

SPECTROMETRY AND REACTIVITY OF PHENALENYL ANIONS

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The aromatic odd-alternant phenalenyl anion and a number of its derivatives were prepared in order to study the perturbation of this conjugated anion by methyl and methoxy groups. The conjugated anions were studied by means of ^1H and ^{13}C NMR spectrometry, alkylation experiments and semi-empirical calculations. It was found that a substituent at a charged carbon atom perturbs the entire conjugated system, whereas substituents at inactive (uncharged) carbon atoms have a large effect on the positions *ortho* to the substituent.

INTRODUCTION

Many conjugated carbanions have been generated from polycyclic aromatic hydrocarbons under Birch reduction conditions^{1,2} and they could be alkylated with high regioselectivity,³ leading to valuable novel polycyclic aromatic hydrocarbons^{4–7} or intermediates for the preparation of natural products such as terpenes.⁸ The use of conjugated anions for synthetic purposes is therefore well established. The structure and charge distribution of a number of conjugated carbanions have been investigated and the regioselectivity towards electrophilic attack could be correlated with the distribution of the negative charge.^{1–3} Little is known, however, about the effect of substituents on charge distribution and reactivity in conjugated anions. Substituents may have a pronounced effect on the reactivity of 1^- . This is illustrated by the 1-hydroropyrenyl anion (Figure 1), a species which is attacked by electrophiles with high regioselectivity.^{9,10}

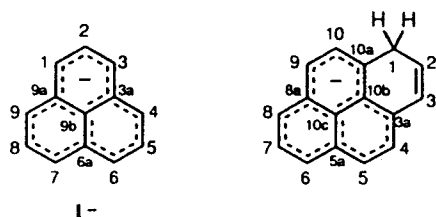


Figure 1. The phenalenyl anion (1^-) and the 1-hydroropyrenyl anion

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In this paper, the influence of methyl and methoxy groups on the regioselectivity of electrophilic attack on the aromatic phenalenyl anion (1^-) is discussed. To establish the influence of alkyl substituents, the symmetrical 1,2,3-trihydroropyrenyl anion (2^-) and the 1-methylphenalenyl anion (3^-) were prepared. These anions have alkyl groups at positions which, in the unsubstituted phenalenyl anion (1^-), bear negative charge. The symmetry of anion 2^- simplifies the study of its charge distribution. The effect of a substituent at a position which in 1^- , does not bear negative charge may be studied on the 2-methylphenalenyl anion (4^-). Further, the 1-methoxyphenalenyl anion (5^-) and the 2-methoxyphenalenyl anion were prepared (6^-), in order to determine the influence of a stronger^{11,12} substituent on the charge distribution.

Information on the charge distribution in these conjugated carbanionic systems was obtained by ^{13}C NMR spectrometry^{1,2,13–16} and semi-empirical calculations^{17,18} and an attempt was made to correlate this with the results of alkylation experiments.^{1,2,19,20}

