connecting ^{1}A′-**2-XN** with **6-XN**, X = Cl, Br, have also not been successful.[30]

Biscarbene 2-ClC. (a) Computational Considerations. The presence of two carbene subunits gives rise to four different isomers: *EE*, *EZ*, *ZE*, and *ZZ*. Their relative energies and computed geometries appear in Tables S3 and S4. Much of the geometrical characteristics and relative energetics discussed above for the carbenonitrenes **2-XN** are applicable in this case as well (Scheme 2, Z = CH). The four different isomers of **2-ClC** exhibit quite similar geometries. Thus for a given state the bond lengths differ in general by 0.01 Å or less among the four isomers. An exception is the C5−C6 bond length of the S_1 state, which varies by 0.04 Å, with *EE*-isomer having the shortest and *ZZ*-isomer the longest. B3LYP and MCSCF predict similar geometries with the exception of the S_1 state of *EE*-**2-ClC**, which does not exist at the MCSCF level, because it ring-closes “spontaneously” to benzochlorocyclobutadiene (**3-ClC**).

The ground state (S_1) is a singlet biradical, with the *Z*,*E* conformer preferred by the three levels of theory. The Q−S_1 splitting is about 22−23 kcal/mol (i.e., around 5 kcal/mol lower than that of carbenonitrenes **2-XN**). The energy difference between singlet and triplet A″ states is ∼18 kcal/mol, similar to that between open-shell singlet and triplet phenylcarbene (22 kcal/mol).[31,32] The halogen substituent stabilizes both A″ states, resulting in the T_2 state being about 18 kcal/mol above the ground

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(26) The reported calculations refer to thermal reactions, which are unlikely to be taking place under our experimental conditions. It is more likely that the diradicals **2-XN** are extremely photochemically reactive and once formed are rapidly converted to the observed products. Alternatively, excited states of the precursors **1-XN** or intermediates resulting from the loss of one nitrogen molecule (e.g., nitrenediazirines) could give rise to the observed products by simultaneous loss of nitrogen. While these more likely processes may give product ratios that reflect the ground-state proclivities of the diradicals, this can neither be proved nor disproved by the current data.

(27) The computed charges for the halogens are relatively more positive for the *Z* isomer than that for the *E*. The computed charges for the Br in *Z*-^{1}A′-**2-BrN**, *E*-**6-BrN**, *Z*-**6-BrN** based on the atomic polar tensor [28] (Mulliken population analysis) are: −0.19 (0.04), −0.25 (0.01), and −0.04 (0.30), respectively. For the Cl in *Z*-^{1}A′-**2-ClN**, *E*-**6-ClN**, *Z*-**6-ClN** these are: −0.26 (0.14), −0.32 (0.06), and 0.00 (0.43), respectively.

(28) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8336.

(29) The ylide of a very electrophilic carbene (tetrakis(trifluoromethyl)-cyclopentadienylidene) with *p*-bromotoluene has been synthesized and characterized by ^{19}F NMR. Janulis, E. P., Jr.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1983**, *105*, 3563.

(30) The biradical is described by a spin-broken symmetry wave function while *Z*-**6-XN** is a closed-shell singlet. Attempts to locate the transition state were unsuccessful, as the calculation seemed to wander from the open-shell surface to the closed one. Apparently an MCSCF treatment is required, and it is quite possible that a conical intersection connects the two singlet surfaces. However, this also may not be enough since the vibrational mode connecting the two isomers may need to be taken into account at the same time. Whatever the case, this is beyond the scope of the current work.

(31) Nicolaides, A. *Mol. Phys.* **2004**, *103*, 1047.

