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Spectrometry and Reactivity of Benzanthrenyl and 1-Hydroperylenyl Anions

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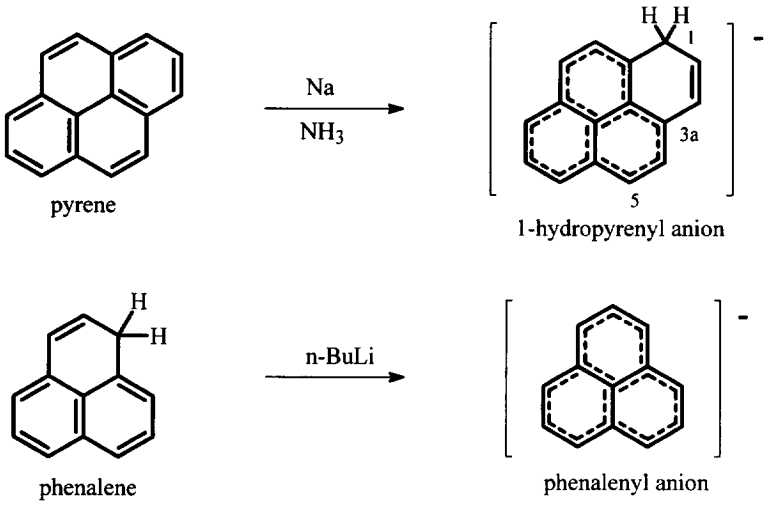
Abstract: Charge distribution and reactivity of benzanthrenyl (1^-) and 1-methyl-1-hydroperylenyl anion (2^-) are examined by means of semiempirical calculations, NMR spectroscopy and reactions with electrophiles. Highest charge density and reactivity are located at position 7 of 1^- and the comparable position 12b of 2^-. A small degree of reactivity is located at positions 4 and 6 of 1^-, as shown by reactions. Generally, a good correlation between calculated charge distribution and charge distribution obtained from ^{13}C NMR is observed.

INTRODUCTION

During the dissolving metal reduction and reductive alkylation of polycyclic aromatic hydrocarbons (PAH), several anionic intermediates are formed, varying in structure, charge, and charge distribution.[1] Most PAH are transformed via the radical mono anion into their dianions. Some of these dianions are stable in liquid ammonia, whereas others are protonated to form the monohydro anions. These dianions and monohydro anions are very useful intermediates in the synthesis of new PAH.[2,3,4]

Much research has been performed on the dissolving metal reduction of pyrene and on determining the charge distribution and reactivity of the intermediates.[5] Upon reduction of pyrene with an alkali metal in liquid ammonia, the pyrene dianion is formed, which is immediately protonated by liquid ammonia to form the 1-hydropyrenyl anion (Scheme 1). Most of the charge in this 1-hydropyrenyl anion is confined to a phenalenyl moiety and therefore the 1-hydropyrenyl anion can be regarded as a vinyl substituted phenalenyl anion. The phenalenyl anion itself is a highly symmetrical singly charged species in which the charge is equally spread over six different carbon atoms (Scheme 1).[6]

A recent study concerning the charge distribution and reactivity of the 1-hydropyrenyl anion showed a large perturbation of the charge distribution in the phenalenyl moiety by the vinyl substituent, causing the reactivity to be mainly concentrated at two positions.[5] Depending on the nature of the electrophile, reaction occurs at position 3a or 5. By using a combination of chemical reactions, NMR spectroscopy and semiempirical calculations, the structure and charge distribution of the anion could be elucidated.



Scheme 1

Upon reduction of perylene to its dianion, followed by alkylation and oxidative workup of the intermediate mono anion, a 1-alkylated perylene is isolated.[4] The mono anion must therefore have the structure depicted in Scheme 2. This 1-alkyl-1-hydroperylenyl anion can be regarded as a vinyl substituted benzanthrenyl anion. The benzanthrenyl anion ($\mathbf{1}^-$) in turn can be regarded as a benzo-annelated phenalenyl anion. It can easily be obtained by deprotonation of one of the possible benzanthrene isomers of which 7*H*-benzanthrene (**1**) is the most stable isomer (Scheme 2).[7]

We are interested in the effect that benzo-annelation of the phenalenyl anion may have on its charge distribution and reactivity and in the effect of a conjugated double bond on the charge distribution and reactivity of the benzanthrenyl anion.

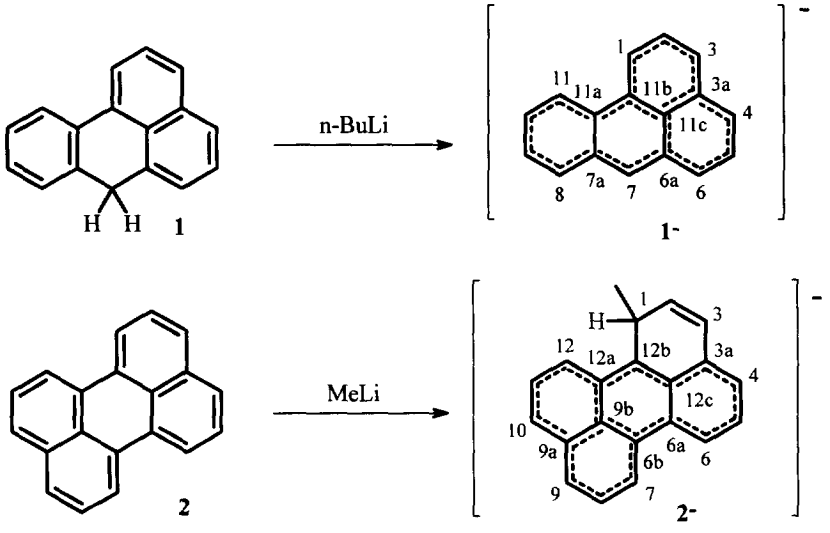
In this study we describe an investigation of the structure and reactivity of the benzanthrenyl and 1-methyl-1-hydroperylenyl anions ($\mathbf{1}^-$ and $\mathbf{2}^-$) by means of NMR spectroscopy, semiempirical calculations and reactions with different electrophiles.

