Acidity of dibasic carbon acids. Part 5.[1–4] The second acidity constant of 9,10-dihydrodibenz[*a*,*h*]anthracene in tetrahydrofuran—geometry, charge distribution of dianion, structure of dimetallic salts

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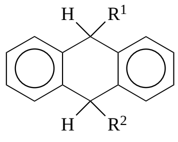
The second equilibrium ion pair acidity constant (pK_2) of 9,10-dihydrodibenz[*a*,*h*]anthracene (DBDHA, $1H_2$) with counter ions sodium (pK_2 28.5) and potassium (pK_2 30.4) has been determined in tetrahydrofuran (THF) at 298 K. This value is considerably lower than for other 9,10-dihydroanthracene derivatives. Disodium, dipotassium and dirubidium salts of DBDHA, *i.e.* 1^{2-}, exist as contact ion triplets in THF at 298 K, although the dilithium salt behaves as a solvent-separated ion triplet under the same conditions. In the dianion of DBDHA (1^{2-}) the negative charge is displaced from the deprotonated carbon atoms towards the outer benzene rings.

This report deals with the dependence of the second acidity constant (pK_2) of 9,10-dihydroanthracene (DHA) derivatives on the structure and size of the π-electron system of the dibasic carbon acid as well as the counter ion. Previously, we measured pK_2 values of DHA, 9-phenyl- and 9,10-diphenyl-9,10-dihydroanthracene (PDHA and DPDHA, respectively) in tetrahydrofuran (THF) with counter ions Na^+, K^+ and Rb^+.[1]



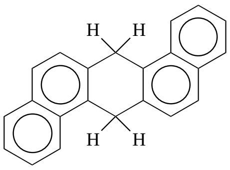
DHA: $R^1 = R^2 = H$
PDHA: $R^1 = H$; $R^2 = Ph$
DPDHA: $R^1 = R^2 = Ph$

It was found that pK_2 values of PDHA and DPDHA are close to those of DHA and they are very strongly dependent on the counter ion.

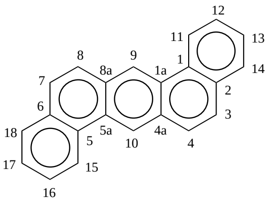
Analysis of the structure of PDHA and DPDHA dianions shows that the angle between the planes of the phenyl substituent and the anthracene ring is 45°.[2] It seems that the contribution of phenyl substituents to stabilization of the negative charge of anions is small and is mainly connected with the inductive effect. It is therefore interesting to estimate the contribution of the conjugation effect of annelated phenyl groups to the stabilization of the negative charge of the dianion of DHA. In view of the possible effect of extending the π-electrons array we studied dihydrodibenz[*a*,*h*]anthracene (DBDHA) ($1H_2$) and the corresponding dianion, *i.e.* 1^{2-}.

According to our calculations (see below) the dianion of DBDHA (1^{2-}) is planar and it follows that the two outer annelated phenyl ring extend the conjugation and thus the stabilization of the negative charge of the dianion of 9,10-dihydroanthracene by conjugation.

Here we report results of the calculations of the dianion geometry and the charge distribution, the structure of ion triplets of dimetallic salts and the pK_2 values of DBDHA ($1H_2$) (counter ions are Na^+ and K^+). Geometry and electron structure were calculated by the AM-1 method.[5] Ion formation of dimetallic salts of $1H_2$ is in the form of an ion triplet as it consists of one anion and two cations. The structure of the ion triplet (*vida supra*) was determined by UV–VIS spectroscopy



$1H_2$



1^{2-}

and pK_2 was found by measuring the equilibrium constant of transmetallation reaction of dimetallic salts of DBDHA ($1H_2$) with several indicator carbon acids with known pK values.

