

m-Phenylene-Linked Bis-(Biradicals). Generation, Characterization and Computational Studies

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m-Phenylene-linked biscarbenes, bisnitrenes and carbenonitrenes can be formed photochemically from appropriate nitrogenous precursors. Generation of such reactive intermediates under matrix-isolation conditions allows for their characterization by spectroscopic techniques such as ESR, UV/vis and IR. The latter method is also useful in characterizing secondary products derived from these reactive intermediates. Computational chemistry methods complement experimental IR data, aiding, thus, in identification of such compounds. In addition electronic structure calculations help in developing qualitative and semi-quantitative models, which can be useful in predicting ground-state multiplicities. The parent systems of *m*-phenylene-linked carbenes and nitrenes have high-spin ground states, but a switching to lower multiplicity can be achieved by chemical substitution. The ground state and various low-lying excited states of *m*-phenylenecarbenonitrenes can be reasonably approximated by simple valence-bond depictions. Finally, *m*-phenylenecarbenonitrenes are photoreactive in the inert matrix isomerizing to cyclopropene derivatives.

key words: 1,3-Phenylene, Carbene, Nitrene, Halocarbene, Matrix isolation, Photochemistry, IR spectroscopy, Electronic structure, Spin coupling

INTRODUCTION

One of the interesting aspects of organic molecules with unpaired electrons is the possibility that they may have high-spin ground states. Such species can serve as the basis for the construction of organic magnetic materials and much research has been carried out in this direction [1-6]. While many problems need to be solved before a high-spin molecule is translated to a magnetic material, understanding the factors that govern the spin-state preferences of organic molecules is in its own right both challenging and interesting. In a sense, it is also a prerequisite for the in depth knowledge needed to design organic magnets.

In the area of high-spin organic molecules, a conceptually useful tool is their dissection into two kinds of fragments; (a) the spin carrier (SC) and (b) the linker or coupler which connects two or more of the SC units. If the linker promotes high-spin coupling between the SCs, it is described as a ferromagnetic coupler (FC) [2].

This approach allows tackling of the problem in a stepwise manner. One part of the problem is the individual SC itself. Usual SCs are radicals or biradicals (*e.g.*, carbenes and nitrenes). These species are now fairly well understood as a consequence of information collected within the last couple of decades. On the other hand, the linking of two or more SCs gives rise to a

more complex system, whose behavior is not necessarily the simple sum of its parts. For this reason, the study of model compounds with two or more SCs continues to attract attention.

An inherent difficulty in dealing with such species is their high reactivity and fleeting existence. The development of time-resolved laser techniques makes possible the detection and characterization of reactive intermediates under ambient conditions [7-12]. Cryogenic methods offer an alternative way to study these species, with conventional spectroscopic methods, by isolating them in inert matrices [13-20]. Finally, computational chemistry [21-23] provides complementary tools in the interpretation of the collected experimental data, not only for characterizing species but also for gaining insight into their electronic structure and, thus, aiding in the development of conceptual models.

Perhaps the most popular FC for radicals and diradical is *m*-phenylene (MP). It is generally considered as a “robust” FC and has been utilized in the design of polycarbenes and polyradicals with impressively high-spin ground states. However, this is not always the case, and the purpose of this paper is to review some of the limitations of MP as a FC between two diradical centers.

DISCUSSION

Carbenes and Nitrenes

Carbenes and their isoelectronic nitrenes are neutral 1,1-

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biradicals with two, non-bonding electrons that are nominally located on the carbon or nitrogen atom, respectively [24-32]. In a simple electronic treatment, four electronic states can be envisioned resulting from the placement of two electrons in two orbitals (Figure 1). In bent carbenes, the two orbitals are of different energy, and are often denoted as σ (in-plane orbital) and π (out-of-plane orbital), with the former having a lower energy due to its higher s character. If the σ - π energy separation is large enough, then a singlet (S_1) ground state is expected. If this energy separation is small, then the order of states cannot be predicted easily. The singlet S_1 benefits from a lower orbital energy as compared to T_1 , but the latter benefits from a reduced electron repulsion since the two electrons occupy different areas of space. Presumably the second factor is more important for the parent methylene (**1**), which has a triplet ground state and a T-S gap of 9.0 kcal/mol [33-35].

Independent of the multiplicity of the ground state (T_1 or S_1), singlet S_2 , which has the same formal occupancy as T_1 , but different overall coupling, will always be higher in energy than T_1 . The reason for this has to do also with electron repulsion. The two orbitals are orthogonal by symmetry and so their overlap is zero. However, they do share some common area spatially and, thus, their exchange integral is far from zero. The electron repulsion of two electrons residing one in each orbital will depend on their relative spins. If both of them have the same spin (T_1), then their motion is better correlated than if they have opposite spins (S_2), since in the former case Pauli's principle forbids them from being present at the same time in the common area of the two orbitals.

