Structures of 9,10-dihydro-9-heteroanthracenes and 9,10-dihydro-9-heteroanthracenide anions; an *ab initio* MO calculation

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The structural parameters and charge distributions of 9,10-dihydroanthracene (DHA) **1a**, xanthene **1b**, *N*-methylacridane **1c** and thioxanthene **1d**, and their monoanions **2a–d** have been calculated by an *ab initio* MO method at the Hartree–Fock SCF level using 6-31G(d) basis set. The calculated dihedral angles (*a*) indicate that xanthene (*a* = 180°) is planar, while DHA (*a* = 142.2°), *N*-methylacridane (*a* = 142.7°) and thioxanthene (*a* = 133.3°) have non-planar geometries. Deprotonation of **1a–d** at C⁹ leads to a completely flat structure for xanthenide **2b** (*a* = 180°) and significantly flattened molecules for DHA⁻ **2a** (*a* = 153.3°), *N*-methylacridanide **2c** (*a* = 157.6°) and thioxanthenide anion **2d** (*a* = 150.0°). The calculated charge distributions of these anions are found to correlate well with the experimentally determined ¹³C NMR chemical shifts. The combined data from net charge distributions and carbon chemical shifts indicate that the heteroanthracenide anions **2b–d** may be characterized as extensively delocalized 16 π-electron systems in which oxygen and nitrogen anions on the one hand and a sulfur analogue on the other exhibit some fundamentally different charge distribution pattern. While the extent of overall delocalization of the benzylic negative charge increases in the order of O < N < S, the reverse order S < N < O is observed with regard to the extent of charge delocalization into the benzenoid moieties. This observed discrepancy may be explained by the second-row nature of the sulfur atom and its ability to stabilize an adjacent negative charge.

Introduction

The structures of 9,10-dihydroanthracene (DHA) **1a**,[1] its monoanion (DHA⁻) **2a**[2] and a host of 9-substituted relatives[2] have been the subject of many theoretical and experimental studies. The focus of attention has been the geometry of the central six-membered ring in these systems. X-Ray analysis[3] of DHA in the solid state has indicated a geometry in which the central ring adopts a boat (or pseudoboat) conformation. A dihedral angle (*a*) of 144.7° between planes containing the two halves of the molecule (Fig. 1) was obtained. In solution, the DHA molecule is presumed to undergo rapid boat-to-boat ring inversion even at very low temperatures. An analysis of the electronic spectra of jet-cooled molecules of DHA has recently led to determination of the inversion potential of 7.4 kJ mol⁻¹ for the ground state.[4] Theoretical[5] as well as NMR[2] studies have indicated that deprotonation of DHA and 9-substituted relatives invariably leads to a flattening of the central ring and, in the case of DHA, a nearly flat monoanion DHA⁻ results.

In related studies, a few conformational analyses of a number of 9,10-dihydro-9-heteroanthracenes, namely, xanthene[6] **1b**, *N*-methylacridane (*N*-methyl-9,10-dihydroacridene)[6a] **1c** and thioxanthene[6a,b] **1d** have been carried out. However, to date, no information on the geometries of 9,10-dihydro-9-hetero-anthracenide anions **2b–d** is available. These anions, which are isoelectronic with the well-documented dianion of DHA, are of special significance because they provide rare examples of 16π-electron conjugated cyclic carbanions in which the degree of delocalization of the negative charge may be controlled by the electronegativity of an existing heteroatom which itself contributes an electron pair to the π-system.

In this work, (1) we have carried out *ab initio* MO calculations at the Hartree–Fock SCF level using a 6-31G(d) basis set on the dihydroheteroanthracenes **1b–d** and the corresponding monoanions **2b–d** as well as on DHA **1a** and DHA⁻ **2a** as the reference structures, and (2) we have studied the correlation between the calculated charge densities and the observed ¹³C NMR chemical shifts[7] in these systems and have compared the effect of the heteroatom on the anionic charge delocalization in monoanions **2b–d**.
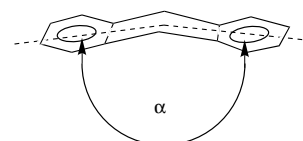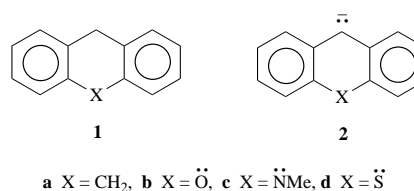

