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Organic Polycarbenes: Generation, Characterization, and Chemistry

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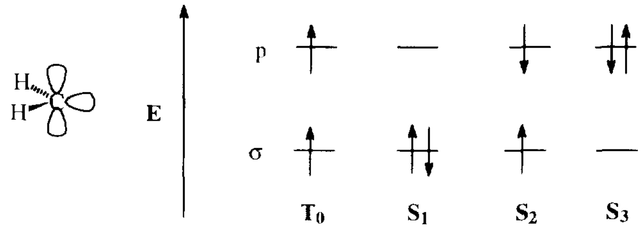
I. Introduction

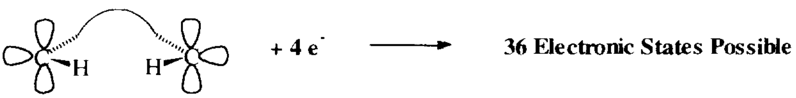
Intermediates incorporating multiple reactive "centers" have long fascinated chemists. More often than not, the poly-reactive intermediate exhibits electronic and chemical properties that transcend those of the corresponding mono-intermediate. For example, the chemistry of biradicals is considerably more complex than that of simple monoradicals.[1] It is thus no surprise that multicarbene containing molecules would attract attention. However, although organic compounds containing more than one diazo group have been known since at least the 1940's,[2] it was not until 1961 that the first evidence for the generation of a biscarbene was presented.[2] Since that time, considerable work has been directed toward organic polycarbenes. The opportunities presented by these species for the study of high-multiplicity organic compounds in particular have attracted much of the attention.

Most organic molecules have equal numbers of spin-up and spin-down electrons, and are thus diamagnetic. One attraction of carbenes is their capacity for unpaired electron spins. The factors that control the spin-states of carbenes are fairly well understood.[3] Carbenes comprise two unshared electrons that occupy two orbitals, σ and p, of similar but unequal energy (Scheme 1). This situation leads to the possibility of four electronic states, one triplet and three singlets, whose relative energies depend on geometry and substitution. The lowest energy state in many organic carbenes, including methylene, phenylcarbene and diphenylcarbene, is a triplet (T_0). Higher in energy by ca. 9 kcal/mole in methylene is a singlet state (S_1), primarily described by an electronic configuration doubly occupied in the σ-orbital (extensive configuration interaction exists in singlet methylene, however).[4] The other singlet states (S_2 and S_3) lie considerably higher in energy.

Scheme 1



The electronic situation becomes considerably more complicated when two carbenic sites interact, as in a simple polycarbene. As noted by Dougherty,[5,6] there are 70 different ways permitted by the Pauli exclusion principle that four electrons can occupy four degenerate orbitals, and these configurations can be condensed to 36 different electronic states. Realistically, however, the potential complexity for two "linked" carbene sites is not quite so severe. Many of the possible electronic states would be inter-center zwitterionic, and can be dismissed on energetic grounds. Moreover, those states involving p^2 carbenic centers are also probably too high in energy to be considered. Excluding these ionic states leaves 11 possibilities: one quintet, five triplets, and five singlets. Formally, one quintet, one triplet, and one of the singlet states arise from the coupling of two triplet carbene centers.[6] Coupling of a closed shell singlet carbene subunit with various configurations at the other center leads to three singlets and two triplets. Finally, one singlet state and two triplet states come from two open-shell singlets interacting and open-shell singlet/triplet interactions, respectively.



Despite these rich electronic possibilities, most investigations of polycarbenes have concentrated on high-spin assemblies of triplet carbene subunits. These studies have been spurred by the hope that they will contribute to the foundation of knowledge necessary to produce organic magnetic materials. Molecules with remarkably high multiplicity have been generated and examined, primarily with EPR spectroscopy and magnetic susceptibility measurements. The high-spin aspects of polycarbene systems have been repeatedly reviewed,[7] with particular focus on magnetic properties. Our concentration will therefore be slightly shifted from this theme, with a somewhat greater emphasis on the structural and chemical properties of these fascinating species. Molecules comprising more than one carbene center are inherently of high energy relative to more covalently satisfied counterparts. Hence, the generation of these unstable species can present special challenges, and deconvoluting mono- from polycarbene chemistry can be non-straightforward. On the other hand, there is the potential for these intermediates to exhibit even greater reactivity than do monocarbenes. Throughout this review, we also direct our attention toward some of these issues.

II. Atomic and Molecular Carbon

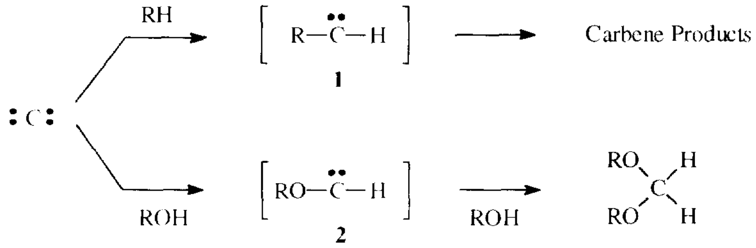
No review of polycarbenes would be complete without discussion of the chemistry of atomic carbon, and that of its related oligomers. Interest in this area has grown in the last few years stemming from its relevance to fullerene formation.[8,9] The generation, spectroscopy, and reactions of these small carbon clusters have been reviewed extensively in the past.[3a,10-13] Coverage of all the facets of this interesting science would be well beyond the bounds of this review. Hence, we survey only very briefly some aspects of these species that are particularly related to the other polycarbenes in this review, striving to be illustrative rather than comprehensive.

A. *Atomic C*

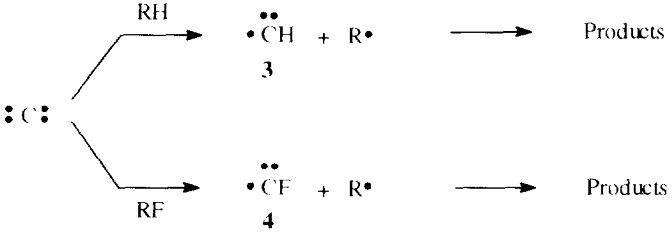
A carbon atom, with four valence electrons distributed among four orbitals, formally might be considered the simplest biscarbene. Carbon possesses a ^3P ground state, consistent with Hund's rule. Open-shell (^1D, corresponding to S_2 in Scheme 1 for CH_2) and closed-shell (^1S, corresponding to S_1 in Scheme 1 for CH_2) singlets lie 30 and 62 kcal/mole higher in energy, respectively.[10-13] The multiplicity-dependent reactivity of carbon thus depends on the energetics of its formation. Since extreme methods are often necessary to produce this high-energy species, however, the observed chemistry can reflect various mixtures of all of these electronic states.

A number of methods have been utilized to produce carbon atoms for the purposes of chemical and spectroscopic investigation.[10-13] The preparations utilized most frequently include nuclear recoil methods (to produce radioactive ^{11}C or ^{14}C), carbon arcs, graphite thermolysis, carbon suboxide photolysis, cyanogen azide photolysis, and thermolysis of 5-tetrazoyldiazonium chloride. These different methods produce different ratios of ground- vs. excited-state carbon. These same methods also serve to produce carbon oligomers.

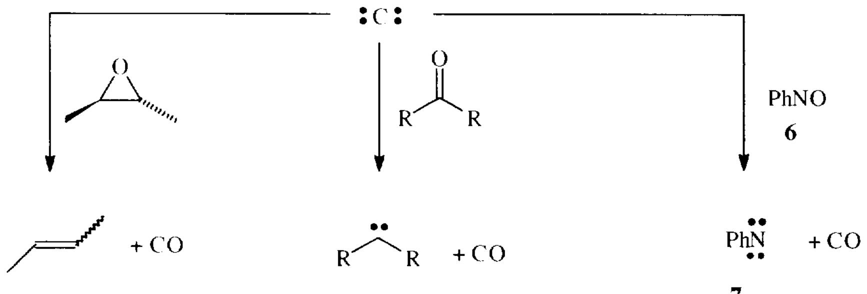
A common reaction of C with organic substrates is insertion into sigma bonds.[10-12] These reactions transform the carbon atom into a carbene (e.g. **1** and **2**). The ultimate products of these reactions have been interpreted on the basis of the presumed multiplicity of these initially formed carbenes. Singlet C (presumably mainly ^{1}D) is considered to produce singlet carbenes. Insertion of triplet ^{3}P carbon is proposed to lead directly to triplet carbenes.



Carbon atoms are also suggested to abstract a wide variety of atoms from organics.[10-12,14-16] Abstraction of monovalent atoms, such as H and halogens, gives carbyne intermediates (e.g. **3** and **4**) along with radicals from the organic substrates. Recombination of these geminate products provides one route to the "insertions" that produce carbene intermediates (e.g. **1**). The interesting chemistry of the carbyne intermediates themselves has also been explored.[14-16]



Perhaps unique among polycarbenes, C can react in a single step to produce a stable, unreactive product, CO.[10,12,17,18] Carbon atoms have been observed to deoxygenate ethers and carbonyl compounds. Since thermolysis of graphite, which produces only ground state carbon atoms, leads to no deoxygenation products, it has been suggested that the reactive species in these reactions is one of the excited singlets. Deoxygenation of epoxides gives varying amounts of stereochemical loss depending on the mode of carbon generation. It has been proposed that the lower energy species (^{1}D) strips oxygen in a stereospecific manner, whereas loss of stereochemistry might be due to ^{1}S carbon. Products of C reaction with other cyclic ethers have been interpreted as arising from biradical intermediates. Carbon atoms will also deoxygenate carbonyl compounds leading to a wide variety of carbenes (**5**). Finally, C has been used to generate phenylnitrene (**7**) via deoxygenation of nitrosobenzene (**6**).[17]



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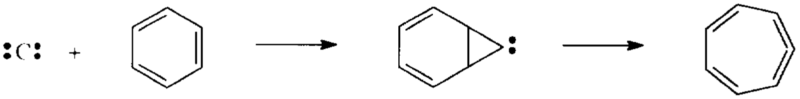
Reflecting their carbenic properties, carbon atoms add to C=C π-bonds. Addition to alkenes gives allenes (e.g. **9**, along with CH insertion products) thought to arise from cyclopropylidenes (e.g. **8**).[10-13]

8 **9**

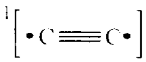
Carbon has also been found to add to the π-system of aromatics and heteroaromatics, producing carbenes (e.g. **10**) that eventually lead to novel products (e.g. **11**).[10-13]



10 **11**

B. C_2

Diatomic carbon has been studied extensively, both spectroscopically and theoretically.[10-13] Only a small amount of information is available on the mechanisms of its chemical reactions, however. A singlet state ($^1\Sigma_g$) is lowest lying, with a triplet state ($^3\Pi_u$) only ca. 2 kcal/mole higher in energy. Although the singlet (**12**) can be described primarily as a diradical, the triplet (**13**) has been suggested to have a bis-carbenic structure.[19]



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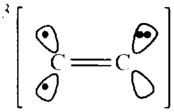

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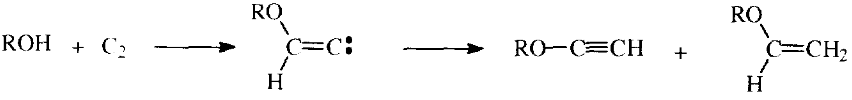
The reactions of C_2 primarily reflect radical-like behavior.[10-13,19,20] Acetylene, formed via hydrogen abstraction, is generally the major product from reaction of C_2 and organics. C_2 adds to alkenes to give 1,4-diradicals, which subsequently undergo various intermolecular reactions to give products. Although kinetic information is available on the individual reactions of the singlets and the triplets with various substrates, the products from the two electronic states have not been differentiated.

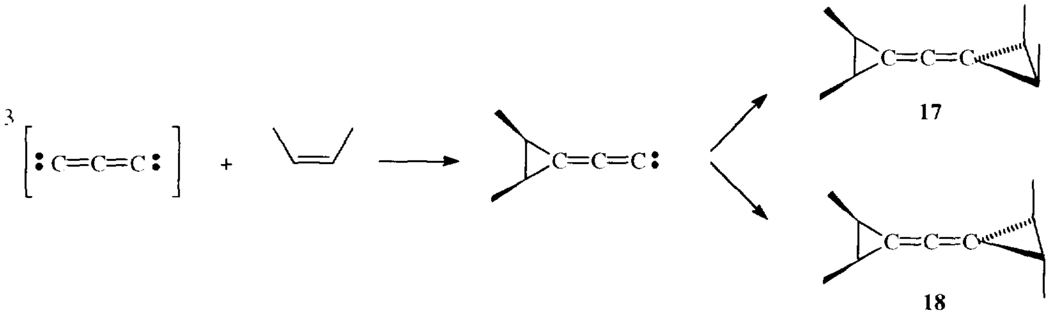
Carbene-like behavior may, however, be signaled by the reactions of C_2 with alcohols. Ethynyl (**15**) and vinyl ether (**16**) products have been proposed to arise from intermediates formed from initial C_2 insertion into the alcohol OH bonds (i.e. **14**).



14 **15** **16**

C. C_3

In contrast to C_2, triatomic carbon clearly reacts as a biscarbene.[10-13] The ground state of C_3 is a singlet. Triplet and excited singlet states are considerably higher in energy. Skell and coworkers[11] have investigated various reactions of C_3. Alkenes add to the two ends of C_3 to give bisethanoallenes (e.g. **17** and **18**), with stereochemistry dependent on mode of generation.[19,21,22] Thermally vaporized graphite, where ground-state singlet C_3 is the major species present, gives adducts with cis- and trans-2-butene with retention of stereochemistry. On the other hand, the more energetic arc-produced C_3 gives bis-adducts with some loss of alkene stereochemistry. It was suggested that singlet C_3 adds stereospecifically to alkene to produce a singlet allenylidine. This intermediate subsequently adds the second alkene also stereospecifically. In contrast, the loss of stereochemistry was attributed to additions of excited triplet C_3 which was proposed to add nonstereospecifically in the second step.



