JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 86–94 (1999)

Substituent-induced polarization of charge in phenalenyl anions

Joost T. M. van Dijk, Steven A. Steggerda, Johan Lugtenburg and Jan Cornelisse

Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Revised 11 February 1998; accepted 28 April 1998

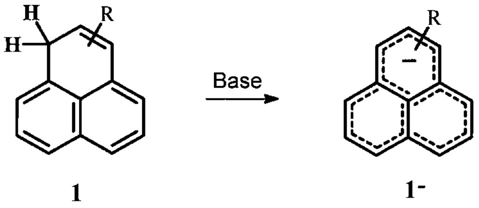
ABSTRACT: The effect of trimethylsilyl, alkynyl and cyano substituents on the charge distribution of the phenalenyl anionic nucleus was examined using semiempirical calculations and NMR spectroscopy. With these techniques it was demonstrated that the trimethylsilyl and cyano substituents are capable of attracting adjacent negative charge. Examples of reactions from the literature confirm the charge-attracting capabilities of the trimethylsilyl substituent. The alkynyl substituent was shown to perturb the charge distribution of the phenalenyl moiety to a much lesser degree than the vinyl substituent in the 1-hydropyrenyl anion. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: charge polarization; charge distribution; substituent-induced polarization; phenalenyl ions

INTRODUCTION

The dissolving metal reduction of arenes with alkali metals is an important method for the preparation of dihydroaromatic compounds or reductively alkylated products.[1,2] Performed in liquid ammonia it is better known as the Birch reduction, but reductions in the absence of liquid ammonia are also possible.[3] The reaction generates various kinds of anionic intermediates, which may react with proton donors or electrophiles. The regioselectivity of the protonations and of many alkylations depends on the charge distribution of these anionic intermediates.[4–6] Reductions of arenes containing functional groups are applied very often[7,8] and are sometimes performed to influence the regioselectivity of the reaction.[9] An example of this is the reduction of 1-methylnaphthalene in the absence or presence of a 4-trimethylsilyl (TMS) substituent.[10]

A useful way of studying the effect of a specific substituent on the charge distribution of an anion is by generating the anion in an NMR tube and measuring and interpreting its ^{1}H and ^{13}C NMR spectra.[4] This has been done previously in order to study the effect of methyl, methoxy and vinyl substituents on the charge distribution of the phenalenyl anion. (Scheme 1).[4,11]



Scheme 1. Formation of phenalenyl anions. R = Me, vinyl, OCH_3; **1**$^-$: R = H

Many examples of stabilization of anions by silyl substituents are known, although little is known about the nature and mechanism of anion stabilization. NMR spectroscopy on silyl-substituted anions may give more insight into this effect.

Cyanoarenes have only recently been used for the first time in Birch-like reactions[12,13] and little is known about the effect of this substituent on the charge distribution of delocalized anions. In order to compare the effect of a CN triple bond with that of a CC triple bond, the 1-(3,3-dimethylbutynyl) derivative (Fig. 1) was also examined.

In this study, the effects of the trimethylsilyl, 3,3-dimethylbutynyl and cyano substituents on the charge distribution of the phenalenyl anion are examined. Anions **2**$^-$, **3**$^-$ and **4**$^-$ were generated in an NMR tube and examined by means of ^{1}H and ^{13}C NMR spectroscopy. The charge distribution and the HOMO coefficients of these anions were calculated by means of semiempirical calculations. It should be kept in mind, however, that the calculated data pertain to the anions in the absence of counterions and solvent.

---

*Correspondence to: Jan Cornelisse, Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

Contract/grant sponsor: Netherlands Foundation for Chemical Research (SON).
Contract/grant sponsor: Netherlands Organization for Scientific Research (NWO).