RESULTS

Generation of the anions

A very efficient way of preparing the benzanthrenyl anion ($\mathbf{1}^-$) is by deprotonation of the stable and readily available 7*H*-benzanthrene (**1**). 7*H*-Benzanthrene was prepared using the procedure of Harvey et al.[8]

The benzanthrenyl anion was generated by addition of n-BuLi to a solution of **1** in THF under an atmosphere of argon at -60°C. Warming up to -20°C resulted in a deep green solution of **1**$^-$ (Scheme 2). As reported previously,[9] addition of methyllithium to a suspension of perylene in THF and stirring for 16 hours results in the formation of a deep green solution of the 1-methyl-1-hydroperylenyl anion (**2**$^-$, Scheme 2).



Scheme 2

Semiempirical calculations

Semiempirical calculations were performed on **1**$^-$ and **2**$^-$ using the PM3 parametrization. These calculations point to carbon atom 7 of **1**$^-$ as the position with the highest negative charge. Carbon atoms 4, 6, 1, 3, 10, 8 and 11a are the other carbons bearing significant amounts of charge. The HOMO coefficients of **1**$^-$ show approximately the same distribution as the charge.

In the case of **2**$^-$, highest charge and HOMO coefficient are located at 12b. The other positions of significant charge and HOMO coefficient are 12, 10, 7, 5, 9, 2, 6a and 3a.

NMR spectroscopy

NMR samples of **1**$^-$ and **2**$^-$ were generated in a glove bag under an atmosphere of argon. In the NMR tube, 50 mg of **1** or **2**, THF-d_8 and methyllithium in diethyl ether were brought together. After three freeze-pump-thaw cycles to remove all traces of oxygen, the NMR tube was sealed under vacuum. Of these samples 400

MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were taken. The assignment of all signals was accomplished by recording proton-proton COSY, NOESY and C-H COSY spectra together with NOE difference spectroscopy.

Table 1. Calculated charges and HOMO coefficients of **1**$^-$ and **2**$^-$.

	charge		HOMO			charge		HOMO	
carbon	**1**$^-$	**2**$^-$	**1**$^-$	**2**$^-$	carbon	**1**$^-$	**2**$^-$	**1**$^-$	**2**$^-$
1	-0.265	0.065	0.321	0.025	3a	0.066	-0.121	0.019	0.238
2	-0.052	-0.168	0.004	0.133	6a	0.113	-0.142	0.006	0.295
3	-0.234	-0.081	0.297	0.006	6b		0.069		0.002
4	-0.300	-0.067	0.398	0.009	7a	0.087		0.042	
5	-0.020	-0.230	0.012	0.260	9a		0.058		0.007
6	-0.296	-0.044	0.412	0.004	9b		-0.066		0.099
7	-0.351	-0.254	0.500	0.318	11a	-0.148		0.298	
8	-0.173	-0.057	0.239	0.001	11b	0.073		0.009	
9	-0.088	-0.222	0.016	0.288	11c	-0.068		0.101	
10	-0.231	-0.287	0.270	0.378	12a		0.123		0.001
11	-0.043	-0.021	0.014	0.002	12b		-0.318		0.497
12		-0.298		0.391	12c		0.116		0.029

In the ^{1}H NMR spectrum of **1**$^-$ we observe two ABC patterns, one ABCD spectrum and a singlet. Irradiation of the singlet belonging to H-7, shows a NOE effect on the signal at 6.39 ppm which is part of the ABCD spectrum and therefore assigned to H-8. Protons 9, 10 and 11 can consecutively be assigned using the H-H COSY spectrum. Furthermore, nuclear Overhauser enhancement on the signal of H-1 at 6.30 ppm was observed upon irradiating H-11. Using the COSY spectrum, the remaining signals belonging to this spin system can be found. The distinction between H-4 and H-6 can be made from the NOE effect between H-3 and H-4.

The assignment of the tertiary ^{13}C signals was achieved by recording a C-H COSY spectrum. This assignment is confirmed by measuring the C-H COSY spectrum optimized for couplings of 10 Hz in which only ^{3}J correlations are observed. With the aid of this ^{3}J C-H COSY spectrum, the quaternary signals could be assigned.

The ^{13}C and ^{1}H NMR spectra of **2**$^-$ were assigned with the aid of a H-H COSY, a C-H COSY and C-H COSY spectrum optimized for ^{3}J C-H couplings. The 400 MHz ^{1}H NMR spectrum of **2**$^-$ consists of three ABC spectra and an $ABCX_3$ spectrum, the X_3 part of which coincides with the methyl signal of ether which is the

solvent of the methyllithium. Protons 1, 2 and 3 can consecutively be found using the H-H COSY spectrum. In the ^{3}J C-H COSY a correlation between C-3 and H-4 is observed. H-5 and H-6 can be found in the H-H COSY spectrum. C-3a can be identified from its ^{3}J couplings with H-5 and H-2. H-2 in turn shows a correlation with the quaternary signal at 100.37 ppm, which is therefore assigned to C-12b. This atom has a second correlation with the proton at 5.54 ppm which is therefore assigned to H-12. H-11 and H-10 can then be found using the H-H COSY spectrum. The ^{3}J C-H COSY shows a correlation between H-10 and a signal at 113.86 ppm which is assigned to C-9. C-8 and C-7 can then be found using the H-H COSY spectrum. The quaternary signals can be assigned using the ^{3}J C-H COSY. Correlations are observed between C-9b and H-7, H-9, H-10 and H-12. C-9a is found from its correlations with H-8 and H-11. Carbon 6a shows a correlation with H-5, C-12a with H-11, C-6b with H-8 and the remaining quaternary signal which does not show any correlation is assigned to C-12c.

Table 2. ^{1}H and ^{13}C NMR chemical shifts of **1**$^-$ and **2**$^-$. ^{1}H chemical shifts are relative to the 1.07 ppm signal of diethyl ether and ^{13}C chemical shifts are relative to the THF signal at 25.3 ppm.