For a linear carbene with cylindrical symmetry ($C_{\infty v}$ or $D_{\infty h}$) or for a $C_{\infty v}$ nitrene, there are two degenerate π orbitals. These are shown as π_y and π_z in Figure 1b. The π_z orbital is perpendicular to the plane of the paper and only its front lobe is shown. By symmetry π_y and π_z are degenerate in energy, so are S_1 and S_2 . Thus, on the basis of Hund's rule a triplet ground state is expected. In agreement with this description, the parent nitrene **5** has a triplet ground state and a ΔE_{ST} of 36.0 kcal mol⁻¹[36].

Phenylnitrene (**3**) [37-43] and phenylcarbene (**4**) [44-49], although more complex, can still be understood qualitatively by using the above simple picture. Both species are well studied and their similarities and differences [44,50,51], as well as some substituent effects [49,52,53] on their electronic structures, have been examined. Both **3** and **4** have triplet ground states, but while the T-S splitting of the former is approximately 18 kcal/mol, that of the latter is 4 kcal/mol. Thus, in both cases, the phenyl group stabilizes the singlet with respect to the triplet (compared to the parent compounds nitrene and methylene, respectively), but this stabilization is more significant in the case of phenylnitrene. Another difference is that the lowest singlet ($^1A'$) of **4** is closed-shell (S_1 of Figure 1a), but of **3** (1A_2 in C_{2v} symmetry or $^1A''$ in C_s) is open-shell (S_1 of Figure 1b) [40]. Perhaps it should be added that, in phenylnitrene, the lack of cylindrical symmetry lifts the degeneracy between states S_1 and S_2 (Figure 1b), and the former becomes more stable [40].

While phenylcarbene has a triplet ground state, replacement of the carbenic hydrogen by a halogen like F, Cl or Br (**5**, **6** and **7**, respectively) switches the ground-state multiplicity to a

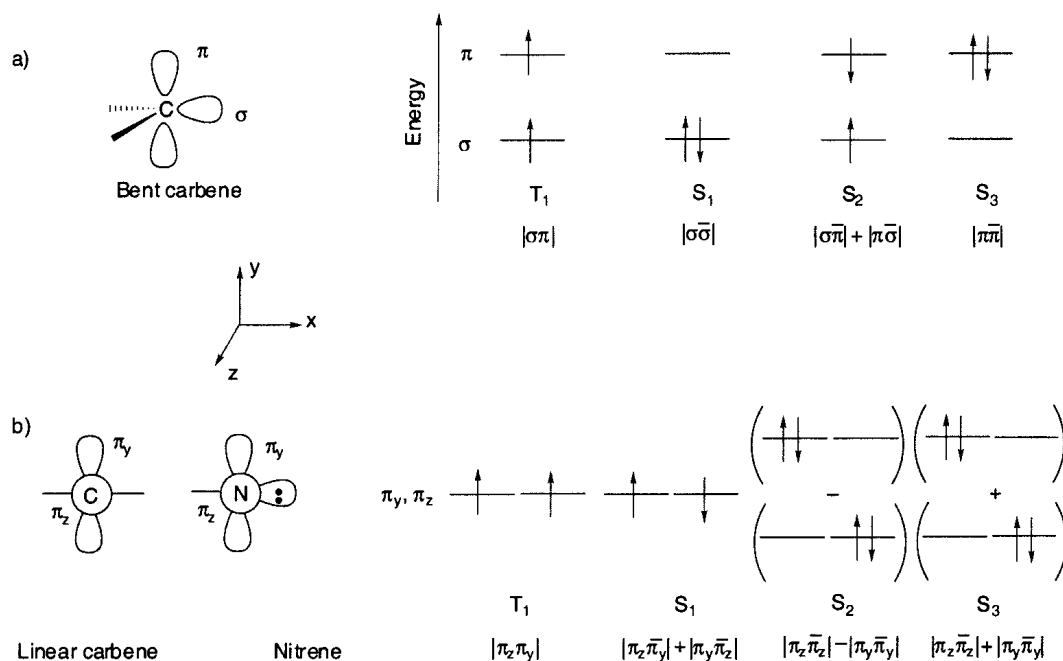
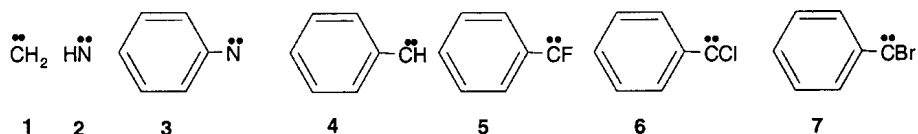


Figure 1. Electronic states of diradical species.



singlet. This switching of electronic configurations can be attributed to the higher electronegativity of the halogen, which inductively stabilizes the σ orbital of the carbene, and/or to the π -donating ability of the lone pair of the halogen, which destabilizes the π orbital of the carbene. Both effects act in the same direction increasing the σ - π separation and, thus, stabilizing the singlet (S_1 in Figure 1a) with respect to the triplet state. While the T-S splittings in the halogen-substituted cases are not as well established as that for the parent **4**, computed estimates of -19, -7 and -7 kcal/mol for **5**, **6** and **7**, respectively, have been reported [54].

