Spectrometry and Reactivity of the 1-Hydropyrenyl Anion

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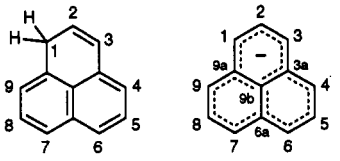
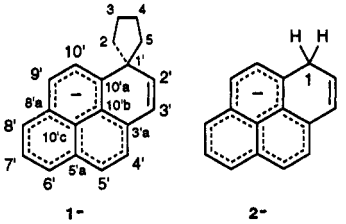
A study of the charge distribution in the 1-hydropyrenyl anion (2^-), and of its regioselectivity toward electrophilic attack was undertaken. In order to obtain reliable information on the reactive positions in 2^-, a model with the same conjugated system was prepared, which has its 1-position fixed with a spirocyclopentane ring. Highly resolved ^1H and ^{13}C NMR spectra of this spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-) and of 2^- were obtained. These spectra could be completely assigned by means of COSY, NOESY, and 2D ^1H–^{13}C COSY techniques. According to the ^{13}C NMR measurements, 5-C of 1^- and 2^- bears the highest negative charge. The results of PM3 semiempirical calculations support this finding and, furthermore, a large HOMO coefficient was calculated at the quaternary 3a-C of 2^-, suggesting that this position is susceptible toward attack by soft electrophiles. In full agreement with the ^{13}C NMR and PM3 results, 5-C of 1^- and 2^- show the highest reactivity toward electrophilic attack, while the quaternary 3a-C of 1^- and 2^- is attacked by soft electrophiles. These new results contradict earlier findings because until now, carbon atom 9-C of the 1-hydropyrenyl anion (2^-) was assumed to be the most reactive position, and soft electrophiles were thought to attack 10a-C of 2^-.

Introduction

Recently[1] we reported an improved preparation of 1*H*-phenalene and we demonstrated the use of the phenalenyl anion as a synthon for the preparation of larger fused PAH.[1,2] Electrophiles were found to react exclusively at

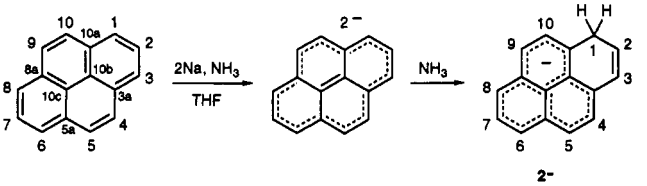


the six equivalent charge-bearing positions of the odd alternant phenalenyl anion, in accordance with earlier findings. Larger conjugated anions have also been used in our group as starting material for the preparation of PAH. An important example is the 1-hydropyrenyl anion (2^-). The 1-hydropyrenyl anion (2^-), which is formed by



treating pyrene in ammonia with 2 equiv of alkali metal (Scheme I), may be regarded as a phenalenyl anion derivative. It has been used as a valuable synthon for preparing cyclopenta[*cd*]pyrene,[3] a potent carcinogen which is widely spread in the environment.[4]

Scheme I



The 1-hydropyrenyl anion (2^-) is attacked with high regioselectivity by electrophiles. The resulting products, dihydropyrene derivatives, readily undergo acid- or base-catalyzed hydrogen shifts which thwart their adequate identification and thereby the establishment of the reactive sites of 2^-.

Recently, we reported an efficient alkylation of the phenalenyl anion with 1,4-dibromobutane and additional base.[1] Initial attack of 1,4-dibromobutane occurs at one of the six equivalent charged positions of the phenalenyl anion. The resulting 1-(4-bromobutyl)phenalene may be deprotonated, after which intramolecular alkylation occurs at the position of initial attack, and a spiro compound is formed. The product does not contain acidic protons and, therefore, it cannot rearrange under the conditions of its formation.

In order to obtain reliable information on the reactivity of 2^-, a model with the same conjugated system was prepared which has its 1-position fixed with a spirocyclopentane ring. This model, the spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-) will be alkylated with 1,4-dibromobutane and additional base. In analogy to the phenalenyl anion, it is expected that a spirocyclopentane ring is introduced at positions of high charge density. Sites at which the spirocyclopentane ring is introduced are established unambiguously relative to the fixed 1-position of 1^-. In addition to this, 2^- will be protonated and alkylated.

The results of these experiments will be correlated with the charge distribution in 1^- and 2^- because generally the charge distribution in conjugated anions is the most important factor[5–7] determining regioselectivity of elec-

(1) Hempenius, M. A.; Lugtenburg, J.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 403.
(2) Hempenius, M. A.; Lugtenburg, J.; Cornelisse, J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 635.
(3) Tintel, C.; Cornelisse, J.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 14.
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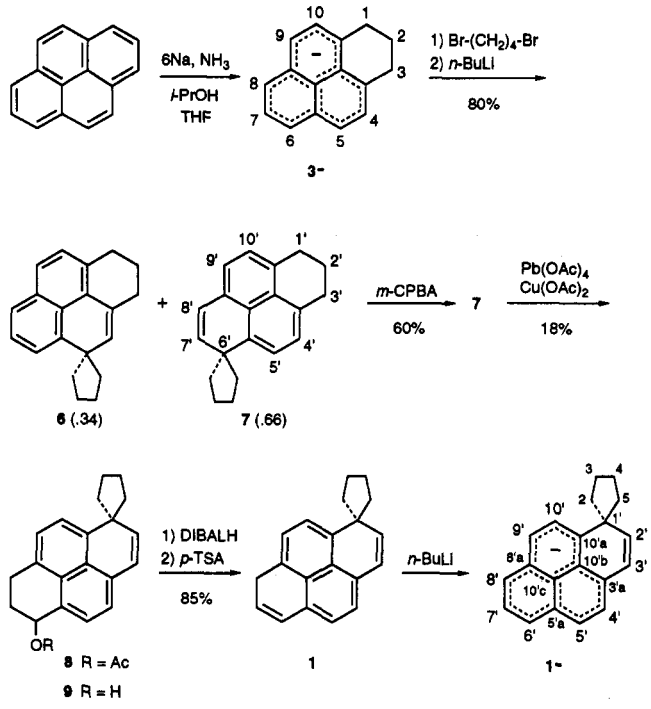
Scheme II



trophilic attack. A fair picture of the charge distribution may be obtained by recording ^{13}C NMR spectra[5-10] of the anions. Furthermore, the charge distribution in 2^- will be calculated using the semiempirical method PM3.[11,12]

Results

Preparation of the Anions 1^- and 2^-. The 1-hydropyrenyl anion (2^-) is a known system which can be easily prepared by two-electron reduction of pyrene in liquid ammonia[3] (Scheme I). For preparing the spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-), the 1,2,3-trihydropyrenyl anion (3^-) (Scheme II) is a suitable starting material. The preparation of this system has been discussed earlier.[1] We found that 3^- can be obtained directly by a four-electron reduction of pyrene in liquid ammonia and 2-propanol. The anion persists in this mixture. In order to obtain solutions of 3^- in THF, which is a more convenient solvent for performing alkylation experiments, NH_4Cl was added and the mixture was worked up, resulting in 1,2,3,5- and 1,2,3,6-tetrahydropyrene (**4** and **5**, not shown in Scheme II) which were reconverted into THF solutions of 3^- by treatment with *n*-butyllithium. The 1-spirocyclopentane ring was introduced by alkylation of 3^- with 1,4-dibromobutane.[1] The symmetrical anion 3^- has four sites available for alkylation. Carbon atoms 5-C and 9-C are equivalent, as are 6-C and 8-C. Alkylation with 1,4-dibromobutane, in the presence of another 1 equiv of base, therefore yields two compounds (**6** and **7**, 80–95%). Compound **7** has a spirocyclopentane ring at the desired position, but **7** could not be separated from **6**. Compound **6**, however, contains a more highly substituted double bond than **7**. It was therefore expected that **6** would be epoxidized more readily[13] than **7**. Treatment of the mixture with *m*-chloroperbenzoic acid in CH_2Cl_2 led to selective epoxidation of **6**, and **7** was readily isolated by means of column chromatography. Compound **7** already has the carbon framework of 1^-. One additional double bond has to be introduced in **7** to form dihydropyrene derivative **1**. In order to introduce the double bond, **7** was functionalized. Benzylic oxidation[14-16] of **7** with a mixture of $Pb(OAc)_4$ and $Cu(OAc)_2$ was accomplished at room temperature, and acetate **8** was isolated exclusively. Acetate **8** was converted into alcohol **9** under mild conditions with DIBALH. Dehydration of this alcohol with *p*-toluenesulfonic acid in toluene afforded dihydropyrene derivative **1**. This compound was deprotonated in THF with *n*-butyllithium to 1^- (Scheme II).

