acidified by 10% HCl. Recrystallization of the precipitate yielded pure product. In one case (**8c**) the product was an oil. **8b** (mp 81°) was isolated by preparative thin layer chromatography, and identified by its ir, nmr, and mass spectra.

8a: mp 105–106° (methanol). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.48; H, 8.17; mol wt 270 (mass spectrometry).

10a: mp 141–142° (hexane). *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.76; H, 7.16; mol wt 306 (mass spectrometry).

10b: mp 145° (ethanol). *Anal.* Calcd for $C_{23}H_{26}O_2$: C, 82.59; H, 7.84. Found: C, 82.32; H, 7.68; mol wt 334 (mass spectrometry).

10c: mp 127–128° (ethanol). *Anal.* Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.49; H, 8.30; mol wt 362 (mass spectrometry).

Acidity of Hydrocarbons. XLVI. Equilibrium Ion-Pair Acidities of Mono-, Di-, and Triarylmethanes toward Cesium Cyclohexylamide[1]

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Abstract: Equilibrium ion-pair acidities relative to 9-phenylfluorene (PF) are reported for 16 hydrocarbons toward cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA). The effects of phenyl and methyl substituents and of cyclic structures on relative p*K*'s illustrate the relative importance of conjugation and inductive effects, rotational entropy and steric effects, and conformational interactions. For the p*K* of PF taken as 18.49, the following p*K* values are obtained: *p*-methylbiphenyl (pMB), 38.7; bis(2,4-dimethylphenyl)methane (DXM, "dixylylmethane"), 36.3; di-*p*-tolylmethane (DpTM), 35.1; di-*o*-tolylmethane (DoTM), 34.8; 5-methyl-5*H*-dibenzo[*a,d*]cyclohepta-1,3-diene (MDCH), 33.6; diphenylmethane (DPM), 33.4; tri-*p*-tolylmethane (TpTM), 33.0; 5-phenyl-5*H*-dibenzo[*a,d*]cyclohepta-1,3-diene (PDCH), 31.6; triphenylmethane (TPM), 31.4; 5*H*-dibenzo-[*a,d*]cyclohepta-1,3-diene (DCH), 31.2; bis-*p*-biphenylylmethane (BBM), 30.8; 9,9-dimethyl-9,10-dihydroanthracene (DDA), 30.3; 9,9,10-trimethyl-9,10-dihydroanthracene (TDA), 30.3; *p*-biphenylyldiphenylmethane (BDPM), 30.2; 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene (PDDA), 28.0; 10-*p*-biphenylyl-9,9-dimethyl-9,10-dihydroanthracene (BDDA), 27.7.

In the construction of thermodynamic acidity scales for hydrocarbons, two important approaches have been the application of H_- techniques in various solvent systems[3] and emf techniques as in the use of the glass electrode in DMSO.[4] These approaches are generally successful down to acidities as low as p*K*'s in the 20's where many fluorene derivatives lie; however, di- and triarylmethanes generally are of still lower acidity and are not measured accurately by these techniques. We have previously reported[5] a number of relative acidities based on competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA).

$$\mathrm{RH} + \mathrm{R'^-Cs^+} \rightleftharpoons \mathrm{R^-Cs^+} + \mathrm{R'H} \tag{1}$$

This method gives quantitative values for equilibrium *ion-pair acidities*, but for hydrocarbons with highly delocalized conjugate bases, such values compare well with the corresponding equilibrium *ionic acidities*, and, especially for closely related systems, serve quite well for assessing substituent and structural effects on carbanion stabilities. In the present paper, we extend this method to a number of di- and triarylmethanes and even to a monoarylmethane, *p*-methylbiphenyl (pMB). The results are used to explore a number of structural effects in carbanions including phenyl and methyl substituent effects, charge distributions, and the effects of rotational entropy.

Experimental Section

Hydrocarbons. Most of the hydrocarbons used in the present study have been reported previously together with spectral data of their cesium salts in CHA:[5–8] diphenylmethane (DPM), triphenylmethane (TPM), 1,1-diphenylethane (DPE), 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene (PDDA), 9,9,10-trimethyl- (TDA) and 9,9-dimethyl-9,10-dihydroanthracene (DDA), 5-methyl- (MDCH) and 5-phenyl-5*H*-dibenzo[*a,d*]cycloheptadiene (PDCH) and the parent hydrocarbon (DCH), *p*-methylbiphenyl (pMB), di-*o*-tolylmethane (DoTM), di-*p*-tolylmethane (DpTM], bis(2,4-dimethylphenyl)methane (DXM), di-*p*-biphenylylmethane (DBM), and tri-*p*-tolylmethane (TpTM).