The rather wide range (+19 to -19 kcal/mol) of T-S splittings between phenylnitrene (**3**), phenylcarbene (**4**), and its halogen analogues (**5-7**) makes these transients suitable for constructing model systems to study systematically both spin-spin interactions, generally, and the factors that control the electronic configuration of the ground states specifically.

m-Phenylene (MP) Linker

The prototypical system for the study of spin-spin interaction across MP is *m*-benzoquinodimethane (**8**), a model that has been extensively studied. It is a non-Kekulé alternant hydrocarbon with a triplet ground state [56-58]. Its high-spin multiplicity can be rationalized either by valence-bond (VB) type arguments [59] or by simple molecular orbital (MO) theory [55]. According to the VB model, each carbon of the starred set [60] forms a π bond with an adjacent carbon of the other (non-starred) set. Thus, in the case of **8**, the excess α spin (given by the difference between starred and non-starred atoms) is two, predicting a triplet ground state. Alternatively, Hückel MO theory suggests that **8** has two degenerate, non-bonding MOs (NBMOs) (Figure 2). Thus, based on Hund's rule a triplet state is expected.

Interestingly, substitution of one or both radical sites of **8** by oxygen (as in **9a** [61] and **9b** [61,62]) does not alter the preference of *m*-phenylene for ferromagnetic coupling. The reasons for this are well understood and have led to the notion that *m*-phenylene is a robust and reliable ferromagnetic linker, something that in practice has been applied successfully in the design of high-spin polyradicals.

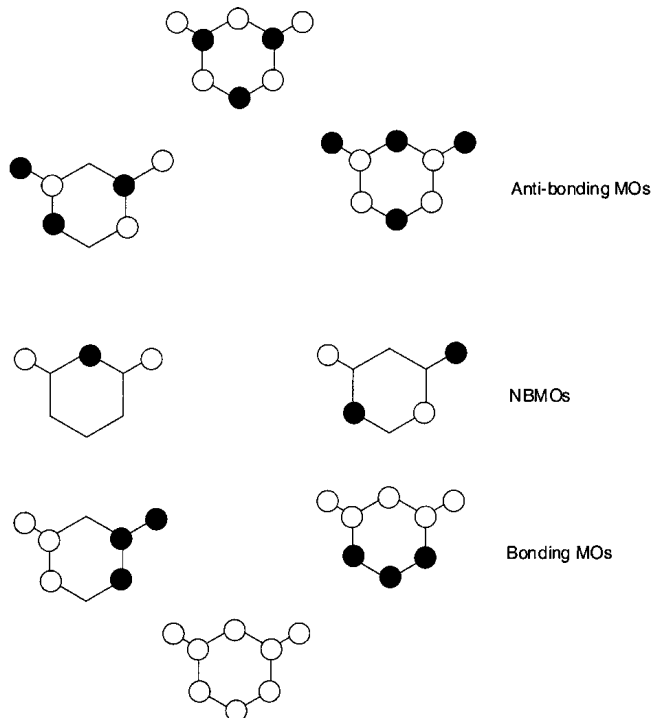
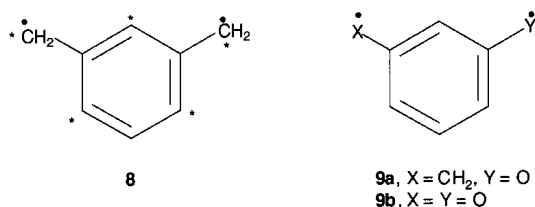
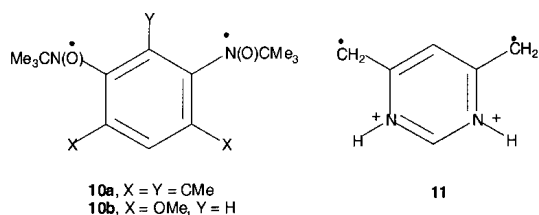


Figure 2. Qualitative π MOs of *m*-phenylene-linked diradicals.

However, recent studies have shown that MP can behave as an anti-ferromagnetic coupler under certain conditions. One case is when the radical centers are twisted out of conjugation from the MP linker. Calculations [63] on **8** have shown that as the angle between the p-orbitals of the methylene units and the p orbitals of the linker increases, the preference for a triplet ground state decreases. At dihedral angles around 90° , the singlet becomes the ground state due to through-bond stabilization of the symmetric combination of the p-orbitals of the substituents. Experimentally this case has been realized by the generation of the bis(alkylnitroxides) **10a** and **10b**, which were found to have singlet ground states [64,65] Presumably the bulky tertiary butyl groups disrupt the conjugation of the π system of the linker with the p-orbitals of the substituents.