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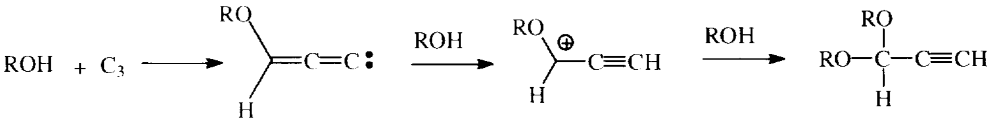
Triatomic carbon has been found to react with alcohols to produce 3,3-dialkoxypropynes (**19**).[23] The carbene-like mechanism shown below was proposed.



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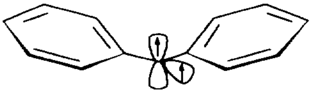
III. Aryl-Linked Triplet Carbene Subunits

A. *Background*

Most of the experimental studies carried out on polycarbenes have revolved around assemblies of diphenylcarbene subunits. Diphenylcarbene (**20**) is a ground state triplet, with one electron in an in-plane σ-orbital, and the other in a p-orbital conjugated with both aromatic π-systems.[3]



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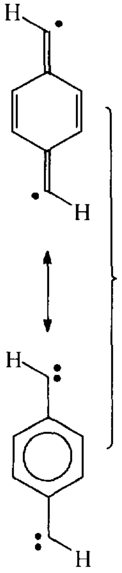
When two phenylmethylene subunits are attached to the same benzene ring, the interaction between the carbene centers is dominated by the coupling of the benzylic radical-like p-electrons through the aromatic ring π-system. Hence, the corresponding quinodimethanes provide a guide for description of the electronic properties of these biscarbenes. In simplest valence bond terms, *p*- and *o*-quinodimethane (**22** and **24**, respectively) possess Kekule π-systems, where all electrons can pair into bonding orbitals. More sophisticated MO approaches confirm this chemical intuition.[24-26] Likewise, *ortho-* and *para*-joined biscarbenes (**21** and **23**, respectively) can covalently couple their π-electrons, with syn- or anti- σ diradical centers remaining. As will be seen later, this coupling destructively interferes with the high-spin configurations of the two carbene centers and leads to low-multiplicity ground states for these situations.

In contrast, *m*-quinodimethane (**25**) is a non-Kekule biradical hydrocarbon.[24-26] No covalent interaction between the benzylic centers is possible, yet the unshared electrons occupy the same π-space. In MO terms, the molecule has two nonbonding MOs, which are each singly occupied. Exchange interaction between the unshared electrons decreases repulsion if they possess the same spin. This situation leads to a triplet ground-state. In the corresponding biscarbene **26**, the carbene centers contribute to a similarly "high-spin" π-system. As in diphenylcarbene (**20**), the strong exchange interaction between the σ and π electrons favors same-spin electron alignment at the carbene centers. Hence, the four unshared electrons all have the same spin, and the ground state of the molecule is a quintet, with a total spin quantum number S = 2.[27] Although simple chemical intuition correctly predicts the electronic structure of these aryl-linked biscarbenes, models of greater sophistication are sometimes needed to describe more complicated situations (vide infra).



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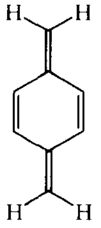

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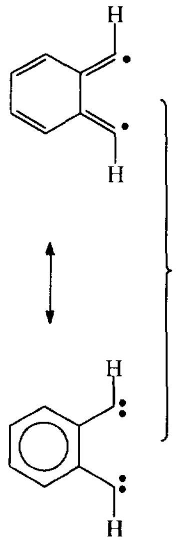

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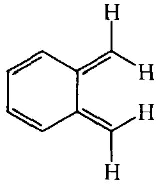

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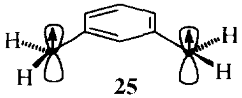

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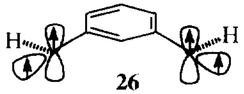

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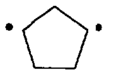

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Because electronic multiplicity issues are of such central importance in polycarbene research, EPR spectroscopy has played a key role. This sensitive technique directly provides information on the spin state of these systems and also can address other electronic and structural questions. A brief discussion of pertinent aspects of high-spin EPR, focusing primarily on results and applications of this technique, is thus worthwhile. Readers desiring a more detailed treatment are referred to the many excellent descriptions in the literature.[7i,24,25,28,29]

Molecules with one unpaired electron interact with an external magnetic field to give two different-energy substates with spin quantum numbers $m_s = \pm 1/2$. EPR spectroscopy probes transitions between these sublevels, that is, the energy required to "flip" an electron spin (i.e. $\Delta m_s = 1$). The situation is more complicated for molecules with two unpaired electrons. In such a triplet molecule there are now three magnetic sublevels, with $m_s = \pm 1$ and 0. The magnetic interactions between the two electrons split the degeneracy of the three sublevels, even in the absence of an external magnetic field. This zero-field splitting can be characterized by two independent energy parameters, D and E. In practice, these energies are reported as $|D|/hc$ and $|E|/hc$ in cm^{-1} units, and their values contain significant information on the structure and electronics of the triplet species. The E value gives some indication of molecular symmetry; if the molecule has three-fold or greater symmetry, E = 0. The D value is approximately inversely proportional to the cube of the average distance between the two unpaired electrons ($1/\langle r^3 \rangle$). Hence, triplets with the parallel-spin electrons localized in close proximity exhibit the largest D values. For example, CH_2 has a $|D|/hc$ of ca. 0.69 cm^{-1}.[28] Diphenylcarbene (**20**), where one of the two unpaired electrons is delocalized, has $|D|/hc$ = 0.405 cm^{-1}, reflecting the greater average interelectronic distance.[28] The unpaired electrons are held farther apart in a biradical such as cyclopentane-1,3-diyl (**27**) where $|D|/hc$ = 0.024 cm^{-1}.[28] It must be kept in mind, however, that spin-polarization in delocalized triplets can strongly influence π-electron interactions and thus complicate simple predictions of D values based on structure.[25]

In a similar fashion, a greater number of unpaired electrons in a molecule leads to more magnetic sublevels. In these higher multiplicity situations, the sublevels are again split in the absence of an external magnetic field by inter-electron magnetic interactions. Although the zero-field splittings are more complicated than is the case for triplets, they can still be characterized approximately by the same two parameters, D and E. These zero-field parameters, however, are less straightforward to interpret in the higher-spin molecules. As in triplets, the absolute value of D in higher multiplicity systems can be related to the $1/r^3$ inter-electronic values averaged over all of the pairwise interactions of the unpaired spins.[29,49,50,59] For subtle reasons based on this averaging, however, the D value generally decreases as the total spin quantum number S increases. Thus $|D|/hc$ = ca. 0.08 cm^{-1} for biscarbene **26**,[27] compared to ca. 0.5 cm^{-1} for triplet phenylcarbene. Itoh and co-workers[7c,59] have suggested that for polycarbenes related to **26** (e.g. **61**, **75**, and **76** in part III.C. below) the D values are inversely proportional to (2S-1).

The zero-field splitting parameters for high-spin systems can be determined by EPR spectroscopy. Since in general the intermediates are highly reactive, they must be produced in rigid media, often at very low temperatures. Precursor molecules are usually imbedded in frozen organic glasses such as 3-methylpentane or 2-methyltetrahydrofuran (2-MTHF), or in single crystals of an appropriate host. Often the diketone corresponding to a bisdiazo precursor is chosen for a single crystal medium to facilitate co-crystallization. In certain cases, argon or nitrogen matrices have also been used. UV irradiation of the precursor then photochemically liberates the species of interest. Irrespective of reactivity considerations, however, the high-spin molecules must be rigidly held in place, since molecular rotation averages the dipolar coupling of the unpaired electrons and renders the EPR spectra uninterpretable. In a magnetic field, the magnetic sublevels of a high-spin intermediate diverge in energy with the splitting dependent on field magnitude. The EPR spectrum measures the magnetic field-dependent energies for allowed $\Delta m_s = 1$ transitions, i.e. those corresponding to "flip" of a single electron spin. For a given triplet, two transitions are allowed at different magnetic fields for a given microwave frequency. To complicate matters further, however, the splitting between the magnetic sublevels also depends on the orientation of the molecule in the external magnetic field. The D and E parameters for a triplet in a single crystal can be extracted by measurement of the angular dependence of the two EPR transitions as the crystal is rotated. In randomly oriented triplets, as occurs in a low temperature glass, up to six transitions can be observed, and from these the zero field parameters are derived.

The EPR spectra of higher multiplicity systems are more complex, depending on the spin state. Quintets, for example, exhibit four allowed $\Delta m_s = 1$ transitions for a given molecular orientation. This number of absorptions can be observed in oriented single crystalline samples, where the angular dependence of the absorption frequencies can be used to extract D and E values. In randomly oriented samples, up to 12 absorptions (actually extrema in the first derivative spectra) can appear. As spin multiplicity increases beyond the quintet state, the complexity of the EPR spectra nearly dictate that oriented single crystals be used.

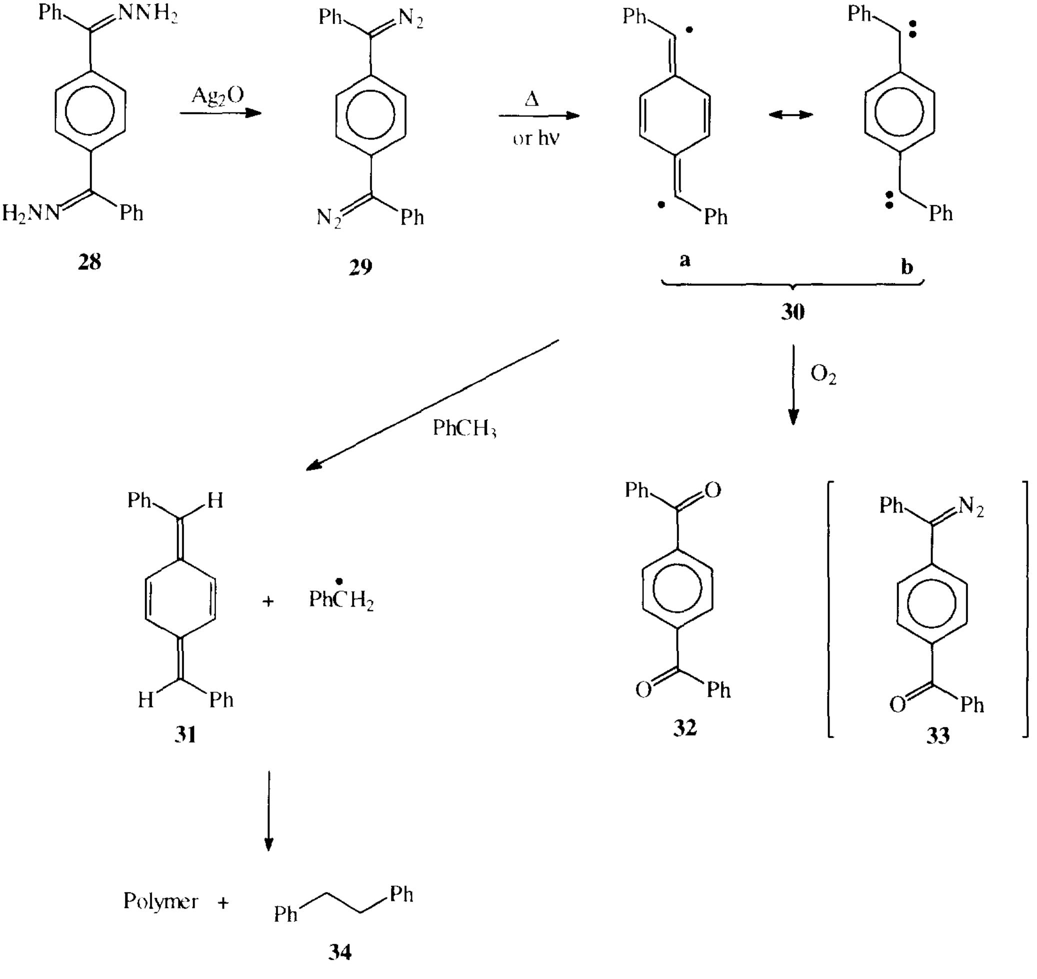
EPR spectroscopy can, in certain cases, also provide information about the energetics of the ground state spin multiplicity. The intensity of any paramagnetic species in the EPR decreases as the temperature is raised, following the Curie law where Intensity = Constant/Temperature. If the observed state is in equilibrium with higher energy states of different multiplicity, then superimposed on the Curie law temperature dependence will be a Boltzmann factor, related to the relative energies of the different states. Qualitatively, if an EPR spectrum is observed at extremely low temperatures (4.2 K or below), it can be safely concluded that this species represents the ground state multiplicity (or is very close in energy to the ground state). Depending on the relative energetics of the electronic states and their respective multiplicities, raising the temperature may simply decrease the EPR signal or may cause the appearance of new peaks from thermally populated states of different spin.

Many polycarbene systems are paramagnetic; indeed this property has led to much of the interest in these species. Measurements of bulk magnetization and magnetic susceptibility have thus played an important role in their characterization. The temperature dependence of the magnetic properties affords information on ground-state multiplicity and energies of low-lying excited states that can complement EPR data. Because such measurements have been repeatedly reviewed in detail, we will refer interested readers elsewhere for discussion of related experiments.[7i,n]

In the following sections, we will describe various studies on systems comprised of triplet carbene subunits linked via aromatic rings. To organize this information along the lines of related compounds, we have borrowed the terminology of many workers in this field.[5] As described above, there are different possible multiplicity outcomes when two triplets interact. At one extreme, antiparallel orientation of the two triplet subunits is energetically favored. Because this situation cancels the overall spin, it is termed "antiferromagnetic coupling." We will first describe polycarbenes that interact conjugatively in this fashion. Then we will delve into polycarbenes at the other extreme, where cooperative coupling favors parallel spin orientation between triplet subunits. In these "ferromagnetically coupled" molecules the overall spin state is maximized. Finally, we will consider mixed systems that fall somewhere in between.