Results

Preparation of salts and UV–VIS spectroscopic measurements

Dimetallic salts were obtained by consecutive two-electron transfer to DBDHA (**1**) with alkali metals in THF. The first step is the formation of an anion radical and the second is the formation of the dimetallic salt [eqn. (1)], where M is an alkali metal.

$$\mathbf{1} \xrightarrow{\text{M, THF}} \mathbf{1}^{\cdot-}\mathrm{M}^+ \xrightarrow{\text{M, THF}} \mathbf{1}^{2-}\ 2\mathrm{M}^+ \qquad (1)$$

The UV–VIS spectra of the anion radical and the dianion are different. Therefore, it is possible to follow the reaction progress and to follow the complete conversion of anion radical to dianion. Dilithium and disodium salts of DBDHA ($1H_2$) are stable for several months. The dipotassium salt is less stable and undergoes decomposition after several days; dirubidium salts were decomposed after 5–6 h. The dicaesium salt is very unstable; it decomposes after several seconds.

UV–VIS spectroscopic data (λ_{max} and the molar extinction coefficients, ε) of the dimetallic salts are given in Table 1. Each extinction coefficient, ε, was determined in four to five concentrations, in the range 10^{-4} to 10^{-3} mol dm^{-3}.

In all cases Beer's law is adhered to over the entire concentration range used for pK_2 determination. The ε values are accurate to within ± 5%.

Equilibrium measurements

Ion triplet acidity (pK_2) of the monometallic salt of DBDHA ($1H_2$), *i.e.* $1H^-M^+$, is determined by measuring the equilibrium constant (K_{eq}) of the transmetallation reaction [eqn. (2)]

$$\mathbf{1}^{2-}\ 2M^+ + InH \overset{K_{eq}}{\rightleftharpoons} \mathbf{1}H^-M^+ + In^-\ M^+ \qquad (2)$$

of dimetallic salt ($\mathbf{1}^{2-}2M^+$) with an indicator (InH) that has a known pK_{InH}.

The pK_2 is determined by eqn. (3).

$$pK_2 = \log K_{eq} + pK_{InH} \qquad (3)$$

The obtained ion triplet acidity constants[1] are related to the scale of ion pair acidities in caesium cyclohexylamide (Cs^+). We used indicator pK values measured in cyclohexylamine (counter ion Cs^+);[6,7] the pK values of these indicators were also determined in THF (counter ions Cs^+) (Table 2).

The K_{eq} is given by eqn. (4), where [$\mathbf{1}H^-\ M^+$], [$In^-\ M^+$], [$\mathbf{1}^{2-}$ $2M^+$] and [InH] are equilibrium concentrations of monometallic salt of DBDHA ($\mathbf{1H_2}$), metallic salt of the indicator, dimetallic salt of DBDHA ($\mathbf{1H_2}$) and indicator, respectively.

$$K_{eq} = ([\mathbf{1}H^-\ M^+]\ [In^-\ M^+])/([\mathbf{1}^{2-}\ 2M^+]\ [InH]) \qquad (4)$$

The scale of the acidity of the indicators was measured in several solvents (cyclohexylamine, dimethoxyethane, THF and dimethyl sulfoxide) with different counter ions (Cs^+, K^+, Li^+).[8,9] It was found that the pK_a values of the indicators—alkylaromatic carbon acids—are practically independent of the solvent and the counter ion. However, the scale of the indicators in cyclohexylamine (counter ion Cs^+) included more carbon acids than other indicator scales.[8] This is the reason for using this scale for the determination of the pK_2 of DBDHA.

Equilibrium concentrations of [$\mathbf{1}H^-\ M^+$], ($In^-\ M^+$] and [InH] were found from the initial [$\mathbf{1}^{2-}\ 2M^+$]^0 and equilibrium [$\mathbf{1}^{2-}\ 2M^+$] concentration of dimetallic salt of DBDHA ($\mathbf{1H_2}$), initial concentration of the indicator acid [InH]^0 and the equations of material balance [eqns. (5–7)], where A_∞, A^0 are the intensities of the equilibrium and initial absorptions of the dimetallic salt of DBDHA, respectively, l is the length of the light path, ε is the extinction coefficient of the dimetallic salt of DBDHA, *i.e.* $\mathbf{1}^{2-}$.

$$[\mathbf{1}^{2-}\ 2M^+] = A_\infty/(l\ \varepsilon) \qquad (5)$$

$$[In^-\ M^+] = [\mathbf{1}H^-\ M^+]_\infty = (A^0 - A_\infty)/(l\ \varepsilon) \qquad (6)$$

$$[InH] = [InH]^0 - [(A^0 - A_\infty)/(l\ \varepsilon]) \qquad (7)$$

The pK_2 values of DBDHA ($\mathbf{1H_2}$) were determined by measuring K_{eq} of the transmetallation reaction of the disodium and dipotassium salts with three different indicators. The obtained pK_2 values are given in Table 3. With each indicator two or three independent determinations were made. With TPM (counter ion K^+) and BDPM (counter ion Na^+) pK_2 was determined only once. All measurements were carried out at a constant temperature of 25.0 ± 0.5 °C. It should be noted that the counter ion did not affect the indicator absorption.

