SOME OBSERVATIONS OF VARIOUS 1,8 NAPHTHOQUINO-DIMETHANE BIRADICALS BY ELECTRON SPIN RESONANCE SPECTROSCOPY

MATTHEW S. PLATZ,* GLEN CARROL, FRANK PIERRAT, JOSÈ ZAYAS and SHEILA AUSTER
Department of Chemistry, The Ohio State University, Columbus, OH 43210, U.S.A.

Abstract—Photolysis of 8-methyl-1-naphthyldiazomethane at 4 K gives the triplet ESR spectrum of 1,8-naphthoquinodimethane but not that of 8-methyl-1-naphthylcarbene. Photolysis of either 8-methyl-1-azido-naphthalene or 8-amino-1-azidonaphthalene does produce the triplet biradical spectra of 8-imino-1-naphthoquinomethane and 1,8-diiminonaphthoquinodimethane, in addition to the triplet nitrene spectra of 8-methyl-1-nitreno-naphthalene and 8-amino-1-nitreno-naphthalene. Curie Law analyses demonstrate that these biradicals are all ground state triplets. Hückel and INDO calculations pertaining to the biradicals are reported. Large charge transfer interactions were observed in the ESR spectra of 8 substituted-1-naphthyl nitrenes.
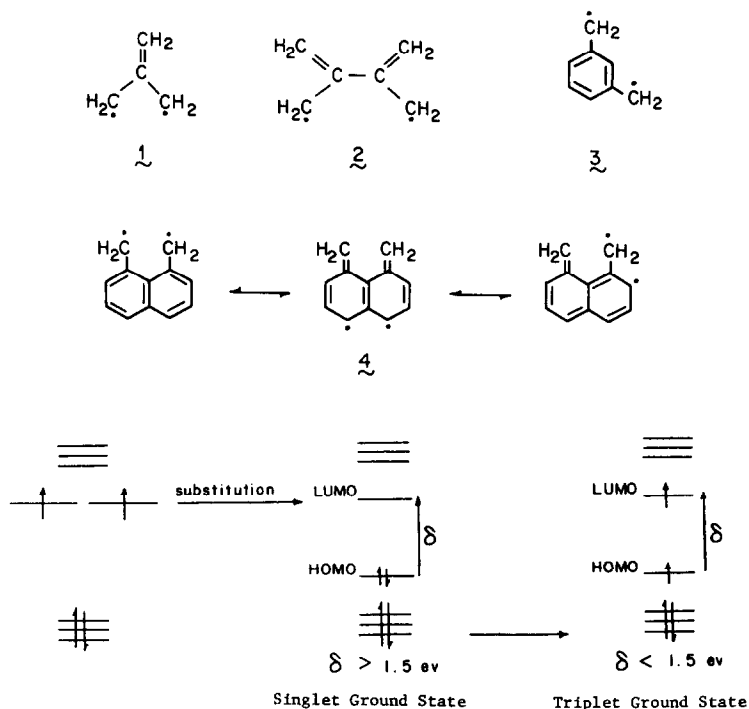
THERE are several hydrocarbons for which no stable Kékulé structure can be written.[1] Some examples of these molecules are trimethylenemethane (**1**), tetramethyleneethane (**2**), metaxylylene (**3**) and 1,8-naphthoquinodimethane (NQM) (**4**). A few valence structures for the last compound are shown.
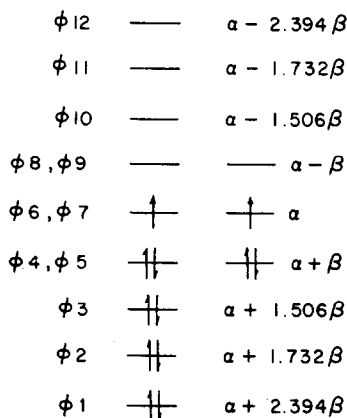
As the biradicaloid valence structures imply, these compounds exhibit very high reactivity and defy conventional attempts at their isolation and characterization. The chemical instability of **1–4** is clearly predicted by MO Theory even at the simple Hückel level (HMO). HMO energy level diagrams of **1–4** are distinguished by the presence of two degenerate nonbonding molecular orbitals (NBMO's). The diagram for **4** pictured in Fig. 1 is representative.[2] Upon following the Aufbau procedure, one finds that the last two electrons must be distributed between the two degenerate orbitals. This energy diagram is highly reminiscent of molecular oxygen, and following Hund's First Rule predicts that, like oxygen, compounds **1–4** should be ground state triplets.[3,4]

Chemical modification of the parent structures **1–4** invalidates the simple HMO prediction of triplet ground states by lifting the degeneracy of the NBMO's ϕ_M and ϕ_N, by an amount of energy δ (ϕ_6 and ϕ_7 in Fig. 1 for diyl **4**).

Elementary theory predicts that if δ is small Hund's Rule applies, and the last two electrons will distribute themselves in different orbitals with their spins parallel, so as to minimize their electrostatic repulsions. If δ is
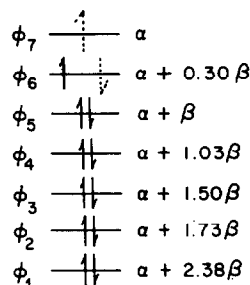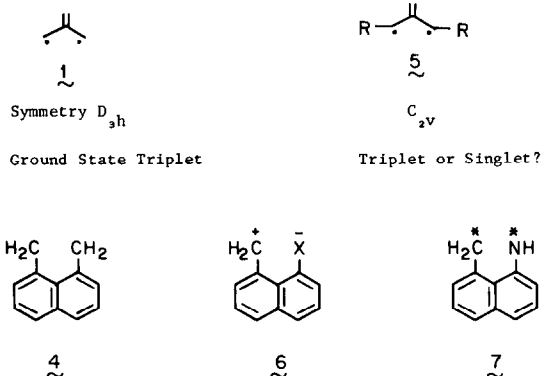
ϕ_{12} ——— $\alpha - 2.394\beta$

ϕ_{11} ——— $\alpha - 1.732\beta$

ϕ_{10} ——— $\alpha - 1.506\beta$

ϕ_8, ϕ_9 ——— ——— $\alpha - \beta$

ϕ_6, ϕ_7 $\dashv\!\!\uparrow$ $\dashv\!\!\uparrow$ α

ϕ_4, ϕ_5 $\dashv\!\!\uparrow\!\!\downarrow$ $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + \beta$

ϕ_3 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 1.506\beta$

ϕ_2 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 1.732\beta$

ϕ_1 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 2.394\beta$

Fig. 1. The simple HMO orbital energy diagram of 4.[2]