CCC 0894–3230/99/020086–09 $17.50

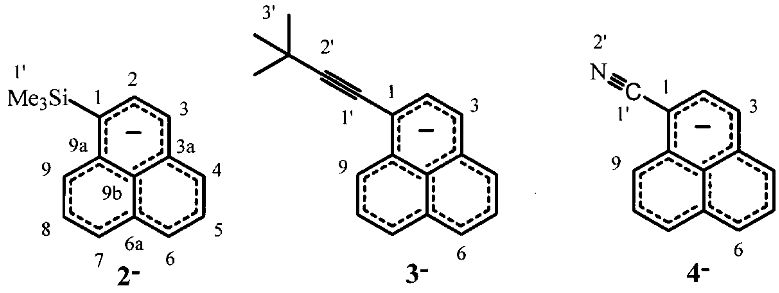
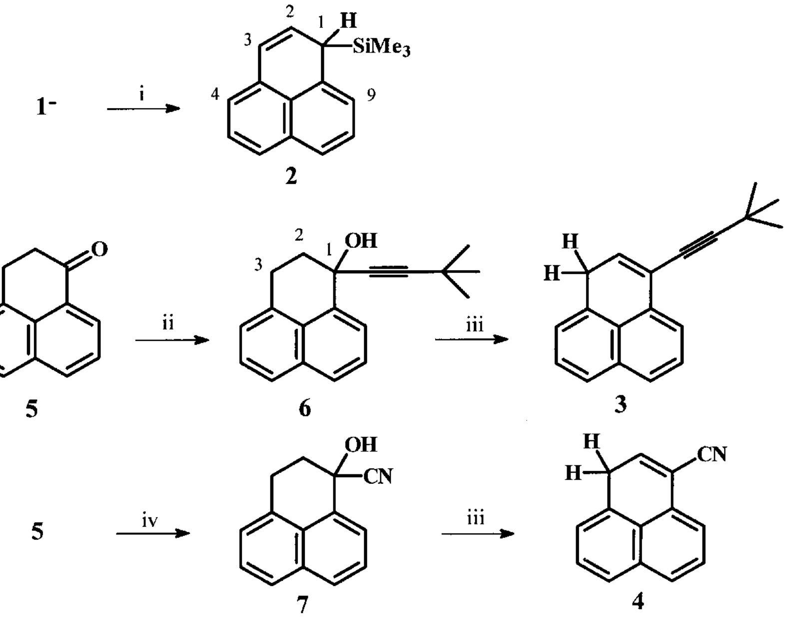


Figure 1. Trimethylsilyl- ($\mathbf{2}^-$), 3′,3′-dimethylbutynyl- ($\mathbf{3}^-$) and cyanophenalenyl ($\mathbf{4}^-$) anions



Scheme 2. (i) TMSCl; (ii) 1-lithium-2-tert-butylacetylide; (iii) *p*-TsOH; (iv) Et$_2$AlCN

RESULTS

Preparation of anions

The easiest way to prepare 1-trimethylsilyl-1*H*-phenalene (**2**) is by reaction of the phenalenyl anion with trimethylsilyl chloride. After work-up, this resulted in the isolation of 71% of 1-trimethylsilyl-1*H*-phenalene (**2**) together with a small amount of 1*H*-phenalene. The structure of **2** was proved by means of ^{1}H NMR spectroscopy.

In their approach to the preparation of 1-substituted phenalenyl anions, Hempenius *et al.*[11] showed that 2,3-dihydro-1*H*-phenalen-1-one (Scheme 2, **5**)[11] is a very useful starting compound. Addition of carbanions to the carbonyl group of the molecule results in the formation of 1-substituted 2,3-dihydro-1-hydroxy-1*H*-phenalene derivatives. Acid-catalyzed dehydration of these compounds results in the formation of substituted phenalenes as mixtures of isomers.

Addition of **5** to lithium *tert*-butylacetylide and work-up resulted in the isolation of **6** in 77% yield after column chromatography. The structure of **6** was proved by means of ^{1}H NMR spectroscopy and by comparison with the known spectrum of 2,3-dihydro-1-hydroxy-1*H*-phenalene.[14] Dehydration with *p*-toluenesulfonic acid resulted in the formation of the unstable phenalene derivative **3**, which was transformed into its anion as soon as possible. Similarly, reaction of **5** with diethylaluminum cyanide and work-up resulted in the formation of **7**, which proved to be a highly unstable compound and was therefore transformed into its phenalenyl derivative **4** and on to its anion ($\mathbf{4}^-$) as soon as possible.

