

**Appendix III: Using the “Ward lattice” for Matrix Isolated
EPR Spectroscopy of a Triplet Biradical**

III.1 Introduction

Matrix isolated EPR spectroscopy of biradicals is of long standing interest to the Dougherty group (Anderson et al., 1997; Jacobs et al., 1993; Silverman and Dougherty, 1993; Snyder and Dougherty, 1989). Typically simple biradicals are measured using cryogenic matrix isolated EPR spectroscopy at 4 K. However, it is not certain how relevant information obtained at 4 K in a frozen solvent is to conventional mechanistic or synthetic conditions of fluid media at room temperature. We postulated that the “Ward lattice” (See Chapters 6 and 7 for discussions of this structure) (Evans et al., 1999; Russell et al., 1994a; Russell et al., 1994b; Russell et al., 1997; Russell and Ward, 1996; Russell and Ward, 1997; Russell and Ward, 1998; Swift et al., 1998a; Swift et al., 1998b; Swift et al., 1997; Swift and Ward, 2000), might be capable of sufficiently isolating biradicals so as to allow room temperature EPR in a guanidinium sulfonate matrix.

To evaluate the potential of the “Ward lattice” as a room temperature matrix for EPR spectroscopy, we choose the well studied 2-isopropylidene-1,3-cyclopentanediyli, the “Berson biradical”. The diazene precursor of the Berson biradical (**1**) is easily prepared, and photolysis of the precursor between 310 and 380 nm in a frozen matrix readily affords the biradical (**2**).

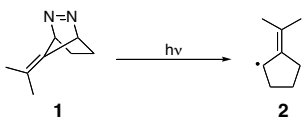


Figure III.1: Photolysis of the diazene precursor of the dimethyl Berson biradical (**1**) readily affords the biradical (**2**)

A “Ward lattice” consisting of guanidinium and 4,4'-biphenyldisulfonic acid was chosen to serve as the isolation matrix, since formation of this lattice has been observed with a variety of guest molecules. Our strategy was to first encapsulate the diazene precursor (**1**) into a guanidinium 4,4'-biphenyldisulfonate matrix, followed by irradiation of this matrix to give biradical. The results of incorporation and irradiation are described here.

III.2 Results and Discussion

The diazene (**1**) was prepared as previously described. Encapsulation in a guanidinium 4,4'-Biphenyldisulfonate matrix was achieved by slow evaporation of a 2:1 methanol: water solution containing one equivalent of diazene (**1**), one equivalent 4,4'-biphenyldisulfonic acid, and two equivalents of guanidinium carbonate under argon flow. The guanidinium sulfonate matrix containing diazene was obtained as a white solid.

Photolysis of the sample was carried out in a vacuum-sealed EPR tube at 77 K. Sample photolysis between ~307 and 386 nm was performed for 25 minutes, and biradical formation was monitored by EPR spectroscopy at 77K. EPR spectra after 0, 5, and 25 minutes of photolysis are shown in Figure III.2. A small amount of biradical was observed prior to photolysis, most likely due to exposure of the sample to ambient light.

Following photolysis, the matrix encapsulated sample was allowed to warm to room temperature. A strong EPR signal persisted for the guanidinium sulfonate matrix encapsulated biradial at room temperature. To confirm the triplet state of the radical, the

half field transition measured and is shown in Figure III.3. The observed half field transition is as expected for this biradical.

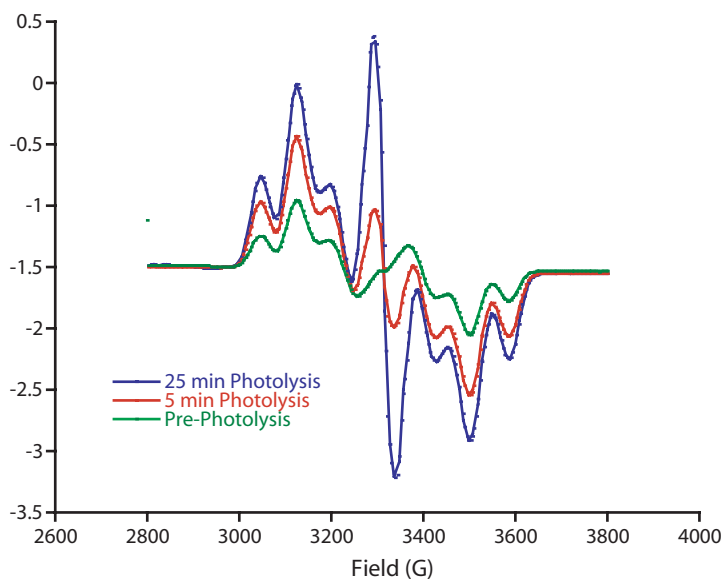


Figure III.2: Photolysis of the diazene precursor to dimethyl Berson (**1**) at 77 K in a guanidinium 4,4'-biphenyldisulfonate matrix.