(32) The lowest singlet of phenylcarbene is of the σ^2 (closed-shell) type in contrast to phenylnitrene, which is of the $\sigma^1\pi^1$ type. Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

state, which is approximately 8 kcal/mol lower in energy than the corresponding stabilization in **2-XN**.[33]

The computations suggest that *E*,*Z*-interconversion between the various geometrical isomers of **2-ClC** is energetically more facile by 8−10 kcal/mol when the process involves the linearization of the methylene (=CH) subunit than the chloromethylene (C=CCl). The barriers for the *E*,*Z*-isomerization when chloromethylene is involved (TS(*ZZ*-*EZ*) and TS(*ZE*-*EE*) of Figure 5a) are higher than those for the isomerization involving the methylene subunit (TS(*ZZ*-*ZE*) and TS(*EZ*-*EE*)) and also for those required for the ring-opening and ring-closing reactions. Thus, under low-temperature conditions, *E*,*Z*- and *E*,*E*-isomers are not expected to equilibrate thermally with the *Z*,*Z* and *Z*,*E* pair because these isomerizations are possible only through TS(*ZZ*-*EZ*) and TS(*ZE*-*EE*), which lie higher in energy than either TS_{ro}(**C**) or TS_{rc}(**C**). The *E*,*E*-isomer is expected to form benzochlorocyclobutadiene (**3-ClC**) essentially without a barrier,[34] and the same product is expected from the *E*,*Z*-isomer (Figure 5). On the other hand, the *Z*,*Z*-isomer is more likely to ring-open to **4-ClC** rather than to ring-close to **3-ClC** via prior isomerization to *Z*,*E*-**2-ClC**. Again a mixture of ring-opened and ring-closure products is predicted and, although the formation of **3-ClC** may be preferred, significant presence of **4-ClC** is also expected.[35]

Vinylidene *Z*-**6-ClC** was also computed (Figures 4 and 5b) in light of the potential presence of *Z*-**6-BrN** in the photolysis of **1-BrN** (vide supra). Interestingly, *Z*-**6-ClC** is found to be much more stable than *Z*,*E*-**2-ClC** (by almost 24 kcal/mol).[36] The C−Cl bond lengths of *Z*-**6-ClC** and *E*-**6-ClC** are virtually the same (Figure 4), while the Cl center of the former is 2.33 Å away from the vinylidene carbon which is a quite different situation from *Z*-**6-ClN** and *Z*-**6-BrN**. Also, *Z*-**6-ClC** is more stable than its *E*-isomer by 6.3 kcal/mol, which is only one-fourth of the stabilization of *Z*-**6-BrN** versus *E*-**6-BrN**. Thus, it is reasonable to describe *Z*-**6-ClC** as a vinylidene. A similar vinylidene (**6-HC**) has been postulated previously as an intermediate in the isomerization of benzocyclobutenylidene (**7-HC**) to methylenecycloheptadienyne **5-HC** (Figure 6).[37]

Attempts to observe benzocyclobutenylidene (**7-HC**) using matrix isolation spectroscopy[37] led instead to the observation of **5-HC** (Figure 6). Calculations suggested that vinylidene **6-HC** lies on the isomerization path from **7-HC** to **5-HC**, but it lies in a shallow potential energy well (Figure 6). Thus, vinylidene **6-HC** is separated by a computed barrier of 7.2 kcal/mol from cycloalkyne **5-HC**, but by a very small barrier (0.6 kcal/mol) from carbene **7-HC**. In contrast, *Z*-**6-ClC** lies in a rather deep potential energy well (Figure 5b). It is separated by a barrier of 14.9 kcal/mol from cycloalkyne **5-ClC** and by 15.4 kcal/mol from benzochlorocyclobutenylidene **7-ClC** and benzochlorocyclobutadiene **3-ClC**, with the latter appearing to be the thermodynamic sink on this potential energy surface. It is noteworthy that these transition structures lie lower in energy than the biscarbene (**2-ClC**) itself.

