# Electronic and Ion-Pairing Effects of a Methyl Group on a Diphenylmethyl Anion Determined by Restricted Aryl Rotation

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The compound [(2,4,6-trideuteriophenyl)(4-methylphenyl)methyl]lithium has been prepared and studied by $^1$H DNMR. A complete line shape analysis of the spectrum allows unambiguous phenyl ring assignment to the differential aryl barriers to rotation. Solvent variation reveals that rotational barriers are solvent dependent and subject to ion-pairing effects. The intrinsic electron donor effect of a methyl group and the ion-pairing effect are of comparable magnitudes.

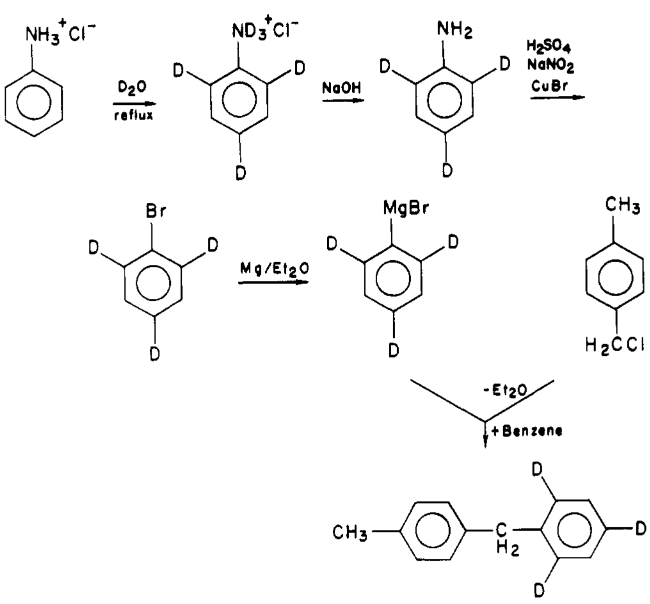
Delocalization in diarylmethyl anions leads to enhanced anion stability and to varying degrees of $\pi$ bonding to the benzylic carbon. This $\pi$ bonding leads in turn to restricted aryl rotation. While inductive, hybridization, and delocalization phenomena can affect anion stability by many orders of magnitude, restricted aryl rotation is determined solely by delocalization, i.e., by the degree of $\pi$ bonding. We have utilized dynamic NMR (DNMR) studies of aryl restricted rotation in the lithium salts of diarylmethyl anions as a measure of $\pi$ bonding.[1-3] Recently others have found value in this method for the quantitative assessment of the effect of a tricarbonylchromium substituent.[4]

The compound [(4-deuteriophenyl)(4-methylphenyl)methyl]lithium shows interesting $^1$H and $^{13}$C [$^1$H] DNMR behavior.[1] At 300 K, the 270-MHz $^1$H spectrum of the aromatic region shows two different overlapping spectra each of which has apparent AB or AA′BB′ characteristics consistent with the nonequivalent phenyl rings. Below 300 K, the spectrum decoalesces, and at 195 K two separate sets of resonances for each ring are seen. It is evident that the $^1$H NMR spectrum of each ring is composed of a four-spin system and is consistent with slow aryl rotation in both rings.

As the temperature is raised above 195 K, complete DNMR line shape analysis for this anion reveals an interesting dynamical situation. One of the two aryl subspectra collapses at a faster rate than the other due to the onset of exchange processes which clearly have different rates. Complete line shape analysis at 208 K reveals that the rate constants for exchange of the two systems are 20 and 2.5 s$^{-1}$. Thus one ring is rotating faster than the other. The phenomenon is further illustrated effectively in the $^{13}$C [$^1$H] DNMR spectra of the anion.[1] These observations provide unequivocal evidence for differential rates of rotation in an unsymmetrical 4,4′-disubstituted diphenylmethyl anion.

This clearcut differential substituent effect could arise from some combination of the intrinsic electron donor properties of a methyl group and ion-pairing phenomena. Assessment is presently not possible for two reasons. Assignment of the $^1$H chemical shifts of the two different phenyl moieties may be done by analogy with chemical shifts derived from symmetrically substituted (diphenylmethyl)lithium anions but really cannot be done rigorously.[2] Thus, one cannot determine unequivocally which ring is rotating faster from the data at hand. Additionally, the effect of solvation is unknown since only data in THF is available. In this paper, we present evidence which allows for unequivocal identification of the individual aromatic rings and evidence for a solvent dependency of the differential barriers to rotation. Clearly, an unequivocal assignment of aryl rotation barriers could be done by a DNMR study of the anion of [(2,4,6-trideuteriophenyl)(4-methylphenyl)methane. In addition, studies of the effect of solvent on this aryl rotation barrier have been performed.