^1H And ^{13}C NMR Spectrometry of the Anions 1^- and 2^-. The NMR samples of 1^- and 2^- were prepared under moisture- and oxygen-free conditions. ^1H and ^{13}C NMR spectra were recorded at $T = 253$ K. At this temperature, the conditions for obtaining highly resolved spectra are optimal. Line broadening, possibly due to electron transfer, was observed above $T = 263$ K. Below $T = 233$ K, line broadening due to increased viscosity of the solvent is observed.

By comparing the spectra of 1^- and 2^- (Figure 1), it can be established that 1^- has a spirocyclopentane ring attached at position 1. A broad singlet of eight sp^3 protons is observed at $\delta = 1.55$ ppm. In the low-field region of the spectrum, three AX patterns and one AXB pattern are observed. The AX pattern of the olefinic 2′-H and 3′-H is readily identified by the coupling constant. Upon irradiation of the signal of the spirocyclopentane protons, a nuclear Overhauser effect was observed on the signal of 2′-H and 10′-H. The signal of 9′-H was found by homonuclear decoupling of the doublet of 10′-H. The shift of 10′-H to low field is a typical example of the *peri* effect and is caused by steric interactions with the spirocyclopentane ring.[18] The remaining AX pattern, which belongs to 4′-H and 5′-H, was identified by means of homonuclear decoupling and assigned by comparison with the odd alternant phenalenyl anion[19] (5′-H is connected to the charged 5′-C whereas 4′-C is not expected to bear negative charge). The AXB pattern in the spectrum of 1^- belongs to 6′-H, 7′-H, and 8′-H and was assigned based on a nuclear Overhauser effect on 6′-H upon irradiation of the signal of 5′-H.

The 300-MHz ^1H NMR spectrum of 2^- is identical to that published by *Schnieders* et al.[17] These authors only assigned the signals of 1-CH_2, 2-H, 3-H, and 7-H of 2^-. By

(5) Müllen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801 and refs cited therein.
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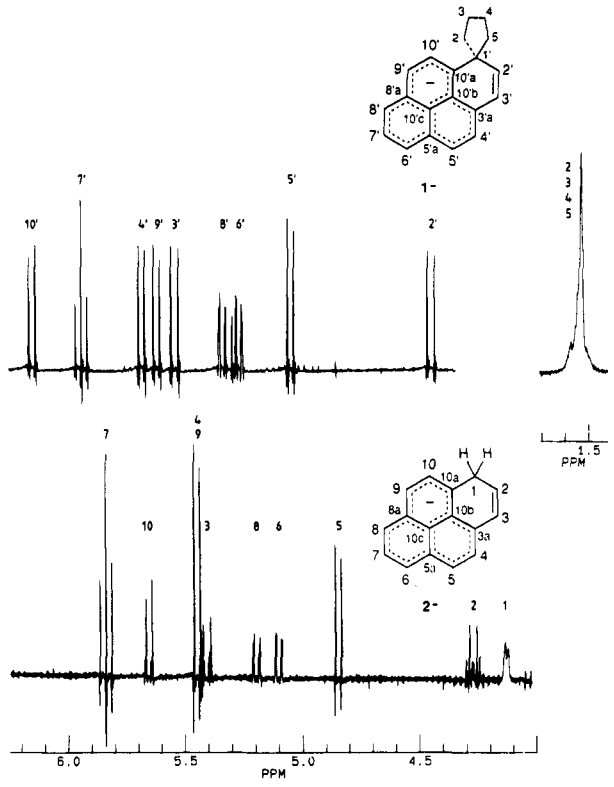

Figure 1. 300-MHz ^{1}H NMR spectra of 1^- and 2^- in THF-d_8–diglyme-d_{14} (1:1) at T = 253 K. Chemical shifts are measured with respect to the THF signal at δ = 3.58 ppm.

means of homonuclear decoupling and NOE experiments, we were able to assign every signal in the ^{1}H NMR spectrum of 2^-.

^{1}H-Noise-decoupled 100-MHz ^{13}C NMR spectra of anions 1^- and 2^- were recorded of the samples from which the ^{1}H NMR spectra were obtained. The spectra are reproduced in Figure 2. In the ^{13}C NMR spectrum of the spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-), three signals are observed at high field which are ascribed to the spirocyclopentane ring.[1] The less intense signal at δ = 49.3 ppm is ascribed to the quaternary 1′-C. In the low-field region of the spectrum, 13 signals are observed. A 2D ^{1}H–^{13}C correlated NMR spectrum shows that the signal at δ = 105.1 ppm belongs to two carbon atoms. Furthermore, two carbon atoms resonate at δ = 135.9 ppm, which leads to the expected number of 15 carbon atoms resonating in the low-field region. By means of the 2D ^{1}H–^{13}C correlated NMR spectrum, all tertiary signals could be assigned. The signals of carbon atoms 2′-C (δ = 118.6 ppm) and 10′a-C (δ = 117.1 ppm) occur at rather low field due to the β-effect[18] of the spirocyclopentane ring.[1]

The ^{13}C NMR spectrum of 2^- is in excellent agreement with the spectra obtained by *Schnieders* et al.[17] and by *Tintel* et al.[20] We, however, were able to assign every signal of the spectrum. In the spectrum of 2^-, which is similar to that of 1^- (Figure 2), one signal at high field (δ = 34.3 ppm) is observed, which belongs to 1-C. In the low-field region of the spectrum, 15 signals are observed, in accordance with expectations. Of these, nine signals are recognized as tertiary because they show correlations in the 2D ^{1}H–^{13}C correlated NMR spectrum (Figure 3). Six, less intense signals, belong to quaternary carbon atoms.

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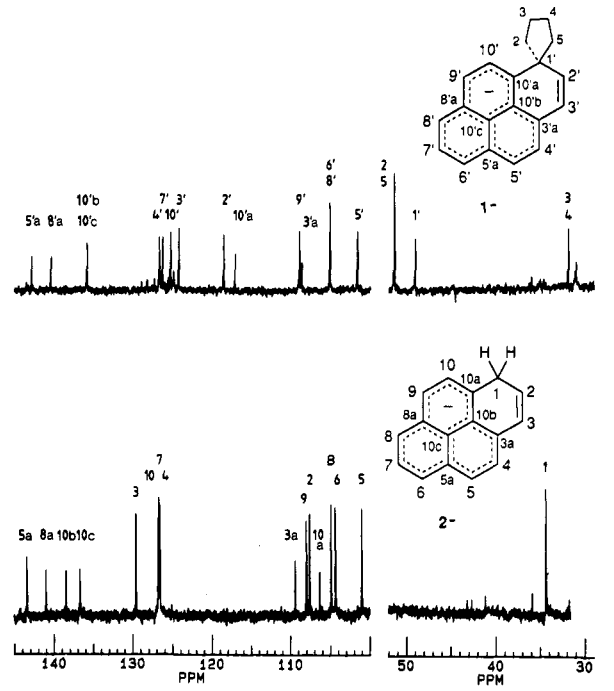


Figure 2. 100-MHz ^{13}C NMR spectra of 1^- and 2^- in THF-d_8–diglyme-d_{14} (1:1) at T = 253 K. Chemical shifts are measured with respect to the THF signal at δ = 67.4 ppm.

Table I. ^{1}H and ^{13}C NMR Chemical Shifts (δ, ppm) of the Spiro[cyclopentane-1,1′-[1*H*]pyrenyl] Anion (1^-) and the 1-Hydropyrenyl Anion (2^-)

1^-			2^-		
position	δ (^{1}H)[a]	δ (^{13}C)[b]	position	δ (^{1}H)[a]	δ (^{13}C)[b]
1′	–	49.3	1	4.12	34.3
2′	4.45	118.6	2	4.27	107.6
3′	5.54	124.3	3	5.40	129.5
4′	5.68	126.7	4	5.44	126.5
5′	5.05	101.7	5	4.84	101.0
6′	5.27	105.1	6	5.10	104.3
7′	5.94	126.4	7	5.83	126.6
8′	5.34	105.2	8	5.19	104.9
9′	5.62	109.0	9	5.44	108.0
10′	6.15	125.3	10	5.65	126.7
3a′		108.7	3a		109.4
5a′		142.9	5a		143.3
8a′		140.5	8a		140.9
10a′		117.1	10a		106.3
10b′		135.9	10b		138.4
10c′		135.9	10c		136.6

[a] 300 MHz, THF-d_8–diglyme-d_{14} = 1:1, T = 253 K. Chemical shifts are measured with respect to the THF-d_8 signal at δ 3.58 ppm. 1^-: 1.55 (8 H, bs, spirocyclopentane). [b] 100 MHz, THF-d_8–diglyme-d_{14} = 1:1, T = 253 K. Chemical shifts are measured with respect to the THF-d_8 signal at δ 67.4 ppm. 1^-: 31.8 (3-C + 4-C), 51.1 ppm (2-C + 5-C).