Chemical substitution at appropriate positions of the MP linker can also transform it to an anti-ferromagnetic coupler. Thus, there is good evidence that dication **11**, if formed, will have a singlet ground state [66]. It was proposed that the presence of the very electronegative NH^+ groups of **11** in places where only one of the two NBMOs has significant density is responsible for the lift in their degeneracy and a switch to a singlet ground state in contrast to the parent **8**.



m-Phenylene-linked Bis(biradicals)

When two diradical centers are present in a molecule (as in biscarbenes, dinitrenes and carbenonitrenes), the number of possible electronic states increases significantly. Within a four-electrons-in-four-orbitals approximation, there are 70 different possible electronic configurations giving rise to 36 electronic states [2]. However, half of these states are of the “donor-acceptor” or “ionic” type, corresponding to formal electron transfer from one diradical site to the other, and therefore of higher energy than the “neutral” or “covalent” ones. Of the remaining “neutral” states (one quintet, 7 triplets and 10 singlets), seven (two triplets and five singlets) have configurations that are locally doubly excited (two electrons in the π orbital in the case of bent carbenes (S_3 of Figure 1a)) and of high energy content [32]. Eleven states are left (one quintet, five triplets and five singlets), which may need to be considered.

The relative energies of the possible electronic states depend among other factors on the topology (connectivity) of the linker. For example, *p*-phenylene, which allows for direct (conjugative) coupling between the radical centers tends to favor low-spin ground states, in contrast to *m*-phenylene (MP).

In Figure 3, VB approximate depictions that are likely to be important when two diradical centers are joined via MP are shown. For simplicity it has been assumed that there exists a plane of symmetry which encompasses the linker and the SCs. Within this approximation, each diradical site contributes one σ (in-plane) and one π (out-of-plane) atomic orbital and two electrons. The resulting states can be classified in several ways: a) overall multiplicity (singlet, triplet or quintet), b) “local” multiplicity of each diradical site (singlet or triplet), c) number of σ and π electrons contributed by each diradical center. For example, $\sigma^2/\sigma\pi$ means that one center has a σ^2 closed-shell singlet “local” configuration and the other has $\sigma\pi$ occupancy. The latter may correspond to triplet or to open-shell singlet “local” configuration). d) A' or A" depending on the number of π -electrons (even or odd, respectively).

According to the simple VB depictions of Figure 3, the quintet state (Q) arises when each diradical center is “locally” in a triplet state and there is high-spin (ferromagnetic) coupling between the centers (Figure 3). On the other hand, there are several ways of forming a singlet state. Singlet S_1 has the same electronic occupancy as Q, i.e. it consists of two “local” triplets, but these are anti-ferromagnetically coupled. Singlets S_2 and S_3 have one center as an open-shell singlet and the other as a closed-shell singlet, whereas singlet S_4 has both centers as “local” singlets of the closed-shell type. Finally, the

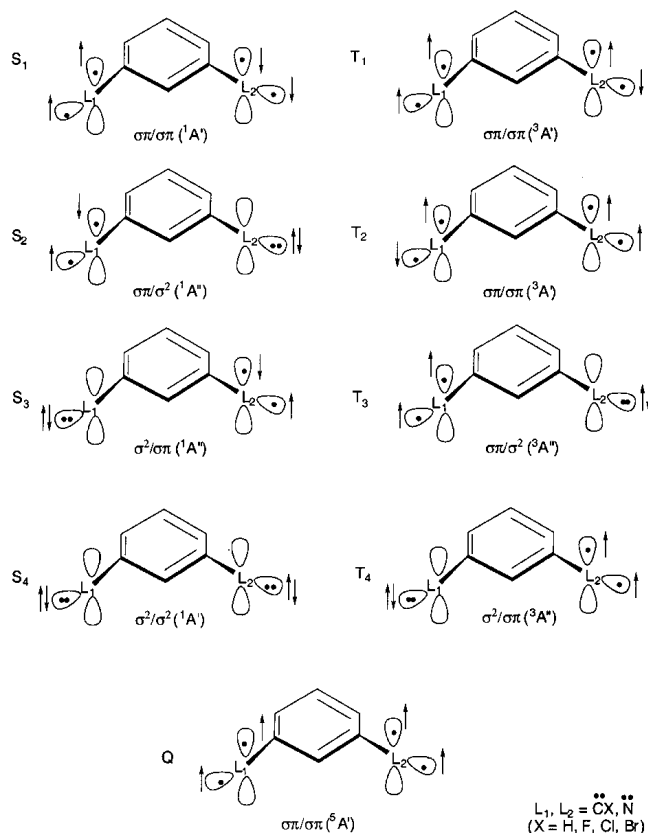
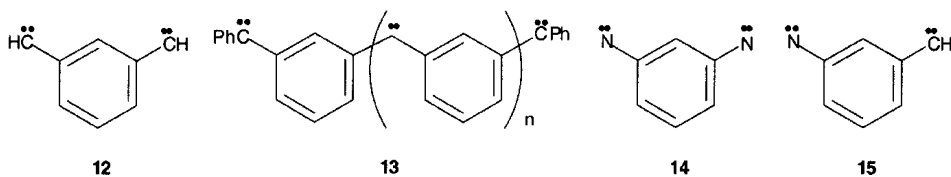


Figure 3. Electronic states arising from the coupling of two diradical centers via the *m*-phenylene linker.

triplet states combine one triplet site with one singlet site. The latter can be open-shell (T_1 and T_2) or closed-shell (T_3 and T_4).