The stability at room temperature and protected from light of the Berson biradical in the guanidinium 4,4'-biphenyldisulfonate matrix was monitored as a function of time. The spectra at 0, 1, 18, 67.5, 192, 355 hours are shown in Figure III.4. The observed EPR signal is stable with little to no degradation for 192 hours. Between the 192 hour time point and the 355 hour time point complete decay of the signal to pre-photolysis levels is observed. It seems likely that the rapid degradation of the signal between 192 and 355 hours resulted from a leak in the vacuum seal of the EPR tube.

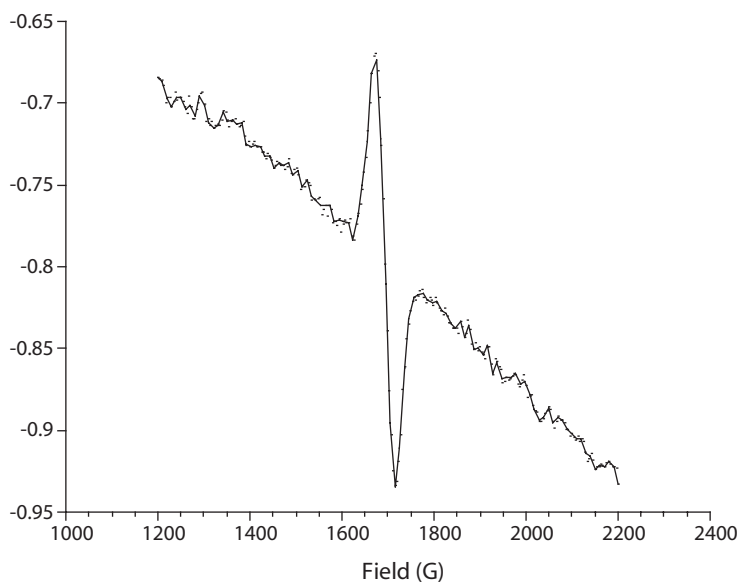


Figure III.3: Half field transition for the dimethyl Berson radical measured at room temperature in a guanidinium 4,4'-biphenyldisulfonate matrix.

III.3 Conclusion

Preliminary results suggest that the “Ward lattice” is useful as a room temperature EPR matrix. Matrix encapsulation of radical precursors is trivial, photolysis of the radical precursors can be carried out in the matrix, and EPR measurements can be obtained at room temperature. The ability to study biradicals by EPR at room temperature may provide useful mechanistic information.

Photolysis of the diazene precursor (**1**) was carried out in a guanidinium sulfonate matrix, and the resulting triplet biradical was observed at 77 K and room temperature. Stability of the biradical within the matrix was determined to be at least 192 hours. Further work is needed to determine the actually decay kinetics of the biradical in the guanidinium sulfonate matrix.