ϕ_7 $\dashv\!\!\uparrow\!\!\cdot$ α

ϕ_6 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 0.30\beta$

ϕ_5 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + \beta$

ϕ_4 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 1.03\beta$

ϕ_3 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 1.50\beta$

ϕ_2 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 1.73\beta$

ϕ_1 $\dashv\!\!\uparrow\!\!\downarrow$ $\alpha + 2.38\beta$

Fig. 2. The HMO calculation of 7 assuming $\alpha_n = 0.5\alpha c$ and $\beta_n = 0.8\beta c$ as suggested by Greenwood.[9]

The lowest singlet configuration is $\phi_1^2, \phi_2^2, \phi_3^2, \phi_4^2, \phi_5^2, \phi_6^2$. The lowest triplet configuration is $\phi_1^2, \phi_2^2, \phi_3^2, \phi_4^2, \phi_5^2, \phi_6^1, \phi_7^1$. The first excited singlet configuration is identical to that of the triplet at the HMO level.

large the energy benefit of placing both electrons in the lower orbital ϕ_M will outweigh the electron repulsion factor, and the singlet will be the ground state.[5] Hoffmann has suggested that if $\delta < 1.5$ eV the former case prevails.[6]

There are several chemical modifications of a biradical structure which can be expected to remove the degeneracy of the two NBMO's. The application of group theory to the linear combination of $2p_z$ atomic orbitals of D_{3h} trimethylenemethane 1 requires that there be two degenerate NBMO's, and consequently, a triplet ground state.[7] Lowering the symmetry of 1 to C_{2v} removes this restriction and a finite splitting of the formerly degenerate NBMO's is now permitted. Unfortunately, group theory does not assess the magnitude of the splitting, and consequently cannot predict the ground state multiplicity of a C_{2v} trimethylenemethane (5).

Another conceptual method of reordering the ground state multiplicity of a biradical is to vary the electronegativity of the biradical termini. One can envision that heteroatomic derivatives of 1,8 NQM, 4, will prefer a zwitterionic singlet 6 as the lowest electronic state.

This idea is supported by the results of a simple HMO calculation of 7. The NBMO's which were degenerate in 4 (Φ_6 and Φ_7 of Fig. 1) are split by 0.3β units in 7 (see Fig. 2).[8,9] Although HMO theory is capable of correlating many molecular properties it is not possible to say what magnitude of the HOMO–LUMO gap (in β units) is sufficient to produce a ground state singlet. Therefore it is not clear from the HMO calculation which multiplicity should be expected for the ground state of 7.

This is not surprising as HMO theory totally ignores spin and electron repulsion effects.[10] Ab initio calculations with large basis sets and extensive configuration interaction are inherently capable of predicting the ground state multiplicities of biradicals.[11] However, these results are not presently available for 1,8 NQM and its derivatives, due to the large size of these systems. The determination of the ground state multiplicities of these non-Kékulé biradicals is a formidable challenge to both theoreticians and experimentalists. In this work the ESR Spectroscopy of several 1,8 NQM's is described, and used to establish the ground state multiplicities of the biradicals.

The determination of the ground state multiplicities of biradicals by electron spin resonance spectroscopy

The most powerful method of characterizing a molecule in the triplet state is Electron Spin Resonance (ESR) Spectroscopy.[12] ESR was first successfully applied to triplets by Hutchison and Mangum.[13] In this pioneering effort, naphthalene in its photochemical triplet state was detected in a single crystal of durene. It was later shown by Wasserman et al. that triplets could be readily detected in polycrystalline and glassy matrices.[14] Low temperatures (4–77 K) and highly viscous matrices are used almost exclusively in the ESR spectroscopy of triplets. These conditions of temperature and phase severely restrict the motion available to the triplets. This has two desirable consequences; (1) it imparts a longer lifetime to the highly reactive triplet species and (2) it preserves the spectral integrity of the triplet by preventing motional averaging and relaxation induced line broadening.[15,16]

A triplet ESR spectrum is dominated by the dipole-dipole interaction of the two unpaired electrons, and gives rise to splittings of hundreds or even thousands of Gauss. As such, a triplet ESR spectrum is readily distinguished from that of a free radical. The radical spectrum consists of the much weaker electron–nuclear interactions which generally lead to spectral envelopes of less than 50–100 G. A triplet ESR spectrum can be analyzed in terms of two parameters, D and E. The D value is proportional to $1/r^3$ where r is the separation of the two unpaired electrons.[12]

The interpretation of a triplet biradical ESR spectrum can yield a wealth of structural information. However, the mere observation of a triplet spectrum does not establish the ground state multiplicity of the biradical. The most compelling evidence for a ground state triplet

1
Symmetry D_{3h}
Ground State Triplet

5
C_{2v}
Triplet or Singlet?

$H_2C \quad CH_2$

4

$H_2\overset{+}{C} \quad \overset{-}{X}$

6

$H_2\overset{*}{C} \quad \overset{*}{N}H$

7

is the conjunction of a paramagnetic ESR spectrum and a linear Curie Law plot.[17] The Curie Law states that the intensity (I) of a stable ESR signal multiplied by the absolute temperature (T) is equal to a constant (C).
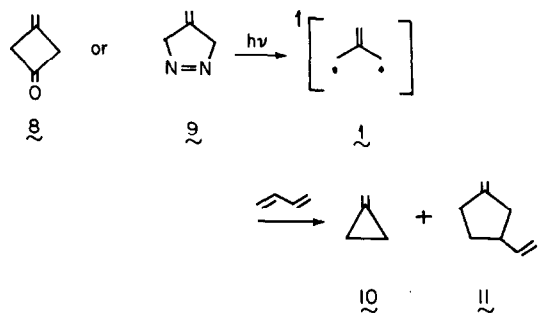
$$I \cdot T = C. \tag{1}$$

When the singlet and ESR active triplet of a biradical are in rapid equilibrium due to a small energy separation, Wasserman's modification of the Curie Law predicts the relationship between signal intensity and temperature.[18]

$$I \cdot T = \frac{C \exp(-\Delta E/RT)}{1 + 3 \exp(-\Delta E/RT)}. \tag{2}$$

Thus, if the triplet is the ground state by more than a few hundred cal/mole, its signal intensity will vary as per eqn (1), but if the triplet is a low lying excited state, and it can be observed by ESR, the signal intensity will change with temperature in accordance with eqn (2).

