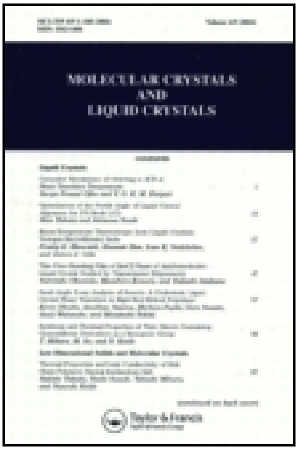

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Recent Studies of Meta-Xylylene and a Diaza Derivative

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To cite this article: K. W. Haider , E. Migirdicyan , M. S. Platz , N. Soundararajan & A. Despres (1989): Recent Studies of Meta-Xylylene and a Diaza Derivative, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 176:1, 85-98

To link to this article: http://dx.doi.org/10.1080/00268948908037470

Mol. Cryst. Liq. Cryst., Vol. 176, pp. 85–98
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Printed in the United States of America

Recent Studies of Meta-Xylylene and a Diaza Derivative

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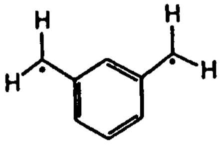
Abstract A new photochemical precursor to meta-xylylene is reported and its mechanism of action discussed. A diaza derivative of meta-xylylene is also reported.

Meta-xylylene **1** is an example of a non-Kekule hydrocarbon, a compound for which there are no non-biradical resonance structures possible.[1] A simple Huckel Molecular Orbital treatment of meta-xylylene reveals the presence of a pair of degenerate non-bonding molecular orbitals.[2] Extension of Hund's first rule to molecules predicts that meta-xylylene should be a ground state triplet molecule.[3] This prediction is also valid for diaza derivative **2**.



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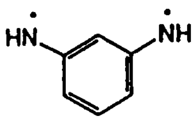

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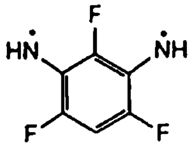

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This prediction was confirmed by Migirdicyan[4] who was the first to prepare biradical **1** and to characterize its fluorescence spectrum. Wright and Platz[5] and Goodman and Berson[6] subsequently detected its triplet EPR spectrum. None of the precursors used previously to prepare meta-xylylene were completely satisfactory, however. We herein report an improved entry into the meta-xylylene system and a facile preparation of diaza derivative **3**.

Photochemistry of α,α'-Dihalo-meta-xylene

We have previously reported[7] that the 254 nm photolysis of α,α'-dichloro-m-xylene **4** in glassy ethanol at 77K gives rise to meta substituted benzyl-monoradicals and m-xylylene biradicals, which are detected by their fluorescence starting at 471 and 438 nm, respectively. The ratio of biradical/monoradical is, however, much higher with the dihalide precursor than that produced on photolysis of meta-xylene.

The fluorescence spectra of the mono and biradicals produced by photolysis of α,α'-dichloro-m-xylene **4** in ethanol at 77K with an excimer laser pulsed at high frequency (5Hz) at 249 nm are presented in figure 1. In the early stages of the photolysis (10 pulses), only the fluorescence of the m-xylylene biradical can be detected, as shown in figure 1. When the number of pulses to which the sample is exposed increases, the fluorescence of the monoradical appears and increases together with that of the biradical. The ratio of monoradical/biradical actually increases as the photolysis progresses (figure 2). Eventually the ratio of monoradical/biradical (5/1) becomes essentially independent of photolysis time. These results are very different from those obtained with the meta-xylene precursor. In this system the monoradical was the major absorbing species in the matrix, even at very brief photolysis times, and the ratio of monoradical/biradical was essentially time independent throughout the experiment.[4]

The increase in the ratio of the fluorescence intensities of the monoradical/biradical at long photolysis exposure times may be explained by secondary photolysis of the biradical, leading to the slow photochemical reaction of m-xylylene with the matrix to form the meta-methylbenzyl radical.