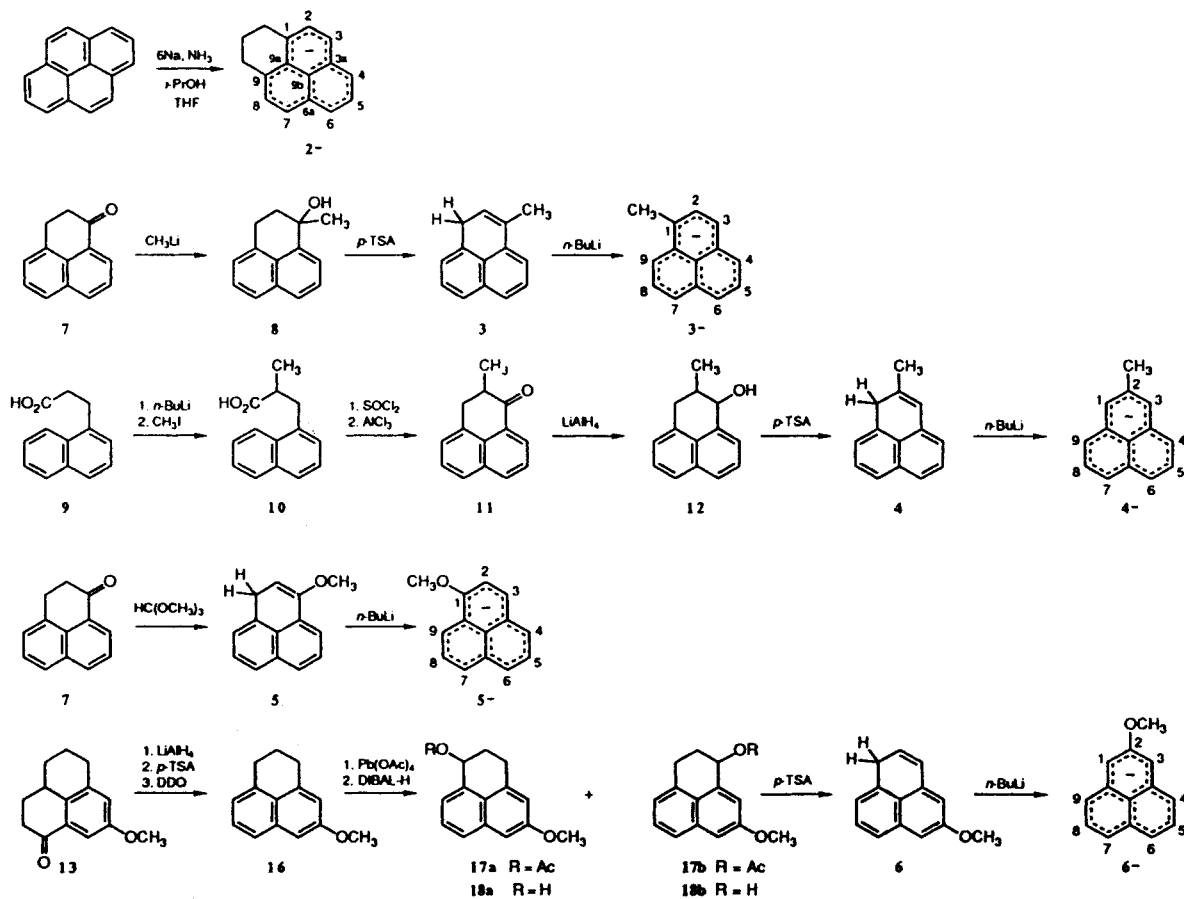
RESULTS

The preparation of the phenalenyl anion (1^-) has been described earlier.²¹ The synthesis of anions 2^- , 3^- , 4^- , 5^- and 6^- is summarized in Scheme 1.

^1H and ^{13}C NMR spectrometry

NMR samples of phenalenyl anions in THF were prepared under exclusion of moisture and oxygen. ^1H NMR spectra and proton-decoupled ^{13}C NMR spectra were recorded at 253 K. Highly resolved spectra could

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Scheme 1. Schematic representation of the synthesis of anions 2⁻, 3⁻, 4⁻, 5⁻ and 6⁻. The numbering of 2⁻ has been adapted for the sake of comparison

be obtained at this temperature. Line broadening was observed at temperatures lower than 233 K, owing to increased viscosity, and at temperatures higher than 273 K. ¹H NMR spectra were assigned by means of homonuclear decoupling and NOE experiments. The tertiary signals in the ¹³C NMR spectra of the anions could then be assigned by means of 2D-correlated ¹H-¹³C NMR spectra. Anions 2⁻, 3⁻ and 4⁻ are soluble in THF-*d*₈ at 253 K. Anions 1⁻, 5⁻ and 6⁻, however, tend to precipitate as lithium phenalenylates, but their solubility could be improved by adding diglyme-*d*₁₄. This had no noticeable effect on ¹H or ¹³C chemical shifts of the anions.

