From bifluorenylidene dianion to dibenzo[*g*,*p*]chrysene dianion: sensitivity of anisotropy changes to bonding structure

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Five polycyclic aromatic hydrocarbons of the C_{26} series having similar bonding structure yield dianions upon reduction with lithium metal. Anisotropy changes, revealed from an advanced charge distribution analysis performed on these dianions, show a correlation to the bonding structure of the dianions. Electron counting and orbital considerations rationalize this correlation in terms of aromatic/anti-aromatic behaviour that is mixed into the character of the aromatic PAH upon reduction. Predictions made regarding relative stability based on this correlation were successfully tested against calculation and experiment. The anisotropy change is suggested as a valid index for the reduction-induced change in the aromatic character of PAHs, which is applicable for both aromatic and anti-aromatic changes.

Introduction

In the current research on polycyclic aromatic hydrocarbons (PAHs), the main attention is being directed toward the understanding of their electronic properties, as a means for prediction of features such as reactivity and regioselectivity.[1] In this regard, aromaticity considerations play a major role in assessing relative stability and electronic behaviour.[2]

An experimental method to reveal the structure of the unoccupied frontier molecular orbitals of a PAH is simply to add electrons to the PAH by an alkali metal reduction (most commonly performed in dry ethereal solutions), and observe the charge distribution over the π-framework in the anion.[3,4] As the negative charge densities induce magnetic shielding on the nuclei, NMR is the method of choice for analyzing the charge distribution in the reduced species. Charge densities on the π-framework carbons are thus calculated from differences between the ^{13}C NMR spectra of the anion and that of the neutral species, employing eqn. (1):[5]

$$\rho_\pi = \Delta\delta_C/K_C \quad (1)$$

where ρ_π is the change in the π-charge on the carbon, $\Delta\delta_C$ is the chemical shift change for that carbon from the anionic to the neutral state, and K_C is a proportionality constant. For annulene (monocyclic) anions, an analogous relation exists for hydrogen atoms, as shown by eqn. (2), in which ρ_π is the change in the π-charge on the proton bearing carbons:[5]

$$\rho_\pi = \Delta\delta_H/K_H \quad (2)$$

Both proportionality constants are calculated as the sum of differences in the chemical shifts of the corresponding nuclei, divided by the total charge of the anion.

This method of evaluation of charge densities is quite reliable for numerous PAHs, provided that the changes in the chemical shifts are dominated by the charge shielding effect. In such cases, values close to 160 and 10.7 ppm per electron are calculated for K_C and K_H, respectively.[5] Yet, when the reduction results in considerable changes in the aromaticity character of the PAH, differences in the dia- or paratropicity of the anion compared to the neutral precursor contribute significantly to the changes in the chemical shifts. In such cases, K_C values can strongly deviate from 160 ppm e^{-1}.[6]

A correction that makes use of the sensitivity exhibited by the K_C measure to anisotropy effects was proposed by Edlund and Müllen.[6] According to this correction, a separation of anisotropy effects from the charge effect can be achieved using the sensitivity of the peripheral protons to both effects, while the peripheral carbons (constituting the ring of the current) are insensitive to the ring current effects.[7] A proton anisotropy term (χ_H) can be calculated from the average change of the ^1H chemical shifts ($\langle\Delta\delta_H\rangle$) and the average change in π-charge at the proton-bearing carbon atoms ($\langle\rho_\pi\rangle$, obtained from quantum mechanical calculations), as shown in eqn. (3) (using the value 10.7 ppm e^{-1} for K_H):[6]

$$\chi_H = \langle\Delta\delta_H\rangle - 10.7\langle\rho_\pi\rangle \quad (3)$$

Using the proton anisotropy term, one can finally isolate the pure chemical shift/charge factor F_C from the value of K_C according to eqn. (4):[6]

$$K_C = F_C + (n_C/Q_\pi)a\chi_H \quad (4)$$

where n_C is the total number of carbon atoms in the π-system, Q_π is the total π-charge change (*i.e.*, −2.0 for dianions) and a is a negative constant.[6] Using NMR data from the reduction of a series of PAHs to di- and tetraanions, F_C was estimated to be 134 ppm e^{-1} and $a = -2.4$.[6]