	1$^-$		**2**$^-$			**1**$^-$	**2**$^-$
posn.	^{1}H	^{13}C	^{1}H	^{13}C	posn.	^{13}C	^{13}C
1	6.31	103.97	3.62	34.87	3a	143.75	127.67
2	6.28	127.23	5.52	130.09	6a	143.85	120.70
3	5.88	113.58	5.99	127.82	6b		136.98
4	5.31	101.92	6.17	124.34	7a	139.59	
5	6.06	128.51	5.89	112.45	9a		142.95
6	5.36	104.18	7.08	122.85	9b		132.37
7	5.24	95.61	6.50	105.20	11a	121.54	
8	6.39	123.50	6.39	126.30	11b	138.89	
9	6.47	125.86	6.06	113.86	11c	135.69	
10	6.01	113.22	5.61	104.71	12a		139.16
11	7.26	123.30	6.30	128.45	12b		100.37
12			5.54	100.22	12c		135.36
1-CH_3			1.10	23.94			

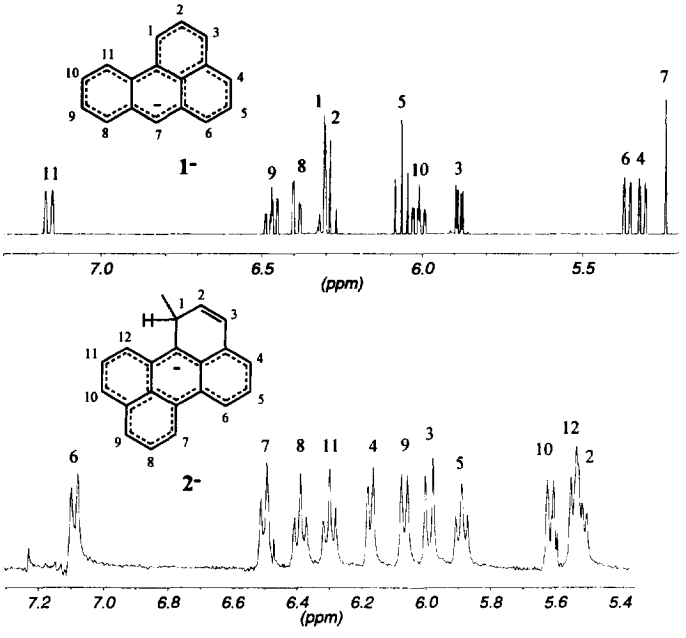


Figure 1. 400 MHz ^{1}H NMR spectra of **1**$^-$ and **2**$^-$ in THF-d_8 at 297 K.

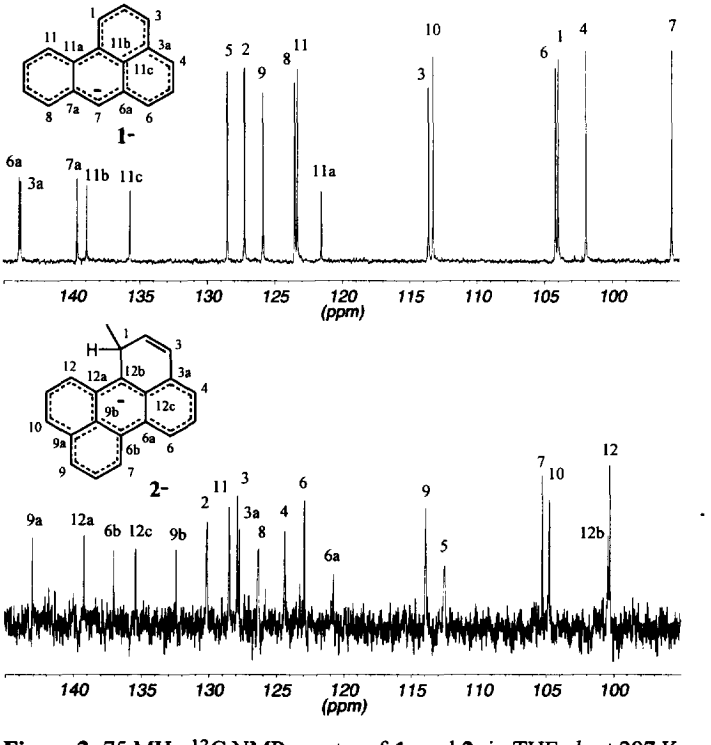


Figure 2. 75 MHz ^{13}C NMR spectra of **1**$^-$ and **2**$^-$ in THF-d_8 at 297 K.

Reactions with electrophiles

Addition of an α,ω-dibromoalkane to a solution of **1**$^-$ at -20°C and stirring for one hour caused the colour of the reaction mixture to change to light-yellow. Upon addition of a second equivalent of base, the colour changed to deep green. Stirring for three hours at -20°C resulted in a light-yellow solution, indicating completion of the reaction.

Reaction of **1**$^-$ with 1,2-dibromoethane and a second equivalent of base, resulted in the isolation of 25% of **3**, after column chromatography. The structure of **3** was confirmed by means of mass spectrometry, ^{1}H NMR, COSY and NOE difference spectroscopy. In the upfield part of the ^{1}H NMR spectrum two multiplets typical for a spiro three-membered ring are observed. A shielding effect by the cyclopropyl group on H-6 and H-8 was observed and confirmed by means of NOE difference spectroscopy. H-1 has a chemical shift typical for a bay-region proton.[10] The rest of the signals were assigned by means of the H-H COSY spectrum.