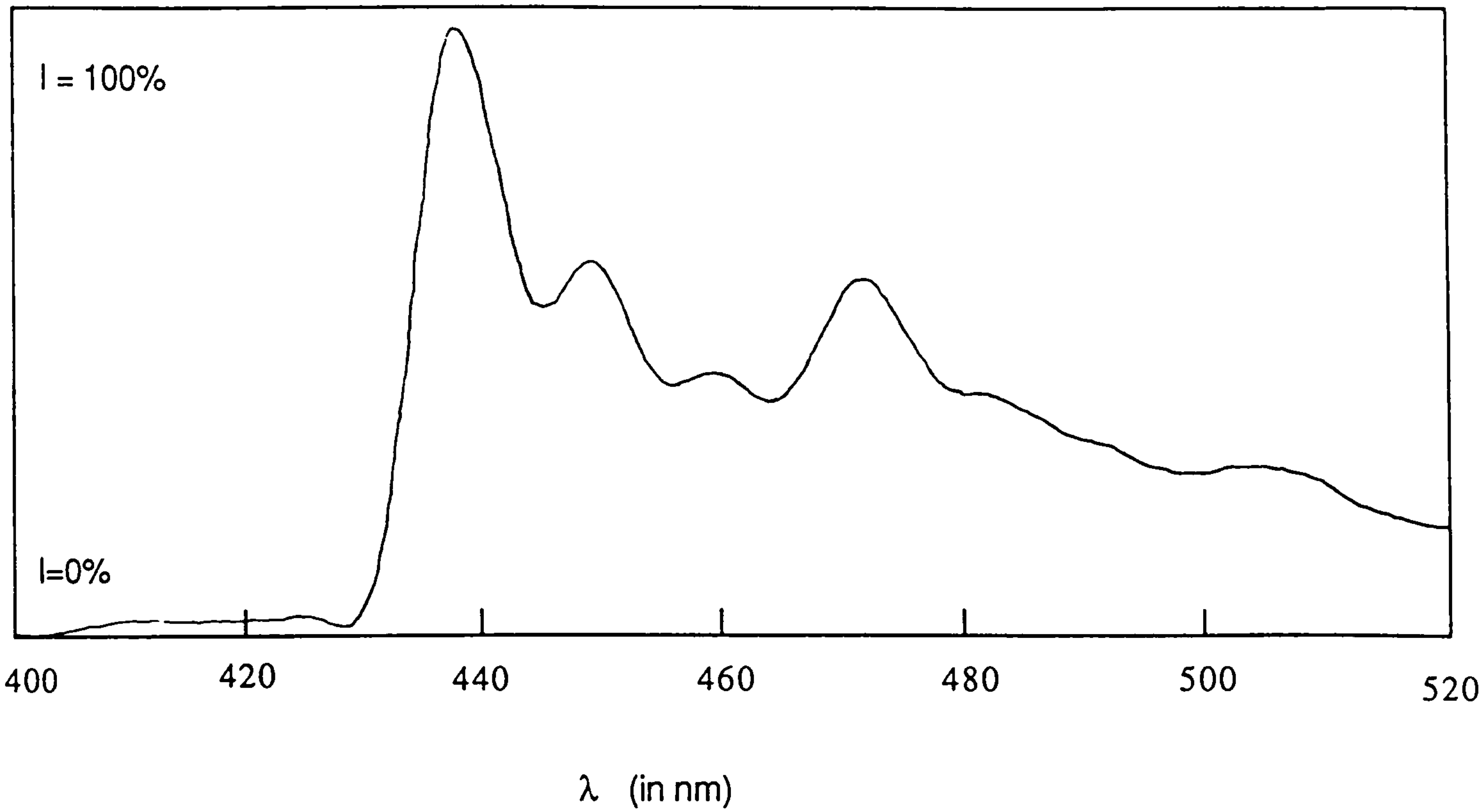


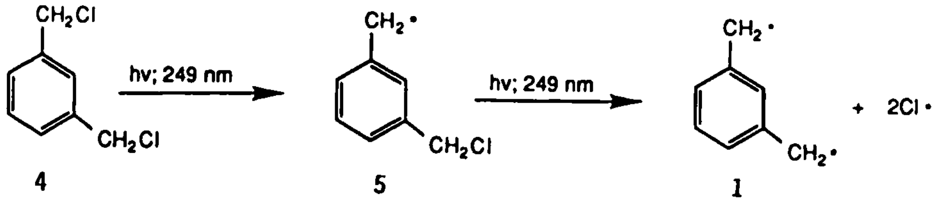
Figure 1

Fluorescence of the m-xylylene biradical (**1**) (438 nm) and m-methylbenzyl radical (5) (471 nm), produced from photolysis of α,α'-(dichloro)-m-xylene (4) (8.0 x 10^{-3} M) in glassy ethanol at 77K using an excimer laser (249 nm, 350 pulses, 5Hz) ($\lambda_{excitation}$ was 296 nm).