Fig. 1   The 'butterfly' conformation of DHA

a X = CH₂, **b** X = Ö, **c** X = N̈Me, **d** X = S̈

Results and discussion

The calculated structural parameters for **1a–d** and **2a–d** are provided in Table 1. The numbering of atoms and angles referred to in Table 1 is shown in Fig. 2. The Mulliken method for charge partitioning[8] was employed to calculate atomic charge distributions for neutrals [Fig. 2(*a*)] and for the anions [Fig. 2(*b*)]. All the structures were fully optimized by the gradient technique[9] at the Hartree–Fock SCF level using the 6-31G(d) basis set.[10] Vibrational analyses were carried out on all of the optimized structures indicating that they were equilibrium structures with all real vibrational frequencies. All the calculations were carried out using the program Gaussian 94.[11]

Neutral structures 1a–d

Previous calculations have provided dihedral angle *a* values of 159[12] and 154.5°[2] for DHA and an inversion barrier of 7.4–8.6 kJ mol⁻¹ in its ground state.[4,13] The structure of xanthene **1b** in crystalline form has not been published. In solution, the molar Kerr constants indicate a folding angle of 160 ± 6°.[6a] Various dipole moment measurements[6a,b] are consistent with a planar or rapidly inverting non-planar conformation. A STO-3G and 4-31G MO calculation[6c] has provided a folding angle of 170°

Table 1 Calculated structural parameters [a] for **1a–d** and **2a–d**

| | Structure | | | | | | | |
| | X = CH$_2$ | | X = O | | X = NMe | | X = S | |
Parameter [b]	**1a**	**2a**	**1b**	**2b**	**1c**	**2c**	**1d**	**2d**
C–X	1.514	1.514	1.359	1.375	1.406	1.414	1.780	1.783
C^4–C^{12}	1.387	1.376	1.389	1.363	1.390	1.372	1.386	1.377
C^3–C^4	1.386	1.395	1.378	1.407	1.387	1.409	1.385	1.393
C^2–C^3	1.384	1.389	1.390	1.376	1.381	1.374	1.384	1.389
C^1–C^2	1.386	1.379	1.380	1.392	1.388	1.392	1.386	1.378
C^1–C^{11}	1.387	1.416	1.393	1.406	1.382	1.404	1.387	1.416
C^{11}–C^{12}	1.394	1.426	1.383	1.423	1.348	1.433	1.393	1.417
C^9–C^{11}	1.514	1.416	1.511	1.412	1.509	1.413	1.513	1.416
C^{12}–X–C^{14}	112.1	112.9	120.4	121.2	117.4	119.8	99.5	101.4
X–C^{12}–C^{11}	118.8	117.1	122.8	120.3	118.1	116.4	119.6	118.2
C^3–C^4–C^{12}	119.7	122.3	119.7	120.9	120.2	121.6	119.9	121.5
C^2–C^3–C^4	120.8	117.6	120.0	117.9	120.6	118.3	119.9	117.7
C^1–C^2–C^3	120.8	121.3	119.4	121.2	119.0	120.9	119.9	121.4
C^2–C^1–C^{11}	119.7	121.9	121.6	122.3	121.2	122.2	120.9	122.3
C^1–C^{11}–C^{12}	119.5	116.2	117.8	115.0	119.5	116.1	118.6	115.0
C^{11}–C^{12}–C^4	119.5	120.7	121.4	122.6	119.3	120.8	120.7	122.0
C^{11}–C^{12}–X	118.8	117.1	122.8	120.3	118.1	116.4	119.6	118.2
C^9–C^{11}–C^1	121.8	123.6	121.2	125.8	122.8	124.8	122.2	122.4
C^9–C^{11}–C^{12}	118.8	120.2	121.0	119.2	117.6	119.0	119.2	122.6
C^{13}–C^9–C^{11}	112.1	120.2	112.0	119.7	110.2	120.2	112.5	123.0
a [c]	142.2	153.3	180.0	180.0	142.7	157.6	133.3	150.0