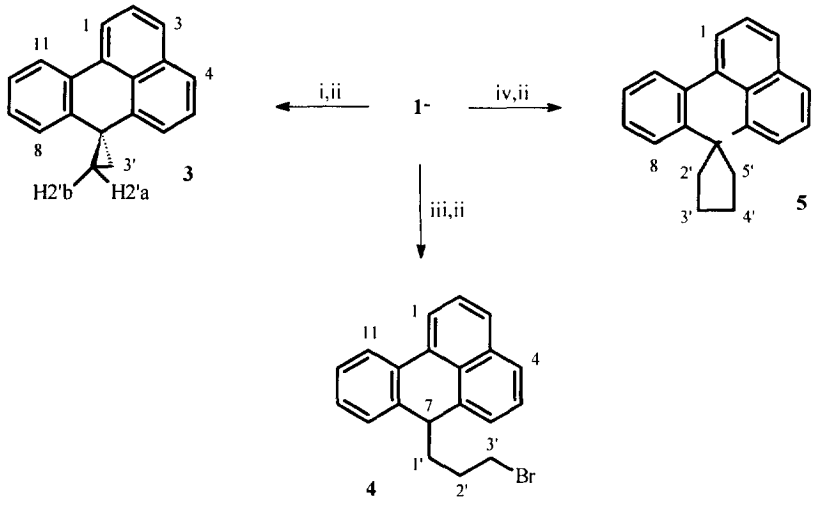
Reaction of **1**$^-$ with 1,4-dibromobutane and a second equivalent of base, resulted in the isolation of 65% **5**, after column chromatography. The structure of **5** was confirmed by means of mass spectroscopy, ^{1}H NMR, COSY and NOE difference spectroscopy. Individual irradiation of the three different groups of aliphatic signals results in NOE effects on the H-6, H-8 multiplet. Again, H-1 has a chemical shift typical for a bay-region proton.[10] The rest of the signals were assigned by means of the COSY spectrum, in which also a correlation between H-3 and H-4 was observed.

Reaction of **1**$^-$ with 1,3-dibromopropane resulted in the isolation of 40% of **4**, after column chromatography. The mass spectrum of **4** clearly proves the presence of a bromine atom. The aromatic part of the ^{1}H NMR spectrum of **4** is almost identical to that of **1**. The signal of H-7 is a triplet with a relative intensity of one proton and is now the A-part of an ABB'CC'D_2 spectrum in the aliphatic region of the spectrum. The BB'CC'D_2 part indicates a 3-bromopropyl chain attached to a chiral position, proving the structure for **4** as depicted in Scheme 3. Reaction of **4** with one equivalent of base resulted in the isolation of 20% of the starting material, together with oligomeric material.

Reaction of the benzanthrenyl anion **1**$^-$ with vinamidinium salt **6** results, after electrocyclization and de-amination, in the formation of benzo[*e*]pyrene as was reported by Jutz.[11] who also isolated a small amount of benzo[*a*]pyrene, a product not found by Lee and Harvey.[12] Stirring of a mixture of benzanthrene (**1**) together with sodium methanolate and vinamidinium salt **6** and heating at 180°C for 16 hours results in the isolation of 45 % of a 1:15 mixture of benzo[*a*]pyrene and benzo[*e*]pyrene (Scheme 4). A trace of perylene was also detected with the aid of TLC.

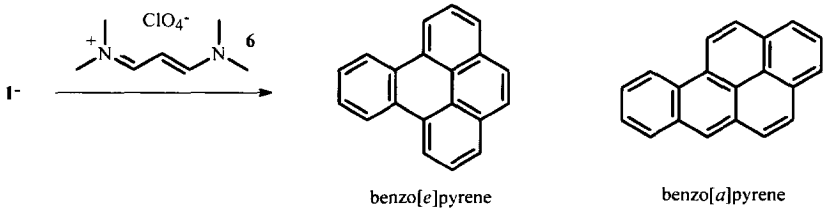
Addition of methyl iodide to a solution of **2**$^-$ at room temperature, workup and column chromatography results in the isolation of 54% of trans-substituted 1,12b-dihydro-1,12b-dimethylperylene (**7**), the ^{1}H NMR spectrum of which is identical to that reported by Ebert et al. (Scheme 5).[13] Addition of methanol to a solution of **2**$^-$ at -40°C, workup and column chromatography results in the isolation of trans-substituted 1,12b-dihydro-1-

methylperylene (**8**, 31%), the structure of which was proven by means of ^{1}H NMR spectroscopy. The aromatic and olefinic parts of the spectrum of **8** are almost identical to those of **7**. The only differences in the aliphatic region are the absence of the signal of 12b-CH_3, the presence of a doublet at 4.76 ppm, which is very similar to the chemical shift of H-7 in benzanthrene and the signal of H-1 which has changed from a quintet into a multiplet, proving the presence of a proton at position 12b in **8**.

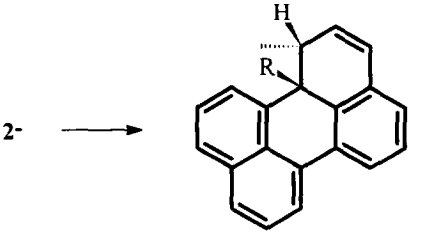


Reaction of **1**$^-$ with dibromoalkanes. i 1,2-dibromoethane; ii n-BuLi; iii 1,3-dibromopropane; iv 1,4-dibromobutane.

Scheme 3



Scheme 4



7 R= Me

8 R= H

Scheme 5

DISCUSSION

Calculation of the charge distribution and HOMO coefficients of the benzanthrenyl anion (**1**$^-$) gives results similar to those found by Pagni et al.[14] Carbon 7 is predicted to bear the highest charge density, followed by carbons 4, 6, 1, 3, 10, 8 and 11a. Our calculations predict only a small amount of negative charge in the newly added ring, but a severe perturbation of the charge distribution in the phenalenyl moiety. The HOMO coefficients obtained from our calculations show approximately the same order as the charge distribution.

The charge distribution in the benzanthrenyl unit of the 1-methyl-1-hydroperylenyl anion (**2**$^-$) differs only slightly from the charge distribution of **1**$^-$. The highest charge density and HOMO coefficient are found at position 12b, which corresponds to position 7 in **1**$^-$. Positions 10 and 12, corresponding with 4 and 6 in **1**$^-$, again are the positions with the second highest charge. The amount of charge predicted at position 2 is smaller compared to the β-positions in the double bonds of the vinylphenalenyl and 1-hydropyrenyl anions.