This treatment allows not only for a more reliable calculation of the charge densities (by dividing the corrected-for-

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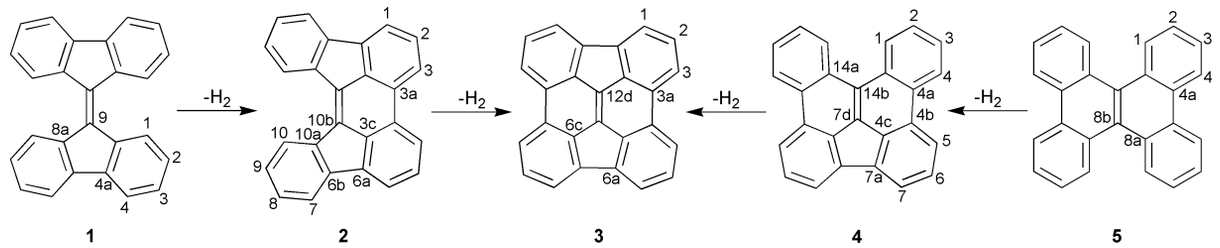

anisotropy ^{13}C chemical shift changes by the pure charge term (F_C), but also for a generation of an aromaticity-variation index according to the proton anisotropy term χ_H. This was implied for 4$n\pi$ dianions, for which negative values of χ_H (and low K_C values) were calculated, evidencing the mixing of anti-aromatic properties into the character of the anions.[6] Consistently, positive values of χ_H that might evidence the "strengthening" of the aromatic character of the anion compared to the neutral species were calculated for (4n + 2)π anions.[6] †

The highly strained diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]-chrysene (**3**) is one of the smallest, symmetrical, bowl-shaped subunits of C_{60}. A general strategy to obtain **3** is to gradually build the curvature by two consecutive ring closures,‡ mainly *via* either one of two routes: from benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (**2**), obtained by an analogous cyclization from bifluorenylidene (**1**), or from benz[*g*]indeno[1,2,3,4-*mnop*]-chrysene (**4**), obtained from dibenzo[*g*,*p*]chrysene (**5**).[8,9] § These five compounds form a series of a gradually changing conjugated skeleton (from **1** to **5**), that is ideally suited to test the sensitivity of the anisotropy-change index to structure.

The formation of dianions of **1**, **3** and **5** has been reported previously.[4,10,12a] Herein we report on the lithium reduction to dianions of the other two compounds, as well as the full assignment of the ^{1}H and ^{13}C NMR spectra. The study includes charge distribution analysis, together with HMO theory, DFT calculations and lithium reduction of binary mixtures, that were performed in order to probe the relation between anisotropy changes and subtle structural differences, as well as to gain insight into the nature of these compounds and their anions.

Results and discussion

The geometries of the five molecules and their dianions have been optimized using DFT calculations (at B3LYP/6-31G* level). Prior to the use of computed charge densities for the evaluation of anisotropy effects, we verified the reliability of the calculation results by comparing the computed NMR shifts (calculated for the optimized structures) to the experimental data. The correlation found is higher than 90% (R value). Based on charge densities obtained by natural bond order (NBO) analysis[11] on the minimum structures we calculated the change in the centre of weight of the ^{13}C spectrum, and the values of K_C, F_C, and χ_H (Table 1), using the previously established estimations K_H = 10.7 ppm e^{-1} and a = −2.4.

Consideration of the values shown in Table 1 reveals that for most dianions (all except $\mathbf{5}^{2-}$) the centre of weight of the ^{13}C spectrum is shifted by *ca.* 11 ppm. This means that for these dianions the charge shielding effect is the dominant one, whereas for $\mathbf{5}^{2-}$ significant changes in the ring current anisotropy diminish the shielding caused by charge on the carbon nuclei. This last observation is evidenced by a small up-field shift of the ^{13}C peaks (reflected in a small K_C value calculated for $\mathbf{5}^{2-}$), as well as by a strong up-field shift of the ^{1}H peaks. Correction for anisotropy effects for all dianions isolates the pure charge contributions (F_C), which show values within the error limits of the previously determined 134 ppm e^{-1} value.[6]