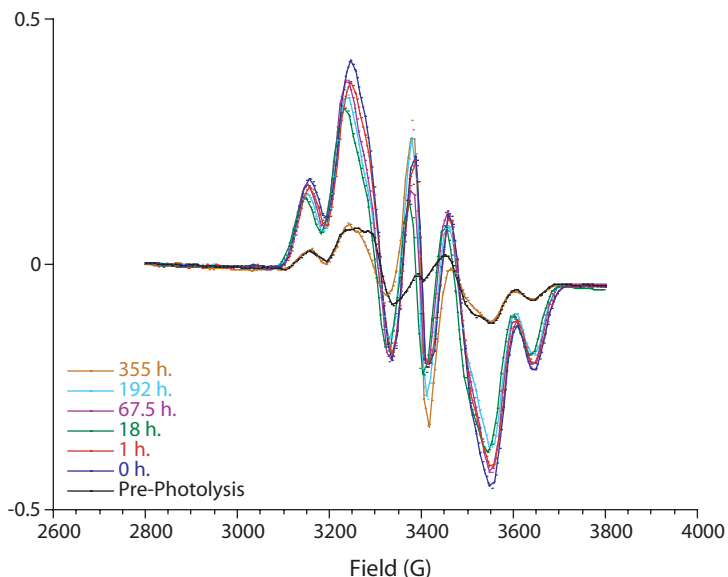


Figure III.4: EPR spectra of the dimethyl Berson radical measured at room temperature in a gadolinium 4,4'-biphenyldisulfonate matrix. This series of spectra indicate that the radical is stable for at least 192 hours.

III.4 Literature Cited

Anderson, K. K., Shultz, D. A., and Dougherty, D. A. (1997). Attempted synthesis of a stable, quintet, tetraphenoxyl tetradical: Facile rearrangement of a substituted bicyclobutane. *Journal of Organic Chemistry* *62*, 7575-7584.

Evans, C. C., Sukarto, L., and Ward, M. D. (1999). Sterically controlled architectural reversion in hydrogen-bonded crystalline clathrates. *Journal of the American Chemical Society* *121*, 320-325.

Jacobs, S. J., Shultz, D. A., Jain, R., Novak, J., and Dougherty, D. A. (1993). Evaluation of Potential Ferromagnetic Coupling Units - the Bis(Tmm) Approach to High-Spin Organic-Molecules. *Journal of the American Chemical Society* *115*, 1744-1753.

Russell, V. A., Etter, M. C., and Ward, M. D. (1994a). Guanidinium Parasubstituted Benzenesulfonates - Competitive Hydrogen-Bonding in Layered Structures and the Design of Nonlinear-Optical Materials. *Chemistry of Materials* 6, 1206-1217.

Russell, V. A., Etter, M. C., and Ward, M. D. (1994b). Layered Materials by Molecular Design - Structural Enforcement by Hydrogen-Bonding in Guanidinium Alkanesulfonate and Arenesulfonate. *Journal of the American Chemical Society* 116, 1941-1952.

Russell, V. A., Evans, C. C., Li, W. J., and Ward, M. D. (1997). Nanoporous molecular sandwiches: Pillared two-dimensional hydrogen-bonded networks with adjustable porosity. *Science* 276, 575-579.

Russell, V. A., and Ward, M. D. (1996). Solid-state structure of a layered hydrogen-bonded salt: Guanidinium 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonate methanol solvate. *Acta Crystallographica Section B-Structural Science* 52, 209-214.

Russell, V. A., and Ward, M. D. (1997). Two-dimensional hydrogen-bonded assemblies: The influence of sterics and competitive hydrogen bonding on the structures of guanidinium arenesulfonate networks. *Journal of Materials Chemistry* 7, 1123-1133.

Russell, V. A., and Ward, M. D. (1998). Interweaving of two-dimensional hydrogen-bonded networks directed by chloride ions. *New Journal of Chemistry* 22, 149-153.

Silverman, S. K., and Dougherty, D. A. (1993). Conformational Effects on High-Spin Organic-Molecules. *Journal of Physical Chemistry* 97, 13273-13283.

Snyder, G. J., and Dougherty, D. A. (1989). 2,4-Dimethylene-1,3-Cyclobutanediyl, the Non-Kekule Isomer of Benzene - Synthesis, Epr, and Electronic Spectroscopy. *Journal of the American Chemical Society* 111, 3927-3942.

Swift, J. A., Pivovar, A. M., Reynolds, A. M., and Ward, M. D. (1998a). Template-directed architectural isomerism of open molecular frameworks: Engineering of crystalline clathrates. *Journal of the American Chemical Society* 120, 5887-5894.

Swift, J. A., Reynolds, A. M., and Ward, M. D. (1998b). Cooperative host-guest recognition in crystalline clathrates: Steric guest ordering by molecular gears. *Chemistry of Materials* *10*, 4159-4168.

Swift, J. A., Russell, V. A., and Ward, M. D. (1997). Organoporous hosts with adjustable molecular environments. *Advanced Materials* *9*, 1183.

Swift, J. A., and Ward, M. D. (2000). Cooperative polar ordering of acentric guest molecules in topologically controlled host frameworks. *Chemistry of Materials* *12*, 1501.