Tetrahedron Letters,Vol.30,No.10,pp 1225-1228,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

EPR SPECTROSCOPY OF A DIAZA DERIVATIVE OF META-XYLYLENE

by

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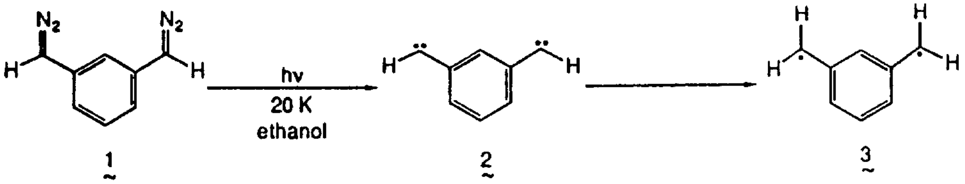
Abstract. Photolysis of 2,4,6-trifluoro-1,3-diazidobenzene in 2-methyltetrahydrofuran at 77K produces a dinitrene quintet. Upon warming the quintet briefly to 100K followed by recooling to 77K the EPR spectrum of the quintet disappears and is replaced by that of a trifluorodiaza biradical.

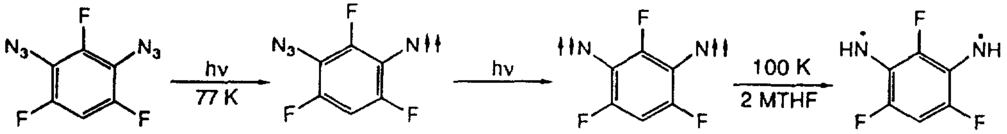
In 1980 Wright and Platz reported that photolysis of bis diazo compound **1** in ethanol-d_6 at 22K produces dicarbene quintet **2** which upon warming to 77K reacts with the matrix by double deuterium atom abstraction to form a deuterated modification of meta-xylylene **3**.[1] In ethanol at 22K the H atom transfer proceeds rapidly between the quintet and the matrix. This spectral assignment was secured subsequently by generation of **3** from several independent precursors.[3]



Wright[4] noted that the corresponding sequence with 1,3 diazidobenzene **4** fails to form diyl **5** even when performed at 77K.

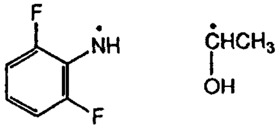
This was attributed to the lower rate of hydrogen atom abstraction reactions of triplet nitrenes as compared to triplet carbenes.[5] However, Reiser and Leyshon[6] have demonstrated that electron withdrawing groups increase the reactivity of triplet nitrenes towards hydrogen atom abstraction thereby prompting this study of diazide **6**.[7]

Photolysis of **6** in 2-methyltetrahydrofuran at 77K produces first the EPR spectrum of triplet mono nitrene **7** and subsequently the spectrum of dinitrene quintet **8**. 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 $|D/hc| = 0.019 \pm 0.0003\ \text{cm}^{-1}$, $|E/hc| \sim 0\ \text{cm}^{-1}$. (Figure 1)



6 7 8 9

We observed no EPR spectra which could be attributed to a nitrene-anilino radical-quartet state, which should be an intermediate between **8** and **9**. The biradical spectral splitting is much too wide to attribute to a radical pair. Radical pairs derived from reaction of fluorinated triplet aryl nitrenes with matrices are known[8] (e.g. **10**) and have zero field parameters on the order of $|D/hc| = 0.007\text{-}0.009\ \text{cm}^{-1}$.