10-Biphenylyl-9,9-dimethyl-9,10-dihydroanthracene. This compound was prepared by a sequence starting with the reaction of *p*-biphenylylmagnesium bromide with 10,10-dimethylanthrone.[9] The formation of the *p*-biphenylylmagnesium bromide, reputedly

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Table I. Absorption Maxima for Cesium Salts in Cyclohexylamine

Hydrocarbon	λ_{max}, nm	$10^{-3}\ \epsilon$
DXM	448	46.4 ± 1.2
DBM	557	102 ± 0.4
BDDA	450	32.1 ± 0.4

Table II. Summary of Equilibrium Constants

	R-H[a]	R′-H[a]	*K* (per H)	Log *K* (per H)	*n*[b]	p*K*[c]
1	*t*-BuF[d]	*PDDA*	5120 ± 1250	3.71 ± 0.11	2	27.94 ± 0.13[g]
2	TPP[e]	*PDDA*	28 ± 2	1.45 ± 0.04	2	28.04 ± 0.08[g]
3	PDDA	*PX*[e]	3 ± 0.4	0.48 ± 0.06	1	28.49 ± 0.10
4	*BDDA*	PX	5.91 ± 0.2	0.77 ± 0.02	2	27.72 ± 0.10
5	PDDA	*BDPM*	145 ± 20	2.16 ± 0.06	2	30.17 ± 0.10
6	BDPM	*TPM*	19 ± 3	1.28 ± 0.07	2	31.45 ± 0.12
7[f]	TPM	*DPM*	76 ± 10	1.88 ± 0.06	2	33.33 ± 0.13[h]
8[f]	TPM	*DPM*	94 ± 12	1.97 ± 0.06	6	33.42 ± 0.13[h]
9	*DBM*	TPM	4.17 ± 0.2	0.62 ± 0.02	2	30.83 ± 0.13
10	*DCH*	TPM	1.75 ± 0.2	0.24 ± 0.04	4	31.21 ± 0.14
11	DCH	*TpTM*	70.5 ± 5	1.85 ± 0.03	3	33.05 ± 0.14[i]
12	*TpTM*	DPM	2.4 ± 0.8	0.38 ± 0.15	5	33.00 ± 0.21[i]
13	*TDA*	TPM	15.0 ± 1.2	1.18 ± 0.04	2	30.27 ± 0.13
14	*DDA*	DCH	9.0 ± 1.0	0.95 ± 0.05	1	30.25 ± 0.15
15	DDA	PDCH	Too large		2	
16	TPM	*PDCH*	1.5 ± 0.5	0.18 ± 0.15	3	31.63 ± 0.19
17	DPM	*MDCH*	1.76 ± 0.2	0.25 ± 0.04	3	33.63 ± 0.13
18	DPM	DPE	Too large		4	
19	TpTM	*DXM*	1818 ± 26	3.26 ± 0.05	2	36.30 ± 0.15
20	DXM	*pMB*	269 ± 29	2.43 ± 0.05	3	38.73 ± 0.16
21	TpTM	*DpTM*	115.5 ± 17	2.06 ± 0.05	3	35.10 ± 0.15
22	TpTM	*DoTM*	53.0 ± 12	1.72 ± 0.09	2	34.76 ± 0.19

[a] Abbreviations are: *t*-BuF, 9-*tert*-butylfluorene; PDDA, 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene; TPP, 1,1,3-triphenylpropene; PX, 9-phenylxanthene; BDDA, 10-*p*-biphenylyl-9,9-dimethyl-9,10-dihydroanthracene; BDPM, *p*-biphenylyldiphenylmethane; TPM, triphenylmethane; DPM, diphenylmethane; DBM, di-*p*-biphenylylmethane; DCH, 5*H*-dibenzo[*a,d*]cyclohèpta-1,3-diene; TpTM, tri-*p*-tolylmethane; TDA, 9,9,10-trimethyl-9,10-dihydroanthracene; DDA, 9,9-dimethyl-9,10-dihydroanthracene; PDCH, 5-phenyl-5*H*-dibenzo-[*a,d*]cyclohepta-1,3-diene; MDCH, 5-methyl-5*H*-dibenzo[*a,d*]cyclohepta-1,3-diene; DPE, 1,2-diphenylethane; DXM, bis(2,4-dimethylphenyl)methane or dixylylmethane; pMB, *p*-methylbiphenyl; DpTM, di-*p*-tolylmethane; DoTM, di-*o*-tolylmethane. [b] Number of determinations. [c] p*K* of the italicized hydrocarbon, followed by the accumulated probable error, relative to p*K* (9-phenylfluorene) = 18.49. [d] Previously reported: A. Streitwieser, Jr., C. J. Chang, and D. M. E. Reuben, *J. Amer. Chem. Soc.*, **94**, 5730 (1972). [e] Previously reported, ref 5. [f] Runs 7 and 8 were done by different workers at different times. [g] Weighted average p*K* of PDDA = 28.01 ± 0.08. [h] Weighted average p*K* of DPM = 33.38 ± 0.12. [i] Weighted average p*K* of TTM = 33.04 ± 0.14.

one of the most difficult Grignard reagents to prepare,[10] was facilitated by the presence of ethylene bromide. (Adding methyl Grignard reagent, iodine crystals, or anhydrous magnesium bromide, either singly or in various combinations, resulted in sluggish and incomplete reaction or no reaction at all.) Stirring a mixture of 1.22 g of 4-bromobiphenyl (Aldrich), 2.18 g of ethylene bromide, and 0.43 g of magnesium turnings in 50 ml of dry ether invariably gave complete reaction of the metal in 0.5 hr.