The charge distribution of the benzanthrenyl anion (**1**$^-$) may cautiously be estimated from its 300 MHz ^{1}H NMR spectrum. Protons 7, 4 and 6 are at the highest field, suggesting a relatively high charge at these positions. ^{13}C NMR spectroscopy however, gives a more reliable indication of the charge at different positions in an anion because these chemical shifts are less sensitive to ring current and concentration effects. At first glance, the ^{13}C NMR chemical shifts of **1**$^-$ appear to agree well with the calculated charge distribution. The signals at highest field are 7, 4 and 6 in that order, in agreement with the calculated charge densities. The same correspondence between ^{13}C NMR and calculations is observed for the other tertiary ^{13}C signals with the exception of C-1 and C-11. These two carbon atoms appear at significantly higher field than C-3, C-10 and C-2, C-5 respectively, although the charge densities are calculated to be similar. This may be due to the fact that both are bay region

positions. The hydrogens in this bay region are very close together, causing a repulsion between their electrons. This results in a polarization of the electron distribution in the σ-bonds towards the carbons, which causes an upfield shift of the two ^{13}C signals. The opposite effect should be found in the ^{1}H NMR spectrum, where H-11 is indeed found upfield of H-2, H-5 and H-1 is found upfield from H-3, H-10. Steric effects like these are well-known in the NMR spectra of neutral compounds containing bay regions.[10] In the case of the quaternary signals again a good correlation between chemical shift and calculated charge density is found.

The use of proton NMR to derive the charge distribution of **2**$^{-}$ is complicated by the fact that position 12b, which has the highest calculated charge, is a quaternary carbon atom. The charge distribution of the tertiary positions may cautiously be derived from the ^{1}H NMR spectrum of **2**$^{-}$. This spectrum shows protons 2, 12 and 10 at the highest field. However, for the reasons described above, ^{13}C NMR spectroscopy is a more reliable tool for determining the charge distribution of **2**$^{-}$.

The ^{13}C NMR spectrum of **2**$^{-}$ implies a charge distribution similar to that found by calculations. Two signals which do not follow this rule are C-6 and C-7. Both are bay-region carbon atoms just as C-1 and C-11 in **1**$^{-}$. The same rationalization as was used in the case of **1**$^{-}$ for the deviation of the charge densities of C-1 and C-11, may now be applied to C-6 and C-7 of **2**$^{-}$. Another signal of which the interpretation is not straightforward is C-12b, because the chemical shifts of tertiary and quaternary positions cannot be compared directly. In going from a tertiary to a quaternary carbon atom, a downfield shift is observed because of the higher electronegativity of carbon. This is known as the α-effect.[15] This implies that, although C-12 and C-12b have a similar chemical shift, the highest charge density is located at position 12b. In the ^{13}C NMR spectrum of **2**$^{-}$, both the signals of positions 2 and 3 are located at relatively low field, in contrast to the chemical shift of C-2 in the 1-hydropyrenyl anion.[5] This indicates that only a small amount of negative charge is located in the double bond of **2**$^{-}$, as was suggested by semiempirical calculations.

Summarizing, the highest charge density according to ^{13}C NMR spectroscopy in **2**$^{-}$ is located at position 12b, followed by positions 12 and 10 respectively. The rest of the signals show a good correlation between calculated charge density and charge density suggested by NMR spectroscopy.

The use of 1,4-dibromobutane proved to be very useful in the investigation of the structure and reactivity of phenalene and substituted phenalenes.[5,6] The intramolecular bi-alkylation procedure results in a spiro annelated product, which indicates the position of reaction. Reaction of **1**$^{-}$ with 1,4-dibromobutane results in the formation of **5** as the sole product. This product arises from initial attack of **1**$^{-}$ by the alkyl bromide at position 7. Deprotonation of the intermediate 7-(ω-bromoalkyl)-7*H*-benzanthrene results in the corresponding ω-bromoalkyl benzanthrenyl anion. Reaction at position 7 results in the formation of a spiro five-membered ring. This indicates highest reactivity of **1**$^{-}$ towards alkyl bromides at position 7, which is in accordance with the position of highest charge density determined by semiempirical calculations and NMR spectroscopy.

The reaction of 1,2-dibromoethane with an aromatic anion and a second equivalent of base is very useful for the introduction of fused five-membered rings to polycyclic ring structures.[16,17] In the case of **1**$^-$, the reaction resulted in the formation of a spiro three-membered ring, similar to the reactions performed on the phenalenyl[17] and 1-hydropyrenyl anions.[16] Initial reaction at the position bearing the highest charge, deprotonation and intramolecular reaction favours the formation of a spiro three-membered ring over the formation of a fused five membered ring. Rearrangement of the spiro three-membered ring by refluxing in xylene for 8 hr under an atmosphere of nitrogen to a fused five-membered ring proved not possible.

The reaction of the phenalenyl anion with 1,3-dibromopropane and a second equivalent of base proved to be useful in the introduction of a new fused six-membered ring to the existing carbon skeleton.[18] Reaction of **1**$^-$ with 1,3-dibromopropane and butyllithium yields the open chain product **4** as the sole isolated product. Apparently, the charge densities at positions 6 and 8 of **1**$^-$ are too low for intramolecular reaction to occur. This is confirmed by deprotonation of the open chain product **4** with one equivalent of base. Stirring for three hours results in the isolation of 20% of the starting compound. The remaining amount of starting material is most likely transformed into oligomers, a well-known reaction in the reductive alkylation of anthracene dianion with 1,3-dibromopropane.[19]

Reaction of **1**$^-$ with **6** results in the formation of benzo[*e*]pyrene together with a small amount of benzo[*a*]pyrene. The formation of benzo[*e*]pyrene arises from initial attack at position 7 and subsequent de-amination, electrocyclization at position 6 and again de-amination. Electrocyclization of this intermediate to position 8 results in the formation of perylene. With the aid of TLC a small amount of this product is indeed observed. In the previously mentioned studies[11,12] no perylene was detected. The isolation of benzo[*a*]pyrene can be rationalized by assuming initial attack of **6** at either position 3 or 4. The charge distribution obtained from calculations and NMR spectroscopy, suggests initial attack at position 4. Reaction of **1**$^-$ with a carbene[14] results in products arising from initial attack at positions 7, 4 and 6, indicating that the highest reactivity of **1**$^-$ towards carbenes is confined to these three positions. This is in accordance with our results obtained from semiempirical calculations and ^{13}C NMR spectroscopy, which indicate positions 7, 4 and 6 to be the positions with the highest charge density and HOMO coefficients.