Scheme I. Synthetic Route Used To Prepare (2,4,6-Trideuteriophenyl)(4-methylphenyl)methane



## Results and Discussion

The synthetic strategy employed the Grignard coupling of (2,4,6-trideuteriophenyl)magnesium bromide and *p*-xylyl chloride as outlined in Scheme I and is detailed in the Experimental Section. The trideuterio isotopic purity of the 2,4,6-trideuteriobromobenzene was 91% determined by a mass spectroscopic procedure described in the Ex-

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† Taken from the M.S. Thesis of R.P.M., State University of New York at Albany, 1979.

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perimental Section. Interestingly the trideuterio isotopic purity of the (2,4,6-trideuteriophenyl)(4-methylphenyl)methane determined by the same procedure was somewhat less (71%). In fact the spectra of the anions further reveals this change (vide infra). Evidently there is some rearrangement during coupling, but the extent of this rearrangement is sufficiently small so as to not obscure the present study. It is nevertheless interesting, and we are pursuing this possibility of rearrangement in other work.

[(2,4,6-Trideuteriophenyl)(4-methylphenyl)methyl]lithium (1) was generated in THF and DME (0.4 M) and sealed in NMR tubes under argon. The $^1H$ DNMR study utilized the Bruker 270-MHz NMR system at the Southern New England High Field NMR Facility at Yale University.

Examination of the $^1H$ DNMR spectrum of 1 (0.4 M in THF) at 297 K reveals two overlapping sets of spectra (Figure 1, supplementary material). One set of resonances appears to have an apparent AB or AA′BB′ characteristic ($^3J_{AB}$ = 8 Hz) while the other resonance appears as a singlet overlapping the low field portion of the low field doublet (see asterisk in Figure 1). As the temperature is lowered, the spectrum decoalesces and resharpens at 196 K, consistent with a slowing of aryl rotation. At 196 K (Figure 1), the dominant features of the spectrum include an AEGM subspectrum ($\delta_A$ 6.77, $\delta_E$ 6.57, $\delta_G$ 6.44, $\delta_M$ 6.28, $^3J_{AE}$ = 8.0 Hz, $^3J_{GM}$ = 8.0 Hz, $^5J_{AG}$ = $^5\mathrm{J}_{EM}$ = 0 Hz, $^4J_{AM}$ = $^4J_{EG}$ = 1.1 Hz) and a CF subspectrum ($\delta_C$ 6.67, $\delta_F$ 6.51, $^4J_{CF}$ = 1.1 Hz). The four-spin AEGM subspectrum is obviously consistent with the structure of the 4-methylphenyl ring under conditions of *slow aryl rotation* and allows unequivocal assignment of the AEGM subspectrum to that ring. The two-spin CF subspectrum, i.e., essentially two broad singlets, is also obviously consistent with the structure of the 2,4,6-trideuteriophenyl ring under conditions of slow aryl rotation. Indeed, the AEGM subspectrum for 1 corresponds exactly to the ADFM subspectrum observed for the (4-deuteriophenyl)(4-methylphenyl)methyl anion at 195 K.[1] The chemical shifts of the CF subspectrum for 1 correspond exactly to the $\delta_C$ and $\delta_E$ values of the BCEN subspectrum of the (4-deuteriophenyl)(4-methylphenyl)methyl anion, thus allowing an unequivical assignment of the BCEN subspectrum to the phenyl group of this anion. All the various resonances for the AEGM and CF subspectra are labeled with appropriate letters in the 196 K spectrum of 1 (Figure 1).