Table 1 ^{13}C NMR centre of weight change (^{13}C ΔCM), chemical shift change per electron (K_C), pure charge term (F_C) and ^{1}H NMR shift anisotropy term (χ_H) for the dianions of **1**, **2**, **3**, **4** and **5**

	^{13}C ΔCM/ppm	K_C/ppm e^{-1}	F_C/ppm e^{-1} [a]	χ_H/ppm [a]
$\mathbf{1}^{2-}$	14.1	183	170	+0.40
$\mathbf{2}^{2-}$	12.1	157	159	−0.07
$\mathbf{3}^{2-}$	8.1	105	128	−0.75
$\mathbf{4}^{2-}$	9.5	123	159	−1.15
$\mathbf{5}^{2-}$	2.6	34	114	−2.54

[a] To isolate the π-charge change used in the calculation of F_C and χ_H we subtracted the NBO charge densities of the neutral compounds from the densities calculated for the corresponding dianions.

Table 2 Calculated HOMO–LUMO energy gaps for the dianions of **1**, **2**, **3**, **4** and **5**

	HMO/β	DFT/kJ mol^{-1} [a]
$\mathbf{1}^{2-}$	0.633 [b]	165.5
$\mathbf{2}^{2-}$	0.432	84.4
$\mathbf{3}^{2-}$	0.358	45.1
$\mathbf{4}^{2-}$	0.349	67.7
$\mathbf{5}^{2-}$	0.194	52.3

[a] DFT calculations were performed at the B3LYP/6-31G* level. [b] In ref. 10 the value 0.658 β is reported, based on ωβ calculations.

Consideration of the values calculated for the proton anisotropy, χ_H, reveals that the discussed series of dianions is ordered on an "aromaticity scale" (represented by χ_H), starting with the "aromatic" $\mathbf{1}^{2-}$ and ending with the most "anti-aromatic" $\mathbf{5}^{2-}$. Interestingly, the order of the dianions on this "aromaticity scale" shows continuity in terms of the bonding structure, as each two adjacent members on this scale differ by only one C–C bond. It should be noted that the dianions of the three compounds located at the "anti-aromatic" end of the scale show broadening of the proton line widths at room temperature, with increasing magnitude from $\mathbf{3}^{2-}$ to $\mathbf{5}^{2-}$. This finding reveals the proximity of a low lying, thermally accessible triplet state in these anions.[6b,12] According to the known relation between anti-aromaticity in 4$n\pi$ dianions and their HOMO–LUMO gap (ΔE),[6b,12] we find that significantly smaller gaps are indeed calculated for the dianions of **3**, **4** and **5** compared to those calculated for $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ (Table 2). Moreover, the values of the HOMO–LUMO gap classify $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ as "aromatic" (with ΔE > 0.4 β), while the rest of the dianions belong to the region in between the aromatic and anti-aromatic extremes (0.2 β < ΔE < 0.4 β),[12b] exhibiting mixed characters of aromatic and anti-aromatic contributions. For the last three dianions ($\mathbf{3}^{2-}$, $\mathbf{4}^{2-}$ and $\mathbf{5}^{2-}$), a change in the ion-pairing equilibrium (*e.g.* with elevation of the temperature) considerably affects their HOMO–LUMO gap, resulting in NMR line

† Although Longuet–Higgins and Salem predicted that 22 π-electrons in an annulene are the borderline for the validity of the Hückel "magic numbers" of electron counting,[22] it has recently been shown that this borderline can be extended beyond 40 π-electrons,[23] as has also been shown by theoretical considerations.[24]

‡ These cyclization reactions occur with dehydrogenation under flash vacuum pyrolysis (FVP) conditions.

