

Triradicals

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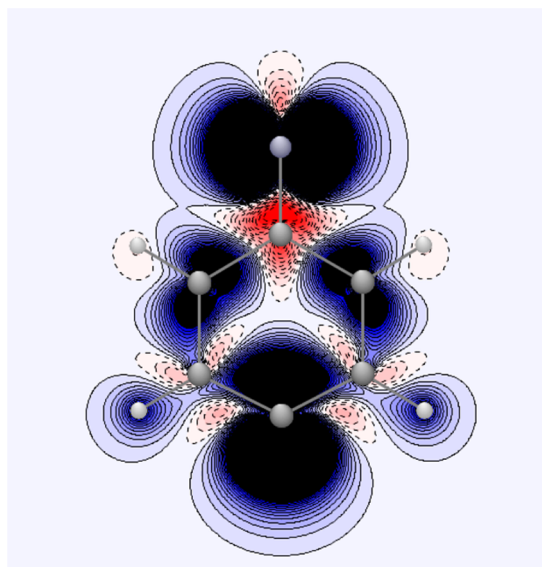
CONSPECTUS

Consistent with the definition of diradicals, triradicals are species in which three electrons occupy three (nearly) degenerate orbitals, resulting in close-lying quartet and doublet states. The same concepts and rules that can be used to predict and rationalize the ground state multiplicity of diradicals also apply to triradicals, but the greater number of states in triradicals generally leads to more complex electronic structures.

Most experimentally accessible triradicals are based on organic π -systems; therefore triradicals are classified according to the σ/π symmetry of the nominally nonbonding molecular orbitals (NBMOs). The tridehydrobenzenes are prototypical $\sigma\sigma\sigma$ triradicals with doublet ground states and significant doublet–quartet energy splittings. In all three isomers, the ordering of electronic states depends critically on the distance between the m -radical centers, which makes computational studies of these systems demanding. The experimental IR spectrum of matrix-isolated 1,2,3-tridehydrobenzene led to a revision of the previous ground state assignment based on computations. This work demonstrates the close interplay between experiment and theory in this realm of reactive intermediate chemistry.

1,3,5-Tridehydrobenzene can be isolated as its trifluoro derivative. The stabilization of dehydrophenyl nitrenes, typical members of the $\sigma\sigma\pi$ family of triradicals, also requires *ortho*-fluorination. Because of their quartet ground states, derivatives of 2-dehydrophenyl nitrene and 4-dehydrophenyl nitrene could be studied using IR or EPR spectroscopy. The zero-field splitting parameters of these systems provide direct evidence for the contribution of carbenoid resonance structures to the resonance hybrid of the high-spin systems. According to computations, the through-bond coupling of the in-plane electrons thermodynamically stabilizes the doublet ground states of m -dehydrophenyl nitrenes. But for the same reasons, these systems are prone to ring-opening reactions, which make them difficult to isolate. Remarkably, the m -phenylene unit leads to strongly antiferromagnetic coupling in $\sigma\sigma\pi$ triradicals, while *o*- or *p*-coupling results in high-spin systems. The more common all- π systems show the opposite pattern because the latter connectivity naturally results in closed-shell arrangements.

Within the family of $\sigma\pi\pi$ triradicals, we could characterize 2-dehydro-*m*-xylylene and 4-dehydro-*m*-xylylene by EPR spectroscopy, whereas the 5-isomer features a doublet ground state. This observation is readily rationalized considering the nodal characteristics of the NBMOs involved and by simple spin polarization models. 1,3,5-Trimethylenebenzene strongly prefers ferromagnetic coupling and features a robust quartet ground state. We have synthesized this $\pi\pi\pi$ triradical in cryogenic matrices and characterized it by IR and EPR spectroscopy. Interestingly, the triradical is photochemically much more stable than *m*-xylylene, a diradical that shows fascinating rearrangements upon irradiation in cryogenic matrices.



Introduction

Diradicals are well-established reactive intermediates in organic chemistry, although the precise definition of this term is far from trivial.^{1–3} In their seminal contribution, Salem and Rowland suggested defining a diradical within the framework

of molecular orbital (MO) theory as a species in which two electrons occupy two degenerate or near-degenerate orbitals, leading to a close-lying singlet–triplet pair of electronic states.¹ This electronic definition avoids the ambiguities of older chemical demarcations (mostly based on indirect stereochemical

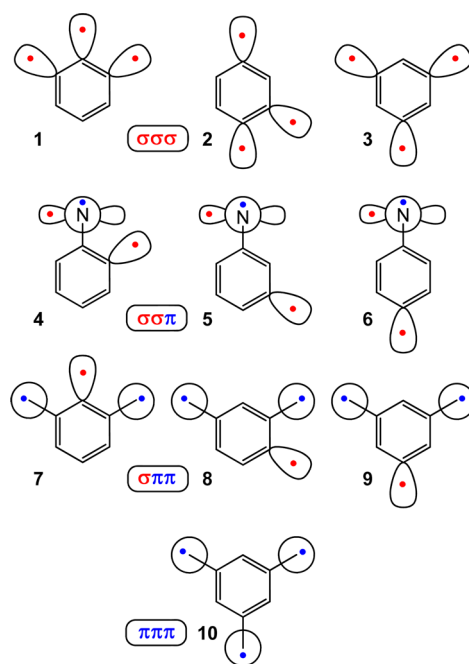
arguments) and is less restrictive than earlier magnetic criteria that either used the term synonymously to triplet systems or even reserved it for species in which electronic coupling is weaker than the hyperfine interaction. The unified treatment of many different types of diradicals within the 3×3 CI model² led to a consistent classification and deeper understanding of the electronic, spectroscopic, and chemical properties of these intermediates.

In parallel with these developments, interest in organic oligo- and polyradicals increased due to their potential application in the field of organic magnetic materials.^{4–7} Accordingly, a great many research efforts have been devoted to the magnetic properties of organic high-spin systems, employing EPR spectroscopy and susceptibility measurements as the primary tools to unravel the spin–spin coupling patterns in (usually) rather extended systems or even solid state structures. More recently, a number of small prototypical tri-, tetra-, and oligoradicals became amenable to experimental studies in the gas-phase⁸ and in low-temperature matrices. Interest in the electronic structure of such molecules increased concomitantly, because they can serve as simple model systems to understand the electronic and magnetic interactions within more complex and extended structures. In a seminal work, Krylov analyzed the general electronic structure of triradicals, defined in the spirit of Salem as species in which three electrons are distributed over three (nearly) degenerate orbitals, and investigated the properties of several members of this class of reactive intermediates using the spin-flip approach.⁹ The 20 Slater determinants that can be obtained from the distribution of three electrons over three orbitals give rise to the four components of a quartet and to eight doublet states. Whereas the low-spin states are generally two-determinantal, the $S_z = \pm 3/2$ components of the high-spin state are always well described by a single configuration. Depending on the symmetry of the three nominally nonbonding molecular orbitals (NBMOs), several of the low-spin states can mix further, leading to complex electronic structures.⁹

In perfect triradicals with exactly degenerate NBMOs, ferromagnetic coupling between the three electrons should result in a preference for high-spin ground states, according to Hund's first rule applied to molecules. Violations of Hund's rule are frequently observed, however, when the exchange interaction between the electrons is weak.^{10,11} This situation is encountered in di- or triradicals in which the NBMOs are disjoint (i.e., can be chosen to have no atoms in common). In these cases, instantaneous correlation effects (e.g., dynamic spin polarization)¹⁰ often give rise to low-spin ground states, but state energy differences are usually much smaller than in nondisjoint systems with significant exchange interaction. Exact orbital degeneracy is the exception rather than the rule, and interactions between

the orbitals or other perturbations tend to split the NBMOs energetically. When the orbital energy separation exceeds the electron repulsion, the orbital occupation pattern starts to follow the Aufbau principle leading to low-spin ground states.

Most triradicals isolated to date are based on organic π -systems that function as rigid spacers to keep the open-shell moieties spatially apart. It is useful to classify these triradicals according to the σ/π symmetry of the NBMOs involved. The tridehydrobenzenes **1–3** are $\sigma\sigma\sigma$ triradicals, whereas the dehydrophenylnitrenes **4–6** are of the $\sigma\sigma\pi$ type. Within the $\sigma\pi\pi$ family, all three dehydro-*m*-xylylenes **7–9** have been subject to recent experimental studies, just as the 1,3,5-trimethylenebenzene **10**, which will be discussed as an example of a typical $\pi\pi\pi$ triradical.