[a] Bond lengths (Å) and angles (°), calculated by *ab initio* Hartree–Fock SCF with the 6-31G(d) basis set. [b] See Fig. 2 for structure, numbering of atoms and definition of angles. The anions are formed by deprotonation at C^9. [c] Dihedral angle between the two halves of the molecule and a measure of planarity of the central ring (Fig. 1).
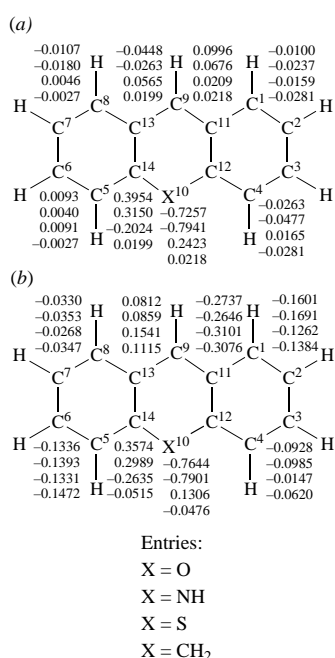
Fig. 2 Mulliken atomic charge distribution analysis for (*a*) **1a–d** and (*b*) **2a–d**

corresponding to its lowest energy. A fluorescence excitation and the dispersed fluorescence spectral analysis of jet-cooled xanthene has established that the molecule is only slightly non-planar in the ground state.[6e] To our knowledge, no theoretical study regarding the conformation of the *N*-methylacridane **1c** has been published. An NMR study of *N*-acylacridanes indicated that the molecule is non-planar in solution.[6b] However, the amide double bond character in this molecule may play as important a role in shaping the molecule as the nature of the acridane moiety. The sulfur analog, thioxanthene **1d**, exists in a non-planar geometry with a folding angle a of 135.3° in the solid state.[14] In CCl$_4$ or C$_6$H$_6$ solutions at ambient temperature, a folding angle of 135 ± 8° is estimated.[15] A number of MO calculations have been carried out on thioxanthene, including a

3-21G(*) basis set which provides a folding angle of 130.0°.[16] Our calculations (Table 1) indicate that molecules of DHA **1a**, acridane **1c** and thioxanthene **1d**, are non-planar with the value of a being 142.2, 142.7 and 133.3° respectively. On the other hand, xanthene **1b** is calculated to be completely planar ($a = 180°$).

A few ^{1}H and ^{13}C NMR studies regarding the structures of xanthene[6c,17,18] and its nitrogen[6c] and sulfur[16,17,19] analogs **1c–d** in solution at 60–100 MHz have been published. We have carried out ^{1}H and ^{13}C NMR studies of **1a–d** at 500 and 125 MHz respectively and observed that in CHCl$_3$ and at ambient temperature, the two methylene hydrogens of C^9 for each compound exhibit no chemical shift differences. Interestingly, the observed singlet for xanthene (δ 4.02) has a slightly lower half-band width (0.086 Hz) compared to those of *N*-methylacridane (δ 3.86, half-band width: 0.091 Hz) and thioxanthene (δ 3.83, half-band width: 0.091 Hz). These data support the results of spectroscopic studies of previous investigators which do not distinguish between rapidly inverting puckered conformations or static planar ones. The difference in the half-band widths points to a lower energy barrier for interconversion or a more planar static structure for xanthene compared to *N*-methylacridane and thioxanthene. Our calculated dihedral angles a for xanthene, *N*-methylacridane and thioxanthene are 180, 142.7 and 133.3° respectively.

Anionic structures 2a–d

The calculated charge distributions for the anions **2a–d** [Fig. 2(*b*)] correlate well with the experimentally determined ^{13}C NMR chemical shifts (Table 2). Specifically, it is found that the change in total carbon chemical shifts for **1b** ⟶ **2b** of +28.6 ppm, for **1c** ⟶ **2c** of +14.7 ppm and for **1d** ⟶ **2d** of −22.1 ppm are in good agreement with the calculated total charge shifts on the carbon atoms (Fig. 2 and Table 3) when neutral molecules are transformed into anions (Fig. 3). An excellent correlation is also observed when the above-mentioned total chemical shift changes are plotted against the calculated net charge shifts on the heteroatoms for neutral to anion transformations (Fig. 4).

