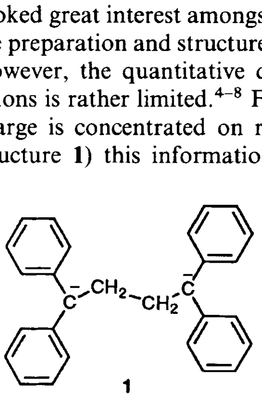
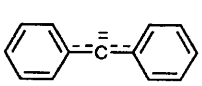
Acidity of Dibasic Acids I: the Second Acidity Constant of 9,10-Dihydroanthracene and its 9,10-Substituted Derivatives: Effect of Substituent and Counter Ion

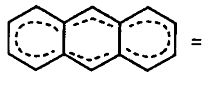
Israel O. Shapiro, Malka Nir, Roy E. Hoffman and Mordecai Rabinovitz*
Department of Organic Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem, Israel 91904

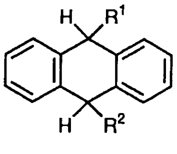
The second equilibrium ion pair acidity constants (pK_2) of 9,10-dihydroanthracene, 9-phenyl-9,10-dihydroanthracene, 9,10-diphenyl-9,10-dihydroanthracene and 9-cyano-9,10-dihydroanthracene with sodium, potassium and rubidium have been determined in tetrahydrofuran (THF) at 25 °C in the concentration range 10^{-5}–10^{-2} mol dm^{-3}. Equilibria were monitored by UV–VIS and ^{1}H NMR spectroscopies and the spectra of the dimetallic and monometallic salts reported. The dimetallic salts of all the dibasic carbon acids studied behave as contact ion pairs in THF. The pK_2 of 9,10-dihydroanthracene is insensitive to substituent effect but is strongly dependent on the cation.

Dianions and polyanions are widely used for organic syntheses.[1] For this reason, information concerning methods of preparation, structure and reactivities of these species has evoked great interest amongst chemists. Information regarding the preparation and structure of dianions has been reported.[1-3] However, the quantitative determination of reactivity of dianions is rather limited.[4-8] For dianions in which the negative charge is concentrated on remote sites in the molecule (*e.g.* structure **1**) this information may be extrapolated from the monoanions.[8-10] However, for dianions, in which the negative charge is concentrated within one π-electron framework (structures **2**, **3**) such extrapolation is unreliable.


1


2


3


4a $R^1 = R^2 = H$
b $R^1 = H, R^2 = Ph$
c $R^1 = R^2 = Ph$
d $R^1 = H, R^2 = CN$

A fundamental data base for assessment of the electronic and steric effects brought about by structural variations in dibasic carbon acids are the second equilibrium acidity constants (pK_2). The first, and so far only, measurements of acidity of dibasic carbon acids were reported by Streitwieser *et al.*[5-8] It has been demonstrated that the scale is also applicable to tetrahydrofuran (THF) solutions.[8] They have measured the first (pK_1) and second (pK_2) ion pair acidity constants of 9,10-dihydroanthracene (DHA), 2,2′-biindenyl, 9,9′-bifluorenyl, 10,12-dihydroindeno[2,1-*b*]fluorene and 6,12-dihydroindeno[1,2-*b*]fluorene (counter ion Cs^+) in cyclohexylamine and in dimethylsulfoxide.[5-8] The pK_1 and pK_2 of 9,9′-bifluorenyl were measured *inter alia* in THF[7] with two counter ions: Li^+ and Cs^+. From their results they concluded that ion interaction exerts more influence on the pK_2 than on the pK_1.[8]

The general goal of our research is the understanding of the dependence of pK_2 of dibasic carbon acids on the structure and size of π-electron systems, substituents at the deprotonating carbon atoms and their cations.

A convenient system for the study of effects of cations and substituents at the deprotonation sites on pK_2 is DHA. The difference between pK_1 and pK_2 of DHA amounts to four.[5] This allows independent measurements of pK_1 and pK_2. Our method allows the measurement of pK_2 prior to that of pK_1. We therefore studied pK_2 in the first instance.[11] The monometallic salt of DHA is a sufficiently strong acid to allow the measurement of pK_2.[5] The dimetallic salt of DHA can be prepared by two methods: by metallation of the hydrocarbon using a strong base or by reducing anthracene using an alkali metal.[2] The dimetallic salt of DHA is stable enough during the time of the transmetallation reaction used for the pK measurements.[5] The mono- and di-metallic salts of DHA and its derivatives absorb at different regions of the UV–VIS spectrum, thus it is possible to measure their absorbances.

In view of the above, our system of choice was DHA and its derivatives. Here we report the pK_2 of DHA, 9-phenyl-9,10-dihydroanthracene (9-PDHA), 9,10-diphenyl-9,10-dihydroanthracene (9,10-DPDHA) and 9-cyano-9,10-dihydroanthracene (9-CNDHA) in THF in the presence of Na^+, K^+ and Rb^+ cations as well as semiempirical calculations for the dianionic forms of these compounds. The progress of the reaction as well as the identity of the products was monitored by UV–VIS and NMR spectroscopies. The application of these spectroscopies enabled us to study the influence of concentration on acidity.