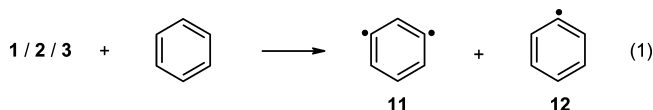
The matrix isolation of triradicals requires appropriate precursors that are sufficiently volatile and stable to be sublimed without significant degradation. Based on our experience with the generation of radicals and diradicals (e.g., arynes),^{12–14} organic iodine compounds fulfill these requirements, and the C–I bond can often be cleaved photochemically *in situ* or thermally in the gas phase by flash-vacuum pyrolysis (FVP) with subsequent trapping of the products in a large excess of an inert gas. The latter approach is restricted to kinetically stable target systems but usually leads to reactive species that are isolated in individual matrix cages. The photochemical decomposition of iodine compounds, on the other hand, necessarily produces radical pairs, with the iodine atoms residing in nearby matrix cages. Upon annealing of these matrices, radical recombination

frequently occurs. This diminishes the radical concentration and is thus unwanted in most cases; however, it can be helpful to disentangle the spectra of complex product mixtures formed upon photolysis of the precursors (e.g., by stepwise loss of two or more iodine atoms or secondary photolysis of radicals). Noteworthy is the only small degree of perturbation caused by the proximity of iodine atoms on the spectroscopic properties of the isolated radical species. Thus, the IR and EPR spectra of oligoradicals generated by FVP with subsequent trapping in a matrix or by photolysis of matrix-isolated precursors in general are very similar. The synthesis and isolation of all triradicals discussed in this work involves cleavage of at least one C–I bond. In some cases, the yield of triradicals is high enough to allow for the measurement of IR spectra. In other cases, only the high-spin systems can be detected by the much more sensitive (and selective) EPR spectroscopy.

Tridehydrobenzenes: $\sigma\sigma\sigma$ Triradicals

The tridehydrobenzenes **1–3** are prototype examples of $\sigma\sigma\sigma$ triradicals. The heats of formation of the three isomers have been determined by Wenthold et al. as 155.1 ± 3.8 , 163.5 ± 5.0 , and 179.0 ± 4.5 kcal/mol,^{15,16} leading to C–H bond dissociation energies (BDEs) for the C2–H, C4–H, and C5–H bonds in *m*-benzyne **11** of 85.3 ± 4.9 , 93.7 ± 5.9 , and 109.2 ± 5.5 kcal/mol, respectively (Figure 1).

Thus, the stabilizing interaction between the formally unpaired electrons is significant in **1** and of intermediate strength in **2**, whereas **3** can be considered as a *m*-benzyne interacting only weakly with an additional radical center at the opposite site of the ring.¹⁵ The strength of interaction between the radical electrons can also be quantified in terms of isodesmic equations that formally separate the triradical into a diradical species and a phenyl radical.^{9,17} Among the different ways to define the triradical stabilization energy (TSE), reference to **11** (eq 1) appears to be most appropriate, because all three tridehydrobenzenes can be looked upon as *m*-benzyne derivatives.



The TSE provides a measure for stabilizing (positive TSE) or destabilizing (negative TSE) interactions, when the three radical centers are combined within the same molecule. The structures, relative energies, and TSEs of several low-lying electronic states of **1–3** computed at the CCSD(T)/cc-pVTZ and CAS(9,9)-RS2/cc-pVTZ level are shown in Figure 2. All three systems are characterized by (at least) two doublet states that are significantly more stable than the quartets.^{9,14,17}

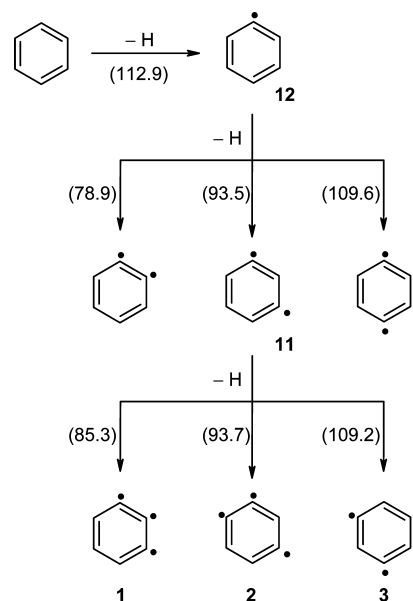


FIGURE 1. C–H bond dissociation energies (in kcal/mol) of benzene, **11**, and **12**.

Just as *m*-benzyne **11** and most of its derivatives, the tridehydrobenzenes are structurally highly flexible along the 1,3 interradsical distance coordinate,^{14,18–20} some states giving rise to bicyclic geometries with a bonding *m*-interaction, and some even show double-well potentials. At the geometry of the quartet state, the three NBMOs of **1** are energetically sandwiched by the occupied and virtual benzenoidic π orbitals (Figure 3). Whereas the $10a_1$ and $11a_1$ orbitals of the σ allylic system are bonding between C1 and C3, the $7b_2$ orbital is antibonding and has a node at C2.

Accordingly, at small distances between C1 and C3, occupation of the three orbitals with three electrons following the Aufbau principle gives rise to a 2A_1 state, whereas at larger separations, the lowest-energy state is of 2B_2 symmetry. Adiabatically, both states are nearly degenerate and both are rather well described by wave functions based on a single reference configuration.^{9,14,17,21,22} At the CCSD(T)/cc-pVTZ level, the equilibrium distance R_{C1C3} of the 2A_1 state is significantly shorter (169.2 pm) whereas in the 2B_2 state it is longer (236.7 pm) than that in *m*-benzyne 1A_1 -**11** ($R_{C1C3} = 205.8$ pm).¹⁴ At this level, the 2A_1 state is more stable than 2B_2 -**1** by 2.2 kcal/mol. In contrast to the low-spin states, the 4B_2 state is destabilized considerably (TSE = -12.2 kcal/mol) because it requires excitation of one electron from the strongly bonding $10a_1$ orbital.

The matrix isolation of **1** was achieved in 2005: irradiation of 3-iodophthalic anhydride **13** in neon matrices at 3 K produces a mixture of monoradical **14** and benzyne **15**.²¹ Both **14** and **15** disappear upon irradiation at 248 nm, whereas several new photoproducts are formed. Subsequent

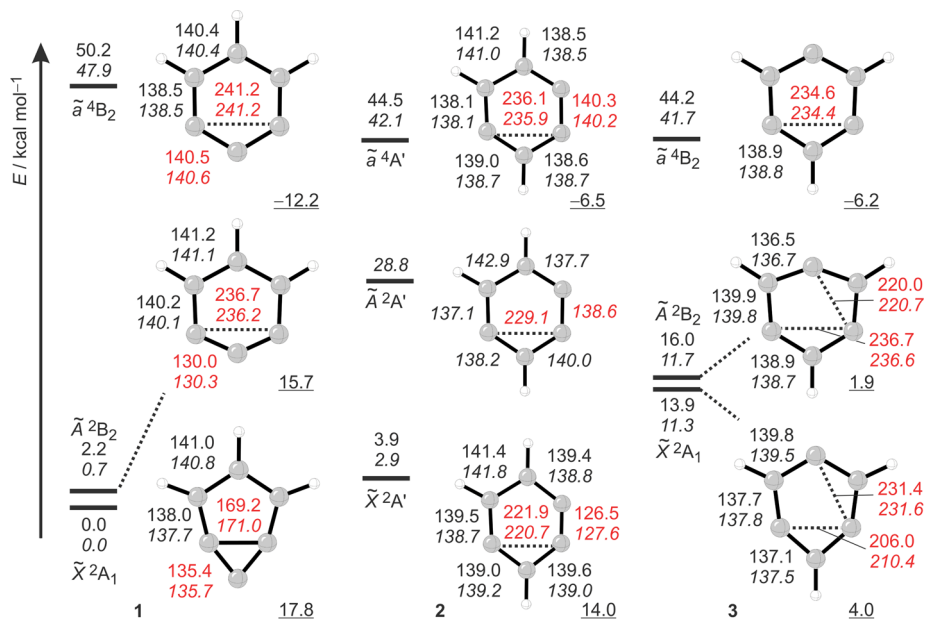
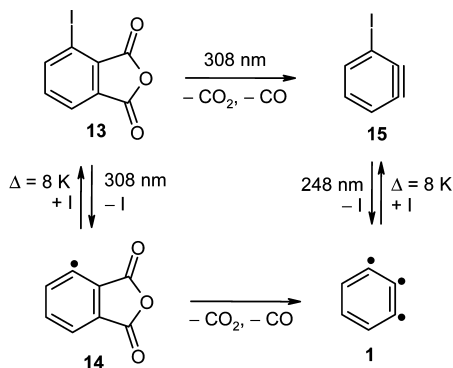


FIGURE 2. Selected structural parameters and relative energies of **1–3** in their two lowest-energy doublet and in the most stable quartet states. Roman type: CCSD(T)/cc-pVTZ; italic type: CAS(9,9)-RS2/cc-pVTZ. Electronic TSEs are underlined.

annealing of the matrix leads to a decrease in intensity of all absorptions assigned to **14**, whereas those of **13** increase concomitantly. Simultaneously, another species with strong absorptions at 524, 753, and 1698 cm⁻¹ disappears, whereas all absorptions of **15** gain intensity. Assuming that thermal recombination with iodine atoms takes place under these conditions, the three absorptions were assigned to **1**.



