

# Acidity of dibasic carbon acids. Part 2.<sup>1</sup> Geometry and electronic structure of mono- and di-anions of 9,10-dihydroanthracene and its derivatives in tetrahydrofuran

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The geometric structure, charge distribution and heats of formation of 9-R<sup>1</sup>-10-R<sup>2</sup>-9,10-dihydroanthracenes (R<sup>1</sup> = R<sup>2</sup> = H; R<sup>1</sup> = Me, R<sup>2</sup> = H; R<sup>1</sup> = R<sup>2</sup> = Me; R<sup>1</sup> = Ph, R<sup>2</sup> = H; R<sup>1</sup> = R<sup>2</sup> = Ph; R<sup>1</sup> = CN, R<sup>2</sup> = H), their mono- and di-anions, deprotonated at positions 9 and 10 have been calculated by the AM-1 method. The <sup>13</sup>C chemical shifts of the mono- and di-alkali metal salts have been determined in [<sup>2</sup>H<sub>8</sub>]THF. The structures of the mono- and di-anions are nearly planar, the dianions being more planar than the monoanions. The hybridization of the deprotonated carbon atoms is nearly sp<sup>2</sup>. Phenyl substituents subtend angles of 56.5° and 45.0° to the anthracene plane in the mono- and di-anions, respectively. With the exception of the cyano group, there is little participation by the substituents in the delocalization of negative charge. There is a correlation between the π-electron densities and the change in <sup>13</sup>C chemical shift upon anion formation from the neutral species. The values of the proportionality constants are equal to 120.3 and 133.1 ppm/electron for mono- and di-anions, respectively. The pattern of negative charge distribution in the monoanions of 9,10-dihydroanthracenes is similar to that of substituted diphenylmethanes. The first and second acidity constants of substituted 9,10-dihydroanthracenes in the liquid phase follow the patterns indicated by the gas phase calculations of their relative thermodynamic stabilities.

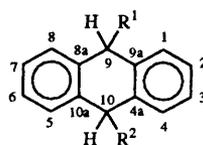
The mono- and di-metallic salts of 9,10-dihydroanthracene (DHA) and its derivatives are the subject of many studies concerning the effect of substituent, cation and solvent on reactivity.<sup>1-8</sup> A measure of the reactivity of the mono- and di-anions is the first (pK<sub>1</sub>) and the second (pK<sub>2</sub>) acidity constants of the corresponding mono- and di-basic carbon acids.

Bordwell,<sup>9,10</sup> Shatenshtein<sup>11,12</sup> and Streitwieser<sup>13,14</sup> measured the pK<sub>1</sub> values of DHA and several of its derivatives in cyclohexylamine, dimethoxyethane, tetrahydrofuran (THF) and dimethylsulfoxide (DMSO). The pK<sub>1</sub> values of these compounds were found to decrease with increasing electron withdrawal by the substituents but not to significantly change with the cation size.<sup>9-12</sup>

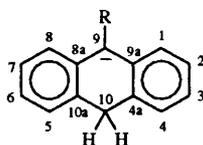
Streitwieser<sup>15,16</sup> was the first to measure the pK<sub>2</sub> value of DHA: 34.1 in cyclohexylamine with a Cs<sup>+</sup> counter ion. He explained its surprisingly low pK<sub>2</sub> value as being due to the high stability of the dimetallic salt of DHA on account of charge delocalization in the dianion and strong interaction between the dianion and its cations. We have previously determined the pK<sub>2</sub> values of DHA and its 9,10-substituted derivatives in THF with Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> as counter ions.<sup>1</sup> It was found that the pK<sub>2</sub> values of these dibasic acids are insensitive to substituent effects but are dependent on the cation size. These results show that the electronic structures and the ion solvation states of the monometallic salts of substituted DHA are different from those of the dimetallic salts. For this reason information regarding the spatial and electronic structures as well as the ion solvation state of the monometallic and dimetallic salts of DHA and its derivatives is very important for understanding the effects of the substituent, cation and solvent on their reactivity.

Here we report the results of semiempirical molecular orbital calculation (AM-1)<sup>17</sup> of the geometric structure and charge distribution of DHA and its derivatives as well as their mono- and di-anions. We also report the experimentally determined values of the <sup>13</sup>C NMR chemical shifts in [<sup>2</sup>H<sub>8</sub>]THF.

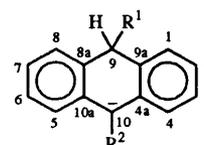
The geometric structures and charge distributions for some of these compounds and their mono- and di-carbanions have been calculated by the MNDO, AM-1, INDO and PM3



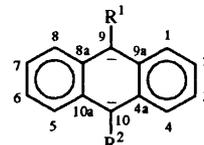
DHA R<sup>1</sup> = R<sup>2</sup> = H  
 MDHA R<sup>1</sup> = Me, R<sup>2</sup> = H  
 DMDHA R<sup>1</sup> = R<sup>2</sup> = Me  
 PDHA R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 DPDHA R<sup>1</sup> = R<sup>2</sup> = Ph  
 CNDHA R<sup>1</sup> = CN, R<sup>2</sup> = H



MDHA-9<sup>-</sup> R = Me  
 PDHA-9<sup>-</sup> R = Ph  
 CNDHA-9<sup>-</sup> R = CN



DHA<sup>-</sup> R<sup>1</sup> = R<sup>2</sup> = H  
 MDHA-10<sup>-</sup> R<sup>1</sup> = Me, R<sup>2</sup> = H  
 DMDHA<sup>-</sup> R<sup>1</sup> = R<sup>2</sup> = Me  
 DPDHA<sup>-</sup> R<sup>1</sup> = R<sup>2</sup> = Ph



DHA<sup>2-</sup> R<sup>1</sup> = R<sup>2</sup> = H  
 MDHA<sup>2-</sup> R<sup>1</sup> = Me, R<sup>2</sup> = H  
 DMDHA<sup>2-</sup> R<sup>1</sup> = R<sup>2</sup> = Me  
 PDHA<sup>2-</sup> R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 DPDHA<sup>2-</sup> R<sup>1</sup> = R<sup>2</sup> = Ph  
 CNDHA<sup>2-</sup> R<sup>1</sup> = CN, R<sup>2</sup> = H

methods,<sup>2-4,18</sup> and have also been determined by X-ray crystallography.<sup>19,20</sup> However, these determinations have been carried out by a variety of different methods, which makes comparison difficult. It is therefore interesting to calculate and to compare the geometric structures and the charge distributions for all the compounds and their mono- and di-anions using only one method.

## Results and discussion

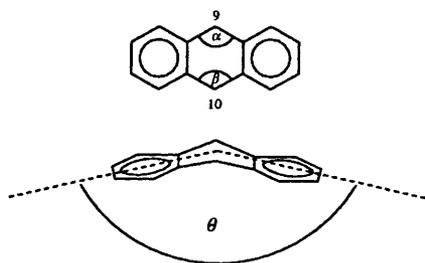
### Geometric structure

The calculations were carried out by the AM-1 method.<sup>17</sup> AM-1 is a quantitative quantum mechanical molecular modelling

**Table 1** Heats of formation ( $\Delta_f H$ , kcal mol<sup>-1</sup>), dihedral angle ( $\theta$ , °) inner angles  $\alpha$  and  $\beta$  (°), bond lengths between deprotonated carbon atoms (C-9 and -10) and neighbouring carbon atoms of the anthracene ring ( $r_{C9-C8a}$ ,  $r_{C10-C4a}$ , Å), bond length between C-9 or -10 and substituents R<sup>1</sup> ( $r_{C9-C1'}$ , Å) or R<sup>2</sup> ( $r_{C10-C1''}$ , Å)