Dowd has generated trimethylenemethane 1 in solution by photolysis of 8 or 9.[19] As expected the major reaction of biradical 1 is closure to methylenecyclopropane 10, but the biradical can also be trapped in low yields with butadiene to give adduct 11.[3] In Berson's trimethylene-

methane derivative 12, ring closure is slowed due to the high strain energy of 13 and quantitative yields of adducts 14 can be realized. In the absence of a suitable trapping agent, a mixture of dimers is obtained.[20]

Dowd has observed the triplet ESR spectrum of 1 upon irradiation of neat 8 at 77 K. Under these conditions 1 is indefinitely stable. The rigid matrix prevents diffusion and dimerization of the biradical, and the low

temperature employed essentially freezes out any reaction associated with an enthalpy of activation greater than 5 kcal/mole. A Curie Law analysis of 1 demonstrated that trimethylenemethane does indeed have a triplet ground state in agreement with simple HMO.[21] Berson et al. have matrix isolated several trimethylenemethane derivatives (16 a–g).[22] The interesting triazadiyl 17 has also been observed by triplet ESR spectroscopy.[23]
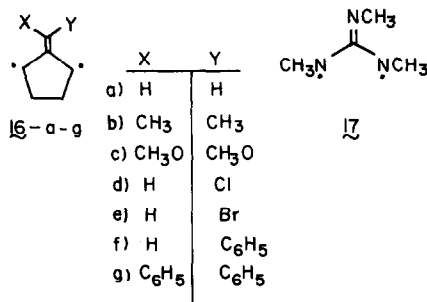
Each of these diyls was subjected to a Curie Law analysis and found to have a triplet ground state. These results indicate that over a large range of substitution patterns and angular distortions the splitting of the two nearly NBMO's of the TMM's remains relatively small.

Tetramethyleneethane 2 and a derivative 18 have both been observed by low temperature ESR.[24] However, to the author's knowledge Curie Law studies have not been performed on these species, hence their ground state multiplicities are not established rigorously. The triplets are either the ground states of 2 and 18 or are within a kcal/mole of the ground state.[18]
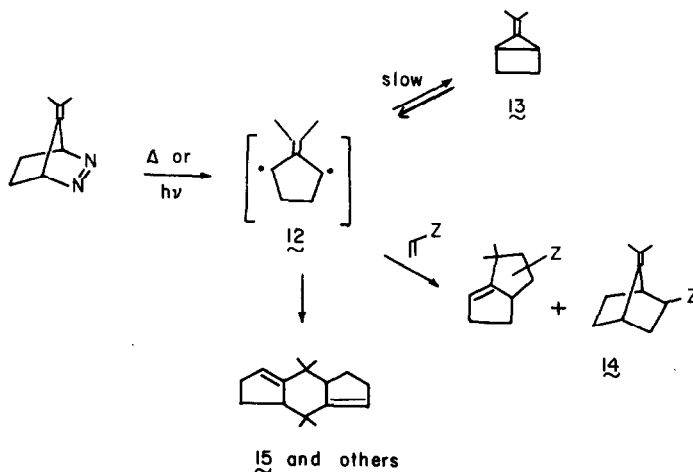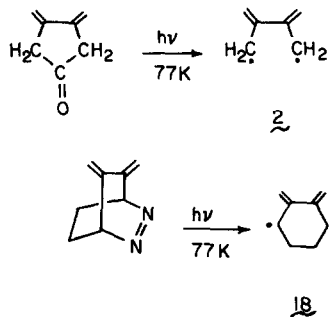
In contrast to the wealth of chemical and spectroscopic data available for ortho and para-xylylene (19 and 20 respectively) very little is known about the *meta* isomer 3.[25]

The first reported cyclophane synthesis, due to Pellegrin in 1899 may proceed by way of *m*-xylylene.[26] Gajewski and Stang have recently described an ingenious method of generation of tetramethyl *m*-xylylene 24.[27]

There is only one report in the literature describing the spectroscopic detection of *m*-xylylene. Migridicyan and Baudet have exhaustively photolyzed ($\lambda = 2537$ Å) *m*-xylylene in a matrix at 77 K.[28] The new emission bands obtained from the irradiated sample have been assigned to *m*-xylylene.

The authors have interpreted the emission spectrum as most consistent with a triplet species. This has not yet been confirmed by ESR studies.

The Berson group has observed the oxa derivatives of *m*-xylylene 27 and 29 by ESR.[29] Curie Law analyses of the biradicals have established that the triplet is the ground state of these species, despite the presence of attractive singlet zwitterionic alternatives 30 and 31.

Several 1,8 NQM biradicals have been observed by ESR. Pagni has observed the triplet ESR spectrum of 4 by low temperature photolysis of Carpino's azo compound 32.[30] The first 1,8 NQM type biradical to be observed spectroscopically was the ethano bridged compound 34.[31] This species was detected by the Pagni
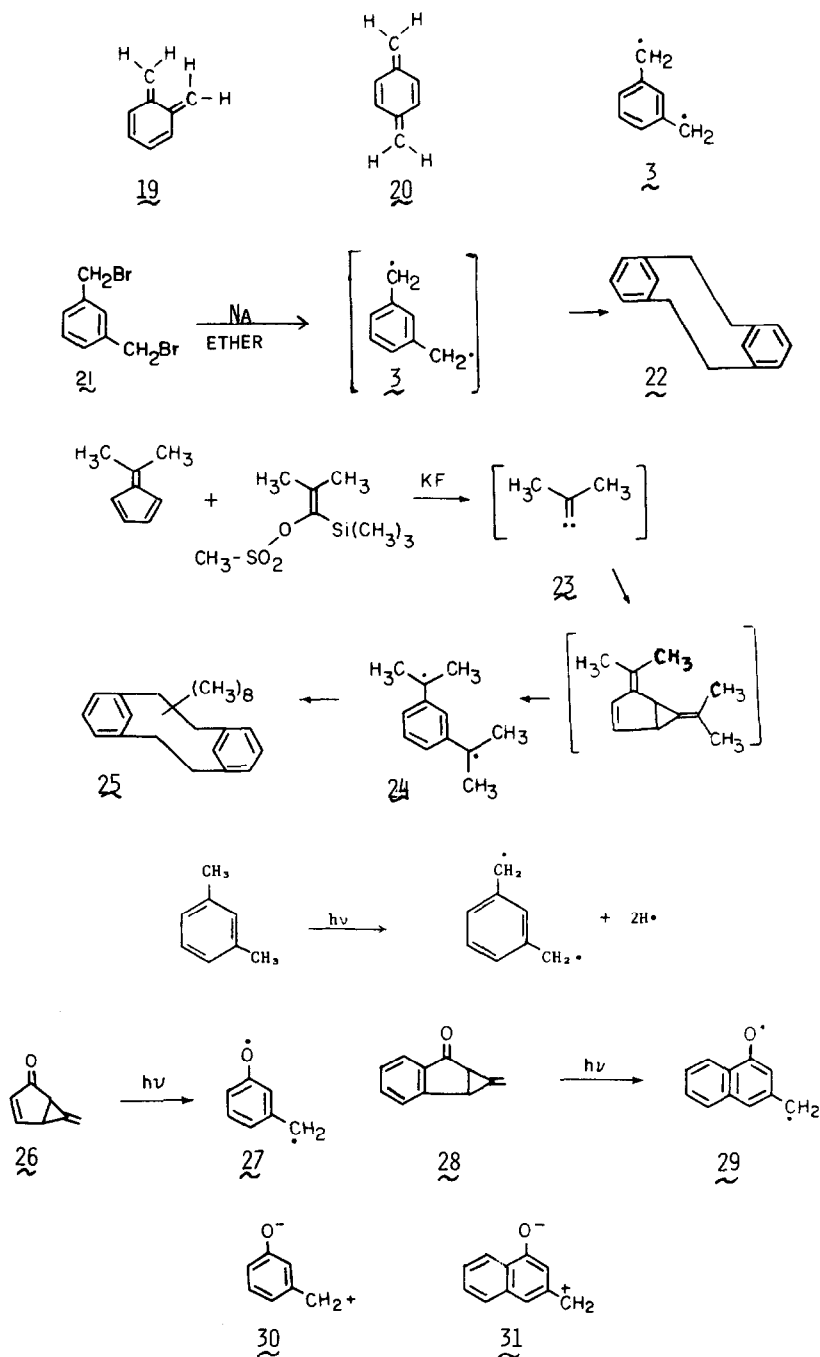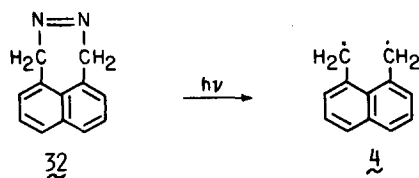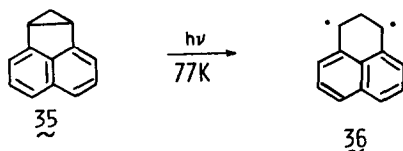
group following low temperature photolysis of azo compound 33.
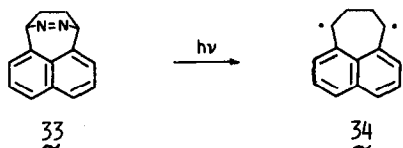
Michl *et al.* have reported the triplet ESR spectrum of the methano bridged biradical 36 following the photolysis of cyclopropane 35.[32]