In addition to the dominant AEGM and CF subspectra, a perusal of the 196 K spectrum of 1 shows other minor resonances, e.g., resonances labeled B and N in Figure 1. Independent evidence shows the carbon skeleton of 1 to be intact. The minor peaks arise from nonregiospecific and/or incomplete deuteriation of the precursor to 1 (see Experimental Section). In fact, the deuteriated phenyl ring is adequately simulated as a composite of *three* subspectra: (1) CF discussed above (67%), (2) BCFN ($\delta_B$ 6.73, $\delta_C$ 6.67, $\delta_F$ 6.51, $\delta_N$ 6.22; $^3J_{BC}$ = 8.0 Hz, $^3J_{FN}$ = −8.0 Hz, $^3J_{BN}$ = $^3\mathrm{J}_{CF}$ = 1.1 Hz, $^5J_{BF}$ = $^5J_{CN}$ = 0 Hz; 25%) and (3) BN ($\delta_B$ 6.73, $\delta_N$ 6.22; $J_{BN} < 1.2$ Hz; 8%). The BCFN subspectrum corresponds exactly to the 4-deuteriophenyl ring of (4-deuteriophenyl)(4-methylphenyl)methyl anion,[1] i.e., a monodeuterio species. The BN spectrum is consistent with the presence of a 3,4,5-trideuteriophenyl ring. The three subspectra and a composite spectrum for the phenyl ring only are illustrated in Figure 2 (supplementary material). The spectrum of 1 at 196 K is then simulated adequately by a superposition of the AEGM subspectrum upon the composite spectrum of the phenyl ring. A decomposition of the complete simulation of the spectrum of 1 at 196 K is illustrated in Figure 3 (supplementary material). In simulating the exchange-broadened $^1H$ DNMR spectra of 1 (Figure 1), the phenyl ring rotation was modeled with CF to FC, BCFN to NFCB, and BN to NB interchanges. At a given temperature, the rate constants for all three of these processes are equal. They all reflect the *same* rate process, i.e., phenyl ring rotation. The 4-methylphenyl ring was simulated by using an AEGM to MGEA exchange.

**Table I. Barriers to Aryl Rotation for [(4-Deuteriophenyl)(4-methylphenyl)methyl]lithium in Various Solvents**

| solvent | ring | $\Delta G^\ddagger$,[a] kcal/mol |
|---|---|---|
| THF | 4-methyl | 10.7 |
| | deuteriophenyl | 11.6 |
| DME | 4-methyl | 11.3 |
| | deuteriophenyl | 12.9 |

[a] At 223 K.

At 218 K (Figure 1), it is evident that the AEGM subspectrum (4-methylphenyl ring) is significantly exchange broadened as compared to the spectrum of the deuterated phenyl group, i.e., the 4-methylphenyl ring is indeed rotating faster than the phenyl ring. The $\Delta G^\ddagger$ value for 4-methylphenyl rotation is 11.0 ± 0.2 kcal/mol and 12.6 ± 0.2 kcal/mol for phenyl rotation in reasonable agreement with the stereodynamics of the (4-deuteriophenyl)-(4-methylphenyl)methyl anion ($\Delta G$ = 10.8 and 11.7 kcal/mol at 223 K).[1]

These data prove unequivocally that the 4-methylphenyl rotation barrier is lower than the phenyl rotation barrier consistent with the expected electron-donor properties of methyl. The magnitude of the effect is assessed by comparison with the unsubstituted compound ($\Delta G^\ddagger$ = 11.2 kcal/mol) and is 0.4 kcal/mol for single ring rotation. Interestingly, this is somewhat less than the 1.1 kcal/mol anion destabilizing effect of a methyl group determined by acidity studies for this same compound.[5]

Having unequivocally assigned the $^1H$ NMR spectrum and determined a lower barrier to 4-methylphenyl rotation in [(4-deuteriophenyl)(4-methylphenyl)methyl]lithium (2), we can confidently examine the effect of solvent on the two different aryl rotation barriers in 2. $^1H$ DNMR studies of 2 were performed in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), total line shape analyses were performed, and $\Delta G^\ddagger$ values for aryl rotation are compiled in Table I.

Attention can now be focused on the effect of solvent on the barriers to aryl rotation. The change from THF to DME has a smaller effect on the activation energy of the barrier of the methyl ring (+0.6 kcal/mol) than for the phenyl ring (+1.3 kcal/mol). This leads to a greater differential between the two barriers in DME (1.6 kcal/mol) as compared to THF (0.9 kcal/mol). In view of the remote site of methyl substitution, it is far more likely that the solvent effect on the barriers is assocd. with ion-pairing changes rather than with substituent donor changes.

A change in solvent from THF to the better cation coordinating solvent DME generally increases charge delocalization into the rings.[6] This should increase $\pi$ bonding and leads to the observed overall increases in aryl rotation barriers (Table I). Additionally, in the more solvent separated ion pair (in DME) the effect of differential charge induced by methyl between the two phenyl rings is magnified. An attractive interpretation is that the two transition states for rotation involve differing amounts of

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charge localized on the $\alpha$ carbon. Thus the magnitude of the substituent effect on the barrier depends upon both the intrinsic electron donor (or acceptor) properties as well as the state of ion pairing. From the values obtained in this study it appears as if magnitudes of these effects are approximately comparable.

