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2-(3,5-Dinitrophenyl)-1,3-dithiane Carbanion: A Benzylic Anion with a Low Energy Triplet State

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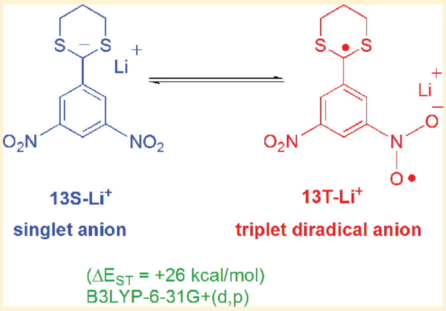
S Supporting Information

ABSTRACT: Calculations at the DFT level predict that benzyl anions with strong π-electron-withdrawing groups in the meta position(s) have low energy diradical or triplet electronic states. Specifically, the 2-(3,5-dinitrophenyl)-1,3-dithiane carbanion is predicted to have nearly degenerate singlet and triplet states at the (U)B3LYP level as a free anion. Its lithium ion pair is predicted to be a ground-state triplet with a substantial (26 kcal/mol) singlet−triplet energy gap. Experiments on this anion using chemical trapping, NMR, and the Evans method strongly suggest that this anion is either a triplet or a ground-state singlet with a very low energy triplet state.



INTRODUCTION

Identifying and characterizing organic species with high-spin states (triplet and higher) is a problem that continues to attract attention for both fundamental and practical reasons. Accurately predicting electronic states in high-spin molecules continues to challenge current theoretical and computational tools, although substantial progress has been made in the past decade.[1−11] High-spin molecules hold promise as building blocks for new materials having interesting electronic and magnetic properties.[12−19] However, a variety of practical problems, not the least of which is the high chemical reactivity of such species, will need to be overcome before commercial products based on these concepts become widely available.

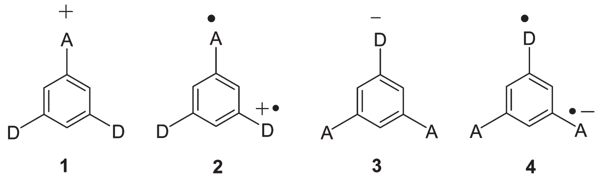
Density functional theory (DFT) has served as a highly valuable tool for organic chemists in predicting various physical properties that would prove otherwise difficult to measure or determine experimentally. For example, DFT has been shown to accurately predict the electronic states,[1−5] spectroscopic,[1] and thermodynamic[6,7] properties of high-spin diradicals.[5−11]

The *m*-xylylene diradical system is known to be a nondisjoint and open-shell species with a triplet ground state ($\Delta E_{ST} = +9.6 \pm 0.2$ kcal/mol).[11,20,21] Its physical and chemical properties have been studied both computationally and experimentally.[13,22,23] The *m*-xylylene diradical and its derivatives has proven to be somewhat of a challenge to study due to their high reactivity. These intermediates tend to be generated and studied in low temperature solid-state matrices or solutions by ESR spectroscopy.[13] Nonetheless, the *m*-xylylene diradical has served as a robust template for designing new high-spin building blocks. Rajca and co-workers have shown that aza-*m*-xylylene diradical derviatives are stable and persistent at room temperature.[24]

One particular reactive intermediate that has been widely investigated as having a triplet ground state are aryl-substituted carbenes.[25−31] Substituted triplet carbenes have been a convenient high-spin intermediate to study by many investigators, due to their ease of generation from the thermal decomposition or photolysis of the corresponding diazo precursors. Carbenes are known to selectively add to alkenes and insert into activated C−H bonds. The predictable chemical reactivity of singlet and triplet carbenes is yet another feature that demonstrates why carbenes have been extensively studied by chemists as reactive intermediates. However, other stable heteroatom-based radical systems that possess high-spin states are known to have interesting magnetic properties[32−37] and are currently being investigated as an alternative source of high-spin building blocks to carbenes.