Matrix isolation of triplet biradicals from carbene precursors

The matrix isolation of biradicals is frequently accomplished by the unimolecular photochemical fragmentation of an azo or carbonyl compound. This process results in the formation of a biradical and a small stable compound such as N_2, CO or CO_2. As inter and intramolecular H atom abstraction reactions are well known triplet carbene and nitrene processes,[33] it was hoped that this reaction might be applicable to the matrix isolation of biradicals.
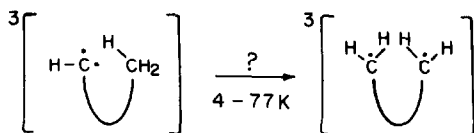
To test the feasibility of this approach 8 methyl - 1 - naphthyldiazomethane 37 was synthesized. Trozzolo, Wasserman and Yager have shown that 1 - naphthyl-carbene has a triplet ground state.[34] Presumably, 8 methyl - 1 - naphthyl carbene 38 should be a triplet species as well.
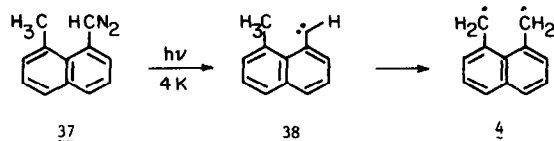

Photolysis of 37 at 4 K in either a glassy 2-methyl-tetrahydrofuran (2MTHF) or hexafluorobenzene poly-crystalline matrix gives rise to an intense ESR spectrum of 1,8 NQM, identical to that previously observed by Pagni.

Curie Law analyses of 1,8 NQM's 4, 34, and 36 were originally interpreted as consistent with the triplet states of these diyls being low lying (20–600 cal/mole) thermally

excited states.[30–32] Our reinvestigation of the Curie dependence of 1,8 NQM 4 revealed an excellent straight line plot (as per eqn 1) between 10 and 77 K.[35] This is strong evidence in favor of a triplet ground state for this species. Deviations from eqn (1) were observed between 4–10 K but these are attributed to saturation of the biradical ESR transitions at cryogenic temperatures. Wirz and Pagni have reexamined the Curie effect upon biradicals 34 and 36 between 4 and 77 K and have demonstrated that the methano and ethano bridged 1,8 NQM's also have triplet ground states.[36]
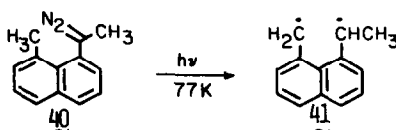
A disappointing aspect of the low temperature photolysis of diazo compound 37 was the failure to observe the triplet spectrum of 8 - methyl - 1 - naphthyl carbene 38. Either the carbene to biradical rearrangement is extremely rapid at 4 K, or the biradical is formed in an alternative process not involving a carbene intermediate. The intramolecular H atom transfer may occur in an excited state of diazo compound 37 as per 39.[37]
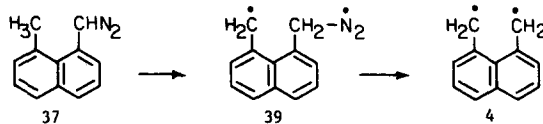

One expects that the hypothetical triplet carbene (38) to biradical (4) rearrangement should involve a finite activation energy (Ea). If Ea were as low as 0.5 kcal/mole, and log A as high as $20 \sec^{-1}$, the Arrhenius equation predicts that the rate constant for the rearrangement would be less than $10^{-7} \sec^{-1}$ at 4 K! This alone seems to contradict the operation of straight-forward hydrogen transfer. However, recent work by Senthilnathan reveals that hydrogen abstraction by triplet carbenes in low temperature matrices occurs via quantum mechanical tunneling.[38] A tunneling process seems particularly appropriate for 8 - methyl - 1 - naphthyl-carbene due to the short distance the migrating hydrogen must traverse. Unlike a classical reaction, a tunneling rate constant does not go to zero at liquid helium temperature but approaches a limiting value.[39] The limiting tunneling rate constant at 4 K may be large in 38 due to the very small barrier width.[40] The mechanism of formation of biradical 4 remains undetermined. Both of the aforementioned routes are viable possibilities.
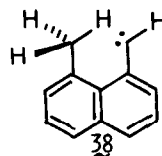
The matrix isolation of 1,8 NQM biradicals from formal carbene precursors has been tested in a few other cases. Photolysis of diazo compound 40 gives rise to the ESR spectrum of a Me derivative of 1,8 NQM 41. As in the parent system, carbenes were not observed by ESR. The spectrum of 41 is much weaker than that of 4. This is presumably a consequence of the availability of 1,2 hydrogen migration in carbene intermediates to give 1 - methyl - 8 - vinylnaphthalene.[35]

Low temperature photolysis of 8 - benzyl - 1 - naphthyldiazomethane **42** was disappointing. In this case neither carbene **43** nor biradical **44** could be observed via ESR. Product analysis of the photolysis mixtures showed that phenylacenaphthene **45** and dihydropleiadene **46** were the only products formed.