Photolysis of dichloride 4 at 77K with 50 rapid 249 nm laser pulses produces primarily the m-xylylene biradical 1 and only traces of a meta substituted monoradical. However, exposure of dichloride 4 to 50 laser pulses spaced 20 seconds apart are equally effective in producing 1 and a monoradical, in marked contrast to the results obtained with mesitylene as precursor. The biradical must therefore be produced from 4 within the 10 ns pulse width of the excimer laser pulse. A single 249 nm photon (115 kcal/mole) has insufficient energy to fragment both carbon-chlorine bonds. (B.D.E. C-Cl = 69 kcal/mole).[8] Thus, a species produced by absorption of a 249 nm pulse, must in turn absorb a second photon, within a single laser pulse, to form the biradical.

The two most reasonable candidates which can undergo secondary photolysis are the lowest triplet state of the dichloride ^{34}, or the m-chloromethyl benzyl radical 5 formed by rapid fragmentation of an excited state of 4. However, the chlorinated monoradical 5 is not detected by fluorescence spectroscopy upon brief photolysis of 4 with 249 nm excimer laser or 254 nm arc lamp radiation at 77K. In fact extremely efficient fragmentation of the putative meta-chloromethylbenzyl radical 5 would explain the absence of detectable emission from this species. In support of this mechanism (Scheme 1), laser flash photolysis (LFP) of α, α' dichloride 4 in solution, produces a new transient with λ_{max} = 324 nm. This transient absorption is at the appropriate wavelength for a meta substituted benzyl radical and is tentatively attributed to meta-chloromethyl benzyl radical 5 (Figure 3).

Scheme 1



Rentzepis[9] and coworkers have studied the photochemistry of the halomethylbenzenes and naphthalenes by picosecond spectroscopy.

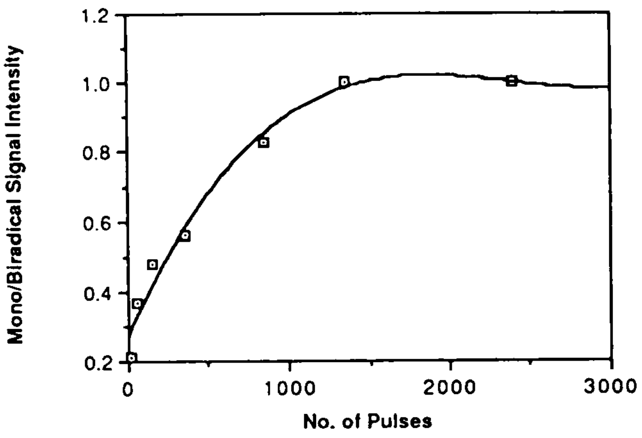
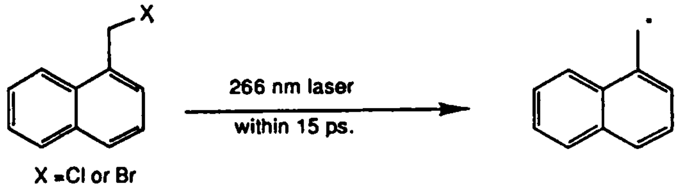


Figure 2

Ratio of monoradical/biradical (5/1) produced from the photolysis of dichloride (4) as described, versus the number of laser pulses delivered. The ratio was calculated by measuring the emission intensities at the maxima of the monoradical and the biradical (471 and 438 nm respectively), with $\lambda_{excitation}$ held constant at 296 nm.

Photolysis (266 nm) of 1-(chloromethyl)naphthalene **6** produces the 1-naphthylmethyl radical **7** within 15 ps of excitation. It was concluded that 266 nm photolysis promotes **6** into a vibrationally excited state of $S_2(\pi, \pi^*)$ which rapidly (< 15 ps) intersystem crosses to a dissociative $T(\sigma^*)$ state.