To this solution was added an ether solution of 0.76 g of 10,10-dimethylanthrone, mp 102–102.5°, and the mixture was stirred overnight under argon. The reaction mixture was quenched with water and extracted with ether. The combined ether extract was evaporated using a rotary evaporator and the residue was extracted with cold pentane which quantitatively removed the biphenyl and any remaining 10,10-dimethylanthrone. The ir spectrum showed absorption at ~3500 cm^{-1} (O—H) and no absorption at 1660 cm^{-1} (C=O). The yield of 10,10-dimethyl-9-biphenylyl-9,10-dihydroanthran-9-ol was 96%. This product should be handled carefully since attempts to remove the biphenyl and excess dimethylanthrone by sublimation at 80–90° led to a dehydration product, probably the corresponding fluorene, 5,5-dimethyl-10-phenyl-5,12b-dihydrobenzo[*a*]fluoranthene. The alcohol, 0.60 g, was reduced to the desired hydrocarbon by catalytic hydrogenation in a mixture of 350 ml of methanol, 0.5 g of 5% Pd on charcoal, and 6 drops of 70% $HClO_4$. The mixture was filtered through Celite and the clear solution was neutralized using aqueous potassium carbonate. The methanol was removed on a rotary evaporator, leaving fine, white crystals. The inorganic salts were washed away with water leaving the hydrocarbon, mp 144–144.7°, in 70% yield. Spectra were consistent with the assigned structure. High resolution mass spectroscopy gave *m/e* 360.1881; $C_{28}H_{24}$ requires 360.1878.

Procedure. The procedure for measuring the spectra of the cesium salts was identical with that used previously.[7] Spectral data not reported previously are summarized in Table I. The equilibrium constants were determined using the previously reported procedure,[5,6] and the results are summarized in Tables II–IV. Table II gives results for the individual equilibrium runs. This table is arranged such that the more acidic hydrocarbon is given as RH in equilibrium 1 and *K* is always >1. Tables III and IV summarize the results as p*K* values. These values actually relate to the equilibrium of each hydrocarbon in eq 1 with 9-phenylfluorene with a p*K* of 18.49 assigned to the latter, and are given on a per-hydrogen basis. Error limits assigned are the total accumulated probable errors. The probable error for Δp*K* between neighboring hydrocarbons on the p*K* scale is much smaller.

Table III. Effect of Bridge Size on Substituent Effects at the α Position of Polyarylmethanes

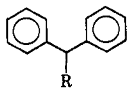
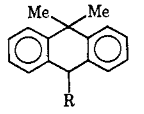
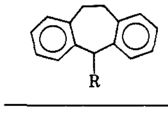
	R = H	R = Ph	R = Me
	33.4 DPM	31.45 TPM	>35 DPE
	30.25 DDA	28.0 PDDA	30.3 TDA
	31.2 DCH	31.6 PDCH	33.6 MDCH

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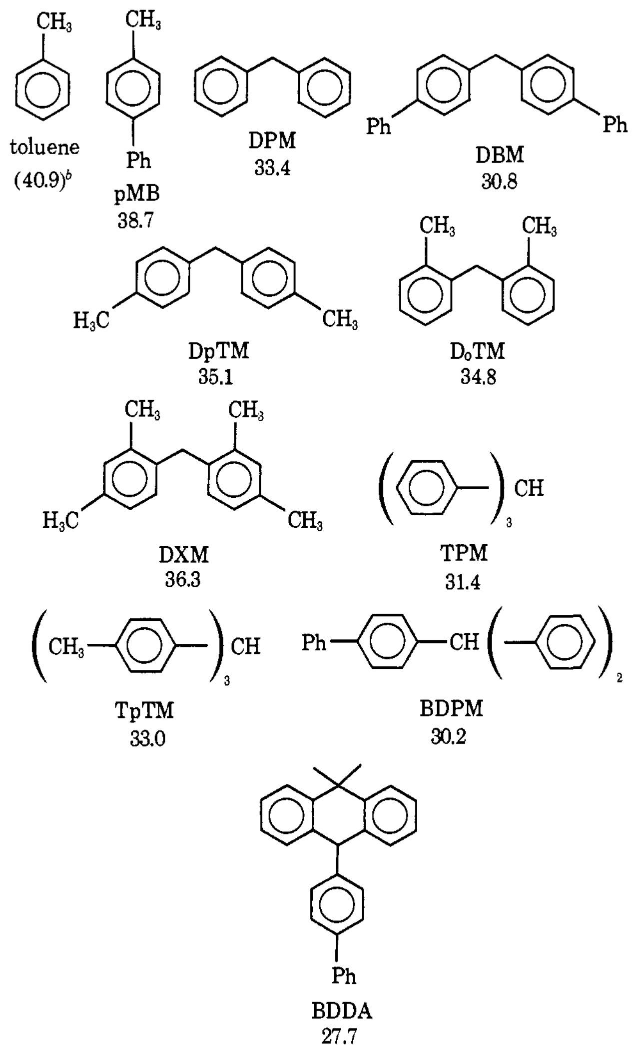
Table IV. Effect of Aryl and Methyl Substituents on pK^a



^{a} CsCHA pK's per hydrogen (Table II). ^{b} Paper XLVIII: A. Streitwieser, Jr., M. R. Granger, F. Mares, and R. A. Wolf, *J. Amer. Chem. Soc.*, **95**, 4257 (1973).