Results

Preparation of Dimetallic Salts of DHA and its Derivatives.—The method of two-electron reduction of anthracene, 9-phenylanthracene, 9,10-diphenylanthracene and 9-cyanoanthracene by alkali metal in THF was used in this study to obtain dimetallic salts. This reaction proceeds in two steps. The first step is the formation of the anion radical and the second is the formation of the dimetallic salt. The UV–VIS spectra of anion radicals and dianions are different enough to be well resolved. Therefore, it is possible to follow the reaction progress. The monoanion radical is paramagnetic and exchanges with the dianion, consequently, no NMR spectrum of the dianion can be observed while the radical is present in significant quantities. As the metallation reaction nears completion and the concentration of radicals falls, an NMR spectrum of the dianion appears and its peaks become narrower.

Table 1 UV Spectra of dialkali metal salts of DHA and its derivatives

Acid	λ_{max} ($\varepsilon \times 10^4$)^a				
	Li^+	Na^+	K^+	Rb^+	Cs^+
DHA	565 (–)^b	605 (2.0), 324 (7.1)	621 (1.8), 327 (6.1)	626 (1.7), 330 (6.1)	633^c
9-PDHA	—	563 (2.4), 320 (7.5)	580 (2.5), 333 (8.6)	583 (2.1), 320 (6.9)	
9,10-DPDHA	527 (–)	529 (1.9), 334 (6.8)	548 (1.7), 336 (7.3)	553 (1.7), 337 (7.5)	554, 333
9-CNDHA	—	537 (1.8), 313 (6.5)	552 (2.0), 315 (6.9)	553 (1.9), 311 (6.2)	

^{a} λ_{max} is the wavelength of absorption in nm; ε is the molar extinction coefficient in $dm^3\ mol^{-1}\ cm^{-1}$. ^{b} Measured in diethoxyethane.[4] ^{c} Measured in cyclohexylamine.[6]

Table 2 UV Spectra of monoalkali metal salts of DHA and its derivatives

Acid	λ_{max} ($\varepsilon \times 10^4$)^a		
	Na^+	K^+	Rb^+
DHA	420 (2.4)^b	442 (2.4)	444 (2.4)^c
9-PDHA	449 (2.6)	447 (2.5)	443 (2.4)
9,10-DPDHA	448 (2.8)	442 (2.8)	443 (2.9)
9-CNDHA	368 (2.3)	380 (2.3)	380 (2.4)

^{a} λ_{max} is the wavelength of absorption in nm; ε is the molar extinction coefficient in $dm^3\ mol^{-1}\ cm^{-1}$. ^{b} For Li^+ in 2-methyltetrahydrofuran, λ_{max} = 398 nm.[33] ^{c} For Cs^+ in cyclohexylamine, λ_{max} = 444 nm.[5]

It is very difficult to prepare the dimetallic salt in the absence of monometallic salts. However, the mixture of dimetallic and monometallic salts of these compounds are stable in THF and their concentrations may be measured during the pK_2 determinations for DHA or its derivatives.

UV–VIS Spectra.—Spectroscopic data of mono- and di-alkali metal salts of DHA, 9-PDHA, 9,10-DPDHA and 9-CNDHA are reported in Tables 1 and 2. Owing to the presence of the mono- and di-metallic salts in solution their extinction coefficients could be determined by calculation [eqns. (1) and (2)]. Where $A^1{}_d$ and $A^1{}_m$ are the absorbances of di- and

$$A^1{}_d/l \times \varepsilon_d + A^1{}_m/l \times \varepsilon_m = C^1 \qquad (1)$$

$$A^2{}_d/l \times \varepsilon_d + A^2{}_m/l \times \varepsilon_m = C^2 \qquad (2)$$

mono-metallic salts of DHA, respectively when the concentration of introduced anthracene is equal to C^1. $A^2{}_d$ and $A^2{}_m$ are the absorbances of di- and mono-metallic salts of DHA, respectively when the concentration of introduced anthracene is equal to C^2. ε_d and ε_m are the extinction coefficients of di- and mono-metallic salts of DHA, respectively. l is the light path length.

Each pair of extinction coefficients was determined at four to six concentrations. These concentrations are in the range of 10^{-4}–10^{-3} mol dm^{-3}. In all the cases studied, Beer's law is adhered to over the concentration range used for pK_2 determination. The ε_d and ε_m values are accurate to within 8%.

Indicator Carbon Acids.—Diphenylmethane (DPM), di-*o*-tolylmethane [D(*o*-T)M], di-*p*-tolylmethane [D(*p*-T)M], and bis-2,5-dimethylphenylmethane [B(2,5-DMP)M] were used as indicator carbon acids. Their UV–VIS spectra and p*K* values are reported in Table 3. The p*K* values of DPM, D(*o*-T)M and D(*p*-T)M were measured by Streitwieser in cyclohexylamine (counter ion Cs^+).[10] As stated earlier, the p*K* values of the indicator carbon acids in cyclohexylamine and in THF are practically the same.[8,10] The p*K* value of B(2,5-DMP)M was measured in THF in this study (counter ion K^+).