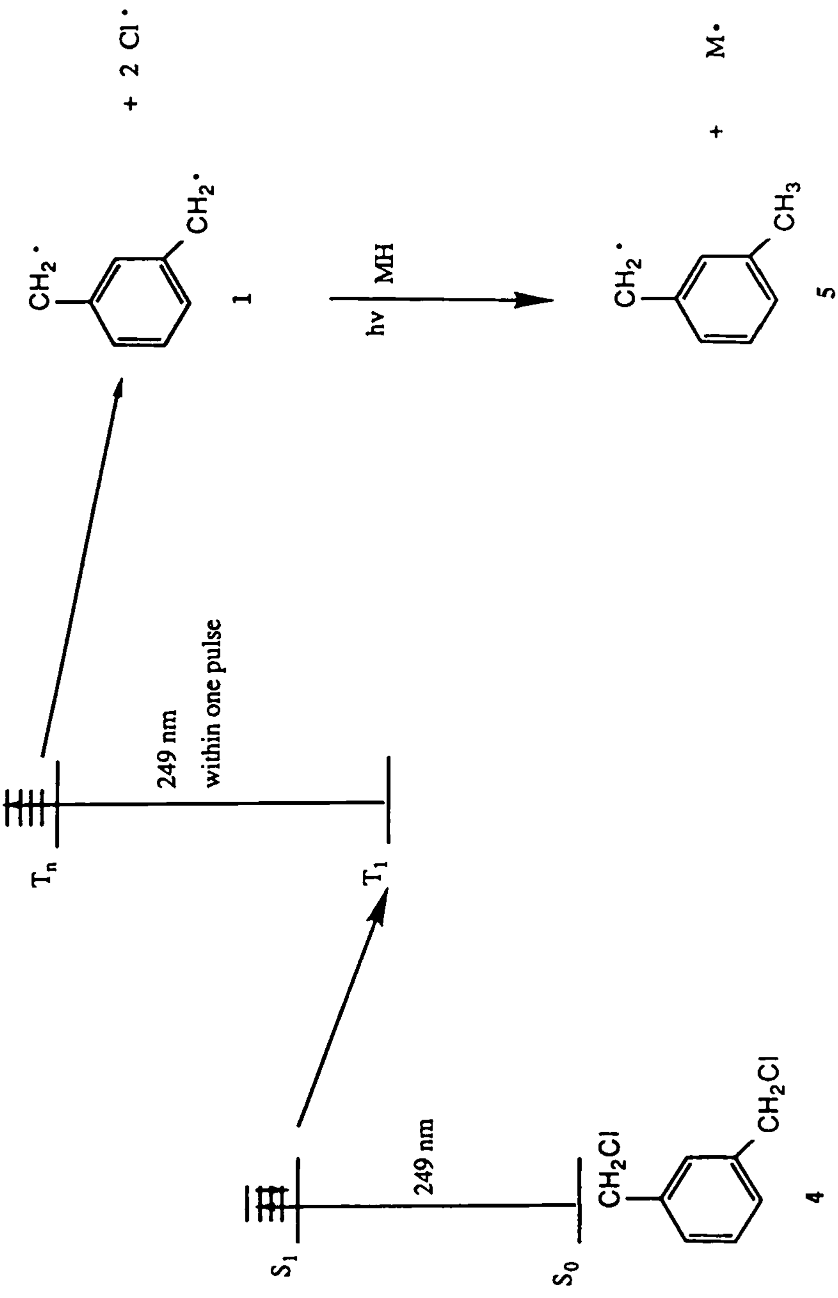
6 **7**

Thus it certainly seems feasible that dichloride **4** can be fragmented by absorption of a single photon to form chloromethylbenzyl radical **5**, which can then be subsequently photolyzed within a 10 ns 249 nm excimer laser pulse (Scheme 1).

The data to this point are also formally consistent with biradical formation produced by photolytic production of triplet dichloride, ^{3}**4**, followed by secondary photolysis of this species. It is well-known[10] that the presence of heavy atoms increases the spin-orbit coupling in aromatic molecules, leading to enhanced rates of radiative and radiationless singlet-triplet transitions. As a consequence of this heavy atom effect, the triplet state of α, α'-dichloro-m-xylene is expected to be more efficiently populated than the triplet state of mesitylene because of fast intersystem crossing from the first excited singlet state. The triplet state of this precursor might then absorb a second photon to produce an upper excited triplet state of, ^{3}**4**, which has sufficient energy to simultaneously cleave two carbon-chloride bonds to form m-xylylene, according to Scheme 2.