¹H NMR chemical shifts and coupling constants are given in Table 1. The ¹H NMR spectrum of the phenalenyl anion (1⁻) consists of an A₂X pattern, in accordance with its high symmetry. The chemical shifts obtained for 1⁻ agree well with recently published values.²² The ¹H NMR spectrum of the 1,2,3-

trihydroxyphenyl anion (2⁻) displays an AX and an A₂X pattern, and the spectra of 2-methylphenalenyl anion (4⁻) and the 2-methoxyphenalenyl anion (6⁻) show a singlet and an AXB pattern, all in accordance with the symmetry of these species. The spectra of the 1-methylphenalenyl anion (3⁻) and the 1-methoxyphenalenyl anion (5⁻) also display the expected patterns.

¹³C NMR chemical shifts are given in Table 2. The ¹³C NMR spectrum of the phenalenyl anion (1⁻) displays the expected four signals (Figure 2). The chemical shifts are in excellent agreement with recently published values.²² The spectrum of the 1,2,3-trihydroxyphenyl anion (2⁻) shows methylene signals at δ = 22.2 and 32.2 ppm. The quaternary signal of C-1 is recognized from its chemical shift. The intense quaternary signal at the lowest field is attributed to the equivalent C-3a and C-6a. The signals at δ = 138.6 and 139.0 ppm belong to C-9a and C-9b.

The methyl group of the 1-methylphenalenyl anion

Table 1. ^1H NMR chemical shifts, δ (ppm), of phenalenyl anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- (300 MHz, $\text{THF}-d_6$, 253 K), measured with respect to the THF signal at $\delta = 3.58$ ppm, and coupling constants (Hz)^a

	1^-	2^-	3^-	4^-	5^-	6^-
H-1	5.06 d	—	—	4.94 s	—	4.80 s
H-2	5.81 t	5.66 d	5.91 d	—	5.84 d	—
H-3	5.06 d	5.05 d	5.23 d	4.94 s	5.13 d	4.80 s
H-4	5.06 d	4.97 d	5.19 dd ^b	5.05 d	5.21 dd ^c	5.14 dd
H-5	5.81 t	5.73 dd	5.90 dd	5.81 dd	5.85 dd	5.87 dd
H-6	5.06 d	4.97 d	5.25 dd ^b	5.05 d	5.03 dd ^c	5.12 dd
H-7	5.06 d	5.05 d	5.26 dd ^b	5.05 d	5.17 dd	5.12 dd
H-8	5.81 t	5.66 d	6.05 dd	5.81 dd	5.97 dd	5.87 dd
H-9	5.06 d	—	4.87 dd	5.05 d	5.20 dd	5.14 dd
J_{12}	7.7					
J_{23}		7.6	7.7		8.0	
J_{45}		7.6	7.6	7.5	7.6	7.5
J_{56}			7.6	7.5	7.6	7.5
J_{78}			7.6		7.6	
J_{89}			7.6		7.6	
J_{46}			1.2		1.2	1.2
J_{79}			1.2		1.2	

^a 2^- , CH_2s $\delta = 1.49$ ppm (*qui*, $6\cdot0$), benzylic CH_2s $\delta = 2.27$ ppm (*t*, $6\cdot0$); 3^- 1-CH_3 $\delta = 1.44$ ppm; 4^- , 2-CH_3 $\delta = 1.63$ ppm; 5^- , 1-OCH_3 $\delta = 3.44$ ppm; 6^- , 2-OCH_3 $\delta = 3.37$ ppm.

^b These values may have to be interchanged.

^c Assignment based on results of alkylation experiments and calculations.

(3^-) resonates at $\delta = 20.5$ ppm. The chemical shifts of C-4, C-6 and C-7 may have to be interchanged. Of the quaternary carbon atoms, C-1 is found at $\delta = 106.1$ ppm. It is assumed that C-6a and C-9a are influenced the least by the presence of the methyl group. After comparison with 1-methylnaphthalene and toluene,^{23,24} it is expected that C-3a resonates upfield from C-9a.