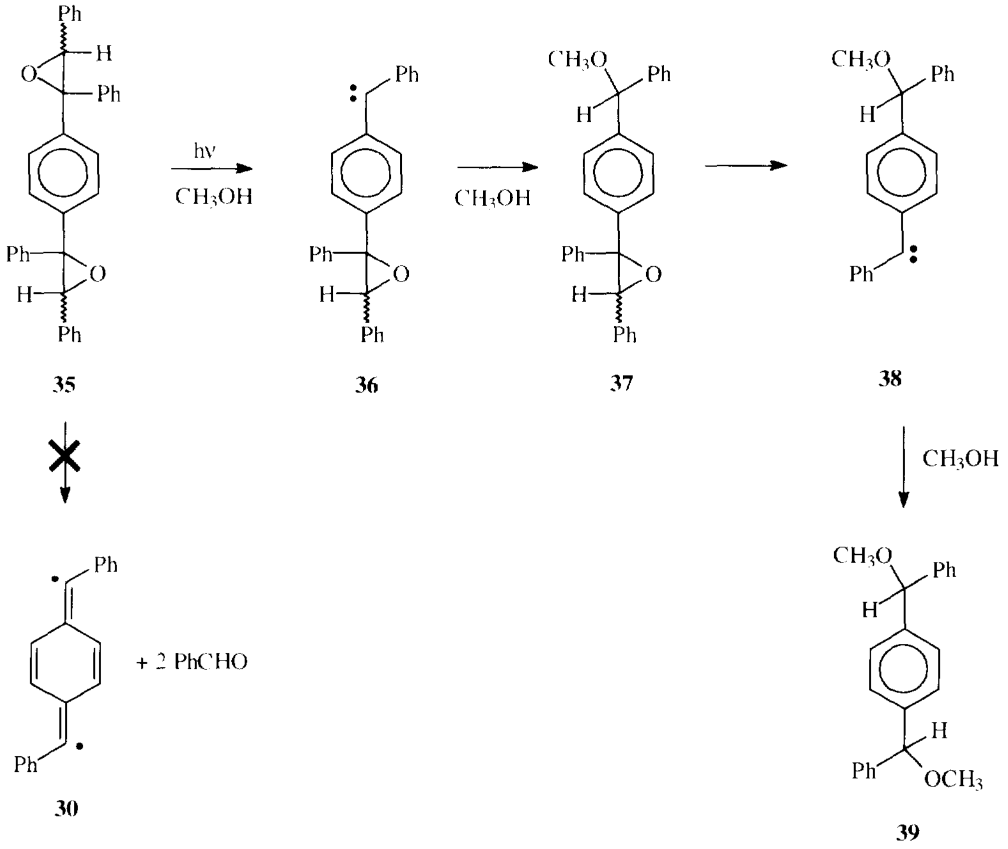
B. Antiferromagnetically Coupled Triplet Carbenes

The first observation of chemistry that could be attributed to a synthetically designed biscarbene came from workers at Bell Laboratories in 1961. Murray and Trozzolo prepared 1,4-bis[α-diazobenzyl]benzene (**29**) from oxidation of the corresponding bishydrazone **28**.[2] Thermolysis of **29** in refluxing toluene produced 1,2-diphenylethane (**34**), along with polymeric materials. They proposed that **30** was best described as a diradical (**30a**) that abstracted hydrogens from the solvent to produce the quinodimethane **31**, and benzyl radicals. The radicals combined to give **34** and the polymeric material was attributed to thermally unstable **31**. It was noted that the observed products might actually arise from monocarbene rather than biscarbene reactions, based on the known H-atom abstraction proclivities of diphenylcarbene. Partial photodecomposition of **29** in the presence of O_2, however, produced only diketone **32**, and no diazoketone **33**. Hence, they suggested that, at least photochemically, double denitrogenation to give **30** was occurring.[2]

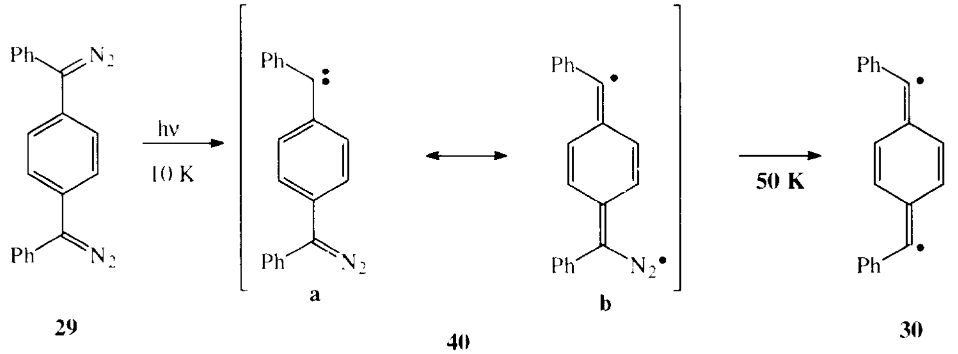


The direct observation of diradical **30** by EPR spectroscopy was reported in a subsequent paper.[31] Irradiation of **29** in polycrystalline diketone **32** at 77 K produced a triplet EPR spectrum with $|D|/hc = 0.0521$ cm^{-1} and $|E|/hc < 0.002$ cm^{-1}. The D value indicated an average separation of 4 Å, consistent with the localized diradical structure **30a**. Since a similar spectrum was observed at 4 K, this triplet was deemed to be the ground state of this species. Using a simple LCAO-MO overlap approach to approximate spin-spin interactions, Higuchi estimated a D value of 0.013 cm^{-1} for **30**.[32] In those calculations, however, he assumed that the radical centers were linear.

Griffin and co-workers explored a different route to **30**, based on their observations that aryl-substituted oxiranes photochemically fragment to carbenes and carbonyls.[33] Irradiations of isomeric bisoxiranes **35** in methanol solution were found to produce doubly trapped product **39**, along with **37** formed from single cleavage. The product ratios, however, fit those expected if the two oxiranyl subunits in **35** reacted independently. It was thus considered unlikely that biscarbene **30** was formed, and the sequential series of reactions shown below was proposed.

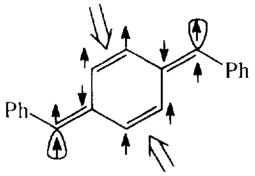


Itoh reported a reinvestigation of the EPR of **30**, photochemically generated at low temperatures from **29**, although few experimental details were given.[34] He suggested that the observed triplet was actually a thermally populated excited state lying 202 cm^{-1} (0.58 kcal/mole) above a *singlet* ground state. This system was subsequently investigated in considerably greater detail by Sixl et al.[35] They found that irradiation of bisdiazo compound **29** in single-crystalline benzophenone at 10 K produced metastable carbene signals in the EPR, which they attributed to monocarbene **40**. Warming the crystal to 40 - 60 K caused the disappearance of these signals with an activation energy of ca. 2.5 kcal/mole. They proposed that the *p*-triplet carbene weakened the remaining diazo group CN bond, as the diazenyl biradical structure **40b** might suggest, permitting facile denitrogenation to give **30**. At temperatures above 60 K, triplet signals for diradical **30** appeared in the EPR, comparable to those reported earlier.[31,34] Below 60 K, these absorptions disappeared reversibly, confirming a singlet ground state for **30**. Based on the temperature dependence of the absorptions, a singlet - triplet energy gap of 0.85 kcal/mole was proposed.



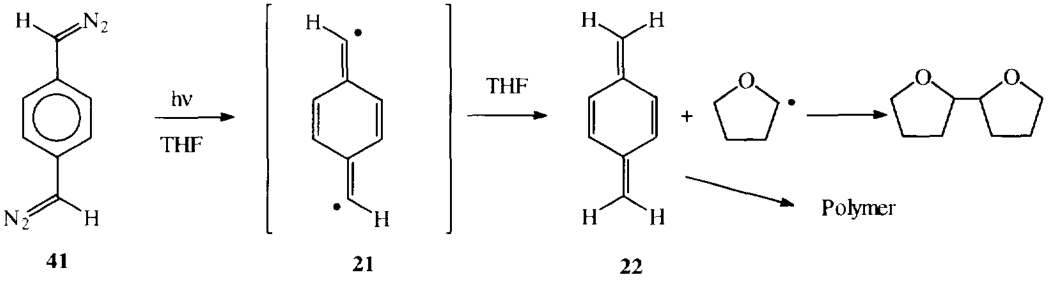
29 **40** **30**

Teki et al., have studied the electron distribution of the excited triplet of **30** using ^{1}H-ENDOR spectroscopy.[36] The derived hyperfine coupling constants suggest the spin-polarization in the π-system shown in the accompanying diagram. Qualitatively, the dangling σ-radicals induce an alternating polarization in the π-electrons. These workers termed this spin-alternation a pseudo π-spin density wave (π-SDW). In **30**, the favored spin polarizations actually cancel in the central phenylene ring, and disrupt the π-SDW. The singlet, in contrast, has perfectly alternating up-down electron spins in the π-system. They have suggested that the "node" in the π-SDW raises the triplet state over that of the singlet.

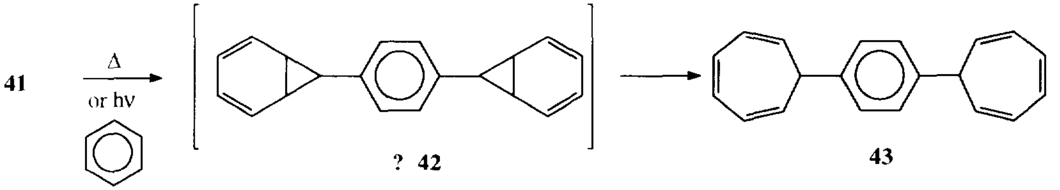


Spin-Density Wave for excited triplet 30
Open arrows indicate disruption

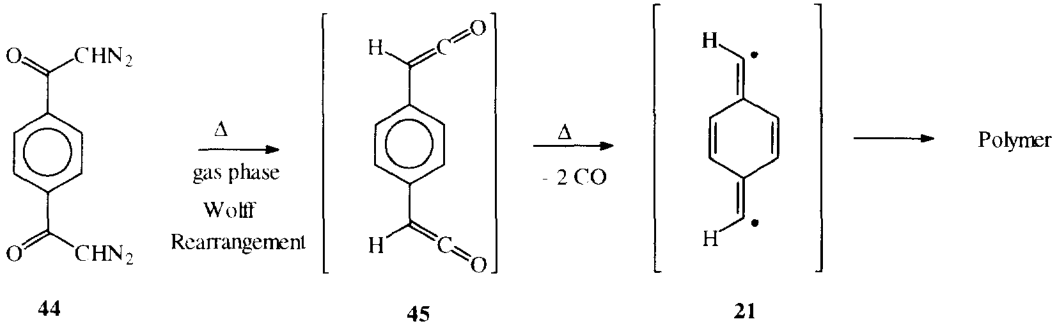
Although Murray and Trozzolo also reported synthesis of the parent bisdiazo compound **41** in 1963,[37] there have been no reports of spectroscopic characterization of the corresponding biscarbene **21**. Moritani, however, reported evidence for the possible photochemical generation of **21** in solution.[38] Irradiation of **41** in THF produced dimers of solvent and polymeric material, suggested to arise from H-abstraction from solvent.



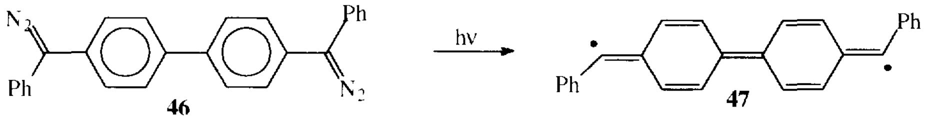
Murray and Kaplan found that photolysis and thermolysis of **41** in benzene produced very small yields of the interesting 1,4-bis(cycloheptatrienyl)benzene **43**, possibly via isomerization of the bisnorcaradiene **42**.[39] Whether **43** arose from biscarbene **21**, or from reaction of monocarbene, was not discussed.



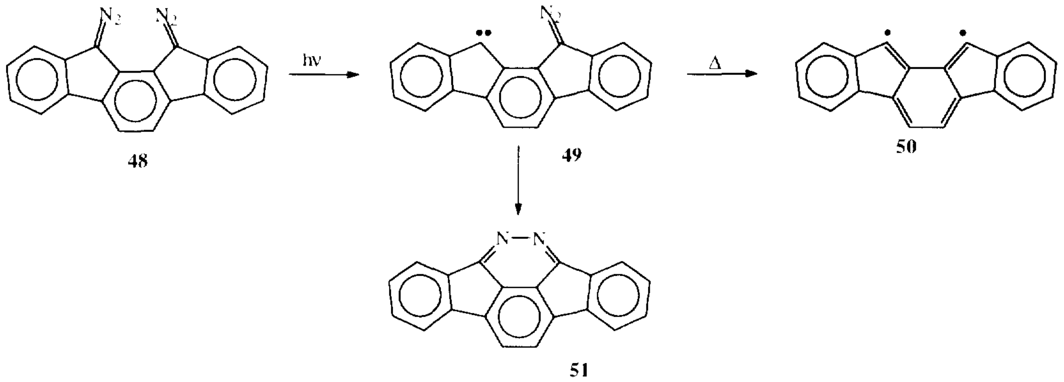
The possibility of controlled polymerization of **21** to conjugated, crystalline materials has also been explored.[40] Gas phase formation of **21** via pyrolysis of bis-diazoketone **44** was attempted by Lee and Wunderlich, as shown. Only amorphous crosslinked material was obtained, however.