Compound	$\Delta_f H$	$\theta$	$\alpha$	$\beta$	$r_{C9-C8a}$	$r_{C9-C1'}$	$r_{C10-C4a}$	$r_{C10-C1''}$
DHA	38.29 <sup>a</sup>	154.5 <sup>a</sup>	113.5	113.5 <sup>a</sup>	1.4881 <sup>a</sup>	1.1278	1.4881	1.1278
DHA <sup>-</sup>	20.77	176.0	121.3	115.6	1.4023	1.0952	1.4880	1.1285
DHA <sup>2-</sup>	97.42	179.7	122.4	122.4	1.4069	1.0962	1.4069	1.0962
MDHA	35.70	162.6 <sup>b</sup>	113.6	114.4	1.4950 <sup>b</sup>	1.5230 <sup>b</sup>	1.4874	1.1271
MDHA-9 <sup>-</sup>	16.20 <sup>c</sup>	170.0	120.0	115.1	1.4132 <sup>c</sup>	1.4769 <sup>c</sup>	1.4856	1.1290
MDHA-10 <sup>-</sup>	18.17 <sup>c</sup>	175.3	114.5	121.2	1.4964	1.5261	1.4020	1.0952
MDHA <sup>2-</sup>	94.19	178.6	121.1	122.2	1.4198	1.4743	1.4056	1.0962
DMDHA( <i>cis</i> )	32.68	156.5 <sup>d</sup>	113.0	113.0	1.4957	1.5220	1.4957	1.5220
DMDHA( <i>trans</i> )	34.55	172.8	114.4	114.4	1.4952	1.5258	1.4952	1.5258
DMDHA <sup>-</sup>	16.67	162.4	119.5	112.1	1.4135	1.4749	1.4980	1.5163
DMDHA <sup>2-</sup>	86.10	171.0	120.7	120.7	1.4169	1.4744	1.4169	1.4744
PDHA	70.88	156.2 <sup>e</sup>	112.9	113.6	1.4995	1.5040	1.4875	1.1279
PDHA-9 <sup>-</sup>	45.53 <sup>e</sup>	176.8	120.0	115.1	1.4213	1.4501	1.4853	1.1289
PDHA <sup>2-</sup>	113.37	179.2	118.6	121.4	1.4485	1.4140	1.4027	1.0953
DPDHA( <i>cis</i> )	104.12	165.2	113.7	113.7	1.4985	1.5041	1.4985	1.5042
DPDHA( <i>trans</i> )	104.40	158.9	113.1	113.1	1.4995	1.5046	1.4995	1.5046
DPDHA <sup>-</sup>	76.44	173.8	120.0	114.0	1.4197	1.4509	1.4962	1.5093
DPDHA <sup>2-</sup>	130.06	176.5	118.8	118.8	1.4353	1.4279	1.4353	1.4279
CNDHA	74.71	151.7	112.6	113.1	1.5008	1.4589	1.4879	1.1280
CNDHA-9 <sup>-</sup>	37.72	175.5	120.7	116.0	1.4179	1.4031	1.4852	1.1281
CNDHA <sup>2-</sup>	103.41	179.7	121.2	122.2	1.4314	1.3974	1.4047	1.0960

<sup>a</sup>  $\Delta_f H = 38.2$  kcal mol<sup>-1</sup>,<sup>21</sup>  $\theta = 159^\circ$ ,<sup>2</sup>  $\theta = 145^\circ$ ,<sup>19,20</sup>  $\alpha = 111 \pm 2^\circ$ ,<sup>19,20</sup>  $r_{C9-C8a} = 1.516$  Å,<sup>19,20</sup> <sup>b</sup>  $\theta = 153.2^\circ$ ,<sup>19,20</sup>  $r_{C9-C8a} = 1.516$  Å,<sup>19,20</sup> <sup>c</sup>  $\Delta_f H = 14.16$  kcal mol<sup>-1</sup> (for MDHA-9<sup>-</sup>) and  $\Delta_f H = 16.96$  kcal mol<sup>-1</sup> (for MDHA-10<sup>-</sup>),<sup>2</sup>  $r_{C9-C8a} = 1.435$  Å,  $r_{C9-C1'}$  = 1.495 Å,<sup>2</sup> <sup>d</sup>  $\theta = 152^\circ$  for *cis*-9-methyl-10-isopropyl-9,10-dihydroanthracene,<sup>21</sup> <sup>e</sup>  $\Delta_f H = 41.63$  kcal mol<sup>-1</sup>,<sup>2</sup>  $\theta = 180^\circ$ ,<sup>2</sup>  $\Delta_f H = 45.7$  kcal mol<sup>-1</sup>.<sup>18</sup>



program which is used as an aid to chemical experiment and in particular for studies of chemical reactions and reaction mechanisms. The initial calculation was carried out for the neutral compound. After optimization, the charge was added, the necessary protons removed and the structure reoptimized. All geometric parameters reported correspond to the optimal structure. The calculation of the structures of DMDHA and DPDHA was carried out for both the *cis* and the *trans* conformations. Monoanions of MDHA, PDHA and CNDHA can be obtained by removal of a proton from C-9 or -10. We calculated the structure and the charge distribution for the monoanion of MDHA obtained by deprotonation at C-9 and at -10 of MDHA. The structures and the charge distributions were calculated for the monoanions of PDHA and CNDHA, which are deprotonated at C-9. The parameters and the charge distributions of dianions were calculated for DHA and its derivatives by deprotonating at C-9 and -10.

The heats of formation and geometric parameters for the neutral compounds, mono- and di-anions of DHA and its derivatives are reported in Table 1. The Table also includes literature values<sup>2,18-21</sup> of the heats of formation, bond lengths,  $\theta$ ,  $\alpha$  and  $\beta$  angles for DHA, MDHA, DMDHA, PDHA, their monoanions and dianions. The dihedral angle ( $\theta$ ) is the angle between the two outer benzene rings of the anthracene framework and characterizes the deviation of the structure of the neutral compound and anions from the plane. The angles

$\alpha$  and  $\beta$  are the internal angles at the deprotonated C-9 and -10 atoms, respectively.

According to the data in Table 1 the C-9 and -10 atoms in the parent carbon acids are sp<sup>3</sup> hybridized. The  $\alpha$  and  $\beta$  angles are always found to be equal to  $113.5 \pm 1.0^\circ$ . This value is close to the value of the tetrahedral angle ( $109.5^\circ$ ) which is characteristic of sp<sup>3</sup> hybridization. The bond lengths of the bonds to C-9 and -10 in the parent compounds are  $1.48 \pm 0.01$  Å, similar to the C-C bond lengths of an sp<sup>3</sup> hybridized carbon atom. Consequently, DHA and its derivatives are non-planar. The central six-membered ring in their molecules has a 'pseudo-boat' structure. The dihedral angle ( $\theta$ ) in DHA and its derivatives depends on the nature of the substituents and their orientation for doubly substituted derivatives.

The heats of formation for the *cis*-isomers of DMDHA and DPDHA are smaller than for the *trans*-isomers and is independent of the degree of planarity of the anthracene unit. The  $\theta$  angle for *trans*-isomer of DMDHA is closer to  $180^\circ$  than for the *cis*-isomer of this compound, but the opposite is true for the  $\theta$  values for *cis*- and *trans*-isomers of DPDHA.

The formation of monoanions changes the hybridization of the deprotonated carbon atom. The angle between the chemical bond of this carbon increases to  $120.0 \pm 1.5^\circ$ . The bond lengths of the bonds between the deprotonated carbon atom and the neighbouring carbon atoms of the anthracene framework decreases by between 0.08 and 0.09 Å and the bond length of the bonds between the deprotonated carbon atoms and the carbon atom of the substituent decreases by between 0.04 and 0.05 Å. Such changes are typical of the change from sp<sup>3</sup> to sp<sup>2</sup> hybridization. The change of hybridization of the deprotonated carbon atom increases the planarity of the central ring of the anthracene unit. The value of the  $\theta$  angle increases by between  $8^\circ$  and  $25^\circ$  and the increase of planarity of the anthracene unit is conducive to the displacement of negative charge from the deprotonated carbon to other carbon atoms.

Dianion formation changes the hybridization of the second deprotonated carbon atom. It also becomes nearly sp<sup>2</sup> hybridized. The result of this process is a further increase of planarity of the central anthracene ring with the  $\theta$  angle

becoming practically equal to 180°. The negative charge is displaced from the deprotonated carbon atoms to all the carbon atoms of the anthracene ring and to the carbon atoms of the substituents. According to our calculations and results reported elsewhere,<sup>2</sup> MDHA-9<sup>-</sup> is more stable than MDHA-10<sup>-</sup> by about 2 kcal mol<sup>-1</sup>. However, during the reaction of the dimetallic salts of MDHA with a proton donor monometallic salts of MDHA-10<sup>-</sup> are formed.<sup>2,5</sup> The main reason for the difference between experimental and calculated results is related to the ionic interaction of the monometallic salts of MDHA. MDHA-10<sup>-</sup> mainly forms contact ion pairs (CIP) with alkali metals, but MDHA-9<sup>-</sup> forms solvent separated ion pairs (SSIP) with the same metals.<sup>22-25</sup> For example we found that MDHA-10<sup>-</sup>Na<sup>+</sup> is 60% CIP and MDHA-9<sup>-</sup>Na<sup>+</sup> is 36% CIP at 260 K.<sup>22</sup>

Interaction with the cation usually increases anion stability. That is why the  $\lambda_{\max}$  of CIP is less than that of SSIP.<sup>26,27</sup> The greater stability of CIP and larger CIP concentration for salts of MDHA-10<sup>-</sup> are reasons for the protonation reaction of dimetallic salts of MDHA to yield preferentially the monometallic salts of this anion.

### Substituent orientation

In 9,10-disubstituted DHA, the connecting atom of the substituent (C-1') is located at one of the vertices of a tetrahedron which has C-9 or -10 as its centre and C-4a and -10a or C-8a and -9a at two of the other vertices. The angle between the substituent and the hydrogen atom is similar to the tetrahedral angle (109.5°) independent of the substituent size. Deprotonation of 9,10-substituted DHA derivatives leads to displacement of the substituent towards the plane of the central anthracene ring. The angle between the bonds of the deprotonated carbon atom, the substituent and the neighbouring carbon atoms of the anthracene unit all became equal to 120.0 ± 0.5°.

