

Substituent Effect on the Electrochemical Oxidation of Arylmethyl Anions.

3. Effect of Methyl Substitution on Diarylmethyl Anions

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Electrochemical oxidation of a series of diarylmethyl anions was examined. Twelve variously substituted groups including methyl, dimethyl, ring, and a $\text{CH}_2\text{N}(\text{CH}_3)_2$ group were studied as the lithium salts in dimethoxyethane/tetramethylethylenediamine by use of cyclic voltammetry. The potentials depend upon the number and positions of the substituents. The effect of a single methyl group at the various positions as well as the effect of multiple substitution is compared with expectations. These electrochemical results are compared with the triarylmethyl series and acidity data.

Electrochemical methods have been very useful for providing stability values of highly reactive species. In previous studies, the reversible one-electron oxidations of triarylmethyl anions and the irreversible second oxidative process were examined for a series of sequentially substituted *p*-methyl¹ and *p*-trimethylsilyl anions.² The substituent effects on stability were measured and compared with other methods. In this way, the electronic effects of the electron-donating methyl group and the electron-withdrawing trimethylsilyl groups were determined. A dominant term in the substituent effect is the propeller geometry of the aryl rings in these species.³ Diarylmethyl species, while of similar stabilities,⁴ have differing geometric factors, and a comparable study of these anions offers interesting comparisons.

In contrast to triarylmethyl anions the increase in π bonding due to charge delocalization leads to well-characterized, restricted phenyl rotation about the benzylic carbon-phenyl bond.⁵ Dynamic (¹H and ¹³C) NMR studies reveal that the barrier is sensitive to the nature and extent of ring substitution.^{6,7} Indeed, the method has provided quantitative assessment of the substituent effect upon charge delocalization. This study included an assessment of the effect of methyl groups in varying positions.⁸ Additionally, the acidity of variously substituted diarylmethanes has been studied.⁹ The effect of methyl substitution on the *pK* value and the alteration of anion basicity for many of these compounds are known quantitatively. Accordingly, the effect of a methyl group on both anion overall stability and delocalization is available for various substituted diarylmethanes.

The desirability of oxidation data to provide further entries for this set has long been noted.¹⁰ For some years

it did not appear to be feasible to obtain uncomplicated information in view of the lack of reversibility of the oxidative process. Recently, experiments with both cyclic and second-harmonic ac voltammetry permit the values from cyclic voltammetry to be used without difficulty.⁴

Accordingly, we have investigated the electrochemistry of a series of diarylmethyl anions with systematic methyl substituent variation. Included in this work are the effect of select ring alkyl substitution and an *o*- CH_2NMe_2 group. For the former, cyclic compounds can provide, by comparison with open chain, important information about steric effects. For the latter, the effect of intramolecular cation solvation is possible,¹¹ and by comparison with the *o*-methyl compound this effect can be assessed.

Results and Discussion

The diarylmethanes (2-9b) were obtained via Grignard syntheses. The remaining compounds were either commercially available or were donated. The lithium anions (1-12a) were prepared from the reaction of the corresponding hydrocarbons with *n*-butyllithium-tetramethylethylenediamine (TMEDA) and diluted with freshly distilled dimethoxyethane (DME). Freshly prepared anion solutions were generated and transferred to the electrochemical cell in a No-Air system (Ace Glass).

The cyclic voltammogram of 1a depicted in Figure 1 reveals a single oxidation peak. The cyclic voltammogram reveals an anodic wave with a well-characterized current maximum, but even at sweep rates up to 500 mV s^{-1} there is no cathodic wave on reverse scan. Similar behavior for this anion has been noted previously by other workers.^{4,10} Several critical features of the electrochemistry allow a reliable value for the reversible potential to be obtained.

The values obtained from consecutive sweeps and independent runs have reproducibilities (± 0.005 V) equal to those of the fully reversible trityllithium oxidation, demonstrating a reliable degree of precision for the measurements. In addition, reversible behavior for (diphenylmethyl)lithium is obtained with second-harmonic ac voltammetry.⁴ Significantly, the $E_{1/2}$ values from that technique agree well with the value derived from cyclic voltammetry. Accordingly, the lack of reversible behavior is due to an extremely rapid chemical decomposition of the radical (vide infra) rather than electrochemical difficulties. Finally, it is noted that for the anions studied there is neither E_p nor $E_{p/2}$ dependence on scan rate, in the available range of 5 mV/s to 5 V/s , or concentration. This