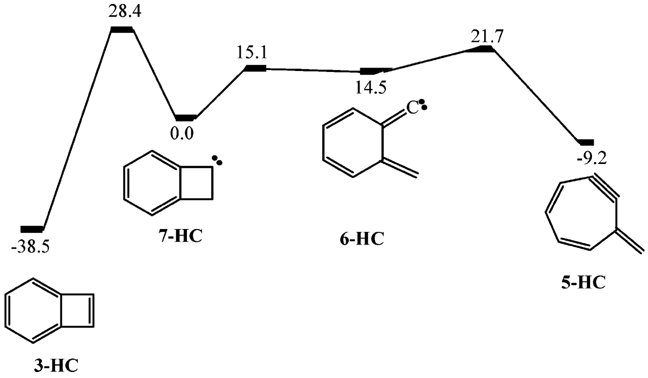
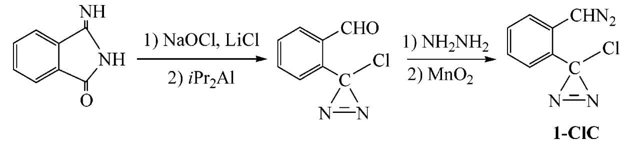


FIGURE 6. G2(MP2,SVP) relative energies (kcal/mol) for isomerization pathways of **6-HC**.[37]

SCHEME 4



(b) Photolysis Study. Photolysis of 3-Chloro-3-(2-diazomethylphenyl)diazirine (1-ClC). Desired precursor of **2-ClC**, diazo-diazirine **1-ClC**, was obtained by rapid oxidation of the corresponding hydrazone by MnO_2 at low temperature (Scheme 4). Compound **1-ClC** was very unstable and hence was deposited in an Ar matrix immediately after preparation without further purification.

Irradiation ($\lambda > 350$ nm) of **1-ClC** in the Ar matrix at 10 K resulted in a clean disappearance of the bands due to the starting diazo-diazirine to give rather weak peaks (Figure 7a). The observed peaks seem to correspond to a mixture of products, but once more we do not find evidence for the observation of the postulated intermediate carbeno(chlorocarbene) **2-ClC** (Figure 7e).

Several of the peaks marked “A” in Figure 7a can be easily assigned to benzochlorocyclobutadiene **3-ClC** based on the computed data (Figure 7b). However, the rest of the major peaks “A” appear to be due to the co-presence of cycloalkyne **5-ClC**, by comparison with the computed values (Supporting Information). In particular, the observation of a weak signal at 2138 cm^{-1} (computed at ~2149 cm^{-1}) compares favorably to the C−C triple bond stretch of **5-HC** that was observed at 2098 cm^{-1} and provides strong support for the presence of **5-ClC**.[37] With the help of computations the observed peaks at 1600, 1513, 1459, 757, and 741 cm^{-1} are also assigned to **5-ClC**.

The very weak peak at 2236 cm^{-1} (peak “B” of Figure 7a) is attributed to the C−C(Cl) triple bond of the ring-opening product **4-ClC** as suggested by the computed data (Figure 7d). The presence of **4-ClC** is further

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[33] A linear relationship between the T_2-S_1 splitting of **2-XC**, X = H, F, Cl, Br, on one hand and the ΔE(S − T) of phenylcarbene has been found.[31] This correlation is similar to that for **2-XN**.

[34] The energy of the transition structure connecting *E*,*E*-**2-ClC** with **3-ClC** is 0.1 kcal/mol higher than that of *E*,*E*-**2-ClC**, but it becomes lower (by 0.2 kcal/mol, Figure 5a) when ZPE corrections are included. Thus, this barrier is small (if it exists at all) and is in agreement with the MCSCF result of “spontaneous” ring closing to **3-ClC**.

[35] Ignoring the small energy differences between the four isomers and assuming that all are formed in equal amounts, the data in Figure 5 suggest that more than 25% of the (**3-ClC** and **4-ClC**) mixture should be **4-ClC**.

[36] For reasons analogous to the ones mentioned in ref 30, attempts to locate a transition structure for the *Z*,*E*-**2-ClC** to *Z*-**6-ClC** isomerization were unsuccessful.