To date, most approaches to high-spin organic molecules have favored building blocks derived from neutral biradicals,[13] carbenes,[38] or nitrenes.[12] However, recent computational studies, including multireference methods, have identified a new class of ion diradicals, described in Scheme 1, wherein a cationic acceptor group (e.g., O$^+$,

Scheme 1. Electronic Effect of Meta π-Donors with Exocyclic Cationic and Anionic Substituents



A = CR$_2^+$, NR$^+$, O$^+$ (R = H or alkyl)
D = NR$_2$, OR (R = H or alkyl)

A = CR$_2^-$, $^-$NR, O$^-$ (R = H or alkyl)
D = CN, NO$_2$, C(O)R (R = H or alkyl)

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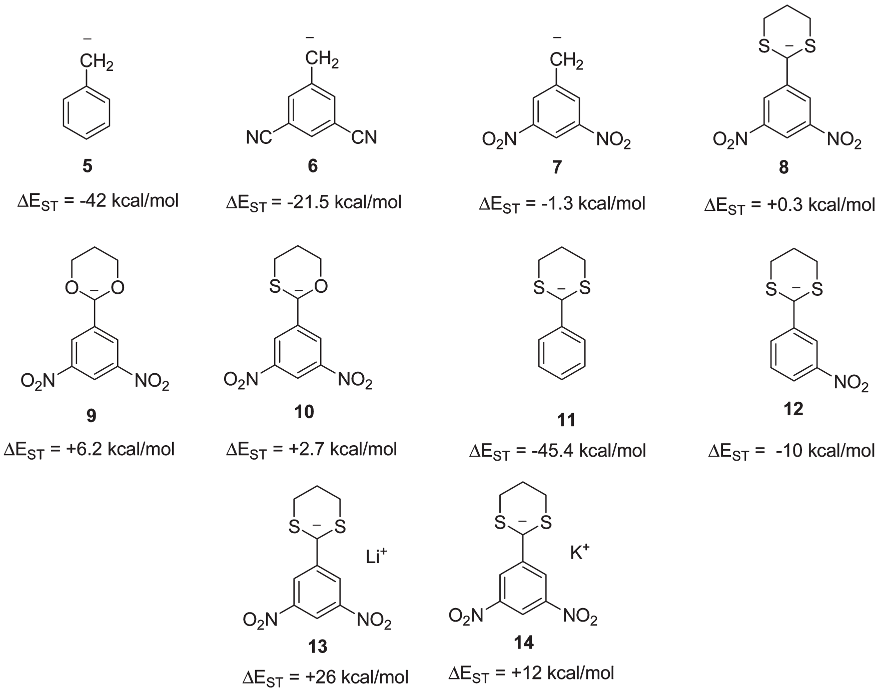
Scheme 2. Predicted Singlet−Triplet Energy Gaps with DFT (B3LYP 6-31+G(d,p)) for Several Benzylic Carbanions



NR^+, CR_2^+) is placed on a benzene ring meta with respect to one or two strong neutral π-electron donors (e.g., NMe_2, NH_2).[39]

In favorable cases, this can result in a species with a π,π^*-triplet ground state. The latter can be viewed as resulting from a formal transfer of a single electron from the donor substituent to the cationic center. A recent experimental study provided evidence for the triplet state of the 3,5-bis(dimethylamino)benzyl carbenium ion.[40] Likewise, β-donor-substituted vinyl cations are also predicted to show low energy triplet states.[41]

The following study was designed to determine if the same reasoning could be applied to anionic species. Specifically, we have generated and characterized a benzylic carbanion having two nitro groups substituted meta with respect to the (formally) anionic center. Calculations using density functional theory (DFT) suggest that this species has a diradical ground state. NMR, UV, as well as chemical trapping experiments provide evidence that this species is both persistent and paramagnetic.

On the basis of these calculations and experiments, it is argued that **8** either has a triplet ground state or has a singlet ground state with a higher energy, but thermally accessible, triplet.

RESULTS AND DISCUSSION

DFT Calculations. To identify anionic species having low energy open-shell and/or triplet electronic states, the anions shown in Scheme 2 were considered. These include the parent benzyl anion **5**, its 3,5-dicyano **6**, and 3,5-dinitro derivatives **7** and **8**. Also investigated were benzylic anions wherein the formally anionic center was substituted with either two sulfur atoms **8**, two oxygen atoms **9**, or one of each **10**. For each anion, geometries of the singlet and triplet states were optimized at the (U)B3LYP/6-31+G(d,p) level, and the reported geometries were verified as local minima on the basis of vibrational energy calculations, which showed no imaginary frequencies. The reported singlet−triplet energy gaps (kcal/mol) include ZPVE, and a negative value indicates a singlet ground state.