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Table I. Summary of Electrochemical Data^a for Lithiodiarylmethyl Anions

compd	anion	$E_{p/2}^{c,e(a)}$, V	$E_p^{d,e(a)}$, V	$(i_p(a))/(V^{1/2} C) \times 10^{-4} f$
1	diphenylmethyl	-1.23 ₁	-1.11 ₄	7.2
2	2-methyldiphenylmethyl	-1.29 ₈	-1.19 ₄	4.6
3	3-methyldiphenylmethyl	-1.25 ₄	-1.12 ₅	6.8
4	4-methyldiphenylmethyl	-1.31 ₀	-1.23 ₆	6.1
5	α -methyldiphenylmethyl	-1.46 ₆	-1.40 ₀	6.8
6	2,2'-dimethyldiphenylmethyl	-1.28 ₉	-1.15 ₃	5.5
7	2,5-dimethyldiphenylmethyl	-1.29 ₅	-1.19 ₆	5.6
8	4,4'-dimethyldiphenylmethyl	-1.36 ₂	-1.24 ₅	6.1
9	4,4', α -trimethyldiphenylmethyl	-1.57 ₃	-1.52 ₀	<i>g</i>
10	2-(dimethylamino)methyldiphenylmethyl	-1.30 ₁	-1.20 ₀	5.9
11	9-isopropyl-9,10-dihydroanthracenyl	-1.34 ₁	-1.25 ₁	6.4
12	phenylindanyl	-1.41 ₂	-1.31 ₂	4.8

^a Determined by cyclic voltammetry at 50 mV s⁻¹ at a platinum wire electrode in DME solution, 0.04 M anion, 0.06 M in TMEDA, and 0.5 M in TBAP. Anthracene added an internal standard during the electroscan and gave for the reversible one-electron reduction $E_{1/2} = 2.01_3$ V vs. Ag/AgCl with a peak separation $\Delta = 69$ mV. ^b For the structures a = Li, b = H, c = 1 electron. ^c Half peak heights are reported conventionally for the totally irreversible process (ref 14). ^d No cathodic wave was observed on the reverse sweep. ^e At the conclusion of each run, ferrocene was added and the well-behaved reversible electrochemistry was recorded under similar conditions. A value of $E_{1/2}$ of $+0.455 \pm 0.08$ mV relative to Ag/AgCl, $\Delta = 70$ mV, was obtained (Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* 1980, 19, 2855). ^f Comparison of these values to that observed for the known one-electron reduction of anthracene, 5.6 V, confirms that these are one-electron oxidations. ^g The concentration of this anion was too low to provide estimation.

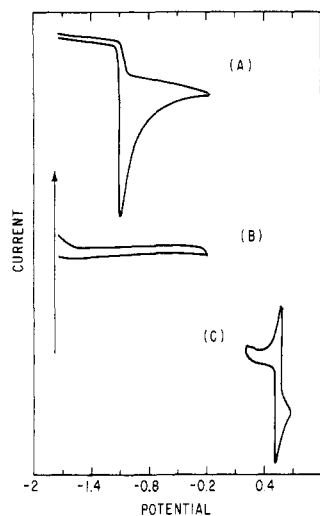


Figure 1. Cyclic voltammogram of (diphenylmethyl)lithium in TMEDA/DME solution at a scan rate of 50 mV s⁻¹. (A) Scan range -2.0 to 0 V. (B) Scan range -2.0 to 0 V after quenching solution with dry oxygen for 30 s followed by 2 min of argon purge. (C) Scan range +0.2 to +0.85 V after addition of ferrocene.

suggests that serious kinetic complications are minimal and of comparable nature for the anions of this study. Under these conditions, accurate E^0 values may be obtained from irreversible waves (vide infra).

The effect of added TMEDA on the peak potential for anion 1a in DME is -130 ± 30 mV. This agrees with the values of -160 mV for the addition of 4-30% vol % hexamethylphosphoramide (HMPA) in THF to the same anion.⁴ Thus TMEDA appears to have a similar effect in DME as HMPA does in THF. This is perhaps not surprising in view of the solvation differences of this anion in THF and DME.¹² For an extended series of diarylmethyl anions, the effect of added TMEDA was -90 ± 30 mV. The function of the TMEDA in producing freer ion pairs and/or ions is likely comparable throughout the set. Thus the degree of carbanion association-dissociation is similar throughout the set and is likely to be highly disassociated ion pairs.¹²

Table II. Effect of Single Methyl Substitution at Various Positions of Diarylmethyl Anions on Oxidation and Calculated Charges

position	$\Delta E_{p/2}^a$, mV	calcd charge ^b
α	236	-35
ortho	67	-0.14
meta	23	+0.06
para	79	-0.14

^a Relative to diphenylmethyl. ^b Derived from geometrically optimized MINDO/3 calculations of the diphenylmethyl anion.³¹

Table I records the electrochemical results of all of the anions that were studied. The potentials depend upon the number and position(s) of the substituent. Attention is focused first on single methyl substitution, followed by disubstitution, and finally, ring effects.

Table II records the comparative effect of a substitution of a single methyl group in each of the various positions; *o*- and *p*-methyl groups have similar effects, which are larger than a *m*-methyl and less than an α -methyl group. Finally, a single *p*-methyl in the diphenylmethyl system has a larger effect (79 mV) than a single *p*-methyl in the triphenylmethyl system (40 mV). The direction of the effect is that expected for a smaller π system, but the magnitude is large and may be related to geometric differences between the diphenylmethyl and trityl anions (vide infra).

The effects of an *o*-CH₂NMe₂ substituent are essentially identical with those of an *o*-methyl group. There appears to be nothing unusual in the oxidation of the anion, and the effect of intramolecular solvation if present at all is slight. Whereas such groups are known to direct lithiation in other systems¹³ and provide coordination,¹¹ the effect in this system is minor or absent.