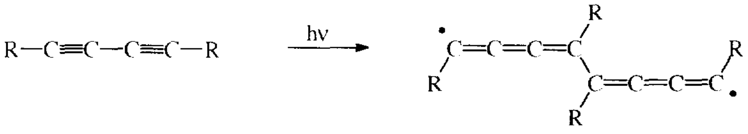
Itoh has reported a biphenyl analog of **30**, namely biphenyl-4,4'-bis(phenylmethylene) (**47**).[7c] Irradiation of the corresponding bis-diazo compound **46**, imbedded in a single crystal of 1,3-dibenzoylbenzene at 77 K, produced the triplet EPR of **47**, with $|D|/hc = 0.0403\ \text{cm}^{-1}$ and $|E|/hc = 0.0007\ \text{cm}^{-1}$. The smaller D value compared to that of **30** is consistent with a greater spatial separation of the unpaired electrons in **47**. Although few experimental details were given, Itoh suggested that the temperature dependence of the triplet absorptions was again consistent with a singlet ground state and a thermally populated triplet.[41]



Iwamura and co-workers have described spectroscopic observations attributed to an *ortho*-linked biscarbene.[42] Irradiation of bis-diazo compound **48** in the presence of benzophenone at 4 K in 2-MTHF/THF in an EPR spectrometer produced the mono-carbene **49**, with $|D|/hc = 0.391$ cm^{-1} and $|E|/hc = 0.0258$ cm^{-1}, similar to values for fluorenylidene. The carbene **49** disappeared irreversibly above 55K. However, reirradiation of the glass gave a new triplet with $|D|/hc = 0.0739$ cm^{-1} and $|E|/hc < 0.003$ cm^{-1}. This triplet was only observed when the light was on. The authors attributed this signal to the photochemically-populated triplet excited state of singlet diradical **50**. They further proposed that monocarbene **21** thermally denitrogenated to produce **50**. UV/Vis spectra taken of 77 K glasses of these materials showed two sets of absorbances. One set, with characteristic vibrational structure between 300 and 400 nm, was shown to be identical to that of azine **51**, which was a major photoproduct of **48** at room temperature. The other set of bands, extending into the visible with maxima at 420 and 535 nm, were attributed to singlet biradical **50**. Control experiments showed that the photochemically-excited triplet observed in the EPR spectrum was not due to azine **51**.

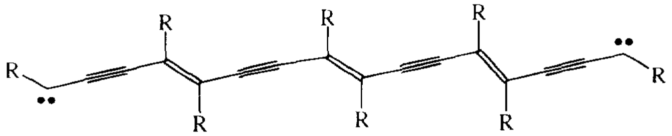


Huber and Sixl, and their co-workers have observed conjugated biscarbene intermediates in photochemical polymerization of diacetylenes and have drawn the analogy to antiferromagnetically coupled biscarbenes such as **21**.[35,43] Irradiation of single crystals of the bis(*p*-toluene sulphonate) ester of 2,4-hexadiyne-1,6-diol (**52**) produced crystals of the corresponding conjugated polymers. Low-temperature EPR spectra of the crystals showed triplet and quintet intermediates that depended on reaction conditions. The triplet species possessed $|D|/hc$ values of ca. 0.03 - 0.05 cm^{-1} and $|E|/hc$ values of ca. 0.001 cm^{-1}. These triplets were thermally populated, and exhibited maximum intensities at ca. 60 K.[43e,f] The authors suggested that these absorptions corresponded to the thermally excited states of dimeric diradical species such as **53**. Based on the temperature dependence of the various triplet signals, singlet-triplet gaps in the range of 0.23 kcal/mole were estimated.



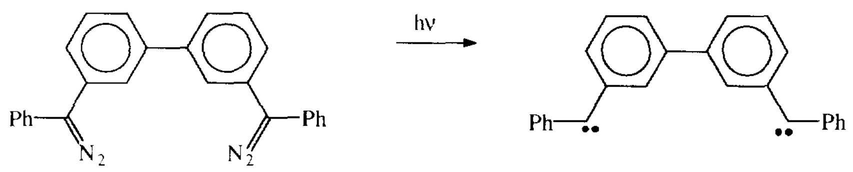
52 (R = CH_2OTs) **53**

Warming the irradiated crystals to 100 K, then cooling, produced signals from several quintet species, with |D|/hc ca. 0.09 cm^{-1} and |E|/hc ca. 0.003 cm^{-1}.[43f,g,i] Again, these signals were thermally reversible, and the temperature dependence suggested a ground state singlet-excited quintet energy gap of 0.12 - 0.5 kcal/mole. It was proposed that the quintet signals arose from biscarbene oligomeric structures of greater length, such as **54**.



54

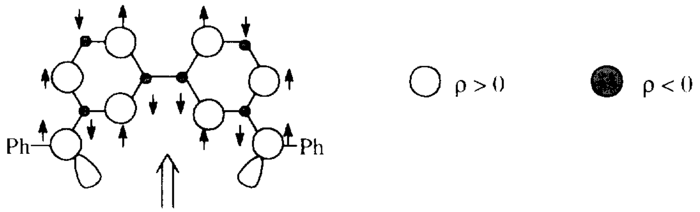
Itoh and co-workers have reported aryl-linked biscarbenes that are antiferromagnetically coupled in yet a different fashion.[7a,b,44,45] Irradiation of bisdiazo compound **55** in single crystals of benzophenone at 4.2 K produced no EPR spectrum. Warming the crystal to 10 K, however, gave triplet absorptions for **56** with |D|/hc = 0.29583 cm^{-1}, and |E|/hc = 0.06032 cm^{-1}. At 34 K, quintet signals were also observed with |D|/hc = 0.10349 cm^{-1} and |E|/hc = 0.01457 cm^{-1}. The temperature dependence of the various EPR signals indicated that **56** has a singlet ground state with triplet and quintet excited states lying only 20 and 60 cm^{-1} (57 and 172 cal/mole) higher in energy, respectively. No mention was made of attempts to observe a corresponding monocarbene/monodiazo intermediate.



55 **56**

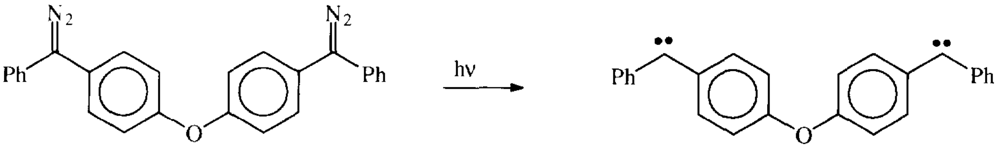
The researchers pointed out that simple MO theory predicts **56** to have a quintet ground state.[7a,b,44,45] The π-system of the biscarbene should have two degenerate nonbonding MOs, occupied by the two carbenic p-electrons. Blind application of Hund's rule would suggest parallel alignment of the spins, or ferromagnetic coupling, of these two electrons. In turn, the σ-carbenic electrons should be strongly coupled ferromagnetically to the π-electrons via one-center exchange interactions, resulting in a quintet state. They note that the failure of this simple-minded approach to predict the correct ground state lies in the inapplicability of Hund's rule to such π-systems. By the Borden-Davidson criterion,[25,46] the non-bonding MOs of **56** are disjoint, that is they can be localized onto separate atomic centers. Hence, the exchange interaction advantage for parallel spins in the two π-electrons is minimized, and weak interactions with the paired electrons in lower level MOs leads to antiferromagnetic coupling.

The observed low spin of **56** was also rationalized from an alternative point of view.[45] The authors noted that the symmetry of the π-system leads to an discontinuity in the natural up-down spin alternation in the π-SDW (vide supra) for the excited triplet and quintet states of this system, but not for the singlet. This approach is supported by ENDOR experiments, which measured the ^{1}H hyperfine coupling in the excited triplet. These experiments, and MO calculations, suggested the spin densities in the excited triplet of **56** shown in the accompanying figure (where the circle size approximately represents spin density magnitude).[7b,45]



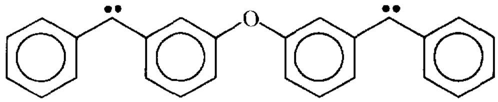
Disruption in alternation of π Spin Density Wave of Triplet 56

Itoh and co-workers have also explored coupling of arylcarbenes through the lone-pair electrons of an oxygen linker.[47] Observation of ferro- or antiferromagnetic interaction depends on the regiochemistry and thus the π-MO topology. Irradiation of the 4,4'-bisdiazoether **57** in single crystal benzophenone at 4.2 K gave only monocarbene EPR triplet signals attributed to monodiazo impurities. Warming the crystal to 20 K, however, caused the appearance of a triplet species attributed to **58**, with $|D|/hc = 0.38821$ cm^{-1} and $|E|/hc = 0.01437$ cm^{-1}. Warming to 31 K, produced quintet signals for **58**, with $|D|/hc = 0.1288$ cm^{-1}, and $|E|/hc = 0.00085$ cm^{-1}. Additionally, the dependencies of the triplet and quintet signals for **58** on crystal orientation were consistent with both arising from the same molecule. A superexchange interaction through the O lone pairs was suggested to couple the two triplet carbene subunits in an antiferromagnetic fashion to produce a singlet ground state. The temperature dependencies of the spectra indicated that the excited triplet and quintet lie 15 and 45 cm^{-1} (43 and 129 cal/mole) respectively, above the ground state.



57 **58**

Although few experimental details were given, Itoh et al. also reported that the 3,3'-ether-linked system **59** was similarly studied.[47] Analogously to the *meta-meta'* directly coupled system **56**, antiferromagnetic interaction was observed. In this case, triplet and quintet excited states were nearly degenerate with a singlet ground state. No zero field parameters were given in this preliminary report.

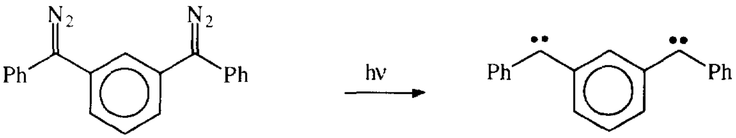


59

C. Ferromagnetically Coupled Triplet Carbenes

In recent years a great deal of work has been directed toward high-spin polycarbenes, where the carbenic subunits are coupled in a ferromagnetic fashion. There is a general hope that these high-multiplicity systems will guide the way to organic ferromagnets.[7] The majority of the high-spin systems that have been investigated center on the *meta*-phenylene linker, as in the prototypical *m*-phenylenebis(methylene) (**26**). In contrast to the examples given earlier in part B, here the unshared π-electrons cannot couple covalently. As described in the Background section, however, exchange interaction is strongly stabilizing when the π-nonbonding electrons have the same spin. Since the one-center exchange coupling between parallel spins is also strong between the carbenic σ and p-electrons, all four electrons in **26** are coupled ferromagnetically, to give a quintet ground state.

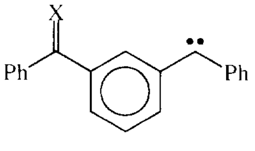
Trozzolo et al.[31] reported the first attempts to analyze the EPR spectrum of a *meta*-coupled biscarbene. Irradiation of bisdiazo compound **60** at low temperatures gave EPR spectra which were "quite complex" and distinct from those of triplet species such as the related *para*-system **30**. They also noted a similarity between the EPR spectra of the photoproducts of **60** and those of the corresponding *m*-bisazidobenzene.



60 **61**

Spurred by these results, Higuchi subsequently reported calculations using a simple LCAO-MO method on the corresponding biscarbene **61**.[32,48] The calculations indicated that **61** should be a ground-state quintet and also predicted D and E values for this species.

Several years later, the Bell Laboratories group[49] and Itoh[50] independently published analyses of the low temperature EPR spectra of **61**. Wasserman et al.[49] found that irradiation of **60** in randomly-oriented organic glasses at 4 K produced signals that could be attributed to quintet **61**. They estimated $|D|/hc = 0.0701$ cm^{-1} and $|E|/hc = 0.020$ cm^{-1}. Absorptions were also observed corresponding to a monocarbene, **62**, arising either from monodenitrogenation or from reaction at one center of **61** with the matrix. Similar measurements on the parent biscarbene **26** gave $|D|/hc = 0.0844$ cm^{-1} and $|E|/hc = 0.0233$ cm^{-1} and on the corresponding bisnitrene **63** gave $|D|/hc = 0.156$ cm^{-1} and $|E|/hc = 0.029$ cm^{-1}.



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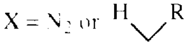

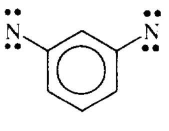

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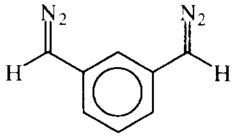
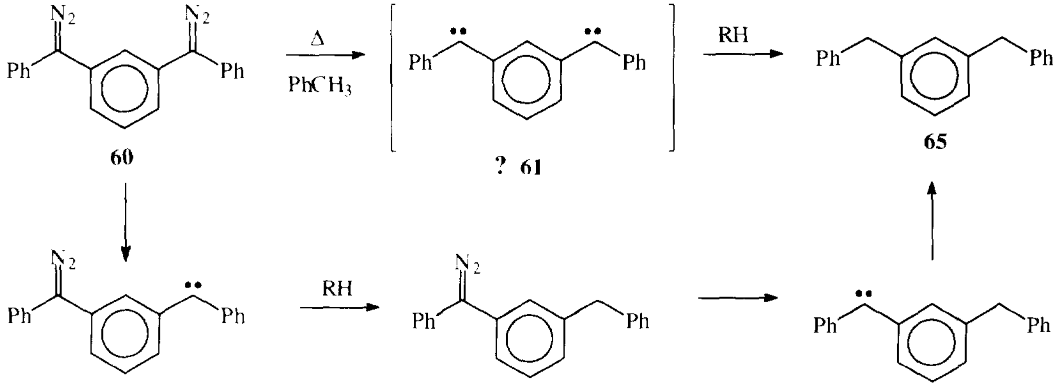


64

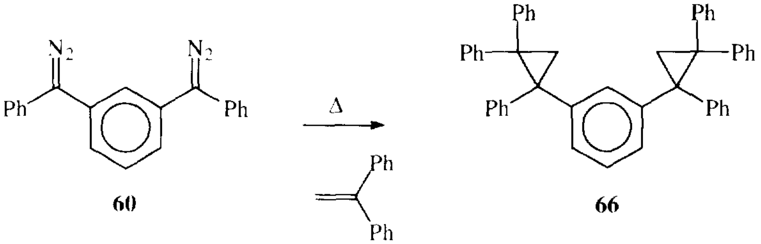
Itoh found that well-resolved EPR spectra of **61** could be obtained from 77 K irradiations of bisdiazo **60** in oriented single benzophenone crystals.[50] Analysis of the spectra gave zero-field parameters in excellent agreement with the randomly oriented spectra of Wasserman et al.[49] The signals were observed at temperatures as low as 2 K, indicating a quintet ground state. At 77 K the spectra decayed with a half-life of approximately 10 hours, to produce a triplet carbene signal suggested to be due to a reaction product such as **62**.