42 → **43** + **44**

45   **46**
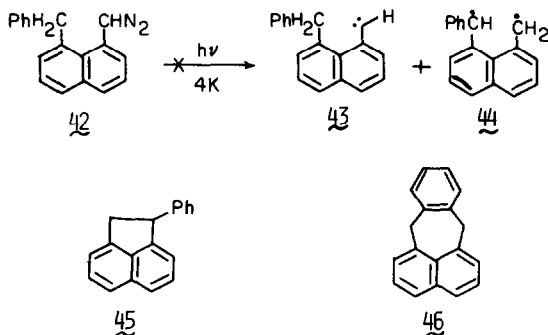
Photolysis of diazo compound **47** in hexafluorobenzene gave rise to a strong spectrum of carbene **48** ($|D/hc| = 0.3458 + 0.0018$ cm^{-1}, $|E/hc| = 0.00178 \pm 0.0018$ cm^{-1}). Incorporation of the peri alkyl moiety into a cyclic structure apparently reduces the availability of a benzylic hydrogen atom for migration. Indeed carbene **48** does not decay at an appreciable rate in the matrix until warmed to 170 K. The anticipated product of unimolecular hydrogen migration in this case is pleiadene **49**, which is known to be a ground state singlet biradicaloid.[41]

47   **48**   **49**
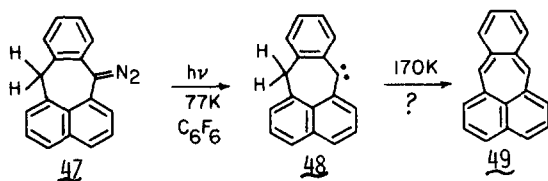
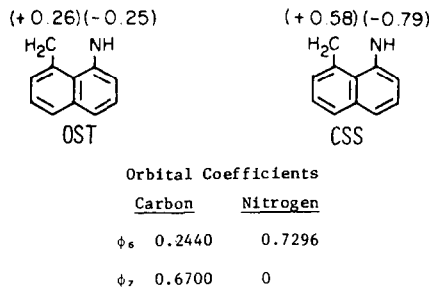### Matrix isolation of nitrogen centered triplet biradicals from nitrene precursors

The successful observation of hydrocarbon biradicals from carbene precursors prompted work on the corresponding nitrenes. Irradiation of 8 - methyl - 1 - azidonaphthalene **50**, in 2MTHF, at 77 K, produced a mixture of heteroatomic biradical **7** ($|D/hc| = 0.0255 \pm 0.0002$ cm^{-1}, $|E/hc| = 0.0008 + 0.0002$ cm^{-1}) and 1 - methyl - 8 - nitrenonaphthalene **51** ($|D/hc| = 0.79 \pm 0.02$ cm^{-1}, $|E/hc| < 0.003$ cm^{-1}). The two sets of triplet resonances are well separated, which facilitates their study.[42]

50   **7**   **51**
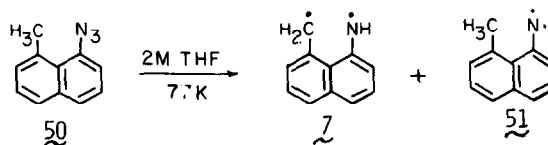
A Curie Law analysis was performed on biradical **7** between 17 and 83.5 K. An excellent linear plot was observed demonstrating that the ground state of **7** is a triplet.

A simple Hückel calculation of **7** (see Fig. 2) reveals an extremely small HOMO–LUMO gap of 0.3β. As electron repulsion and electron correlation effects are not treated at this level, HMO theory makes no clear prediction of

ground state multiplicity. The lowest HMO electron configuration (ϕ_1^2, ϕ_2^2, ϕ_3^2, ϕ_4^2, ϕ_5^2, ϕ_6^2) is an extremely ionic closed shell singlet (CSS). The first excited electron configuration (ϕ_1^2, ϕ_2^2, ϕ_3^2, ϕ_4^2, ϕ_5, ϕ_6, ϕ_7) is much less ionic, and open shell (singlet or triplet; OST) in nature.


(+0.26)(−0.25)   (+0.58)(−0.79)

OST   CSS

Orbital Coefficients

	Carbon	Nitrogen
ϕ_6	0.2440	0.7296
ϕ_7	0.6700	0

Inspection of the orbital coefficients of ϕ_6 and ϕ_7 is particularly revealing. The singlet–triplet interconversion (OST ⇌ CSS) is essentially electron transfer from the exocyclic C to N. This is the ideal circumstance for spin orbit assisted intersystem crossing.[43] Preliminary kinetic studies to be reported elsewhere indicate a larger intersystem crossing rate in biradical **7**, compared, with the hydrocarbon 1,8 NQM **4**.

The HMO results for **7** are in qualitative agreement with previous work on nitrogen centered radicals. The ESR and INDO studies of Wood on the anilino radical have demonstrated considerable charge separation (−0.19 charge on nitrogen) indicative of the contribution of a zwitterionic resonance form.[44]


INDO calculations for the planar, anticonformation of **7** have been performed using the optimized C–N and N–H bond lengths and C–N–H bond angle found by Wood for the anilino radical.[45] The geometries of the


7 anti
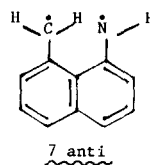
ring carbons were not optimized. The geometry of the parent naphthalene ring system was assumed for **7**, despite the fact that the peri substituents must certainly cause some distortion of the ring system.[46] The INDO calculation finds that the triplet of **7** anti is the ground state. The singlet–triplet splitting is 60 kcal/mole. The magnitude of the energy gap obtained via INDO is likely to be an exceedingly high upper limit. This is a consequence of the poor description of the singlet state obtained without configuration interaction.[47]