At the time these experiments were carried out, it was commonly believed that **1** possesses a 2B_2 ground state, based on high-level computations published one year earlier.¹⁷ However, the spectrum calculated at the DFT level for 2B_2 -**1** did not fit the experimental data. A careful investigation showed that the B3LYP functional gives structures and relative energies in excellent agreement with our higher level computations for both low-lying doublet states (B3LYP/cc-pVTZ: $R_{C1C3}(^2A_1) = 169.2$ pm; $R_{C1C3}(^2B_2) = 234.2$ pm) with the 2A_1 isomer being 1.7 kcal/mol lower in energy.^{21,22} A comparison of measured and computed IR data clearly indicated that indeed tridehydrobenzene **1** in its

2A_1 ground state was isolated in the neon matrix. With anharmonic corrections, three strong absorptions are computed for 2A_1 -**1** at 548, 756, and 1708 cm⁻¹, whereas no intense absorptions are calculated around 1700 cm⁻¹ for the 2B_2 state.^{14,21,22}

For the lower-symmetry 1,2,4-tridehydrobenzene **2**, there are also two doublet states (\tilde{X}^2A' and \tilde{A}^2A') that arise from single occupation of a 1,3-bonding or 1,3-antibonding orbital. Because the doublet states both have the same symmetry, they mix and thus repel each other energetically, so that the energy gap between them is much larger than that in **1**.^{9,14,17}

The high-spin state of **3** has D_{3h} symmetry, whereas single occupation of a degenerate pair of orbitals in the doublet state leads to a Jahn–Teller unstable situation and symmetry lowering to C_{2v} . Similar to **1**, the 2A_1 ground state of **3** is characterized by a shortened C1–C3 distance that is of similar size as the one in **11**, whereas the C1–C3 separation is much larger in the 2B_2 state. The ground state structure and small calculated TSE of 2A_1 -**3** nicely underline the weakness of interaction between the *m*-benzyl moiety and the additional radical center in the 5 position.¹⁵ Just as in **1**, the energy difference between the 2A_1 and 2B_2 states of **3** amounts to only 1–2 kcal/mol. The latter does not correspond to a minimum energy structure, however, but rather to a transition state for the mutual interconversion of equivalent 2A_1 structures. The doublet PES of **3** forms a Jahn–Teller doublecone potential in which three equivalent 2A_1 minima and three 2B_2 transition states are arranged symmetrically around the D_{3h} cusp.

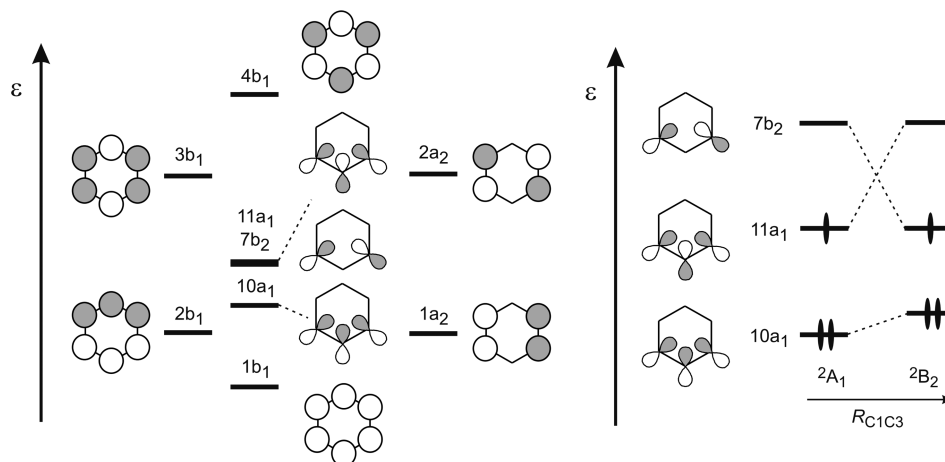
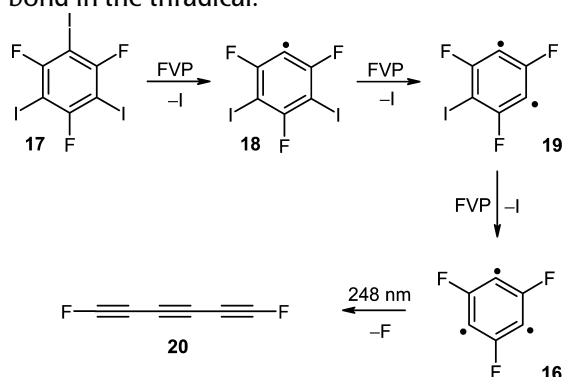


FIGURE 3. (a) Schematic representation and energies (CASSCF(9,9)/cc-pVTZ) of the NBMOs and π orbitals of **1** at the geometry of the 4B_2 state. (b) Qualitative changes in NBMO energies with increasing distance between C1 and C3.

Whereas all attempts aimed at the generation of **1** or **3** by FVP or photolysis of the corresponding triiodo compounds turned out to be unsuccessful,^{21,23} trifluoro-1,3,5-tridehydrobenzene **16** could be isolated in small yields after thermolysis of trifluorotriiodobenzene **17**.²⁴ Photolysis of **17** in neon matrices produced phenyl radical **18** and *m*-benzynes **19** in good yields, but no traces of **16** could be detected under these conditions.^{23,24} Interestingly, **16** turns out to be photolabile: the detection of difluorohexatriyne **20** after irradiation at 254 nm of a matrix containing the pyrolysis products of **17** points toward photochemical fission of a C–F bond in the triradical.²⁴



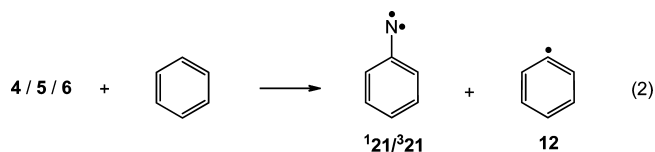
According to computations, fluorine substitution in **3** only has a marginal effect on the structures and relative energies of the lowest doublet and quartet states.¹⁴

$\sigma\sigma\pi$ Triradicals: Dehydrophenylnitrenes

The nitrene radicals **4–6** belong to the $\sigma\sigma\pi$ category. It is well established that the ground state of phenylnitrene **21** is of 3A_2 symmetry and dominated by the electronic configuration $(8b_2)^1(3b_1)^1$. The $3b_1$ orbital closely resembles the singly occupied molecular orbital (SOMO) of the benzyl radical

with large coefficients at the methylene carbon as well as in the *o*- and *p*-positions of the aromatic ring, whereas the $8b_2$ orbital is largely localized on the nitrogen atom of **21**. The two-determinantal 1A_2 open-shell singlet state with the same orbital occupation pattern is less stable by 15–17 kcal/mol.^{25,26} The next higher states are totally symmetric two-configurational closed-shell singlets, \tilde{b}^1A_1 and \tilde{c}^1A_1 , with leading configurations $(8b_2)^2$ and $(3b_1)^2$, respectively.

The electronic structure of **4–6** has been studied computationally by Bettinger and Sander.²⁷ Structures, relative energies, and TSEs of **4–6** in their lowest electronic states are given in Figure 4. Because most of the low-spin states are strongly multiconfigurational, only the TSEs of the quartet states are determined directly at the CCSD(T)/cc-pVTZ level according to eq 2.