As expected, simple benzylic anions lacking strong π-acceptors in the meta positions (**5** and **11**) are straightforward ground-state singlets having negative ΔE_{ST} values. Substitution of π-acceptors in the meta positions does have the effect of moving ΔE_{ST} in favor of the triplet. However, in cases with modest acceptors **6**−**7** or a single acceptor **12**, the singlet is still clearly the ground state. In fact, even the 3,5-dinitrobenzyl anion is predicted to be a singlet at the DFT level, although at this point the gap is very small. Only when additional π-donating groups (**8**−**10** and **13**−**14**) are included on the anionic center does DFT predict a triplet ground state (Scheme 2).

Analysis of the computed NBMOs in which the unpaired electrons of structure **7** reside gives a qualitative picture showing clear overlap of electron density. This overlap occurs largely on the positions ortho to the nominally, carbanionic center and slightly on the para positions and nitro groups (see the Supporting Information). Such overlap establishes the nondisjointness of the nonbonding molecular orbitals, reinforcing the conclusion that a triplet state is favored. Similar results are seen with structure **8**. However, the orbitals are more complex due to the lower symmetry of this anion.

It should be noted that DFT is a single-reference method and so does not explicitly account for nondynamical correlation in any rigorous way. Because nondynamical correlation is usually more important for singlet states than for triplet states, DFT often underestimates the singlet stability relative to the triplet by several kcal/mol.

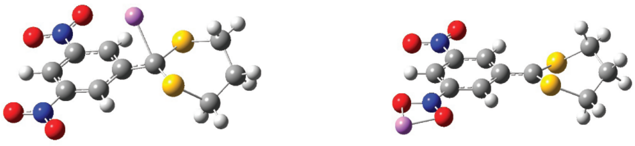
To benchmark the accuracy of B3LYP 6-31+G(d,p) methods, both CASSCF and CBS-QB3 calculations were performed on the parent benzyl anion. CASPT2/cc-pVDZ and the CBS-QB3 method yielded results of −46.3 and −44.0 kcal/mol, respectively. These numbers are in reasonable agreement with previous calculations. While still a single reference method, CBS-QB3 has been known to give extremely accurate energetic values by accounting for both static and dynamic electron correlation as well as extrapolating to an infinite basis set limit.

It is also the case that the calculations shown in Scheme 2 represent free gas-phase anions. We considered the possibility that ion pairing might affect ΔE_{ST}. Specifically, calculated charge distributions for **13S-Li$^+$**−**13T-Li$^+$** show that the singlet state favors negative charge on the benzylic carbon, whereas the triplet state accumulates more negative charge on the nitro groups. This picture is consistent with the general structure depicted in Scheme 1. Moreover, it implies that differential counterion binding to these sites might affect ΔE_{ST}.

DFT calculations, therefore, were carried out on the singlet and triplet states of ion pairs consisting of anion **8** and lithium or potassium cations. While several local minima were located with respect to the positioning of the cations, the lowest energy minima for each spin state are depicted in Figure 1. As expected, the triplet state has the Li$^+$ or K$^+$ counterion associated with the nitro group, whereas in the singlet state the same counterions are associated with the carbon.

More surprising is the effect of counterion binding on ΔE_{ST}. For lithium, this value increases to +26 kcal/mol as compared to nearly degenerate for the free anion. For potassium, the effect is smaller (+12 kcal/mol), presumably due to its weaker coordination to the anionic sites. Of course, coordinating solvents, like ethers, would be expected to bind to the counterions competitively with the anions. As such, we would expect the magnitude of the counterion effect on ΔE_{ST} to be diminished relative to what is calculated in the gas phase. Indeed, reoptimization of **13S** and **13T** using the Polarizable Continuum model (Integral Equation Formalism-PCM) in Gaussian 03 at the 6-31+G(d,p) level with THF as solvent showed a decrease in ΔE_{ST} to a value of +17 kcal/mol (including correction for ZPVEs). Nonetheless, it is reasonable to expect that the lithium salt of ion **8** will be a triplet or at least have a low-energy triplet state if it is generated in solution.