The methyl signal of the 2-methylphenalenyl anion (4^-) is found at $\delta = 22.5$ ppm. The large quaternary signal at $\delta = 144.7$ ppm is ascribed to the equivalent C-3a and C-9a and the signal at $\delta = 144.5$ ppm to C-6a (Figure 3). The methoxy signal of the 1-methoxyphenalenyl anion (5^-) is found at $\delta = 55.6$ ppm. The assignment of C-4 and C-6 may have to be inter-

Table 2. ^{13}C NMR chemical shifts, δ (ppm), of phenalenyl anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- (100 MHz, $\text{THF}-d_6$, 253 K), measured with respect to the $\text{THF}-d_6$ signal at $\delta = 67.4$ ppm^a

	1^-	2^-	3^-	4^-	5^-	6^-
C-1	103.3	108.4	106.1	104.3	138.6	88.0
C-2	128.1	126.8	129.2	135.2	113.2	161.1
C-3	103.3	101.9	102.5	104.3	99.3	88.0
C-4	103.3	101.5	102.6 ^b	103.1	102.5 ^c	103.4
C-5	128.1	127.1	127.1	128.1	126.5	128.2
C-6	103.3	101.5	104.2 ^b	103.1	99.5 ^c	103.1
C-7	103.3	101.9	104.4 ^b	103.1	102.9	103.1
C-8	128.1	126.8	128.4	128.1	127.6	128.2
C-9	103.3	108.4	99.1	103.1	95.0	103.4
C-3a	144.9	143.8	141.9	144.7	140.0	145.6
C-6a	144.9	143.8	144.4	144.5	144.2	144.0
C-9a	144.9	139.0 ^b	143.1	144.7	134.3	145.6
C-9b	139.5	138.6 ^b	138.3	137.6	138.5	135.0

^a 2^- , CH_2s $\delta = 22.2$ ppm, benzylic CH_2s $\delta = 32.2$ ppm; 3^- , 1-CH_3 $\delta = 20.5$ ppm; 4^- , 2-CH_3 $\delta = 22.5$ ppm; 5^- , 1-OCH_3 $\delta = 55.6$ ppm; 6^- , 2-OCH_3 $\delta = 53.8$ ppm.

^b These values may have to be interchanged.

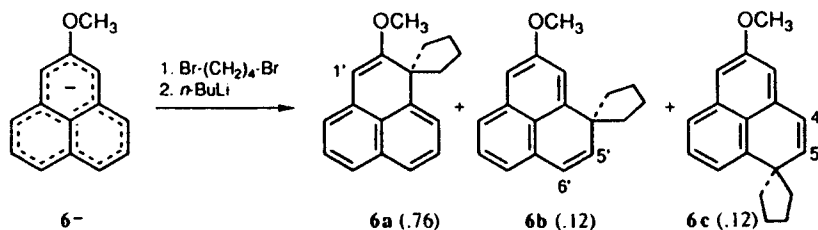
^c Assignment based on the significantly higher reactivity of C-6 than of C-4. This is in accordance with calculations, which predict a higher charge at C-6 than at C-4.

changed. The quaternary signals could be assigned by means of a 2D long-range ^1H - ^{13}C correlated NMR spectrum.

The methoxy signal of the 2-methoxyphenalenyl anion (6^-) is found at $\delta = 53.8$ ppm. The signals of C-6a and of the equivalent C-3a and C-9a are readily assigned. The *ipso* carbon atom C-2 resonates at low field ($\delta = 161.1$ ppm) owing to the large α -effect of the methoxy group, whereas C-9b ($\delta = 135.0$ ppm), being *para* to the methoxy group, is shielded ($\Delta\delta = -4.5$ ppm) compared with C-9b of the unsubstituted 1^- .