Substitution of two methyl groups brings about two kinds of effects. For di-*para* and *ortho*-*meta* the second methyl has a slightly diminished effect relative to the first and the effect is not strictly additive. The oxidation potential of the disubstituted compounds is clearly greater than that of the monosubstituted analogues. However, for di-*ortho* substitution, the combined effect of the two me-

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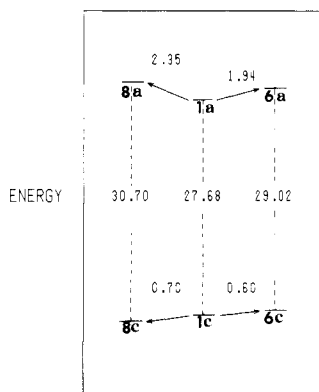


Figure 2. Energy relationships for the stabilities of di-*p*-tolylmethyl (8a and 8c), diphenylmethyl (1a and 1c), and di-*o*-tolylmethyl (6a and 6c) anions and radicals in kcal/mol.

thyls brings about a lower oxidation potential than that of the single methyl substitution compound. This suggests a conformational change due to a steric effect for this compound, which is discussed in a subsequent section.

Analysis of these data in somewhat greater detail is possible using related anion stability data and calculations of E_0 from the oxidation potentials.¹⁴ The relative stabilities of the di-*o*- and di-*p*-tolylmethyl and diphenylmethyl anions are derived from the pK measurements of Streitwieser.⁹ When the oxidation data in Table I is used, the di-*p*-tolylmethyl radical is some 0.70 kcal/mol more stable than the diphenylmethyl radical. In similarity with the effect of a *p*-methyl in the triaryl series, the effect on radical stability is 0.35 kcal/mol per methyl compared to 0.50 kcal/mol for the triarylmethyl compound.¹ Energy differences for radicals are given as energy differences in the C-H bond dissociation energy relative to the diaryl- or triarylmethane.

A similar analysis for the di-ortho compound reveals that the radical is some 0.6 kcal/mol less stable than the unsubstituted compound. A steric effect of 1.3 kcal/mol is indicated since in the absence of steric effects a stabilizing effect of 0.7 kcal/mol is expected. Interestingly, there are data for the cation that shows a similar effect.

Equilibrium constants for carbonium ion formation from diarylmethanols in H_2SO_4 have been obtained for the corresponding cations.¹⁵ Substitution of di-*p*-methyls brings about an increase in carbonium ion formation amounting to 4.0 kcal/mol in ΔG° (or 2.0 kcal/mol per methyl).¹⁵ Corresponding substitution by di-*o*-methyl brings about a stabilization amounting to only 1.1 kcal/mol or 0.55 kcal/mol per methyl.¹⁵

From these data and the preceding analyses we can compare the relative effects of methyl on cation, anion, and radical stabilities for the same system, focusing first on the para species where only electronic effects prevail. The magnitude of the para effect per methyl in a diaryl species for the cation, radical, and anion is respectively 2.0, 0.35, and -1.1 kcal/mol. As expected, the charged species show a greater sensitivity, and in accord with many other find-

ings, cations are more sensitive to a substituent than anions.¹⁶ These data provide an interesting quantitative comparison for the same system.

For the di-*o*-methyl species, clearly both electronic and steric terms contribute. A qualitative estimate of the steric effect in the cation can be obtained in the following way. If we assume that in the absence of a steric effect, the di-*o*-methyl-substituted cation would be as stabilized as the di-*para*-substituted cation than there is some 2.9 kcal/mol strain in this cation which is similar to the estimated 1.3 kcal/mol strain in this cation which is similar to the estimated 1.3 kcal/mol strain for the radical. An independent estimate of the strain of the 2,2'-dimethyldiphenylmethyl anion can be obtained from spectroscopic data. For the cesium salts in cyclohexylamine the 2,2'-dimethyldiphenylmethyl anion reveals a decrease in ϵ_{max} (40 500) as compared to the diphenylmethyl anion ϵ_{max} (47 100) at similar wavelengths.¹⁷ By use of these data estimates of delocalization for the diphenylmethyl anion¹⁸ and relationships for changes in ϵ_{max} with energy¹⁹ a value of 2.0 kcal/mol strain can be assigned to the 2,2'-dimethyl-substituted compound. This treatment estimates ortho methyl strain in the anion independently of the pK measurement. It agrees quite well with the destabilization value in the ortho anion of some 1.9 kcal/mol obtained by pK measurement. Accordingly, the three diarylmethyl species with 2,2'-dimethyl substituents have estimated values of steric destabilization of 2.9, 2.0, and 1.3 kcal/mol for the cation, anion, and radical, respectively.