Generation of the Anions. Benzylic anion **8** was generated from deprotonation of the corresponding dithiane **15** using various strong bases (for the synthesis and characterization of **15**, see the Supporting Information). Anion formation was verified by observing the incorporation of deuterium into the benzylic position after the solutions were subsequently quenched with CD_3OD. For example, dithiane **15** in anhydrous THF was allowed to equilibrate with KH at room temperature for 1 h. This mixture was then quenched with CD_3OD. The resulting ^{1}H NMR spectrum showed little to no signals for the benzylic proton, and 86% H/D incorporation was determined from this spectrum (Scheme 3). Essentially identical results were obtained with other strong bases including CH_3Li, *n*-BuLi, as well as in other aprotic media including benzene and dioxane (see the Supporting Information for NMR spectra). For comparison purposes, the unsubstituted analogue **16** was also investigated, and similar results were obtained. On the basis of these experiments, we conclude that the targeted anions are generated through straightforward deprotonation of the corresponding dithianes.



13S-Li$^+$ **13T-Li$^+$**

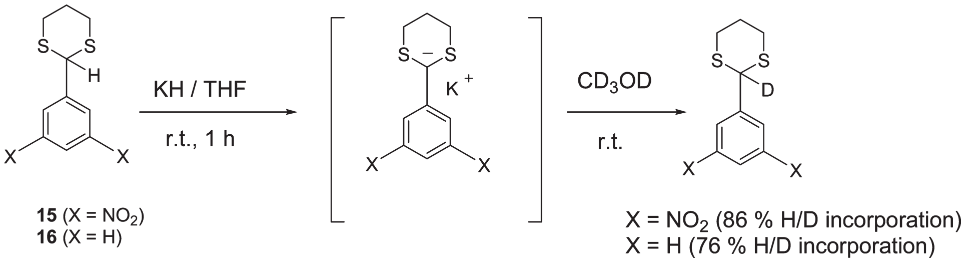
Figure 1. Computed DFT (B3LYP-6-31+G(d,p)) geometries for the singlet **13S-Li$^+$** (left) and **13T-Li$^+$** triplet (right) with lithium counterions.

In contrast, similar attempts to generate the corresponding O-substituted anions **9** and **10** resulted in exchange of the aromatic proton that is between the two nitro groups, rather than the desired benzylic proton.

Chemical Trapping Experiments. Carbanions derived from 1,3-dithianes are well-known to carry out S_N2 reactions with primary alkyl halides.[42−51] The anion generated from dithiane **16** is no exception. Generation of the latter and treatment with methyl iodide or 1-bromopropane results in good yields of the alkylated products (60%) and (57%), respectively (see the Supporting Information for characterization details). However, the dinitro-derivative **15**, when subjected to the same conditions, provided no detectable alkylation products, even after 24 h of reaction time (see the Supporting Information). While this experiment does not unambiguously identify the electronic configuration of **8**, it does illustrate that this species differs qualitatively from the unsubstituted dithiane in its chemical behavior.

UV−Vis Spectra of Anion 8. Shown in Figure 2 is the spectrum of the anion generated through the deprotonation of dithiane **15** using CH_3Li/TMEDA. The main features are a maximum at 390 nm along with a shoulder at ca. 425 nm. These features only appear when a base is added and are rapidly quenched upon addition of water or alcohols. Thus, these signals are confidently attributed to the anion. Similar spectra were obtained with other bases and/or in other solvents (specific bands are listed in a table in the Supporting Information). Unfortunately, the UV−vis bands computed using TD-DFT for the singlet and triplet anion are not sufficiently different to make a definitive assignment of the spin state by absorption spectroscopy, given the inherent approximations in the computational method and that the absorption spectra that we obtained for the anion are highly dependent on additives (such as TMEDA), solvent, and counterion. Nonetheless, these experiments indicate that anion **8** can be generated and is persistent in the absence of oxygen, alcohols, or water.