[37] Nicolaides, A.; Matsushita, T.; Yonezawa, K.; Shinji, S.; Tomioka, H.; Stracener, L. L.; Hodges, J. A.; McMahon, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 2870.

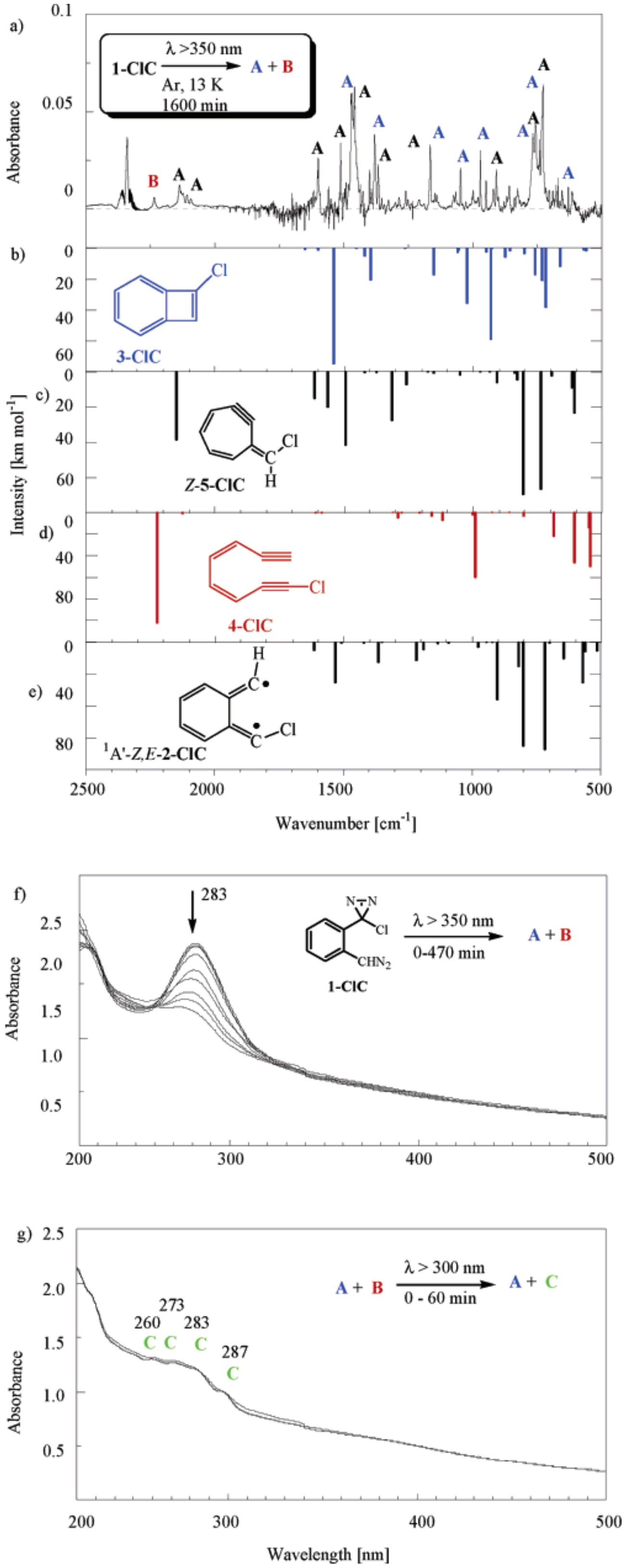

FIGURE 7. Photolysis of **1-ClC** in an Ar matrix at 13 K. (a) Total IR spectrum after 1600 min of irradiation of **1-ClC**. Calculated (B3LYP/6-31G(d)) spectra of (b) benzochlorocyclobutadiene (**3-ClC**), (c) cycloalkyne *Z*-**5-ClC**, (d) *Z*,*Z*-octadiendiyne **4-ClC**, and (e) singlet quinoidal diradical (^{1}A′-*E*,*Z*-**2-ClC**). (f) UV spectrum obtained by irradiating **1-ClC** from 0 to 470 min at λ > 350 nm. (g) UV/vis spectrum obtained by additional irradiation of the sample (f) for 60 min at λ > 300 nm.