However, ^{3}**4** can not be observed in absorption following ambient temperature laser flash photolysis of **7** in 3-methylpentane (Figure 3).

At the present time we can not determine the identity of the photolabile intermediate produced on photolysis of dichloride **7** with complete certainty. However, our ambient temperature LFP experiment (Figure 3) provides evidence for mono radical **5** but not for ^{3}**4**. Thus, the meta-(chloro-methyl)benzyl radical is the preferred photochemical precursor to the meta-xylylene biradical **1** at present.


S₁
S₀
249 nm
CH₂Cl
CH₂Cl
4
T₁
Tₙ
249 nm
within one pulse
CH₂•
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CH₃
5
+ M•

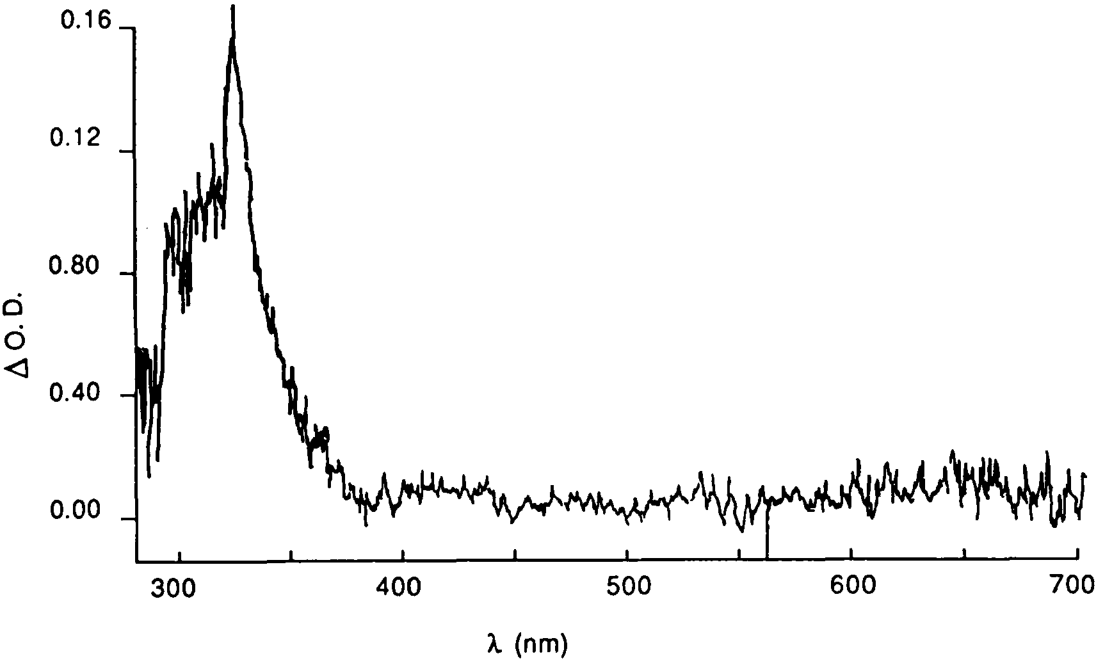


Figure 3

The transient absorption spectrum produced from laser flash photolysis (LFP) of α,α'-(dichloro)-m-xylene (4). The spectrum was recorded 250 ns following the laser pulse of a 3-methylpentane solution of dichloride 7 (optical density = ~ 1.0 at 249 nm).

