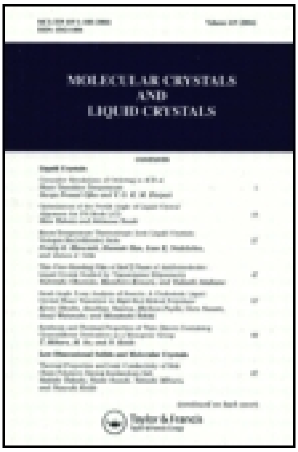

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Nitroxyl-Galvinoxyl - A New Biradical

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NITROXYL-GALVINOXYL — A NEW BIRADICAL

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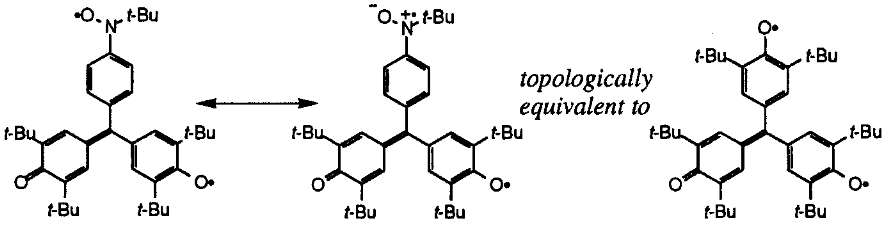
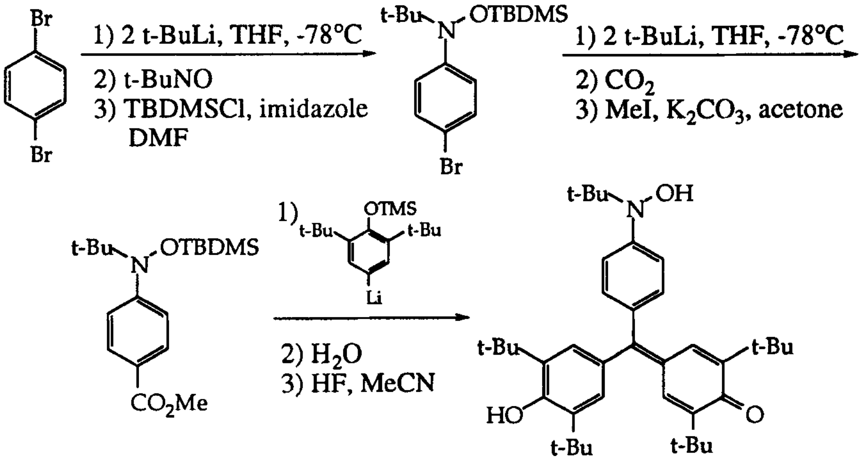
Abstract The synthesis and solution phase EPR spectrum of a new biradical is presented. The H-hyperfine coupling constants of the biradical indicate interaction of the unpaired electrons in the molecule.

The synthesis of novel, paramagnetic organic molecules is an essential component to the preparation of organic-based magnetic materials.[1] There are many examples of the preparation of high-spin organic molecules constructed using a pi-topology approach. For example, the "meta-through-a-benzene" motif is a successful one if near-planarity of the pi-system is maintained and certain substituent effects are avoided.[2] Our program involves, in part, the preparation of new paramagnetic organic molecules which can act as transition metal ligands. An example is the biradical shown below. This molecule is composed of galvinoxyl and nitroxide radical units that are connected through a phenyl group such that high-spin coupling should result. Indeed, this molecule is topologically equivalent to Yang's biradical — a stable, ground state triplet molecule. The nitroxide group of this biradical can act as a ligand for a number of transition metals as well as lanthanides and actinides.

As with Yang's biradical, ferromagnetic coupling between the unpaired electrons is expected based on the non-disjoint nature of the two SOMOs.[3-5] However, there are relatively few examples of different paramagnetic groups attached to a coupling unit as compared to identical paramagnetic groups attached to a coupling unit. Examination and modeling of spin-spin coupling in these former cases (relative to the latter case) is an important area in the study of high-spin organic molecules.



The compound was synthesized according to the scheme below. The synthesis of the protected nitroxide follows the general procedure of Iwamura,[6] while galvinol formation follows a modified procedure of Kurreck.[7,8] The galvinol *tert*-butyldimethylsilyl-protected-hydroxyamine has been characterized by IR, ^{1}H NMR, and high-resolution mass spectrometry.



The final deprotection step is rather difficult. Occasionally, a paramagnetic by-product formed, which when oxidized yielded an EPR spectrum consistent with an arylnitroxide monoradical (e.g., $a_N \approx 11$ G). In fact, this by-product can be seen in the spectrum of the biradical. The EPR spectrum of the title biradical, formed by stirring with PbO_2, is shown below along with a simulated spectrum. The spectrum of the biradical is consistent with a species with $J \gg a$.