The low-spin TSEs are derived from these values by addition of the adiabatic doublet–quartet energy splittings of **4–6** (CAS(9,9)-CID+Q/cc-pVTZ//CAS(9,9)-RS2c/cc-pVTZ) and the singlet–triplet energy splitting of **21** ($\Delta E_{ST} = 17.1$ kcal/mol) computed at the CAS(8,8)-CID+Q/cc-pVTZ//CAS(8,8)-RS2c/cc-pVTZ level, following a procedure devised by Krylov et al.¹⁷ Although this procedure is formally correct, it is often more convenient to refer to the diradical ground state (i.e., the 3A_2 state of **21** in eq 2). The difference between doublet and quartet TSEs then simply equals the doublet–quartet energy splitting of the triradical, in accord

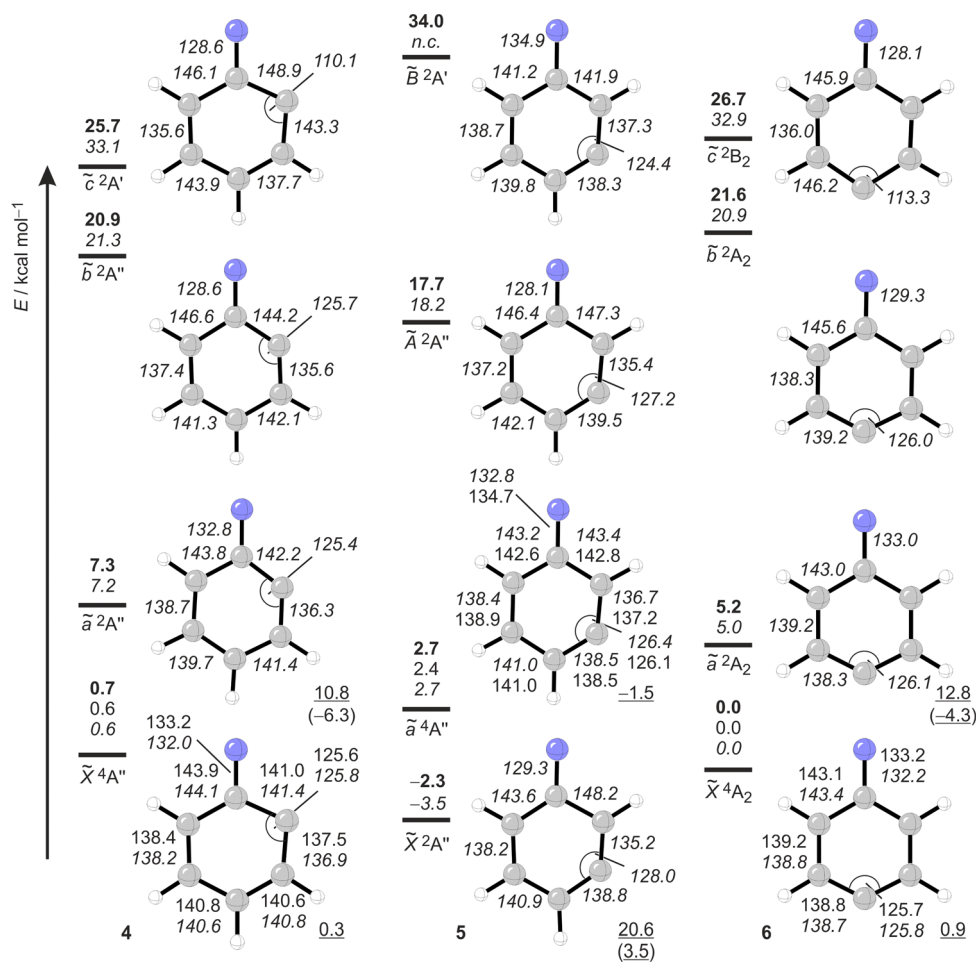
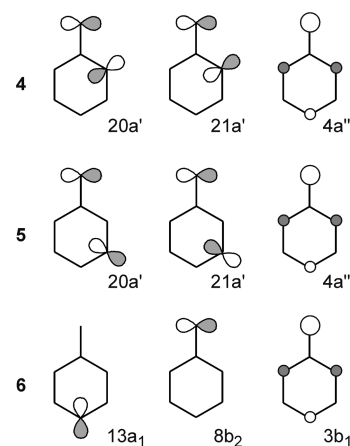


FIGURE 4. Selected structural parameters and energies (relative to 4A_2 -**6**) of **4–6** in their lowest electronic states; Roman type, CCSD(T)/cc-pVTZ; italic type, CAS(9,9)-RS2c/cc-pVTZ; bold type, CAS(9,9)-CISD+Q/cc-pVTZ//CAS(9,9)-RS2c/cc-pVTZ. TSEs are underlined; values in parentheses make reference to the triplet ground state of **21**; see text for details. Due to intruder state problems, structure $^2A'$ -**5** was optimized at the CASSCF(9,9)/cc-pVTZ level.

with the analogous definition of the diradical stabilization energy (DSE).

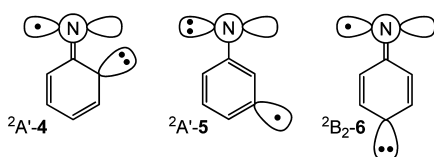
The quartet ground states of **4** and **6** are slightly stabilized, whereas $^4A''$ -**5** shows a negative TSE. These findings are in line with qualitative spin-polarization considerations (Figure 5): in the high-spin states of **4** and **6**, σ/π exchange interaction leads to stabilization (or less destabilization); in **5** the Coulomb repulsion between the in-plane electron and the π -density destabilizes the system. In contrast, the lowest-energy doublet states of **4** and **6** are destabilized significantly as compared with $^2A''$ -**5**, because in the former the parity-dictated alternating pattern of the spin density distribution is disrupted:

In the quartet and two lowest doublet states of **4–6**, the three NBMOs of the nitrene radicals remain essentially singly occupied, with the exception of $^2A''$ -**5** in which 20a' has a somewhat higher occupation number than 21a' (*vide infra*).

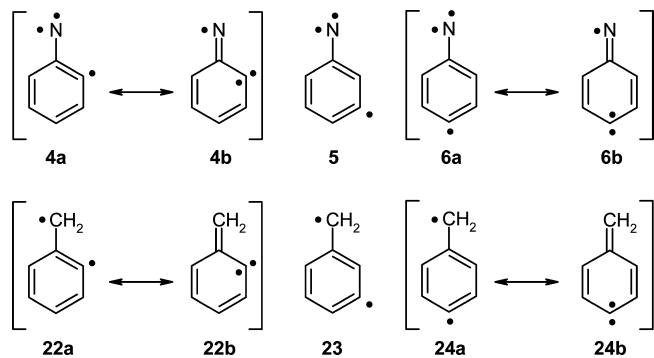


The next higher excited doublet states reveal some interesting differences between the three isomers. In $^2A'$ -**4**, one electron is transferred from the $4a''$ into the $20a'$ orbital, which now has its largest coefficient at the dehydrocarbon. Similarly, in 2B_2 -**6** $13a_1$ is essentially doubly and $3b_1$ singly

occupied. In contrast, the ${}^2A'$ state of **5** is two-configurational and apart from the leading configuration $(20a')^2(21a')^1(4a'')^0$, a doubly excited configuration $(20a')^0(21a')^1(4a'')^2$ makes strong contributions to the wave function of that state. As discussed in more detail by Bettinger et al.,²⁷ ${}^2A'$ -**4** and 2B_2 -**6** can be considered as closed-shell carbene/iminy radicals with short C–N bonds and acute CCC angles at the dehydrocarbons. In contrast, ${}^2A'$ -**5** can be looked upon as phenylnitrene **21** in its \bar{b}^1A_1 closed shell singlet state in weak interaction with a phenyl radical moiety in the *m*-position.



It is illuminating to compare the doublet–quartet splittings of **4–6** to the singlet–triplet energy differences of the α,n -didehydrotoluenes **22–24** (Figure 6). These differ from the nitrene radicals by the absence of the in-plane orbital corresponding to $8b_2$ in **21**.



Whereas **22** and **24** show a similar preference for the high-spin states with singlet–triplet energy splittings in almost perfect match with the doublet–quartet energy splittings of **4** and **6**, the low-spin preference of **23** is less pronounced than that of **5**. Apparently, the $8b_2$ in-plane orbital at nitrogen in the nitrene radicals has little influence on the lowest doublet and quartet states of **4** and **6** but plays a more active role in **5**, where it leads to a stabilization of the low-spin and a destabilization of the high-spin state. As for many other $\sigma\sigma$ 1,4-diradicals, this additional degree of interaction is attributable to through-bond coupling via the $\sigma^*(C1-C2)$ orbital.²⁷ Structurally, increased occupation of this orbital shows up in a significant lengthening of the C1–C2 and shortening of the C–N and C2–C3 bonds in the doublet state (Figure 4).