Both nitrene **51** and biradical **7** are long lived at 77 K in 2MTHF. Warming the mixture to 98 K results in the rapid and complete dissipation of the biradical signal **7**, but very little change of the nitrene signal intensity. Clearly the triplet biradical is not formed sequentially from the triplet nitrene in a thermally activated process at 77 K.
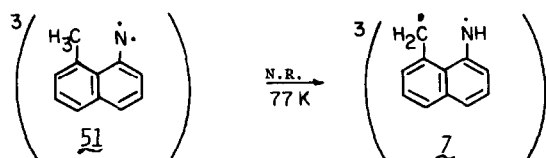
Conceivably, the biradical might be formed in the matrix in a secondary photochemical process. To test this possibility the signal intensities of the nitrene 51 and biradical 7 were studied as a function of irradiation time. The ratio of 7/51 was invariant with the duration of the photolysis at 77 K. The nitrene and biradical are formed simultaneously, not sequentially. Photolysis of the long-lived triplet nitrene in the matrix is not the source of the biradical. Control experiments with cyclic amine 52 demonstrate that it is not photochemically cleaved, and therefore it cannot be the source of the diradical.
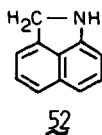
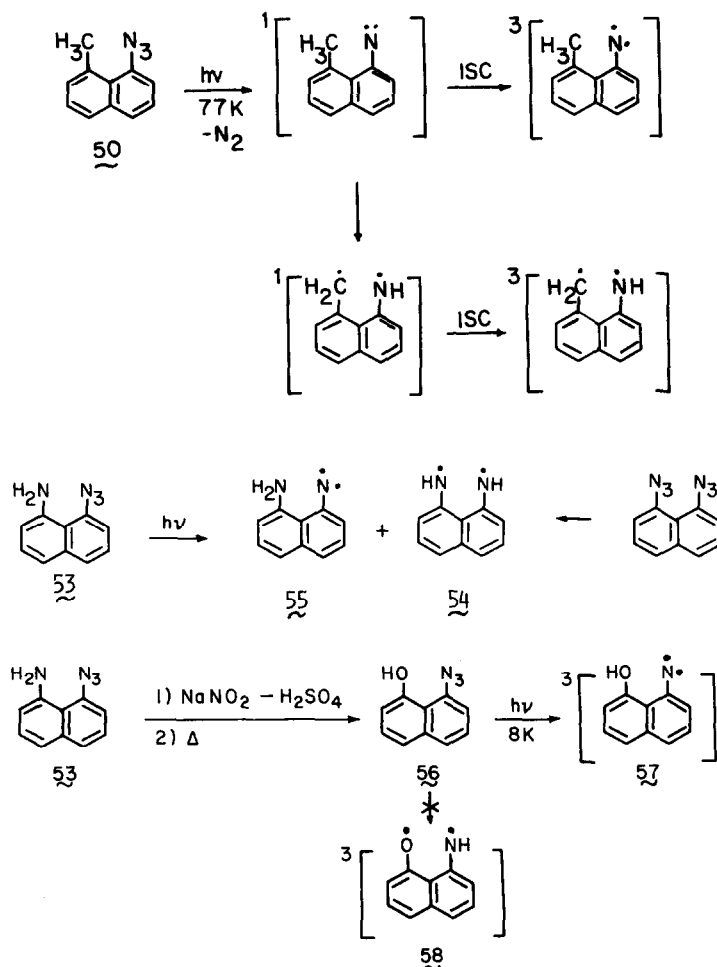A simple explanation of the ESR results is that photolysis of azide 50 produces an intermediate which partitions itself between formation of triplet nitrene and

triplet biradical. A likely candidate for the common intermediate is the singlet state of 8 - methyl - 1 - nitrenonaphthalene (Scheme 1) but this remains to be established.

Analogs of 8 - methyl - 1 - azidonaphthalene were photolyzed at 77 K in an attempt to observe other N centered biradicals. Low temperature irradiation of Rees' aminoazide 53 produced the well-separated triplet resonance absorptions of diazabiradical 54 ($|D/hc|$ = $0.0257 + 0.0002$ cm^{-1}, $|E/hc| < 0.0004$ cm^{-1}) (Fig. 3) and aminoitrene 55 ($|D/hc| = 0.62$ cm^{-1}). Both triplets are indefinitely stable at 77 K. A weak spectrum of 54 was also observed upon photolysis of 1,8 - diazidonaphthalene at 77 K. A Curie Law analysis of 54 over the temperature range 12.5–77.5 K indicates that the triplet is the ground state of the biradical.

The amino azido compound 53 was used to prepare the hydroxy derivative 56. The amine was diazotized with aqueous H_2SO_4-$NaNO_2$ at 0°C, diluted with water and steam distilled. After work-up a mixture of 1-azidonaphthalene and 8 - hydroxy - 1 - azidonaphthalene was obtained which was separated into its components by a simple extraction procedure. Upon photolysis of 56 at 77 K no triplet ESR spectra were observed. When the photolysis was repeated at 8 K only a weak spectrum of the nitrene 57 was observed. The isomeric triplet biradical 58 could not be observed, even at 4 K.
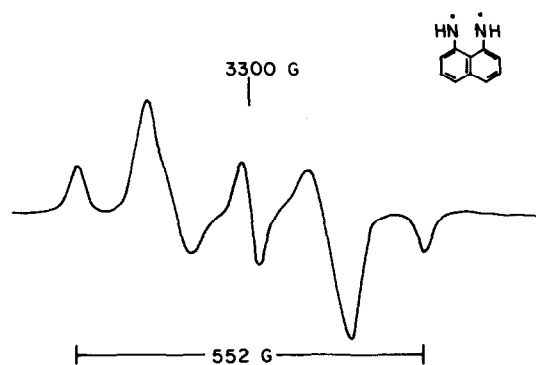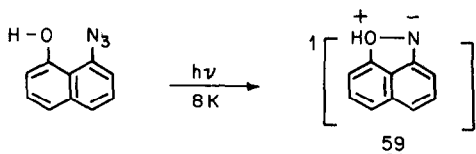
Scheme 1.

HN NH

3300 G

Fig. 3.

Table 1. The $|D/\hbar c|$ parameters of some 8-substituted 1-naphthyl nitrenes

8-Substituent	$|D/\hbar c|(cm^{-1})^b$	Ref.
NH_2	0.62	a
OH	0.75	a
N_3	0.76	a
NO_2	0.78	a
CO_2H	0.78	a
Cl	0.72	a
Br	0.57	a
I	——	a
CH_3	0.79	42
H	0.79	48

(a) this work   (b) $|D/\hbar c|$ are ± 0.02 cm^{-1}

All spectra were run in a 2-methyltetrahydrofuran glass.

The low signal intensity of nitrene 57 implies that there may be a rapid interaction between the peri moieties following the extrusion of nitrogen. This diverts the reaction course from the formation of triplet species. One possibility of this type is ylid formation 59. Low temperature IR spectroscopy is in progress to probe for ylid type intermediates.