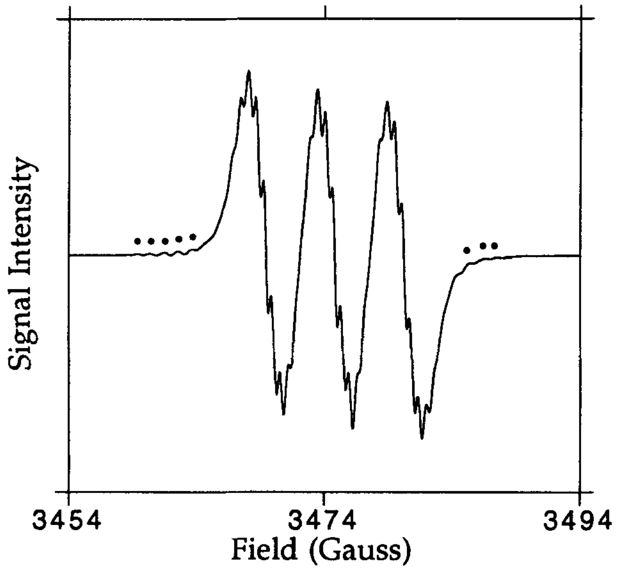


FIGURE 1. X-band solution phase EPR spectrum of title biradical in toluene at 298K; • denotes nitroxide by-product.

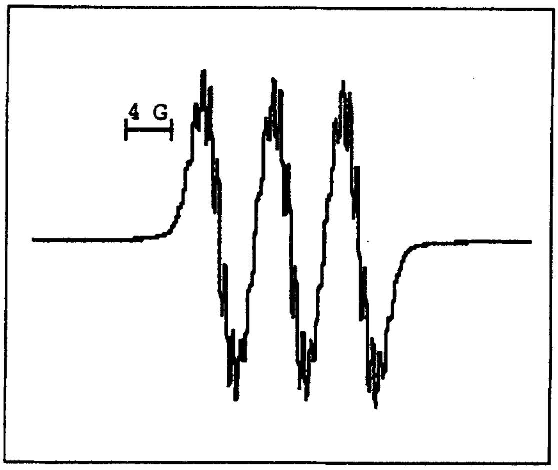


FIGURE 2. Simulation of the biradical with a_H(meta) = 0.5 G; a_H(ortho) = 1.1 G; a_H(Gal) = 0.69 G; a_N = 5.5 G; gaussian lineshape with linewidth = 0.38 G.

Frozen solution spectra and Curie plots for this compound and the *meta*- isomer will be reported elsewhere.

EXPERIMENTAL

All reactions were performed using oven dried glassware under an atmosphere of argon, employing Schlenk techniques where appropriate. ^{1}H spectra were recorded on a 300 MHz Varian Spectrometer using $CDCl_3$ as the solvent. EPR spectra were taken on a IBM-Bruker E200SRC Spectrometer. Samples were prepared inside a glove box with toluene as the solvent. IR were recorded on a Perkin-Elmer 1525 FTIR Spectrometer. All reagents were purchased from Aldrich or Fischer chemicals and used as received. Tetrahyrdofuran and diethyl ether were distilled under argon from purple or blue benzophenone/sodium metal solutions. Acetone and dimethylformamide were purchased as reagent grade from Aldrich, and used as received.

1-Bromo-4-(N-*tert*-butyl-hydroxyamino) benzene: 1,4-dibromobenzene (3.00 g, 12.7 mmol) is added to a 200 mL Schlenk flask and dissolved in 60 mL THF. The solution is then cooled to -78°C in an acetone/dry ice bath. *Tert*-butyl lithium (15 mL of a 1.7 M solution, 25.4 mmol) is then added dropwise via syringe. The resulting colorless solution is then stirred for one hour at -78°C. *Tert*-butyl nitroso dimer (2.22 g, 12.7 mmol) is then added to a 25 mL conical round bottom flask and dissolved in 10 mL of THF. The sapphire blue dimer solution is then cannulated into the aryllithium solution. The reaction solution is then allowed to stir an additional 18 hours (allowing the bath to evaporate) to yield an emerald green solution. The reaction is quenched with 5 mL deoxygenated water, then washed with saturated NH_4Cl and saturated NaCl solutions and dried over $CaCl_2$. The solvent is evaporated to yield a golden brown oil from which, upon addition of petroleum ether, the product precipitates as a white solid.

***tert*-Butyl -dimethylsilyl ether protection the hydroxyamine**: In a 250 mL round bottom flask the product of the previous reaction (1.68 g, 6.88 mmol) is added to TBS chloride (1.15 g, 7.57 mmol) and pyrazole (1.17 g, 17.2 mmol). These are dissolved in 45 mL anhydrous DMF and heated to 55°C on an oil bath with stirring under argon for 22 hours. After cooling to room temperature, the solution is added to a sepratory funnel containing equal amounts of petroleum ether and saturated NH_4Cl solution. The layers are separated, and the aqueous layer is washed twice with petroleum ether. The organics are then combined and dried over $CaCl_2$, after which the solvent is removed under reduced pressure. The product is then purified on a silica gel column using 10% diethyl ether/petroleum ether as the eluting solvent. The product, a lightly colored oil, is collected in a 91% yield (2.25 g).