The extinction coefficients of the metallic salts of DPM and D(*o*-T)M were determined in THF (counter ion Cs^+).[12] Streitwieser has shown that the extinction coefficients of alkali metal salts of indicator acids in THF are independent of the cation within 10%.[13] The extinction coefficients for potassium salts of D(*p*-T)M and B(2,5-DMP)M were measured in THF. These salts were prepared by the reaction of D(*p*-T)M and B(2,5-DMP)M with cumylpotassium.

NMR Spectra.—For determination of the equilibrium constants by ^1H NMR spectroscopy in [$^2H_8$]THF, relative concentrations were determined by integration of the multiplets. Spectra were acquired using 90° excitation pulses and delays of 13 s were allowed between transients for complete relaxation to occur. 13 s is equal to at least five times the longitudinal relaxations times (T_1) of all the signals except for the solvent and some aromatic protons of the indicator acids. Neither of the latter two groups of signals were used for determining relative concentrations. Precisions of up to ±1% can be achieved depending on signal overlap.

Absolute concentrations were determined by calibrating the concentration of [$^2H_7$]THF in each batch of [$^2H_8$]THF using a solution of known concentration. The T_1 of the proton in [$^2H_7$]THF is typically 120 s so only one transient was acquired in order to obviate the necessity of waiting 15 min between transients. Accuracies of ±3% in absolute concentration were achieved by this method.

NMR measurements were only possible for some of the dimetallic salts. The dipotassium and dirubidium salts of anthracene exhibit paramagnetism at room temp. arising from thermal population of a triplet state.[14] The dicaesium salts were not soluble enough to obtain good spectra in a reasonable amount of time. The dirubidium salt of 9-phenylanthracene reacted with the indicator anion and dissolved rubidium to generate small quantities of paramagnetic radicals; enough to make the spectrum of the dirubidium salt unobservable over a period of a few days. Therefore, no equilibrium measurements could be made by NMR spectroscopy in these cases.

Equilibrium Measurements.—Equilibrium constants of the transmetallation reaction [eqn. (3)] were determined by UV–VIS and NMR spectroscopies.

$$R^{2-}2M^+ + InH \rightleftharpoons RH^-M^+ + In^-M^+ \qquad (3)$$

Where $R^{2-}2M^+$ is a dimetallic salt of substituted DHA, InH is an indicator carbon acid, RH^-M^+ is a monometallic salt of substituted DHA and In^-M^+ is the salt of an indicator carbon acid.

The equilibrium constant, K_{eq}, of this reaction is given by eqn. (4) and the p*K* by eqn. (5).

$$K_{eq} = ([RH^-M^+][In^-M^+])/([R^{2-}2M^+][InH]) \qquad (4)$$

$$\log(K_{eq}) = pK_{RH^-M^+} - pK_{InH} \qquad (5)$$

Table 3 UV Spectra and pK values of indicator carbon acids

	$\lambda_{max}{}^a$					
Indicator	Na^+	K^+	Rb^+	Cs^+	$\varepsilon \times 10^{4\,b}$	pK
DPM	424	442	442	443^c	5.06^c	33.4^d
D(o-T)M	426	445	445	447^c	4.03^c	34.8^d
D(p-T)M	—	442	445	446^d	4.5	35.1^d
B(2,5-DMP)M	425	449	449	—	4.8	35.0^e

[a] λ_{max} is the wavelength of absorption in nm. [b] ε is the molar extinction coefficient in $dm^3\ mol^{-1}\ cm^{-1}$. [c] Measured in THF, counter ion Cs^+.[12] [d] Measured in cyclohexylamine, counter ion Cs^+.[10] [e] Counter ion K^+ (THF).

Table 4 p$K_2{}^a$ values of DHA and its derivatives

Acid	Na^+	K^+	Rb^+	p$K_2(K^+)$ − p$K_2(Na^+)$
DHA	34.1	35.0	—	0.9
9-PDHA	33.6 (33.5)	35.2 (34.9)	35.1	1.6
9,10-DPDHA	32.0 (31.0)	34.8 (35.3)	34.7 (35.3)	2.8
9-CNDHA	32.6	35.0	—	2.4

[a] Figures in parentheses indicate pK determined by NMR spectroscopy. The remaining pK values were determined by UV–VIS spectroscopy.

For the determination of K_{eq}, by UV–VIS spectroscopy we used the same technique which was applied in the literature.[5] Spectra of the reaction mixture usually contain three peaks. The absorption at *ca.* 600 nm corresponds to the dimetallic salt of DHA or its derivatives. The absorption at *ca.* 440 nm corresponds to both the monometallic salt of DHA and the metallic salt of the indicator carbon acid. The third absorption at *ca.* 330 nm corresponds to the dimetallic salt of DHA. The equilibrium concentration of the monometallic salt of DHA and the metallic salt of the indicator carbon acid (InH) are determined by the absorption of the dimetallic salt and equations of material balance [eqns. (6)–(10)]. Where $[R^{2-}2M^+]_0$ and $[R^{2-}2M^+]_\infty$