The π MOs of biscarbene **12** are qualitatively the same as for **8**. Thus, eight π electrons in **12** should be overall coupled in a triplet fashion for the same reason as in *m*-benzoquinodimethane. However, **12** has two additional σ NBMOs, which are essentially degenerate in energy. By taking appropriate linear combinations, these two MOs can be localized one on each carbene center in the form of essentially pure (σ) atomic orbitals (AOs) with almost zero spatial overlap. If one electron is placed in each orbital, then their coupling should be very weak and the energy difference between the two modes, singlet or triplet, should be small. However, for reasons similar to those discussed above for the energy difference between the T_1 and S_2 states of a simple carbene, when the π electrons are also taken into account (Figure 1a) both σ non-bonding electrons will tend to be high-spin coupled with the excess α spin density in the π space. This results in an overall quintet state.

Indeed biscarbene **12** and its phenyl-substituted derivative **13** ($n=0$) were the first hydrocarbons for which quintet states were demonstrated [67,68]. The hetero-analogue bisnitrene **14** was also reported at the same time to have a quintet ground state [68]. Of interest was also the finding that the same multiplicity was assigned to the ground state of the “mixed”



carbenonitrene **15** [69]. Due to the large difference in electronegativity between carbon and nitrogen, the two NBMOs are no longer degenerate, and thus there is no *a priori* reason to expect high-spin coupling. However, these findings are in agreement with those of **8** and its oxygen derivatives **9a** and **9b**, demonstrating once more the intrinsic preference of the MP linker for ferromagnetic coupling. This preference has been exploited in the design of polycarbenes with very high ground state multiplicities as for example with the series **13** ($n=1-3$) [70-72].

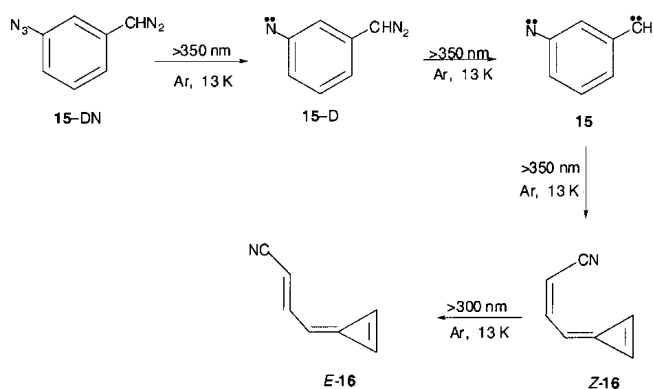
The generation of **12-15** was carried out at low temperatures in inert matrices by photochemically decomposing appropriate nitrogenous precursors. For example, carbenonitrene **15** was produced by irradiation of **15-DN** (Scheme 1) in a 2-methyltetrahydrofuran (MTHF) matrix at 18 K and its multiplicity was assigned by ESR spectroscopy [69]. Interestingly when the same precursor was irradiated under similar conditions (Ar matrix, 13 K, Scheme 1) and the reaction was monitored by IR spectroscopy, no significant amount of **15** could be detected, although at the initial stage of the irradiation an intermediate diazo-compound (assigned the structure **15-D**)

was observed [73].

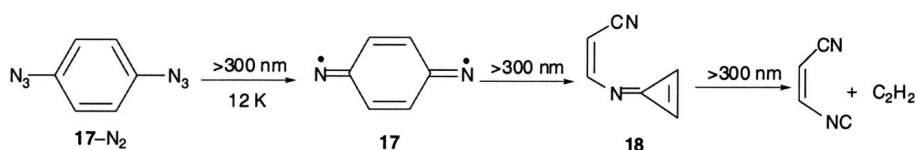
The failure of IR spectroscopy to detect **15** was attributed to the lower sensitivity of this technique as compared to ESR and to the intrinsically weak IR absorptions computed for the Q state. On the other hand IR spectroscopy made possible the detection of secondary photoproducts, which could not have been detected by ESR due to their singlet multiplicity. These were identified with the help of calculations as the substituted cyclopropenes *Z*- and *E*-**16**. A similar transformation has been observed in the photolysis of *p*-phenylenebisazide (**17-N₂**, Scheme 2). At the early stages of the irradiation, bisnitrene **17** is formed, which subsequently gives rise to cyclopropene **18** [74]. It has been speculated that these isomerizations are photochemical, but their mechanisms have not been established yet.