confirmed by the observation of weak absorbances at 3413 and 3429 cm^{-1} (Figure S6), attributable to its terminal *sp*-C−H stretch. Since in the case of **4-ClN** the C−C(Cl) triple-bond stretch was clearly observed as a medium-intensity absorption (Figure 2a), the very weak C−C(Cl) bond stretch of **4-ClC** (Figure 7a) suggests that it is formed in a relatively small amount.[38]

(c) Reactivity of 1-ClC. Once more the observed mixture of ring-closed and ring-opened photoproducts is in qualitative agreement with the computational results. In this case as well, it is hard to explain why cyclobutene **3-ClC** is so much favored over dienediyne **4-ClC**. Perhaps the high [**3-ClC**]/[**4-ClC**] ratio reflects a preference for the formation of *E*,*E*- and *E*,*Z*-isomers over *Z*,*Z*- and *Z*,*E*-isomers upon photolysis of **1-ClC**, but as mentioned in the case of the carbenonitrenes, this simply shifts the question to why these isomers may be forming in significantly different ratios despite their similar energies. Another possibility is that the ring-opening of *Z*,*E*- and *Z*,*Z*-**2-ClC** (via *Z*,*Z*-**2-ClC**) can compete effectively with the ring-closing reaction (via *E*,*E*-**2-ClC**) since the energy difference between the two barriers (TS$_{ro}$(**C**) and TS(*ZE-EE*)) is computed to be only 1.5 kcal/mol, which must be less than the expected error of our calculations. However, in this case the relation of the two barriers must be such that only a small part of the *Z*,*E* and *Z*,*Z* pair of isomer forms **4-ClC** (via *Z*,*Z*-**2-ClC**) and the rest gives **3-ClC** (via *Z*,*E*- and subsequently *E*,*E*-**2-ClC**). Finally, it is also conceivable that a (photochemical) pathway exists that enhances the formation of **3-ClC** from *Z*,*Z*- or *Z*,*E*-isomers without the need of prior isomerization to *E*,*Z*- or *E*,*E*-isomers. A plausible way of this happening is shown in Figure 5b. If under our experimental conditions a (photochemical) pathway to form vinylidene *Z*-**6-ClC** from *Z*,*E*-**2-ClC** is operative,[36] then it is conceivable that *Z*,*E*-**2-ClC** (and presumably *Z*,*Z*-**2-ClC**) can “leak” to **3-ClC** without having to overcome the barrier required for linearizing the chloromethylene subunit. This is supported by the presence of methylenecycloheptadienyne **5-ClC** in our experiments. In turn, observation of **5-ClC** implies the formation of vinylidene **6-ClC**. The finding that photolysis of **1-BrN** under very similar conditions forms at least in part *Z*-**6-BrN** (vide supra) shows that it is not unreasonable to expect formation of vinylidene **6-ClC** during the photolysis of **1-ClC**.

A question that arises is why in the photolysis of **1-ClC** cycloalkyne **5-ClC** is observed, but in the case of **1-BrN** the reaction path seems to be intercepted at the *Z*-**6-BrN** stage. According to the calculations, a likely answer is that the energy of the transition state structure leading from *Z*-**6-BrN** to cycloalkyne **5-BrN** is 31 kcal/mol *higher* than the energy of the biradical ^{1}A′-*Z*-**2-BrN** (Figure S7), in contrast to the case of **1-ClC** where the corresponding transition state (TS(*Z*-**6-ClC** → **5-ClC**)) is *lower* in energy by 9 kcal/mol with respect to the corresponding diradical (Figure 5b). In addition, the transition state leading to aminocarbene **7-BrN** is also higher in energy than birad-