For the mono- and di-anions of phenyl substituted DHA, the orientation of the substituents relative to the plane of the anthracene unit is also very important because p- $\pi$ -conjugation between the p-electrons of the anionic centre and the  $\pi$ -electron system of the substituent is possible if they are co-planar. According to our calculations the dihedral angle between the planes of the phenyl substituent and the anthracene unit for monoanions of PDHA and DPDHA is equal to 56.5°. A similar value was reported by Rabideau *et al.*<sup>18</sup>

Dianion formation leads to a decrease in the dihedral angle between the planes of the phenyl substituents and the anthracene unit. In dianions of PDHA and DPDHA this angle is equal to 45.0°. There is a significant change in the bond lengths of the C-9-C-8a and C-9-C-1' bonds upon conversion of monoanion to dianion for PDHA, DPDHA, and to a lesser extent, CNDHA (Table 1). The bond length C-9-C-8a in the anthracene ring increases by between 0.013 and 0.027 Å while the bond length C-9-C-1' of the substituent decreases by between 0.006 and 0.035 Å. This shows that the outer benzene rings of the anthracene unit hinder the approach of bulky substituents to the anionic centres of PDHA and DPDHA.

Increasing p- $\pi$ -conjugation between the p-electrons of deprotonated carbon atoms and the  $\pi$ -electron system of substituents in the dianions decreases the C-9-C-1' bond length. However, repulsion between the outer benzene rings of the anthracene unit and the phenyl substituents hinders this process. Therefore the substituents are twisted out of the anthracene ring plane. On the other hand, the approach of the phenyl substituents to the anionic centre causes repulsion of the outer benzene rings of the anthracene unit. Hence, the bond lengths C-9-C-8a and C-9-C-9a as well as C-10-C-4a and C-10-C-10a (for DPDHA<sup>2-</sup>) increase, *i.e.* in dianions, the outer rings of the anthracene unit twist the phenyl substituents from its plane.

### Charge distribution in mono- and di-anions

Changes in the hybridization of the deprotonated carbon atoms and the geometric structure of the anthracene framework upon formation of mono- and di-anions leads to a redistribution of the  $\pi$ -electron density in the anthracene ring. The negative charge is displaced from the deprotonated carbon atoms to the outer benzene rings of the anthracene unit because of p- $\pi$ -interaction.

The calculated values of the total and  $\pi$ -electron density on the carbon atoms of the mono- and di-anions of DHA and its derivatives are shown in Tables 2 and 3. In monoanions, over 40% of the  $\pi$ -electron density remains on the deprotonated carbon atom. The remainder is dispersed around the anthracene unit and concentrated on the *ortho* (to the deprotonated carbon atom, C-10), (C-4, -5, -8a and -9a) and *para* carbons (C-2 and -7) of the outer benzene rings (Table 2). Dianion formation changes the  $\pi$ -electron density. About 85% of the density remains on the deprotonated carbon atoms. The remaining significant part is concentrated on C-1, -4, -5 and -8, while a small amount of  $\pi$ -electron density is located at C-2, -3, -6 and -7 (Table 3).

Because of the orientation of the phenyl substituents relative to the anthracene unit in the anions of PDHA and DPDHA, p- $\pi$ -conjugation of the negative charge with the  $\pi$ -electron system of the substituents is very limited. The carbon atoms of the phenyl substituents are even positively charged (Table 2). The dianions of PDHA and DPDHA have a smaller dihedral angle between the substituents and the anthracene plane than for the monoanions and the  $\pi$ -electron density on the substituents is slightly greater (Table 3) as compared to the monoanions. The *ortho* (C-2') and *para* (C-4') carbons of the phenyl substituent in the dianions of PDHA and DPDHA are negatively charged.

Comparison of the total and  $\pi$ -electron densities on the deprotonated carbon atoms (C-9 and -10) of mono- and di-anions of derivatives of DHA, with the exception of MDHA and DMDHA, shows that the  $\pi$ -electron density is larger than the total electron density. It may therefore be concluded that there is a charge stabilization on deprotonated carbon atoms in mono- and di-anions arising from an inductive effect of the substituent for PDHA, DPDHA and even CNDHA. Consequently, the monoanions and dianions of DHA and its derivatives are mainly stabilized by distribution of negative charge around the anthracene unit. The substituent effect on charge distribution is weak.

### Heats of idodesmic reaction for anion formation

The heats of formation ( $\Delta_f H$ ) of DHA and its 9,10-substituted derivatives and their mono- and di-anions are given in Table 1. It is noteworthy that the  $\Delta_f H$  values of DHA and its derivatives are larger than those of their corresponding monoanions. This has also been established for other species.<sup>4</sup> This effect arises from an artifact of the semiempirical SCF-MO method. The heat of formation of molecules and anions is obtained by subtracting the electronic energies ( $E_{el}^A$ ) from the total energy ( $E_{tot}^{mol}$ ) of these species and adding the experimental heats of formation ( $\Delta_f H^A$ ) of the atoms in the molecule or anion [eqn. (1)].<sup>28</sup>

$$\Delta_f H = E_{tot}^{mol} - \Sigma E_{el}^A + \Sigma \Delta_f H^A \quad (1)$$

The total energy ( $E_{tot}^{mol}$ ) is the sum of electronic energy ( $E_{el}$ ) and the repulsions ( $E_{AB}^{core}$ ) between the cores of atoms A and B [eqn. (2)].<sup>28</sup>

$$\Delta E_{tot}^{mol} = E_{el} + \Sigma \Sigma E_{AB}^{core} \text{ for all } A < B \quad (2)$$

A limitation of semiempirical methods is that, the repulsions ( $E_{AB}^{core}$ ) are not evaluated analytically but are determined either

**Table 2** Calculated  $\pi$ - and total ( $\sigma + \pi$ )-electron densities on carbon atoms of monoanions of DHA and its derivatives<sup>a</sup>

R <sup>1</sup>	R <sup>2</sup>	C1,8	C2,7	C3,6	C4,5	C4a,10a	C8a,9a	C9	C10	C1'	C2'	C3'	C4'
H	H	-0.001 (-0.095)	-0.175 (-0.265)	-0.004 (-0.101)	-0.132 (-0.231)	0.110 (0.109)	-0.114 (-0.163)	0.023 (-0.029)	-0.369 (-0.412)				
Me	H	0.004 (-0.091)	-0.174 (-0.266)	-0.003 (-0.101)	-0.130 (-0.230)	0.110 (0.109)	-0.115 (-0.161)	0.060 (0.019)	-0.367 (-0.412)				
Me	Me	0.001 (-0.096)	-0.154 (-0.256)	-0.003 (-0.105)	-0.112 (-0.226)	0.104 (0.110)	-0.096 (-0.151)	0.014 (0.013)	-0.372 (-0.371)	0.033 (-0.095)			
H <sup>b</sup>	Ph <sup>b</sup>	-0.005 (-0.102)	-0.145 (-0.242)	-0.006 (-0.108)	-0.103 (-0.217)	0.111 (0.123)	-0.104 (-0.153)	0.018 (-0.037)	-0.413 (-0.358)	0.106 (0.094)	0.013 (-0.159)	0.026 (-0.137)	0.029 (-0.188)
Ph	Ph	0.012 (-0.089)	-0.140 (-0.241)	-0.001 (-0.106)	-0.098 (-0.215)	0.111 (0.123)	-0.120 (-0.160)	0.091 (0.048)	-0.409 (-0.360)	0.104 (0.092)	0.013 (-0.157)	0.030 (-0.137)	0.039 (-0.186)
H <sup>b</sup>	CN <sup>b</sup>	-0.006 (-0.105)	-0.131 (-0.232)	-0.005 (-0.109)	-0.093 (-0.205)	0.111 (0.123)	-0.097 (-0.145)	0.014 (-0.040)	-0.437 (-0.321)	0.092 (-0.060)	-0.214(N) (-0.232N)		

<sup>a</sup> The total ( $\sigma + \pi$ )-electron densities are in brackets. <sup>b</sup> The numbering in this Table is done so that the deprotonation is at C-10 which is not the standard numbering for PDHA-9<sup>-</sup> and CNDHA-9<sup>-</sup>. This was done to allow comparison of the  $\pi$ -electron densities with other derivatives of DHA. The standard notation is used in the remainder of this work.