Results and Discussion

Experimental Errors. The general errors present in this type of work have been discussed in previous papers.[5,6] Several cross-checks have been employed in determining the pK values relative to 9-phenylfluorene, and the agreement has been excellent. For example, the pK of PDDA is 27.94 or 28.04, using *tert*-butylfluorene or 1,1,3-triphenylpropene, respectively, as indicators (Table II). Other cross-checks are entries 7 and 8, where two different workers have independently carried out the measurements, and entries 11 and 12, in which two indicators give essentially identical pK's for TTM. One surprising result in Table III is the acid-weakening effect that a phenyl substituent has on DCH. This cannot be the result of experimental or other error, since a cross-check was made by running PDCH against DDA (pK = 30.2), where the initial ratio of DDA/PDCH varied from 13.5 to 81 (entry 15, Table II). When a small amount of CsCHA was added, only the anion of DDA was formed, showing that PDCH does not have a pK less than DDA. The excellent agreement of the cross-checks establish that the probable errors assigned to log K in Table II are realistic and that the original assumptions[5] for setting up a pK scale in a single solvent–base system are valid for structurally similar hydrocarbons. Consequently, differences in relative pK's greater than about ±0.2 pK unit are probably significant.

Configuration of the Carbanion Carbon. The question of the configuration of the carbanion carbon is not as straightforward as that for carbonium ions. In the latter case, both simple alkyl and conjugated carbonium ions prefer a planar carbon of the sp^2 type. In the case of carbanions, however, simple alkyl anions are undoubtedly pyramidal in structure,[11-13] but conjugated systems require planar carbanions for greatest conjugation stabilization. In the case of highly conjugated systems, there would seem to be little question of the essential planarity of the carbanion carbon; for example, salts of triphenylmethyl anion are highly colored whereas 9-triptycyllithium is colorless.[14] SCF-π-MO methods that assume a planar π system give a reasonable account of the spectra of conjugated hydrocarbon carbanions.[15] However, in solvents of low polarity it is well known that carbanion salts exist as various forms of ion pairs. The considerable electrostatic interaction between cation and anion expected in an ion pair may be considered as an additional driving force favoring a pyramidal carbanion with its more concentrated negative charge. Waack, McKeever, and Doran[16,17] have recently interpreted the α-^{13}C, ^{7}Li, and ^{1}H nmr spectral changes of benzyllithium as a function of solvent in terms of a variation of covalent bonding to lithium. The most pronounced effect occurs in benzene in which the lithium is likely to be poorly solvated and more dependent on interaction with the negative charge of the carbanion. Nevertheless, in cation-solvating solvents such as ethers and amines, covalent interactions between carbanion and cation are minimized[18] and delocalized carbanion ion pairs result. This conclusion is supported by ^{1}H, ^{7}Li, and α-^{13}C nmr spectral studies of triphenylmethyllithium, diphenylmethyllithium, and benzyllithium in THF by Waack, *et al.*,[19] who conclude that the carbanion carbons in these compounds are essentially sp^2 hybridized. From proton nmr data, Nicholls and Szwarc[20] have reached a similar conclusion regarding the 9 position of 10-alkyl-9,10-dihydro-9-anthracyllithiums in THF. Since THF and CHA are known to be comparable in terms of contact and solvent-separated ion-pair equilibria,[21,22] these conclusions undoubtedly

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apply to the CHA system as well. Furthermore, Sandel and Freedman[23] have reported that the proton nmr spectra of triphenylmethyl anion salts are independent of cation (Li^+ and Na^+ in THF) and solvent (Li^+ in THF, DMSO, and HMPA). The implications are that the structures of these diarylmethyl and triarylmethyl anions are not appreciably dependent on either ion pair or solvent interactions and that the α-carbon atoms of these anions are sp^2 hybridized, at least in basic solvents where the lithium cation is extensively solvated. Other alkali metals, including cesium, show little or no tendency toward forming covalent bonds to carbon[24] and so the hybridization of the central carbon atom for cesium salts should also be approximately trigonal. Recently, the crystal structure of triphenylmethyllithium tetramethylethylenediamine was reported;[25] the three C–C–C bond angles about the central carbon atom were found to be close to 120°, indicating predominantly sp^2 hybridization. Such a structure is likely to persist in solution; hence, our fundamental assumption of a planar central carbanion carbon appears to be well founded.