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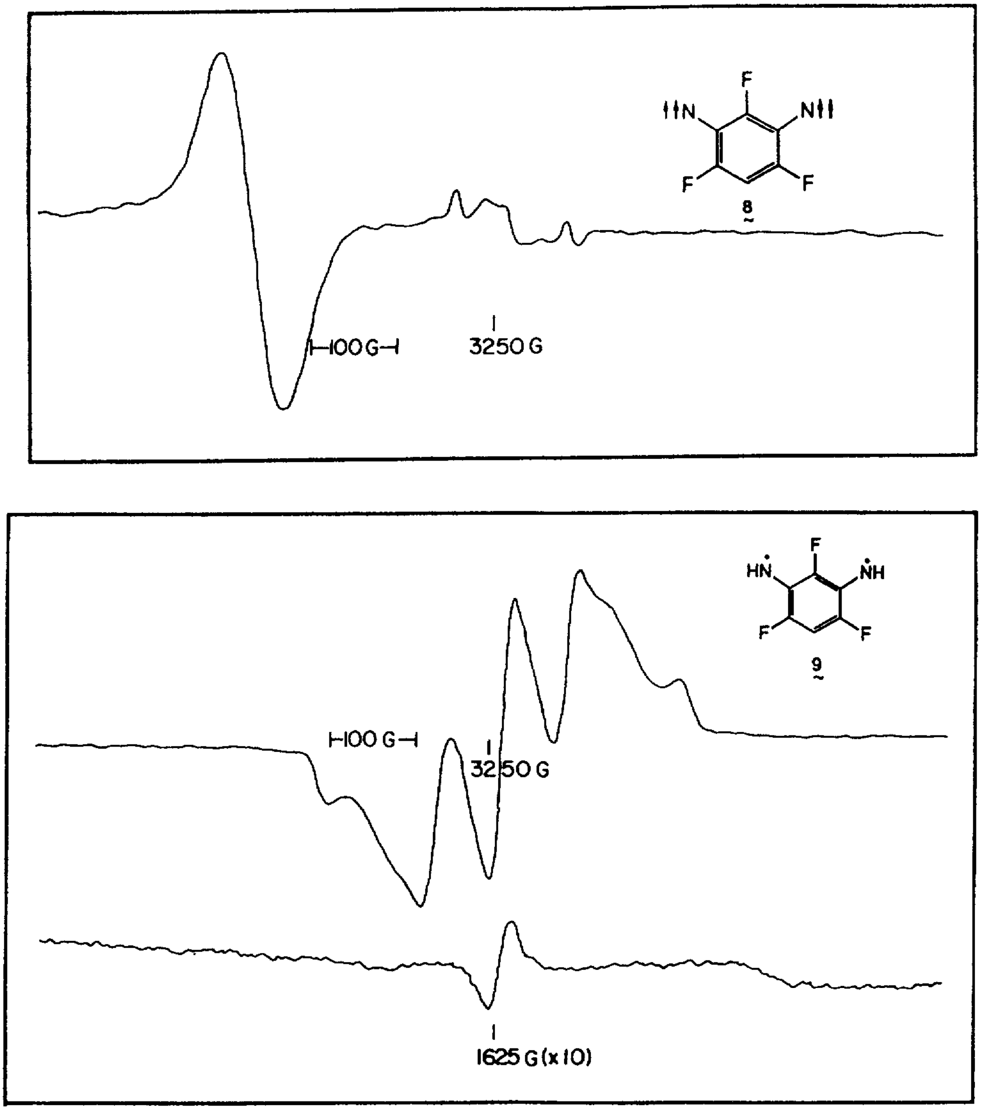
The fact that the biradical spectrum is constant with variation of the matrix (2MTHF, CH_3OH, CD_3OD and 3-methylpentane) and absent in a perfluorinated matrix, is further evidence against a radical pair interpretation. Thus diaza diyl **9** is the most reasonable assignment of the spectrum.

The zero field parameter $|D/hc|$ of **9** is considerably larger than that of meta-xylylene **3**[1] which has $|D/hc| = 0.011\ \text{cm}^{-1}$. This is expected because of the increased spin orbit contribution to the zero field parameter in nitrogen centered diyls relative to hydrocarbons.[9] The observed zero field parameter is in agreement with a value calculated by Lahti[10] ($|D/hc| = 0.021\ \text{cm}^{-1}$) for diyl **5**.

Acknowledgement Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Figure 1



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.

References

1. Wright, B. B.; Platz, M. S.; J. Am. Chem. Soc. (1983) **105**, 628. The quintet has been observed initially by Trozzolo et al., reference 2.

2. Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. J. Am. Chem. Soc. (1963) **85**, 2526.

3. (a) Goodman, J. L.; Berson, J. A. J. Am. Chem. Soc. (1985) **107**, 5409.
   (b) Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. J. Am. Chem. Soc. (1988) **110**, 2318.

4. Wright, B. B., Ph.D., The Ohio State University (1983). Upon photolysis of **4** at 77K a very complex EPR spectrum is produced which may be due in part to a dinitrene quintet species. There is however no evidence for biradical **5**.

5. See Platz, M. S. in "Azides and Nitrenes" Scriven, E. F. V. ed., Academic Press (1984) Ch. 7, pp. 374-381.

6. Reiser, A.; Leyshon, L. J. J. Am. Chem. Soc. (1971) **93**, 4051.

7. Acetylation (acetic anhydride, acetic acid) of 2,4,6-trifluoroaniline (Aldrich Chemical Co.) followed by nitration (fuming nitric, sulfuric acid) afforded 3-nitro-2,4,6 trifluoroacetanilide. Reduction of the nitro group by catalytic hydrogenation followed by ethanolic acidic hydrolysis (HCl, ethanol) gave 2,4,6-trifluoro-1,3-phenylene diamine as a hydrochloride salt. Diazatization followed by treatment with sodium azide gave 2,4,6-trifluoro-1,3-diazobenzene as a pale yellow oil. M.S.: calcd for $C_6HF_3N_6$ = 214.0215; obsd = 214.0202; diff = 0.0013. ^{19}F(NMR): -129.5 (m, 2F, 4,6 aromatic fluorines); -136.2 (m, 1F, 2 aromatic fluorine). ^{1}H(NMR): 6.80-6.92 (m, 1H, aromatic H). IR: 2110, 2200, azide stretch).

8. Leyva, E.; Young, M. J. T.; Platz, M. S. J. Am. Chem. Soc. (1986) **108**, 8307.

9. Quest, H.; Bieber, L.; Danen, W. C. J. Am. Chem. Soc. (1978) **100**, 1306.

10. Personal communication from Professor P. Lahti.

(Received in USA 28 September 1988)