§ Dehydrobromination of appropriate brominated precursors is an improved variation of the general strategy outlined herein, leading to better yields.[9]

broadening due to thermal population of a close triplet state.[6b,12]

Structural aspects and π-electron counting may provide a simple explanation for the location of the dianions on the scale of anisotropy changes.¶ Although all five dianions are 28 (4*n* number) π-electron systems, $\mathbf{1}^{2-}$ is fundamentally different with respect to its structure, as its central double bond is not a member of any ring. Therefore, while all other dianions have increasing paratropic contributions due to the 4*n* number of π-electrons in them, $\mathbf{1}^{2-}$ is split into two aromatic fluorenyl-anion units, each bearing 14 (4*n* + 2 number) π-electrons (Fig. 1).[10]

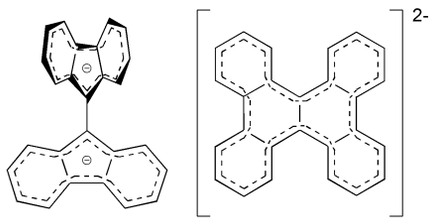

Fig. 1 The different modes of delocalization of 28 π-electrons in $\mathbf{1}^{2-}$ and $\mathbf{5}^{2-}$.

This situation is accounted for by DFT calculations, which show an increase of the dihedral angle from 34° in the neutral to 57° in the dianion along with planarization of the fluorenyl units. Bay proton overcrowding effects on ^{1}H NMR shifts apparently reflect this situation, as the proton peak appearing at the lowest field is H-4 (in contrast to the most deshielded H-1 in the neutral compound). This observation may evidence the relief of the H-1 proton crowding in their bays due to an increased twisting angle of the double bond. The high twisting of the central double bond lowers significantly the "electronic communication" between the two fluorenyl-anion units, as the π-overlap orbital over this double bond fragment bridging the two units becomes poor. These considerations rationalize the finding that $\mathbf{1}^{2-}$ is the only dianion having increased aromaticity (positive χ_H value) compared to the other dianions, that due to their rigid skeleton cannot escape the situation of a 28 π-electron delocalization over the entire conjugated skeleton.

The fact that $\mathbf{5}^{2-}$ sustains the strongest "anti-aromatic" contributions in this series is rationalized by viewing **5** as a bridged analogue of the anti-aromatic [26]annulene dianion, as all the carbons in $\mathbf{5}^{2-}$ are peripheral, located on an overall monocycle (Fig. 1).

The location of $\mathbf{4}^{2-}$ as the second most paratropic dianion may be explained on the basis of its electronic structure. As shown in Fig. 2, the frontier orbitals of **4** remarkably resemble those of corannulene (**6**), whose dianion is a prominent example of an anti-aromatic anion.[13]

In a previous report we have shown that the electronic structure of **3** is best modelled by four benzene fragments connected to a central double bond.[4] In this respect, **3** stands as a true middle point on the "aromaticity scale" between the dianions showing anti-aromatic annulene type behaviour (*i.e.* $\mathbf{4}^{2-}$ and $\mathbf{5}^{2-}$) and the two dianions consisting of aromatic fluorenyl-anion moieties (*i.e.* $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$).

As the terms "aromaticity" and "anti-aromaticity" are synonyms for enhanced stability and instability, respectively, a comparison of the dianions' relative stability is desired. Correlations between the energetic and magnetic criteria of aromaticity have already been previously evoked.[14] Direct comparison of calculated total energies, which is meaningful only for the couples of isomers existing in the line, shows a preference of $\mathbf{1}^{2-}$ over $\mathbf{5}^{2-}$ and of $\mathbf{2}^{2-}$ over $\mathbf{4}^{2-}$ as expected. In order to compare the relative stability of non-isomers, one should calculate the enthalpy changes in homodesmotic reactions (a subclass of isodesmic reactions).[15] Table 3 shows the results of the enthalpy changes in the imaginary homodesmotic reaction $A + B^{2-} \rightleftharpoons A^{2-} + B$, involving a two-electron exchange between the species.‖ The trend found in Table 3 is clear: in an imaginary binary mixture, in which one system exists as a neutral compound and the other as a dianion, the dianion exhibiting less paratropic influences will be preferred. This preference gradually becomes smaller for systems that are close in character.