Inductive and Resonance Effects. From the differences in p*K* of DPM and TPM and from estimates of the p*K*'s of methane and toluene, it was previously concluded[5] that the phenyl rings in diphenylmethane and benzyl anion were close to being fully conjugated with the central carbon atom, whereas the phenyl groups of triphenylmethyl anion were seriously twisted from coplanarity. Because of mutual interactions of the ortho hydrogens in diphenylmethyl anion, it is probable that either the rings are twisted somewhat from coplanarity or that the angle between the two rings and the α-carbon atom is opened substantially from 120°. If the usual MO resonance integral, β, is taken as approximately proportional to $\cos \theta$,[26] where θ is the angle of twist, rotating a phenyl ring 25° out-of-plane will reduce $|\beta|$ by only 10%. Consequently, rotation of the phenyl rings by a few degrees in opposite directions should result in relatively small destabilization and should be an efficient mechanism for relieving at least part of the ortho H interference. On this basis, it seems reasonable to assume that diphenylmethyl anion has a slight twist propeller conformation, analogous to that for trityl cation[27] and anion,[25] with perhaps some enlargement of the angle between the central carbon atom and the phenyl rings.

The effect of replacing a phenyl group with a *p*-biphenylyl substituent shows an interesting contrast that provides some support for ring twist in diaryl- and triarylmethyl anions. Substitution of a phenyl group into the para position of toluene gives a p*K* decrease of 2.1 units. Substitution of two phenyl groups into both para positions of diphenylmethane gives a larger decrease of 2.6 p*K* units; this result is expected because more total charge is delocalized in the benzhydryl anion compared to benzyl anion. However, the effect of a single *p*-phenyl substituent is expected to be about $2.6/2 = 1.3$ p*K* units, substantially less than in toluene where one benzene ring must support the entire charge. It seems remarkable, therefore, that a single *p*-phenyl substituent in triphenylmethane causes an equally large p*K* lowering of 1.3 units. This result must arise from the seriously twisted nature of the triarylmethyl system. The *p*-biphenylyl group is undoubtedly more coplanar because of its greater capacity for delocalization and the remaining two phenyl groups are probably twisted more seriously from coplanarity. We would expect a second and third *p*-phenyl substituent to have far smaller ΔpK increments. This prediction could not be tested because of the low solubility of tri-*p*-biphenylylmethane but the dihydroanthracene system is striking. In PDDA two benzene rings are forced by the central ring into closer coplanarity with the carbanion carbon and the 10-phenyl substituent is undoubtedly twisted seriously from this coplanarity. Accordingly, the *p*-phenyl substituent in BDDA gives a p*K* lowering of only 0.3 unit; the 10-aryl substituent is essentially not conjugated with the carbanion center! This effect appears to pertain to 9-phenylfluorenyl anion as well. 9-*p*-Biphenylylfluorene is more acidic than 9-phenylfluorene by only 0.4 p*K* unit[3c] and 9-phenylfluorene almost follows the σ^* correlation defined by 9-alkylfluorenes.[28] The latter observation suggests that a 9-phenyl substituent in fluorene exerts principally an inductive effect with little additional conjugative stabilization. Likewise, Cockerill and Lamper[29] have correlated the p*K*'s of a series of substituted 9-phenylfluorenes with σ_I and σ_R and have concluded that the 9-phenyl group of the anion is only partially conjugated with the fluorenyl moiety. In close analogy, the phenyl substituent in the 9-phenylxanthyl *cation* also appears to be essentially unconjugated since the carbonium ion stabilization energies follow σ^0 rather than σ^+.[30]

The effects of methyl substitutions on the ring positions of diphenylmethane are approximately additive. A single methyl substituent in the para position results in an increase in p*K* by 0.85 unit, whereas a single *o*-methyl group raises the p*K* by only 0.70 unit. This leads to a predicted p*K* for bis(2,4-dimethylphenyl)methane of 36.5 compared with an observed p*K* of 36.3. Methyl substitution into the para positions of triphenylmethane also results in an increase in p*K* (0.53 unit per methyl group), but the change per methyl group is smaller, undoubtedly a reflection of the lower negative charge in a given ring compared to diphenylmethyl anion.

These results can be expressed in $\sigma\rho$ terms. The effect of single substitution in diphenylmethane corresponds to $\rho = 5.0$ and in triphenylmethane to $\rho = 3.1$. Extrapolation to a corresponding ρ value for toluene involves a number of approximations and arguments that we will not belabor here; however, such a ρ value should be at least 7 and could be even higher. This value puts into better perspective the value of $\rho = 3.7$

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for the kinetic acidity of toluene determined from hydrogen isotope exchange rates of substituted toluenes with lithium cyclohexylamide,[31,32] and provides a further demonstration that delocalization has proceeded only partially at the transition state of this reaction.[33] These experiments also demonstrate that methyl groups attached to aromatic rings are effectively electron releasing in both kinetic and equilibrium acidities of hydrocarbons. However, when a methyl-substituted tetrahedral carbon is converted to a trigonal carbon in forming a carbanion the resulting increased C–C σ bond strength can offset the inductive effect of the methyl substituent, particularly in highly delocalized carbanions in which only a part of the negative charge is in the region of methyl substitution. This effect has recently been discussed thoroughly by us[28] especially in connection with the acidities of 9-alkylfluorenes.[34] We note here that methyl substitution in the 10 position of DDA causes no change in p*K* (Table III); the two effects apparently just balance in this case. The large acid-weakening effect of methyl substitution in diphenylmethane to form 1,1-diphenylethane (DPE) is undoubtedly associated with a steric effect that is discussed below.