Alkylation experiments

The alkylation of the phenalenyl anion (1^-) with the bifunctional electrophile 1,4-dibromobutane has been discussed.²¹ It was shown that a spirocyclopentane ring



Scheme 2. Alkylation of the 2-methoxyphenalenyl anion (6^-)

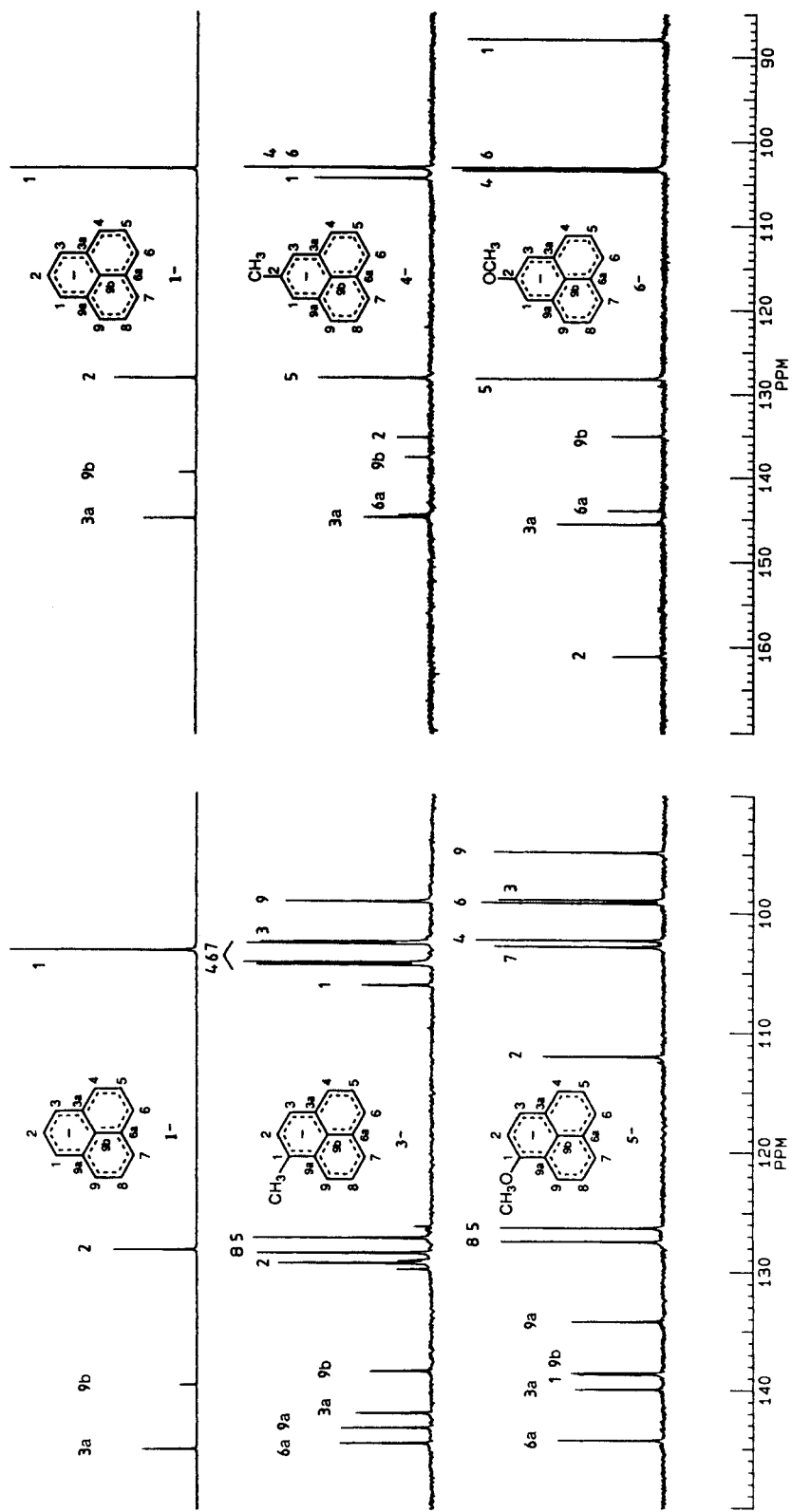


Figure 2. ^{13}C NMR spectra (low-field region) of 1-, 3- and 5- (100 MHz, THF- d_6 , 253 K). Chemical shifts are measured with respect to the THF- d_6 signal at $\delta = 67.4$ ppm

Figure 3. ^{13}C NMR spectra (low-field region) of 1-, 4- and 6- (100 MHz, THF- d_6 , 253 K). Chemical shifts are measured with respect to the THF- d_6 signal at $\delta = 67.4$ ppm

is introduced at the position of initial attack, with high efficiency. The resulting product cannot isomerize and is therefore readily identified by means of ^1H NMR spectrometry.