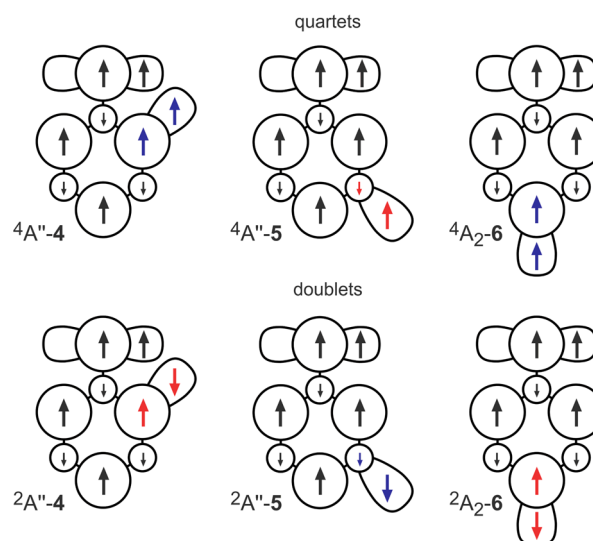
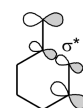
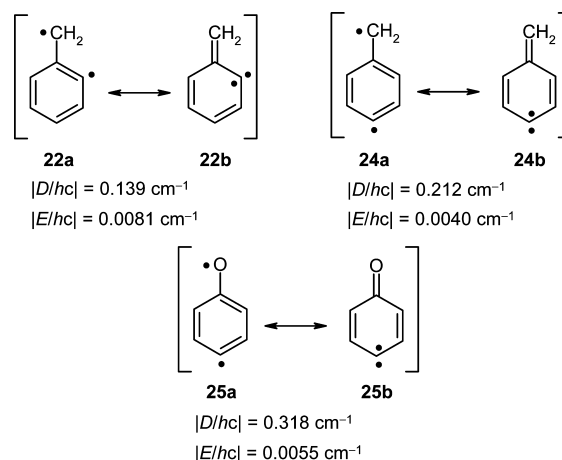


FIGURE 5. Qualitative spin polarization patterns in the lowest quartet and doublet states of **4–6**.



20a'

Triplet ground states of **22** and **24** have been demonstrated by matrix EPR spectroscopy.²⁸ The measured zero field splitting (zfs) parameters are comparative large, providing evidence for the contribution of carbenoidic resonance structures **22b** and **24b**. The *D* parameter of 3B_1 -**24** comes already close to that of 4-oxo-cyclohexadienylidene **25**.



Arylnitrenes are easily accessible by photolysis of aryl azides. It is well-known, however, that intersystem crossing of singlet nitrenes into their triplet ground states is a rather slow process and photochemically reversible and that rearrangement into azirines and ketenimines readily occurs on the singlet PES.²⁹ The three systems are therefore

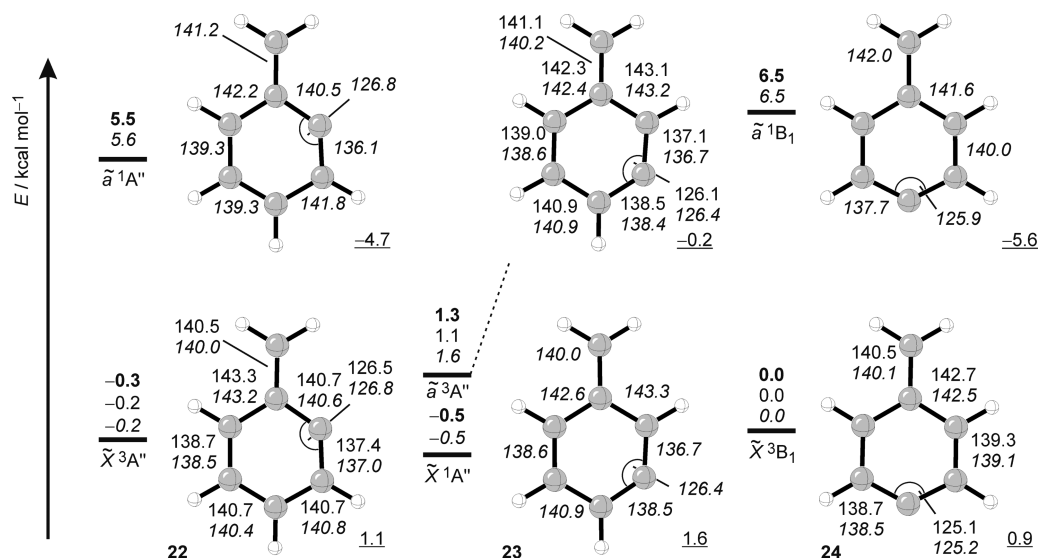


FIGURE 6. Selected structural parameters and energies (relative to 3B_1 -**24**) of **22**–**24** in their lowest electronic states. Roman type, CCSD(T)/cc-pVTZ; italic type, CAS(8,8)-RS2c/cc-pVTZ; bold type, CAS(8,8)-CISD+Q/cc-pVTZ//CAS(8,8)-RS2c/cc-pVTZ. DSEs are underlined.

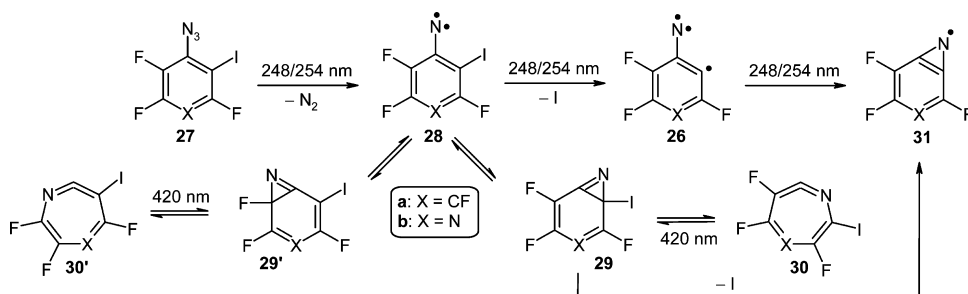
obtained in photostationary equilibrium and the yield of nitrene strongly depends on the irradiation conditions. Although iodophenyl azides are potential precursors of dehydrophenylnitrenes, these rearrangements compete with the C–I bond cleavage, which usually requires extended times of irradiation. Fluorine substitution in the *ortho* positions of the aromatic ring decreases the tendency for rearrangements, so fluorinated aryl nitrenes are generally obtained in much higher yields than those of the unsubstituted systems.²⁹

Two fluorinated derivatives of *o*-nitrene radical **4**, 3,4,5,6-tetrafluorophenylnitrene-2-yl **26a** and the heterocyclic 2,5,6-trifluoropyridylnitren-3-yl **26b**, have been isolated in cryogenic matrices and characterized as quartet species by EPR spectroscopy.^{30,31}

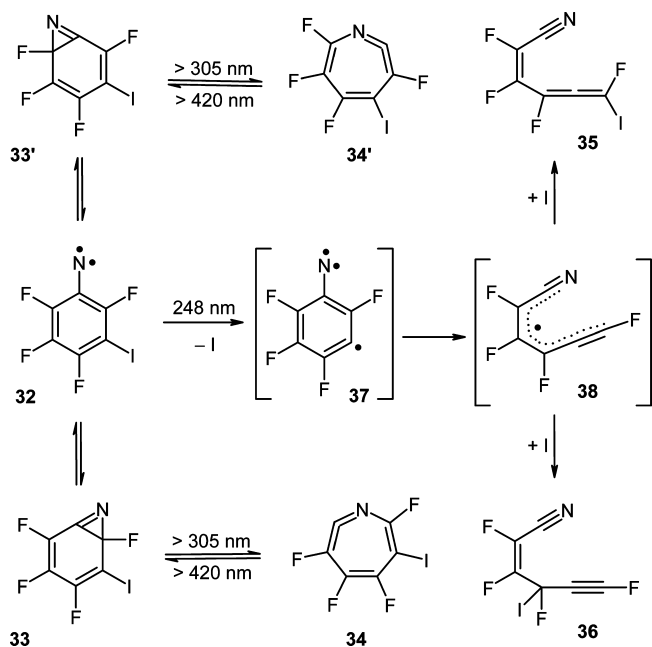
Irradiation of iodoaryl azides **27** at 248 nm results in the rapid formation of triplet nitrenes **28** that could be characterized by IR and EPR spectroscopy. Continued photolysis leads to the formation of ketenimines **30** and azirines **29** (at 420 nm). The selectivity is higher in the heterocyclic system, giving rise mainly to **29b'**/**30b'**, whereas all four

species are involved in the photochemistry of **28a**. The photostationary concentration of **26** is too low in both cases to allow for its characterization by IR spectroscopy. Involvement of nitrene radicals **26** in these rearrangements can nevertheless be demonstrated by the observation of a characteristic quartet EPR spectrum upon irradiation of **27**. Annealing the matrices after photolysis causes rapid disappearance of these signals due to recombination with iodine atoms. Prolonged irradiation at short wavelengths leads to the disappearance of all species discussed above and to the quantitative formation of new compounds that were identified by IR spectroscopy as aziriny radicals **31a** and **31b**. According to DFT calculations, these unusual planar radicals are more stable than **26a** and **26b** by 18.5 and 14.5 kcal/mol, respectively.^{30,31} Whether bond formation in **26** proceeds photochemically on the lowest doublet PES or involves C–I bond cleavage in **29** cannot be decided on the basis of available experimental data.