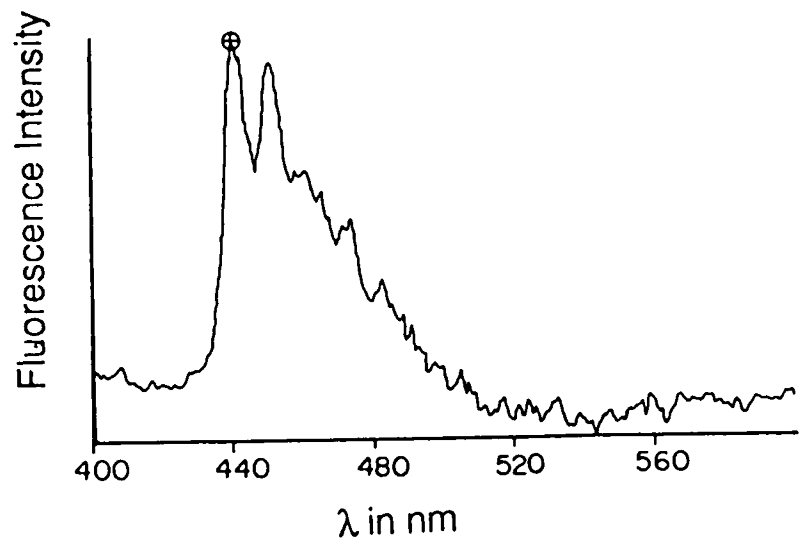


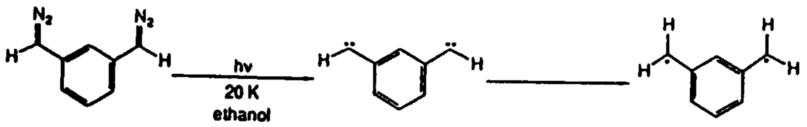
Figure 4

Room Temperature Laser Induced Fluorescence (LIF) spectrum of m-xylylene (1). The spectra were produced from α,α'-(dichloro)-m-xylene (4) by exposure to a pulse of 249 nm light. The spectrum was recorded in isopentane solution at room temperature. Fluorescence was collected beginning cooincident with the laser pulse for a total of 100 ns. (Optical density of the dihalide was 1.2 at 249 nm).

The results obtained by solution phase laser induced fluorescence (LIF) experiments performed at ambient temperature corroborate the mechanism proposed above. In these experiments, a single pulse from an excimer laser (249 nm, 10 ns) was used to irradiate a fluid solution of the dichloride (4). The laser pulse serves to dissociate the precursor, as well as to excite the nascent radicals or biradicals. The (LIF) emission spectrum recorded in this manner (Figure 4) from dihalide (4) is in excellent agreement with the matrix fluorescence emission spectrum previously assigned to m-xylylene. An identical LIF spectrum was recorded using α, α'-(dibromo)-m-xylene as the precursor. Only a very low intensity band corresponding to the 0-0 transition of monoradical (5) can be seen along with the liquid phase emission spectrum of m-xylylene. Clearly, the m-xylylene biradical (1) formed by the stepwise or simultaneous cleavage of 2 C-Cl bonds is formed within a single 249 nm laser pulse. To our knowledge this is the first ambient temperature direct spectroscopic detection of meta-xylylene in fluid solution.

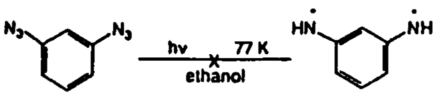
Photochemistry of 1,3 Diazido,2,4,6 Trifluorobenzene

In 1980 Wright and Platz[5] reported that photolysis of bis diazo compound 8 in ethanol-d_6 at 22K produces dicarbene quintet 9 which upon warming to 77K reacts with the matrix by double deuterium atom abstraction to form a deuterated modification of meta-xylylene 1-d_2. In ethanol at 22K the H atom transfer proceeds rapidly between the quintet and the matrix.



8 9 1

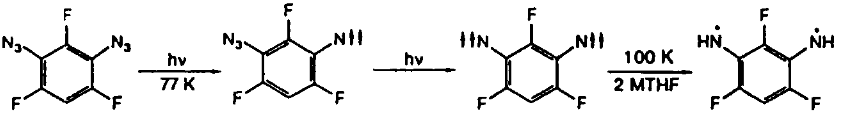
Wright[5] noted that the corresponding sequence with 1,3 dizidobenzene 10 fails to form diyl 2 even when performed at 77K.



10 2

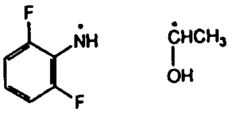
This was attributed to the lower rate of hydrogen atom abstraction reactions of triplet nitrenes as compared to triplet carbenes. However, Reiser and Leyshon[11] have demonstrated that electron withdrawing groups increase the reactivity of triplet nitrenes towards hydrogen atom abstraction thereby prompting this study of diazide **11**.