This alkylation method therefore seemed suitable for obtaining a picture of the reactivity of anions 2^- , 3^- , 4^- , 5^- and 6^- . The alkylation experiments were carried out several times, giving highly reproducible results. Alkylation products (e.g. Scheme 2) were obtained in combined yields ranging from 75% to 95%. The products resulting from each alkylation experiment were separated, if possible, by means of column chromatography and their identity was ascertained by the use of ^1H NMR homonuclear decoupling, NOE experiments and high-resolution mass spectrometry. The isomer proportions in the alkylation of anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- are shown in Figure 4.

Semi-empirical calculations

Charges and orbital coefficients were calculated by means of the semi-empirical PM3 method. For all anions, a pre-optimization 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 was used, followed by Bartel's non-linear least-squares method, in order to achieve a further reduction of the gradients. In 5^- , the methoxy group can be directed at H-2 or at H-9 or be at an angle with the plane of the anion. Charges

and orbital coefficients were calculated for the structure in which the methoxy group is directed at H-2. If the methoxy group is directed at H-9, significant hindrance between this proton and the methoxy group occurs. Therefore, the latter conformation seems less likely than the former. The most stable conformation of the 2-OCH₃ group of 6^- is in the plane of the anion, thereby making the 1- and 3-positions significantly inequivalent. The average charge and orbital coefficient of these positions are given in Table 3.

The negative charge in the phenalenyl anion (1^-) is found exclusively at the expected carbon atoms C-1, C-3, C-4, C-6 C-7 and C-9. The introduction of alkyl groups on to charged positions, as in the symmetrical 1,2,3-trihydroxyphenyl anion (2^-), does not seem to have a significant influence on charge distribution. The propano bridge only decreases charge at the substituted C-1 and C-9. The same holds true for the 1-methylphenalenyl anion (3^-). Less charge is calculated at C-1 than at the other negatively charged carbon atoms where almost equal charges are found. The symmetrical 2-methylphenalenyl anion (4^-) has somewhat less charge at the positions *ortho* to the methyl group than at its other charged positions.

Methoxy groups have a larger influence on charge distribution in the phenalenyl system. In the 1-methoxyphenalenyl anion (5^-), the negative charge at the substituted C-1 has decreased considerably. At C-3, C-4, C-6 and C-7, which have no steric interaction with the methoxy group, significant differences in the charges and the HOMO coefficients are calculated. The highest negative charge and coefficient are found at C-6. If the methoxy group is set at an angle of 90° with the plane of the anion, the methoxy group does not seem to interact with the conjugated system. For the 2-

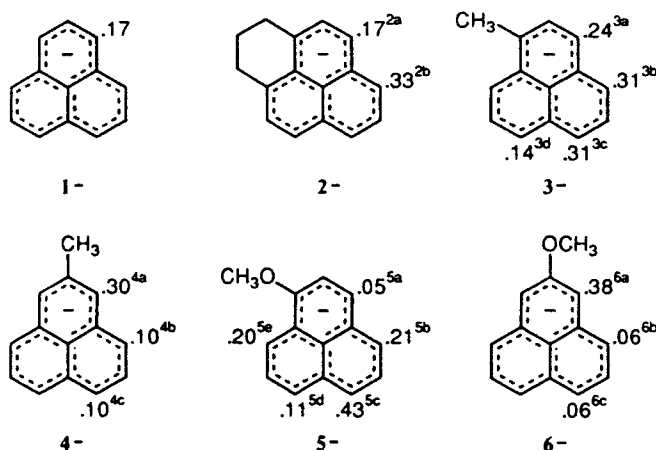


Figure 4. Isomer proportions in the alkylation with 1,4-dibromobutane of anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- . The corresponding products are given as superscripts