Semiempirical calculations

Substitution of the phenalenyl anion at position 1, as in $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$, results in a relatively large HOMO coefficient at this position (Table 1). In general, the

Table 1. Charge distribution and HOMO coefficients of **2**$^-$, **3**$^-$ and **4**$^-$

	Charge			HOMO		
Position	**2**$^-$	**3**$^-$	**4**$^-$	**2**$^-$	**3**$^-$	**4**$^-$
1	−0.374	−0.196	−0.225	0.421	0.450	0.417
2	−0.012	−0.022	0.027	0.014	0.019	0.064
3	−0.315	−0.298	−0.298	0.408	0.405	0.397
4	−0.299	−0.280	−0.271	0.402	0.386	0.384
5	−0.030	−0.074	−0.044	0.006	0.010	0.030
6	−0.291	−0.264	−0.255	0.394	0.364	0.376
7	−0.297	−0.271	−0.264	0.399	0.377	0.383
8	−0.029	−0.075	−0.040	0.001	0.006	0.020
9	−0.310	−0.269	−0.263	0.401	0.386	0.389
3a	0.092	0.073	0.090	0.011	0.020	0.056
6a	0.080	0.050	0.061	0.003	0.005	0.007
9a	0.132	0.094	0.105	0.011	0.022	0.061
9b	−0.075	−0.059	−0.058	0.007	0.020	0.007
1′	0.399	0.004	−0.017	0.042	0.007	0.097
2′		−0.322	−0.259		0.236	0.246

relative magnitudes of the HOMO coefficients are very similar to the calculated charge distribution. The negative charge in the phenalenyl moieties is still located at the same six positions as in the phenalenyl anion, but of course in a less symmetric way.

The effects of the cyano and *tert*-butylethynyl groups on the charge distribution and HOMO coefficients of the phenalenyl anion were compared with the effects of the same substituents in naphthalene. The charge distribution and HOMO coefficients of naphthalene, 1-cyanonaphthalene and 1-(3,3-dimethyl-1-butynyl)naphthalene were calculated (Table 2). The presence of these substituents on the naphthalene skeleton results in a positive charge at C-1. A lowering of the negative charge on the other naphthalene carbon atoms is observed in the case of 1-cyanonaphthalene. In the case of 1-(3,3-dimethyl-1-butynyl)naphthalene, similar but less pronounced effects are observed.

Table 2. Charge distribution and HOMO coefficients of naphthalene (N), 1-cyanonaphthalene (CN) and 1-(3,3-dimethyl-1-butynyl)naphthalene (DBN)

	Charge			HOMO		
Position	N	DBN	CN	N	DBN	CN
1	−0.088	0.077	0.040	0.416	0.419	0.412
2	−0.101	−0.091	−0.061	0.303	0.317	0.259
3		−0.102	−0.112		0.253	0.277
4		−0.087	−0.063		0.419	0.397
5		−0.091	−0.084		0.360	0.412
6		−0.100	−0.096		0.227	0.263
7		−0.102	−0.086		0.259	0.275
8		−0.087	−0.094		0.356	0.414
4a	−0.037	−0.039	−0.043	0.002	0.008	0.017
8a		−0.022	−0.012		0.048	0.002
1′		−0.126	−0.091		0.151	0.057
2′		−0.148	−0.066		0.273	0.198

NMR spectroscopy

The anions **2**$^-$, **3**$^-$ and **4**$^-$ were generated in an NMR tube under water- and oxygen-free conditions. The 300 MHz ^{1}H NMR spectra (Fig. 2) were assigned with the aid of H–H COSY and NOE difference experiments. In addition, 75 MHz ^{13}C NMR spectra were recorded, which were assigned with the aid of C–H HETCOR and gated decoupling techniques.