## Experimental Section

The 60-MHz proton NMR spectra were obtained by using a Varian A-60A and Varian EM-360A spectrometers. The 90-MHz proton spectra and 25.2-MHz carbon-13 spectra were run on a Bruker WH-90. The 270-MHz NMR were run on the Southern New England High Field NMR facility at Yale University. Mass spectra were obtained by using an AEI MS-902 mass spectrometer. Gas chromatographic analysis were performed on a HP-5750. A 10 ft × $^1/_8$ in. stainless steel column, packed with 10% Carbowax (20 m, 60–80 mesh), was used to analyze all compounds. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected.

**2,4,6-Trideuterioaniline.** The trideuterated aniline was prepared in a manner similar to that used by Streitwieser and Klein.[7] To a 100-mL flask containing 31.3 g of aniline hydrochloride (0.24 mol, Aldrich) was added 50 mL of $D_2O$ (SIC, 99.8% d) and the solution was refluxed for 24 h. The spent $D_2O$ was distilled and placed in a second 100-mL flask containing 31.3 g (0.24 mol) of fresh aniline hydrochloride. A 50-mL portion of fresh $D_2O$ was added to flask 1 and both solutions were refluxed for another 24 h. The $D_2O$ was then distilled from both flasks. The $D_2O$ in flask 2 was discarded and the $D_2O$ from flask 1 was placed into flask 2 and both reactions were again refluxed for 24 h. This procedure was repeated a total of four times. Then the $D_2O$ was removed by distillation from flask 1 and the flask was stoppered. The $D_2O$ in flask 2 was also removed, however a fresh 50-mL portion of $D_2O$ was added to the flask and refluxed for an additional 24-h period. The $D_2O$ was then distilled from flask 2 and the crude dark blue aniline-*2,4,6-*$d_3$·HCl was combined with the contents from flask 1.

At this point enough sodium hydroxide (1 N, Fisher) was added to the solid to form two layers. The basic aqueous layer was removed leaving 43.8 g of crude aniline-*2,4,6-*$d_3$ (0.47 mol, 99% yield) which was stored in a brown glass bottle. Aniline-*2,4,6-*$d_3$: $^1$H NMR (A-60A, neat) 7.05 (S, 2 H), 3.42 (s, 2 H).

**2,4,6-Trideuteriobromobenzene.** The synthesis was patterned after one described by Vogel for toluidine.[8] The reaction components are prepared in two separate flasks: a copper bromide solution and a diazonium salt of aniline-*2,4,6-*$d_3$. The two are mixed while heating, and the final product is steam distilled from the solution.

The copper bromide solution was prepared by adding 15.8 g of cupric sulfate (0.105 mol, Baker), 5.1 g of copper powder (0.079 mol, Baker), 38.0 g of sodium bromide (0.364 mol, Aldrich), 4.1 mL of 18 M $H_2SO_4$ (Fisher), and 250 mL of distilled water to a 1-L flask. The solution was refluxed for $3^1/_2$ h, and then sufficient sodium bisulfate was added (0.1–1.0 g) to change the color of the solution from light blue to yellow which indicates that the reduction is complete.

During the same period, to 500 mL of copper bromide solution was added 24.2 g of aniline-*2,4,6-*$d_3$ (0.25 mol), 27.0 mL of $H_2SO_4$ (Fisher), and 200 mL of distilled water. This reaction mixture was stirred until all solids had dissolved and was brought to 0 °C (ice–salt bath). Then 17.5 g of $NaNO_2$ (0.25 mol, Allied) dissolved in 30 mL of distilled water was added at a rate of 2–3 mL per addition maintaining the temperature between −5 and 5 °C. As the last 5% of the sodium nitrite solution was being added, sample drops indicated the presence of nitrous acid and the conversion of all the aniline-*2,4,6-*$d_3$ to diazonium salt. This solution was stored at −5 °C pending addition to the CuBr solution.