UV/Vis spectra attributed to biscarbene **61** have also been reported by Itoh et al.[51] The structured spectra, with distinct maxima at 316 and 450 nm, were observed on irradiation of **60** in mixed decalin-cyclohexane glasses at 77 K. The electronic spectra increased during irradiation in proportion to the increase of the EPR absorptions of **61**. An isosbestic point was located between the absorbance maxima of starting material and product, suggesting that only one species was formed. Although the spectra were very similar to those reported for diphenylcarbene (**20**), the researchers suggested that the approximately measured extinction coefficient of the spectra were about twice as large as that of the monocarbene. Thus, a monocarbene reaction product such as **62** was ruled out. Fluorescence spectra with a 485 nm maximum and a 150 ns lifetime were also attributed to **61**

Moritani and co-workers[52] have carried out an extensive investigation of the thermal and photochemical reactions of bisdiazo compound **60**, and of the corresponding parent compound **64**, in solution. They interpreted their results in terms of reactions of the corresponding biscarbenes **61** and **26**, although the more likely possibility of monocarbene reaction was not explicitly considered. Thus, for example, thermolysis of **60** in toluene produced 1,2-diphenylethane, reduction product **65**, and oligomeric material. It was suggested that these products resulted from hydrogen abstractions by biscarbene **61**. However, given the propensity for H-abstraction by arylcarbenes, it is equally probable that these products arise from sequential denitrogenation/monocarbene reactions, as shown in the accompanying scheme.

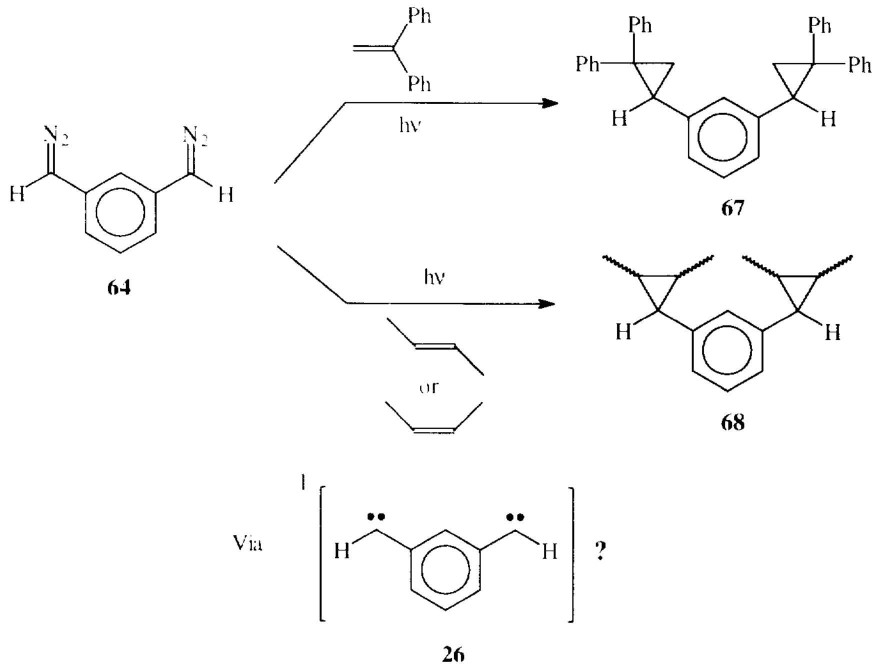


Thermolysis of **60** in the presence of 1,1-diphenylethene gave the bisaddition product **66**, as a mixture of diastereomers, in 84% yield.[52]

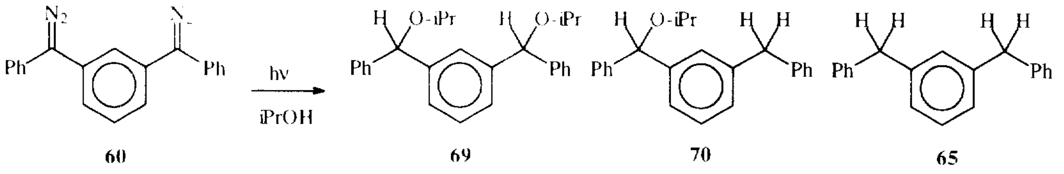


Flash photolysis of bisdiazo compound **60** at 20°C in deoxygenated liquid paraffin produced a UV/vis spectrum similar to that previously reported for biscarbene **61** (vide supra) in low temperature glasses. The lifetime of this intermediate, attributed to **61**, was found to be 10^{-5} s.[52]

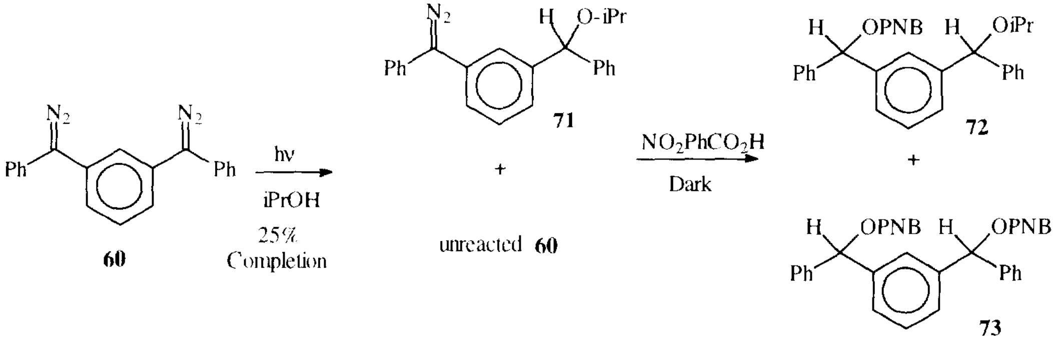
The stereochemistry of olefin addition by the parent system **64** was also investigated.[52] Photolysis of **64** in the presence of 1,1-diphenylethylene gave an 87% yield of a diastereomeric mixture of adducts **67**. Photolysis in neat *cis*- or *trans*-2-butene gave 17% and 15% yields, respectively, of a mixture of stereoisomeric adducts **68**. Only very minor amounts of products formed with loss of olefin stereochemistry were detected. However, when **64** was irradiated in a 1:100 solution of *cis*-2-butene in cyclohexane, 25% of *cis-trans* and 7 % *trans-trans* isomers of **68** were observed. The authors ascribed the stereospecific additions to excited singlet biscarbene **26**, initially formed in the photolysis. Dilution with cyclohexane then was considered to permit intersystem crossing to higher multiplicity states, which added to olefin in nonstereospecific manner. Again, however, the results may be equally well accommodated by reactions of incipient monocarbenes.



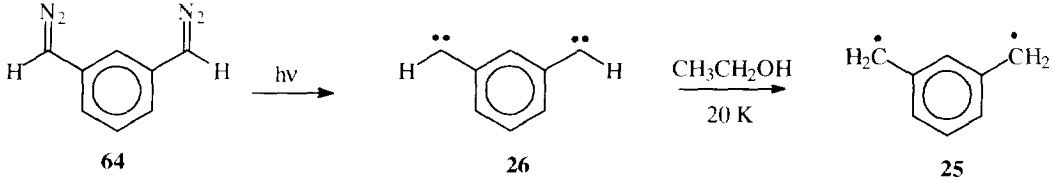
Iwamura and co-workers explored in more detail the question whether photolysis of bisdiazo compound **60** proceeds via a trappable monocarbene in solution, or whether one photon might cause double denitrogenation.[53] Low-temperature matrix experiments have, in fact, suggested that single photon - multidenitrogenations can occur in polydiazocompounds (vide infra). Two experiments were carried out. In the first, they found that irradiation of **60** in an isopropyl alcohol/ether solution gave a 32:9:1 ratio of **69**, **70**, and **65**. In similar trapping of diphenylmethylene, OH insertion products such as **69** have been attributed to the singlet state of the carbene, whereas reduction products are due to H-abstraction in the triplet. The authors suggested that the ratio of products was statistically consistent with either initial monocarbene formation, or biscarbene reaction where the two carbene centers reacted independently.



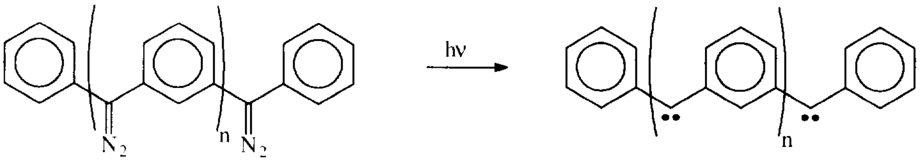
In their second experiment, **60** was irradiated to 25% completion in isopropyl alcohol. The mixture was then treated in the dark with *p*-nitrobenzoic acid (PNB) to destroy unreacted diazo groups. Mainly **72** and **73** were obtained, and no biscarbene isopropanol adducts **69** or **70** were detected. It was thus concluded that no biscarbene was formed in the solution photolyses. Thus, earlier reports[52] of solution trapping of biscarbene **61** (vide supra) were likely in error.



Wright and Platz directly observed H-abstraction reactions of the parent biscarbene **26**, leading to the first EPR characterization of *m*-xylylene (**25**).[30] Bisdiazo compound **64** was irradiated in ethanol-d_6 at 22 K to give quintet **26**. Warming to 77 K caused the disappearance of the EPR quintet signals and concurrent growth of triplet signals of **25** (d_2). Irradiation of **64** in natural abundance ethanol, on the other hand, gave EPR signals of both **26** and **25** even at 20 K. The quintet biscarbene was not stable at these temperatures in the protonated glass, and it decayed to the biradical. A monocarbene - monoradical intermediate was not observed in either experiment.

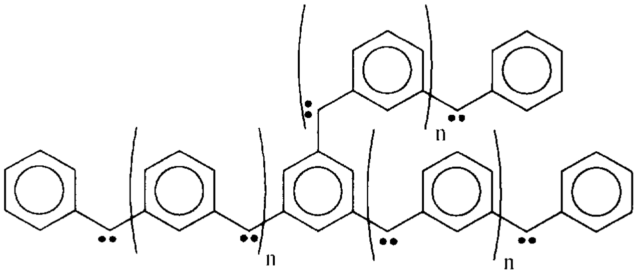


Itoh and Iwamura, together with their co-workers, have extended this *m*-phenylene-coupled polycarbene motif to produce hydrocarbons with very high spin, e.g. **75**.[7,55-63] After the first suggestion by Mataga[64] that these systems might form the basis for organic ferromagnets, there has been considerable interest in their possible practical application. The analogy has been drawn between the electronic interactions in these polycarbenic systems and those between conducting s-electrons and localized d-electrons in ferromagnetic transition metals. The alternant π-networks in these systems have n+1 nominally degenerate, non-disjoint, nonbonding MOs, each singly occupied. There are similarly n+1 localized σ-unshared electrons. For reasons analogous to those described earlier, this situation for **75** affords ground-state multiplicities of 2n+3.



74 **75**

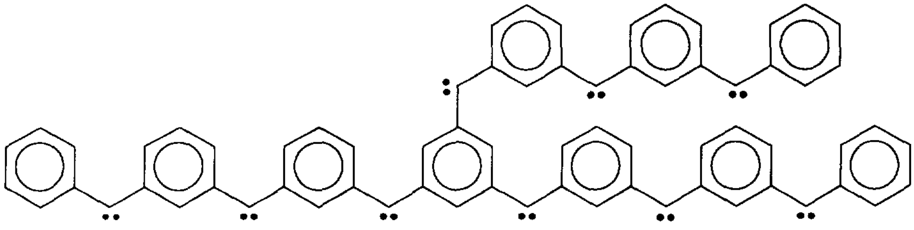
The linearly attached *m*-phenylene-coupled carbenes serve as models for one-dimensional ferromagnets. This work has also been extended to two-dimensional systems of the form **76**. Here again, the MO topology is such that each phenylmethylene unit contributes one additional singly-occupied nonbonding π-MO to the system.