These calculated homodesmotic reactions are unreal, as mixing of any couple of systems in the described conditions would yield both systems' radical anions. Experimentally, one can determine the relative order of stability of two systems for a certain reduction state compared to the former reduction state only, *e.g.* of radical anions compared to neutral species. This

Table 3 Enthalpy changes[a](B3LYP/6-31G*) in the homodesmotic reactions between the neutral and dianion species of **1**, **2**, **3**, **4** and **5**

$A + B^{2-} \rightleftharpoons A^{2-} + B$

	A	1	2	3	4	5
	1	0.0				
	2	−84.0	0.0			
B	**3**	−128.7	−44.7	0.0		
	4	−163.9	−80.3	−35.5	0.0	
	5	−185.6	−101.6	−56.8	−21.3	0.0

[a] Values are given in kJ mol^{-1}. A negative value indicates the thermodynamic preference of A^{2-} over B^{2-}. As this matrix is anti-symmetric by its nature, the positive values in the upper half were omitted for clarity.

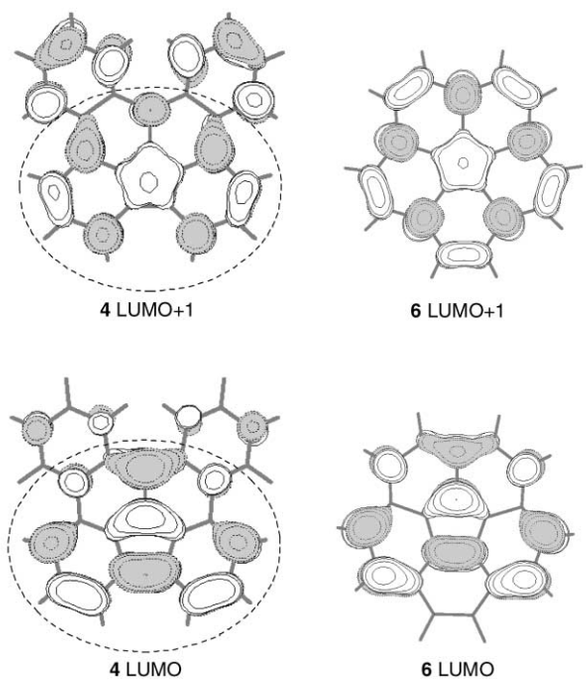

Fig. 2

¶ When large systems, especially polycycles, are discussed, one should take into account that 4*n*π systems are not necessarily anti-aromatic. In polycyclic compounds a modified way of electron counting is necessary.[2b,25] However, it seems that the Hückel counting rule may apply to some polycycles.[6] For example, C_{60}^{6-} is more aromatic than the neutral C_{60}, as has been previously demonstrated by us.[26]

‖ Calculation of radical anions for a more realistic one-electron transfer homodesmotic reaction is more complicated and less reliable because of the electronic structure of an open shell.

may be qualitatively achieved by a gradual alkali metal reduction of a mixture of two compounds, existing in similar concentrations. Soon after the reduction begins, and after the partially reduced solution has equilibrated, the only radical anions present will be those corresponding to the system that yields the energetically favoured radical anion. Radical anions do not exhibit NMR spectra and they also cause broadening of the NMR spectra of the corresponding neutral molecules *via* a degenerate reaction of electron exchange. If no similar electron exchange occurs between the two systems under equilibrium conditions, then the beginning of the reduction should result in a disappearance of one system's spectrum while the other's spectrum should be retained. Under the restrictions mentioned, the same should apply for each step of the reduction.

The sum of two consecutive homodesmotic reactions involving a single-electron transfer, *i.e.* $A + B^{\bullet -} \rightleftharpoons A^{\bullet -} + B$ and $A^{\bullet -} + B^{2-} \rightleftharpoons A^{2-} + B^{\bullet -}$, is the two-electron transfer homodesmotic reaction for which calculations have been made. Since in both the radical anion and the dianion of each system the extra electrons populate the same molecular orbital (the system's LUMO), it is expected that the same order of relative stability would be observed in both stages of reduction for each couple of systems. In other words, the tendency of the equilibrium in the first homodesmotic reaction (reflecting the relative stability of the radical anions compared to the neutral species) should be the same in the second homodesmotic reaction and thus in the whole process. Therefore the summation of the qualitative results from both stages should yield an unambiguous comparison between the experimental results and the calculated energy values outlined in Table 3.