Table 1 UV–VIS spectra of dimetallic salts of DBDHA–($\mathbf{1H_2}$) in THF at 298 K

Cation	λ_{max}/nm (ε/dm^{-3} mol^{-1} cm^{-1})	
Li^+	435 (—)	673 (—)
Na^+	406 (3.75×10^4)	656 (2.29×10^4)
K^+	409 (4.42×10^4)	665 (2.26×10^4)
Rb^+	412 (—)	669 (—)

All our attempts to measure the equilibrium constant of the reaction of the dilithium salt of DBDHA ($\mathbf{1H_2}$) with different indicators were unsuccessful. The reaction is extremely slow. The absorption of the dilithium salt in the reaction with 9-phenylxanthene (9-Phx) did not change during 30 d.

Discussion

Geometry and electronic structure of the dianion

Geometry, electron structure and heat of formation of the dianion were calculated by the AM-1 method. According to the results obtained DBDHA ($\mathbf{1H_2}$)$^{2-}$, *i.e.* $\mathbf{1}^{2-}$ dianion, is planar. The carbon–carbon bond lengths and the net charge on carbon atoms of the dianions are given in Table 4. Dianion formation leads to an alteration of the length of the carbon–carbon bonds of the dibenzoanthracene system.[1] Electron density is displaced from the deprotonated carbon atoms to the carbon atoms of the outer annelated benzene rings. The negative charge that is concentrated on the deprotonated carbon atoms is considerably less for the dianion of $\mathbf{1H_2}$ than for the dianions of other dihydroanthracene derivatives studied.[2] The heat of formation of the dianion of $\mathbf{1H_2}$ is also lower than that of the dianion of phenyl-substituted derivatives of dihydroanthracene. (Table 5). These results show that the dianion of $\mathbf{1H_2}$ is more stable than the dianion of dihydroanthracene and its phenyl substituted derivatives.

Structure of ion triplet of dimetallic salts

The structure of the ion triplets of dimetallic salts of $\mathbf{1H_2}$ was studied by UV–VIS spectroscopy. UV–VIS spectra of dimetallic salts of DBDHA ($\mathbf{1H_2}$) display absorptions in two regions: *ca.* 435 and at *ca.* 673 nm (Table 1). The absorption maxima of the dilithium salt is displaced towards longer wavelengths relative to the maxima of other salts. The absorption of disodium, dipotassium and dirubidium salts is successively displaced towards longer wavelengths as the cation radius is increased. (Table 1).

These results show that disodium, dipotassium and dirubidium salts of $\mathbf{1H_2}$ exist as contact ion triplets (CIT) in THF at 289 K, however, the dilithium salt exists as a solvent separated ion triplet (SSIT) under the same conditions.[4,11] Previously, we found that dialkali metal salts (including dilithium salt) of 9,10-dihydroanthracene and its derivatives exist as CIT in THF at 298 K.[4] Formation of SSIT for dilithium salts of $\mathbf{1H_2}$ indicates that there is a high degree of charge delocalization in its dianion.

The maxima of absorption of the monometallic salts of $\mathbf{1H_2}$ are displaced towards longer wavelengths relative to those of the dimetallic salts of dihydroanthracene. These results show that the mechanism of the negative charge stabilization of dimetallic salts of $\mathbf{1H_2}$ and phenyl substituted derivatives of dihydroanthracene is different.