**Table 3** Calculated  $\pi$ - and total ( $\sigma + \pi$ )-electron densities on carbon atoms of dianions of DHA and its derivatives<sup>a</sup>

R <sup>1</sup>	R <sup>2</sup>	C1,8	C2,7	C3,6	C4,5	C4a,10a	C8a,9a	C9	C10	C1'	C2'	C3'	C4'
H	H	-0.256 (-0.313)	-0.132 (-0.194)	-0.132 (-0.194)	-0.256 (-0.313)	0.087 (0.079)	0.087 (0.079)	-0.399 (-0.430)	-0.399 (-0.430)				
Me	H	-0.235 (-0.299)	-0.138 (-0.203)	-0.119 (-0.183)	-0.253 (-0.312)	0.089 (0.081)	0.085 (0.081)	-0.420 (-0.395)	-0.401 (-0.434)	0.057 (-0.067)			
Me	Me	-0.232 (-0.296)	-0.128 (-0.195)	-0.128 (-0.195)	-0.232 (-0.296)	0.085 (0.088)	0.085 (0.088)	-0.410 (-0.394)	-0.410 (-0.394)	0.056 (-0.067)			
Ph	H	-0.093 (-0.193)	-0.157 (-0.238)	-0.065 (-0.144)	-0.207 (-0.283)	0.102 (0.093)	0.034 (0.032)	-0.322 (-0.275)	-0.390 (-0.435)	0.088 (0.079)	-0.028 (-0.223)	0.012 (-0.116)	-0.114 (-0.332)
Ph	Ph	-0.117 (-0.225)	-0.093 (-0.189)	-0.093 (-0.189)	-0.117 (-0.225)	0.065 (0.068)	0.065 (0.068)	-0.369 (-0.332)	-0.369 (-0.332)	0.111 (0.111)	-0.013 (-0.201)	0.014 (-0.123)	-0.068 (-0.269)
CN	H	-0.163 (-0.242)	-0.149 (-0.221)	-0.090 (-0.162)	-0.232 (-0.298)	0.068 (0.072)	0.099 (0.094)	-0.467 (-0.347)	-0.412 (-0.446)	0.106 (0.018)	-0.298(N) (-0.344N)		

<sup>a</sup> The total ( $\sigma + \pi$ )-electron densities are in brackets.

from experimental data or from semiempirical expressions which contain numerical parameters that can be adjusted to fit the experimental data.<sup>28</sup> Therefore the simplifications and assumptions accepted for calculation of  $E_{AB}^{\text{core}}$  may lead to a systematic error leading to an abnormal relationship between the  $\Delta_r H$  values of the monoanions and the neutral molecules.

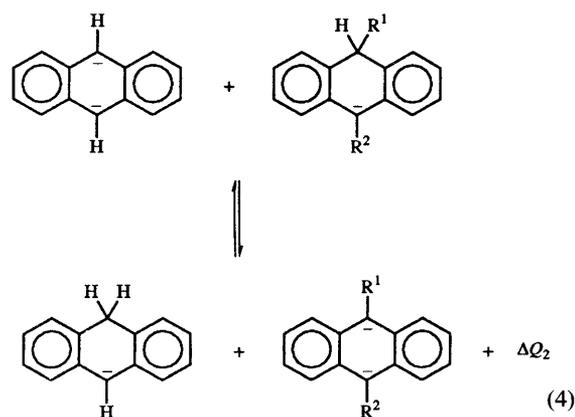
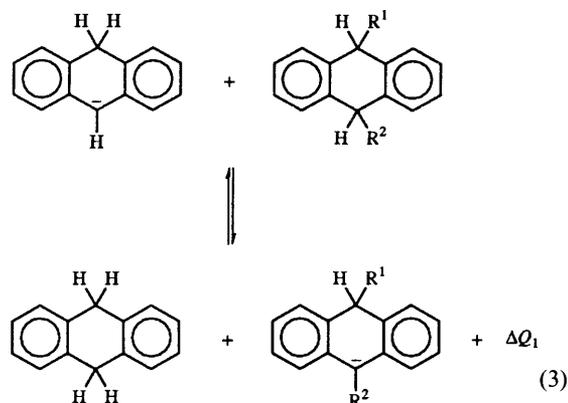
From the  $\Delta_r H$ , it is possible to calculate the heat of isodesmic reaction ( $\Delta Q_1$ ) of monoanions of DHA with substituted derivatives of DHA [eqn. (3)] and the reaction ( $\Delta Q_2$ ) of dianions of DHA with monoanions of substituted derivatives of DHA [eqn. (4)].

The  $\Delta Q_1$  and  $\Delta Q_2$  values characterize the relative thermodynamic acidities of substituted DHA ( $pK_{a1}$ ) and their monoanions ( $pK_{a2}$ ) in the gas phase [eqn. (5)] where  $R$  is the gas constant,  $T$  is temperature,  $a$  is a constant and  $n = 1$  or 2].

$$\Delta Q_n = -RTpK_n + a_n \quad (5)$$

In Table 4, the heat of isodesmic reaction [ $\Delta Q_1$ , eqn. (3)] between the monoanion of DHA and substituted DHA are compared with the  $pK_1$  values (determined in DMSO with a K<sup>+</sup> counter ion) of the corresponding substituted DHA<sup>9,10</sup> and with  $pK_1$  values of 9,9-dimethyl-9,10-dihydroanthracene, 9,9,10-trimethyl-9,10-dihydroanthracene and 9,9-dimethyl-10-phenyl-9,10-dihydroanthracene (determined in cyclohexylamine with a Cs<sup>+</sup> counter ion).<sup>13</sup> In Table 5, the heat of isodesmic reaction [ $\Delta Q_2$ , eqn. (4)] between the dianions of DHA and the monoanions of substituted DHA are compared with the  $pK_2$  values of substituted DHA, determined in THF with a Na<sup>+</sup> counter ion.<sup>1</sup>

The  $pK_1$  and  $pK_2$  values display the same trends as observed for  $\Delta Q_1$  and  $\Delta Q_2$  for the corresponding isodesmic reactions. This shows that the stability of the mono- and di-anions



**Table 4** Heat of isodesmic reactions [ $\Delta Q_1$ , eqn. (3)] and  $pK_1$  values of DHA and its derivatives

Property	DHA	MDHA	PDHA	CNDHA
$\Delta Q_1^a$	0	-1.98	-7.83	-19.47
$pK_1^b$	30.1	—	28.8	14.3
$pK_1^c$	30.3	30.3	28.1	—

<sup>a</sup> In kcal mol<sup>-1</sup>. <sup>b</sup> Measured in dimethyl sulfoxide with a K<sup>+</sup> counter ion. <sup>9,10</sup> <sup>c</sup>  $pK_1$  values for corresponding derivatives of 9,9-dimethyl-9,10-dihydroanthracene in cyclohexylamine with a Cs<sup>+</sup> counter ion.<sup>13</sup>

**Table 5** Heat of isodesmic reactions [ $\Delta Q_2$ , eqn. (4)] and  $pK_2$  values of DHA and its derivatives

Property	DHA	PDHA	CNDHA	DPDHA
$\Delta Q_2^a$	0	-8.81	-10.96	-23.03
$pK_2^1$	34.1	33.6	32.6	32.0

<sup>a</sup> In kcal mol<sup>-1</sup>.

determines the first and second acidity constants of DHA and its derivatives. Changes in the anion stability ( $\Delta Q$ ) have a greater influence on the  $pK_1$  than on the  $pK_2$  of DHA and its derivatives (Tables 4 and 5). A decrease of  $\Delta Q_1$  by 19.5 kcal mol<sup>-1</sup> increases  $pK_1$  by about 15 units while a decrease of  $\Delta Q_2$  by 23 kcal mol<sup>-1</sup> increases  $pK_2$  by about 2 units. This is due to the greater influence of cation-anion interaction on the stability of dimetallic salts than on monometallic salts. The interaction between mono- and di-anions of DHA and its derivatives with cations is the subject of a forthcoming paper.<sup>22</sup>

### <sup>13</sup>C NMR analysis of hybridization of carbon atoms and of charge distribution in mono- and di-anions

One of the most effective experimental methods to study the atomic state and the charge distribution in charged species in solution is NMR spectroscopy. The one-bond <sup>13</sup>C-<sup>1</sup>H coupling constants, the chemical shifts and the direction of their displacement upon conversion of the parent compound to its corresponding charged species permits the establishment of the existence of the hybridization of carbon atoms and charge distribution.<sup>29,30</sup> The <sup>13</sup>C chemical shifts for derivatives of DHA and anthracene, their mono- and di-alkali metal salts are shown in Table 6.

The <sup>13</sup>C chemical shifts of the C-9 atoms for DHA, MDHA and PDHA are 36.7, 41.1 and 52.4 ppm, respectively. Deprotonation at C-9 and/or C-10 displaces the <sup>13</sup>C-chemical shift of these atoms by about 40 ppm downfield. As a result, the chemical shifts of C-9 and -10 in anions are closer to the chemical shifts of C-9 and -10 of anthracene and its corresponding derivatives. From these results it can be assumed that anion formation changes the hybridization of the deprotonated carbon atoms from sp<sup>3</sup> to nearly sp<sup>2</sup>.

The <sup>13</sup>C chemical shifts of *ortho* (to the site of deprotonation) and especially *para* carbons in monometallic salts are displaced upfield. However, the <sup>13</sup>C chemical shifts of the *ipso* carbons are displaced downfield. This change is similar to the situation for carbanions of alkyaromatic compounds, in particular, for diphenylmethane and its  $\alpha$ -substituted derivatives.

In Table 7 the <sup>13</sup>C chemical shifts of the monometallic salts of diphenylmethane, triphenylmethane, DHA, PDHA are compared. The <sup>13</sup>C chemical shifts of the deprotonated site of the monoanions of DHA, PDHA and the anions of diphenyl- and triphenyl-methane are practically the same.