Incidentally, the p*K* of di(*p*-tolyl)methane has been found to be 27.1 in liquid ammonia at −33°.[35] This measurement is based on the dilute solution in ammonia as the standard state, whereas our CsCHA value of 35.1 for this hydrocarbon is approximately that for an aqueous solution standard state. For this highly delocalized carbanion, solvation differences should be minimized[22b] and, if the activities of the hydrocarbon are approximately the same, the difference of 8 p*K* units refers mostly to the lower activity of the solvated hydrogen ion in ammonia compared to water.

Rotational Entropy Effect. It is surely significant that an *o*-methyl substituent in diphenylmethane is *less* acid weakening than a *p*-methyl group. Its rate-retarding electronic influence should be at least as great as a *p*-methyl[31] and any steric interference between the ortho substituents that results in reduced planarity should only further increase the p*K* of the hydrocarbon. One attractive explanation is that the two ortho substituents reduce the rotational entropy of the hydrocarbon compared to diphenylmethane; we have made use of this interpretation before in similar contexts.[5,31] This effect is based on the premise that aryl groups are more free to rotate in the hydrocarbon than in the conjugated carbanion. Any restriction of rotation in the hydrocarbon, such as by ortho-ring formation or by the steric effect of *o*-methyl groups, will result in a lower rotational entropy loss in forming the carbanion, equivalent to a lower hydrocarbon p*K*. The effect of bridging the ortho positions is quite striking. The change from diphenylmethane to DDA gives a p*K* decrease of 3.1 units. Some of this change may be a coplanarity effect but it seems reasonable to associate at least part of this p*K* difference to the rotational entropy effect. The p*K* of DCH is lower than DPM by 2.2 units and again the rotational entropy effect would appear to be largely responsible; according to Dreiding models, the degree of ring twist is roughly comparable in both anions.

The magnitude of this entropy effect may be estimated in several ways. It has been suggested that the entropy decrease due to loss of hindered internal rotations about alkyl carbon bonds amounts to about 4.0 eu/rotation.[36] This value is confirmed by an examination of the entropy differences between *n*-alkanes and the corresponding cyclic hydrocarbons (C_4 through C_8).[37] The average entropy loss per rotation is about 3.6 ± 0.5 eu. This figure may be a little high since the *n*-alkanes have two extra hydrogens, but the difference between 1-alkenes and their cycloalkane isomers is still 3.4 eu/rotation.

An interesting example that may illustrate this entropy effect is afforded by the lithium cyclohexylamide catalyzed protodetritiation of *o*-methyl- and *p*-methyltoluene-α-*t*.[31] The exchange rate of the ortho isomer is about twice that of the para analog. The explanation given is that, in the reaction of *p*-xylene, a freely rotating methyl group is converted to a rotationally rigid methylene group. Assuming that the methyl groups of *o*-xylene already experience restricted rotation, the entropy loss in going to the transition state should be less for the ortho compound than the para. The barrier to methyl rotation in toluene is close to zero, whereas the barrier of *o*-xylene is about 2 kcal/mol.[38,39] Assuming that methyl rotation in *p*-xylene is as unrestricted as that in toluene, this difference in rotational barriers would correspond to a relative entropy difference of about 0.8 eu[37] at 50° between *o*-xylene and *p*-xylene on going from the hydrocarbon to the anion. This entropy difference at 50° corresponds to a free energy difference of ~0.26 kcal/mol or to a rate enhancement of about 1.5, which is comparable to the observed factor of 2. One plausible assumption in this simple treatment is that the rotational barrier for the second methyl group is assumed to remain unchanged on conversion to the anion.

A maximum limit on this entropy effect for diphenylmethane can be estimated by assuming free rotation of the phenyl groups in the hydrocarbon and complete restriction of rotation in the anion. Using the method of Pitzer and Gwinn,[39] the reduced moments of inertia were calculated for two freely rotating phenyl rings attached to a rigid methylene frame. Tetrahedral geometry was assumed for the methylene group, along with C–H bond distances of 1.09 Å and C–C bond distances of 1.54 Å. Aryl C–H bond distances were taken as 1.08 Å and aromatic C–C bond distances were assumed to be 1.39 Å. One phenyl group of diphenylmethane was placed in the plane bisecting the two methylene hydrogens and the other was situated perpendicular to the first. Since the two phenyl groups are nonequivalent, their reduced moments of inertia are not identical, but the difference is unimportant for

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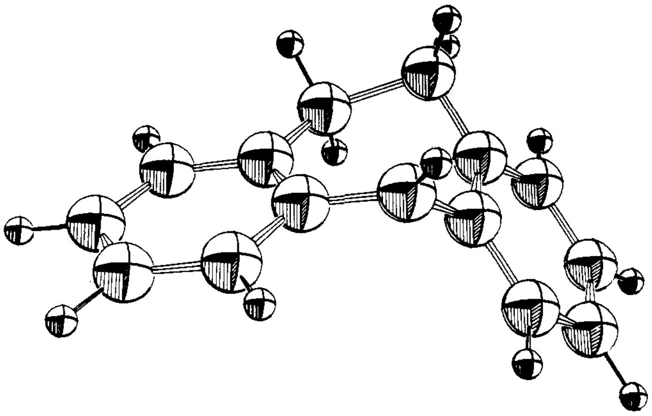

Figure 1. Perspective diagram of the boat-like conformation of dibenzocycloheptadienyl anion from DCH.