An apparatus for steam distillation was constructed using the 1-L flask containing the CuBr solution. The warm copper bromide solution was again brought to boiling. Steam was then passed through the solution and distilled into a 300-mL receiving flask. At this point, approximately 50-mL portions of cold diazonium solution were added to the boiling copper bromide solution via the addition funnel; the stem of the addition funnel was placed well below the surface of the solution. The total amount of diazonium salt was added during 0.3–0.5 h. The steam distillation was continued until no further orange organic matter was collected. The distillate was rendered basic (NaOH) and the organic layer was separated. The organic layer was then washed with 40 mL of concentrated $H_2SO_4$ and 40 mL of $H_2O$, 40 mL of 20% NaOH, and 40 mL of $H_2O$ and finally dried over $CaCl_2$. GLPC analysis showed the formation of bromobenzene-*2,4,6-*$d_3$ and a minute amount of benzene-*1,3,5-*$d_3$. Since benzene is used as a solvent in the following reaction, further purification was not required (18 g, 0.11 mol, 44% yield). Bromobenzene-*2,4,6-*$d_3$: $^1$H NMR (A-60A, neat) 7.0 (s, 2 H); mass spectrum, *m/e* 161, 159, 80. The mass spectra of bromobenzene-*2,4,6-*$d_3$ and bromobenzene-$d_0$ were obtained under identical conditions. In the undeuterated bromobenzene spectrum, the ratio of molecular ion height (*m/e* 156, $^{79}$Br) to the total integration of the cluster of peaks (*m/e* 154–159) was 0.460. Similarly, in the spectrum of bromobenzene-*2,4,6-*$d_3$, the ratio of the molecular ion peak (*m/e* 159, $^{79}$Br) to the entire cluster (*m/e* 157–162) was 0.417. Therefore, the percent of trideuterated material in this product is (0.417/0.460) × 100 = 91%. This technique is accurate to ±5%.[9]

Proton NMR was also used to support the analysis of the deuteration although the error is higher (±10–15%). The bromobenzene spectrum consisted of a complex aromatic region while that of bromobenzene-*2,4,6-*$d_3$ was a spectrum of one broad singlet at $\delta$ 7.0 (2 H) thus confirming the presence of two symmetrical hydrogens and the trideuteration of bromobenzene.

**(2,4,6-Trideuteriophenyl)(4-methylphenyl)methane.** The preparation of this compound is similar to the synthesis of (3-methylphenyl)(4-deuteriophenyl)methane A Grignard reagent was prepared by adding 17.7 g of bromobenzene-*2,4,6-*$d_3$ (0.110 mol) in 65 mL of dry $Et_2O$ (Fisher) to 2.91 g of Mg (0.12 mol, Baker) and a vaporized iodine crystal. After the addition of the deuterated bromobenzene, the solution was refluxed for an additional 0.5 h. The ether was removed and replaced with dry benzene (Fisher). The solution was heated to reflux (72 °C) and a solution containing 18.3 g of *p*-methylbenzyl chloride (0.13 mol) in 5 mL of dry benzene (Fisher) was added dropwise. After 1 h refluxing, a GLPC analysis confirmed the complete consumption of *p*-methylbenzyl chloride. The reaction was cooled and worked up in standard manner. Vacuum distillation afforded 9.4 g of pure phenyl-*2,4,6-*$d_3$-(4-methylphenyl)methane (0.51 mol, 46% yield, bp 90–95 °C (1.5 mmHg)): $^1$H NMR (WH-90, $CDCl_3$) 7.0–7.25 (m, 6 H), 3.88 (s, 2 H), 2.26 (s, 3 H); mass spectrum, *m/e* 186, 170. The mass spectra of (2,4,6-trideuteriophenyl)(4-methylphenyl)methane and phenyl(4-methylphenyl)methane were obtained under identical conditions. In the undeuterated compound the ratio of the intensity of the molecular ion, *m/e* 182, to the intensities of the cluster of peaks *m/e* 175–184 was 0.669. The corresponding ratio for the deuterated compound of *m/e* 185 to the cluster of peaks 178–187 was 0.481. Therefore, the percent of trideuterated material is 71%. Thus, even with the ±5% accuracy of the method some trideuterio material was lost in the synthetic scheme.

**Registry No.** $D_2O$, 7789-20-0; $H_2SO_4$, 7664-93-9; $NaNO_2$, 7632-00-0; CuBr, 7787-70-4; Mg, 7439-95-4; $Et_2O$, 60-29-7; aniline hydrochloride, 142-04-1; aniline-*2,4,6-*$d_3$ hydrochloride, 93041-26-0; sodium hydroxide, 1310-73-2; aniline-*2,4,6-*$d_3$, 7291-08-9; 2,4,6-trideuteriobromobenzene, 13122-41-3; *p*-methylbenzyl chloride, 104-82-5; (2,4,6-trideuteriophenyl)(4-methylphenyl)methane, 93041-27-1; benzene, 71-43-2; [(4-deuteriophenyl)(4′-methylphenyl)methyl]lithium, 67402-26-0.

**Supplementary Material Available:** Full NMR spectra, simulated spectra, and subspectra (4 pages). Ordering information is given on any current masthead page.

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