The *para* carbon atoms (to the deprotonated site) of monoanions of diphenylmethane, DHA and their phenyl derivatives are shielded between 14–19 ppm and the chemical shifts of the *ortho* carbon atoms are shielded by between 6

and 19 ppm compared to their precursors. Chemical shifts for the *ipso* carbon atoms of the monoanions of these compounds are displaced downfield by between 5 and 9 ppm. The shielding of the *meta* carbon atoms of the monoanions is practically unchanged compared to their precursors. The  $\Delta\delta_C$  values for the deprotonated carbon atoms of DHA and PDHA are close to the maximum known value for a deprotonated carbon atom of a salt of a delocalized carbanion.<sup>29</sup> Such large shifts can be explained by the deprotonated carbons of monoanions of DHA and its derivatives being sp<sup>2</sup> or nearly sp<sup>2</sup> hybridized.

Dianion formation changes the hybridization of the second deprotonated carbon atom. Its <sup>13</sup>C chemical shift is equal to the <sup>13</sup>C chemical shift of the monoanionic centre. The <sup>13</sup>C chemical shifts of all the carbons of the outer benzene rings of the anthracene unit also change. The chemical shifts of C-1, -2, -3 and -4 are displaced upfield by between 9 and 27 ppm, while those of C-4a and -8a shift downfield by between 7 and 17 ppm (Table 6). These results confirm the sp<sup>2</sup> or near sp<sup>2</sup> hybridization of C-9 and -10. The phenomenon is in line with the charge alternation observed in other dianionic systems.<sup>33,34</sup>

The hybridization of carbon atoms can be estimated from the one-bond <sup>13</sup>C-<sup>1</sup>H coupling constant (<sup>1</sup>J<sub>CH</sub>). The dependence <sup>1</sup>J<sub>CH</sub> and the contribution of s-character (*s*) to the C-H bond is expressed by eqn. (6) and corresponds to sp<sup>*n*</sup> hybridization where  $n = 1/s - 1$  [eqn. (7)].<sup>35</sup> This expression is, however,

$${}^1J_{CH} = 500s \quad (6)$$

$$n = 500/{}^1J_{CH} - 1 \quad (7)$$

only approximate as electronegativity and bond length also affect the coupling constant slightly.

To estimate the hybridization of the carbon atoms of anthracene, DHA, its mono- and di-anions, the <sup>1</sup>J<sub>CH</sub> was measured (Table 8). The results are equally applicable to derivatives of DHA, whose deprotonated carbons are not connected to protons. The C-9 and -10 of DHA are sp<sup>3</sup> hybridized while the remaining carbons are sp<sup>2</sup> hybridized. Deprotonation of DHA increases the s-character of the CH bond at the carbanion centre to approximately sp<sup>2.4</sup>.

Comparison of the  $\Delta\delta_C$  values for carbon atoms of the anthracene framework of mono- and di-anions of salts of DHA with those for substituted DHA shows, with the exception of anions of CNDHA, that  $\Delta\delta_C$  is relatively insensitive to substituent effects. The  $\Delta\delta_C$  values for the mono- and di-metallic salts of DHA derivatives are very similar to the  $\Delta\delta_C$  for the corresponding carbon atoms of mono- and di-metallic salts of DHA (Table 6). The  $\Delta\delta_C$  values for the deprotonated C-9 and -10 of dianions which would be expected to be the most sensitive to substituent effects all fall between 47 and 51 ppm except for anions of CNDHA. The change in <sup>13</sup>C chemical shifts of carbon atoms of substituents are also small. For example, the <sup>13</sup>C chemical shifts of the *ortho* (C-2') and *para* (C-4') carbons of the phenyl substituents of anions of PDHA and DPDHA are displaced by less than 10 ppm. The influence of the CN group on the <sup>13</sup>C chemical shifts of the anthracene unit is somewhat larger than that caused by other substituents. All the <sup>13</sup>C chemical shifts for the mono- and di-anions of CNDHA significantly differ from those of other anions of derivatives of DHA. This difference is especially large for the deprotonated carbon (C-9) and the *para* carbon (C-3) (Table 6).

It is well established that there is a linear relationship between <sup>13</sup>C chemical shifts and charge densities on the corresponding carbon atoms.<sup>30,36–39</sup> This relationship can be expressed by eqn. (8).  $\Delta\delta_C$  is the difference between <sup>13</sup>C chemical shifts of

$$\Delta\delta_C = K_C\Delta q^i + b \quad (8)$$

carbon atom C<sub>i</sub> of the charged species and its neutral precursor.

**Table 6**  $^{13}\text{C}$  chemical shifts of anthracene, its derivatives, mono- and di-alkali metal salts of DHA and its derivatives

Compound	Anthracene unit								Substituent			
	C-1	C-2	C-3	C-4	C-4a	C-8a	C-9	C-10	C-1'	C-2'	C-3'	C-4'
Anthracene	128.9	126.1	126.1	128.9	132.8	132.8	126.9	126.9				
DHA	126.7	128.0	128.0	126.7	137.7	137.7	36.7	36.7				
DHA <sup>-</sup> Na <sup>+</sup>	126.7	110.7	126.3	114.7	146.4	120.5	39.9	72.1				
DHA <sup>2-</sup> 2Na <sup>+</sup>	101.8	116.0	116.0	101.8	152.2	152.2	77.7	77.7				
$\Delta_1^a$	-2.2	-15.4	0.2	-14.2	13.6	-12.3	-87.0	-54.8				
$\Delta_2^b$	-27.1	-10.1	-10.1	-27.1	19.4	19.4	-49.2	-49.2				
9-Methylanthracene	125.4	126.0	125.5	129.8	132.6	131.2	128.0	126.1	23.6			
MDHA <sup>31</sup>	127.1	126.6	126.2	127.9	136.0	142.0	41.1	35.1	23.6			
MDHA-10 <sup>-</sup> Na <sup>+</sup>	127.1	110.1	126.3	114.9	143.0	125.4	43.4	79.1	24.9			
MDHA <sup>2-</sup> 2Na <sup>+</sup>	100.6	116.3	116.0	101.2	151.8	149.2	77.5	79.0	11.8			
$\Delta_1^a$	1.7	-15.9	0.8	-14.9	10.4	-5.8	-84.6	-47.0	1.3			
$\Delta_2^b$	-24.8	-9.7	-9.5	-28.6	19.2	18.0	-50.5	-47.1	-11.8			
9,10-Dimethylanthracene	126.0	125.3	125.3	126.0	131.0	131.0	128.9	128.9	23.4			
<i>cis</i> -DMDHA <sup>31</sup>	128.0	126.4	126.4	128.0	140.6	140.6	40.0	40.0	28.6			
<i>trans</i> -DMDHA <sup>31</sup>	126.0	126.4	126.4	126.0	141.5	141.5	38.5	38.5	18.8			
DMDHA <sup>2-</sup> 2Na <sup>+</sup>	99.9	116.1	116.1	99.9	148.9	148.9	77.8	77.8	12.0			
$\Delta_2^b$	-26.1	-9.2	-9.2	-26.1	17.9	17.9	-51.1	-51.1	-11.4			
9-Phenylanthracene	127.4	126.1	125.8	129.2	132.5	131.2	139.8	127.4	137.8	132.0	129.2	128.3
PDHA	129.2	127.1	127.0	128.5	140.7	137.4	52.4	36.2	145.0	128.7	129.0	126.8
PDHA-9 <sup>-</sup> Na <sup>+</sup>	112.2	125.8	110.8	126.5	121.5	142.5	90.8	40.5	147.3	133.3	128.8	121.0
PDHA <sup>2-</sup> 2Na <sup>+</sup>	101.6	114.4	118.1	103.9	147.9	151.4	89.9	78.6	146.9	132.8	129.1	119.7
$\Delta_1^a$	-15.2	-0.3	-15.0	-2.7	-11.0	11.3	-49.0	-86.9	9.5	1.3	-0.4	-7.3
$\Delta_2^b$	-25.8	-11.7	-7.7	-25.3	15.4	20.2	-49.9	-48.8	9.1	0.8	-0.1	-8.6
9,10-Diphenylanthracene	127.6	125.6	125.6	127.6	130.9	130.9	140.2	140.2	138.0	132.1	129.1	128.3
DPDHA <sup>-</sup> Na <sup>+</sup>	128.5	110.5	125.7	113.5	140.4	123.4	54.8	91.5	147.3	127.8	127.8	125.0
DPDHA <sup>2-</sup> 2Na <sup>+</sup>	102.4	116.3	116.3	102.4	148.1	148.1	90.5	90.5	151.0 <sup>c</sup>	133.7 <sup>c</sup>	128.6 <sup>c</sup>	121.6 <sup>c</sup>
$\Delta_1^a$	0.9	-15.1	0.1	-14.1	9.5	-7.5	-85.4	-48.7	147.1	134.0	129.6	120.9
$\Delta_1^a$									13.0 <sup>c</sup>	1.6 <sup>c</sup>	-0.5 <sup>c</sup>	6.7 <sup>c</sup>
$\Delta_2^b$	-25.2	-9.3	-9.3	-25.2	17.2	17.2	-49.7	-49.7	9.1	1.9	0.5	-7.4
9-Cyanoanthracene	125.8	130.0	127.2	130.0	131.8	134.1	117.2	133.7	106.4			
CNDHA-9 <sup>-</sup> Li <sup>+</sup>	117.0	126.4	116.1	126.9	123.9	141.2	55.4	36.5	132.7			
CNDHA <sup>2-</sup> 2Na <sup>+</sup>	111.8	112.0	121.2	106.5	140.4	149.0	53.9	74.2	136.5			
$\Delta_1^a$	-8.8	-3.6	-11.1	-3.1	-7.9	7.1	-61.8	-97.2	26.3			
$\Delta_2^b$	-14.0	-18.0	-6.0	-23.5	8.6	14.9	-63.3	-59.5	30.1			

<sup>a</sup>  $\Delta_1$  is the chemical shift difference between the monometallic salt and its corresponding anthracene derivative. <sup>b</sup>  $\Delta_2$  is the chemical shift difference between the dimetallic salt and its corresponding anthracene derivative. <sup>c</sup> Values corresponding to the phenyl substituent at the deprotonated 10 position.