$$[R^{2-}2M^+]_\infty = A_{600}/l \times \varepsilon_d \qquad (6)$$

$$[RH^-M^+]_\infty = [R^{2-}2M^+]_0 - A_{600}/l \times \varepsilon_d \qquad (7)$$

$$[In^-M^+]_\infty = A_{In^-}/l \times \varepsilon_{In^-} \qquad (8)$$

$$A_{In^-} = A_{440} - [RH^-M^+]_\infty \times l \times \varepsilon_m = A_{440} - \{[R^{2-}2M^+]_0 - A_{600}/l \times \varepsilon_d\} \times l \times \varepsilon_m \qquad (9)$$

$$[In^-M^+]_\infty = \{A_{440} - [R^{2-}2M^+]_0 \times l \times \varepsilon_m + A_{600}\,\varepsilon_m/\varepsilon_d\}/l \times \varepsilon_{In^-} \qquad (10)$$

are the initial and equilibrium concentrations of the dimetallic salt, respectively; $[RH^-M^+]_\infty$ is the equilibrium concentration of the monometallic salt of DHA; $[In^-M^+]_\infty$ is the equilibrium concentration of metallic salt of the indicator carbon acid; A_{440} and A_{600} are the intensities of the absorptions arising from the equilibrium reaction; and ε_{In^-} is the extinction coefficient of the metallic salt of the indicator carbon acid.

The pK_2 values of DHA, 9-PDHA, 9,10-DPDHA and 9-CNDHA (Table 4) were determined from the K_{eq} of the transmetallation reaction [eqn. (3)] for each carbon acid with two or three indicators. With each of the indicators two or three independent determinations were made. The pK_2s (Table 4) are mean values.

All measurements were carried out at 25.0 ± 0.5 °C. The accuracy of pK_2 (Table 4) is estimated to be within 0.3 pK units. The reproducibility of log K_{eq} values is usually ±0.1. Sources of measurement errors of K_{eq} stem from determination of the extinction coefficients applied to convert absorbance to concentration, and from the indirect method used for determination of the concentrations of In^-M^+ and RH^-M^+. It was reported that the pK_2 values for DHA in cyclohexylamine (counter ion Cs^+) is 34.1.[5] The pK_2 for this compound in the present study is 35.0 (Table 4). Taking into account the difference between solvents and counter ions, one can say that these values are similar.

Discussion

Depending on the counter ion and substituent the pK_2 values (Table 4) vary from 31.0 to 35.3. It follows that the acidities of the monometallic salts of DHA and its derivatives are relatively high. The primary cause of this phenomenon is the efficient delocalization of charge in the dianion.[5] The second most important factor in dimetallic salts of these dibasic carbon acids is the interion interaction.[5] It is known that in non-polar solvents such as THF the organometallic compounds exist as ion pairs.[8] The stability of these ion pairs depends on the charge and structure of anions, cation size and solvent polarity. The ion pair stability varies with the structure and the charge of anion and cation size. This variation may displace the equilibrium of the transmetallation reaction. Such considerations are very important in the reaction [eqn. (3)], in which three organometallic compounds, one of which is a dimetallic salt, take part.

Solvation State of Metallic Salts of Dibasic Carbon Acids and Indicators.—The system of mono- and di-metallic salts of DHA, 9-PDHA, 9,10-DPDHA and 9-CNDHA is analysed by UV–VIS and NMR spectroscopies. The UV–VIS spectra of dimetallic salts of these acids have two maxima. The maximum between 527 and 626 nm is sensitive to cations and to substituents on the anthracene ring. The other absorption between 311 and 333 nm is much less sensitive to these factors. The change from Li^+ to Cs^+ displaces the first maximum towards longer wavelengths. According to Smid,[15,16] such a displacement indicates that the dimetallic salts are contact ion pairs (CIP). As the anion charge in dimetallic salts of these acids is twice as high as the charge of the anions of the monometallic salts, the energy of ion interaction for the former is larger than for the latter. The displacement of λ_{max} for dimetallic salts by replacing of Na^+ with K^+ is larger than that for replacing K^+ with Rb^+ which is in turn larger than that for replacing Rb^+ for Cs^+ (Table 1). These results show that interion interaction of dianions with Na^+ is stronger than with K^+ and Rb^+, *i.e.* the order of stability of dimetallic salts is $Na^+ > K^+ \geq Rb^+ \geq Cs^+$.