Irradiation of 3-iodo-2,4,5,6-tetrafluorophenyl azide in cryogenic neon or argon matrices at $\lambda > 305$ nm likewise produces triplet nitrene **32** as the primary product in



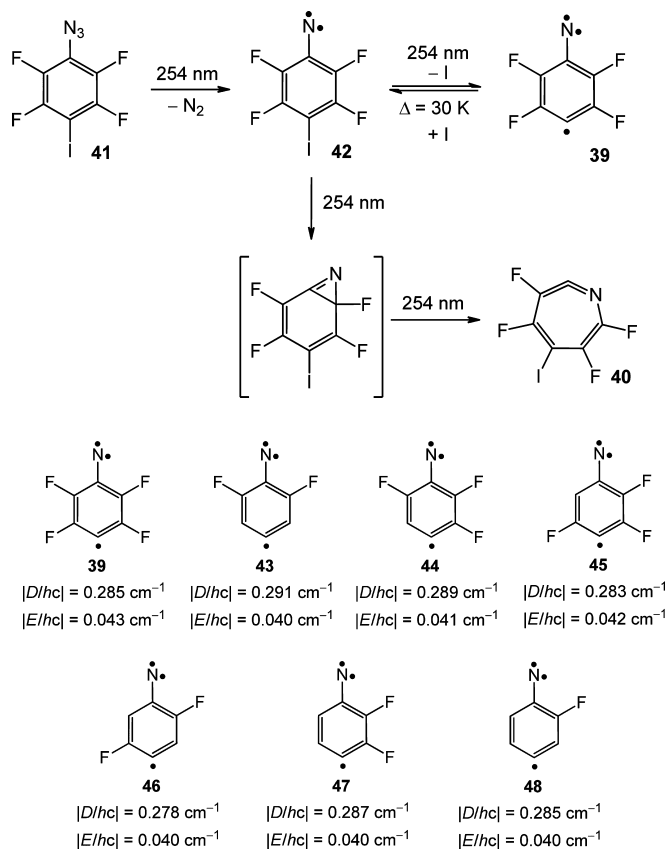
photostationary equilibrium with the corresponding azirine and ketenimine isomers **33/33'** and **34/34'**.³² Subsequent photolysis at 248 nm leads to the formation of two new products that were identified as allene **35** and its acetylene isomer **36**. No evidence for the formation of nitrene radical **37** could be extracted from the IR spectra, and no characteristic quartet signals could be observed by EPR spectroscopy.



Although numerous pathways for the formation of **35** and **36** from **32** are feasible, it is plausible to assume that C–I bond cleavage in **32** leads to doublet nitrene radical **37**, which rapidly undergoes a ring-opening reaction to radical **38**, which in turn recombines with iodine atoms to produce the final products. The low barrier (~6 kcal/mol) for the exothermic rearrangement **37** → **38** is a natural consequence of the through-bond interaction in 3-dehydrophenylnitrenes.

Whereas 2-dehydrophenylnitrenes readily and irreversibly rearrange to aziriny radicals and the *m*-isomers are prone to ring rupture, no such exit channels are available to 4-dehydrophenylnitrenes. 2,3,5,6-Tetrafluorophenylnitrene-4-yl **39** was the first nitrene radical that was identified as a quartet species by IR spectroscopy.³³ Owing to its higher symmetry only one ketenimine isomer, **40**, is formed as a byproduct upon irradiation of azide **41** at 254 nm. Annealing the matrix causes all absorptions of **39** to disappear, whereas those of triplet nitrene **42** grow concomitantly, underpinning the assignment to the nitrene radical. The quartet ground state was confirmed by EPR measurements.³⁴

In a similar vein, a number of *p*-nitrene radicals **43–48** with different substitutional patterns could be isolated and spectroscopically characterized during the last years, all of which contain at least one fluorine atom in *o*-position to the nitrene moiety.^{33–35}

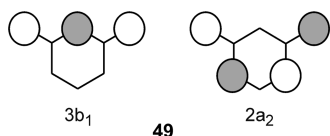


The unusual *zfs* parameters of these systems, which all fall in a narrow range, have been rationalized by comparison with computed magnetic properties. Most aryl nitrenes show *D* values between 0.8 and 1.1 cm^{-1} and *E* values close to or exactly zero. The iodine-containing nitrenes (e.g., **42**, $|D/hc| = 1.108 \text{ cm}^{-1}$, $|E/hc| = 0.012 \text{ cm}^{-1}$) deviate somewhat from this behavior, and especially the *E* parameters are larger than expected. This finding has been attributed to spin–orbit coupling (SOC) due to the heavy iodine atom: the principal axis of the **D** tensor points along the C–N bond, whereas, for the SOC contribution, the easy axis is oriented perpendicular to the C–N bond and the molecular plane, resulting in an overall increase in rhombicity.³⁴ A similar geometric rationale has been found for the nitrene radicals, where SOC contributions are of minor importance; however, The spin–spin (SS) coupling in **39** accounts for 87% of the computed $D/hc = 0.261 \text{ cm}^{-1}$ and is essentially local (i.e., one-center integrals make the largest contributions). The large *E* parameter can be ascribed to the fact that **39**

simultaneously exhibits nitrene and carbene character: The nitrene SOMOs are comprised of p_x and p_y orbitals causing a dipolar field along the z -axis (C–N bond). The carbene (cyclohexadienylidene) SOMOs are comprised of p_x and p_z orbitals with a resulting dipolar field along the y -axis (in-plane). Because the nitrene character dominates, the main axis points still along the C–N bond, but the carbene contribution causes deviations from the pseudocylindrical symmetry with magnetically inequivalent x - and y -directions. The small D parameter results mainly from the prefactor $1/[S(2S - 1)]$ in the expression for D^{SS} , which amounts to 1 for triplets but 1/3 for quartet systems. The additional lowering is again attributable to the cancellation of nitrene and carbene contributions, which oppose each other along the magnetic z -direction. Thus, the non-vanishing E value as well as the small D parameter directly reflect the carbene character of the quartet p -nitrene radicals. The measured zfs parameters of the o -radicals (**26a**: $|D/hc| = 0.357 \text{ cm}^{-1}$, $|E/hc| = 0.0136 \text{ cm}^{-1}$; **26b**, $|D/hc| = 0.384 \text{ cm}^{-1}$, $|E/hc| = 0.0088 \text{ cm}^{-1}$) can be rationalized on similar grounds: Due to the carbene contribution, the easy axis of the \mathbf{D} tensor is rotated in-plane by approximately 1° away from the C–N bond. The spin population at the nitrene center is higher in **26b** than in **26a** causing the larger D value. In turn, the spin population at the carbene carbon is slightly lower in **26b**, leading to a smaller E parameter.

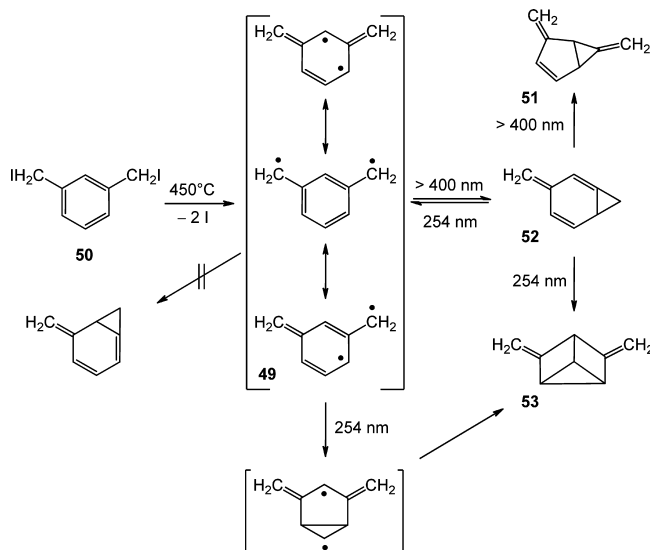
$\sigma\pi\pi$ Triradicals: Dehydro-*m*-xylylenes (Dehydrobenzoquinodimethanes)

m-Xylylene **49** features a robust triplet ground state ($\Delta E_{ST} = 9.6 \pm 0.2 \text{ kcal/mol}$)³⁶ due to its strongly nondisjoint NBMOs and is one of the principle high-spin building blocks employed in the design of organic magnetic materials.^{5,7} At the CAS(8,8)-CISD+Q/cc-pVTZ//CAS(8,8)-RS2c/cc-pVTZ level, the $\tilde{a} \ ^1A_1$, $\tilde{b} \ ^1B_2$, and $\tilde{A} \ ^3A_1$ states are less stable than the $\tilde{X} \ ^3B_2$ state by 11.6, 23.7, and 70.7 kcal/mol, respectively.