All tertiary signals were assigned on the basis of the ^{1}H NMR assignments. The quaternary signals were assigned by means of a 2D long-range ^{1}H–^{13}C correlated NMR spectrum.

It is established beyond doubt that the signals of 5′-C of 1^- and 5-C of 2^- occur at the highest field in the ^{13}C NMR spectra, which implies that the highest negative charge resides at these positions.

Calculation of the Charge Distribution in 2^-. Calculation of the charge distribution in the 1-hydropyrenyl anion (2^-) was performed using the semiempirical method PM3.[11,12] The calculated charges and HOMO coefficients are presented in Table II. The results for 2^- indicate that most of the negative charge is present at the expected

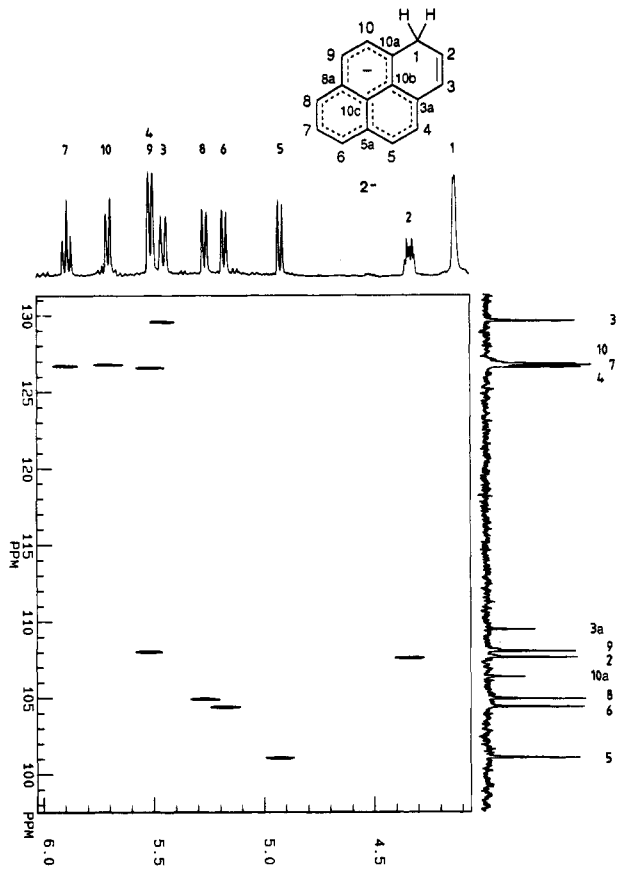


Figure 3. 2D ^1H–^{13}C correlated NMR spectrum of 2^- (^1H at 400 MHz, ^{13}C at 100 MHz) in THF-d_8 at T = 253 K.

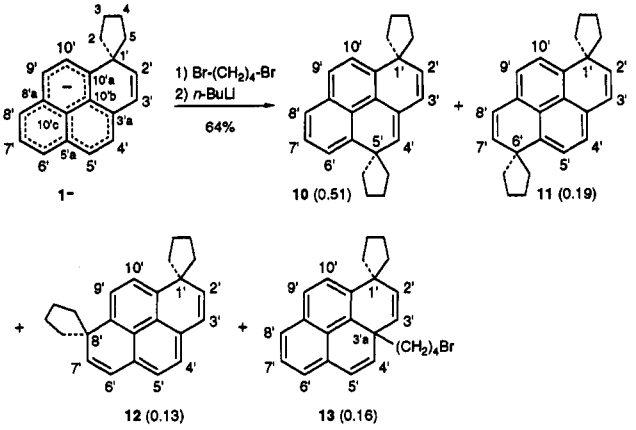
Table II. PM3 Calculated Charges and HOMO Coefficients of the 1-Hydropyrenyl Anion (2^-)

position	charge	coefficient
1-C	0.066	0.050
2-C	−0.264	0.265
3-C	−0.014	0.015
4-C	0.004	0.010
5-C	−0.297	0.388
6-C	−0.285	0.369
7-C	−0.038	0.007
8-C	−0.270	0.354
9-C	−0.279	0.372
10-C	−0.029	0.021
3a-C	−0.261	0.432
5a-C	0.086	0.003
8a-C	0.068	0.016
10a-C	−0.249	0.397
10b-C	0.116	0.013
10c-C	−0.064	0.017

positions in the phenalenyl part of 2^- (3a-C, 5-C, 6-C, 8-C, 9-C, and 10a-C). A rather large negative charge is also calculated for the conjugated carbon atom 2-C (−0.264), which indicates that the 2,3-double bond of 2^- delocalizes a significant part of the negative charge. Of the positions in the phenalenyl-part of 2^-, the largest negative charge is calculated at position 5-C (−0.297). Markedly less negative charge is found at 9-C (−0.279). Furthermore, the charge at the quaternary position 3a-C (−0.261) is larger than the charge at 10a-C (−0.249). Noteworthy is the large HOMO coefficient at 3a-C (0.432).

Reaction of 1^- and 2^- with Electrophiles. The spiro-[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-) was generated from its neutral precursor **1** in THF, using *n*-butyllithium as base. Alkylation (Scheme III) was carried out by treating 1^- with 1 equiv of 1,4-dibromobutane and 1 equiv

Scheme III



of base, as described earlier[1] for the phenalenyl anion. Two fractions were obtained. In the first fraction, according to ^1H NMR, three compounds are present. By means of high-resolution mass spectrometry, it became clear that the mixture consists of isomers, for which the molecular formula $C_{24}H_{24}$ was established. The three sets of signals in the ^1H NMR spectrum were readily distinguished using homonuclear decoupling and NOE. In the mixture, three compounds are present of which two are symmetrical and one, the major constituent, is asymmetrical. One of the symmetrical compounds possesses an $(AM)_2$ pattern formed by aromatic protons and an $(AX)_2$ pattern of olefinic protons. The chemical shifts of the latter protons indicate that the double bond is conjugated with the aromatic moiety. This combination of signals is realized only in **11**. The other symmetrical compound has olefinic protons, conjugated with the aromatic moiety, which appear as an $(AX)_2$ pattern, and aromatic protons which appear as two A_2 patterns. These results can only be matched with the structure of **12**.

The remaining set of signals, five aromatic and three olefinic, belongs to a less symmetrical species. Two aromatic signals form an AX pattern. The other three aromatic protons appear as an ABC pattern. By means of nuclear Overhauser enhancement it was established that the two double bonds, containing three protons, are connected. The chemical shifts of the olefinic protons clearly indicate that the structure has no olefinic protons in a position *peri* to an aromatic moiety, since such protons are found at δ = 6.5 ppm (see compounds **11** and **12**). The only structure in accordance with these findings is **10**. The coupling constants of its higher order (ABC) pattern were obtained by means of simulation. The ^1H NMR chemical shifts and coupling constants of products **10**, **11**, and **12** are given in Table III.

The second fraction consists of a pure compound, for which the molecular formula $C_{24}H_{25}Br$ was found. It was identified as compound **13** (Table V). The major product in the reaction of 1^- with 1,4-dibromobutane clearly is the result of electrophilic attack at 5′-C (Scheme III).