In the 300 MHz ^{1}H NMR spectrum of **2**$^-$, two AMX spectra, one AX spectrum and a singlet are observed. Next to the signals of **2**$^-$, those of 14% of **1**$^-$ are present.[11] The singlet at 0.01 ppm with a relative intensity of 9H is assigned to the TMS group. Irradiation of this singlet causes NOE effects on the doublet at 5.46 ppm and on the doublet at 6.08 ppm. The doublet is part of the AX spin system and is therefore assigned to H-2 and the doublet at 5.46 ppm is assigned to H-9. Using the H–H COSY spectrum, H-3, H-7 and H-8 can easily be found. The remaining triplet can be assigned to H-5. A distinction between H-4 and H-6 could not be made.

Two AMX spectra, one AX spectrum and a singlet with a relative intensity of 9H are observed in the 300 MHz ^{1}H NMR spectrum of **3**$^-$. Irradiation of the doublet at 5.34 ppm causes an NOE effect on the signal at 5.17 ppm, which is part of the AX spectrum. The former signal is therefore assigned to H-4 and the latter to H-3. H-2, H-5 and H-6 can subsequently be found using the H–H COSY spectrum. In the remaining AMX spectrum belonging to H-7, H-8 and H-9, the signal with two *ortho* couplings can be assigned to H-8. The ^{13}C NMR signals belonging to these positions can be found using the C–H HETCOR spectrum. A distinction between the two remaining tertiary ^{13}C signals, C-7 and C-9, could be made by recording a 75 MHz gated decoupled ^{13}C NMR spectrum (Fig. 3). In this spectrum C-7 appears as a double double doublet, arising from the ^1J coupling with H-7 and two ^3J couplings with H-6 and H-9. Carbon 9 has one ^1J and one ^3J coupling and therefore it appears as a double doublet. The signals of H-7 and H-9 in the ^{1}H NMR spectrum can subsequently be found using the C–H HETCOR spectrum. Because C-1 has two ^3J couplings, with H-3 and H-9, the double doublet at 90.93 ppm can be assigned to this atom. Similarly, the doublet at 83.20 ppm is assigned to C-1′ because of its ^3J coupling with H-2. The signal of C-2′ appears at 95.33 ppm as a multiplet because of its ^3J couplings with the nine protons of the *tert*-butyl group. The downfield quaternary signals belong to C-3a, C-6a, C-9a and C-9b. The first three appear as triplets and cannot be further distinguished. The signal of C-9b can be recognized because it appears as a multiplet, arising from its five ^3J couplings.

In the 300 MHz ^{1}H NMR spectrum of **4**$^-$, two AMX spectra and one AX spectrum are observed. Assignment of these signals is achieved using ^1J C–H, ^3J C–H HETCOR and gated decoupled ^{13}C NMR spectra. The five tertiary carbon atoms of **4**$^-$ bearing a pronounced