Our calculations (Table 1) indicate that the deprotonation of neutral molecules **1a–d** at C^9 leads to a completely flat structure,

Table 2 ^{13}C NMR Characteristics[a] of **1a–d** and **2a–d**

Compound	Chemical shifts,[b] δ					Total carbon shift
	C^1–C^8	C^{11},C^{13}	C^{12},C^{14}	C^9	C^{10}	
1a[c]	127.3, 125.9, 125.9, 127.3 (1012.8)[d]	136.5	136.5	35.9	35.9	1630.8
2a[e]	114.7, 126.3, 110.7, 126.7 (956.8)	146.4	120.5	72.1	39.9	1602.6
				(+36.2)[f]		(−28.2)[g]
1b	128.9, 122.9, 127.6. 116.5 (991.8)	120.6	152.0	27.9	—	1564.9
2b	112.3, 118.8, 109.4, 126.4 (933.8)	143.0	152.4	68.9	—	1593.5
				(+41.0)		(+28.6)
1c	127.5, 120.6, 126.8, 111.9 (973.6)	124.3	143.6	33.2	—	1542.6
2c	109.1, 124.0, 108.0, 110.3 (902.8)	142.9	146.7	75.3	—	1557.3
				(+42.0)		(+14.7)
1d	127.4, 126.5, 126.4, 126.8 (1014.2)	133.8	136.2	39.2	—	1593.4
2d	114.5, 128.0, 112.6, 114.5 (939.2)	149.2	125.5	82.7	—	1571.3
				(+43.9)		(−22.1)

[a] ^{13}C NMR spectra for neutral molecules **1b–d** were obtained at 125 MHz in CHCl$_3$ and for the anions **2b–d** were obtained at 20 MHz in NH$_3$ (liq.).
[b] Chemical shifts (δ) in ppm from TMS. [c] From Ref. 17. [d] Total chemical shifts. [e] From Ref. 2. [f] Change in chemical shift ($\Delta\delta$) for neutral $\longrightarrow$ anion.
[g] Change in total chemical shift ($\Delta\delta$) for neutral $\longrightarrow$ anion.

Table 3 Total net charge distribution for **1a–d** and **2a–d**

Compound	C^1–C^8	Charge shift[a]	C^9	Charge shift	$C^{12} + C^{14}$	Charge shift
1a	−0.1232		0.0218		0.0398	
2a	−0.7646	−0.6414	−0.3076	−0.3294	−0.1030	−0.1428
1b	−0.0754		0.0996		0.7908	
2b	−0.8350	−0.7596	−0.2737	−0.3733	0.7148	−0.0760
1c	−0.1694		0.0676		0.7100	
2c	−0.8844	−0.7150	−0.2646	−0.3322	0.5978	−0.1122
1d	−0.0143		0.0209		−0.4048	
2d	−0.6016	−0.5873	−0.3101	−0.3310	−0.5270	−0.1222

[a] The net charge distribution difference between the neutral molecules and the corresponding anions.
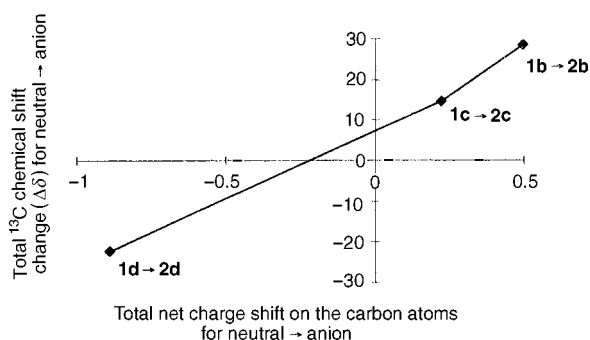

Fig. 3 Plot of total ^{13}C chemical shift change *vs.* the calculated total net charge shift on the carbon atoms on going from neutral molecules **1b–d** to anionic molecules **2b–d** respectively (values from Tables 2 and 3)