From the UV–VIS spectra of monometallic salts of DHA and 9-CNDHA it may be concluded that these salts are CIP. The absorptions arising from these salts are displaced to longer wavelengths with increasing cation size (Table 2). Such a displacement is characteristic of CIP.[15,16] However, the absorptions attributed to the monometallic salts of 9-PDHA and 9,10-DPDHA are displaced towards shorter wavelengths with increasing cation size. A similar shift has been observed for the absorptions corresponding to the alkali metal salts of triphenylmethane.[17,18] Such variations in the λ_{max} of monometallic salts of 9-PDHA and 9,10-DPDHA can be explained by their structure, *i.e.* two of the phenyls are coplanar while the third is perpendicular as is the case for alkali metal salts of triphenylmethane.[17,18] According to our calculations by semiempirical methods (AM-1)[18b] of monocarbanions of 9-PDHA and 9,10-DPDHA, the phenyl groups are approximately perpendicular to the plane of the carbanion. Therefore, the approach of the cation, surrounded by a solvent layer, to the deprotonated carbon atom is hindered. That is why the concentration of solvent separated ion pairs (SSIP) for monometallic salts of 9-PDHA and 9,10-DPDHA is greater than for monometallic salts of the planar DHA and 9-CNDHA anion. In addition, the interion distance in the CIP of monometallic salts of 9-PDHA and 9,10-DPDHA is larger than in monometallic salts of DHA and 9-CNDHA. For these reasons, the differences between the λ_{max} of CIP and SSIP for 9-PDHA and 9,10-DPDHA are smaller than for DHA and 9-CNDHA. The UV–VIS spectra of these salts display one wide maximum formed by the overlap of the two absorptions. As the cation size increases, the CIP concentration rises resulting in a blue-shift of the absorption (Table 2).

The system of metallic salts of carbon acids used in this study as indicators was reported, with the exception of B(2,5-DMP)M, in several papers.[17–20] The alkali metal salts of DPM and D(*p*-T)M have been shown to be CIP in THF and in several ethereal solutions.[17–20] The same conclusion follows from our results. The wavelengths of the absorbances of alkali metal salts of DPM increase with the change of cation from Na^+ to Cs^+ (Table 3). The displacement of absorbance of alkali metal salts of D(*o*-T)M and B(2,5-DMP)M shows the same effect (Table 3) implying that the metallic salts of all indicator acids used in this study exist as CIP in THF.

Second Acidity Constants.—According to the aforementioned analysis, the dimetallic salts of DHA, 9-PDHA, 9,10-DPDHA and 9-CNDHA; monometallic salts of DHA and 9-CNDHA; and metallic salts of indicator carbon acids exist in THF as CIPs. However, monometallic salts of 9-PDHA and 9,10-DPDHA exist as a mixture of CIP and SSIP in THF. The stability of CIP depends on ion interaction.

The energy of ion interaction decreases as the cation size increases. The thermodynamic stability of dimetallic salts must be more sensitive to cation size because the energy of ion–ion interactions of these organometallic compounds is twice as large as that of monometallic salts. That is why the disodium salts of DHA and its derivatives must be more stable than the dipotassium and dirubidium salts of these compounds. In accordance with this conclusion the pK_2 of these dibasic acids for counter ion Na^+ is lower than for counter ions K^+ and Rb^+ (Table 4).

The differences between pK_2(K^+) and pK_2(Na^+) for 9,10-DPDHA (34.8 and 32.0, respectively) and 9-CNDHA (35.0 and 32.6, respectively) are larger than two. It should be noted that such a large change of pK is typical of carbon acids with localized carbanions.[7]

The phenyl and cyano groups are strong electron acceptors. Usually, their presence increases the acidity of the compounds, considerably. For example, the series Ph_2CH_2, Ph_2CH–Ph and Ph_2CH–CN have pK values of 33.5,[21] 30.7[22] and 18.3,[23] respectively (dimethoxyethane, Cs^+ counter ion). Also the series fluorene, 9-phenylfluorene, and 9-cyanofluorene have p*K*s of 22.0,[22] 17.5[22] and 9.4,[23] respectively under similar conditions. The pK_2(Na^+) values also depend on the electron acceptor properties of these groups. There is a correlation between the pK_2(Na^+) values of 9-substituted DHA and the σ_m constant of the substituent. A correlation with σ_p constants was not as good thus showing that an inductive effect predominates over the resonance effect. However, the pK_2 values of these acids are fairly insensitive to substituent effects. Thus the difference, 1.5, between the p*K*s of DHA and 9-CNDHA is considerably smaller than those found for the diphenylmethane and fluorene series mentioned above.

According to eqn. (3), the pK_2 values are determined by the relative stability of the mono- and di-metallic salts of dibasic carbon acids, *i.e.* the ratio $[R^{2-}2M^+]:[RH^-M^+]$. When the substituent is introduced into the DHA molecule, the stabilities of mono- and di-metallic salts may be changed. However, if the changes are similar, the above ratio will not change much. In such a case the pK_2 values for the dibasic acid and for its derivatives will be similar.

The charge densities on the deprotonated carbon atoms of monoanions and dianions of DHA and its derivatives are compared in Table 5. The charge densities were calculated by the semiempirical AM-1 method.[18b] For DHA, 9-PDHA and 9,10-DPDHA, the ratio of charge densities on the deprotonated carbon atoms of monoanions to those of the dianions is approximately equal but this is not the case for 9-CNDHA, therefore, the pK_2(K^+) of DHA and its derivatives are very close (Table 4). The difference between pK_2(Na^+) for DHA from that of 9-PDHA and 9,10-DPDHA are apparently connected to considerable decrease of thermodynamic stability of monometallic salts of the latter compounds. The monometallic salts of 9-PDHA and 9,10-DPDHA are a mixture of CIP and SSIP. Upon the transition from potassium to sodium, the SSIP concentration of these salts increases. As SSIP is less thermodynamically favoured to that of CIP, there is an increase in the ratio $[R^{2-}2M^+]:[RH^-M^+]$ for the sodium salts. CIP of mono- and di-metallic salts of 9-CNDHA are formed by the interaction of cations with the nitrogen atom.[23] The negative charge on the nitrogen of the dianion is greater than that of the monoanion (Table 5). For this reason, the interaction between the cations and the dianion of 9-CNDHA is stronger than for the monoanion. This effect is larger for the smaller Na^+ cation than for the larger K^+ cation. Therefore, the ratio $[R^{2-}2M^+]:[RH^-M^+]$ for the sodium salts of 9-CNDHA is found to be larger than for the potassium salts.