Table 3. Calculated charges and (in italics) HOMO coefficients in anions 1⁻, 2⁻, 3⁻, 4⁻, 5⁻ and 6⁻

	1 ⁻	2 ⁻	3 ⁻	4 ⁻	5 ⁻	6 ⁻
C-1	-0.304 <i>0.408</i>	-0.278 <i>0.414</i>	-0.283 <i>0.420</i>	-0.296 <i>0.406</i>	-0.111 <i>0.400</i>	-0.353 <i>0.411</i>
C-2	-0.025 <i>0</i>	-0.018 <i>0.009</i>	-0.018 <i>0.006</i>	-0.008 <i>0</i>	-0.090 <i>0.039</i>	0.154 <i>0.014</i>
C-3		-0.298 <i>0.400</i>	-0.303 <i>0.407</i>		-0.287 <i>0.415</i>	
C-4		-0.298 <i>0.396</i>	-0.299 <i>0.402</i>	-0.304 <i>0.408</i>	-0.306 <i>0.406</i>	-0.301 <i>0.408</i>
C-5		-0.028 <i>0</i>	-0.028 <i>0.002</i>	-0.025 <i>0</i>	-0.021 <i>0.008</i>	-0.025 <i>0.008</i>
C-6			-0.299 <i>0.400</i>	-0.304 <i>0.408</i>	-0.312 <i>0.409</i>	-0.298 <i>0.404</i>
C-7			-0.300 <i>0.401</i>		-0.295 <i>0.393</i>	
C-8			-0.025 <i>0.001</i>		-0.033 <i>0.010</i>	
C-9			-0.306 <i>0.405</i>		-0.278 <i>0.394</i>	
C-3a	0.087 <i>0</i>	0.083 <i>0.004</i>	0.085 <i>0.004</i>	0.087 <i>0</i>	0.075 <i>0.022</i>	0.108 <i>0.015</i>
C-6a	0.087 <i>0</i>	0.083 <i>0.004</i>	0.084 <i>0.002</i>	0.088 <i>0</i>	0.085 <i>0</i>	0.086 <i>0.003</i>
C-9a	0.087 <i>0</i>	0.109 <i>0.001</i>	0.100 <i>0.006</i>	0.087 <i>0</i>	0.072 <i>0.017</i>	0.108 <i>0.015</i>
C-9b	-0.065 <i>0</i>	-0.062 <i>0</i>	-0.062 <i>0</i>	-0.065 <i>0.003</i>	-0.052 <i>0.016</i>	-0.080 <i>0.007</i>

methoxyphenalenyl anion (6⁻), a large positive charge is calculated at C-2 and a large negative charge at the *ortho* positions C-1 and C-3.

DISCUSSION

¹³C NMR spectrometry is useful for obtaining a picture of the charge distribution in conjugated systems. The signal of the equivalent carbon atoms of 1⁻ which, according to calculations, bear negative charge (C-1, C-3, C-4, C-6, C-7 and C-9) is found at significantly higher field than the signals of the carbon atoms which bear very little charge. Steric factors, however, must be taken into account in the case of substituted carb-anions, because they may have an effect on carbon chemical shift. In the ¹³C NMR spectrum of the 1-methylphenalenyl anion (3⁻), the signal of the *peri* carbon atom C-9 appears at the highest field as a result of steric interaction²³ between H-9 and 1-CH₃. Calculations do not suggest a significantly higher charge at C-9. Therefore, even though its signal appears at the highest field, it cannot be concluded that C-9 is the most reactive position of 3⁻. Similarly, in the ¹³C NMR spectrum of the 1-methoxyphenalenyl anion (5⁻), the signal of C-9 is present at unusually high field. It may be expected that C-9 of 5⁻ is a reactive position, but less reactive than it appears from the ¹³C NMR spectrum. Steric hindrance by the substituent groups also has an effect on the reactivity of charged carbon atoms situated *ipso* and *peri* to the substituent. C-1 and C-9 of anions 2⁻, 3⁻ and 5⁻ are expected to be less reactive compared with unhindered atoms. Indeed, no product resulting from attack at C-1 of anions 2⁻, 3⁻ and 5⁻ was observed. At C-9 of 3⁻, which bears a similar charge as C-3, C-4, C-6 or C-7, no electrophilic attack was observed.