Reaction of **2**$^-$ with methyl iodide results in the formation of 1,12b-dihydro-1,12b-dimethylperylene as the sole product of alkylation. Protonation of **2**$^-$ also results in reaction at position 12b as is proven by the isolation of 1-methyl-1,12b-dihydroperylene as the sole protonation product. This indicates that the reactivity of **2**$^-$ towards either hard or soft electrophiles is confined to position 12b. These findings agree with the performed calculations and NMR spectroscopy, which indicate highest charge density and HOMO coefficient at position 12b.

Benzo annelation of the phenalenyl anion has a large effect on the charge distribution and HOMO coefficients of the anion. Highest charge and reactivity are located at positions 7, 4 and 6, according to

semiempirical calculations, ^{13}C NMR spectroscopy and reactions with electrophiles, instead of being equally spread over six different positions.

Only a minor effect is observed on the charge distribution of the benzanthrenyl moiety in $\mathbf{2}^-$ as a consequence of the introduction of a conjugated double bond connected at position 8 of $\mathbf{1}^-$. This is in contrast to the drastic effect of the conjugated double bond on the charge distribution in the phenalenyl nucleus in the 1-hydropyrenyl anion.[5] As a result, the charge distribution and reactivity of $\mathbf{1}^-$ and $\mathbf{2}^-$ are very similar. The major amount of charge and reactivity are located at the comparable positions 7 of $\mathbf{1}^-$ and 12b of $\mathbf{2}^-$. One exception is the charge density according to ^{13}C NMR spectroscopy of positions 10 and 12 of $\mathbf{2}^-$, which have switched in their relative order compared to the corresponding positions 4 and 6 of $\mathbf{1}^-$.

EXPERIMENTAL

Benzanthrene was obtained via the method of Harvey et al.[8] Perylene was synthesized using our earlier reported method.[4] n-Butyllithium (1.6 M in hexane) was purchased from Janssen Chimica (Belgium). Methyllithium (1.6 M in diethyl ether) was obtained from Aldrich. 1,2-Dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane were obtained from Merck. Tetrahydrofuran from Janssen Chimica was distilled from $LiAlH_4$ directly before use. Tetrahydrofuran-d_8 and diglyme-d_{14} were purchased from Aldrich. Column chromatography was performed on silica gel 60 (230-400 mesh) obtained from Merck. The 400-MHz ^1H NMR and 100-MHz ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer. The 300-MHz ^1H NMR, 75-MHz ^{13}C NMR, H-H COSY, NOESY, NOE-difference and ^{13}C-^1H correlated spectra were recorded on a Bruker WM-300 spectrometer. The 200 MHz ^1H NMR spectrum was recorded on a Jeol JNM-FX-200. All chemical shifts (δ) of the neutral compounds are given in ppm relative to tetramethylsilane (TMS); the chemical shifts of the ^1H NMR spectra of the anions are given relative to the 1.07 ppm signal of diethyl ether and the ^{13}C NMR shifts relative to the 25.3 ppm signal of THF; the coupling constants (J) are given in Hz. Observed NOE effects from NOE difference experiments are printed as: NOE: irradiated proton (observed correlation proton). UV-VIS spectra were recorded on a Varian DMS 200 spectrophotometer. Mass spectra were recorded using a Finnigan MAT 900 with a direct insertion probe, in E.I. mode. Accurate masses in E.I. mode were measured with perfluorokerosine as standard compound.

Generation of the benzanthrenyl anion ($\mathbf{1}^-$) in an NMR tube. In a glove bag, under an atmosphere of argon, a solution of 56 mg of benzanthrene (0.26 mmol) in a 1:1 mixture of THF-d_8 and diglyme-d_{14} (total volume 1 ml) was transferred to an NMR tube. By means of a long needle, the solution was purged with argon. After this, 0.32 ml methyllithium (0.52 mmol) was added and the NMR tube was transferred to a vacuum line connected to the glove bag. The solution was cooled in a hexane bath (-125°C), submitted to four freeze-pump-thaw cycles,

sealed under vacuum and separated from the vacuum line. After thorough mixing, a deep green solution was obtained. Stored at -80°C the sample is stable for months.

^{1}H NMR (300 MHz, THF-d_8, diglyme-d_{14}) δ (ppm): 5.24 (1H, s, 7-H), 5.31 (1H, dd, *J* 1.2, 7.5, 4-H), 5.36 (1H, dd, *J* 1.2, 7.5, 6-H), 5.88 (1H, dd, *J* 2.2, 6.7, 3-H), 6.01 (1H, ddd, *J* 1.5, 6.5, 8.0, 10-H), 6.06 (1H, t, *J* 7.5, 5-H), 6.27-6.30 (1H, m, 2-H), 6.29-6.32 (1H, m, 1-H), 6.39 (1H, ddd, *J* 0.6, 1.5, 8.2, 8-H), 6.47 (1H, ddd, *J* 1.3, 6.5, 8.2, 9-H), 7.16 (1H, ddd, *J* 0.6, 1.3, 8.0, 11-H). ^{13}C NMR (300 MHz, THF-d_8, diglyme-d_{14}) δ (ppm): 95.61 (7-C), 101.92 (4-C), 103.97 (1-C), 104.18 (6-C), 113.22 (10-C), 113.58 (3-C), 121.54 (11a-C), 123.30 (11-C), 123.50 (8-C), 125.86 (9-C), 127.23 (2-C), 128.51 (5-C), 135.69 (11c-C), 138.89 (11b-C), 139.59 (7a-C), 143.75 (3a-C), 143.85 (6a-C). NOESY: 4-H, 3-H; 1-H, 11-H; 7-H, 8-H.