After the establishment of the reactivity of 1^-, it was checked if the 1-hydropyrenyl anion (2^-) displays a similar reactivity. Quenching experiments with the hard electrophile NH_4Cl and with the soft electrophile benzyl iodide were carried out. Treatment of a solution of 2^- in ammonia with 2.5 equiv of NH_4Cl (Scheme IV) afforded a white solid (**2**) as the only product (85–90%). Its melting point (110 °C) is identical to that reported by *Harvey* and

Table III. ^{1}H NMR Chemical Shifts[a] (δ, ppm, relative to TMS) and Coupling Constants (J, Hz) of 10, 11, and 12

	10	11	12
2′-H	5.88 d	6.01 d	6.00 d
3′-H	6.19 d	6.52 d	6.51 d
4′-H	5.80 s	7.16 d	7.00 s
5′-H	–	7.34 d	7.00 s
6′-H	7.46 dd	–	6.51 d
7′-H	7.46 dd	6.01 d	6.00 d
8′-H	7.58 dd	6.52 d	–
9′-H	7.69 d	7.16 d	7.46 s
10′-H	7.41 d	7.34 d	7.46 s
$J_{2',3'}$	9.8	9.7	9.7
$J_{4',5'}$		7.5	
$J_{6',7'}$	7.1[b]		9.7
$J_{6',8'}$	1.5[b]		
$J_{7',8'}$	8.0[b]	9.7	
$J_{9',10'}$	8.8	7.5	

[a] 10, 11, and 12: 1.86–2.13 (m, spirocyclopentane). 300 MHz, $CDCl_3$, T = 293 K. [b] Coupling constants were obtained by means of simulation and are given in hertz.

Scheme IV

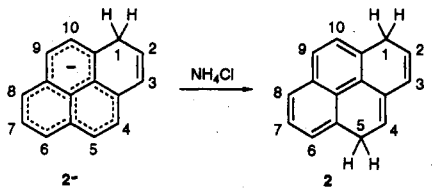


Table IV. ^{1}H NMR Chemical Shifts[a] (δ, ppm, relative to TMS) and Coupling Constants (J, Hz) of 1,5-Dihydropyrene (2)

	δ		J
1-CH_2	3.73 m	$J_{1,2}$	3.1
2-H	5.91 dt	$J_{1,3}$	2.2
3-H	6.32 dt	$J_{1,4}$	2.2
4-H	5.71 m	$J_{1,5}$	5.2
5-CH_2	4.09 m	$J_{2,3}$	9.9
6-H	7.20 dq	$J_{2,4}$	1.0
7-H	7.31 dd	$J_{2,5}$	1.0
8-H	7.52 dd	$J_{4,5}$	4.0
9-H	7.52 d	$J_{5,6}$	1.5
10-H	7.09 d	$J_{6,7}$	7.1
		$J_{6,8}$	1.5
		$J_{7,8}$	8.0
		$J_{9,10}$	8.6

[a] 300 MHz, $CDCl_3$, T = 293 K. Coupling constants were obtained by means of simulation and are given in hertz.

Rabideau.[21] Furthermore, its ^{1}H NMR spectrum is identical to the spectra obtained by *Harvey* and *Rabideau* and by *Tintel* et al.[3]

In the spectrum, two high-field signals of two protons each and three olefinic and five aromatic signals are observed (Table IV). The high-field signals belong to the two methylene groups. By means of nuclear Overhauser experiments, it was established that the methylenes are both located next to the aromatic moiety and that the two double bonds are connected to each other, as in **10**. There is only one structure in which such an arrangement is possible: 1,5-dihydropyrene (**2**) (Scheme IV). The ^{1}H NMR spectrum of **2** was simulated by means of the Bruker Panic program. The simulated and the recorded spectrum of **2** are in excellent agreement. The finding, that protonation of the 1-hydropyrenyl anion (2^-) occurs at 5-C, is in full agreement with the observed reactivity of the spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion (1^-).

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Scheme V

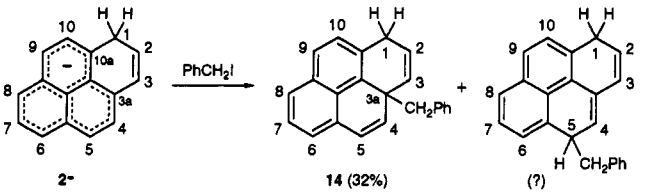
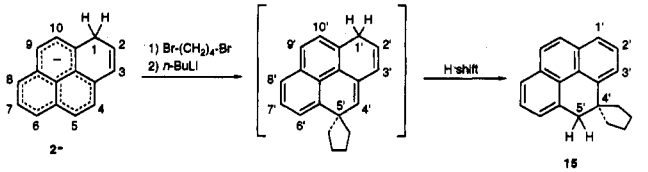


Table V. ^{1}H NMR Chemical Shifts[a] (δ, ppm, relative to TMS) and Coupling Constants (J, Hz) of 13 and 14

13		14	
2′-H	5.90 d	2-H	6.03 m
3′-H	5.94 d	3-H	6.03 m
4′-H	6.19 d	4-H	6.18 d
5′-H	6.72 d	5-H	6.77 d
6′-H	7.16 dd	6-H	7.18 dd
7′-H	7.35 dd	7-H	7.37 dd
8′-H	7.64 dd	8-H	7.70 dd
9′-H	7.67 d	9-H	7.66 d
10′-H	7.50 d	10-H	7.22 d
$J_{2',3'}$	9.8		
$J_{4',5'}$	9.5	$J_{4,5}$	9.6
$J_{6',7'}$	7.0	$J_{6,7}$	7.0
$J_{6',8'}$	1.1	$J_{6,8}$	1.0
$J_{7',8'}$	8.2	$J_{7,8}$	8.2
$J_{9',10'}$	8.6	$J_{9,10}$	8.3

[a] 13: 1.84–2.15 (8 H, m, spirocyclopentane), 1.24–1.55 (8 H, m, bromobutyl), 3.17 (2 H, t, J 6.9 Hz, CH_2Br). 14: 2.60 + 2.73 (2× 1 H, 2× d, J 12.5, benzyl), 2.62 (1 H, dd, $J_{1'1}$ 21.5, $J_{1'2}$ 1.8, 1′-H); 3.19 (1 H, dd, $J_{11'}$ 21.5, J_{12} 4.3, 1-H); 6.61 (2 H, m, *o*-H); 7.05 (2 H, m, *m*-H); 7.13 (1 H, m, *p*-H).

Scheme VI



In the alkylation of the 1-hydropyrenyl anion (2^-) with benzyl iodide (Scheme V), 1,5-dihydropyrene (**2**) in THF was converted into 2^- by adding only 0.9 equiv of *n*-butyllithium, in order to prevent reaction of this strong base with the alkylation product. Upon the addition of 1.0 equiv of benzyl iodide, the deep-red color of the reaction mixture instantly changed into lemon-yellow. After workup and column chromatography, 3a-benzyl-1,3a-dihydropyrene (**14**) was isolated (32%, based on 2^-). Its chemical shifts and coupling constants are given in Table V. Another alkylation product was formed but it could not be identified due to its instability. Because the high reactivity of 5-C of 2^- has been established here, the unstable product is assumed to be 5-benzyl-1,5-dihydropyrene.

Alkylation of the 1-hydropyrenyl anion (2^-) with 1,4-dibromobutane (Scheme VI), as described for 1^-, gave product **15** (28%). *Tintel* et al.[23] obtained this compound from the reaction of 2^- with 1,4-diiodobutane in liquid ammonia, but assumed that it was *cis*-8b,9,10,11,12,12a-hexahydrobenzo[*e*]pyrene, although the ^{1}H NMR spectrum clearly shows a singlet (δ = 3.16 ppm) of a benzylic CH_2 group. Three typical spirocyclopentane signals,

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(23) Tintel, C.; Lugtenburg, J.; van Amsterdam, G. A. J.; Erkelens, C. Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 228.

among which the signal of a quaternary carbon atom at δ = 46.6 ppm (4'-C), give evidence of **15**. This product must have undergone a hydrogen shift (Scheme VI), because it no longer contains a 1-CH_2 group. It shows the importance of using 1^-, yielding alkylation products which cannot isomerize under the conditions of their formation.