Although **49** had been subject to early experimental studies employing fluorescence and EPR spectroscopy in organic glasses, a detailed characterization of *m*-xylylene in cryogenic matrices by IR, UV–vis, and EPR spectroscopy was achieved only recently.³⁷ FVP of 1,3-bis-iodomethyl-benzene **50** at 450 °C produces **49** in excellent

yields, whereas photochemically, just as in earlier studies, only trace amounts of the diradical could be obtained. Upon visible light irradiation, **49** rearranges to three isomeric hydrocarbons, **51–53**, in photostationary equilibrium.



According to DFT calculations, all three photoproducts are considerably less stable than **49** (but do not absorb significantly at long wavelengths) and partly form back *m*-xylylene upon 254 nm photolysis.³⁷ The longest-wavelength UV–vis absorption of **49** at 433 nm (66 kcal/mol) is in excellent agreement with the computed excitation energy for the $\tilde{A} \ ^3A_1 \leftarrow \tilde{X} \ ^3B_2$ transition. The measured zfs parameters ($|D/hc| = 0.011 \text{ cm}^{-1}$; $|E/hc| = 0.001 \text{ cm}^{-1}$) are small, indicating that the unpaired spins stay well separated from each other (only two-center integrals contribute to the computed D^{SS}).^{37,38}

Removing a ring-hydrogen atom from **49** leads to the dehydro-*m*-xylylenes **7–9**. Structures and relative energies of the three lowest electronic states of these triradicals are given in Figure 7. Whereas **7** and **8** feature high-spin ground states with doublet-quartet energy splittings between 7 and 10 kcal/mol, the 2B_2 open-shell doublet state of **9** lies 1–2 kcal/mol below the 4B_2 high-spin state.

The computed ground state multiplicities are in accord with expectations based on qualitative spin polarization considerations (Figure 8): the quartet ground states of **7** and **8** are stabilized by 2.4 and 1.9 kcal/mol, respectively, which slightly exceeds the high-spin stabilization of **4** and **6** (Figure 4) and **22** and **24** (Figure 6) due to the higher spin density at these positions in 3B_2 -**49** compared with the respective positions in the benzyl radical (2B_1) and phenylnitrene 3A_2 -**21**.³⁸ The destabilization of 4B_2 -**9**, on the other hand, is very moderate, because the NBMOs of **49** both have

a node in the 5 position, so that Coulomb repulsion between the σ electron and the π electron density of the aromatic ring is comparable in 4B_2 -**9** to that of the phenyl radical **12**. In the low-spin manifold, 2B_2 -**7** and ${}^2A'$ -**8** are destabilized by 7.7 and 5.9 kcal/mol, respectively, whereas the TSE of 2B_2 -**9** is positive by 1.6 kcal/mol, which matches the weak stabilization of ${}^1A''$ -**23**.

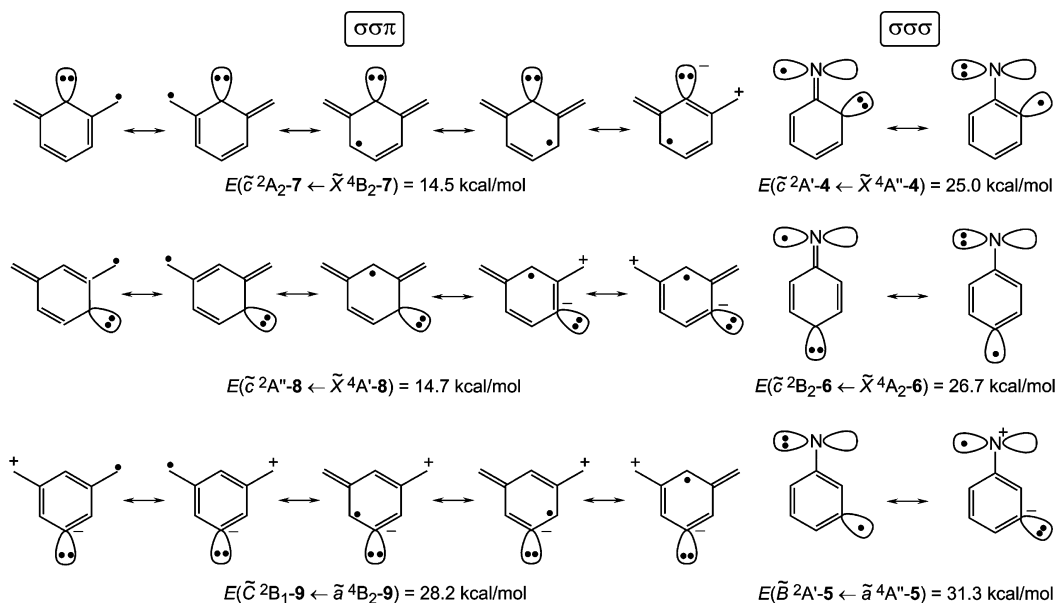
In analogy to the dehydrophenylnitrenes, the three lowest electronic states of **7–9** show little structural variations, because the three NBMOs remain essentially singly occupied. The structures and energies of the lowest $\sigma\sigma\pi$ states are given in Figure 9. The excitation energies to these states are significantly lower in **7** and **8** compared with **4** and **6** by more than 10 kcal/mol, because resonance stabilization is more efficient in the former than in the $\sigma\sigma\sigma$ states of the nitrene radicals. The corresponding excitation energies of **5** and especially **9** are significantly higher, because only charge-separated structures contribute to the resonance hybrid of the $\sigma \leftarrow \pi$ excited states. The “zwitterionic” nature of 2B_1 -**9** shows up directly in the exceedingly high dipole moment of 5.4 D.

The doublet ground state of **9** was established by mass spectrometric methods in the gas phase.³⁹ The weak interaction between the σ radical electron and the π system of the *m*-xylylene framework was determined experimentally to 1 ± 4 kcal/mol, in agreement with the computed low-spin TSE.^{9,39} Quartet ground states of **7** and **9** were demonstrated recently by EPR spectroscopy.³⁸ Irradiation (308 nm) of 2,4- or 2,6-bis(iodomethyl)iodobenzenes in argon matrices at 5 K led to the formation of characteristic quartet signals (among a broad doublet and partially hidden triplet patterns). In

contrast, photolysis of matrix-isolated 3,5-bis(iodomethyl)iodobenzene leads to a simpler EPR spectrum without any evidence for the formation of a quartet species. The measured zfs parameters of **7** ($|D/hc| = 0.0920 \text{ cm}^{-1}$; $|E/hc| = 0.0033 \text{ cm}^{-1}$) and **8** ($|D/hc| = 0.0935 \text{ cm}^{-1}$; $|E/hc| = 0.0009 \text{ cm}^{-1}$) are rather similar. The *D* values are almost 1 order of magnitude larger than that of **49** and, according to computations,³⁸ one-center interactions make the most significant overall contributions, which are counteracted by two-center terms that are of similar magnitude as the ones calculated for *m*-xylylene. Although it is appealing to associate the former with the carbene character (π spin density) at the dehydrocarbon, simple classical interpretations are hampered by the fact that exchange contributions account for roughly 30% of the computed D^{SS} in these systems and are even dominant in *m*-xylylene.³⁸

1,3,5-Trimethylenebenzene: A $\pi\pi\pi$ Triradical

1,3,5-Trimethylenebenzene **10** forms the basis for numerous high-spin polyradicals described in the literature,^{4,7} but remarkably few experimental studies have been devoted to this prototypical triradical till recently.^{40,41} The third $C(sp^3)$ –H BDE in trimethylbenzene (88.2 ± 5.0 kcal/mol) is rather identical to that in toluene (89.8 ± 0.6 kcal/mol) or the first and second BDEs in *m*-xylene ($BDE(1) = 90.1 \pm 1.7$ and $BDE(2) = 90.7 \pm 2.9$ kcal/mol, respectively), indicating that the interaction between the unpaired electrons is rather weak.⁴⁰ Two of the strongly nondisjoint NBMOs ($2a_2$ (e_x'') and $4b_1$ (e_y'')) of ${}^4A_1''$ -**10** are exactly degenerate in D_{3h} symmetry, whereas $3b_1$ (a_2'') lies slightly lower in energy.



