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 (pK₂) 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 ¹H 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 pK₂ 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.⁴-⁶ 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.

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 (pK₂). 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 (pK₁) and second (pK₂) ion pair acidity constants of 9,10-dihydroanthracene (DHA), 2,2'-bindenyl, 9,9'-bifulloerylen 10,12-dihydroindenom[2,1-b]fluorene and 6,12-dihydroindenom[1,2-b]fluorene (counter ion Cs⁺) in cyclohexylamine and in dimethyl sulfoxide.⁵-⁸ The pK₁ and pK₂ of 9,9'-bifulloerylen were measured inter alia in THF with two counter ions: Li⁺ and Cs⁺.

From their results they concluded that ion interaction exerts more influence on the pK₂ than on the pK₁.⁸

The general goal of our research is the understanding of the dependence of pK₂ 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 pK₂ is DHA. The difference between pK₁ and pK₂ of DHA amounts to four.¹ This allows independent measurements of pK₁ and pK₂. Our method allows the measurement of pK₂ prior to that of pK₁. We therefore studied pK₂ in the first instance.¹¹ The monometallic salt of DHA is a sufficiently strong acid to allow the measurement of pK₂.³ 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.¹ The dimetallic salt of DHA is stable enough during the time of the transmetallation reaction used for the pK measurements.¹ 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 pK₂ of DHA, 9-phenyl-9,10-dihydroanthracene (9-PDHA), 9,10-diphenyl-9,10-dihydroanthracene (9,10-DPPDA) 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

<table>
<thead>
<tr>
<th>Acid</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHA</td>
<td>565 (1.5)</td>
<td>605 (2.0), 324 (7.1)</td>
<td>621 (1.8), 327 (6.1)</td>
<td>626 (1.7), 330 (6.1)</td>
<td>633 (1)</td>
</tr>
<tr>
<td>9-PDHA</td>
<td>—</td>
<td>563 (2.4), 320 (7.5)</td>
<td>580 (2.5), 333 (8.6)</td>
<td>583 (2.1), 320 (6.9)</td>
<td>—</td>
</tr>
<tr>
<td>9,10-DPDHA</td>
<td>527 (—)</td>
<td>9,10-DPDHA</td>
<td>529 (1.9), 334 (6.8)</td>
<td>548 (1.7), 336 (7.3)</td>
<td>553 (1.7), 337 (7.5)</td>
</tr>
<tr>
<td>9-CNDHA</td>
<td>—</td>
<td>537 (1.8), 313 (6.5)</td>
<td>552 (2.0), 315 (6.9)</td>
<td>553 (1.9), 311 (6.2)</td>
<td>—</td>
</tr>
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</table>

The extinction coefficients of the metallic salts of DPM and D(o-T)M were determined in THF (counter ion Cs⁺). Streitwieser has shown that the extinction coefficients of alkali metal salts of indicator acids in THF are independent of the cation within 10%. 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 [1H₃]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 relaxation times (T₁) of all the signals except for the solvent and some aromatic protons of all 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 [1H₃]THF in each batch of [1H₃]THF using a solution of known concentration. The T₁ of the proton in [1H₃]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. 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.

\[
R₂^⁺ + 2M^+ + InH \rightleftharpoons RH^⁺ M^+ + In^⁻ M^+ \quad (3)
\]

Where \(R₂^⁺\) 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 \(pK\) by eqn. (5).

\[
K_{eq} = \left(\frac{[RH^⁺ M^+][In^⁻ M^+]}{[R₂^⁺ 2M^+][InH]}\right) \quad (4)
\]

\[
\log(K_{eq}) = pK_{RH^⁺ M^+} - pK_{InH} \quad (5)
\]
used the same technique which was applied in the literature. 

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 monometallic salt of DHA and the metallic salt of the indicator carbon acid.

For the determination of \(K_{eq}\) by UV-VIS spectroscopy we used the same technique which was applied in the literature. 

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order of stability of dimetallic salts is Na\(^+\) > K\(^+\) > Rb\(^+\) > Cs\(^+\).