Scheme 3. H/D Exchange Experiment of Dithianes 15 and 16 in Anhydrous THF with Excess KH at Room Temperature (1 h) and Quenching with Excess CD_3OD



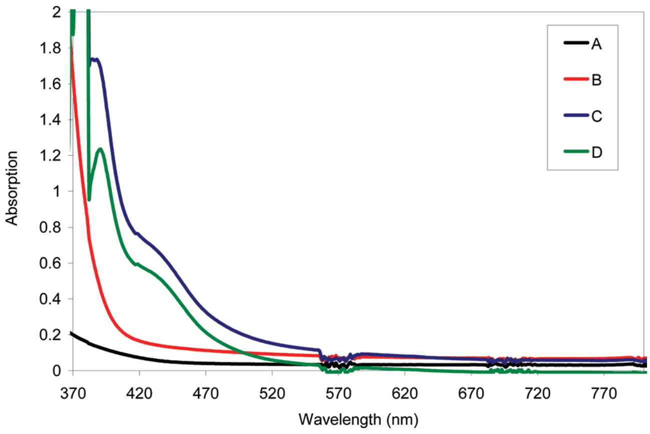


Figure 2. UV−vis spectrum of 2-(3,5-dinitrophenyl)-1,3-dithiane (**15**) and 156 mM TMEDA/benzene with no base added (A). Difference UV−vis absorption spectra of **15** (0.061 mM) in benzene with TMEDA (164 mM) and titration of excess base (addition of 25 μL of 3.0 M MeLi/DEM) (C), which is subtracted from a blank solution (B) containing 164 mM TMEDA, benzene, and 36.1 mM MeLi/DEM ((D) benzyl anion **8** difference spectrum). See the Supporting Information for additional UV−vis spectra.

^{1}H NMR Spectra of the Anion.

Several years ago, Eliel et al. demonstrated that the benzylic anion **11**, derived from deprotonation of 2-phenyl-1,3-dithiane, could be directly detected and characterized using ^{1}H NMR spectroscopy.[52] Similar experiments were carried out on **16**, and the results are shown in Figure 3.

Following the earlier work, the protons meta and para with respect to the anionic center show a substantial upfield shift relative to the conjugate acid, while the ortho protons show a downfield shift. The latter is presumably due to the coordination of the lithium counterion at the benzylic site. Quenching with CD_3OD restores the original dithiane. The broadening of the peaks in the latter spectrum is attributed to the formation of insoluble lithium salts from the quenching reaction.

The dinitro derivative **15** shows qualitatively different behavior. In this case, deprotonation of the dithiane using *n*-BuLi in dioxane-d_8 results in the broadening of the aromatic resonances to the point where they disappear (Figure 3e). As with **16**, quenching with CD_3OD restores the aromatic signals of the dithiane (Figure 3f). Similar results were obtained with other bases (CH_3Li) and using other solvents (TMEDA/C_6D_6). This behavior is consistent with what would be expected for a paramagnetic species having significant spin density localized on the phenyl ring. In general, paramagnetic species are observed to be NMR silent due to rapid spin−spin relaxation. Other causes, such as chemical exchange, aggregation, and formation of precipitates, could also explain such peak broadening. However, these causes would also have to be consistent with nearly quantitative reformation of dithiane **15** upon quenching with proton donors.

To determine whether the observed peak broadening was due to the formation of a paramagnetic species, an Evans experiment was carried out. In addition to relaxation effects, paramagnetic additives can also cause deshielding of species that are in the same solution. Through comparison of chemical shifts of the solvent in the presence and absence of a paramagnetic solute, it is possible to determine if the anion shows paramagnetic character. For the present study, this was accomplished using the Evans method wherein ^{1}H NMR spectra were carried out using a two-compartment NMR sample tube.[53−64] In these experiments, the inner compartment contains solvent (C_6D_6) alone, and the outer compartment was charged with a solution containing the anion in the same solvent.