The pK_2 values of 9-PDHA and 9,10-DPDHA were determined by measuring the reagent and product concentrations by UV–VIS and NMR spectroscopies. The application of these two methods permitted estimation of the influence of reagent and product concentration on the pK_2. The pK_2 values in the range of concentrations between 10^{-3} and 10^{-2} mol dm^{-3} were determined by NMR spectroscopy and the range 10^{-5}–10^{-4} mol dm^{-3} were determined by UV–VIS spectroscopy. The differences between the values determined by the two methods is small. From these results, it can be concluded that the effect of the formation of ionic aggregates of dimetallic salts of DHA and its derivatives in the concentration range 10^{-5}–10^{-2} mol dm^{-3} is insignificant.

Experimental

General Considerations.—^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer in $CDCl_3$ at 25 ± 1 °C with

Table 5 Calculated charge densities[a] on C_α and on the substituents of monoanions and dianions of DHA and its derivatives

	Monoanion		Dianion		
Acid	C_α	Substituent	C_α	Substituent	$C_{\alpha di}/C_{\alpha mono}$
DHA	−0.442	—	−0.860	—	1.95
9-PDHA	−0.353	−0.211	−0.710	−0.496	1.98
9,10-DPDHA	−0.360	−0.110	−0.663	−0.650	1.90
9-CNDHA	−0.321	−0.238	−0.768	−0.322	2.39

[a] In units of electron charge.

TMS (0 ppm) as an internal chemical shift standard or in $[^2H_8]$THF (*vide infra*) using the H_2 of $[^2H_7]$THF (3.575 ppm) as a chemical shift standard. NMR spectra for the determination of reagent and product concentrations of transmetallation reactions were recorded in $[^2H_8]$THF. UV–VIS spectra were recorded on a UVIKON 860 spectrometer fitted with a thermostatically controlled cell holder. All equilibrium experiments were carried out at a constant temperature (25.0 ± 0.5 °C) maintained by a refrigerated and heated recirculating bath (Forma Scientific 2095). Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

Materials.—Commercial samples of anthracene, 9-phenylanthracene, 9,10-diphenylanthracene and 9-cyanoanthracene were purified by multiple recrystallization (methanol) and/or vacuum sublimation. Their UV–VIS spectra were identical with those in the literature.[24–28] The hydrocarbons had the following melting points: anthracene, m.p. 217–218 °C (lit.,[24,25] 216–218 °C); 9-phenylanthracene, m.p. 154–155 °C (lit.,[26] 153–155 °C); 9,10-diphenylanthracene, m.p. 246–248 °C (lit.,[27] 245–248 °C); 9-cyanoanthracene, 175–177 °C (lit.,[28] 173–177 °C). The indicator carbon acids: diphenylmethane, di-*o*-tolylmethane, di-*p*-tolylmethane and bis-2,5-dimethylphenylmethane were purified by multiple vacuum distillation or recrystallization from alcohol.

Diphenylmethane. DPM was recrystallized from a commercial sample: m.p. 25.2 °C (lit.,[29] 25 °C).

*Di-*o*-tolylmethane.* [D(*o*-T)M] was prepared from the corresponding aryl magnesium bromide and ethyl formate in diethyl ether followed by the reduction of the corresponding polymethylbenzhydrols on 10% Pd/C under hydrogen pressure of three bars for 12–20 h at room temp.[30] D(*o*-T)M was obtained as a colourless solid: m.p. 31.6 °C (lit.,[30] 31–32 °C); δ_H(400 MHz, $CDCl_3$) 2.26 (s, 6 H), 3.91 (s, 2 H), 6.88 (d, 2 H, *J* 7.2 Hz), 7.10 (t, 2 H, *J* 7.3 Hz), 7.14 (t, 2 H, *J* 7.1 Hz) and 7.18 (d, 2 H, *J* 7.2 Hz) (Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.7; H, 8.0%).

*Di-*p*-tolylmethane.* [D(*p*-T)M] was prepared as for D(*o*-T)-M[30] and was obtained as a colourless liquid: $[\alpha]_D^{20}$ 1.5620 (lit.,[30] 1.5616); δ_H(400 MHz, $CDCl_3$) 2.23 (s, 6 H), 3.89 (s, 2 H), 7.06 and 7.08 (AA'BB', 8 H, *J* 7.3, 7.3, 2.0, 1.5 Hz) (Calc. for $C_{15}H_{16}$; C, 91.78; H, 8.22. Found: C, 91.5; H, 8.0%).