There is yet another system that permits comparison of the three species. This remarkable system is the 9-isopropyl-9,10-dihydroanthracenyl anion and related species. For this compound, some greater analysis and comparison with other species is possible. The dihydroanthracenyl anion is some 4.7 pK units or 6.5 kcal/mol more stable than open analogues.^{20a} With the reasonable assumption that the 9-isopropyl-substituted compound would have a similar basicity and the oxidation data in Table I, the radical can be estimated to be some 5.5 kcal/mol more stable than an open analogue. This value compares with an independent estimate of approximately 10 kcal/mol derived from hydrocarbon oxidation data.^{20b}

These estimates can be compared with cation stabilities. For the cation the solvolysis rates of 9,10-dihydro-9-anthracenyl acetate in aqueous acetone solutions have been measured.²¹ By the use of data for benzhydryl chloride²² and a leaving group factor²³ of $10^{4.86}$, benzhydryl acetate is estimated to solvolyze at a rate of $9.7 \times 10^{-10} s^{-1}$ at 25 °C in 80% acetone. Since the dihydroanthracenyl acetate solvolyzes at a rate of $1.26 \times 10^{-8} s^{-1}$, the rate acceleration is 1.3×10^4 . In another extrapolation, the rate of hydrolysis of benzhydryl *p*-nitrobenzoate at 25 °C in 90% acetone can be estimated to be $2.0 \times 10^{-11} s^{-1}$ from data at higher temperatures.²⁴ Under these conditions the dihydro-

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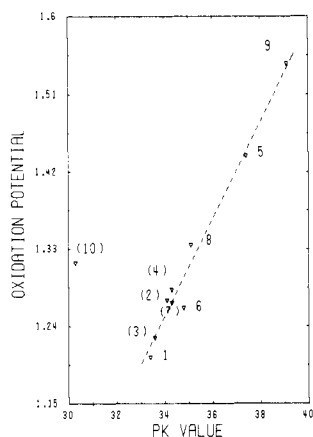


Figure 3. Relationship between calculated¹⁴ oxidation potentials and equilibrium acidities of diarylmethyl anions. Values of pK indicated by parenthesis are calculated assuming additivity.

anthracenyl acetate solvolyzes at a rate of $9.9 \times 10^{-7} \text{ s}^{-1}$. The acceleration is $\sim 5 \times 10^4$, in remarkable agreement with the previous value. The dihydroanthracenyl cation is thus some 6.1 kcal/mol more stable than the diphenylmethyl cation. Once again all three species show similar effects and in this case, stabilizing. For the cation, anion, and radical these are 6.1, 6.5, and 5.5 kcal/mol, respectively. It would seem that a common structural effect is indicated. This effect is stabilizing due to the enhanced ability to achieve coplanar aryl rings due to the absence of van der Waals repulsion of the ortho hydrogens.

Two different kinds of structural effects are noted in comparing cations, anions, and radicals. For para substitution, where electronic factors dominate, greater effects are seen for cations than anions than radicals. In ortho substitutions where steric effects can prevail, the effect can be stabilizing or destabilizing, but all three species show comparable effects. This argues for a common geometrical explanation based on the size of the groups, which is in fact common throughout.

Some insight into the relationship between base strength and oxidation is possible. For many of the compounds studied, values for the equilibrium acidities are available.⁹ For the remaining compounds, values can be estimated assuming substituent additivity. By the use of these data and the measured peak potentials, Figure 3 depicts the relationship between these quantities. With the exception of the dihydroanthracenyl and di-ortho compounds, which are probably special for reasons discussed above, a good linear relationship is obtained. Three points from this correlation merit comment.

First, base strength and oxidation potential are related in a straightforward manner. Thus the choice of a stronger base additionally gives a stronger reducing agent. Second, the slope of 0.068 is similar to slopes obtained for two other known cases. From the limited data on para-substituted triarylmethyl anions, a slope of 0.076 is obtained.^{1,2} Federlin has obtained a slope of 0.085 for very different types of carbanions in the pK range of 9–15.²⁵ This remarkable correspondence bridging differences in ranges of some 20 pK units suggests similarities in contributions. Of these, perhaps the central factor is the greater importance of anion stability relative to radical stability in the determination of the oxidation energies. A slope of 0.059 would be obtained if anion stability were the sole contribution to the relationship. Slopes greater than this value indicate

the contribution of substituent effect on radical stability. From this slope we can estimate that anion stability factors contribute about 75% to the oxidation process. Related data for phenols lead to a slope of 0.17.²⁶ Radical stability appears to be a more important contributor for these oxyanions. Third, while the slopes are similar, the lines appear to be displaced and are characteristic of the parent structure. This last observation suggests that changes in the basic system could lead to significant deviation from the relationship of base strength and oxidation potential. For example, tris(4-trimethylsilylphenyl)methyl anion has a comparable base strength to the substituted dihydroanthracenyl anion but differs in oxidation potential by more than 0.25 V.

In preceding sections it was noted that a para methyl group has a larger effect on the oxidation of a diaryl compound compared to a triarylmethyl compound. The anions in the diaryl- and triarylmethyl series reveal another difference in electrochemical behavior that merits comment. Oxidation of triarylmethyl anions is reversible by cyclic voltammetry. Base strength is not dominant since this includes anion basicities in the same ranges. Moreover, since the oxidation potentials are similar, thermodynamic radical stability cannot be a dominant term.⁴ A likely important factor is effectiveness in the rates of subsequent radical reaction.