The contribution of p,π-conjugation to the charge stabilization of dimetallic salts of $\mathbf{1H_2}$ is more significant than that for

Table 2 Maxima of absorption (λ_{max}) of caesium salt (in THF) and pK values of the indicator acids

Indicator	λ_{max}/nm THF (Cs^+)[6,7]	pK (CHA, Cs^+)[10]	pK (THF, Cs^+)[6,7]
9-Phenylxanthene (PhX)	491	28.5	28.7
Triphenylmethane (TPM)	488	31.4	31.3
Biphenyl-4-yldiphenylmethane (BDPM)	568	30.2	30.1
Bis(biphenyl-4-yl)methane (BBM)	557[a]	30.8	—

[a] In cyclohexylamine, counter ion Cs^+.

Table 3 Sodium, pK_2 (Na$^+$), and potassium, pK_2 (K^+), ion pair acidity constants of 9,10-dihydrodibenz[*a*,*h*]anthracene **1** in THF at 298 K

Indicator	pK_2 (Na$^+$)	pK_2 (K$^+$)
9-PhX	28.4 ± 0.1	—
TPM	28.6 ± 0.3	30.1
BDPM	28.5	30.3 ± 0.2
BBM	—	30.5 ± 0.3
Average	28.5 ± 0.3	30.4 ± 0.3

Table 4 The C–C bond lengths and net atomic charge on the carbon atoms of $\mathbf{1}^{2-\,a}$

C–C Bond	Length/Å	Carbon atom	Net charge
C1–C2 (C5–C6)	1.4423	C1 (C5)	−0.121
C2–C3 (C6–C7)	1.4107	C2 (C6)	+0.065
C3–C4 (C7–C8)	1.4107	C3 (C7)	−0.354
C4–C4a (C8–C8a)	1.3747	C4 (C8)	−0.113
C4a–C10 (C8a–C9)	1.4434	C4a (C8a)	−0.089
C10–C5a (C9–C1a)	1.3678	C1a (C5a)	+0.040
C5a–C5 (C1a–C1)	1.4570	C11 (C15)	−0.069
C5–C15 (C1–C11)	1.3946	C12 (C16)	−0.313
C15–C16 (C11–C12)	1.3952	C13 (C17)	−0.099
C16–C17 (C12–C13)	1.4009	C14 (C18)	−0.252
C17–C18 (C13–C14)	1.3951	C9 (C10)	−0.241
C18–C6 (C14–C2)	1.4296		
C1a–C4a (C5a–C8a)	1.4545		

[a] Calculated by the AM-1 method.

Table 5 Negative charge on the deprotonated carbon atoms, heat of dianion formation (ΔH_f) and pK_2 of DHA and its derivatives[1,2]

Dianion	Net electron density on the deprotonated carbon atoms	ΔH_f/kcal mol$^{-1\,b}$	pK_2 (Na$^+$)
DHA$^{=}$	−0.860	97.42	34.1
9-PDHA$^{=}$	−0.701	113.37	33.6
DPDHA$^{=}$	−0.664	130.06	32.0
DBDHA$^{=}$($\mathbf{1}^{2-}$)	−0.492^a	111.2^a	28.5 ± 0.3^a

[a] This paper. [b] 1 cal = 4.184 J.

the dimetallic salts of dihydroanthracene (long-wavelength displacement of $\lambda_{\max}$). For dimetallic salts of the phenyl and diphenyl derivative of dihydroanthracene, *i.e.* PDHA or DPDHA, the contribution of p,π-conjugation to the negative charge stabilization is reduced as compared with the dimetallic salts of dihydroanthracene DHA (short-wavelength displacement of $\lambda_{\max}$[1]). It follows that the dimetallic salts of 9-phenyl- and 9,10-diphenyl-dihydroanthracene, PDHA or DPDHA, respectively are mainly stabilized by cation–anion interaction.

Second acidity constant

The values of second acidity constants of $\mathbf{1H_2}$ are equal to 28.5 ± 0.3 (counter ion Na$^+$) and 30.4 ± 0.3 (counter ion K$^+$). The values are related to ion pair acidity scale in cyclohexylamine (counter ion Cs).[8,10] The p*K* values of the indicators are also measured in THF;[6,7] therefore, the pK_2 of $\mathbf{1H_2}$ can be related to the ion pair acidity scale in this solvent. In the ion pair acidity scale in THF the pK_2 of $\mathbf{1H_2}$ is equal to 28.5 ± 0.3 (counter ion Na$^+$) and 30.1 ± 0.2 (counter ion K$^+$).