Bis-2,5-dimethylphenylmethane. [B(2,5-DMP)M] was prepared in a similar manner to D(*o*-T)M and D(*p*-T)M[30] although its synthesis by this method has not been previously reported. Ethyl formate (3 g; 0.04 mol dm^{-3}) was added to Grignard reagent which had been prepared from magnesium metal (2.4 g; 0.1 mol dm^{-3}) and 1-bromo-2,5-dimethylbenzene (18.5 g; 0.1 mol dm^{-3}) in anhydrous diethyl ether. The reaction mixture was stirred for 6 h and quenched with 10% HCl. The organic layer was washed with water, 10% $NaHCO_3$, then water. The ether solution was dried ($MgSO_4$) and the solvent evaporated to yield the carbinol. The carbinol was reduced by hydrogen in methanol solution containing 0.5 g of 10% Pd/C and one drop of 70% perchloric acid for 15 h at three bars (room temp.). The suspension was neutralized with 5% aqueous sodium carbonate then filtered. The methanol was evaporated from the solution and the remaining solid dissolved in diethyl ether. The solution was washed with water, dried over $MgSO_4$ and filtered. The solvent was evaporated and the solid recrystallized three times from methanol to yield [B(2,5-DMP)M] (3.2 g, 15%) as a colourless solid: m.p. 60–61 °C (lit.,[31] 60–60.5 °C); δ_H(400 MHz, $CDCl_3$) 2.22 (s, 6 H), 2.24 (s, 6 H), 3.84 (s, 2 H), 6.70 (s, 2 H), 6.95 (d, 2 H, *J* 7.6 Hz) and 7.07 (d, 2 H, *J* 7.6 Hz) (Calc. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.8; H, 8.9%).

Bicumyl. 2,3-Dimethyl-2,3-diphenylbutane was prepared from α-cumyl alcohol according to a published procedure[32] and obtained as a white solid: m.p. 118 °C (lit.,[32] 118–119 °C); δ_H(400 MHz, $CDCl_3$) 1.31 (s, 12 H), 7.06 (d, 4 H, *J* 8.1 Hz), 7.15 (t, 2 H, *J* 8.1 Hz) and 7.18 (t, 4 H, *J* 8.4 Hz) (Calc. for $C_{18}H_{22}$: C, 87.70; H, 12.30. Found: C, 87.5; H, 12.0%).

Cumylpotassium was prepared by reaction of bicumyl with potassium in THF was obtained as a red solution: UV–VIS λ_{max}, 338 nm; ε, 1.7 × 10^4. The cumyl potassium solution was used for the preparation of THF solution of potassium salts of B(2,5-DMP)M and D(*p*-T)M.

THF. The commercial solvent was predried over sodium wire for several days followed by refluxing over potassium for several days under argon and distilled into a flask equipped for a vacuum line. $[^2H_8]$THF was transferred directly from a commercial sealed ampoule without predrying. The solvent was degassed in several freeze pump thaw cycles and then vacuum transferred into a flask containing distilled Na : K 5 : 1 alloy and sonicated until a blue colour developed. The flask was allowed to stand overnight then sonicated again until a permanent blue colour developed. $[^2H_8]$THF was redistilled into another similar flask containing the alloy to make up for the lack of predrying. The THF was then distilled under vacuum into the reaction vessel.

Equilibrium Measurements.—For UV–VIS spectroscopy, the transmetallation reaction was carried out in an all glass apparatus equipped with an optical quartz cell and graduated cylinder for determining the quantity of solvent. The apparatus has three sections: (1) for the preparation of an alkali metal mirror; (2) for the solvent, and (3) for a ball of glass and sealed fragile ampoules, one containing preweighed anthracene or its derivative and the other containing a preweighed indicator carbon acid. All the manipulations were carried out under vacuum.

The glass ball, the fragile ampoules and the alkali metal were placed into their respective positions in the apparatus; the apparatus connected to a vacuum line; and a vacuum pulled. The alkali metal mirror was formed by distillation of the metal in section 1. The solvent was vacuum transferred into section 2. The apparatus was sealed and cut off by a flame from the vacuum line. The fragile ampoule of anthracene or a derivative of it was broken. The substrate was dissolved and transferred around the apparatus, including section 1, many times over a period of several hours to form the dimetallic salt. The formation of the salt was monitored by UV–VIS spectroscopy. The solution was transferred into section 2 and frozen. Section 1 was sealed and cut off by a flame. The solution was thawed and the indicator ampoule broken and mixed. The reaction was then followed to equilibrium at constant temperature over a typical period of several days by UV–VIS spectroscopy.

The pK value of B(2,5-DMP)M was measured by the above procedure (cation K^+) and found to be 35.0 (Table 3), using the monometallic salts of DHA and 9-PDHA as indicators.