A triarylmethyl species is more persistent since the recombination rates of these twisted and strained radicals are known to be slow.²² The diarylmethyl species are less persistent in view of greater rates of recombination.²⁸ Interestingly, the types of dimers differ as well. For the diarylmethyl species studied in this work, tetraarylethane dimers (head to head) are the products.²⁹ For the triarylmethyl species, methylenecyclohexadienyl type dimers (head to tail) are obtained. Whereas the triphenylmethyl species are twisted, the diphenylmethyl species may in fact be much closer to planar. In actual fact, many of the electrochemical differences described above may signal this geometric change.

Some insight into the structure of the diphenylmethyl species can be derived from the electrochemistry data of this work and from spectroscopic data. From calculations, we conclude that an essential geometrical feature is that the anion (and perhaps the cation as well) has phenyl groups close to planar (if not actually planar).³¹ The important and required reduction of steric effect is achieved via a bond angle opening which is energetically favorable for the small hydrogen atom. Clearly, substitutions that inhibit bond angle opening would lead to a less planar and less stable species. One way to achieve this is with di-*o*- (2,2'-) methyl substitution and another is with α -methyl substitution.

Methyl groups in the 2 and 2' position have an anomalous effect on the electrochemistry, which as discussed above is suggestive of a conformational difference for this anion. This di-ortho substitution would inhibit an opening of the central carbon to phenyls bond angle. This par-

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Table III. Absorption Data for Diarylmethyl Ions

anions	cation/solvent	λ_{\max}^a	ϵ_{\max}	ref
diphenylmethyl	Cs/CHA ^b	443	47 100	17
	Li/Et ₂ O	407	30 800	33
	Li/THF	443, 418		33
	Li/DME	448	37 000	33
	Cs/CHA ^b	449	40 500	17
2,2'-dimethyldiphenylmethyl	Cs/CHA ^b	477	30 700	17
α -methyldiphenylmethyl	Cs/CHA ^b	447		17
9,10-dihydroanthracenyl	Cs/CHA	400	42 500	33, 35
9-alkyl-9,10-dihydroanthracenyl	Li/THF	450, 400		33, 35
	Li/THF	415		33, 35
	Li/Et ₂ O			
cations	media	λ_{\max}^a	ϵ_{\max}	ref
diphenylmethyl	FSO ₃ H/SbF ₅	440	38 000	34
	H ₂ SO ₄	440	31 620	34
2,2'-dimethyldiphenylmethyl	H ₂ SO ₄	470	19 952	34
α -methyldiphenylmethyl	FSO ₃ H/SbF ₅	422	37 000	34
9,10-dihydroanthracenyl	H ₂ SO ₄	430	31 622	34

^a In nm. ^b Cyclohexylamine.

ticularly strong effect of the methyls is consonant with a structure for the parent diphenylmethyl anion that is close to planar.

A methyl group in place of hydrogen at the central carbon atom similarly causes large effects. For comparison the results of single methyl substitution can be compared with the charges derived from geometrically optimized MINDO/3 calculations on the diphenylmethyl anion³¹ (Table II). For substitution on the aromatic ring the results are in agreement. The ortho and para have the same charges and similar effects on the oxidation. These effects are clearly larger than that of the meta position, which is calculated to have far less negative charge. Substitution at the α carbon atom brings about a 3.2-fold change in oxidation peak potential relative to the ortho and para position. This is substantially larger than the 2.5-fold increase in charge at this position calculated for this anion in a planar form. The effect is some 50 mV greater than expected based on the planar form. In fact, if the rings are twisted, there would be increased negative charge at the α carbon and therefore substitution of methyl would have a larger effect. MINDO/3 calculations reveal that this anion is twisted and has a greater charge at the α position and less at the ortho and para positions.³¹ The increase in charge at C _{α} to -0.40 V leads to an expected effect of 2.9 on the oxidation potential, in reasonable agreement with the observed 3.2-fold change.

The anion of phenylindan poses an interesting counterpoint. The effect of the ring that places a substituent in the ortho and α positions is an increase of some 200 mV compared to the unsubstituted anion. This is less than would be expected from the combined effects of an *o*-methyl (68 mV) and an α -methyl (230 mV). Models reveal (and calculations support) that the ring coplanarity is far more probable in the indanyl structure than in the corresponding analogue 2-methyldiphenylethyl anion.³² Indeed the covalent bond greatly reduces the steric interactions and an essentially planar diaryl anion is possible. Accordingly, the effect of the central alkyl group would be expected to be considerably less since the steric contribution of the alkyl group is largely absent. Indeed, the charge-only estimated effect of the ortho and α group is 234 mV, assuming that the α position should have an effect 2.5 times that of the ortho. The observed value is close to the predicted and the conclusion is that greater twisting is the source of the larger effect for the α -methyl compound.