Discussion

The charge distribution in the spiro[cyclopentane-1,1'-[1*H*]pyrenyl] anion (1^-) and the 1-hydropyrenyl anion (2^-) may cautiously be derived from the ^{1}H NMR data. Of the protons in the conjugated system, the signals of 5'-H of 1^- and 5-H of 2^- are observed at the highest field, followed by those of 6'-H and 6-H, 8'-H and 8-H, and 9'-H and 9-H which occur at much lower field (Table I). This suggests that a relatively high charge is present at the 5-position of the anions. A better method for obtaining a picture of the charge distribution in conjugated ions is measuring ^{13}C chemical shifts, which strongly depend on charge density[10] but are less sensitive to ring-current effects and concentration effects. The signals which occur at high field belong to 2-C, 3a-C, 5-C, 6-C, 8-C, 9-C, and 10a-C, which implies that the negative charge resides mainly at these carbon atoms. The sequence in ^{13}C chemical shift values of 5'-C, 6'-C, 8'-C, and 9'-C of 1^- and 5-C, 6-C, 8-C, and 9-C of 2^- is similar to that of the corresponding ^{1}H chemical shifts. The signals of carbon atom 5'-C (δ = 101.7 ppm) of 1^- and carbon atom 5-C (δ = 101.0 ppm) of 2^- are found at the highest field and, therefore, the highest charge resides at these atoms. The signals of 9'-C (δ = 109.0 ppm) of 1^- and 9-C (δ = 108.0 ppm) of 2^- occur at much lower field which indicates that these atoms bear significantly less charge than 5'-C and 5-C. It must be noted that comparison of the chemical shifts of the charged quaternary carbon atoms 3a-C and 10a-C of 2^- is not meaningful, because 3a-C is vinyl substituted while 10a-C is alkyl substituted. Differences in chemical shift of these carbon atoms, therefore, cannot be attributed solely to the amount of charge.

The ^{13}C NMR spectra of 1^- and 2^- show that replacing the 1-CH_2 group by a spirocyclopentane ring does not strongly influence the distribution of the negative charge in the conjugated system. The tertiary carbon atoms of the phenalenyl moiety of 1^- and those of 2^- have almost identical chemical shifts (Table I). It may therefore be expected that carbon atoms of 1^- which are not in the vicinity of the spiro ring have a similar reactivity as corresponding carbon atoms of 2^-. The spirocyclopentane ring strongly influences the chemical shifts of 2'-C and 10'a-C of 1^-. The shift of these carbon atoms to lower field is caused by the β-effect[18] of the spiro ring. It is not known whether the spiro ring causes a large decrease of the charge at these carbon atoms. It is, however, clear that 10'a-C is sterically hindered by the spiro ring.

The ^{1}H chemical shift values of 2^- are in very good agreement (within 0.05 ppm) with the values obtained by *Schnieders* et al.[17] for their 1-hydropyrenyl anion. Furthermore, they obtained ^{1}H and ^{13}C NMR spectra of a closely related species: the 1-LiO$(CH_2)_4$-1-hydropyrenyl anion. Although the ^{1}H NMR chemical shift values of 2^- and this species are similar, the assignments are different. These authors assigned the ^{1}H NMR spectrum of the 1-LiO$(CH_2)_4$-1-hydropyrenyl anion on the basis of SCF-π-charge density calculations. This risky manner of assigning a ^{1}H NMR spectrum led to the wrong attribution of the signals of 4-H, 5-H, 9-H, and 10-H. The ^{13}C NMR assignment of this anion was based on the ^{1}H NMR assignment and is therefore also incorrect. Noteworthy is the difference in assignment of 5-C (δ = 101.0 ppm) and 9-C (δ = 108.0 ppm) of the 1-hydropyrenyl conjugated system. *Schnieders* et al. report δ = 108.40 ppm for 5-C and δ = 101.70 ppm for 9-C.

In accordance with the ^{13}C NMR measurements, alkylation of 1^- occurs predominantly at 5'-C. Some reactivity of positions 6'-C and 8'-C of 1^- was also found. Indeed, the signals of these carbon atoms are found at the next highest field (δ = 105.1 ppm and δ = 105.2 ppm, respectively). Since carbon atoms 6-C and 8-C (δ = 104.3 ppm and δ = 104.9 ppm, respectively) of 2^- are not known to be reactive but have a similar chemical shift, the spirocyclopentane ring probably has some influence on the conjugated system of 1^-. No product resulting from attack on 9'-C could be detected. Of the quaternary positions, 3'a-C is susceptible toward attack by 1,4-dibromobutane.

The reactivity of the tertiary carbon atom 5'-C of 1^- is not in agreement with the protonation product of 2^- reported by *Harvey* and *Rabideau*[22] and *Tintel* et al.[3] These authors treated pyrene in ammonia with 2 equiv of sodium metal and reported the formation of 1,9-dihydropyrene, after quenching the mixture with ammonium chloride. We have therefore repeated the experiments of these authors. Protonation of the 1-hydropyrenyl anion (2^-) in diethyl ether and ammonia with ammonium chloride affords one product which was shown to be 1,5-dihydropyrene (**2**). The properties of 1,5-dihydropyrene (**2**) and the product obtained by *Harvey* and *Rabideau* and *Tintel* et al. are identical and therefore, 1,5-dihydropyrene instead of 1,9-dihydropyrene has been obtained by these authors.

The reactivity of the quaternary carbon atom 3'a-C of 1^- does not agree with the findings of *Brandsma* et al.[22] who added benzyl iodide to the reduction mixture of pyrene and reported formation of 3a-benzyl-3,3a-dihydropyrene, a product formed by attack at the 10a-position of 2^-. We identified one product, 3a-benzyl-1,3a-dihydropyrene (**14**) from the reaction of 2^- with benzyl iodide. It is very similar (see Table V) to compound **13** which results from attack of 1,4-dibromobutane on the quaternary 3'a-C of 1^-. Since, next to 2^-, 1 equiv of the strongly basic sodium amide is always formed when pyrene is reduced in diethyl ether and ammonia with 2 equiv of alkali metal, the product of *Brandsma* et al. probably is the result of electrophilic attack at 3a-C of 2^-, followed by a base-catalyzed [1,3] H shift. The protonation product 1,5-dihydropyrene (**2**) most likely has not undergone such a rearrangement, because on addition on ammonium chloride to the mixture of 2^- and sodium amide in diethyl ether and ammonia, the amide ions are neutralized instantly.

Very interesting in the ^{1}H NMR spectrum of 1,5-dihydropyrene (**2**) are the long-range couplings. Especially noteworthy is the seven-bond coupling between 1-CH_2 and 5-CH_2 ($^7J_{25}$ = 5.2 Hz). From homonuclear decoupling experiments and from the simulations, equal seven-bond coupling constants were obtained between methylene protons which are at the same side of the plane of 1,5-dihydropyrene (**2**) (cis) and methylene protons which have a trans orientation. Five-bond homoallylic coupling between methylene groups, with almost equal coupling constants between protons oriented cis and trans, has been

well-established[24] for 1,4-cyclohexadienes and related systems such as 1,4-dihydronaphthalenes. This coupling, which can be quite large ($^5J_{14}$ = 12 Hz), is transmitted through the p-orbitals and decreases as the orbital overlap decreases. Measurement of homoallylic coupling constants is, therefore, an important method for determining the geometry of substituted cyclohexadienes. For obtaining large coupling constants, it is essential that the methylene groups are close to the π-system. If more paths[25] are available along which the coupling can be transmitted, larger constants are also found. In 1,5-dihydropyrene, these structural requirements are fulfilled. Four different seven-bond paths can be imagined from the 1-methylene group to the 5-methylene group.

A number of compounds which possess extended π-systems are known for long-range proton–proton couplings. Pentatetraenes[26] are capable of efficient spin transmission through the π-system as is evident from seven-bond couplings (^7J = 2.3–3.5 Hz) observed in these systems. Another linear conjugated system, 1,2,4,5-hexatetraene,[27] displays seven-bond couplings ^7J = 3.5 Hz. Phenylacetylenes[28] and polyacetylenes are known to display nine-bond couplings ^9J = 0.1–0.4 Hz. It is generally accepted that these long-range couplings are dominated by π-contributions.[25,28]

The results of the semiempirical PM3 calculations of the 1-hydropyrenyl anion (**2**$^-$) are in agreement with the ^{13}C NMR measurements and the alkylation and protonation experiments. The highest negative charge was calculated at 5-C (−0.297), whereas significantly less negative charge was found at 9-C (−0.279). Therefore, the calculations predict 5-C as the most reactive position of **2**$^-$. At the reactive quaternary position 3a-C of **2**$^-$, a higher charge (−0.261) is calculated than at position 10a-C (−0.249). Of special interest is the large HOMO coefficient at 3a-C (0.432) (Table II). Reaction sites with a large frontier orbital coefficient are considered to be soft[29] and are therefore expected to react more readily with soft electrophiles.

Conclusion

The reactivity of the 1-hydropyrenyl anion (**2**$^-$) has been elucidated. Carbon atom 5-C shows the highest reactivity toward electrophilic attack, while the quaternary carbon atom 3a-C is susceptible toward attack by soft electrophiles. The strong perturbation of the phenalenyl moiety of **2**$^-$ by the conjugated 2,3-double bond is evident from the results of ^{13}C NMR measurements. PM3 calculations, and alkylation experiments, which all are in very good agreement. Electrophilic attack at 5-C is charge controlled, whereas orbital control is relatively important for electrophilic attack at 3a-C.