Irradiation of the nitrogenous precursors **19-NR**, **20-NR** and **21-NR** was carried out essentially under the same experimental conditions as for **15-DN** [73]. In the fluorine case (**19-NR**, Scheme 3a), partial isomerization of the diazirine precursor to its diazo isomer (**19-DN**) was detected. With the chloro and bromo derivatives (**20-NR** and **21-NR**, respectively) the intermediate formation of azidocarbenes **20-N** and **21-N**, respectively, was inferred from the IR data (Scheme 3b). In all three cases, the carbenonitrenes **19-21** were detectable by IR spectroscopy, unlike their parent **15** (Scheme 1). Interestingly, the computed spectra for **19-21** could differentiate between ³A' and ⁵A' and by comparison with the experimental data, the presence of the triplet states was inferred. Additional (indirect) evidence that **19-21** have triplet ground states was provided by irradiating precursors **19-NR**, **20-NR** and **21-NR** in MTHF matrix at 77 K and detecting ESR signals due to triplet nitrene species.

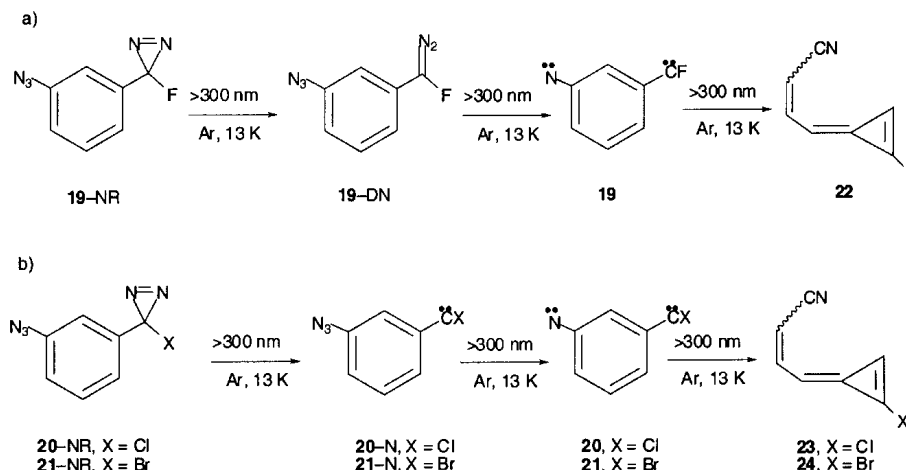
Under the conditions of their formation halocarbenonitrenes **19-21** are photolabile and give rise to new products which were identified with the help of IR spectroscopy and theoretical calculations as substituted cyclopropenes (**22-24**, respectively, Scheme 3). These isomerizations are very similar to the reaction observed for the parent **15** (Scheme 1).



Scheme 1. Photochemical formation of **15** and its rearrangement to **16**.



Scheme 2. Photochemical formation of **17** and photoproducts derived from it.



Scheme 3. Photochemical formation of carbenonitrenes **19**, **20** and **21** and photoproducts derived from them.

Carbenonitrenes **15** and **19-21** were considered computationally in some detail. Five electronic states were computed: one quintet ($^5A'$), two triplets ($^3A'$ and $^3A''$) and two singlets ($^1A'$ and $^1A''$). It was found that halogen substitution hardly affects the relative energies of A' states. Thus, the quintet state ($^5A'$) is computed to be the lowest in energy, while $^3A'$ and $^3A''$ lie higher by about 6 and 10 kcal/mol, respectively (Figure 4). The same is true for the A'' states, for

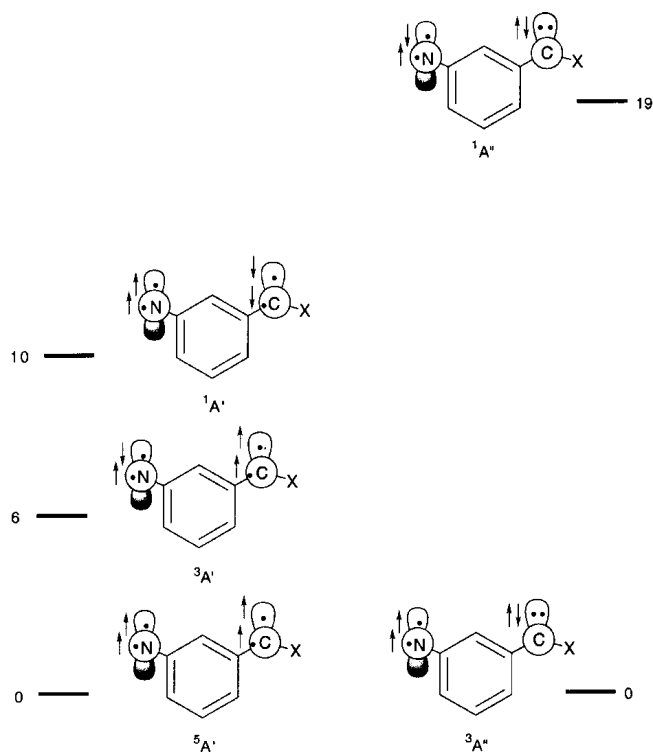


Figure 4. Relative energies (kcal/mol) of the A' and A'' states for **15** ($X=H$) and **19-21** ($X=F, Cl, Br$).