For NMR spectroscopy, the transmetallation was carried out in an all glass apparatus. The final sample tube was a 14 mm diameter tube attached to a 4 mm diameter tube. A few milligrams of the anthracene derivative was placed in the bottom of the 4 mm tube and a sealed fragile ampoule containing the indicator carbon acid under vacuum and a glass ball were placed in the 14 mm tube above. This was connected to glass tubing suitable for redistillation of alkali metal and for connection to a vacuum line. The alkali metal was introduced, the apparatus sealed, and a vacuum attained. The anthracene derivative was resublimed in the 4 mm tube. The metal was distilled into the 14 mm tube and [$^2H_8$]THF vacuum transferred into the 4 mm tube. The final sample tube was sealed and cut off by a flame from the vacuum line. The solution was transferred around the apparatus many times over a period of several hours to days so as to react with the metal until a good permanent NMR spectrum of the dianion could be observed. The ampoule containing the indicator was then broken and the reaction followed to equilibrium while keeping the sample upright and at a constant temperature. If the spectrum of the dianion broadened or disappeared then inverting the sample for a few minutes restored it. Inverting for much longer than this leads to side reactions with the metal which upset the equilibrium.

Acknowledgements

We thank the Rich Foundation of the Ministry of Science and Technology for financial support and the Margaret Thatcher Center for Interdepartmental Scientific Equipment for NMR facilities.

References

1 C. M. Thompson and D. L. C. Green, *Tetrahedron*, 1991, **47**, 4223.
2 W. Schlenk, J. Appenrodt, A. Micahel and A. Thal, *Berichte*, 1914, **47**, 473.
3 R. B. Bates, *Comprehensive Carbanion Chemistry*, ed. E. Buncel and T. Durst, Elsevier: Amsterdam, 1980, part A.
4 E. S. Petrov, M. I. Tezekhova and A. I. Shatenshtein, *Russ. Chem. Rev.*, 1973, **42**, 1574.
5 A. Streitwieser, C. M. Berke and K. Robbers, *J. Am. Chem. Soc.*, 1978, **100**, 8271.
6 A. Streitwieser and J. T. Swanson, *J. Am. Chem. Soc.*, 1983, **105**, 2502.
7 M. Stratakis and A. Streitwieser, *J. Org. Chem.*, 1993, **58**, 1989.
8 A. Streitwieser, *Acc. Chem. Res.*, 1984, **17**, 353.
9 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.
10 A. Streitwieser, E. Juaristi and L. L. Nebenzahl, *Comprehensive Carbanion Chemistry*, ed. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, part A.
11 pK_1 studies are underway, I. O. Shapiro, M. Nir, R. E. Hoffman and M. Rabinovitz, to be published.
12 A. Streitwieser, J. C. Ciula, J. A. Krom and G. Thiele, *J. Org. Chem.*, 1991, **56**, 1074.
13 S. Gronert and A. Streitwieser, *J. Am. Chem. Soc.*, 1986, **108**, 7016.
14 A. Minsky, A. Y. Meyer, R. Poupko and M. Rabinovitz, *J. Am. Chem. Soc.*, 1985, **107**, 6975.
15 T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 1965, **87**, 669.
16 T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 1966, **88**, 307.
17 E. Buncel, B. C. Menon and J. P. Colpa, *Can. J. Chem.*, 1979, **57**, 999.
18 (*a*) B. C. Menon and E. Buncel, *J. Organometal. Chem.*, 1978, **159**, 357; (*b*) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
19 J. B. Grutzner, J. M. Lawlor and L. M. Jackman, *J. Am. Chem. Soc.*, 1972, **94**, 2306.
20 D. H. O'Brien, C. R. Russell and A. J. Hart, *J. Am. Chem. Soc.*, 1979, **101**, 633.
21 I. O. Shapiro, M. I. Terkhova, I. Ya, E. S. Petrov and A. I. Shatenshtein, *Zhur. Obshch. Khim.*, 1982, **53**, 1386.
22 E. S. Petrov, M. I. Terekhova and A. I. Shatenshtein, *Zhur. Obshch. Khim.*, 1974, **44**, 1118.
23 T. I. Lebedeva, E. S. Petrov and A. I. Shatenshtein, *Zhur. Organ. Khim.*, 1977, **13**, 905.
24 G. M. Badger, *J. Chem. Soc.*, 1952, 1175.
25 V. Gold and F. L. Tye, *J. Chem. Soc.*, 1952, 2172.
26 E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, 1952, **74**, 6235.
27 Y. Hirshberg, *Trans. Faraday Soc.*, 1948, **44**, 285.
28 A. Mielert, C. Braig, J. Sauer, J. Martelli and R. Sustmann, *Liebig Ann. Chem.*, 1980, 954.
29 G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, *J. Am. Chem. Soc.*, 1946, **68**, 2524.
30 G. Häfelinger and A. Streitwieser, *Chem. Ber.*, 1968, **101**, 657.
31 R. C. Huston and D. T. Ewing, *J. Am. Chem. Soc.*, 1915, **37**, 2394.
32 D. A. Bors, M. J. Kaufman and A. Streitwieser, *J. Am. Chem. Soc.*, 1985, **107**, 6975.
33 N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, 1965, **87**, 4529.

Paper 4/00835I
Received 10*th February* 1994
Accepted 6*th April* 1994