H-O   N₃ $\overset{h\nu}{\underset{8 K}{\longrightarrow}}$ 1 ⎡ HO—N ⎤ ⁺ ⁻
                                                                            ⎣   ⎦
                                                                                59

Finally, the zero field parameters of 8-substituted nitrenonaphthalenes are worthy of note. The $|D/\hbar c|$ parameter of 8 - amino - 1 - nitreno naphthalene is 16% smaller than that of 1-nitrenonaphthane. Wasserman has found that the $|D/\hbar c|$ parameter of matrix isolated carbenes and nitrenes is decreased in electron donating and accepting hosts. Interactions of this type lower the value of $|D/\hbar c|$ of aryl nitrenes relative to that observed in more inert matrices by less than 2%.[48] The large effect in 55 indicates that there is substantial electron donation from the amine to the electron deficient perinitrene. This interaction puts spin density on the amino nitrogen and lessens the spin density on the nitrene. As $|D/\hbar c|$ is proportional to $(1/r^3)$, where r is the average separation of the two unpaired electrons, $|D/\hbar c|$ decreases with increasing spin delocalization.

δ•   δ•
H₂N   N•

55
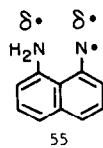
The $|D/\hbar c|$ parameters of 8-hydroxyl, and 8-azido, 1-nitrenonaphthalene display modest charge transfer interactions (Table 1). 8-methyl, 8-nitro and 8-carboxyl-1 - nitrenonaphthalene show essentially no charge transfer interaction. 8-Chloro and 8-bromo substitution produce very large effects on $|D/\hbar c|$. In fact, the bromo compound has the largest effect on $|D/\hbar c|$ of all the substituents examined. The halogen substituent effect is likely a combination of charge transfer and spin orbit interactions. The ESR spectrum of 8 - iodo - 1 - nitreno - naphthalene was not observed upon low temperature photolysis of the azide. This may also be due to rapid ylid formation which bypasses triplet potential minima.

EXPERIMENTAL

Materials. Many of the azides used in this work have been prepared previously. The preparations of 8-amino,[49] 8-chloro,[50] 8-bromo,[50] 8-iodo,[50] 8-nitro,[51] 8 - methyl - 1 - azido[42] naphthalene and 1,8-diazidonaphthalene[52] are reported in the literature. The preparations of 12-H-7 Diazopleiadene (33) and 8 benzyl - 1 - naphthyl diazomethane (35) are described elsewhere.[53]

8-Hydroxy-1-azidonaphthalene (56) 0.1 g of aminoazide 53 was stirred with 3 ml of a soln of 6 ml conc H_2SO_4 and 35 ml water. This was cooled to 0° and then 0.2 ml of a soln of 8.58 NaNO₂ in 50 ml water was added. The dark soln was stirred for 10 min then poured into 250 ml water and steam distilled behind a safety shield until 100 ml distillate was collected. The distillate was brought to pH 10 and washed twice with CH_2Cl_2 to remove 1-azidonaphthalene. The aqueous phase was brought to pH 4 with conc HCl and extracted $(3 \times 50$ ml) with CH_2Cl_2. The combined extracts were dried over $MgSO_4$, filtered and solvent removed to give 20 mg of a waxy tan solid. Mass Spectroscopy shows $m/e - 185.0596568$ (Calc. 185.0589077) and no peaks above 186; IR, 3,300; 2080 cm^{-1}.

Spectroscopy. All ESR spectra were obtained on a Varian E-112 spectrometer. Samples were prepared by weight between 0.1 and 1.0 M and syringed into 4 mm quartz tubes. These were degassed by three freeze thaw cycles and sealed under vacuum. Spectra at 77 K were obtained by immersion of the sample tubes into a quartz dewar filled with liquid nitrogen. Temperatures below 77 K were achieved by flowing liquid helium through an Air Products Helitrans dewar system. Temps above 77 K were achieved and regulated with the Varian variable temp accessory. Temps were measured by means of an Omega digital thermometer. The samples were irradiated using a 150 watt xenon lamp.

Computations. The HMO and INDO programs used in this work were obtained from the Quantum Chemistry Program Exchange, Bloomington, Indiana (programs 81 and 141, respectively).

Product analyses. 8 - benzyl - 1 - naphthyldiazomethane was directly photolyzed and subjected to xanthone sensitized photolysis at room temp and at 77 K in 2-methyltetrahydrofuran. The photochemistry was performed in the chamber of a Rayonet Reactor equipped with four 3500 Å lamps. The only products observed by NMR and Gas Chromatography were 1-phenyl-acenaphthene and 7, 12-dihydropleiadene. These compounds were identified by comparison with authentic samples by both NMR and G. C. A Hewlett-Packard Model 5830A G.C. was employed along with a 6 ft 10% SE30 column. A mass balance (internal standard biphenyl) accounted for greater than 90% of the starting azo compound.

CONCLUSIONS

Low temperature photolysis of appropriately 8 sub-stituted 1 - naphthyldiazomethanes or 1-naphthylazides

in rigid matrices can produce hydrocarbon and nitrogen centered 1,8 naphthoquinodimethane biradicals. These biradicals can be readily detected in their triplet states by ESR Spectroscopy. Curie Law analyses of the biradicals reported herein establish that they are all ground state triplets.

REFERENCES

[1]For early considerations see W. E. Moffitt, Footnote to C. A. Coulson, *J. Chim. Phys.* **45**, 243 (1948) and W. E. Moffitt, *Trans. Far. Soc.* **45**, 373 (1949).

[2]C. A. Coulson, A. Streitwieser, *A Dictionary of π Electron Calculations.* Freeman, San Francisco (1965).

[3]F. Hund, *Linienspektren und periodisches System der Elemente,* p. 124. Springer-Verlag, Berlin (1927).

[4]F. Brescia, J. Arents, H. Meislich and A. Turk, *Fundamentals of Chemistry,* p. 366. Academic Press, New York (1975).

[5]For a valuable discussion of electron repulsion effects in biradicals see W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **99**, 4587–4594 (1977).

[6]R. Hoffmann, *J. Am. Chem. Soc.,* **90**, 1475–1485 (1968).

[7]F. A. Cotton, *Chemical Applications of Group Theory.* Wiley-Interscience, New York (1971).

[8]The authors are indebted to Mr. M. Skoglund for his help with these computations.

[9]H. H. Greenwood, *Computing Methods in Quantum Organic Chemistry.* Wiley-Interscience, New York (1972).

[10]A. Streitwieser, *Molecular Orbital Theory for Organic Chemists.* Wiley, New York (1961).

[11]For representative examples see: [a]M. P. Conrad, R. M. Pitzer and H. F. Schaefer III, *J. Am. Chem. Soc.* **101**, 2245 (1979); [b]W. F. Borden and E. Davidson, *Annu. Rev. Phys. Chem.* **30**, 125 (1979).