which the $^1A'$ is higher in energy than the $^3A''$ by about 19 kcal/mol. These energy differences can be rationalized to some extent by the VB approximations shown in Figure 4 and which are based on those of Figure 3. Thus, the energy splitting $^1A'-^3A''$ in **15** and **19-21** is approximately equal to the S-T gap of phenylnitrene (**3**). On the other hand, the $^1A'-^5A'$ splitting can be taken as a measure for the intrinsic preference of the MP linker for a high-spin coupling in its π space.

On the other hand, significant stabilization of the A'' states with respect to A' states occur when halogen is substituted at the carbene center (Figure 5). This results in a switching of ground state multiplicities. Thus, while the parent **15** has a quintet ground state, halogen substitution at the carbene center (**19-21**) gives rise to a triplet ($^3A''$) ground state. The effect is most significant for fluorine ($Q-T(^3A'')$ about -12 kcal/mol), whereas with chlorine and bromine substitution the Q-T splittings are very small (-3 and -1.5 kcal/mol, respectively). A plot of the $Q-T(^3A'')$ gap in **15**, **19-21** against the T-S gap of

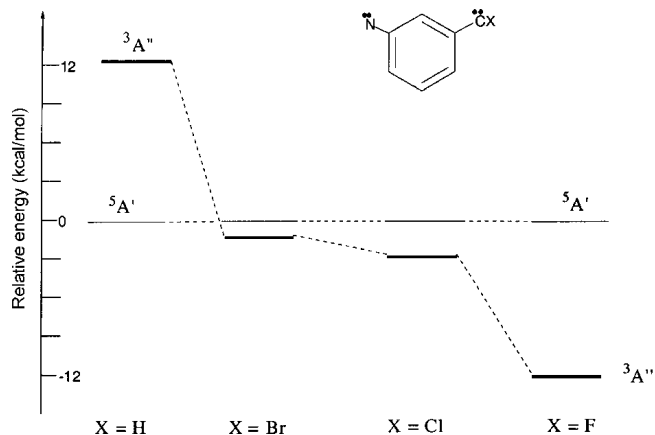


Figure 5. Effect of halogen substitution on the $^5A'-^3A''$ splitting of **15** and **19-21**.

the corresponding phenylcarbene (**4**, **5**, **6** and **7**, respectively) gives essentially a linear relationship which is described by the following equation (units in kcal/mol) [72]:

$$\Delta E_{TQ} = 6.6 + 1.1 \times \Delta E_{TS} \quad (1)$$

This linear dependence signifies that the VB depictions are reasonable approximations, at least for the $^3A''$ and $^5A'$ states. Furthermore it shows that for the $^3A''$ state to become the ground state the intrinsic preference of the carbene subunit for a closed-shell singlet (σ^2) configuration must be at least 6 kcal/mol greater than for the triplet ($\sigma\pi$) configuration.

It would be interesting to test the above predictions on derivatives of the parent biscarbene **13**, such as **25** and **26**. To the extent that a methylene subunit resembles a nitrene subunit (in the sense that both have an intrinsic preference for "local" triplet multiplicity), then, by analogy to **19** and **20**, both **25** and **26** are expected to have triplet ($^3A''$) ground-states. While for **25** there seems little reason to doubt this prediction, for **26**, the two states are likely to be close in energy and perhaps other factors will dominate reversing the predicted energy order. However, this remains to be shown since these systems have not been reported so far.

On the basis of the above, halogen substitution in both methylenes of **13** may result in a singlet ground state of the S_4 type (Figure 3), where both carbene units are in a closed-shell "local" singlet state (σ^2/σ^2). Obviously the difluoro compound **27** is the best candidate among the dihalogen derivatives, but this is not known yet. Nevertheless the dichloro derivative **28** has been reported and was actually the first example of configuration switching in this type of systems [75].