To test the predictions made in Table 3 (as well as the aforementioned assumptions), three binary mixtures were prepared: **1** with **2**, **2** with **4** and **4** with **5**.** This is the minimal set of mixtures needed to be tested in order to confirm the relative stability order of $\mathbf{1}^{2-} > \mathbf{2}^{2-} > \mathbf{4}^{2-} > \mathbf{5}^{2-}$. Fig. 3 shows the results

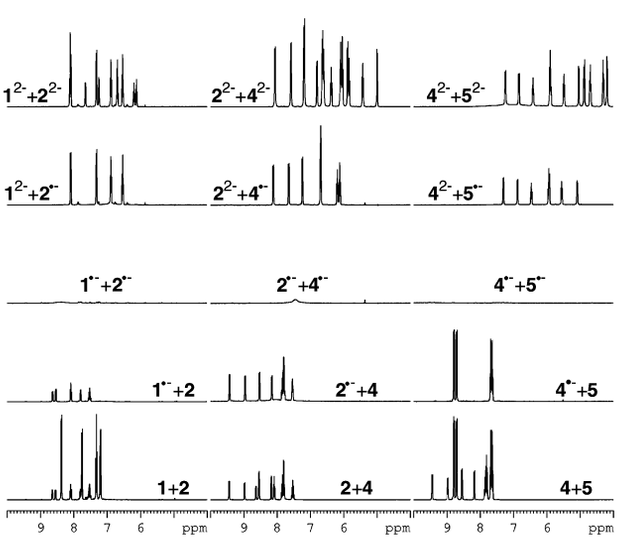

Fig. 3 ^{1}H NMR of binary mixtures at different reduction stages (as denoted by the labels). The species of **1** and **5** exhibit 4 proton peaks, while 7 peaks (some of them overlapping) are exhibited by the species of **2** and **4**. Note the increasing paratropic effect on the protons upon reduction to dianions when advancing from **1** to **5**. All spectra were recorded at 298 K, except for the spectra of $\mathbf{2}^{2-} + \mathbf{4}^{2-}$ and $\mathbf{4}^{2-} + \mathbf{5}^{2-}$, which were recorded at 220 and 250 K, respectively, due to line broadening of the corresponding dianions at room temperature.

of the gradual reduction of these three mixtures. Our previous assumption regarding the retaining of relative order of reduction in both stages is proven correct, as each system that forms the favourable radical anion in every couple also yields the energetically preferred dianion. Moreover, it is clearly noticed that **1** is preferentially reduced to a radical anion over **2**, the radical anion formation of **2** is preferred over that of **4**, and $\mathbf{4}^{\bullet -}$ formation precedes the formation of $\mathbf{5}^{\bullet -}$, and as mentioned, the same applies in an analogous way to the dianion formation. The results of these experiments confirm the relative stability order predicted by both the calculated enthalpy changes in homodesmotic reactions involving a two-electron exchange and the anisotropy-change index.

Conclusions

Dianions of five related PAHs have been analyzed for the changes occurring in their aromatic character, according to charge distribution analysis that employs corrections for anisotropy effects. The results show a clear correlation between the dianions' bonding structure and the ordering of the dianions according to the changes in anisotropy compared to the neutral precursors. Electron counting and structural considerations, as well as molecular orbital structure, rationalize the anisotropy-change index as an "aromaticity scale", which is applicable for both aromatic and anti-aromatic changes.

Based on the anisotropy-change index and Hückel calculations a complete picture is obtained, which describes all dianions as aromatic in nature with increasing anti-aromatic behaviour mixed into their character. Relative stability predictions based on this picture have been proven correct by calculations and experiments on binary mixtures.

The sensitivity of the anisotropy-change index to structural differences may suggest its use as a tool for prediction of properties of other structurally related anions.