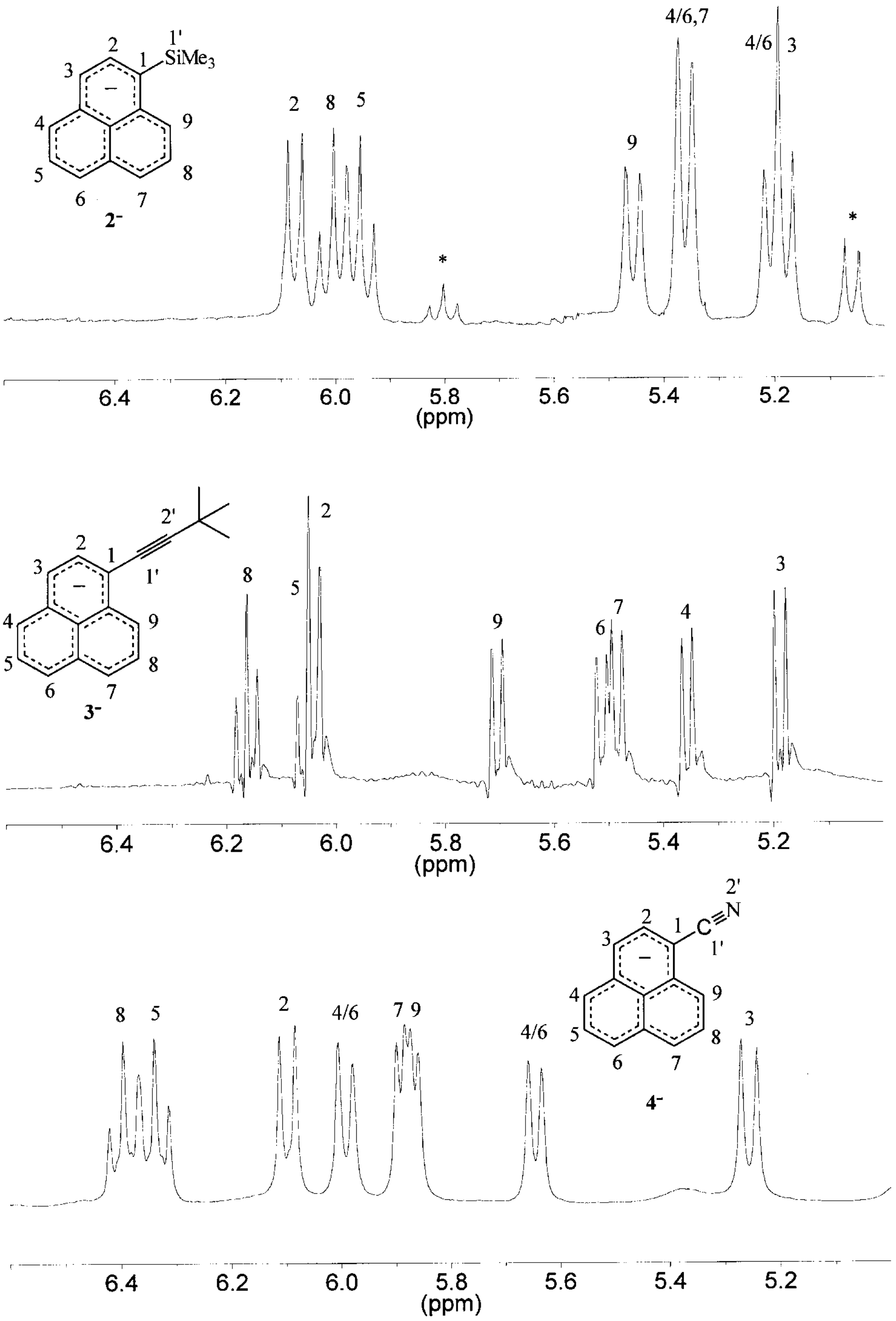


Figure 2. 300 MHz ^{1}H NMR spectra of $\mathbf{2}^-$, $\mathbf{3}^-$ and $\mathbf{4}^-$. * $\mathbf{1}^-$

negative charge appear in the range of 106–113 ppm. Three of these signals appear as double double doublets in the gated decoupled ^{13}C NMR spectrum. Because of the absence of a proton at position 1, two of the signals appear as double doublets and are therefore assigned to C-3 and C-9. A distinction between these signals can be made by inspecting the ^1J C–H HETCOR spectrum. From this spectrum it can be seen that the signal at 107.08 ppm is coupled to one of the signals of the AX spectrum and it is therefore assigned to C-3. The carbon signal at 106.09 ppm is coupled to a proton of an AMX spectrum and is therefore assigned to C-9. With the aid of the H–H COSY spectrum, H-2, H-7 and H-8 can easily be found. From the remaining AMX spectrum, the signal with two ortho couplings is assigned to H-5. A distinction between positions 4 and 6 could not be made. Carbon 1 could be identified from its cross-correlation with H-3 in the ^3J C–H HETCOR spectrum. In the gated decoupled