76

The EPR and magnetic susceptibility measurements on these arrays of high-spin coupled polycarbenes have been reviewed repeatedly,[7,55-63] and hence only a brief description will be given here. In all cases, the polycarbenes have been generated at low temperatures by irradiation of the corresponding polydiazocompounds **74**, usually in single crystals of benzophenone or other arylketones. Interestingly, the completely denitrogenated polycarbene is in general the only species observed by EPR; no intermediate mixed diazo-carbenes of lower spin are observed. The signals for the polycarbene appear immediately on irradiation of the low-temperature crystals, and the rate of growth of the EPR signals depends linearly on light intensity. These observations have led to the remarkable suggestion that absorption of a single photon causes complete multiple denitrogenations in these starting materials.[7,55-63] The exact mechanism of this unusually efficient photochemical process is still unknown. It has been proposed, however, that the thermal energy liberated in each exothermic denitrogenation remains in the molecule to give a vibrationally "hot" intermediate, which undergoes subsequent denitrogenation in competition with cooling.[53] As described earlier, this multidenitrogenation process does not seem to occur in solution, where vibrational relaxation may be more facile.[53]

The EPR results for the *m*-phenylene-coupled polycarbenes that have thus far been characterized are summarized in Table 1. It can be seen that the D values decrease with increased multiplicity, as discussed earlier. Itoh and co-workers[7c,59,63] have proposed that the D values for these polycarbenes are dominated by the one-center interactions of the n and p carbene electrons. They have derived the approximate relationship that |D| should be inversely proportional to 2S-1, where S is the total spin of the system. As can be observed in Table 1, (2S-1)|D| is approximately constant over this series of systems. In all these molecules, only the highest multiplicity electronic states are observed up to temperatures of decomposition, generally >160 K. Thus, the high-spin ground states are separated from lower-multiplicity excited states by at least 0.85 kcal/mole. Finally, multiple conformations showing slightly different zero field parameters are generally observed and can often be interconverted thermally. In this fashion, systems with amazingly-high spin have been generated, with the current record holder being **77** with a multiplicity of 19, confirmed by magnetic susceptibility measurements. The EPR spectrum was not analyzed but was reported to exhibit a complexity consistent with a nonadecet ground state.[71,65]

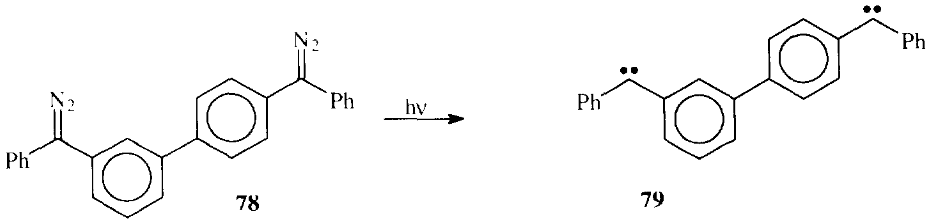


77

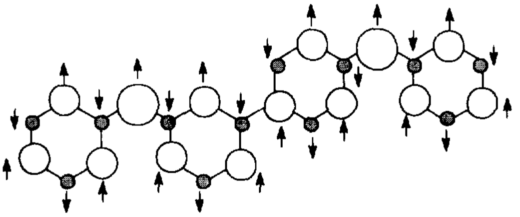
Table 1. Zero-Field Parameters for *meta*-phenylene coupled polycarbenes

Polycarbene	Multiplicity	|D|/hc (cm^{-1})	|E|/hc (cm^{-1})	(2S-1)|D|	References
26	5	0.0844	0.0233	0.253	27
61	5	0.0713	0.019	0.214	49, 50
75:					
n = 2	7	0.0487	0.0089	0.244	55
n = 3	9	0.0332	0.0031	0.232	7d,55 - 59
n = 4	11	0.0168	0.0036	0.151	60
76:					
n = 0	7	0.04158	0.01026	0.208	61
n = 1	13	0.01909	0.00193	0.210	62,63

As described earlier in part B, the carbene-coupling properties of the biphenyl unit are more complicated than those of a simple benzene. Teki et al. have reported EPR spectra of the 3,4'-isomer of bis(phenylmethylene)biphenyl, **79**, which they have termed a π-topological isomer of the 3,3'- (**56**) and 4,4'- (**47**) derivatives described earlier.[45,46] Biscarbene **79** was generated by low temperature irradiation of the corresponding bisdiazo compound **78** in benzophenone. In contrast to **56**, this *meta* - *para* isomer is a ground state quintet, with |D|/hc = 0.1256 cm^{-1} and |E|/hc = 0.0058 cm^{-1}. The quintet signal follows the Curie Law from 4.2 to 250 K, so it was suggested that lower multiplicity excited states are at least 300 cm^{-1} (0.86 kcal/mole) higher in energy. In this case, the unpaired carbenic π-electrons occupy non-disjoint NBMOs, so exchange interaction favors parallel spins (Hund's rule followed). The authors also suggest the alternative interpretation that a pseudo π-spin density wave is possible in this hydrocarbon (in contrast to the case for **56**). Spin density distributions calculated by Hubbard type UHF calculation, shown in the accompanying figure, were consistent with ENDOR experiments.

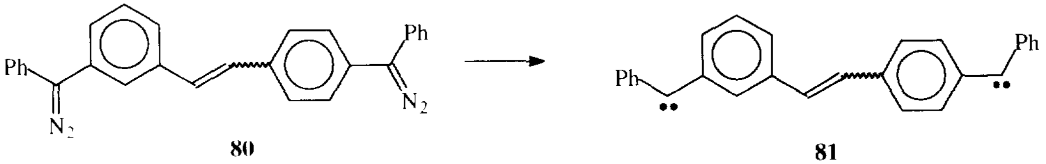


78 **79**



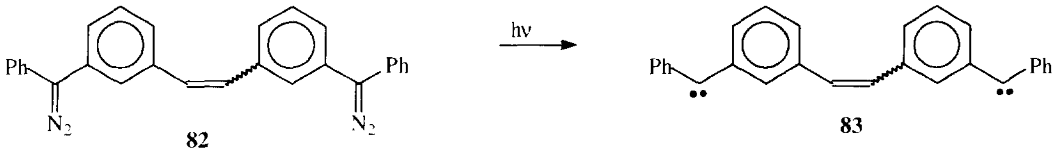
Spin density distribution for 79 and π - SDW

Iwamura's group has investigated a related set of π-topological isomers.[67] Irradiation of the ethylene-linked bisdiazo compound **80** (cis or trans) at 16 K in 2-MTHF gave complex EPR signals attributed to the *meta - para* quintet biscarbene **81**. The spectra were not analyzed to obtain zero-field parameters, however. The signals decreased with increasing temperature following the Curie law. The authors indicated that the unpaired π-electrons in **81** occupy non-disjoint NBMOs, and thus should be high-spin coupled as confirmed by the experimental results.



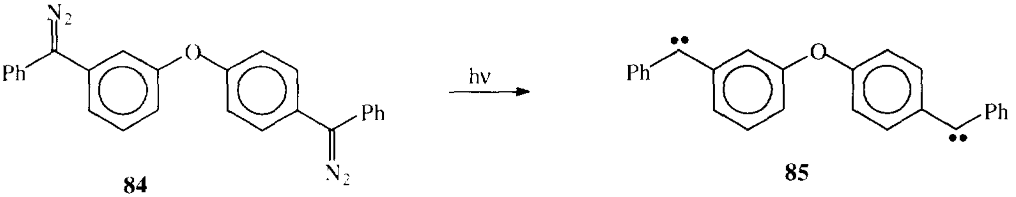
80 **81**

In contrast, irradiation of the *meta-meta* isomer **82** at 16 K gave a triplet carbene signal, as well as a quintet absorption that they attributed to biscarbene **83**.[67] The workers proposed that the triplet arose from monodiazo-monocarbene or from monocarbene formed by reaction with surroundings. The quintet signals increased as the temperature of the matrix was raised, to a maximum at 50 K, and then decreased irreversibly at higher temperatures. It was proposed that **83** possesses a singlet ground state with an excited quintet state lying ca. 200 cal/mole higher in energy. The triplet excited state expected to lie between the singlet and quintet was not observed, however.



82 **83**

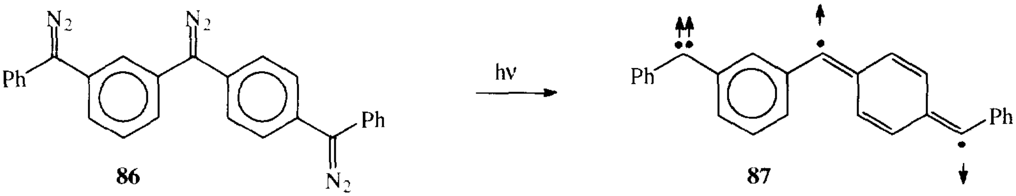
Itoh and co-workers have found that an oxygen bridging atom can also serve as a ferromagnetic coupler (in contrast to the cases of **58** and **59** described earlier).[47] Irradiation of the 3,4'-ether linked bisdiazo compound **84** in single benzophenone crystals at 4.2 K gave biscarbene **85** by EPR. Few details have been reported thus far, but **85** was indicated to have a quintet ground state with a close lying triplet (40 cal/mole higher). Thus, it appears that the "superexchange coupling" between the triplet carbene subunits is only weak.



84 **85**

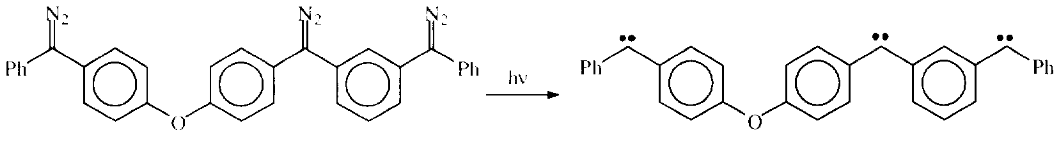
D. *Mixed Coupled Triplet Carbenes*

Itoh and co-workers have investigated an interesting triscarbene system that combines aspects of both ferromagnetic and antiferromagnetic coupling.[68-70] Irradiation of trisdiazocompound **86** at 4.2 K in single crystals of benzophenone gave a triplet EPR signal, with $|D|/hc = 0.23356\ cm^{-1}$ and $|E|/hc = 0.01073\ cm^{-1}$. Warming the crystal to 50 K reversibly gave a quintet signal with $|D|/hc = 0.06845\ cm^{-1}$ and $|E|/hc = 0.00237\ cm^{-1}$. The authors suggest that these signals arise from carbene-diradical **87**. The three σ-unshared carbenic electrons were considered to adopt a low-spin (S=1/2) subsystem, because of through bond and through space interactions. Ferromagnetic coupling with the solitary π-unshared electron then leads to the triplet ground state. The excited state quintet, higher in energy by ca. 114 cal/mole, arises from ferromagnetic coupling of the π-electron with a high-spin (S=3/2) σ-electron subsystem.[68-70]



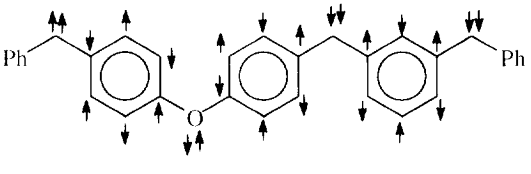
86 **87**

Antiferromagnetic coupling between two subsystems with different multiplicity can lead to inexact cancellation resulting in residual spin; such interaction has been termed ferrimagnetic.[45] An *intramolecular* ferrimagnetic system has been described by Itoh, Teki, and co-workers.[45,47,71] Irradiation of *para-para* ether-linked trisdiazo compound **88** at 4.2 K in benzophenone single crystals gave strong triplet signals attributed to the ground state of triscarbene **89**. Zero-field parameters $|D|/hc = 0.24465\ \mathrm{cm}^{-1}$ and $|E|/hc = 0.03433\ \mathrm{cm}^{-1}$ were assigned. Triplet monocarbene and quintet biscarbene signals were also observed, and were ascribed to partially decomposed diazo precursors formed during sample preparation. Warming the crystal to 10 K caused the appearance of quintet signals for **89**, with $|D|/hc = 0.047\ \mathrm{cm}^{-1}$, and warming to higher temperatures produced septet **89** with $|D|/hc =$ ca. $0.067\ \mathrm{cm}^{-1}$. The authors [45,47,71] propose that the triplet and quintet subunits are antiferromagnetically coupled by superexchange with the lone pairs of the oxygen bridging atom, giving an overall triplet ground state. The interaction between the spin-systems is weak, however, giving only small energy separations between different electronic states.



88 **89**

ENDOR experiments are consistent with this superexchange coupling in triplet **89**.[71] In particular, they show reversal of the spin-density signs at corresponding carbons in the biscarbene and triscarbene moieties. The observed hyperfine couplings were consistent with a perfectly alternating π-spin density wave in the triplet ground state, as shown in **89a**.



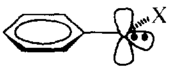
89a

IV. Aryl Linked Singlet Carbene Subunits

A. Background

As can be seen from the previous discussion, the emphasis on high-spin polycarbenes has led to extensive investigations centered around triplet diphenylcarbene, and to a lesser extent around phenylcarbene, subunits. However, to probe various other possible electronic states in polycarbenes (see Introduction), it is necessary to consider interactions involving singlet carbene moieties in these systems. Toward this end, our research group has begun to explore combinations of aryl-coupled halocarbenes.

It is worthwhile to consider briefly some pertinent aspects of arylhalocarbenes. In contrast to phenyl- and diphenylcarbene, the phenylhalocarbenes (**90**) are ground state singlets with "closed shell" electronic structures as shown.[3,72,73] The singlet states of these halocarbenes are favored by lone-pair donation from the halogen to the p-orbital of the singlet, along with stabilization of the carbenic σ-electrons via a through-bond inductive effect. Although the singlet-triplet gaps in aryl carbenes **90** are not known with certainty, calculations on simpler systems indicate that F is the most strongly singlet stabilizing, followed by Cl, and then Br.[73] Consistent with this picture, the IR spectra of arylhalocarbenes measured under low temperature matrix isolation conditions bear close resemblance to the non-carbonyl regions of the corresponding benzoyl halides.[72] The UV/vis spectra of **90** are dominated by strong absorption at ca. 300 nm, possibly due to π,π* transitions. Weaker visible σ,π* transitions are also observed, in the region 700 - 800 nm for Cl, and Br, and 500 - 600 nm for F substituted carbenes.[74,78]

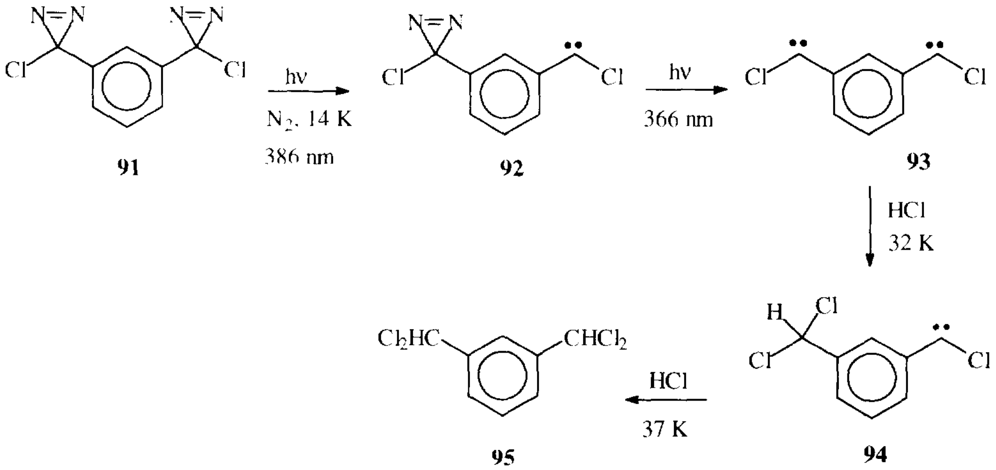


90 **X = F, Cl, Br**

In the following sections, we describe several systems comprising singlet carbenes linked across aromatic rings. Since these are nonmagnetic subunits, it is something of a misnomer to describe these systems as ferromagnetically or antiferromagnetically coupled. However, for consistency between this section and the previous discussions of triplet subunits, we will retain this organization.