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[38] As pointed out by a reviewer, weak signals in the 2100 cm^{-1} area can be attributed to weak hot bands of acetylenic compounds (Klaboe, P.; Klosterjensen, E.; Bjarnov, E.; Christensen, D. H.; Nielsen, O. F. *Spectrochim. Acta* **1975**, *31A*, 931), thus making doubtful the observation of **4-ClC**. However, this would only increase the observed [**3-ClC**]/[**4-ClC**] ratio, strengthening the argument presented in the next section.

ical ^{1}A′-*Z*-**2-BrN** (by 38.5 kcal/mol). Thus, the possible isomerization pathways of *Z*-**6-BrN** require energies higher than that of its postulated precursor ^{1}A′-*Z*-**2-BrN** and are presumably not allowed. However, in the case of *Z*-**6-ClC** if its energy difference from *Z*,*E*-**2-ClC** (23.9 kcal/mol, Figure 6b) is not dissipated fast enough, it is reasonable that it isomerizes to **5-ClC** and perhaps **3-ClC** before it can be observed.

Finally, it is of interest to note that the energy difference between **3-ClC** and **4-ClC** is about 50 kcal/mol, in favor of the former, which is 10 kcal/mol larger than the energy difference between **3-FN** and **4-FN**. Thus, again the higher [**3**]/[**4**] ratio correlates with the overall thermodynamics at least in the cases where the intermediates (**2-XN** and **2-ClC**) are not observed. For the parent biscarbene (**2-HC**), the energy difference between ring-closed (**3-HC**) and ring-opened product (**4-HC**) is halfway between the two previous cases (~30 kcal/mol).[9] Thus, photolysis of **1-HC** under similar conditions and assuming that no intermediates (**2-HC**) will be observed will likely give a mixture of both **3-HC** and **4-HC**, with the former being the dominant one and the ratio [**3-HC**]/[**4-HC**] lying between the ratios [**3-FN**]/[**4-FN**] and [**3-ClC**]/[**4-ClC**]. However, if the intermediates **2-HC** can be observed and the ring-opened and ring-closed products are the result of a thermal reaction then only **3-HC** is expected to form.[9]

Conclusions

Halogen substitution in the series **2-XN**, X = H, F, Cl, Br, affects the relative energies of the excited A″ states by stabilizing them relative to the singlet (A′) quinoidal biradical ground state. This stabilization is greatest for fluorine and results in the smallest T_2-S_1 splitting among the four cases. Halogen substitution also affects the barrier and exothermicity of the ring-opening reaction (formation of **4-XN**), but its effect on the ring-closing reaction (formation of **3-XN**) is smaller. In the parent case (photolysis of **1-HN**), intermediate **2-HN** was observed by IR and the only final photoproduct was **4-HN**. In contrast, the halogenated carbenonitrenes **2-XN**, X = F, Cl, Br, were not observed and the final photoproducts were a mixture of **3-XN** and **4-XN**, in agreement with the computational results. In the case of the bromo derivative, there is evidence that small amounts of *Z*-**6-BrN** may be formed along with **3-BrN** and **4-BrN**. In the case of the fluoro derivative, the relative amount of **3-XN** seems to be favored more than in the cases of Cl and Br. This is in agreement with a "phenomenological" explanation that the stability of **3-XN** (relative to **4-XN**) is greatest for X = F, but a detailed mechanistic understanding of this is not available yet.