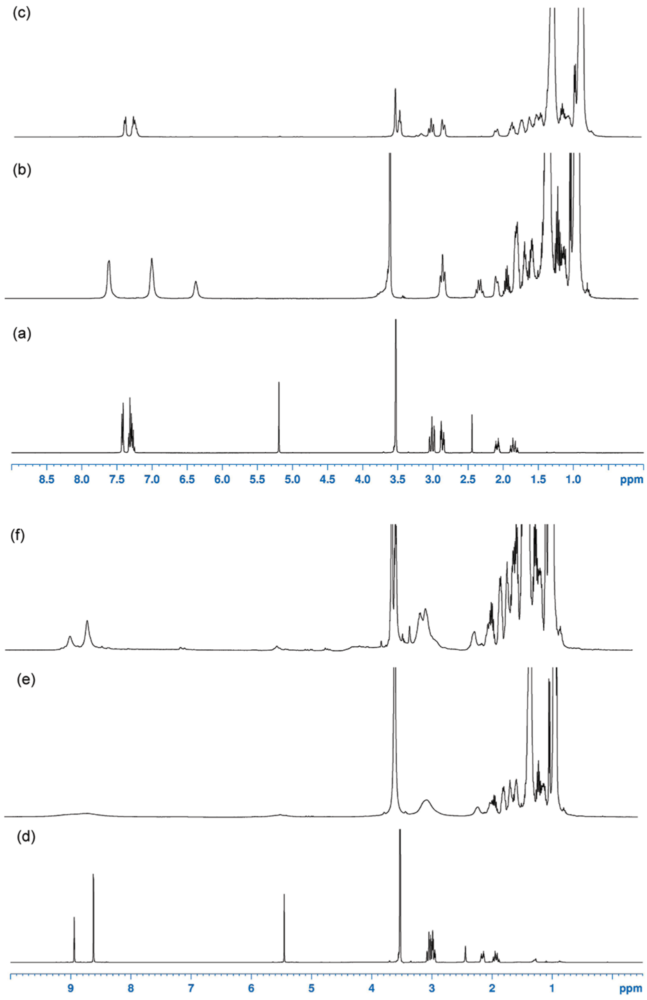


Figure 3. Room-temperature ^{1}H NMR (400 MHz) spectra of the generation of the 2-phenyl-1,3-dithiane anion and the 2-(3,5-dinitrophenyl)-1,3-dithiane anion in a sealed Young tube in d_8-dioxane. (a) **16** (124 mM) in d_8-dioxane (no base added). (b) **16** (124 mM) in d_8-dioxane after 0.45 mL of 2.5 M *n*-butyllithium/hexanes was added. (c) **16** (124 mM) in d_8-dioxane after 0.45 mL of 2.5 M *n*-butyllithium/hexanes was added and quenched with 0.2 mL of CD_3OD. (d) **15** (89.0 mM) in d_8-dioxane (no base added). (e) **15** (89.0 mM) in d_8-dioxane after 0.20 mL of 2.5 M *n*-butyllithium/hexanes was added. (f) **15** (89.0 mM) in d_8-dioxane after 0.2 mL of 2.5 M *n*-butyllithium/hexanes was added and quenched with 0.2 mL of CD_3OD.

In the absence of anion, there is a single solvent peak (Figure 4a). However, as the concentration of anion is increased, solvent peaks for the inner and outer two begin to separate, signaling the formation of a paramagnetic species (see the Supporting Information for more detailed NMR spectra and a table that summarizes all Evans method experiments on **15** in C_6D_6/TMEDA with *n*-BuLi). Control experiments wherein *n*-BuLi/TMEDA but no dithiane was added to the outer compartment showed no chemical shift differences (see the Supporting Information).

Figure 4 shows the ^{1}H NMR resonances in the region 6.5−7.5 ppm from an Evans experiment wherein the anion was generated in C_6D_6 using *n*-BuLi/TMEDA. The peaks shown in these figures correspond to the residual protonated solvent.