B. "Ferromagnetically" Coupled Singlet Carbenes

The *meta*-phenylene unit has played a key role in communicating spin information between triplet carbene subunits. In contrast, however, we have found that singlet carbenes linked across a *meta*-benzene show little

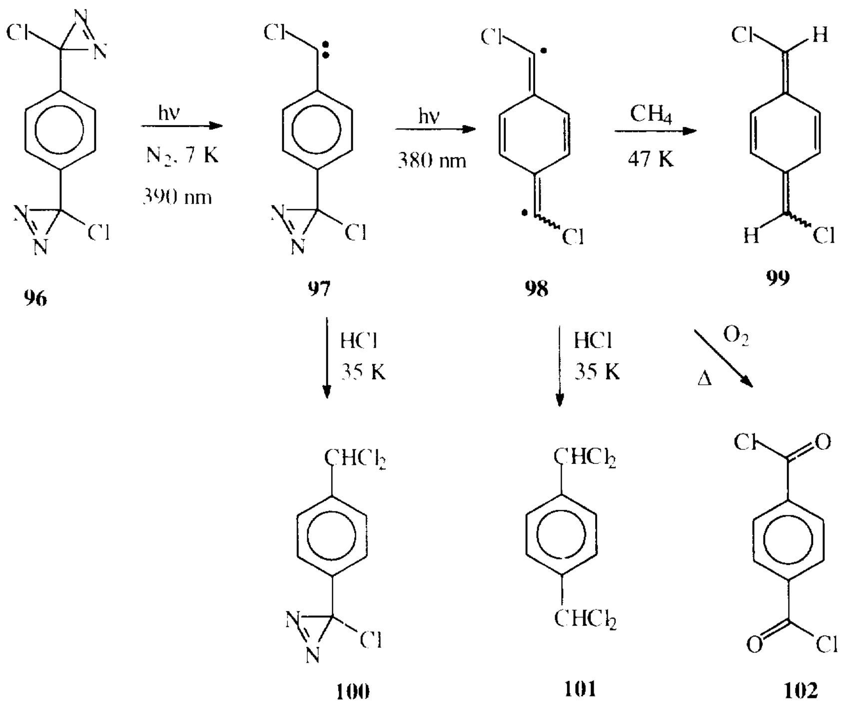


difference from the separate subunits.[74] Irradiation of *meta*-bisdiazirine **91** in a N_2 matrix at 14 K with 386 nm light produced monodiazirine **92**, characterized by IR, UV/vis, and *in situ* trapping with HCl. Subsequent irradiation with 366 nm light converted **92** into biscarbene **93**. Warming an HCl-doped N_2 matrix of **93** to 32 K produced mono-trapped product **94**, assigned through its IR spectrum. Continued warming to 37 K gave bis-adduct **95**. Both monocarbene **92** and biscarbene **93** had strong 300 nm UV and weak 740 nm visible absorptions.

The IR spectrum of biscarbene **93** is very similar to that of isophthaloyl chloride (minus the carbonyl bands).[74] This evidence supports the assignment of a bis-singlet carbene structure for **93**. The vibrational spectrum predicted by 6-31G* ab initio calculations for this structure also strongly resembles the experimental IR. No peculiarities in the electronic spectra signifying any radical character, as might be expected for higher multiplicity states, were observed. Finally, triplet carbenes characteristically trap molecular oxygen at low temperatures to give carbonyl oxides.[75] Biscarbene **93**, however, was unreactive to O_2 at low temperatures. All of these data confirm that **93** represents a closed-shell bis-singlet carbene species, as distinct from *m*-phenylenebiscarbenes previously investigated.

C. *"Antiferromagnetically" Coupled Singlet Carbenes*

Work in our group,[76] and similarly by Tomioka et al.[77] has indicated that *p*-phenylene-linked singlet carbenes can behave profoundly differently than the corresponding isolated carbenes. Irradiation (390 nm) of *p*-bischlorodiazirine **96** matrix isolated at 7 K in N_2 gave monocarbene **97**. The nπ* diazirine absorption of **97**



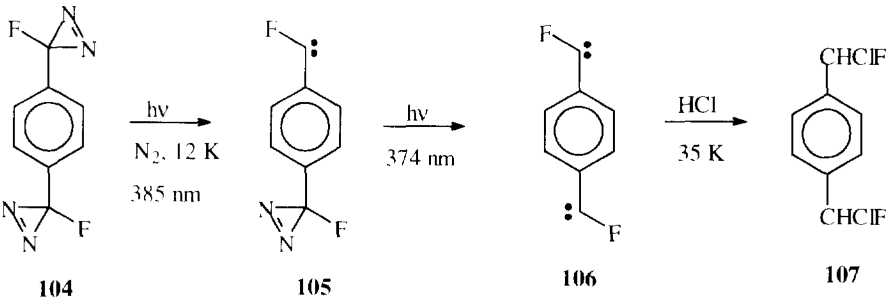
shifts to shorter wavelength (relative to that in the precursor **96**) and thereby protects the monocarbene from the 390 nm irradiation. The monocarbene **97** was characterized by IR, UV/vis, and trapping with HCl to give**100**. Shifting the wavelength of irradiation to 380 nm converted **97** to biradical **98** in the IR. Warming an HCl-doped N_2 matrix containing **98** to 35 K caused disappearance of the IR bands (and UV/vis spectrum) of **98** and growth of those of trapped product **101**.[76]

Considerable evidence supports the biradical structure **98**, rather than a bis-singlet carbene electronic configuration akin to **103**.[76] (1) The IR spectrum of **98** does not resemble that of terephthaloyl chloride (**102**). In particular, **102** lacks ring-breathing modes in the 1600 cm^{-1} region for symmetry reasons. Terephthaloyl chloride's (**102**) strongest bands, attributed to exocyclic C-C stretching, are in the region of 1300 - 1000 cm^{-1}. In contrast, **98** has its strongest IR absorption at 1582 cm^{-1} (C=C), and only minor absorption in the 1200 cm^{-1} region. (2) The quinonoid diradical **98** exhibits highly structured UV/vis absorption in the region 400-500 nm, where phenylchlorocarbene is transparent. This electronic spectrum, which resembles that of phenyl radical and which may similarly arise from a $\pi \rightarrow \sigma$ transition, lends a golden-yellow color to matrices containing **98**. (3) Diradical **98** is extremely reactive with hydrocarbons. Warming in a CH_4 matrix to 47 K converted **98** to quinodimethane **99** and methyl radical. Phenylchlorocarbene, in contrast, is stable in even more reactive organic glasses at 77 K. (4) Diradical **98** abstracts hydrogen from hydrocarbons, in contrast to the usual CH insertion observed for singlet carbenes. (5) Diradical **98** readily reacts with O_2 under matrix conditions to give terephthaloyl chloride (**102**), likely via the corresponding biscarbonyloxide.[77] Singlet phenylchlorocarbene only reacts reluctantly with O_2 under similar conditions.[72]

103 (syn/anti)

In the case of **98**, the potential gain in extra π-bonding in a quinonoid structure must override the closed-shell σ^2 tendencies of the chlorocarbene moieties. Fluorine is known to stabilize singlet carbenes more strongly than does chlorine. Thus, we reasoned that the *p*-bisfluoro system might more resemble a biscarbene.[78] Irradiation (385 nm) of bisdiazirine **104** matrix isolated in N_2 at 12 K gave the deep-blue monocarbene **105**. The monodenitrogenated **105** was characterized by IR, UV/vis, and HCl trapping. Subsequent irradiation at shorter wavelengths (374 nm) converted **105** into biscarbene **106**. As before, **106** could be trapped in situ with HCl to give **107**.[78]

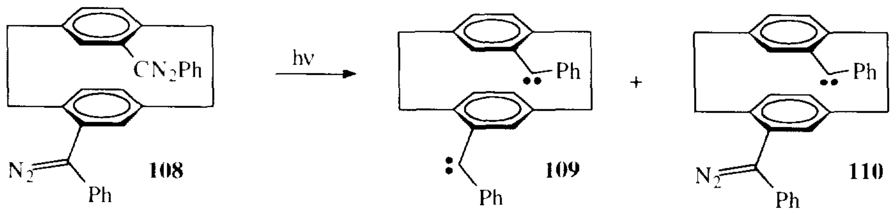
In this case, the following experimental evidence strongly supports a bis-singlet carbene structure for **106**.[78] (1) The IR spectrum of **106** closely resembles that of terephthaloyl fluoride. In particular, no strong ca. 1600 cm^{-1} absorptions for exocyclic double bonds are observed. The IR spectrum could be nicely simulated by ab initio 6-31G* calculations. (2) The UV/vis spectra for **106** (300 and 600 nm) are only slightly shifted from those of phenylfluorocarbene. (3) No H-abstraction of hydrocarbon matrices by **106** is observed up to at least 60 K. (4) Biscarbene **106** does not react with O_2 under cryogenic conditions.



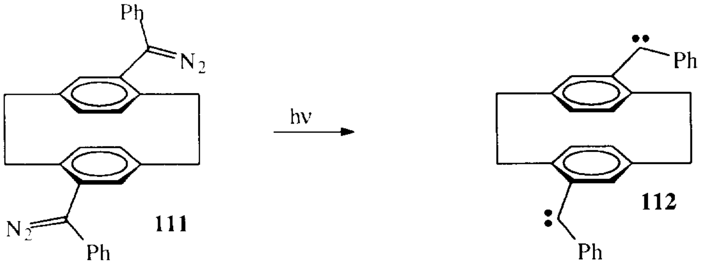
V. Unconjugated Polycarbenes

A handful of reports have described systems incorporating biscarbenes that are not directly conjugatively coupled. For true ferromagnetic materials to be realized from combinations of organic high-spin subunits it will be necessary to engineer systems where three-dimensional ferromagnetic interactions are favorable. Random aggregates of triplet carbenes, however, have been shown to interact through space in an overall antiferromagnetic manner.[79] Iwamura's group has cleverly designed and investigated biscarbenes built onto [2.2]-paracyclophanes, where the facial interaction of triplet carbene subunits can be controlled. The exchange interaction between the carbenes, and hence the overall multiplicity, depends on their relative orientation.[80]

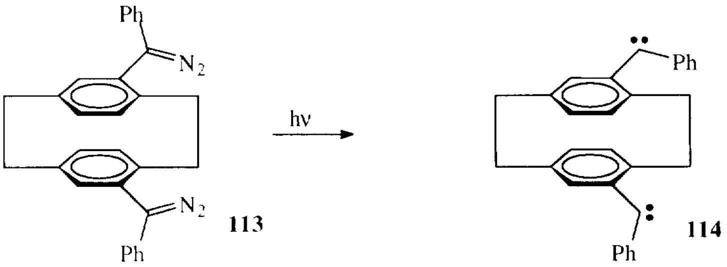
A pseudo-*ortho* orientation of two phenylmethylenes was found to be overall ferromagnetic.[80] Irradiation of the pseudo-*ortho* bisdiazo compound **108** at 11 K in 2-MTHF gave a strong quintet EPR signal for biscarbene **109** with |D|/hc = 0.0624 cm^{-1} and |E|/hc = 0.0190 cm^{-1}. A triplet signal attributed to monocarbene **110** was also observed. The time dependence of the EPR intensities suggested that **110** was the photochemical precursor of **109**. A triplet biradical absorption with a small D value increased in intensity as the quintet spectrum decreased above 50 K, and was suggested to arise from the products of H-abstraction by **109** from the matrix. Finally, at temperatures higher than 20 K, a new triplet species was detected, with estimated values of |D|/hc = 0.1872 cm^{-1} and |E|/hc = 0.0570 cm^{-1}. The workers suggested that the triplet represents the excited state of **109**, and lies 0.18 kcal/mole above the ground state.



Photolysis of the pseudo-*para* bisdiazo compound **111** similarly gave a quintet biscarbene **112**, with |D|/hc = 0.1215 cm^{-1} and |E|/hc = 0.0085 cm^{-1}. Monocarbene and the biradical product from H-abstraction were again observed. In this case, the biscarbene **112** reacted with the matrix even in the temperature range 15 - 41 K. Although this reactivity complicated matters, they did not observe a thermally-populated triplet excited state, suggesting a larger quintet-triplet energy gap in **112** compared to **109**.[80]

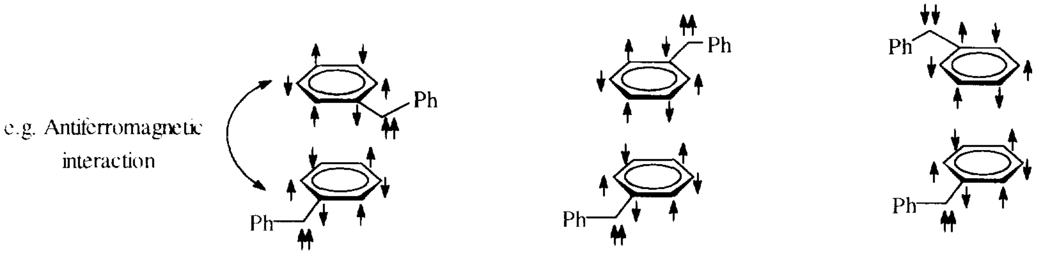


The pseudo-*meta* system gave different results. Irradiation of bisdiazocompound **113** in 2-MTHF at 12 K produced no biscarbene signal, and only monocarbene and H-abstraction product were observed in the EPR at these temperatures. Warming to 25 K, however, gave a triplet spectrum with $|D|/hc = 0.1840$ cm^{-1} and $|E|/hc = 0.0023$ cm^{-1}. The triplet signals reached a maximum intensity at 65 K, and began to decay irreversibly