Generation of the 1-methyl-1-hydroperylenyl anion (2$^-$) in an NMR tube. According to the same procedure as described above, 50 mg of perylene was allowed to react with 0.20 ml of methyllithium in 1 ml of THF-d_8. This resulted in a deep green colour.

^{1}H NMR (300 MHz, THF-d_8) δ (ppm): 1.10 (3H, m, 1-CH_3), 3.62 (1H, m, 1-H), 5.52 (1H, t, *J* 9.5, 2-H), 5.54 (1H, d, *J* 7.3, 12-H), 5.61 (1H, d, *J* 7.5, 10-H), 5.89 (1H, dd, *J* 6.7, 7.8, 5-H), 5.99 (1H, d, *J* 9.5, 3-H), 6.06 (1H, d, *J* 7.5, 9-H), 6.17 (1H, d, *J* 6.7, 4-H), 6.30 (1H, t, *J* 7.7, 11-H), 6.39 (1H, d, *J* 7.5, 8-H), 6.50 (1H, d, *J* 7.7, 7-H), 7.08 (1H, d, *J* 7.8, 6-H). ^{13}C NMR (300 MHz, THF-d_8) δ (ppm): 23.94 (CH_3), 34.87 (1-C), 100.22 (12-C), 100.37 (12b-C), 104.71 (10-C), 105.20 (7-C), 112.45 (5-C), 113.86 (9-C), 120.70 (6a-C), 122.85 (6-C), 124.34 (4-C), 126.30 (8-C), 127.67 (3a-C), 127.82 (3-C), 128.45 (11-C), 130.09 (2-C), 132.37 (9b-C), 135.36 (12c-C), 136.98 (6b-C), 139.16 (12a-C), 142.95 (9a-C).

Reaction of 1$^-$ with 1,4-dibromobutane; Spiro[*7H*-benzanthrene-7,1'-cyclopentane] (5). 1.00 g *7H*-Benzanthrene (4.63 mmol) was dissolved in dry tetrahydrofuran (THF) and kept under an atmosphere of argon in a three-necked flask. The solution was cooled to -70°C in a liquid nitrogen/ethanol bath. Through a septum 2.90 ml (4.64 mmol) of n-butyllithium was syringed into the reaction mixture. The clear solution immediately turned deep black/green. The temperature was raised to -25°C and 553 µl (1.00 g, 4.63 mmol) 1,4-dibromobutane in 8 ml of dry THF was added through a dropping funnel. After two hours of stirring at -25°C the colour disappeared and a second portion of 2.90 ml n-butyllithium was added at -70°C. The temperature was raised again to -25°C and stirring continued until the colour disappeared again after 3 hours. The reaction mixture was quenched with water and extracted with hexane. The organic layer was washed with water until neutral, dried over magnesium sulphate, filtered and concentrated under reduced pressure. A white solid was obtained which was purified by means of column chromatography, using petroleum ether as eluent. This yielded 807 mg of product (2.97 mmol, 65%) as a white solid.

UV-VIS (hexane): λ_{max}: 225.9 nm; other maximum at: 325.2 nm. Exact mass calc. for $C_{21}H_{18}$: 270.1409; Found: 270.1383. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.00-2.11 (4H, m, 3'-CH_2, 4'-CH_2), 2.15-2.25 (2H, m, 2'-H, 5'-H), 2.31-2.41 (2H, m, 2'-H', 5'-H'), 7.27 (2H, m, 9-H, 10-H), 7.47 (1H, dd, *J* 7.6, 7.9, 5-H), 7.48 (1H, dd, *J* 7.4, 8.2, 2-H), 7.51-7.55 (2H, m, 6-H, 8-H), 7.67 (1H, dd, *J* 1.8, 7.6, 4-H), 7.74 (1H, dd, *J* 1.2, 8.2, 3-H), 8.04 (1H, dd, *J* 2.0, 7.4, 11-H), 8.06 (1H, dd, *J* 1.2, 7.4, 1-H). NOE: 3-CH_2, 4-CH_2 (6-H, 8-H); 2'-H', 5'-H' (6-H, 8-H); 2'-H, 5'-H (6-H, 8-H). *m/z* 270 (M^+, 100%), 241 (M^+-29, 75%) and 215 (M^+-55, 44%).

Reaction of 1$^-$ with 1,2-dibromoethane; Spiro[*7H*-benzanthrene-7,1'-cyclopropane] (3). According to the same procedure 1.00 g of benzanthrene (4.63 mmol) was converted to 256 mg of spiro[7*H*-benzanthrene-7,1'-cyclopropane] (**3**,1.06 mmol, 23%) using 2.90 ml (4.64 mmol) n-BuLi and 399 µl (870 mg; 4.63 mmol) 1,2-dibromoethane and again 2.90 ml n-BuLi. UV-VIS (hexane): λ_{max}: 235.1 nm; other maxima at: 329.4 nm; 343.6 nm; 360.8 nm. Exact mass calc. for $C_{19}H_{14}$: 242.1096; Found: 242.1080. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.50 (2H, dd, *J* 4.6, *J* 7.2, 2'a-H, 3'a-H), 1.83 (2H, dd, *J* 4.6, 7.2, 2'b-H, 3'b-H), 6.83 (1H, dd, *J* 1.2, 7.4, 6-H), 6.88 (1H, dd, *J* 3.3, 6.0, 8-H), 7.22-7.28 (2H, m, 9-H, 10-H), 7.40 (1H, dd, *J* 7.4, 8.1, 5-H), 7.48 (1H, dd, *J* 7.4, 8.0, 2-H), 7.71 (1H, dd, *J* 1.2, 8.0, 3-H), 7.76 (1H, dd, *J* 1.2, 8.1, 4-H), 8.04 (1H, dd, 1.2, 7.4, 1-H), 8.09 (1H, dd, *J* 3.3, 6.1, 11-H). NOE: 2'b-H, 3'b-H (8-H); 2'a-H, 3'a-H (6-H). *m/z* 242 (100%) and 215 (M^+- 27, 60%).