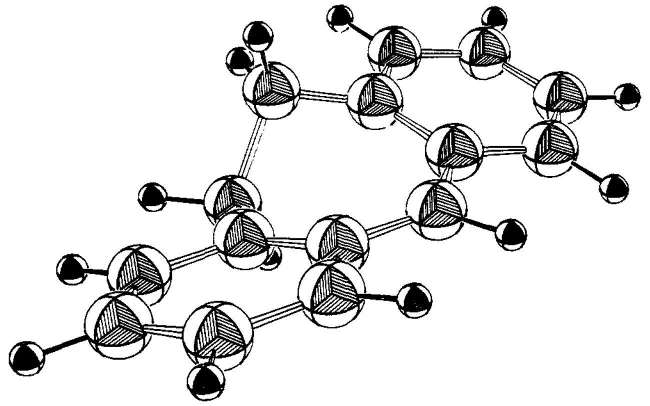

Figure 3. Perspective diagram of the chair-like conformation of carbanion from DCH.

our present purpose. The calculated reduced moments of inertia for internal rotation are 104.3×10^{-40} and 100.8×10^{-40} g cm^2, respectively. The reduced moments of inertia were used to calculate the partition function for internal rotation from

$$Q = (I_{\mathrm{R}}T)^{1/2}(2.7835 \times 10^{19})/N$$

where Q is the partition function, I_{R} is the reduced moment of inertia, T is the temperature, and N is the symmetry number of the internal rotation (2).[40] The entropy, S, of free internal rotation was calculated from[40]

$$S = R(^1/_2 + \ln Q)$$

At 25°, the total entropy associated with the two freely rotating phenyl groups was calculated to be 14.65 eu. Loss of this entropy in going to diphenylmethyl anion where both phenyl substituents are assumed to be rotationally frozen would correspond to a free energy difference of about 4.36 kcal/mol at 25°. Relative to a diphenylmethane with two frozen phenyl groups (*e.g.*, our model for DDA) this would be equivalent to an increase in pK of about 3.2 pK units. However, the phenyl rings in diphenylmethyl anion are certainly not completely frozen. Sandel, McKinley, and Freedman[41] have investigated phenyl rotation in phenylallyllithium in THF solution. Analysis of the temperature dependent proton nmr spectra yields a $\Delta H^{\ddagger}$ for internal rotation of 13.9 ± 0.5 kcal/mol. Assuming that this figure represents the barrier to rotation of the phenyl group, the difference in entropy between the free and restricted rotations of a phenyl group can be calculated using the tables given by Pitzer and Gwinn.[39] This entropy difference is about 3.1–3.3 eu per phenyl rotation, corresponding to a pK difference between fixed and rotating diphenylmethane of about 1.4 units. This figure must be regarded as a rough one since the exact barrier height for phenyl rotation in diphenylmethyl anion is unknown, as is the rotational barrier in diphenylmethane itself. Nevertheless, these simple calculations set a maximum limit of ~3.2 pK units for this entropy effect and suggest that 1.0–1.5 pK units is probably a reasonable estimate. The rotational entropy effect is thus of the right order of magnitude to account for a substantial portion of the pK difference between cyclic and acyclic diphenylmethanes. The remaining difference is probably due to increased planarity in the cyclic carbanions.

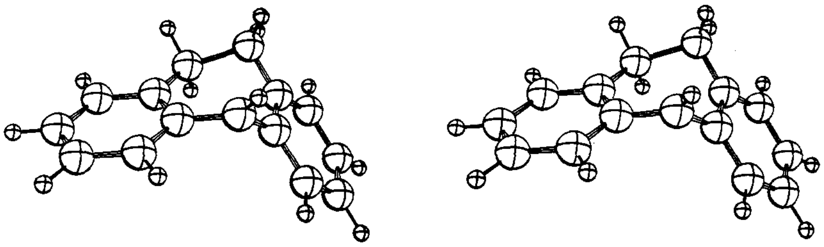

Figure 2. Stereoview of the boat-like conformation of dibenzocycloheptadienyl anion from DCH.

Dibenzocycloheptadiene. The acidity decrease of 0.4 pK unit produced by phenyl substitution at the 5 position of 5*H*-dibenzo[*a*,*d*]cycloheptadiene (DCH) presents an interesting paradox compared to analogous systems. Both the inductive and conjugative effects of a phenyl group normally, as we have seen, produce a significant increase in acidity. For example, in the dihydroanthracene series, PDDA is 2.3 pK units more acidic than the unsubstituted compound. The key to understanding the cycloheptadiene anomaly is clearly that the pK difference between the phenyl (PDCH) and methyl (MDCH) compounds of 2.0 pK units is comparable to that for substitution in 9,9-dimethyldihydroanthracene (pK(TDA) − pK(PDDA) = 2.3). Thus, the two substituted dibenzocycloheptadienes are "normal" between themselves but differ in some significant way from the unsubstituted hydrocarbon, DCH.