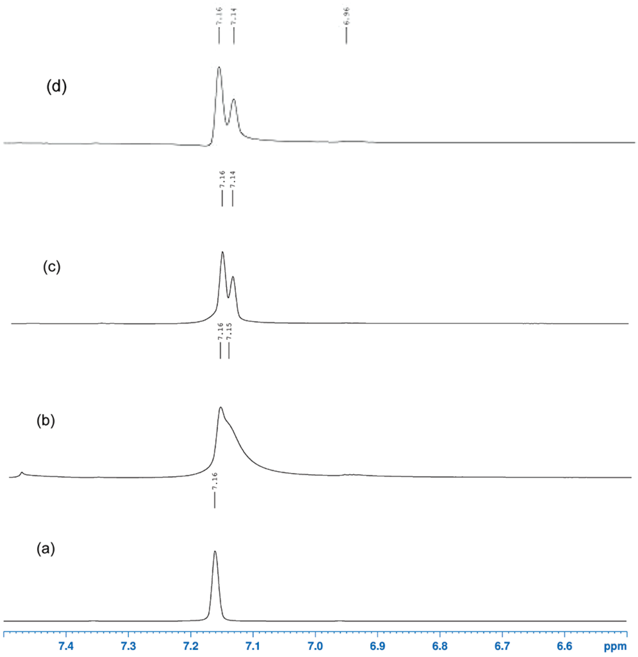


Figure 4. Representative ^{1}H NMR (400 MHz) Evans method experiments at room-temperature expansions (7.5−6.5 ppm). (a) 85.0 mM **15** in C_6D_6 with 132 mM TMEDA. (b) 54.8 mM **15** in C_6D_6 with 132 mM TMEDA and 0.1 mmol of 2.5 M *n*-butyllithium/hexanes. (c) 85.0 mM **15** in C_6D_6 with 132 mM TMEDA and 0.125 mmol of 2.5 M *n*-butyllithium/hexanes. (d) 113.5 mM **15** in C_6D_6 with 258 mM TMEDA and 0.250 mmol of 2.5 M *n*-butyllithium/hexanes.

A quantitative analysis of the chemical shift change data suggests a lower limit of 1% triplet is formed under these conditions. This could indicate that the singlet is the ground state with a slightly higher energy triplet or a lack of quantitative formation of anion **8** (see the Supporting Information for more details).[64−66]

Also considered was the possibility that a radical anion resulting from one electron reduction of dithiane **15** is responsible for the ^{1}H NMR peak broadening and Evans shift seen in Figures 3 and 4. While such an intermediate could, in principle, account for these observations, it is difficult to reconcile with three observations.

First, the high level of deuterium incorporation at the benzylic position is inconsistent with the formation of an anion radical as the latter would retain the hydrogen at the benzylic position.

Second, no products attributable to the anion radical were detected by GC or ^{1}H NMR. Similar nitroarene anion radicals have been generated in aprotic media. These species seem to decay by protonation on the nitro group followed by disproportionation to form hydroxylamines.[67] To verify this, we generated the anion radical of **15**. Samarium(II) diiodide (SmI_2) is known to carry out one electron reduction reactions with aliphatic and aromatic nitro groups to yield hydroxylamines, amines, and various other reduced adducts.[68,69] Therefore, dithiane **15** was combined with an excess of SmI_2/THF (ca. 6−10 equiv) at reflux for 20.5 h. Following the quenching of this reaction with CD_3OD, the formation of 3−4 major products was observed by GC, GC−MS, and NMR (see the Supporting Information). We did not observe any of these products in the deprotonation experiments (Scheme 3). While it is impossible to exclude trace formation of anion radical under these conditions, we feel that the data are much more consistent with the formation of anion **8**.

Third, the same peak broadening and Evans shift effects are seen with a variety of bases (CH_3Li, *n*-BuLi, KH) as well as in different solvents (THF, benzene, dioxane). While it is not strictly impossible that similar trace amounts of anion radical could be formed under these different conditions, we regard this as far less likely than a more straightforward assignment of the paramagnetic effects to a thermally accessible triplet state of **8**.

CONCLUSION

The calculations and experiments described provide evidence that anion **8** is a persistent ground state triplet or has a singlet ground state with a triplet state that is very low in energy. The DFT calculations summarized in Scheme 2 are consistent with the general picture developed for analogous cationic intermediates. Combining an anionic center with two strong π-electron-withdrawing groups results in a low energy triplet state. This can be viewed as a formal electron transfer, creating a diradical that is similar to the well-characterized *meta*-xylylene system. H/D exchange experiments establish that the anion is being formed, and the ^{1}H NMR and Evans experiments show that this species is paramagnetic. Future efforts will be directed at identifying other carbanions with this electronic configuration and characterizing these species by X-ray crystallography.

ASSOCIATED CONTENT

Supporting Information. Detailed syntheses and characterization of benzyl anion precursor **15** as well as additional H/D exchange spectra, chemical trapping characterization, UV−vis/NMR titration spectra, and Evans method spectra of benzyl anion **8** under a variety of different conditions. An Evans method control spectrum and a detailed table summarizing the Evans method results from the deprotonation of **15**. Computational data including *Z*-matrices, ZPVEs, singlet−triplet energy gaps for anions **8**−**14**, and TD-DFT data for anion **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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