Reaction of 1$^-$ with 1,3-dibromopropane; 7-(3-Bromopropyl)-*7H*-benzanthrene (4). Following the same procedure as above 2.00 g benzanthrene (9.26 mmol) was converted to 1.32 g 7-(3-bromopropyl)-7*H*-benzanthrene (3.92 mmol, 42%) using 5.80 ml n-butyllithium (9.28 mmol) and 944 µl 1,3-dibromopropane (1.88 g; 9.30 mmol). The reaction was worked up after the first decolorization. UV-VIS (hexane): λ_{max}: 230.4 nm; other maxima at: 206.7 nm; 223.8 nm; 313.6 nm; 325.8 nm; 342.0 nm. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.35-1.63 (2H, m, 1'-CH_2), 1.83-1.95 (2H, m, 2'-CH_2), 3.09 (2H, t, *J* 6.8, 3'-CH_2), 4.42 (1H, t, *J* 5.8, 7-H), 7.27-7.39 (3H, m, 8-H, 9-H, 10-H), 7.37 (1H, dd, *J* 1.2, 7.1, 4-H), 7.47 (1H, dd, *J* 7.1, 8.1, 5-H), 7.51 (1H, dd, *J* 7.4, 8.2, 2-H), 7.70 (1H, dd, *J* 1.2, 8.1, 6-H), 7.76 (1H, dd, *J* 1.1, 8.2, 3-H), 8.01 (1H, dd, *J* 2.0, 5.2, 11-H), 8.03 (1H, dd, 1.1, 7.4, 1-H). NOE: 7-H (6-H, 8-H). *m/z* 338 (M^+ ^{81}Br, 10%), 336 (M^+ ^{79}Br, 10%) and 215 (100%).

Reaction of 1$^-$ with 6; Benzo[*e*]pyrene and benzo[*a*]pyrene. A solution of 347 mg (1.63 mmol) benzanthrene (**1**), 386 mg (1.60 mmol) **6** and 95 mg (1.8 mmol) of sodium methanolate in 7 ml of quinoline was stirred under an atmosphere of argon at rt for three hours. After this, the methanol formed during the reaction was evaporated. The mixture was then heated at 180°C for 16 hours under an atmosphere of argon. Cooling, addition of 10 ml of 97% perchloric acid, 100 ml of water, extraction with toluene, drying over magnesium sulphate and evaporation of the solvent in vacuo resulted in the isolation of the crude product. Filtration over a glass funnel filled with

silica with hexane as the eluent and evaporation of the solvents, resulted in the isolation of 185 mg (0.73 mmol, 45%) of a 15:1 mixture of benzo[*e*]pyrene and benzo[*a*]pyrene, the ratio of which was determined by means of NMR spectroscopy.[2,20]

Reaction of 2^- with methyl iodide; 1,12b-Dihydro-1,12b-dimethylperylene (7). To a suspension of 0.50 g (1.98 mmol) perylene in 40 ml of THF, 1.24 ml (1.98 mmol) methyllithium was added via a syringe. After stirring for 16 hours a deep green solution of 2^- is obtained. To this solution 123 µl (281 mg, 1.98 mmol) of methyl iodide was added via a syringe. This resulted in a change of the colour of the solution from deep green to yellow. Addition of toluene, washing with water until neutral, drying over magnesium sulphate and evaporation of the solid resulted in the isolation of the crude product. This could be further purified by means of column chromatography, using petroleum ether as the eluent. This resulted in the isolation of 302 mg (1.07 mmol, 54%) of pure **7**, together with 225 mg of perylene (45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.78 (3H, d, *J* 6.7, 1-CH_3), 1.41 (3H, s, 12b-CH_3), 3.04 (1H, quint, *J* 6.7, 1-H), 6.23 (1H, dd, *J* 6.7, 9.5, 2-H), 6.51 (1H, d, *J* 9.5, 3-H), 7.06 (1H, dd, *J* 1.3, 7.3, 4-H), 7.29 (1H, dd, *J* 7.3, 8.1, 5-H), 7.50 (1H, m, 11-H), 7.51 (1H, dd, *J* 7.6, 7.9, 8-H), 7.53 (1H, m, 12-H), 7.72 (1H, dd, *J* 2.8, 6.5, 10-H), 7.78 (1H, dd, *J* 1.2, 7.9, 9-H), 8.03 (1H, dd, *J* 1.3, 8.1, 6-H), 8.10 (1H, dd, *J* 1.2, 7.6, 7-H). NOE: 1-H (12-H, 12b-CH_3); 1-CH_3 (2-H, 12-H); 3-H (4-H); 12b-CH_3 (1-H, 12-H).

Reaction of 2^- with CH_3OH; 1,12b-Dihydro-1-methylperylene (8). To a solution of 2^- at -40°C, generated from 0.50 g (1.98 mmol) of perylene and 1.20 ml (1.98 mmol) of methyllithium, 81 µl (2.0 mmol) of methanol was added, causing the colour of the solution to change from deep green to yellow. Workup and column chromatography over silica gel using petroleum ether as the eluent, yielded 164 mg of **8** (0.614 mmol, 31%), together with 340 mg (68%) of perylene. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 0.70 (3H, d, *J* 6.9, 1-CH_3), 3.15 (1H, m, 1-H), 4.76 (1H, d, *J* 6.2, H-12b), 6.36 (1H, dd, *J* 6.2, 9.6, 2-H), 6.55 (1H, d, *J* 9.6, 3-H), 7.04 (1H, dd, *J* 8.9, 4-H), 7.29 (1H, dd, *J* 8.6, 8.9, 5-H), 7.43-7.53 (3H, m, 8-H, 11-H, 12-H), 7.69 (1H, d, *J* 6.9, 9-H), 7.73 (1H, d, *J* 7.6, 10-H), 7.98 (1H, d, *J* 8.6, 6-H), 8.02 (1H, d, *J* 7.2, 7-H).

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