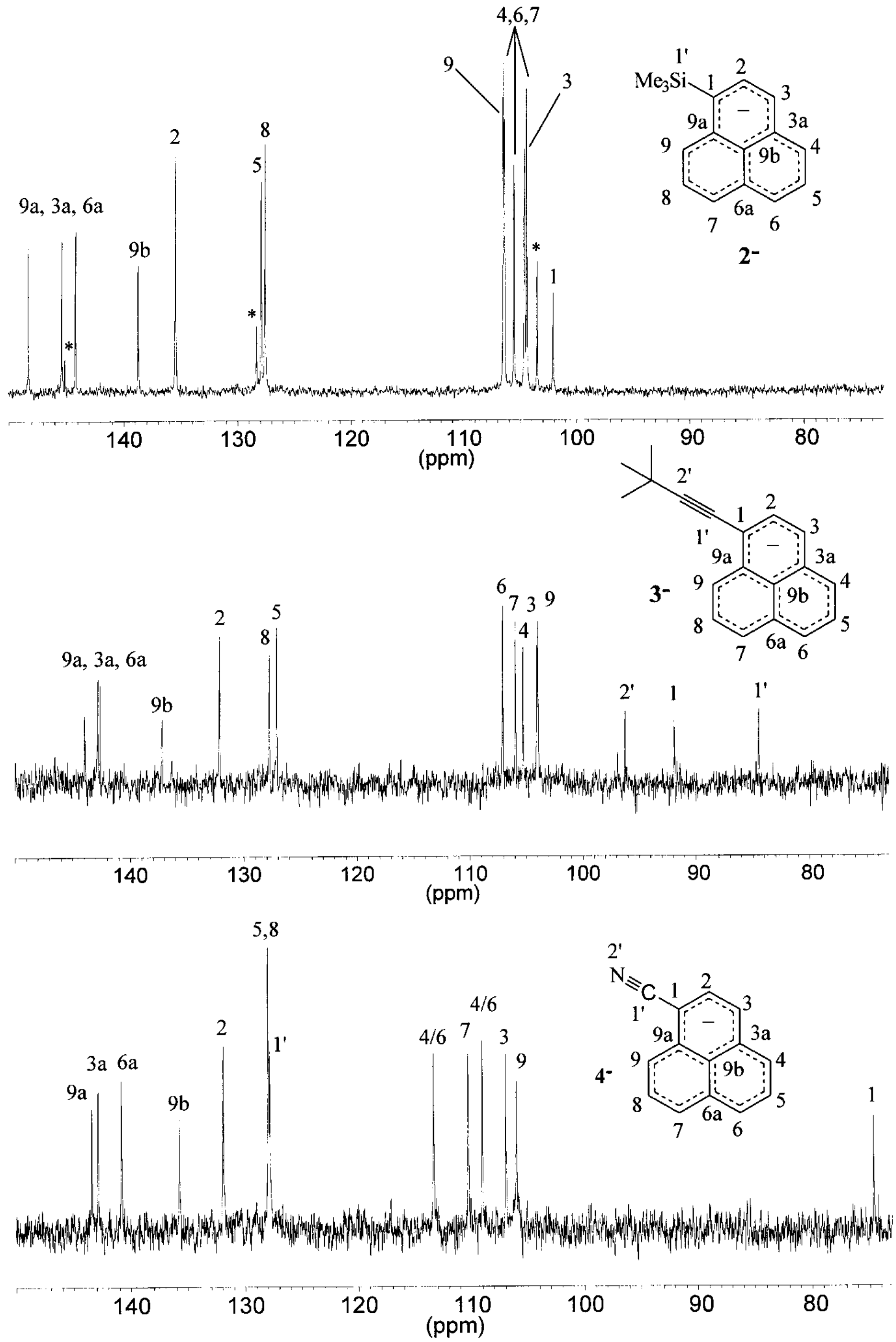


Figure 3. 75 MHz ^{13}C NMR spectra of **2**$^-$, **3**$^-$ and **4**$^-$. * **1**$^-$

^{13}C NMR spectrum, the cyano carbon appears as a doublet with a ^3J coupling at 127.84 ppm. In the ^3J C–H HETCOR spectrum, correlations between C-3a, H-5, H-2; C-6a, H-5, H-8 and C-9a, H-8 are observed. C-9b is observed at a chemical shift similar to C-9b in other phenalenyl anions.