There are data from other spectroscopic methods that are supportive of a nearly planar diphenylmethyl anion. The UV absorption spectra of key diarylmethyl anions depicted in Table III reveal two kinds of effects.^{33,34} First, di-*o*-methyl and α -methyl substitutions bring about decreases in absorption intensity with bathochromic shifts of the absorption maximum. These are the predicted absorption changes for twisting of the aryl rings out of the central plane of the ion. Second, the spectrum of dihydroanthracenyl anions is very similar in detail (λ_{\max} , ϵ_{\max} , and ion pairing) to that of the diphenylmethyl anion.³⁵ There is considerable reason to conclude that the dihydroanthracenyl anion is planar,³⁶ and this spectral agreement invites by comparison that the diphenylmethyl species is planar. Thus the spectral data confirm in two ways the planar form of the anion by similarity with a known planar system and by predictable differences with twisted systems. This view is quite similar to that derived from the first set of data. The 2,2'-dimethyl and α -methyl anions are twisted relative to the unsubstituted, which is consonant with their expected effect on an unsubstituted planar species. Interestingly, parallel behavior is observed for the carbocations.

NMR chemical shift data similarly support these conclusions (Tables IV and V). The proton and more helpfully the ¹³C chemical shifts of the α and para carbons are revealing.^{37,38} The charges calculated at C _{α} and C_{*p*} are indicative, if anything, of greater dispersal for diphenylmethyl than for dihydroanthracenyl anions. The expected value of $\delta^{13}\text{C}$ for the C _{α} methyl compound is 86 ppm using the average value of 7 ppm as the effect of a methyl group on the sp²-hybridized carbon. The observed value of 75.2 is some 11 ppm at higher field. This calculates to some 0.068 more charge than expected. A similar but less pronounced analysis can be made for the 2,2'-dimethyl-sub-

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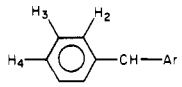
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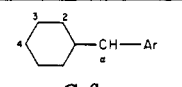
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Table IV. ¹H NMR Chemical Shifts^a of Aromatic Protons of Lithiodiarylmethyl Anions in THF at 25 °C


	H ₂ ^a	H ₃ ^a	H ₄ ^a	ref
diphenylmethyl	6.51	6.54	5.65	<i>b</i>
2-methyldiphenylmethyl ^c	7.15	6.63	5.77	this work
2-methyldiphenylmethyl ^d	6.74	6.60		this work
4-methyldiphenylmethyl ^c	6.50	6.42		this work
4-methyldiphenylmethyl ^d	6.46	6.50		this work
α-methyldiphenylmethyl	6.84	6.51	5.60	39
2,5-dimethyldiphenylmethyl	6.97	6.44	5.61	this work
2,5-dimethyldiphenylmethyl ^d	6.72	6.56		this work
4,4'-dimethyldiphenylmethyl	6.41	6.36		39
4,4',α-trimethyldiphenylmethyl	6.79	6.38		39
9,10-dihydroanthracenyl	6.21	6.47/6.50	5.97	35
9-isopropyl-9,10-dihydroanthracenyl	6.12	6.36/6.44	5.79	35

^a PPM downfield from Me₄Si (internal). ^b Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* 1963, 85, 2328. ^c Substituted ring. ^d Unsubstituted ring.

Table V. ¹³C NMR Chemical Shifts of Lithiodiarylmethyl Anions in THF at 25 °C


	C _α ^a	C ₂ ^a	C ₃ ^a	C ₄ ^a	ref
diphenylmethyl	76.2	117.4	127.9	107.2	37
2-methyldiphenylmethyl ^b	74.5	123.4, 113.7	129.1, 126.2	107.3	this work
3-methyldiphenylmethyl ^b	72.0	115.3, 118.2	135.7, 129.1	109.0	this work
4-methyldiphenylmethyl ^b	74.7	117.9	128.9	115.8	39
α-methyldiphenylmethyl	75.8	115.9	127.8	106.4	39
2,2-dimethyldiphenylmethyl ^b	73.8	123.4, 113.7	129.1, 126.2	107.6	this work
2,5-dimethyldiphenylmethyl	73.0	121.2, 114.6	133.7, 129.1	108.9	this work
4,4'-dimethyldiphenylmethyl	72.1	117.4	128.9	114.7	39
4,4',α-trimethyldiphenylmethyl	73.6	115.6	128.6	112.5	39
9,10-dihydroanthracenyl	69.3	115.7, 121.7	126.1, 125.7	111.8	<i>c</i>

^a PPM downfield from Me₄Si (internal). ^b Substituted ring. ^c O'Brien, D. H., personal communication.

stituted compound. These NMR data are consistent with a planar diphenylmethyl and dihydroanthracenyl anions and a twisted anion for the α-methyl- and di-*o*-methyl-substituted compounds.