Experimental Section

Pyrene (99+%), diisobutylaluminum hydride (1.0 M in toluene), and 2-propanol (99+%) were obtained from Aldrich. Tetrahydrofuran, *m*-chloroperbenzoic acid (70%), *n*-butyllithium (1.6 M in hexane), and methyllithium (1.6 M in diethyl ether) were purchased from Janssen Chimica. 2-Propanol (Baker Grade), 1,4-dibromobutane (97%) and lead tetraacetate (98%) were obtained from Merck. Tetrahydrofuran-d_8 (99.5 atom% D) was obtained from Janssen Chimica, and diglyme-d_{14} (99 atom% D) was obtained from Cambridge Isotope Laboratories. Dichloromethane, diethyl ether, petroleum ether (bp 60–80 °C) and toluene were distilled before use. Tetrahydrofuran was distilled from $LiAlH_4$ immediately before use. The purity of the prepared compounds was checked by means of high-resolution mass spectrometry and ^{1}H and ^{13}C NMR spectrometry. The 300-MHz ^{1}H NMR spectra were recorded on a Bruker WM-300 spectrometer. The 400-MHz ^{1}H NMR spectra, 100-MHz ^{13}C NMR spectra, and ^{1}H–^{13}C correlated 2D NMR spectra were recorded on a Bruker MSL-400 spectrometer. All chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (J) are given in hertz. Simulations were performed by means of the Bruker Panic program and the Laocoon fitting procedure. The electron impact (EI) mass spectra were recorded at 70 eV on a V.G. Micromass ZAB-HFQ mass spectrometer which was coupled to a V.G. data system. The samples were introduced *via* the direct insertion probe into the ion source. The source temperature generally was 150 °C. During the high-resolution EIMS measurements, a resolving power of 15000 (10% valley definition) was used. Low-resolution FAB mass spectra were recorded of **8** and **9**. Column chromatography was carried out on Merck (230–400 mesh) silica gel. Method of calculation: for anion **2**$^-$, a preoptimization was carried out using the program MODEL, which includes an MM2-derived optimization mode. Further reduction of the heat of formation was achieved with a restricted Hartree–Fock calculation using the standard PM3 parameters as implemented in the VAMP program (based on AMPAC 1.0 and MOPAC 4.0 and run on a CONVEX C-120 computer). For this purpose the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS) was used, followed by Bartel's nonlinear least squares method (NLLSQ), in order to achieve a further reduction of the gradients.

1,2,3,5-Tetrahydropyrene (4) and 1,2,3,6-Tetrahydropyrene (5).[1] Pyrene (10.1 g, 0.05 mol) was dissolved in a mixture of THF (250 mL) and 2-propanol (77 mL, 1 mol), under an atmosphere of argon. The mixture was cooled (−78 °C) and liquid ammonia (500 ml) was added. With vigorous stirring, 6 equiv of sodium (6.9 g, 0.3 mol) were added in small portions. The solution immediately turned deeply red. Vigorous stirring was continued for 6 h, followed by the addition of NH_4Cl (24 g, 0.45 mol). The cooling bath was removed. After stirring for 15 min, the solution turned lemon-yellow. The ammonia was allowed to evaporate, the residue was poured into water (750 mL) and extracted with petroleum ether. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. A yellow solid, consisting of **4** and **5** (ratio 1:2), was obtained in quantitative yield.

Spiro[cyclopentane-6,6′-[6*H*]-1,2,3,6-tetrahydropyrene] (7). A solution of **4** + **5** (10.3 g, 50 mmol) in THF (750 ml) was cooled (−78 °C) under argon. *n*-BuLi (34.5 ml, 55 mmol) was syringed into the mixture and the resulting red solution of **3**$^-$ was stirred for a few minutes. The anion **3**$^-$ was alkylated with 1,4-dibromobutane, as described earlier for the phenalenyl anion,[1] yielding a mixture of **6** and **7** (ratio 1:2) and combined yield 10.4 g (40 mmol, 80% based on **4** + **5**). Compound **6** could be removed selectively from the mixture by means of epoxidation. The epoxidation procedure of *Masamune* et al.[30] was followed. After workup, the organic layer was dried over Na_2SO_4 and concentrated, and the residue was purified by means of column chromatography (SiO_2; petroleum ether). The epoxidized **6** remains on the column, and pure **7** is collected (6.25 g, 24 mmol, 60%) as an almost colorless oil.

6: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.95–2.08 (10 H, m, 2′-CH_2 and 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 2.57 (2 H, m, 3′-CH_2), 2.92 (2 H, m, 1′-CH_2), 5.75 ppm (1 H, t, J 1.7, 4′-H), 7.17 (1 H, d, J 8.3, 10′-H), 7.42 (1 H, dd, J 7.1, 1.5, 6′-H), 7.42 (1 H, dd, J 8.0, 7.1, 7′-H), 7.55 (1 H, d, J 8.3, 9′-H), 7.57 (1 H, dd, J 8.0, 1.5, 8′-H). J values of 6′-H, 7′-H, and 8′-H were obtained by means of simulation.

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7: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.95–2.08 (10 H, m, 2′-CH_2 and 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 3.06 (4 H, m, 1′-CH_2 + 3′-CH_2), 5.99 (1 H, d, *J* 9.7, 7′-H), 6.52 (1 H, d, *J* 9.7, 8′-H), 7.02 (1 H, d, *J* 7.0, 9′-H), 7.10 (1 H, dt, *J* 7.0, 1.2, 10′-H), 7.26 (1 H, dt, *J* 7.5, 1.2, 4′-H), 7.36 (1 H, d, *J* 7.5, 5′-H); MS *m/z* (%) 101 (13), 165 (10), 178 (26), 189 (16), 191 (14), 202 (43), 203 (22), 204 (22), 205 (47), 206 (25), 218 (20), 219 (29), 231 (55), 232 (74), 259 (42), 260 (100); exact mass calcd for $C_{20}H_{20}$ ($M^{\cdot+}$) 260.1565, found 260.1549.

1′-Acetoxyspiro[cyclopentane-6,6′-[6*H*]-1,2,3,6-tetrahydropyrene] (8). Compound 7 (5.2 g, 20 mmol) was dissolved in a mixture of acetic acid (100 mL) and $Cu(OAc)_2 \cdot H_2O$ (4.0 g, 20 mmol) while stirring under argon. Subsequently, $Pb(OAc)_4$ (9.0 g, 20 mmol) was added in small portions in 15 min.[14,15] The mixture was stirred for 0.5 h, poured into water (500 mL), and extracted with diethyl ether (4 × 75 mL). The organic layer was extracted with aqueous $NaHCO_3$, separated, and dried over Na_2SO_4. The diethyl ether was evaporated, and the residue was purified by means of column chromatography (SiO_2; CH_2Cl_2–hexane 1:4 v/v). One acetoxylated compound (8), a yellow oil, was obtained (1.15 g, 3.6 mmol, 18% based on 7), next to unidentifiable oxidation products.

8: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.82–2.06 (8 H, m, 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 2.05 (3 H, s, OAc), 2.15 + 2.27 (2 H, 2m, 2′-CH_2), 3.03 + 3.29 (2 H, m, 2 m, 3′-CH_2), 6.07 (1 H, d, *J* 9.7, 7′-H), 6.24 (1 H, m, 1′-H), 6.54 (1 H, d, *J* 9.7, 8′-H), 7.09 (1 H, d, *J* 7.1, 9′-H), 7.34 (1 H, d, *J* 7.6, 4′-H), 7.40 (1 H, d, *J* 7.1, 10′-H), 7.41 (1 H, d, *J* 7.6, 5′-H); MS *m/z* (%) 57 (42), 91 (11), 165 (17), 178 (14), 179 (17), 189 (18), 191 (21), 202 (47), 203 (63), 204 (21), 205 (25), 215 (46), 216 (23), 217 (29), 218 (14), 219 (36), 227 (12), 228 (11), 229 (24), 230 (10), 231 (16), 232 (14), 233 (18), 255 (12), 257 (25), 258 (27), 259 (89), 260 (46), 261 (38), 262 (12), 263 (20), 273 (17), 275 (15), 289 (22), 290 (19), 291 (12), 315 (42), 316 (24), 317 (100), 318 (32) ($M^{\cdot+}$), 319 (32) ($[M + H]^+$).