Experimental

NMR experiments were carried out using a Bruker DRX-400 spectrometer equipped with a BGUII z-gradient, operating at 400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively. All samples were dissolved in THF-d_8 and the reported chemical shifts were calibrated to the downfield THF signal (δ_H 3.575; δ_C 67.393). Complete NMR assignment was obtained by applying standard 2D-NMR techniques such as COSY, NOESY, CH-correlation and long-range CH-correlation. Reported *J* values are given in Hz.

General procedure for the reduction process

A lithium wire was freshly produced and directly inserted into the upper part of an extended NMR tube, which had been previously filled with argon and contained the material (*ca.* 5 mg). Dry THF-d_8 (*ca.* 0.5 ml) was vacuum transferred from a reservoir to the tube. The sample was degassed under vacuum using the freeze–pump–thaw technique and flame sealed. The solution was brought into contact with the lithium wire by turning the tube upside down.

Quenching of the anions

After completing the analyses on the samples they were quenched with oxygen to verify the reversibility of the reduction process by recovering the neutral materials. The oxidation experiments were carried out by opening the samples under anhydrous conditions and blowing the gas *via* a syringe into the tube. The deep color gradually disappeared and the ^{1}H NMR spectra of the recovered neutral species were recorded.

Computational details

All computations described herein were carried out using the GAUSSIAN '98 program package[16] with the exception of

** Due to the significantly lower solubility of neutral **3** compared to the other compounds, which might add an unwanted effect, we omitted this compound from the binary mixture reduction experiments.

NBO[11,17] analyses, which employed JAGUAR 4.0 software (Schrödinger, Inc., Portland, Oregon, 1998).

Most of the calculations were carried out at the DFT level of calculation employing Becke's three-parameter hybrid density functional with the non-local correlation functional of Lee, Yang and Parr (B3LYP)[18] and the 6-31G* basis set.[19]

All structures calculated were geometrically optimized within their symmetry point groups. Only minimum structures were considered for NMR and NBO calculations. NMR chemical shifts were derived from additional single point calculations employing the GIAO[20] method as implemented in GAUSSIAN '98. The isotropy values obtained in this way were subtracted from the isotropy values obtained for optimized TMS (B3LYP/6-31G*//B3LYP/6-31G*: H 32.18 ppm; C 189.75 ppm).

Bifluorenylidene (1)

The full assignment of the NMR spectra of the neutral material is published elsewhere.[21]

Dianion (1^{2-}/2Li$^+$). The reported assignment of the dianion NMR spectra[10] is now corrected: δ_H(400 MHz, THF-d_8; 220 K) 6.33 (4 H, t, *J* 6.8, 3-H), 6.69 (4 H, t, *J* 7.0, 2-H), 7.30 (4 H, d, *J* 8.1, 1-H) and 7.98 (4 H, d, *J* 7.4, 4-H); δ_C(100 MHz, THF-d_8; 220 K) 96.6 (C-9), 106.6 (C-3), 117.7 (C-2), 118.3 (C-4), 118.5 (C-1), 123.1 (C-4a) and 134.4 (C-8a).

Benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (2)

δ_H(400 MHz, THF-d_8; 298 K) 7.50 (2 H, t, *J* 7.3, 8-H), 7.54 (2 H, t, *J* 7.3, 9-H), 7.79 (2 H, t, *J* 7.6, 2-H), 8.07 (2 H, d, *J* 7.6, 7-H), 8.10 (2 H, d, *J* 7.5, 1-H), 8.54 (2 H, d, *J* 8.1, 3-H) and 8.63 (2 H, d, *J* 6.8, 10-H); δ_C(100 MHz, THF-d_8; 298 K) 120.5 (C-1), 122.2 (C-7), 123.0 (C-3), 126.9 (C-10), 128.7 (C-9), 128.8 (C-3a), 129.4 (C-2), 129.6 (C-8), 133.9 (C-10b), 135.4 (C-3c), 138.6 (C-10a), 138.7 (C-6a) and 142.9 (C-6b).