$\Delta q^i$  is the charge on carbon atom  $C_i$  in the charged species.  $K_C$  is a proportionality constant.  $b$  is a constant.

The proportionality constant ( $K_C$ ) is strongly dependent on the molecular structure of the charged species and its neutral precursor, hybridization of the carbon atoms, and the method of calculation of  $\Delta q^i$ . Each family of charged species requires its own factor ( $K_C$ ).<sup>40</sup>

We calculated the relationships between  $\Delta\delta_{C_i}$  and  $\Delta q^i$  for mono- and di-anions of DHA and its derivatives. Two kinds of  $\Delta q^i$  were used for calculation of the relationship: one used only the  $\pi$ -electron density ( $\Delta q_\pi^i$ ) and the other used the total ( $\sigma + \pi$ )-electron density ( $\Delta q_{\sigma+\pi}^i$ ). The relationships obtained are expressed by eqns. (9) and (10) for the monoanions.

$$\Delta\delta_{C_i} = 120.3 \Delta q_\pi^i - 0.40 \quad r = 0.966 \quad (9)$$

$$\Delta\delta_{C_i} = 62.3 \Delta q_{\sigma+\pi}^i + 1.20 \quad r = 0.630 \quad (10)$$

Eqns. (11) and (12) show the relationships for the dianions.

$$\Delta\delta_{C_i} = 133.1 \Delta q_\pi^i + 2.80 \quad r = 0.960 \quad (11)$$

$$\Delta\delta_{C_i} = 97.53 \Delta q_{\sigma+\pi}^i + 1.72 \quad r = 0.743 \quad (12)$$

The correlation coefficients ( $r$ ) for eqns. (10) and (12) are less satisfactory, implying that the delocalization of negative charge in the mono- and di-anions of DHA and its derivatives is mainly *via* the  $\pi$ -electron system.

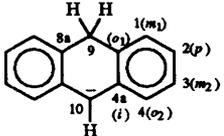
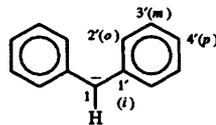
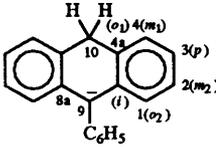
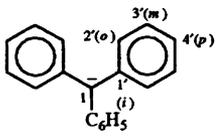
As mentioned earlier, the proportionality constant [ $K_C$ , eqn. (8)] may vary widely from  $-1$  to 316 ppm per electron<sup>36-39,41,42</sup> the average being 160 ppm per electron. The relationship between  $^{13}\text{C}$  chemical shifts of anthracene, its doubly charged species and  $\pi$ -electron density on these atoms was reported previously and the correlation coefficient ( $K_C$ ) found to be smaller than average.<sup>3,41,42</sup> The  $K_C$  value from eqn. (11) is similar to that found for other anthracene dianions.<sup>3,41</sup> However, the value obtained for the dianion of unsubstituted anthracene was reported to be 89.<sup>42</sup> It is assumed that the main reason for the large reduction of  $K_C$  for the dianions of DHA and its derivatives is paratropicity.<sup>42</sup>

The pattern of charge delocalization in monoanions of DHA and its derivatives is similar to that of diphenylmethane and triphenylmethane. The  $K_C$  value for the latter anions is between 90 and 140 ppm/electron, smaller than 160 ppm per electron.<sup>29</sup> The proportionality constant for related monoanionic DHA systems is also smaller than 160 ppm/electron [eqn. (9)]. The difference between the  $K_C$  values of mono- and di-anions of DHA and its derivatives is connected with a difference in the mechanism of delocalization of negative charge.

## Conclusions

The results of semiempirical (AM-1) calculation of structure and charge distribution in mono- and di-anions of DHA and its 9,10-substituted derivatives conform with  $^{13}\text{C}$  chemical shift

**Table 7** Comparison of  $^{13}\text{C}$  chemical shifts and  $\Delta\delta_{\text{C}}$  of monometallic salts of DHA, diphenylmethane and their phenyl derivatives

	$\alpha$	$i$	$o_1$	$o_2$	$m_1$	$m_2$	$p$	Ref.	
	$\delta$	72.1	146.4	120.5	114.7	126.7	126.3	110.7	
	$\Delta\delta$	35.4	8.7	-17.2	-12.0	0.0	-1.7	-17.3	
	$\delta$	76.8	147.3	117.5	117.5	128.0	128.0	107.3	32
	$\Delta\delta$	34.4	5.4	-11.9	-11.9	-0.8	-0.8	-19.1	
	$\delta$	90.8	142.5	121.5	112.2	126.5	125.8	110.8	
	$\Delta\delta$	38.4	5.1	-19.2	-17.0	-2.0	-1.3	-16.2	
	$\delta$	90.2	149.6	123.8	123.8	127.9	127.9	113.0	32
	$\Delta\delta$	32.7	4.9	-6.2	-6.2	-0.9	-0.9	-13.7	

$\alpha$  = anion centre,  $i$  = *ipso*,  $o$  = *ortho*,  $m$  = *meta* and  $p$  = *para*.

**Table 8** One-bond  $^1\text{H}$ - $^{13}\text{C}$  coupling constants in Hz ( $^1J_{\text{CH}}$ ) and  $sp^2$  hybridization for anthracene, DHA and its anions

	Carbon	1	2	3	4	9	10
Anthracene	$^1J_{\text{CH}}$	161.1	159.8	159.8	161.1	156.9	156.9
	$n$	2.1	2.1	2.1	2.1	2.2	2.2
DHA	$^1J_{\text{CH}}$	159.3	155.6	155.6	159.3	127.0	127.0
	$n$	2.1	2.2	2.2	2.1	2.9	2.9
$\text{DHA}^- \text{Na}^+$	$^1J_{\text{CH}}$	149.5	157.8	150.2	149.8	123.1	146.7
	$n$	2.2	2.2	2.3	2.3	3.1	2.4
$\text{DHA}^{2-} 2\text{Na}^+$	$^1J_{\text{CH}}$	149.8	151.5	151.5	149.8	146.7	146.7
	$n$	2.3	2.3	2.3	2.3	2.4	2.4

measurements in  $[\text{H}_8]\text{THF}$ . The planarity of the dihydroanthracene unit increases on transition from the neutral compound to the mono- and di-anion. The deprotonated carbon atoms of the mono- and di-anions become nearly  $sp^2$  hybridized. The negative charge in mono- and di-anions of most derivatives of DHA is mainly concentrated on the carbon atoms of the anthracene unit. However, a significant proportion of the negative charge in anions of CNDHA is sited on the substituent. The  $pK_1$  and  $pK_2$  of DHA and its derivatives in the liquid phase follow the patterns indicated by the gas phase calculations of their relative thermodynamic stabilities  $[\Delta Q, \text{eqn. (5)}]$ . This shows that the charge distribution in mono- and di-anions of DHA and its derivatives is the major determinant of the  $pK_1$  and  $pK_2$  values.

### Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-400

spectrometer in  $[\text{H}_8]\text{THF}$  between 295 and 302 K. The temperature effect on  $^{13}\text{C}$  chemical shifts of the compounds studied is 0.01 ppm  $\text{K}^{-1}$  or less at these temperatures and the effect of concentration is also small. As alkali metal anions react with tetramethylsilane (TMS), the chemical shifts were referenced to the most downfield solvent peaks which are the better resolved signals of the solvent. The solvent chemical shifts were determined for pure  $[\text{H}_8]\text{THF}$  containing TMS ( $< 5 \text{ mmol dm}^{-3}$ ). Varying the concentration of TMS up to 5  $\text{mmol dm}^{-3}$  had no perceptible ( $< 0.001 \text{ ppm}$ ) effect on the chemical shift. The temperature was determined using a standard methanol NMR thermometer.<sup>43,44</sup> In the temperature range 295 to 302 K, the chemical shift of the 1-H of  $[\text{H}_7]\text{THF}$  (260  $\text{mmol dm}^{-3}$ ) in  $[\text{H}_8]\text{THF}$  was found to be  $3.5749 + 4.71 \times 10^{-5} T \text{ ppm}$ , and the chemical shift of C-1 of  $[\text{H}_8]\text{THF}$  (containing 260  $\text{mmol dm}^{-3}$  of  $[\text{H}_7]\text{THF}$ ) was found to be  $67.3937 + 8.242 \times 10^{-4} T \text{ ppm}$  to within  $\pm 0.001 \text{ ppm}$  where  $T$  is temperature  $-295 \text{ K}$ .