From the UV–VIS spectra of monomeric 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 monomeric salts of 9-PDHA and 10,10-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 \(\lambda_{\max}\) of monomeric salts of 9-PDHA and 10,10-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)\(^{18}\) of monocarbanions of 9-PDHA and 10,10-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 monomeric salts of 9-PDHA and 10,10-DPDHA is greater than for monomeric salts of the planar DHA and 9-CNDHA anion. In addition, the interion distance in the CIP of monomeric salts of 9-PDHA and 10,10-DPDHA is larger than in monomeric salts of DHA and 9-CNDHA. For these reasons, the differences between the \(\lambda_{\max}\) of CIP and SSIP for 9-PDHA and 10,10-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(p-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, 10,10-DPDHA and 9-CNDHA; monomeric salts of DHA and 9-CNDHA; and metallic salts of indicator carbon acids exist in THF as CIPs. However, monomeric salts of 9-PDHA and 10,10-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 dibarium 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 32.4, respectively) and 9-CNDHA (35.0 and 32.6, respectively) are larger than two. It should be noted that such a large change of \(pK\) for the phenyl and cyano groups 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\(_2\)CH\(_2\)Ph, Ph\(_2\)CH–Ph and Ph\(_2\)CH–CN have \(pK\) values of 33.5,\(^{21}\) 30.7\(^{22}\) and 18.3,\(^{23}\) respectively (dimethoxyethane, Cs\(^+\) counter ion). Also the series 9-phenylfluorene, 9-pheynyl-9-eyano-fluorene have \(pK\)s of 22.0,\(^{24}\) 17.5\(^{22}\) and 9.4,\(^{23}\) respectively under similar conditions.

The \(pK_2\) values of these acids are fairly insensitive to substituent effects. Thus the difference, 1.5, between the \(pK\)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 \([RZ-2M+]:[RH-M+]\). 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.\(^{18}\) For DHA, 9-PDHA and 10,10-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 \(pK_2\) of 9-PDHA and its derivatives are very close (Table 4). The difference between \(pK_2\) (Na\(^+\)) for DHA from that of 9-PDHA and 10,10-DPDHA are apparently connected to considerable decrease of thermodynamic stability of monometallic salts of the latter compounds. The monometallic salts of 9-PDHA and 10,10-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 \([RZ-2M+]:[RH-M+]\) 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.\(^2\) 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 \([RZ-2M+]:[RH-M+]\) 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 10,10-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\(^{-2}\)–10\(^{-3}\) mol dm\(^{-3}\) is insignificant.

**Experimental**

**General Considerations.**—\(^{13}\) H NMR spectra were recorded on a Bruker AMX-400 spectrometer in CDCl\(_3\), at 25 ± 1 °C with...
TMS (0 ppm) as an internal chemical shift standard or in 
$[^1]H_2$THF (vide infra) using the $H_2$ of $[^1]H_2$THF (3.575 ppm) as a chemical shift standard. NMR spectra for the determination of reagent and product concentrations of transmetalation reactions were recorded in $[^1]H_2$THF. UV-VIS spectra were recorded on a UVKON 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. The hydrocarbons had the following melting points: anthracene, m.p. 217–218 °C (lit., 25 246–248 °C); 9-phenylanthracene, m.p. 154–155 °C (lit., 25 246–255 °C); 9,10-diphenylanthracene, m.p. 246–248 °C (lit., 25 245–248 °C); 9-cyanoanthracene, 175–177 °C (lit., 25 173–177 °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 poly- methylbenzyldrols on 10% Pd/C under hydrogen pressure of three bars for 12–20 h at room temp. [D(o-T)M] was obtained as a colourless solid: m.p. 3 1.6 °C (lit., 31 30–32 °C); $\delta$ (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, 12.0%). Found: C, 91.7; H, 12.30.

Di-p-tolylmethane. [D(p-T)M] was prepared from l-bromo-2,5-dimethylbenzene (2.4 g; 0.1 mol dm$^{-3}$) 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 60–65.5 °C); $\delta$ (400 MHz, CDCl$_3$) 2.22 (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$_{15}$H$_{16}$: C, 91.70; H, 12.30). Found: C, 90.8; H, 8.9%).

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Diphenylmethane. DPM was recrystallized from a commercial sealed ampoule without 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 dimetallate 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 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.

Followed to equilibrium at constant temperature over a typical period of several days by UV–VIS spectroscopy.

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 was 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 permanent NMR spectrum of the dianion could be observed.

The ampoule containing the indicator was then broken and the derivative was resublimed in the 4 mm tube. The metal was distilled into the 14 mm tube and [2H₄]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.

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References

11 pKₐ studies are underway, I. O. Shapiro, M. Nir, R. E. Hoffman and M. Rabinovitz, to be published.

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