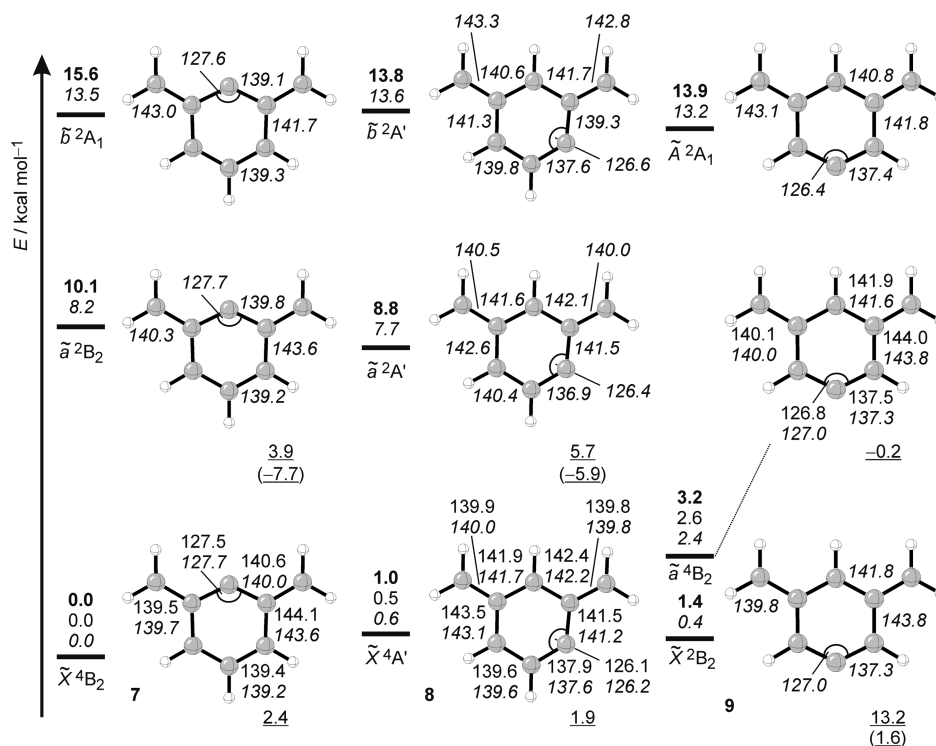


FIGURE 7. Selected structural parameters and relative energies of **7–9** in their lowest electronic states. Roman type, CCSD(T)/cc-pVTZ; italic type, CAS(9,9)-RS2c/cc-pVTZ; bold type, CAS(7,7)-CISD+Q/cc-pVTZ//CAS(9,9)-RS2c/cc-pVTZ. TSEs are underlined; values in parentheses make reference to the triplet ground state of **49**.

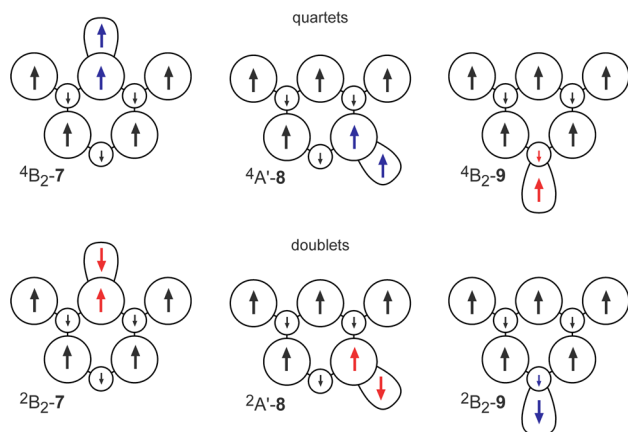


FIGURE 8. Qualitative spin polarization patterns in the lowest quartet and doublet states of **7–9**.

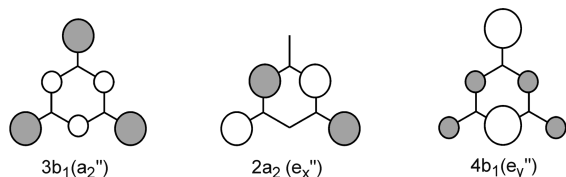


FIGURE 9. Selected structural parameters, energies (relative to $^4B_2-7$), and dipole moments (RS2) of **7–9** in their lowest-energy $\sigma\sigma\pi$ states computed at the CAS(9,9)-RS2c/cc-pVTZ (in italics) and CAS(7,7)-CISD+Q/cc-pVTZ//CAS(9,9)-RS2c/cc-pVTZ level (in bold).

first-order Jahn–Teller distortion. After symmetry breaking to C_{2v} , both components (2A_2 and 2B_1) are stabilized only slightly and to a similar extent (1–2 kcal/mol). In contrast to 1,3,5-tridehydrobenzene, the lowest 2B_1 and 2A_2 states both have real vibrational frequencies, so that the potential energy landscape on the lowest doublet surface is extremely flat.⁴²

The matrix isolation of **10** was achieved recently by FVP of 1,3,5-tris(iodomethyl)benzene at temperatures around 500 °C.⁴¹ The quartet ground state was confirmed by IR, UV–vis, and EPR spectroscopy. Although various species are formed as byproducts, two absorptions at 255 and 367 nm have been assigned to **10**. The longest-wavelength absorption is in good agreement with the vertical excitation energy

Based on computations, the adiabatic doublet quartet energy splitting of **10** amounts to 12–14 kcal/mol.^{9,42} Vertical excitation in D_{3h} symmetry leads to a degenerate $^2E''$ pair of states on the first (and second) doublet PES that is subject to a

computed for the first allowed $\tilde{A}^4A_2 \leftarrow \tilde{X}^4A_2$ transition (CAS(9,9)-RS2c/cc-pVTZ: 83 kcal/mol, 345 nm). The very same EPR spectrum of **10** has been obtained after FVP of tris(iodomethyl)benzene in the gas-phase with subsequent trapping of the products in argon at 5 K and after photolysis of the precursor at 308 nm. The centrosymmetric five-line EPR spectrum centered at 3427 G is in perfect agreement with a quartet molecule with a 3-fold or higher axis of symmetry. The zfs parameter $|D/hc| = 0.0128 \text{ cm}^{-1}$ ($|E/hc| = 0 \text{ cm}^{-1}$) is somewhat larger than expected based on comparison with triplet *m*-xylylene. A remarkable feature of **10** is the photostability of this triradical that stands in marked contrast to the rich photochemistry of **49** under similar experimental conditions. Although not yet fully understood, this finding might be of practical importance when it comes to the design of high-spin materials for which photostability is required.

Conclusions and Outlook

During the last years, organic iodine compounds emerged as suitable precursors that allow for the matrix isolation of a large variety of carbon-centered organic triradicals, provided that appropriate conditions for their controlled decomposition can be found. IR, UV–vis, and EPR spectra of these highly reactive systems, complemented by high-level *ab initio* computations, offer detailed insight into their molecular and electronic structure, as well as their magnetic properties. The classification according to the σ/π symmetry of the occupied NMBOs allows one to compare the properties and energies of different electronic states of various triradicals in a systematic fashion and to put individual (measured or computed) data into a broader perspective. Whereas the ground state multiplicity of all-carbon di-, tri-, and oligoradicals can often be predicted with some confidence by paper-and-pencil methods employing parity-type (or equivalent) models, the same does not always hold true for systems containing heteroatoms or substituents (for various examples, see ref 7). Especially, the development of a simple and universal precursor chemistry for the matrix isolation of nitrogen- and oxygen-centered oligoradicals will be one of the next challenges to tackle. A deeper understanding of how structural modifications influence the electronic and magnetic interactions in organic high-spin systems is one of the prerequisites for the rational design of improved magnetic materials and for fine-tuning of their properties.

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BIOGRAPHICAL INFORMATION

Michael Winkler (b. 1974) received his Ph.D. from Ruhr-Universität Bochum in 2004 under the supervision of Prof. Wolfram Sander. After postdoctoral work with Prof. Ken Houk (UCLA) and Prof. Frank Würthner (University of Würzburg), he is currently working as a guest scientist at the Ruhr-Universität Bochum.

Wolfram Sander (b. 1954) is a Professor of Organic Chemistry at the Ruhr-Universität Bochum (RUB). He obtained his Ph.D. at the University of Heidelberg in 1982 and was a postdoctoral fellow at UCLA with Prof. O. L. Chapman from 1982 to 1984. He was Associated Professor at the Technische Universität Braunschweig from 1990 to 1993 before accepting his present position in 1993. His main research interest in the field of Physical Organic Chemistry is the investigation of reactive intermediates, organic high-spin molecules, and noncovalently bound species using a variety of experimental and computational techniques.

FOOTNOTES

The authors declare no competing financial interest.

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