The photolysis of **1-ClC** is the first attempt to verify the hypothesis that *o*-phenylenebiscarbene at low temperature is more likely to cyclize to benzochlorocyclobutadiene (**3-ClC**) than to ring-open to oct-3,5-diene-1,6-diyne **4-ClC**. The major photoproducts in this case are **3-ClC** and **5-ClC**, while small amounts of **4-ClC** are likely to be formed. Again the postulated intermediate **2-ClC** was not observed. Computations show that (thermal) equilibration between the different geometrical isomers of **2-ClC** via linearization of the chloromethylene subunit requires more energy than the corresponding ring-closing or ring-opening reaction. Also, the Cl substituent changes the potential energy surface of **2-ClC** as compared to its parent **2-HC** in several ways, one of which is that vinylidene **6-ClC** is computed to lie in a reasonably deep energy well. Although this was not observed, evidence for its intermediacy is given by the observation of weak peaks near 2100 cm^{-1}, which is attributed to cycloalkyne **5-ClC**.

Overall, it should be stated that the experimental data prompted us to explore the potential energy surface of **2-XN** and **2-ClC** in mode depth. Thus, the not so good match between the computed and experimental spectra of **2-BrN** and **4-BrN** led us to investigate other possible isomers, and although further work is required to secure the presence of *Z*-**6-BrN** in these experiments, there are strong indications that it is formed under our conditions. Similarly, the great preference for the formation of **4-ClC** over **3-ClC** and in particular the formation of cycloalkyne **5-ClC** opens the possibility that vinylidene **6-ClC** may be participating in the observed photochemistry. It is intriguing that these vinylidenes may be true intermediates since a connection to the benzocyclobutenylidene potential energy surface emerges. Attempts to observe by IR matrix isolation spectroscopy benzocyclobutenylidene failed, and cycloalkyne **5-HC** was observed instead. The formation of the latter was postulated to go via vinylidene **6-HC**. Although **6-HC** may not be easy to observe because it lies in a very shallow potential energy well, vinylidene **6-ClC** should be in principle observable. And by analogy to the benzocyclobutenylidene potential energy surface, one may be able to make **6-ClC** by trying to make 2-chloro-benzocyclobutenylidene.

Computational Details

Ab initio molecular orbital calculations were carried out using the Gaussian 94 and 03,[39] GAMESS,[40] and MOLCAS[41] programs. Optimized geometries were obtained at the B3LYP/6-31G(d)[39,42] 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.[43] Open-shell singlet diradicals were calculated within the UB3LYP formalism. As expected for open-shell singlets, the UB3LYP computations correspond to about 50:50 mixtures of singlet and triplet states (as judged by the spin contamination). These open-shell singlets are the best descriptions for the lowest singlet state within the DFT formalism. Since the singlet−triplet splitting of these biradicals is small, spin contamination does not pose a serious problem for using these calculations.[44] This is also in agreement with our past experience[8b,c,9] that these levels of theory are adequate for the study of the species under consideration. Reported MCSCF and CASPT2 energies (absolute and relative) do not include ZPE corrections. In general, B3LYP and MCSCF give similar geometries and relative energies. One exception is the relative energy of the

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(39) (a) Frisch, M. J. et al. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995. (b) Frisch, M. J. et al. *Gaussian 03*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(40) Gordon, M. S. et al. *J. Comput. Chem.* **1993**, *14*, 1347.

(41) Roos, B. O. et al. *MOLCAS*, version 5.2; Lund University: Lund, Sweden 2000.

(42) (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.

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

(44) 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.

$^3A''$ states, which B3LYP overestimates by 9 kcal/mol compared to MCSCF and CASPT2 methods.

For the active space of the MCSCF wave functions, 11 molecular orbitals (MOs) and 12 electrons were used. Nine active MOs were of A″ symmetry (the three π and three π^* of the phenylene linker, one π and MO per diradical center, and the π MO of the halogen substituent) and two of A′ symmetry (one σ MO per diradical center).

Energy differences (ΔE(X − Y)) between states X and Y (X−Y splittings) are defined as E(X) − E(Y). Thus, T−S splittings with negative values correspond to triplet ground states. The T−S splittings for phenylcarbenes PhCX, X = H, F, Cl, Br, used for data of Figure 1 were taken from ref 31.

Energy differences mentioned in the text that are not immediately derivable from the tables can be obtained with little effort from the data in the Supporting Information.