The value of pK_2 of $\mathbf{1H_2}$ is considerably lower than that of other DHA derivatives and in particular the pK_2 of DPDHA.[1]

The difference between the pK_2 of DBDHA and DPDHA is equal to 3.5 p*K* units (Na$^+$ as counter ion) and 4.4 p*K* units (K$^+$ as counter ion). Comparison of the pK_2 of DHA (34.1; K$^+$), DPDHA (32.0; K$^+$) and $\mathbf{1H_2}$ (30.4; K$^+$) as well as the structure of their dianions shows that increase of the second acidity constant of the latter compound is related to the extended annelation with the outer benzene rings in the $\mathbf{1}^{2-}$ dianion. As these benzene rings are in the same plane of the anthracene moiety, they take part in the stabilization of the dianion by p,π-conjugation. Therefore, the displacement of the negative charge from the deprotonated carbon atoms into the π-array of $\mathbf{1H_2}$ is larger than the shift of charge delocalization into the π-array of DPDHA or DHA. The negative charge which is placed on the deprotonated carbon atoms is equal to 0.492 (electron charge) for the dianion of $\mathbf{1H_2}$ and 0.664 (electron charge) for the dianion of DPDHA (Table 5).

The increase of the contribution of the effect of p,π-conjugation which stabilizes the dianion of $\mathbf{1}^{2-}$ leads to a decrease of the contribution of the cation effect. The difference between pK_2 (K$^+$) and pK_2 (Na$^+$) is equal to 2.8 p*K* units and 1.6 p*K* units for DPDHA and $\mathbf{1H_2}$, respectively (Table 3). Nevertheless, this result shows that the cation–anion interaction still plays an important role in the stabilization of the dimetallic salts of $\mathbf{1H_2}$.

In conclusion, the high value of the second acidity constant pK_2 $\mathbf{1H_2}$ is rationalized by a considerable increase of the contribution of p,π-conjugation effect and the cation–anion interaction on the dianion stabilization of $\mathbf{1}^{2-}$.

Experimental

General

UV–VIS spectra were recorded on UVICON-860 spectrometer fitted with a thermostatically controlled cell holder. All experiments were carried out at constant temperature (25.0 ± 0.5 °C) maintained by a thermostatted bath (Forma Scientific 2095). Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Materials

Dibenz[*a*,*h*]anthracene 1. Commercially available dibenz-[*a*,*h*]anthracene (Aldrich) was twice crystallized from benzene–methanol, mp 266–268 °C (lit.,[12] 261–162 °C). Its UV–VIS spectrum was identical with that in the literature.[12]

Triphenylmethane (TPM). Commercially available TPM (Aldrich) was recrystallized from ethanol, mp 94 °C (lit.,[13] 94 °C).

9-Phenylxanthene (9PhX). 9PhX was prepared by reduction of a commercially available sample of 9-phenylxanthene-9-ol over 10% Pd/C under hydrogen pressure (2 bar) at room temp., and recrystallized from ethanol, mp 146–147 °C (lit.,[14] 147.8–148.1 °C).

Bis(biphenyl-4-yl)methane (BBM). BBM was prepared by hydrogenation of bis(biphenyl-4-yl)methanol over Pd/C. After twice recrystallizing from methanol, the white crystals showed mp 160–162 °C (lit.,[14] 162 °C). Bis(biphenyl-4-yl)methanol was prepared by the procedure given in ref. 14.

Biphenyl-4-yldiphenylmethane (BDPM). BDPM was obtained by reduction of biphenyl-4-yldiphenylmethanol over 10% Pd/C under hydrogen pressure (2 bar). The product obtained was recrystallized twice from methanol, mp 113–114 °C (lit.,[14] 113.5–114.5 °C). Biphenyl-4-yldiphenylmethanol was prepared from benzophenone and biphenyl-4-yllithium.[14]

Tetrahydrofuran (THF). The procedure for the purification of the commercial solvent and its preparation for the transmetallation reaction was given in ref. 1.

Equilibrium measurements. Apparatus and technical details of equilibrium experiments were described in a previous paper.[1]

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