Fig. 4 Plot of total ^{13}C chemical shift change *vs.* calculated net charge shift on the heteroatom on going from neutral molecules **1b–d** to anions **2b–d** respectively (values from Tables 2 and 3)

for **2b** ($a = 180°$) and significantly flattened molecules for **2a** ($a = 153.3°$), **2c** ($a = 157.6°$) and **2d** ($a = 150.0°$). From the net charge distribution for the anions [Fig. 2(*b*)] it is clear that the negative charge, formally located at the 'benzylic' carbon atom, is extensively delocalized. The values of C^{11}–C^9–C^{13} angles for these anions, as well as the observed ^{13}C chemical shifts (Table 2), are also indicative of this delocalization. Furthermore, the combined data from net charge distributions and ^{13}C chemical shifts indicate that the nature of the delocalization of the 'benzylic' negative charge is significantly different for **2b** and **2c** on the one hand and **2d** on the other. The comparison of the charge shifts on going from the neutral molecules **1b–d** to the corresponding anions **2b–d**, shown in Table 3, as well as the total ^{13}C NMR chemical shifts given in Table 2, reveal the following salient features. (a) The carbanionic center C^9 of thioxanthenide **2d** exhibits the largest chemical shift increase (+43.9 compared to +41.0 and +42.0 ppm for **2b** and **2c** respectively) and the smallest charge shift (−0.331 compared to −0.3733 and −0.3322 for **2b** and **2c** respectively) relative to
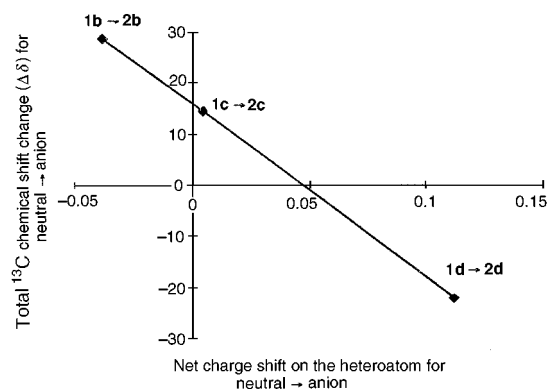
thioxanthene and therefore is the least localized of **2b–d**; (b) the degree of the overall delocalization of the negative charge over the benzenoid tertiary carbons (C^1–C^8) is larger for xanthenide **2b** [C^1–C^8 chemical shift change ($\Delta\delta$) of +58.0 ppm and charge shift of −0.7596] and *N*-methylacridanide **2c** (C^1–C^8 $\Delta\delta$ 70.8 ppm and charge shift of −0.7150) than for thioxanthenide **2d** (C^1–C^8 $\Delta\delta$ 75.0 ppm and charge shift of −0.5873); and (c) in contrast, the degree of spacially limited delocalization of the negative charge, *i.e.* delocalization within the central ring, as judged by the change in net charge distribution on carbons C^{12} and C^{14}, in passing from neutral molecules to anions (−0.076, −0.1122 and −0.1222 for **2b**, **2c** and **2d** respectively) as well as from the change in total chemical shifts of C^{12} and C^{14} (+0.80, +6.20 and −21.40 ppm for **2b**, **2c** and **2d** respectively) is largest for the thioxanthenide anion **2d**.

In summary, the dihedral angle a, calculated by our method, of 142.2° for DHA, 180° for xanthene, 142.7° for *N*-methylacridane and 133.3° for thioxanthene show the closest agree-

ment published to date to the experimentally obtained data regarding the geometries of these molecules (*vide infra*). Hetero-anthracenide anions **2b–d**, may be best characterized as extensively delocalized 16π-electron systems with oxygen and nitrogen analogues on the one hand and a sulfur anion on the other exhibiting some fundamentally different characteristics. While the extent of the delocalization of the benzylic negative charge increases in the order O < N < S, the reverse order S < N < O is observed with regard to the extent of charge delocalization into the benzenoid moieties. This observed discrepancy may be explained by the second-row nature of the sulfur atom and its ability to stabilize an adjacent negative charge.[20]

Experimental

Xanthene (Aldrich Chemical Co.) was recrystallized from light petroleum. *N*-Methylacridane and thioxanthene were prepared according to the literature procedures.[7b] The anions **2b–d** were generated upon treatment of the carbon acids **1b–d** with KNH_2 in liq. NH_3.[7] ^{1}H NMR spectra at 500 MHz and ^{13}C NMR at 125 MHz were recorded on a Bruker DRX-500 spectrometer. ^{13}C NMR spectra at 20 MHz were obtained on a Varian CFT-20 spectrometer.

Acknowledgements

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