[12][a]A. Carrington and A. D. McGlaughlin, *Introduction to Magnetic Resonance.* Harper & Row, New York (1976); [b]N. Atherton, *Electron Spin Resonance.* Wiley, New York (1973).

[13]C. A. Hutchinson, Jr. and B. W. Magnum, *J. Chem. Phys.* **34**, 908–922 (1961).

[14]E. Wasserman, L. C. Snyder and W. A. Yager, *Ibid.* **41**, 1763 (1964).

[15]S. I. Weissman, *Ibid.* **29**, 1189 (1958).

[16]S. I. Weissman, *Accts. Chem. Res.* **6**, 233. (1973).

[17]R. Resnick and D. Halliday, *Physics Part II,* p. 22. Wiley, New York (1962).

[18]R. Breslow, H. W. Chang, R. Hill and E. Wasserman, *J. Am. Chem. Soc.* **89** 1112 (1967).

[19][a]P. Dowd, *Accts. Chem. Res.* **5**, 242 (1972); [b]P. Dowd, *J. Am. Chem. Soc.* **88**, 2587 (1966); [c]P. Dowd and K. Sachdev, *Ibid.* 713 (1967); [d]P. Dowd, A. Gold and K. Sachdev, *Ibid.* **90**, 2173 (1968).

[20]J. A. Berson, D. M. McDaniel, L. R. Corwin and J. H. Davis, *Ibid.* **94**, 3308 (1972).

[21]R. J. Baseman, D. W. Pratt, M. Chow and P. Dowd, *Ibid.* **98**, 5726–6726 (1976).

[22]M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter and J. A. Benson, *Ibid.* **98**, 5725–5726 (1976).

[23]H. Quast, L. Bieber and W. C. Danen, *Ibid.* **100**, 1306 (1978).

[24][a]P. Dowd, *Ibid.* **92**, 1066–1068 (1960); [b]V. W. R. Roth and G. Erker., *Angen, Chem.* **85**, 510–511 (1973).

[25][a]W. Oppolzer, *Synthesis* **11**, 793 (1978); [b]W. Oppolzer, *Angew. Chemie. Int. Ed. Engl.* **16**, 10 (1977); [c]V. Boekelheide, *Accts.*

Chem. Res. **13**, 65 (1980); [d]J. J. McCullough, *Ibid.* **13**, 270 (1980).

[26][a]M. Pellegrin, *Recl. Trav. Chim. Pays-Bas.* **18**, 457–465 (1899); [b]W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.* 1114–1118 (1951).

[27]J. J. Gajewski, M. J. Chang, P. J. Stang and T. E. Fisk, *J. Am. Chem. Soc.* **102**, 2096–2097 (1980).

[28]E. Migirdicyan and J. Baudet, *Ibid.* **97**, 7400–7404 (1975).

[29][a]M. Rule, A. R. Matlin, E. F. Hilsinki, D. A. Dougherty and J. A. Berson, *Ibid.* **101**, 5098 (1979).

[30][a]L. A. Carpino, *Ibid.* **83**, 2144 (1963); [b]R. M. Pagni, M. N. Burnett and J. R. Dodd, *Ibid.* **99**, 1972 (1977).

[31]C. R. Watson, Jr., R. M. Pagni, J. R. Dodd and J. E. Bloom, *Ibid.* **98**, 2551 (1976).

[32]J. F. Muller, D. Muller, H. Dewey and J. Michl, *Ibid.* **100**, 1629–1630 (1978).

[33]Kirmsen, *Carbene Chemistry.* Academic Press, New York (1971).

[34]A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.* **87**, 129 (1965).

[35]M. S. Platz, *Ibid.* **10**, 1192–1193 (1980).

[36]M. Gisin, E. Rommel, J. Wirz, M. N. Burnett and R. M. Pagni, *Ibid.* **101**, 2216 (1979).

[37]H. Tomioka, H. Kitagawa and Y. Izawa, *J. Org. Chem.* **44**, 3072 (1979).

[38]V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.* **102**, 7637–7643 (1980).

[39]E. F. Caldin, *Chem. Rev.* **69**, 135–156 (1969).

[40]Preliminary Eckart Barrier calculations or Prof. C. W. McCurdy Jr. predicts large tunneling rate constants for very small barrier widths.

[41][a]J. Kolc and J. Michl, *J. Am. Chem. Soc.* **92**, 4147 (1970); [b]J. Michl and J. Kolc, *Ibid.* **92**, 4148 (1970). [c]*Ibid.* **95**, 7391 (1973).

[42]M. S. Platz and J. R. Burns, *Ibid.* **101**, 4425–4426 (1979).

[43][a]S. P. McGlynn, T. Azumi and M. Kinoshita, *Molecular Spectroscopy of the Triplet State.* Prentice Hall, Englewood Cliffs, New Jersey (1969); [b]L. Salem and C. Rowland, *Angew. Chem. Int. Ed Engl.* **11**, 92–111 (1972); [c]J. Michl, *Mol. Photochem.* **4**, 243–255, 257–286, 287–314 (1972); [d]S. Shaik and N. D. Epiotis, *J. Am. Chem. Soc.* **100**, 18–29 (1978); [e]J. J. Turro, *Modern Molecular Photochemistry,* pp. 46–51. Benjamin Cummins, Reading, Mass. (1978). Biradical ISC can also occur by nuclear hyperfine interaction, see reference 37, G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.* **95**, 2735–2736 (1973).

[44]R. V. Lloyd and D. E. Wood, *Ibid.* **96**, 659–665 (1974).

[45]Wood's optimized parameters are N–H = 1.074 Å, C–N = 1.379 Å and a CNH bond angle of 111.5°, see Ref. 44.

[46]J. F. Blount, F. Cozzi, J. R. Damewood, Jr., L. D. Iroff, Sjostrand and K. Mislow, *J. Am. Chem. Soc.* **102**, 99 (1980).

[47]See W. T. Borden, *Reactive Intermediates* (Edited by M. Jones, Jr. and R. A. Moss), Vol. 2. Wiley, New York (1980).

[48]E. Wasserman, *Adv. Physical Org. Chem.* **8**, 328.

[49]S. Bradbury, C. W. Rees and R. C. Storr, *J. Chem. Soc.* Perkin I, 68–71 (1972).

[50]The 8 halo-1-azidonaphthalenes were prepared by the method of Schechter and Yang, unpublished research, The Ohio State University.

[51]M. O. Forster and H. E. Fierz, *J. Chem. Soc.* 1942–1953 (1970).

[52]R. W. Hoffman, G. Gutin M. Preiss and B. Ditreich, *Ibid.* (C), 769–772 (1969).

[53]Frank Pierrat, Masters Thesis, The Ohio State University (1981).