Dianion (2^{2-}/2Li$^+$). δ_H(400 MHz, THF-d_8; 200 K) 6.03 (2 H, t, *J* 7.1, 2-H), 6.08 (2 H, t, *J* 6.9, 8-H), 6.60 (2 H, t, *J* 7.2, 9-H), 6.64 (2 H, d, *J* 6.7, 3-H), 7.18 (2 H, d, *J* 7.6, 1-H), 7.58 (2 H, d, *J* 7.4, 7-H) and 8.06 (2 H, d, *J* 8.4, 10-H); δ_C(100 MHz, THF-d_8; 200 K) 102.9 (C-10b), 105.3 (C-8), 108.2 (C-3), 112.0 (C-2), 116.9 (C-9), 117.3 (C-1), 119.0 (C-10), 119.5 (C-7), 121.2 (C-6b), 122.3 (C-6a), 126.4 (C-10a), 132.3 (C-3a) and 138.5 (C-3c).

Diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (3) and dianion (3^{2-}/2Li$^+$)

The full assignment of the NMR spectra of the neutral material and its dianion is published elsewhere.[4]

Benz[*g*]indeno[1,2,3,4-*mnop*]chrysene (4)

δ_H(400 MHz, THF-d_8; 298 K) 7.78 (2 H, t, *J* 9.2, 3-H), 7.80 (2 H, t, *J* 7.6, 6-H), 7.84 (2 H, t, *J* 7.7, 2-H), 8.16 (2 H, d, *J* 7.1, 7-H), 8.54 (2 H, d, *J* 8.1, 5-H), 8.96 (2 H, d, *J* 7.9, 4-H) and 9.43 (2 H, d, *J* 8.2, 1-H); δ_C(100 MHz, THF-d_8; 298 K) 122.7 (C-5), 123.0 (C-7), 123.7 (C-14b), 126.2 (C-4), 127.1 (C-3), 128.0 (C-2), 128.4 (C-1), 128.7 (C-4b), 129.9 (C-6), 132.7 (C-7d), 133.3 (C-4c), 133.4 (C-14a), 134.2 (C-4a) and 138.6 (C-7a).

Dianion (4^{2-}/2Li$^+$). δ_H(400 MHz, THF-d_8; 200 K) 4.98 (2 H, d, *J* 6.5, 5-H), 5.41 (2 H, t, *J* 7.3, 6-H), 5.83 (2 H, t, *J* 7.0, 3-H), 5.87 (2 H, d, *J* 8.3, 7-H), 6.36 (2 H, t, *J* 7.3, 2-H), 6.79 (2 H, d, *J* 7.4, 4-H) and 7.17 (2 H, d, *J* 8.6, 1-H); δ_C(100 MHz, THF-d_8; 200 K) 92.0 (C-5), 102.3 (C-14b), 109.5 (C-7a), 111.2 (C-3), 112.0 (C-7d), 113.6 (C-7), 116.9 (C-6), 121.4 (C-1), 124.6 (C-4), 124.6 (C-2), 127.8 (C-4a), 132.3 (C-4c), 137.6 (C-14a) and 140.1 (C-4b).

Dibenzo[*g*,*p*]chrysene (5)

δ_H(400 MHz, THF-d_8; 298 K) 7.59 (4 H, t, *J* 7.5, 2-H), 7.66 (4 H, t, *J* 7.5, 3-H), 8.68 (4 H, d, *J* 8.5, 1-H) and 8.77 (4 H, d, *J* 8.1, 4-H); δ_C(100 MHz, THF-d_8; 298 K) 124.5 (C-4), 127.3 (C-2), 127.4 (C-3), 128.3 (C-8b), 129.6 (C-1), 130.1 (C-8a) and 131.9 (C-4a).

Dianion (5^{2-}/2Li$^+$). The dianion has been obtained before,[12a] but its NMR spectra and assignment have never been reported. δ_H(400 MHz, THF-d_8; 250 K) 4.21 (4 H, d, *J* 7.2, 4-H), 4.31 (4 H, t, *J* 7.0, 3-H), 4.70 (4 H, t, *J* 7.4, 2-H) and 4.89 (4 H, d, *J* 8.2, 1-H); δ_C(100 MHz, THF-d_8; 250 K) 94.9 (C-8b), 107.7 (C-1), 114.3 (C-3), 121.7 (C-4), 129.6 (C-2), 145.7 (C-4a) and 151.3 (C-8a).

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