Inspection of Dreiding models does not reveal a

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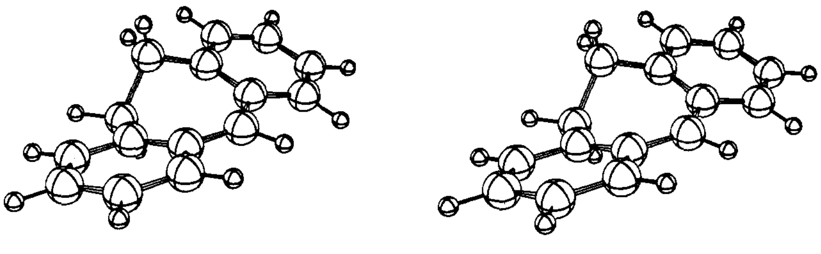

Figure 4. Stereoview of the chair-like conformation of carbanion from DCH.

significant difference between the methylene- or ethano-bridged series that could be attributed to a release or increase of ring strain on going from the hydrocarbon to the anion or to any differences in interactions between nonbonded atoms. The ethano bridge present in DCH leaves the two phenyl rings with some degree of torsional freedom and allows at least two accessible conformations for both the hydrocarbon and the anion.

In one possible conformation of the anion (Figures 1 and 2), the seven-membered ring of DCH is in a boat-shaped arrangement. This leaves the 5 position poorly conjugated to both benzo rings but a 5 substituent is well removed from the neighboring peri hydrogens. In this conformation the two benzo rings are twisted out-of-plane in the same direction relative to a plane that is perpendicular to the vertical axis of the p orbital of the 5 carbon. In another conformation (Figures 3 and 4), the benzo rings are twisted slightly out-of-plane in opposite directions, similar to diphenylmethyl anion, allowing excellent conjugation with the 5 position, but leaving the 5 substituent directly between the peri hydrogens, which are pointing essentially toward each other. We suggest that in DCH itself, where the 5 substitutent is hydrogen, the conformation in Figures 3 and 4 predominates; however, for a 5-substituted compound, interactions with the peri hydrogens are important and the conformation in Figures 1 and 2 now predominates. Consequently, the "anomaly" results from a change in reference. If DCH itself had the "boat" conformation, its p*K* value would be higher and methyl or phenyl substitution would produce a "normal" effect on p*K*.

A related situation occurs with diphenylmethane itself. In the corresponding methyl-substituted compound, 1,1-diphenylethane, the methyl substituent now interacts sterically with the ortho or "peri" hydrogen. The resulting ΔpK change of >2 units is more positive than for most methyl-substituted hydrocarbons (*e.g.*, 9-methylfluorene, $\Delta pK = 0.4$, TDA, $\Delta pK = 0.0$) but is comparable to the change for MDCH ($\Delta pK = 2.4$).

Acidity of Hydrocarbons. XLVII. Primary Kinetic Isotope Effects and Internal Return in Hydrogen Isotope Exchange of Toluene and Triphenylmethane with Lithium Cyclohexylamide[1]

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Abstract: Experimental primary isotope effects for LiCHA-catalyzed proton exchange are compared for toluene and triphenylmethane. For toluene at 25°, $k^{\mathrm{D}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = 2.82$ in cyclohexylamine (CHA) and $k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = 27.2$ in cyclohexylamine-*N*,*N*-d_2 (CHA-d_2). For triphenylmethane at 25°, $k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = 2.79$ in CHA and $k^{\mathrm{H}}_{\mathrm{exptl}}/k^{\mathrm{T}}_{\mathrm{exptl}} = 19.2$ in CHA-d_2. Derived internal return values show that internal return is greater for triphenylmethane than for toluene. Mechanistic primary isotope effects for the proton transfer step are also derived. The resulting $k_{\mathrm{I}}^{\mathrm{H}}/k_{\mathrm{I}}^{\mathrm{D}}$ value is about 11 for both hydrocarbons.

Base-catalyzed hydrogen isotope exchange reactions are frequently complicated by internal return phenomena[3,4] (eq 1). The primary hydrogen isotope

$$\mathrm{RL} + \mathrm{B}^- \underset{k_{-\mathrm{I}}^{\mathrm{L}}}{\overset{k_{\mathrm{I}}^{\mathrm{L}}}{\rightleftharpoons}} \mathrm{R}^-\mathrm{LB} \xrightarrow{k_{\mathrm{II}}} \mathrm{RH} \qquad (1)$$

effect has been a useful criterion for detecting the presence of significant amounts of internal return; k_{II} is a diffusion step which is expected to have but a weak isotope effect and, if $k_{-\mathrm{I}}$ becomes competitive with k_{II}, *low* isotope effects necessarily result (eq 2). In ex-

$$k^{\mathrm{L}}_{\mathrm{exptl}} = k_{\mathrm{I}}^{\mathrm{L}}/(1 + k_{-\mathrm{I}}^{\mathrm{L}}/k_{\mathrm{II}}) \qquad (2)$$

change reactions of methylarenes with lithium cyclo-

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