Assignments of the  $^{13}\text{C}$  spectra were made by  $^1\text{H}$  detected  $^1\text{H}$ - $^{13}\text{C}$  correlation spectroscopy,<sup>45</sup> the  $^1\text{H}$  NMR spectrum being assigned, either by simple inspection or by NOESY.<sup>46</sup> Assignment of quaternary carbons was often straightforward, but where there was uncertainty, long-range  $^1\text{H}$  detected  $^1\text{H}$ - $^{13}\text{C}$  correlation spectroscopy<sup>47</sup> was used.

Concentrations were determined by calibrating the concentration of  $[\text{H}_7]\text{THF}$  in each batch of  $[\text{H}_8]\text{THF}$  using a solution of known concentration.<sup>1</sup> The  $T_1$  value of the proton in  $[\text{H}_7]\text{THF}$  is typically 120 s so only one transient was acquired after waiting 15 min with the sample in the magnet for magnetic equilibration. Accuracies of  $\pm 2\%$  were achieved by this method.

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. Alkali metals were of commercial origin.

### [<sup>2</sup>H<sub>8</sub>]THF

The commercial solvent was purified as previously reported.<sup>1</sup> The [<sup>2</sup>H<sub>8</sub>]THF was placed in a flask equipped for a vacuum line, then degassed in several freeze-pump-thaw cycles before being vacuum transferred into a flask containing distilled Na-K 5:1 alloy. This was then sonicated until a blue colour developed. The flask was allowed to stand overnight then sonicated again until a permanent blue colour developed. The solvent was then vacuum transferred into another flask containing distilled Na-K alloy.

### Preparation of anions

Sodium metal was distilled into the upper part of an extended NMR tube containing the anthracene derivative ( $\approx 5$  mg) then dry [<sup>2</sup>H<sub>8</sub>]THF was vacuum transferred and the tube sealed under vacuum. The solution was brought into contact with the sodium by repeatedly inverting the tube. Formation of the dianion was detected by <sup>1</sup>H NMR spectroscopy. The monoanions were prepared in the same way, except that a stoichiometric quantity of methanol was introduced with the anthracene derivative.

### Anthracene

Mp 217–218 °C (lit.,<sup>48,49</sup> 216–218 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 297.2 \text{ K}; 55 \text{ mmol dm}^{-3})$  7.425 (2-H) and 7.998 (1-H) (AA'XX', each 4 H) and 8.444 (s, 2 H, 9-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 91 \text{ mmol dm}^{-3})$  126.07 (d, <sup>1</sup>J<sub>CH</sub> 159.8, C-2), 126.92 (d, <sup>1</sup>J<sub>CH</sub> 156.9, C-9), 128.93 (d, <sup>1</sup>J<sub>CH</sub> 161.1, C-1) and 132.83 (s, C-4a).

### 9,10-Dihydroanthracene

Mp 108–109 °C (lit.,<sup>50</sup> 108–110 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 208 \text{ mmol dm}^{-3})$  3.891 (s, 4 H, 9-H), 7.119 (2-H) and 7.247 (1-H) (AA'XX', each 4 H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 208 \text{ mmol dm}^{-3})$  36.72 (t, <sup>1</sup>J<sub>CH</sub> 127.0, C-9), 126.71 (d, <sup>1</sup>J<sub>CH</sub> 159.3, C-1), 127.97 (d, <sup>1</sup>J<sub>CH</sub> 155.6, C-2) and 137.72 (s, C-4a).

### 9-Methylanthracene

Mp 81–82 °C (lit.,<sup>51</sup> 81.5 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 297.0 \text{ K}; 34 \text{ mmol dm}^{-3})$  3.083 (s, 3 H, 1'-H), 7.421 (t, 2 H, 3-H), 7.474 (t, 2 H, 2-H), 7.988 (d, 2 H, 4-H), 8.302 (d, 2 H, 1-H) and 8.347 (s, 1 H, 10-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 297.0 \text{ K}; 34 \text{ mmol dm}^{-3})$  23.59 (C-1'), 125.39 (C-1), 125.50 (C-3), 125.97 (C-2), 126.12 (C-10), 127.99 (C-9), 129.81 (C-4), 131.18 (C-8a) and 132.65 (C-4a).

### 9-Cyanoanthracene

Mp 175–177 °C (lit.,<sup>52</sup> 173–177 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K})$  7.60 (t, 2 H, 3-H), 7.75 (t, 2 H, 2-H), 8.16 (d, 2 H, 4-H), 8.38 (d, 2 H, 1-H) and 8.35 (s, 1 H, 10-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K})$  106.40 (C-1'), 117.23 (C-9), 125.80 (C-1), 127.24 (C-3), 129.97 (C-2), 130.02 (C-4), 131.83 (C-4a), 133.72 (C-10) and 134.08 (C-8a).

### 9-Phenylanthracene

Mp 154–155 °C (lit.,<sup>53</sup> 153–155 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K})$  7.31 (d, 2 H, 2-H), 7.40 (d, 2 H, 2'-H), 7.42 (t, 2 H, 3-H), 7.52 (t, 1 H, 4'-H), 7.58 (t, 2 H, 3'-H), 7.61 (d, 2 H, 1-H), 8.05 (d, 2 H, 4-H) and 8.54 (s, 1 H, 10-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 301.5 \text{ K}; 37.8 \text{ mmol dm}^{-3})$  125.81 (C-3), 126.07 (C-2), 127.39 (C-10), 127.43 (C-1), 128.28 (C-4'), 129.16 (C-4), 129.22 (C-3'), 131.18

(C-8a), 132.05 (C-2'), 132.54 (C-4a), 137.81 (C-1') and 139.81 (C-9).

### 9-Phenyl-9,10-dihydroanthracene

This was prepared in a similar manner to that previously reported.<sup>54</sup> 9-Phenylanthracene (130 mg) in THF (30 cm<sup>3</sup>) was placed in contact with an excess of potassium under a vacuum. After six days, the mixture was treated with propan-2-ol then the solvent was evaporated. Recrystallization from ethanol yielded yellowish-white needles, mp 89–90 °C (lit.,<sup>54</sup> 89–90 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 6.27 \text{ mmol dm}^{-3})$  3.893 (10<sub>ax</sub>-H), 3.980 (AB, J<sub>gem</sub> 18.3, 2 H, 10<sub>eq</sub>-H), 5.280 (s, 1 H, 9-H), 7.053 (d, 2 H, 2'-H), 7.067 (t, 1 H, 4'-H), 7.144 (t, 2 H, 3'-H) and 7.145 (3-H) 7.172 (2-H), 7.289 (4-H) and 7.313 (1-H) (ABXY, J<sub>1,2</sub> 7.5, J<sub>2,3</sub> 3.7, J<sub>3,4</sub> 7.5, 8 H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 6.27 \text{ mmol dm}^{-3})$  36.21 (C-10), 52.35 (C-9), 126.77 (C-4'), 127.02 (C-3), 127.05 (C-2), 128.46 (C-4), 128.74 (C-2'), 129.01 (C-3'), 129.20 (C-1), 137.45 (C-8a), 140.68 (C-4a) and 144.94 (C-1').

### 9,10-Diphenylanthracene

Mp 246–248 °C (lit.,<sup>55</sup> 245–248 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K})$  7.30 (2-H) and 7.65 (1-H) (AA'XX', each 4 H), 7.45 (d, 4 H, 2'-H), 7.61 (t, 4 H, 3'-H) and 7.54 (t, 2 H, 4'-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 295.0 \text{ K})$  125.58 (C-2), 127.63 (C-1), 128.33 (C-4'), 129.07 (C-3'), 130.85 (C-4a), 132.10 (C-2'), 138.00 (C-1') and 140.16 (C-9).

### 9,10-Dimethylanthracene

Mp 179–181 °C (lit.,<sup>56</sup> 180–181 °C);  $\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 298.0 \text{ K}; 18.6 \text{ mmol dm}^{-3})$  3.079 (s, 3 H, 1'-H), 7.472 (2-H) and 8.339 (1-H) (AA'XX', each 4 H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 298.0 \text{ K}; 18.6 \text{ mmol dm}^{-3})$  23.41 (C-1'), 125.32 (C-2), 126.03 (C-1), 128.90 (C-9) and 130.96 (C-4a).