Photolysis of **11** in 2-methyltetrahydrofuran at 77K produces first the EPR spectrum of triplet mono nitrene **12** and subsequently the spectrum of dinitrene quintet **13**. Upon brief warming of the quintet to ~ 100K, followed by recooling to 77K the quintet spectrum disappears and is replaced by that of a biradical with $|D/hc| = 0.019 \pm 0.0003\ cm^{-1}$, $|E/hc| \sim 0\ cm^{-1}$. (Figure 5)



11 **12** **13** **2**

We observed no EPR spectra which could be attributed to a nitrene-anilino radical-quartet state, which should be an intermediate between **12** and **13**. The biradical of Figure **5** has a spectral splitting which is much too wide to attribute to a radical pair. Radical pairs derived from reaction of fluorinated triplet aryl nitrenes with matrices are known[12] (e.g. **14**) and typically have zero field parameters on the order of $|D/hc| = 0.007\text{-}0.009\ cm^{-1}$.



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The fact that the biradical spectrum remains constant with variation of the matrix (2MTHF, CH_3OH, CD_3OD and 3-methylpentane) and is absent in a perfluorinated matrix, is further evidence against a radical pair interpretation. Thus diaza diyl **3** is the most reasonable assignment of the EPR spectrum.

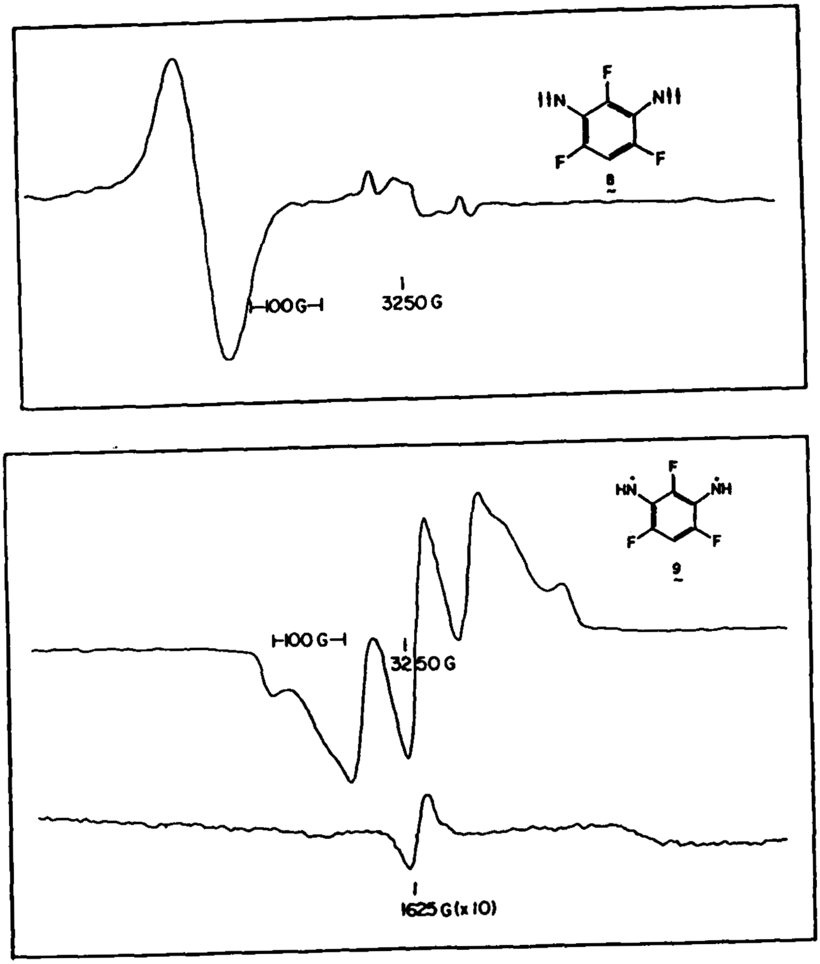

Figure 5

EPR Spectra produced upon irradiation of diazide 6 at 77 K in 2-Methyltetrahydrofuran. Upper spectrum recorded immediately following broad band photolysis at 77 K. Lower spectrum recorded following brief warming of 8 to 100 K and recooling to 77 K.

The zero field parameter |D/hc| of **3** is considerably larger than that of meta-xylylene **1** which has |D/hc| = 0.011 cm^{-1}.[5] This is expected because of the increased spin orbit contribution to the zero field parameter in nitrogen centered diyls relative to hydrocarbons.[13] The observed zero field parameter is in agreement with a value calculated by Lahti[14] (|D/hc| = 0.021 cm^{-1}) for diyl **2**.

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