The ¹³C NMR results and the PM3 calculations for 2⁻ and 3⁻ suggest that an alkyl group at a position

bearing negative charge does not cause a significant redistribution of charge in the conjugated system. The low regioselectivity of electrophilic attack on 2⁻ and 3⁻ is in agreement with this. An alkyl group at an inactive position, as in the 2-methylphenalenyl anion (4⁻), does have a stronger effect on the regioselectivity of electrophilic attack. The positions *ortho* to the methyl group are clearly more reactive than C-4, C-6, C-7 and C-9 of 4⁻. This finding is not in agreement with the ¹³C NMR results and the calculations, which suggest that a methyl group at C-2 barely perturbs the conjugated system.

As expected, a methoxy group perturbs the phenalenyl system more than a methyl group does. A methoxy group at a position bearing negative charge has a polarizing effect throughout the conjugated system, as is apparent from the ¹³C NMR spectrum of the 1-methoxyphenalenyl anion (5⁻) and from the PM3 calculations. In addition to this polarization of the π -electron cloud, the methoxy group has an inductive electron-withdrawing effect at C-1. The reactivity of 5⁻ correlates reasonably well with the results of the ¹³C NMR measurements and the calculations.

In the case of the 2-methoxyphenalenyl anion (6⁻), both the ¹³C NMR measurements and the calculations predict an increased charge density at the positions *ortho* to the methoxy group. Compared with 1⁻, the signal of the *ortho* carbon atoms C-1 and C-3 is shielded by 15.3 ppm, whereas the signal of C-2 is shifted downfield by 33.0 ppm. Since the influence of the 2-methoxy group is observed only at C-1, C-2, C-3 and C-9b, it may be assumed that the inductive effect of the methoxy group (a short-range effect) predominates here. The reactivity of 6⁻ correlates very well with the ¹³C NMR results and the calculated charge distribution. Even alternant systems with the same symmetry as 6⁻, 2-methoxypyrene and the 2-methoxypyrene dianion, show identical shielding and increase in reactivity of the *ortho* positions.^{20,25}

CONCLUSION

Although a good correlation between ^{13}C NMR chemical shifts, charge distribution or HOMO coefficients and regioselectivity of electrophilic attack for alkyl-substituted phenalenyl anions could not be obtained, a reasonable correlation was found in the case of the more strongly perturbed methoxy-substituted phenalenyl anions.

EXPERIMENTAL

Details of the preparation of the anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- and spectroscopic data for all the compounds are available from the authors on request.

Preparation of NMR samples of the anions 1^- , 2^- , 3^- , 4^- , 5^- and 6^- . In a flexible glove-bag, under an atmosphere of dry argon, a solution of 1*H*-phenalene²¹ (25 mg, 0.15 mmol) in a 1:1 mixture of THF-*d*₈ and diglyme-*d*₁₄ (total volume 0.4 ml) was transferred into an NMR tube. The solution was purged with argon, 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, sealed under vacuum and separated from the vacuum line. The ^1H and ^{13}C NMR spectra were recorded at -20°C . NMR samples of anions 2^- , 3^- , 4^- , 5^- and 6^- were prepared analogously from 0.15 mmol of the appropriate phenalene derivative (1,2,3,5- and 1,2,3,6-tetrahydropyrene, **3**, **4**, **5** or **6**), THF-*d*₈ (0.4 ml) or a 1:1 mixture of THF-*d*₈ and diglyme-*d*₁₄ (total volume 0.4 ml), and methyllithium (0.2 ml).

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