The temperature dependence of the ¹³C C_α chemical shift provides still another experimental indicator of a structure change for the α-methyl compound.³⁹ For diphenylmethyl anion (and many others) substantial changes of ¹³C_α with temperature are useful probes of ion-pairing changes.¹² In direct contrast the ¹³C δ of C_α for α-methyldiphenylmethyl anion is the same within experimental error over a 100 °C temperature variation.³⁸ Therefore, there is no change of ion pairing, which indicates greater steric requirements at the carbanion site. Of direct interest, the trityl anion, whose geometry is known to be twisted, exhibits similar behavior.⁴⁰

Experimental Section

The proton NMR spectra were recorded on a Varian A60A spectrometer in CDCl₃ solutions. The carbon-13 NMR spectra were recorded on a Bruker WH90 spectrometer in CDCl₃. Chemical shifts are reported in ppm downfield from Me₄Si. The mass spectra were obtained by using an AEI MS-902 high-resolution electron-impact mass spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5750 instrument. A 10 ft × 1/8 in. stainless steel column packed with 10% Carbowax, 20 m, 60–80 mesh, and a 2 ft × 1/8 in. silicone

rubber column were used. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The solvent, dimethoxyethane (DME), was distilled prior to use from the sodium benzophenone ketyl. Tetrabutylammonium perchlorate (TBAP) recrystallized from ethyl acetate was used as the supporting electrolyte.

For the hydrocarbons 1b–2b diphenylmethane (1b) was commercially available (Eastman). The compounds (dimethylamino)-2-methyldiphenylmethane (10b) and phenylindan (12b) were gifts of Mr. Larry Anderson. 9-Isopropyl-9,10-dihydroanthracene (11b) was a gift of Dr. M. Daney. The remaining compounds are described below. In select cases, the actual compound was a deuterio-substituted compound prepared for ease in analysis of other studies. The presence of deuterium in these compounds and of the anion for the electrochemical studies provides neither assistance nor ambiguity of interpretation.

2-Methyl-, 4-methyl-, 2,2'-dimethyl-, and 4,4'-dimethyldiphenylmethanes were obtained by Grignard coupling reactions. Physical and spectroscopic data obtained are as follows: 2-methyldiphenylmethane, bp 72–80 °C (0.4–0.5 mm) [lit.⁴¹ 148–152 °C (16 mm)]; NMR δ 2.0 (3 H, s), 3.7 (2 H, s) 6.9–7.2 (9 H, m); mass spectrum, *m/e* 182. (4-Methyldiphenyl)methane, bp 125 °C (9 mm), [lit.⁴² 138–139 °C (14 mm)]; NMR (CDCl₃) δ 2.15 (3 H, s), 3.73 (2 H, s) 6.8–7 (9 H, m). (2,2'-Dimethyldiphenyl)methane, bp 103–113 °C (0.5 mm) [lit.⁴³ 105 °C (2 mm)]; NMR (neat) 1.88 (6 H, s), 3.38 (2 H, s) 6.4 (8 H, m); mass spectrum, *m/e* 196 (M⁺) 181, 166. (4,4'-Dimethyldiphenyl)methane, bp 84–90 °C (0.07 mm) [lit.⁴³ 110 °C (2 mm)]; NMR 2.2 (6 H, s), 3.7 (2 H, s); 6.0 (8 H, s).

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1,1-Di-*p*-tolylethane and 1,1-diphenylethane were prepared by catalytic hydrogenation (10% Pd on carbon) of the corresponding olefins. Physical and spectroscopic data obtained are as follows: 1,1-Di-*p*-tolylethane, bp 120 °C 0.2–0.3 mm [lit.⁴⁸ 155 °C (12 mm)]; ¹H NMR (neat) 7.1 (4 H, d, *J* = 8 Hz), 6.9 (4 H, d, *J* = 8 Hz), 4.0 (1 H, q, *J* = 7 Hz), 2.2 (6 H, s), 1.5 (3 H, d, *J* = 7 Hz); IR (neat) 3020, 2965, 2920, 2870, 1510, 1451, 1047, 1021, 812, 734 cm⁻¹; Mass spectrum, *m/e* 210. 1,1-Diphenylethane,⁴⁵ NMR 1.6 (3 H, d, *J* = 8 Hz), 4.15 (1 H q, *J* = 8 Hz), 7.1–7.4 (10 H, m).

***p*-Deuteriobromobenzene.** A Grignard solution prepared from 146.6 g (0.60 mol) of *p*-dibromobenzene and 16.0 g (0.66 mol) of magnesium in ether (333 mL) was reacted with 56 g (2.8 mol) of D₂O. After hydrolysis and solvent removal the liquid was dried over CaCl₂. Distillation afforded 67.5 g (0.44 mol, 71% yield) of the product, bp 95–106 °C (160–170 mm) [lit.⁴⁶ 177–181 °C (760 mm)]; ¹H NMR (neat) 6.7–7.3 (4 H, q); mass spectrum, *m/e* 159, 157, 78. Mass spectral determination of isotopic purity by comparison with bromobenzene gives the % d₁ ≈ 98%.

3-Methyl-4'-deuteriodiphenylmethane. To a Grignard solution prepared from 33.1 g (0.21 mol) of *p*-deuteriobenzene and 5.61 g (0.23 mol) of magnesium in ether (110 mL) and replaced by benzene (70.5 mL) was added 14.76 g (0.105 mol) of α -chloro-*m*-xylene in 40 mL of benzene. After an additional 0.5 h at reflux, the flask was cooled in an ice bath and 100 mL of 4 N HCl was added (exothermic). After separation of phases and extraction with 150 mL of benzene, the combined organic phases were washed with distilled water (150 mL) and dried over MgSO₄, the benzene removed via rotary evaporation, and vacuum distillation provided 17.4 g (0.095 mol, 91% yield) of 3-methyl-4'-deuteriodiphenylmethane, bp 75–80 °C (0.3–4 mm) [lit.⁴⁷ 120 °C (2 mm)]; ¹H NMR (neat) 2.1 (3 H, s), 3.7 (2 H, s), 6.8–7.1 (8 H, m).