### Sodium 9,10-dihydroanthracenide

$\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 46 \text{ mmol dm}^{-3}$  in the presence of DHA<sup>2-</sup> {21 mmol dm<sup>-3</sup>}) 3610 (s, 2 H, 9-H), 4.513 (s, 1 H, 10-H), 5.861 (t, 2 H, 2-H), 6.163 (d, 2 H, 4-H), 6.417 (t, 2 H, 3-H) and 6.460 (d, 2 H, 1-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 46 \text{ mmol dm}^{-3}$  in the presence of DHA<sup>2-</sup> {21 mmol dm<sup>-3</sup>}) 39.87 (t, <sup>1</sup>J<sub>CH</sub> 123.1, C-9), 72.06 (d, <sup>1</sup>J<sub>CH</sub> 146.7, C-10), 110.74 (d, <sup>1</sup>J<sub>CH</sub> 157.8, C-2), 114.66 (d, <sup>1</sup>J<sub>CH</sub> 149.8, C-4), 120.48 (s, C-8a), 126.31 (d, <sup>1</sup>J<sub>CH</sub> 150.2, C-3), 126.67 (d, <sup>1</sup>J<sub>CH</sub> 149.5, C-1) and 146.42 (s, C-4a).

### Sodium 9-methyl-9,10-dihydroanthracen-10-ide

$\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 34 \text{ mmol dm}^{-3}$  in the presence of MDHA<sup>9-</sup> {3.4 mmol dm<sup>-3</sup>}) and MDHA<sup>2-</sup> {17 mmol dm<sup>-3</sup>}) 1.009 (d, 3 H, 1'-H), 3.684 (q, 1 H, 9-H), 4.597 (s, 1 H, 10-H), 5.847 (t, 2 H, 2-H), 6.177 (d, 2 H, 4-H), 6.429 (t, 2 H, 3-H) and 6.525 (d, 2 H, 1-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 296.8 \text{ K}; 34 \text{ mmol dm}^{-3}$  in the presence of MDHA<sup>9-</sup> {3.4 mmol dm<sup>-3</sup>}) and MDHA<sup>2-</sup> {17 mmol dm<sup>-3</sup>}) 24.88 (C-1'), 43.37 (C-9), 79.10 (C-10), 110.10 (C-2), 114.85 (C-4), 125.35 (C-8a), 126.30 (C-3), 127.13 (C-1) and 142.98 (C-4a).

### Sodium 9-phenyl-9,10-dihydroanthracen-9-ide

$\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 298.0 \text{ K}; 11.0 \text{ mmol dm}^{-3}$  in the presence of PDHA<sup>10-</sup> {3.9 mmol dm<sup>-3</sup>}) and PDHA<sup>2-</sup> {5 mmol dm<sup>-3</sup>}) 3.685 (s, 2 H, 10-H), 5.883 (t, 2 H, 3-H), 6.338 (t, 2 H, 2-H), 6.440 (d, 2 H, 1-H), 6.487 (d, 2 H, 4-H), 6.764 (t, 1 H, 4-H), 7.120 (t, 2 H, 3'-H) and 7.310 (d, 2 H, 2'-H);  $\delta_{\text{C}}([\text{}^2\text{H}_8]\text{THF}; 300.0 \text{ K}; 11.0 \text{ mmol dm}^{-3}$  in the presence of DPDHA<sup>10-</sup> {3.9 mmol dm<sup>-3</sup>}) PDHA<sup>2-</sup> {5 mmol dm<sup>-3</sup>}) 40.54 (C-10), 90.80 (C-9), 110.80 (C-3), 112.22 (C-1), 121.01 (C-4'), 121.53 (C-4a), 125.76 (C-2), 126.52 (C-4), 128.83 (C-3), 133.26 (C-2'), 142.51 (C-8a) and 147.32 (C-1').

### Sodium 9,10-diphenyl-9,10-dihydroanthracenide

$\delta_{\text{H}}([\text{}^2\text{H}_8]\text{THF}; 297.3 \text{ K}; 7.6 \text{ mmol dm}^{-3}$  in the presence of

DPDHA<sup>2-</sup> {16 mmol dm<sup>-3</sup>} 4.850 (s, 1 H, 9-H), 5.888 (t, 2 H, 2-H), 6.369 (t, 2 H, 3-H), 6.581 (d, 2 H, 4-H), 6.615 (d, 2 H, 1-H), 6.774 (t, 1 H, 4'-H), 6.844 (t, 1 H, 4'-H), 6.969 (t, 2 H, 3'-H), 7.116 (t, 2 H, 3'-H), 7.262 (d, 2 H, 2'-H) and 7.288 (d, 2 H, 2'-H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 297.3 K; 7.6 mmol dm<sup>-3</sup> in the presence of DPDHA<sup>2-</sup> {16 mmol dm<sup>-3</sup>} 54.77 (C-9), 147.28 (C-1'), 91.54 (C-10), 110.51 (C-2), 113.52 (C-4), 121.60 (C-4'), 123.44 (C-8a), 124.98 (C-4'), 125.70 (C-3), 127.77 (C-3'), 127.85 (C-2'), 128.46 (C-1), 128.64 (C-3'), 133.69 (C-2'), 140.35 (C-4a) and 151.19 (C-1').

#### Disodium 9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 298.4 K; 43 mmol dm<sup>-3</sup> 1.485 (s, 2 H, 9-H), 2.796 (1-H) and 3.780 (2-H) (AA'XX', each 4 H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 298.4 K; 21 mmol dm<sup>-3</sup> in the presence of DHA<sup>-</sup> {46 mmol dm<sup>-3</sup>} 77.72 (d, <sup>1</sup>J<sub>CH</sub> 146.7, C-9), 101.83 (d, <sup>1</sup>J<sub>CH</sub> 149.8, C-1), 115.95 (d, <sup>1</sup>J<sub>CH</sub> 151.6, C-2) and 152.19 (s, C-4a).

#### Disodium 9-methyl-9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 297.0 K; 32 mmol dm<sup>-3</sup> 0.035 (s, 3 H, 1'-H), 1.758 (s, 1 H, 10-H), 2.977 (d, 2 H, 1-H), 2.994 (d, 2 H, 4-H), 3.942 (t, 2 H, 3-H) and 4.067 (t, 2 H, 2-H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 297.0 K, 32 mmol dm<sup>-3</sup> 11.80 (C-1'), 77.53 (C-9), 78.97 (C-10), 100.58 (C-1), 101.23 (C-4), 116.01 (C-3), 116.26 (C-2), 149.21 (C-8a) and 151.82 (C-4a).

#### Disodium 9-cyano-9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 297.4 K; 22 mmol dm<sup>-3</sup> 2.419 (s, 1 H, 10-H), 4.058 (d, 2 H, 4-H), 4.569 (d, 2 H, 1-H), 4.652 (t, 2 H, 2-H) and 4.906 (t, 2 H, 3-H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 296.7 K; 22 mmol dm<sup>-3</sup> 53.95 (C-9), 74.18 (C-10), 106.53 (C-4), 111.80 (C-1), 111.96 (C-2), 121.19 (C-3), 136.46 (C-1'), 140.40 (C-4a) and 149.03 (C-8a).

#### Disodium 9-phenyl-9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 297.0 K; 13.6 mmol dm<sup>-3</sup> 1.801 (s, 1 H, 10-H), 3.227 (d, 2 H, 4-H), 3.720 (d, 2 H, 1-H), 3.893 (t, 2 H, 2-H), 4.141 (t, 2 H, 3-H), 6.342 (t, 1 H, 4'-H), 6.769 (t, 2 H, 3'-H) and 6.814 (d, 2 H, 2'-H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 297.0 K; 13.6 mmol dm<sup>-3</sup> 78.63 (C-10), 89.86 (C-9), 101.62 (C-1), 103.86 (C-4), 114.39 (C-2), 118.08 (C-3), 119.75 (C-4'), 129.13 (C-3'), 132.76 (C-2'), 146.95 (C-1'), 147.93 (C-4a) and 151.41 (C-8a).

#### Disodium 9,10-dimethyl-9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 297.8 K; 48 mmol dm<sup>-3</sup> 0.157 (s, 6 H, 1'-H) and 3.187 (1-H) and 4.222 (2-H) (AA'XX', each 4 H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 297.8 K; 48 mmol dm<sup>-3</sup> 11.98 (C-1'), 77.76 (C-9), 99.91 (C-1), 116.14 (C-2) and 148.94 (C-4a).

#### Disodium 9,10-diphenyl-9,10-dihydroanthracenediide

$\delta_{\text{H}}([{}^2\text{H}_8]\text{THF})$ ; 296.3 K) 3.77 (1-H) and 4.07 (2-H) (AA'XX', each 4 H), 6.47 (t, 2 H, 4'-H), 6.86 (d, 4 H, 2'-H) and 6.88 (t, 4 H, 3'-H);  $\delta_{\text{C}}([{}^2\text{H}_8]\text{THF})$ ; 297.7 K) 90.46 (C-9), 102.38 (C-1), 116.28 (C-2), 120.86 (C-4'), 129.57 (C-3'), 134.00 (C-2'), 147.13 (C-1') and 148.09 (C-4a).

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