Biscarbene **28** was generated and characterized in a low-temperature (14K) N_2 matrix (Scheme 4) [75]. Irradiation of

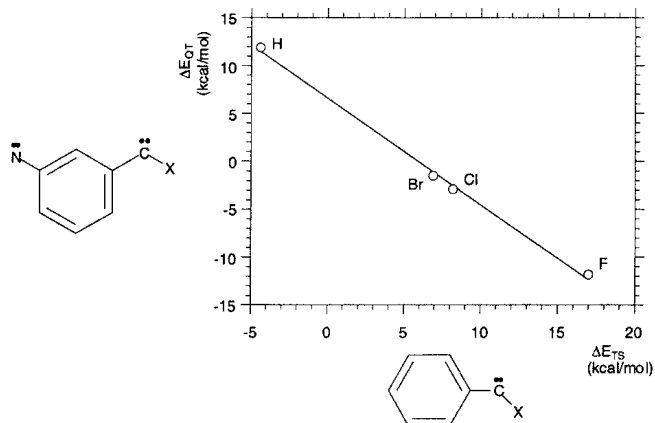
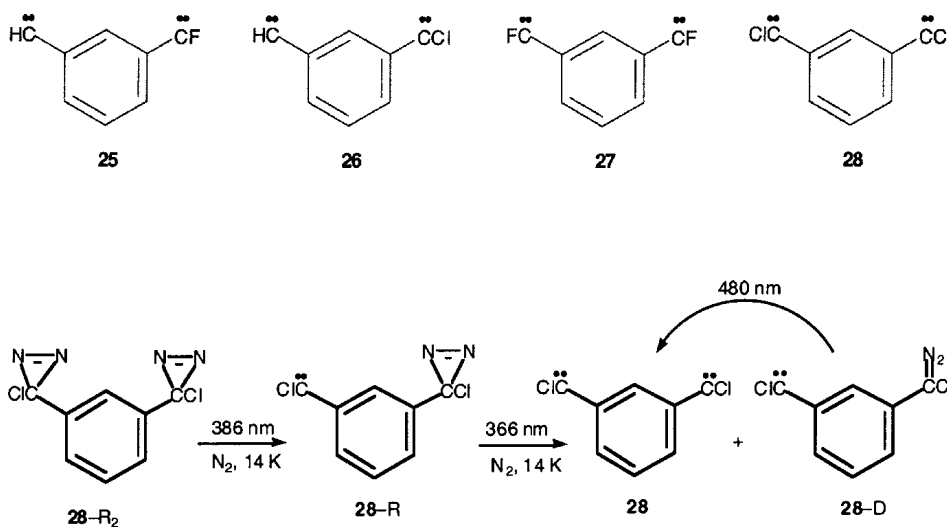


Figure 6. Plot of the Q-T(A'') splitting (ΔE_{QT} , kcal/mol) of **15** ($X=H$) and **19-21** ($X=F, Cl, Br$) against the T-S splitting (ΔE_{TS} , kcal/mol) of the corresponding carbene **4-7** ($X=H, F, Cl, Br$).

bisdiazirine **28-R₂** gave mainly the monocarbene **28-R**, which upon further irradiation with slightly longer wavelength gave its diazo isomer (**28-D**) and the desired biscarbene **28**. **28-D** could be transformed to the latter by selective irradiation at 480 nm.

Biscarbene **28** was characterized by IR and UV/vis spectroscopy [75]. The analysis of the experimental data showed that these are compatible with the presence of two phenylchlorocarbene subunits in **28**. This interpretation was further supported by the reactivity behavior of **28** and computations at the SCF level. From the calculations it was concluded that **28** is a singlet (σ^2/σ^2) biscarbene (S_4 of Figure 3). Subsequent calculations at definitive levels of theory established that the quintet state of **28** lies 11.5 kcal/mol higher in energy than the lowest singlet [73].



Scheme 4. Photochemical formation of **28**.

CONCLUDING REMARKS

In the study of reactive species matrix isolation continues to play a key role. The matrix provides an inert environment, which increases the lifetime of the “reactive” species to the extent that it may be thought of as a “stable” species. Under such conditions the species can be characterized spectroscopically by ESR, IR and UV. ESR is most useful in detecting and characterizing species with higher than singlet multiplicity. On the other hand, IR spectroscopy offers structural information and this method has become increasingly popular in the recent years due to developments in computational chemistry, which allow interpretation of the IR spectra with high confidence. IR spectroscopy is also useful in identifying secondary products, which are often singlet species and are formed in the matrix despite the cryogenic temperatures.

In the particular case of *m*-phenylene linked bis(biradicals), the topology of the linker does not allow for a direct (conjugative) interaction of the two diradical centers. This permits for the possibility of ferromagnetic coupling between the odd electrons, a property that has been amply exploited in the design of organic molecules with impressive high-spin ground states. This property is also exemplified by the quintet ground states of the model systems discussed above. The intrinsic preference of MP for high-spin coupling is estimated to be about 6-10 kcal/mol. However, this preference can be overridden by chemical substitution at a carbene site (if such a site is available). So far this has been achieved by chemical substitution at a carbene site. Thus, carbenonitrenes **19-21** were found to have triplet ground states, while bis(chlorocarbene) **28** is a singlet.

From the accumulated data, it seems that several of the electronic states in these systems can be approximated by simple VB depictions. In certain cases, this has permitted quantification of their relative energies, but more work needs to be done before such expressions are generalized. Finally, several of the *m*-phenylene-linked bis-biradicals exhibit photochemical reactivity in the matrix, giving products of rather unexpected structures. However, the mechanisms of these processes are not understood yet.

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