1′-Hydroxyspiro[cyclopentane-6,6′-[6*H*]-1,2,3,6-tetrahydropyrene] (9). Acetate 8 (1.0 g, 3.1 mmol) was dissolved in dry toluene (50 mL) and stirred under argon. The mixture was cooled (−78 °C) and DIBALH in toluene (7.8 ml, 7.8 mmol) was added. The cooling bath was removed and stirring was continued for 4 h. The reaction mixture was worked up by subsequent addition at 0 °C of methanol (1 mL), a 1:1 methanol–water mixture (1 mL), and by extraction with water (200 mL) and toluene (3 × 50 mL). The organic layer was dried over Na_2SO_4, concentrated, and purified by means of column chromatography (SiO_2; CH_2Cl_2), yielding pure 9 (0.74 g, 2.7 mmol, 87% based on 8) as a lemon-yellow oil.

9: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.83–2.10 (8 H, m, 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 2.16 (2 H, m, 2′-CH_2), 3.04 + 3.29 (2 H, 2m, 3′-CH_2), 5.05 (1 H, t, *J* 4.6, 1′-H), 6.07 (1 H, d, *J* 9.7, 7′-H), 6.55 (1 H, d, *J* 9.7, 8′-H), 7.12 (1 H, d, *J* 7.1, 9′-H), 7.34 (1 H, dt, *J* 7.5, 1.3, 4′-H), 7.41 (1 H, d, *J* 7.5, 5′-H), 7.44 (1 H, d, *J* 7.1, 10′-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 25.9 (2′-C), 26.0 (3-C + 4-C), 30.8 (3′-C), 48.4 (2-C + 5-C), 48.5 (6′-C), 69.3 (1′-C), 122.0 (9′-C), 122.2 (8′-C), 123.3 (10′-C), 123.6 (5′-C), 125.1 (4′-C), 137.9 (7′-C), 127.5, 127.8, 131.0, 132.2, 135.9, 142.1 (3′a-C, 5′a-C, 8′a-C, 10′a-C, 10′b-C, 10′c-C); MS *m/z* (%) 55 (29), 57 (32), 67 (13), 69 (23), 81 (19), 83 (13), 95 (18), 189 (13), 191 (17), 202 (26), 203 (19), 215 (25), 216 (12), 217 (14), 219 (17), 229 (13), 231 (11), 232 (23), 233 (29), 257 (15), 258 (18), 259 (100), 260 (26), 275 (31), 276 (38) ($M^{\cdot+}$), 277 (19) ($[M + H]^+$).

Dihydropyrene Derivative 1. Alcohol 9 was dehydrated in refluxing toluene with a catalytic amount of *p*-TSA.[1]

Preparation of an NMR Sample of the Spiro[cyclopentane-1,1′-[1*H*]pyrenyl] Anion (1⁻). In a flexible glove bag, under an atmosphere of dry argon, a solution of 1 (39 mg, 0.15 mmol) in a 1:1 mixture of THF-d_8 and diglyme-d_{14} (total volume 0.4 mL) was transferred to an NMR tube. By means of a long needle, the solution was purged with argon. After this, the solution was cooled (−80 °C) and methyllithium in diethyl ether (0.2 mL, 0.32 mmol) was added. The NMR tube was transferred to a vacuum line connected to the glove bag, submitted to three freeze-pump-thaw cycles, and sealed under vacuum. This procedure allows the preparation of moisture- and oxygen-free NMR samples. When stored at −20 °C, the sample is stable for months. The ^{1}H and ^{13}C NMR spectra were recorded at −20 °C.

1: ^{1}H NMR (300 MHz, THF-d_8–diglyme-d_{14} = 1:1, 253 K) δ (ppm) 1.55 (8 H, bs, 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 4.45 (1 H, d, *J* 9.4, 2′-H), 5.05 (1 H, d, *J* 7.8, 5′-H), 5.27 (1 H, dd, *J* 7.6, 1.2, 6′-H), 5.34 (1 H, dd, *J* 7.6, 1.2, 8′-H), 5.54 (1 H, d, *J* 9.4, 3′-H), 5.62 (1 H, d, *J* 8.2, 9′-H), 5.68 (1 H, d, *J* 7.8, 4′-H), 5.94 (1 H, dd, 7.6, 7.6, 7′-H), 6.15 (1 H, d, *J* 8.2, 10′-H); ^{13}C NMR (100 MHz, THF-d_8–diglyme-d_{14} = 1:1, 253 K) δ (ppm) 49.3 (1′-C), 101.7 (5′-C), 105.1 (6′-C), 105.2 (8′-C), 108.7 (3′a-C), 109.0 (9′-C), 117.1 (10′a-C), 118.6 (2′-C), 124.3 (3′-C), 125.3 (10′-C), 126.4 (7′-C), 126.7 (4′-C), 135.9 (10′b-C), 135.9 (10′c-C), 140.5 (8′a-C), 142.9 (5′a-C).

Alkylation of 1⁻ with 1,4-Dibromobutane.[1] Compound 1 (186 mg, 0.72 mmol) was stirred in dry THF (50 mL) under argon. The solution was cooled to −60 °C and *n*-BuLi (0.5 ml, 0.8 mmol) was syringed into the mixture. A deeply red solution of the anion 1⁻ was obtained. 1,4-Dibromobutane (163 mg, 0.75 mmol) was added in hexane (1 mL), and the mixture was stirred at −20 °C for 1.5 h. The mixture was cooled to −60 °C and *n*-BuLi (0.5 ml) was added. After stirring at −20 °C for 2 h, the mixture had turned yellow. NH_4Cl (0.5 g, 9 mmol) was added in order to remove traces of base, and the mixture was poured into water (200 mL) and extracted with petroleum ether. The organic layer was dried over Na_2SO_4, concentrated, and fractionated by means of column chromatography (SiO_2; petroleum ether). Two fractions were obtained. The first fraction contained three compounds, 10, 11, and 12 (3.9:1.4:1, total yield 120 mg, 0.38 mmol, 53%, based on 1), the second consisted of the pure compound 13 (31 mg, 0.08 mmol, 11% based on 1). The compounds of the first fraction form a colorless oil and 13 is a lemon-yellow oil.

10: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.80 (1 H, s, 4′-H), 5.88 (1 H, d, *J* 9.8, 2′-H), 6.19 (1 H, d, *J* 9.8, 3′-H), 7.41 (1 H, d, *J* 8.8, 10′-H), 7.46 (1 H, dd, *J* 7.1, 1.5, 6′-H), 7.46 (1 H, dd, *J* 8.0, 7.1, 7′-H), 7.58 (1 H, dd, *J* 8.0, 1.5, 8′-H), 7.69 (1 H, d, *J* 8.8, 9′-H), *J* values of 6′-H, 7′-H, and 8′-H obtained by means of simulation.

11: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.01 (2 H, d, *J* 9.7, 2′-H + 7′-H), 6.52 (2 H, d, *J* 9.7, 3′-H + 8′-H), 7.16 (2 H, d, *J* 7.5, 4′-H + 9′-H), 7.34 (2 H, d, *J* 7.5, 5′-H + 10′-H).

12: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.00 (2 H, d, *J* 9.7, 2′-H + 7′-H), 6.51 (2 H, d, *J* 9.7, 3′-H + 6′-H), 7.00 (2 H, s, 4′-H + 5′-H), 7.46 (2 H, s, 9′-H + 10′-H).

10 + 11 + 12: 1.86–2.13 (m, spirocyclopentane-CH_2s); MS *m/z* (%): 250 (13), 258 (10), 269 (12), 270 (12), 283 (19), 312 (100); exact mass calcd for $C_{24}H_{24}$ ($M^{\cdot+}$) 312.1878, found 312.1878.

13: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.24–1.55 (6 H, m, bromobutyl), 1.84–2.15 (8 H, m, 2-CH_2 + 3-CH_2 + 4-CH_2 + 5-CH_2), 3.17 (2 H, t, *J* 6.9, CH_2Br), 5.90 (1 H, d, *J* 9.8, 2′-H), 5.94 (1 H, d, *J* 9.8, 3′-H), 6.19 (1 H, d, *J* 9.5, 4′-H), 6.72 (1 H, d, *J* 9.5, 5′-H), 7.16 (1 H, dd, *J* 7.0, 1.0, 6′-H), 7.35 (1 H, dd, *J* 8.3, 8.2, 7′-H), 7.50 (1 H, d, *J* 8.6, 10′-H), 7.64 (1 H, dd, *J* 8.1, 1.2, 8′-H), 7.67 (1 H, d, *J* 8.6, 9′-H); MS *m/z* (%) 257 (100), 258 (22), 310 (26), 311 (15), 312 (72), 313 (20), 392 (14), 394 (14), exact mass calcd for $C_{24}H_{25}Br$ ($M^{\cdot+}$) 392.1140, found 392.1150.