4-(N-*tert*-butylhydroxyamino-TBS ether) benzoic acid: The protected hydroxyamine (1.00 g, 2.79 mmol) is added to a 50 mL Schlenk flask and dissolved in 25 mL of THF. The solution is then cooled to -78°C in an acetone/dry ice bath. *Tert*-butyl lithium (3.3 mL of a 1.7 M solution, 5.58 mmol) is then added dropwise via syringe. The resulting orange solution is then stirred for two and a half hours at -78°C. Carbon dioxide (excess, 12.27 g, 279 mmol) is then added to a 250 mL round bottom Shlenk flask , the side arm connected via tygon tubing to a mineral oil bubbler and cooled to -78°C in an acetone/dry ice bath. The aryllithum solution is then cannulated onto the dry ice and the bath is removed. The solution is allowed to stir until the vigorous evolution of CO_2 ceases. This solution is slowly acidified with 1M HCl until the pH ≈ 4. This solution is then washed with a saturated NaCl solution and dried over $CaCl_2$. TLC in 10% diethyl ether/petroleum ether shows a major baseline spot, this spot is assumed to be the carboxylic acid and is used without purification in the next step.

Methyl 4-(N-*tert*-butylhydroxyamino-TBS ether) benzoate: The carboxylic acid (900 mg, 2.79 mmol) is added to a 250 mL round bottom flask and dissolved in 40 mL reagent grade acetone. Methyl iodide (15.8 g, 15.8 mmol) and K_2CO_3 (0.58 g, 4.2 mmol) are then added and the solution is allowed to stir for 17 hours under argon. The solution is then filtered through celite and the acetone removed under reduced pressure. The resulting solid is purified using silica gel and 10% diethyl ether/petroleum ether as the eluting solvent to yield a light yellow oil in 69% yield (647 mg, based on the bromide).

[4-(N-*tert*-butylhydroxyamino-TBS ether) phenyl] galvinol: 4-Bromo-2,6-di-*tert*-butyl-phenol-TMS ether (1.36 g, 3.79 mmol) is added to a 100 mL Schlenk flask and dissolved in 30 mL THF. The solution is then cooled to -78°C in an acetone/dry ice bath. *Tert*-butyl lithium(4.46 mL of a 1.7 M solution, 7.59 mmol) is then added dropwise via syringe. The resulting colorless solution is then stirred for one hour at -78°C. The methyl ester from the previous step (640 mg, 1.90 mmol) is then added to a 25 mL conical round bottom flask and dissolved in 10 mL of THF under argon. The ester is then cannulated into the aryllithum solution, and the color of the solution immediately changed to orange. This solution is then allowed to stir at -78°C for two hours and then warmed to room temperature. The solution is then quenched first with 5 mL deoxygenated water and then 10 mL of a deoxygenated saturated NaOH solution. This was allowed to stir overnight and resulted in a sapphire blue solution. The solution was then washed with both saturated NH_4Cl (after which the organic layer was orange) and saturated NaCl solutions and dried over $CaCl_2$. The resulting solid is purified using silica gel and 10% diethyl ether/petroleum ether as the eluting solvent to yield 700 mg of an orange solid (%).

Deprotection of The TBS Ether: The galvinol from the last step (50 mg, 0.07 mmol) is dissolved in 10 mL of a 10:1 CH_3CN:CH_2Cl_2 solution. HF (1.43 mg, from a 5% by weight solution in CH_3CN, 0.07 mmol) is added and the resulting red solution is stirred for 17 hours under argon. The product is then added to a sepratory funnel containg CH_2Cl_2 and saturated NaCl and the layers are separated (organic layer is orange) and the organic is then dried over $CaCl_2$. The solvent is then removed to yield the deprotected product quantitatively as an orange solid (42 mg).

^{1}H NMR: 7.12 ppm, 2H, doublet (J = 9 Hz); 7.25 ppm, 2H, doublet (J = 9 Hz); 6.96 ppm, 1H, doublet (J = 2 Hz); 7.06 ppm, 1H, doublet (J = 2 Hz); 7.18 ppm, 2H, singlet; 5.44 ppm, 1H (OH); 1.34 ppm, 9H; 1.22 ppm, 18H; 1.17 ppm, 9H; 1.13 ppm, 9H. IR: υ_{OH} = 3327 cm^{-1} (ArOH) and υ_{OH} = 3226 cm^{-1} (NOH). Mass Spec: m/z(calc): 700.51250; m/z(exp): 700.50869; ΔM = 10 ppm.

Oxidation: The hydroxyamino-galvinol (20 mg, 0.034 mmol) is dissolved in diethyl ether in an 30 mL amber glass vial. PbO_2 (excess, 500 mg, 2.09 mmol) is added and the solution is stirred for two hours under argon. The resulting suspension is filtered through a plug of cotton and the solvent removed under a stream of argon to yield a red solid that was used for EPR studies.

ACKNOWLEDGMENT

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