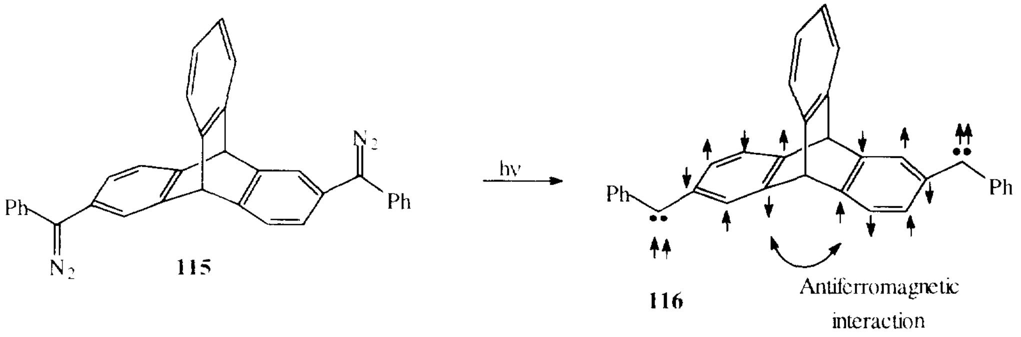
at higher temperatures. The authors suggested that pseudo-*meta* biscarbene **114** is a ground-state singlet, with a thermally accessible triplet state 0.28 kcal/mole higher in energy.[80]

These results have been interpreted[80] on the basis of an earlier suggestion by McConnell[81] for the possible ferromagnetic facial interaction between odd-alternant radicals. Through-space face-to-face interaction between two radicals is inherently antiferromagnetic. That is, the covalent interaction between two radical centers always favors electron pairing. Because of the natural alternation of up and down spins in the π-systems of diphenylcarbene, however, these through-space interactions can lead to overall high-spin coupling if two carbenes are oriented in the right fashion. The pseudo-*ortho* (**109**) and pseudo-*para* (**112**) biscarbenes, as shown, are aligned such that through-space antiferromagnetic interactions between the benzene rings give parallel spins in the carbene subunits. In the pseudo-*meta* system **114**, however, the antiferromagnetic overlaps between the rings produce antiparallel carbene spins.[82]



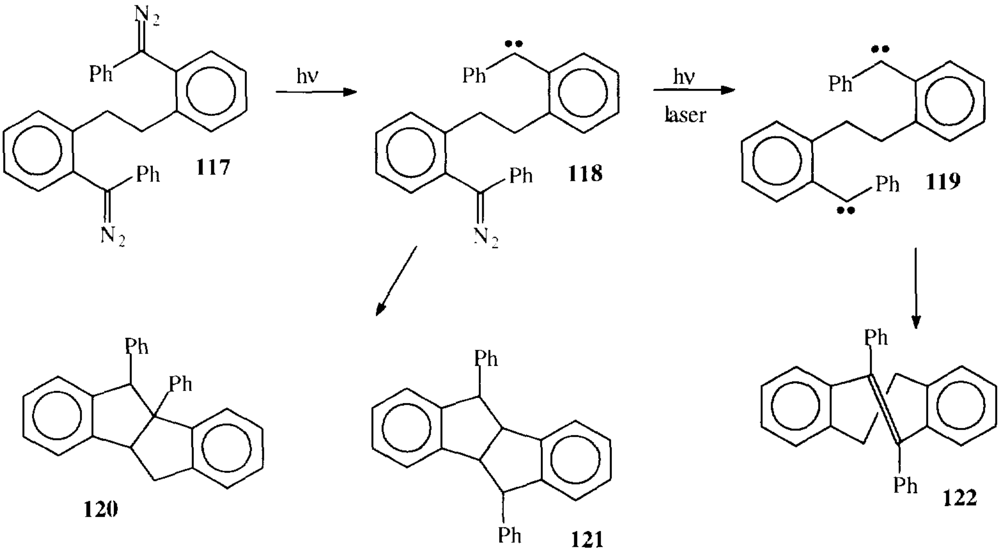
ψ - ortho ψ - para ψ - meta

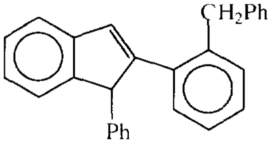
Tukada and Mutai have investigated a bis(diphenylcarbene) where the aromatic rings interact through space in a different fashion.[83] Photolysis of a 2-MTHF glass of tryptycenyl bisdiazocompound **115** at 22 K gave a quintet signal assigned to biscarbene **116**, with |D|/hc = 0.0665 cm^{-1} and |E|/hc = 0.0043 cm^{-1}. Although a triplet monocarbene signal was also observed, possibly from a stepwise intermediate on the way to **116**, no triplet corresponding to the excited state of **116** was detected up to 80 K. In analogy to the paracyclophane results described above, the favored antiferromagnetic through-space interaction shown in **116** was suggested to lead to overall high spin coupling.[83]



115 **116**

Hannemann and Wirz have used high-intensity laser irradiation to generate a system comprising two independent carbene centers.[84] Conventional irradiation of bisdiazo compound **117** at 254 nm in solution lead to products **120**, **121**, **123**, and **124**, attributed to sequential monocarbene formation and reaction. In contrast, photolysis of **117** with a pulsed excimer laser at 248 nm gave the olefinic product **122** in 49% yield. The authors suggest that under the more intense laser irradiation conditions, the initially formed monodiazocompound absorbs an additional photon, producing biscarbene **119** before intermolecular reaction can occur. The bis-triplet carbene was then suggested to dimerize to the twisted triplet excited state of **122**, relaxation of which gives the observed E-isomer of product.





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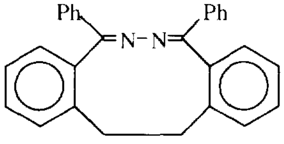
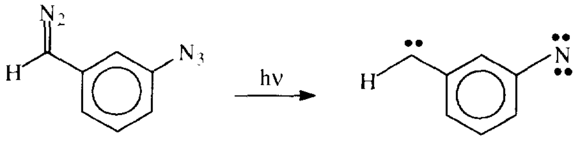


124

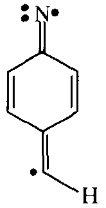
VI. Miscellaneous Related Systems

Considerable work has been published on polyarylnitrenes.[7i,n,85,91] These systems share many theoretical and experimental features with the polycarbenes described above, and have similarly been considered as prototypes for high-spin organic materials. Unfortunately, space does not permit us to discuss all the elegant studies carried out in this area. We will mention, however, two reported systems that combine carbene and nitrene functionalities.

Tukada et al.[86] found that irradiation of *meta*-diazoazide **125** in 2-MTHF at 18 K gave quintet **126** in the EPR with |D|/hc = 0.124 cm^{-1} and |E|/hc = 0.002 cm^{-1}. The D value lies between that for the biscarbene **26** (0.0844 cm^{-1}) and the corresponding *meta*-bisnitrene **63** (0.156 cm^{-1}). A mononitrene triplet signal was also observed. The carbene-nitrene **126** exhibited Curie law dependence up to 77 K, at which point the signals disappeared irreversibly. Interestingly, a high-multiplicity ground state is again observed as in the biscarbenes, even though the singly occupied π-NBMOs must now be nondegenerate. Similar heteroatomic biradicals and tetraradicals have been observed to exhibit high multiplicity by Berson[25a] and by Platz.[87]



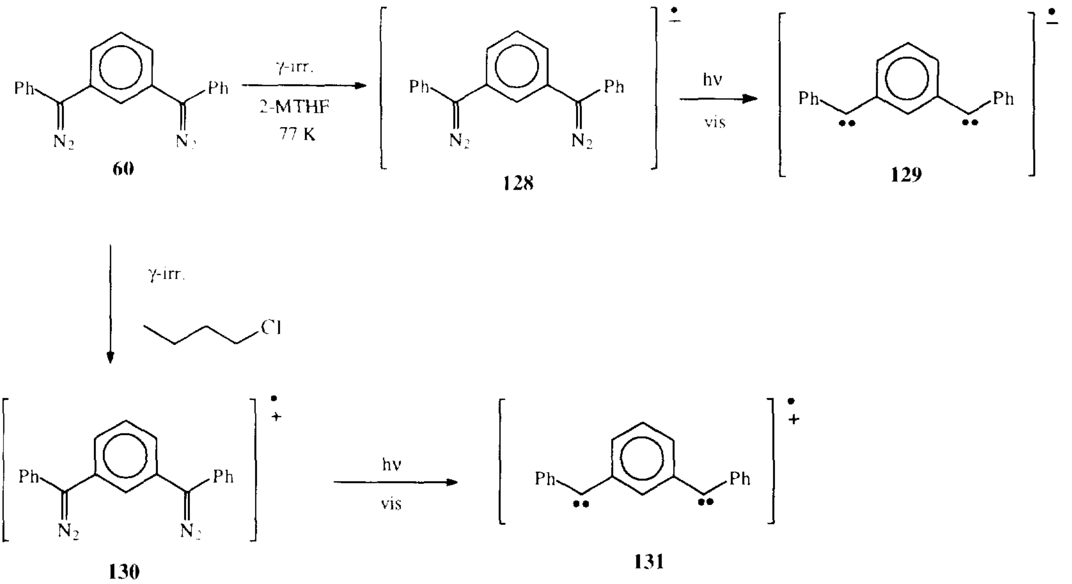
125 **126**



127

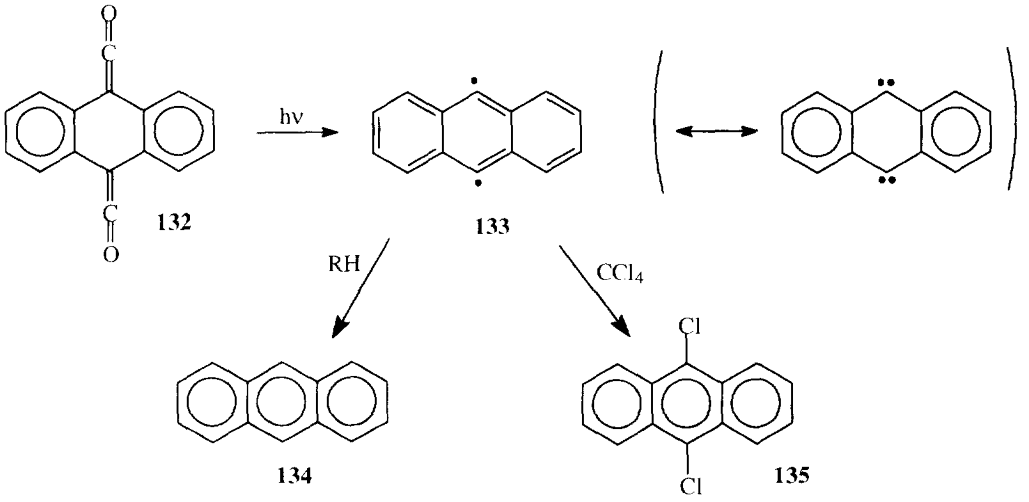
Koseki et al. have reported preliminary IR results on the *para*-nitrenocarbene **127**, photochemically generated from the corresponding diazoazide in a low temperature Ar matrix.[88] MCSCF calculations (although with a minimal basis set) favor the singlet quinoidal biradical structure shown. The authors suggested that facile reaction with O_2 at cryogenic temperatures indicates a close lying triplet state. The singlet biradical, however, may also react with oxygen readily (cf. **98**).

Workers have recently begun to investigate radical ions of polycarbenes.[89] On γ-irradiation, matrices of the *meta*-bisdiazo compound **60** in 2-MTHF (acting as an electron-donating medium) at 77 K gave the corresponding radical anion **128**, characterized by strong visible absorption. Irradiation of **128** with visible light caused bleaching together with the appearance of quartet signals in the EPR, with $|D|/hc = 0.12$ cm^{-1} and $|E|/hc = 0.0045$ cm^{-1}. These EPR spectra were attributed to radical anion **129**. Similarly, γ-irradiation of **60** in a chlorobutane glass (acting as an electron-accepting medium) gave the bisdiazo radical cation, **130**. Subsequent photolysis with visible light produced the radical cation of the biscarbene, **131**, with $|D|/hc = 0.1350$ cm^{-1} and $|E|/hc = 0.0040$ cm^{-1}. The EPR and electronic spectra of **129** and **131** were very similar to each other, as expected by the pairing theorem for alternant hydrocarbons.[89]



60 **128** **129** **130** **131**

Finally, we have noted[76] the analogy between quinoidal *para*-biscarbenes (such as **21**) and 1,4-didehydroaromatics. Chapman and co-workers[90] have, in fact, reported a "carbenic" route to a didehydroaromatic compound. Irradiation of bisketene **132** at 77 K in 3-methylpentane gave a new species in the UV with structured absorption ranging from 300 - 460 nm, which they attributed to 9,10-didehydroanthracene (**133**). Warming led to anthracene (**134**); warming in the presence of 3 % CCl_4 also produced 9,10-dichloroanthracene (**135**). Irradiation of **132** in Ar at 8 K gave CO and a new species with strong IR absorptions at 710 and 760 cm^{-1}, also assigned to **133**. No monocarbene intermediate was observed in the UV or EPR spectra, suggesting either that double decarbonylation occurs, or that the intermediate ketocarbene is photochemically destroyed more rapidly than starting material.



VII. Conclusions and Future Outlook

Available evidence convincingly demonstrates that the chemistry of polycarbenes does in fact extend beyond that of carbenes. It should also be clear that, despite considerable effort over the past 30 years, this area still has great untapped potential. The high reactivity of triplet carbenes presents a problem for real-life applications, yet the study of high spin polycarbenes will continue to help shape the development of organic magnetic materials. To fulfill this potential, however, design of polycarbene systems will need to move from two-dimensional to three-dimensional arrays.

Other obvious areas also warrant further attention. Few of the polycarbenes that have been studied have been characterized by methods other than EPR (including ENDOR) or magnetic susceptibility. Other spectroscopic techniques might shine a clearer light on the structural properties of these species. There also exists a paucity of information on the chemical reactivity of these species, especially in relation to their multiplicity. Finally, most of the investigations thus far have concentrated on high-multiplicity polycarbenes.

As stated in the introduction, 11 physically realistic electronic states are in fact possible for a biscarbene. Work in our laboratories and elsewhere is beginning to probe these other electronic situations.

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