1-Hydropyrenyl Anion (2⁻) and 1,5-Dihydropyrene (2). Pyrene was reduced according to the method of *Tintel* et al.,[3] and the reaction mixture was quenched with NH_4Cl. After evaporation of the ammonia, the residue was poured into water and extracted with petroleum ether. The organic layer was dried over Na_2SO_4 and concentrated. The resulting lemon-yellow solid was purified by means of column chromatography (SiO_2 impregnated with 10% caffeine;[31] petroleum ether). 1,5-Dihydropyrene (2) was obtained in 85–90% yield, as a white solid, mp[21] 110 °C. Solutions of 2⁻ in THF were prepared from 2 and *n*-BuLi at −60 °C under argon.

2: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.73 (2 H, m, 1-CH_2), 4.09 (2 H, m, 5-CH_2), 5.71 (1 H, m, *J* 4.0, 2.2, 1.0, 4-H), 5.91 (1 H, dt, *J* 9.9, 3.1, 1.0, 1.0, 2-H), 6.32 (1 H, dt, *J* 9.9, 2.2, 3-H), 7.09 (1 H, d, *J* 8.6, 10-H), 7.20 (1 H, dq, *J* 7.1, 1.5, 1.5 6-H), 7.31 (1 H, dd, *J* 8.0, 7.1, 7-H), 7.52 (1 H, dd, *J* 8.0, 1.5, 8-H), 7.52 (1 H, d, *J* 8.6, 9-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 31.3 (5-C), 31.8 (1-C), 121.1 (4-C), 124.9 (8-C), 125.0 (2-C), 125.1 (6-C), 125.3 (7-C), 125.9 (10b-C), 126.6 (9-C), 126.8 (3a-C), 127.0 (10-C), 127.5 (10a-C), 127.7 (3-C), 128.6 (10c-C), 132.2 (8a-C), 133.6 (5a-C).

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Preparation of an NMR Sample of the 1-Hydropyrenyl Anion (2⁻). An NMR sample of 2⁻ was obtained in the same way as described for 1⁻. The sample was prepared from dihydropyrene 2 (30 mg, 0.15 mmol) in a 1:1 mixture of THF-d_8 and diglyme-d_{14} (0.4 mL).

2⁻: ^{1}H NMR (300 MHz, THF-d_8–diglyme-d_{14} = 1:1, 253 K) δ (ppm) 4.12 (2 H, m, 1-CH_2), 4.27 (1 H, dt, J 9.4, 3.8, 2-H), 4.84 (1 H, d, J 7.7, 5-H), 5.10 (1 H, dd, J 7.6, 1.1, 6-H), 5.19 (1 H, dd, J 7.6, 1.1, 8-H), 5.40 (1 H, dt, J 9.5, 1.5, 3-H), 5.44 (2 H, d, J 7.7, 4-H + 9-H), 5.65 (1 H, dd, J 7.7, 1.0, 10-H), 5.83 (1 H, dd, J 7.6, 7.6, 7-H); ^{13}C NMR (100 MHz, THF-d_8–diglyme-d_{14} = 1:1, 253 K) δ (ppm) 34.3 (1-C), 101.0 (5-C), 104.3 (6-C), 104.9 (8-C), 106.3 (10a-C), 107.6 (2-C), 108.0 (9-C), 109.4 (3a-C), 126.5 (4-C), 126.6 (7-C), 126.7 (10-C), 129.5 (3-C), 136.6 (10c-C), 138.4 (10b-C), 140.9 (8a-C), 143.3 (5a-C).

Alkylation of the 1-Hydropyrenyl Anion (2⁻) with Benzyl Iodide. 1,5-Dihydropyrene (2) (1.43 g, 7.0 mmol) was stirred in dry THF (200 mL) under argon. The solution was cooled to −60 °C and n-BuLi (4.0 ml, 6.4 mmol, 0.9 eq) was syringed into the mixture. A deeply red solution of 2⁻ was obtained. Subsequently, a solution of benzyl iodide (1.53 g, 7.0 mmol) in toluene (2 mL) was syringed into the solution. The red color immediately changed into yellow. NH_4Cl (0.5 g, 9 mmol) was added and the reaction mixture was poured into water (600 mL) and extracted with petroleum ether. The organic layer was dried over Na_2SO_4 and concentrated, and the residue was purified by means of column chromatography (SiO_2; petroleum ether). One product, 14 (a colorless oil), could be identified (0.60 g, 2.04 mmol, 32% based on 2⁻).

14: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.60 and 2.73 (2 H, 2 d, J 12.5, CH_2Ph), 2.62 (1 H, dd, J 21.5, 1.8, 1′-H), 3.19 (1 H, dd, J 21.5, 4.3, 1-H), 6.03 (2 H, m, 2-H + 3-H), 6.18 (1 H, d, J 9.6, 4-H), 6.61 (2 H, m, o-H), 6.77 (1 H, d, J 9.6, 5-H), 7.05 (2 H, m, m-H), 7.13 (1 H, m, p-H), 7.18 (1 H, dd, J 7.0, 1.0, 6-H), 7.22 (1 H, d, J 8.3, 10-H), 7.37 (1 H, dd, J 8.2, 7.0, 7-H), 7.66 (1 H, d, J 8.3, 9-H), 7.70 (1 H, dd, J 8.2, 1.0, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 31.2 (CH_2Ph), 44.5 (3a-C), 51.6 (1-C), 123.2 (6-C), 125.1 (9-C), 125.2 (7-C), 125.6 (2-C), 125.9 (p-C), 126.2 (5-C), 126.7 (10-C), 126.8 (m-C), 127.0 (8-C), 131.1 (o-C), 133.0 (3-C), 136.3 (4-C), 126.5, 130.5, 131.7, 133.7, 134.7, 135.9 (5a-C, 8a-C, 10a-C, 10b-C, 10c-C, $ipso$-C); MS m/z (%) 146 (16), 147 (17), 200 (68), 201 (57), 202 (100), 203 (100), 204 (56), 215 (26), 289 (36), 290 (14), 291 (24), 292 (100), 293 (37), 294 (24); exact mass calcd for $C_{23}H_{18}$ ($M^{\cdot+}$) 291.1408, found 294.1411.

Alkylation of the 1-Hydropyrenyl Anion (2⁻) with 1,4-Dibromobutane. A solution of 2⁻ was prepared from 1,5-dihydropyrene (2) (0.82 g, 4.0 mmol) and n-BuLi (2.5 ml, 4.0 mmol) in THF (150 ml) at −60 °C. It was alkylated with 1,4-dibromobutane (0.9 g, 4.2 mmol) and worked up as described for 1⁻. After purification by means of column chromatography (SiO_2 impregnated with 6% caffeine; petroleum ether), one product (15), a colorless oil (0.292 g, 1.12 mmol, 28% based on 2), could be identified. Its ^{1}H NMR spectrum is identical to the spectrum described by *Tintel* et al.[23]

15: ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 25.0 (3-C + 4-C), 38.9 (5′-C), 42.1 (2-C+5-C), 46.6 (4′-C), 121.4 (3′-C), 125.3–126.9 (1′-C, 2′-C, 6′-C, 7′-C, 8′-C, 9′-C, 10′-C), 127.1, 127.8, 130.7, 131.2, 135.0 (5′a-C, 8′a-C, 10′a-C, 10′b-C, 10′c-C), 143.9 (3′a-C); MS m/z (%) 101 (13), 165 (10), 178 (26), 189 (16), 191 (14), 202 (43), 203 (22), 204 (22), 205 (47), 206 (25), 218 (20), 219 (29), 231 (55), 232 (74), 259 (42), 260 (100); exact mass calcd for $C_{20}H_{20}$ ($M^{\cdot+}$) 260.1565, found 260.1549.

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Supplementary Material Available: Copies of ^{1}H NMR spectra for compounds 2, 4, and 5, 6 and 7, 7, 8, 9, 10 and 11 and 12, 13, 14, and 15 (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.