Experimental Section

The following products were observed in the irradiation of 3-(2-azidophenyl)-3-halodiazirine and of 3-(2-diazomethylphenyl)-3-chlorodiazirine in argon matrix at 13 K.

2-Fluorobenzo(aza)cyclobutadiene (3-FN): IR (Ar, 13 K) ν 1673, 1620, 1594, 1438, 1411, 1390, 1283, 1258, 1057, 805, 736, 613 cm^{-1}.

1-Cyano-6-fluoro-1-*Z*,*Z*-1, 3-hexadien-5-yne (*Z*,*Z*-4-FN): IR (Ar, 13 K) ν 2316, 1200, 873, 782, 743, 716 cm^{-1}; UV (Ar, 13 K) λ_{max}278 nm.

1-Cyano-6-fluoro-1-*E*,*Z*-1, 3-hexadien-5-yne (*E*,*Z*-4-FN): IR (Ar, 13 K) ν 2321, 984, 852, 799 cm^{-1}; UV (Ar, 13 K) λ_{max}257, 267, 279 nm.

2-Chlorobenzo(aza)cyclobutadiene (3-ClN): IR (Ar, 13 K) ν 1622, 1486, 1435, 1429, 1410, 1121, 1107, 1051, 990, 950, 805, 752, 734 cm^{-1}.

1-Cyano-6-chloro-*Z*,*Z*-1,3-hexadien-5-yne (*Z*,*Z*-4-ClN): IR (Ar, 13 K) ν 2231, 2176, 1593, 1378, 1300, 1291, 828,781, 716, cm^{-1}; UV (Ar, 13 K) λ_{max} 281 nm.

1-Cyano-6-chloro-*E*,*Z*-1,3-hexadien-5-yne (*E*,*Z*-4-ClN): IR (Ar, 13 K) ν 2220, 2205, 1618, 1162, 983, 944, 838, 732 cm^{-1}; UV (Ar, 13 K) λ_{max} 268, 279, 293 nm.

1-Bromobenzo(aza)cyclobutadiene (3-BrN): IR (Ar, 13 K) ν 1476, 1432, 1101, 1071, 1041, 971, 949, 798, 749, 733, 661 cm^{-1}. Peaks at 1600, 1445, 1405, 1257, 1164, 749, 661 cm^{-1} are thought to be due to ***Z*-6-BrN**.

1-Cyano-6-bromo-*Z*,*Z*-1,3-hexadien-5-yne (*Z*,*Z*-4-BrN): IR (Ar, 13 K) ν 2227, 2206, 1593, 826, 780, 716 cm^{-1}; UV (Ar, 13 K) λ_{max} 284 nm.

Cyano-6-bromo-*E*,*Z*-1,3-hexadien-5-yne (*E*,*Z*-4-BrN): IR (Ar, 13 K) ν 2222, 2177, 1617, 1261,1161, 983, 838 cm^{-1}; UV (Ar, 13 K) λ_{max} 271, 283, 297 nm.

1-Chlorobenzocyclobutadiene (3-ClC): IR (Ar, 13 K) ν 1470 (m) 1400 (w), 1381 (m), 1161 (m), 1047 (m), 970 (m), 949 (w), 767 (m), 727 (m), 629 (w) cm^{-1}.

7-(Chloromethylene)cyclohepta-3,5-diene-1-yne (5-ClC): IR (Ar, 13 K) ν 2138 (w) 1600 (m), 1513 (m), 1459 (m), 757 (m), 741 (m).

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Supporting Information Available: Tables S1−S4, Figures S1−S7, Cartesian coordinates of optimized geometries, absolutes energies (B3LYP, MCSCF, CASPT2), vibrational frequencies and intensities, experimental details concerning preparation of compounds and measurements, and experimental data related to irradiation experiments. Complete refs 39, 40, and 41. This material is available free of charge via the Internet at http://pubs.acs.org.

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