2,5-Dimethyl-4'-deuteriodiphenylmethane. To a Grignard solution prepared from 31.6 g (0.20 mol) of *p*-deuteriobenzene and 5.35 g (0.22 mol) of magnesium in ether and replaced by benzene was added 15.5 g (Aldrich, 0.10 mol) of 3,5-dimethylbenzylchloride in 40 mL of dry benzene. After reaction and workup as described above, distillation afforded 9.57 g (0.05 mol, 49% yield) of 2,5-dimethyl-4'-deuteriodiphenylmethane, bp 114–118 °C (0.5 mm) [lit.⁴⁸ 124–125 °C (1 mm)]; NMR (neat) 1.95 (3 H, s), 2.05 (3 H, s), 3.7 (2 H, s), 6.7 (3 H, d), 6.95 (4 H, s).

Anion Preparation for Electrochemical Measurement. 1,2-Dimethoxyethane (DME) was distilled immediately prior to use from the sodium benzophenone ketyl under purified argon gas. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was used from a fresh bottle kept under argon without further purification. Commercially available Tetra-*n*-butylammonium perchlorate

(TBAP) was recrystallized three times from ethyl acetate, dried for 36 h at 110 °C (10 mmHg), and stored until use in a desiccator. *n*-Butyllithium in hexane was commercially available.

The electrochemical cell designed to record cyclic voltammograms consists of a 25 mL three-necked, pear-shaped flask equipped with a AgCl reference electrode (DME, 0.5 M TBAP), a platinum wire working electrode, and a platinum auxiliary electrode. The working electrode was constructed by sealing a short length of platinum wire to a short length of soft glass tubing. Contact was afforded by a mercury seal between the platinum wire and a copper lead. Before use, the platinum working electrode was electrolyzed at 0.0 V in a 0.1 M perchloric acid solution to clean the metal surface.

Cyclic voltammograms were measured on a Princeton Applied Research Model 170 Electroanalytical System. The residual current of the system (DME, 0.5 M TBAP) did not exceed 5 μ A between the limits of -2.9 V and +0.90 V vs Ag/AgCl. Cyclic voltammograms were typically recorded for systems with approximately 20 μ A Faradaic current. Oxidative peak potentials were reproducible within ± 0.005 V overall.

Anions were prepared for electrochemical measurement via reaction of the corresponding hydrocarbon with *n*-butyllithium in TMEDA solvent on an Ace Glass No-Air System. Glassware used was prepared by thorough cleaning in an alcoholic base bath, followed by rinsing with distilled water, and pure acetone. All glassware was dried overnight in a 120° oven.

The apparatus is assembled hot on the No-Air System and fitted with septa and a stir bar. The apparatus is evacuated to at least 0.5 mmHg and purged with purified argon, alternately three times. Finally, the flask is flamed under vacuum to remove residual moisture. *n*-Butyllithium (2 equiv) is introduced into the flask via syringe and the flask cooled to -5 °C in an ice-salt bath. TMEDA (1 equiv) is added dropwise via syringe and the ice bath removed. The solution is warmed to room temperature and 1 equiv of hydrocarbon added dropwise. Within a few minutes the characteristic red color of the anion appears. Reaction is continued for approximately 1/2 h. The anion solution is diluted to a concentration of 0.04 M with freshly distilled DME. This solution is transferred with a cannula into a prepared flask containing sufficient TBAP to yield a solution which is 0.5 M TBAP. Final transfer is into the electrochemical cell, and then the voltammogram is measured.

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Registry No. 1a, 881-42-5; 1c, 18802-87-4; 2a, 86846-57-3; 2b, 713-36-0; 2c, 86846-58-4; 3a, 86846-59-5; 3c, 86846-60-8; 4a, 86846-61-9; 4b, 620-83-7; 4c, 74088-21-4; 5a, 67997-44-8; 5c, 23171-61-1; 6a, 86846-62-0; 6b, 1634-74-8; 6c, 86846-63-1; 7a, 86846-64-2; 7c, 86846-65-3; 8a, 68695-92-1; 8b, 4957-14-6; 8c, 74088-22-5; 9a, 67997-45-9; 9c, 86846-66-4; 10a, 86853-46-5; 10c, 86846-67-5; 11a, 86846-68-6; 11c, 86853-47-6; 12a, 86846-69-7; 12c, 86846-70-0; 1,1-di-*p*-tolylethane, 530-45-0; 1,1-diphenylethane, 612-00-0; *p*-deuteriobromobenzene, 13122-33-3; *p*-dibromobenzene, 106-37-6; α -chloro-*m*-xylene, 620-19-9; 3,5-dimethylbenzyl chloride, 2745-54-2.

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