As indicated in Table 3, some of the assignments may have to be interchanged. The given assignments of these signals are based on the calculated charge densities and therefore have to be interpreted with care.

DISCUSSION

Semiempirical calculations of the charge distribution of **2**$^-$ show the highest charge density to be located at

Table 3. ^{1}H NMR and ^{13}C NMR chemical shifts of **2**$^{-}$, **3**$^{-}$ and **4**$^{-}$

H	**2**$^{-}$	**3**$^{-}$	**4**$^{-}$	C	**2**$^{-}$	**3**$^{-}$	**4**$^{-}$
				1	102.13	90.93	74.65
2	6.08	6.04	6.10	2	135.53	131.14	131.96
3	5.18	5.17	5.26	3	104.65	103.05	107.08
4	5.21[a]	5.34	5.65[a]	4	104.47[a]	104.39	109.13[a]
5	5.95	6.05	6.34	5	127.99	126.28	127.97
6	5.36[a]	5.49	6.00[a]	6	106.35[ab]	106.16	113.50[a]
7	5.36	5.47	5.91	7	105.60[b]	105.05	110.38
8	6.00	6.15	6.40	8	127.65	126.87	127.98
9	5.46	5.68	5.88	9	106.45	103.12	106.09
R	0.01	1.20		3a	145.45[c]	141.80[a]	142.89
				6a	144.25[c]	141.61[a]	140.77
				9a	148.38[c]	142.94[a]	143.29
				9b	138.77	136.24	135.79
				1′	−2.64	83.20	127.84
				2′		95.33	
				3′		31.69	

[a,b,c] These values may be interchanged.

position 1.[15] The second and third highest charge density are located at positions 3 and 9.[11]

In the case of **3**$^{-}$, semiempirical calculations predict a significant lowering of the charge density of position 1 compared with that of C-1 in the unsubstituted phenalenyl anion (−0.304).[14] The highest charge density of the phenalenyl moiety is located at position 3. The charge distribution at positions 3–9 of **3**$^{-}$ is similar to that of the 1-vinylphenalenyl anion and the 1-hydropyrenyl anion.[4]

In the calculated charge distribution of the cyanophenalenyl anion (**4**$^{-}$), a lowering of the charge in the phenalenyl moiety can be observed compared with the unsubstituted phenalenyl anion. The highest charge density in the phenalenyl moiety is located at position 3.

The relatively small upfield shift of 1 ppm (11 ppm in the corresponding naphthalene compounds),[16] observed on going from C-1 of the phenalenyl anion[11] to C-1 of the 1-(trimethylsilyl)phenalenyl anion (**2**$^{-}$), may be attributed to an accumulation of negative charge at position 1 of **2**$^{-}$. Positions 3–9 are shifted slightly downfield compared with the unsubstituted phenalenyl anion, confirming a slight shift of negative charge from the rest of the phenalenyl moiety to C-1. These findings are in accordance with the relative charge distribution predicted by semiempirical calculations.

An upfield shift of 12.4 ppm for C-1 is observed on going from the phenalenyl anion to **3**$^{-}$, which is significantly larger than the 6 ppm upfield shift observed for the same substitution on neutral naphthalene.[17,18] This suggests accumulation of more charge at C-1 of **3**$^{-}$ than on the same position in 1-(3,3-dimethyl-1-butynyl)-naphthalene. The tertiary positions 3–9 of **3**$^{-}$ are shifted slightly downfield relative to the same positions in **1**$^{-}$, which suggests a slight withdrawal of negative charge from these positions. The chemical shift of the β-carbon atom in 1-(3,3-dimethyl-1-butynyl)naphthalene is 103.4 ppm.[18] Substituting the naphthyl for an anionic phenalenyl substituent causes an upfield shift of 8.1 ppm for this β-carbon atom, which suggests the accumulation of a small amount of charge at this position. These facts combined imply a shift of electron density from positions 3–9 to C-1 and C-2′. The exact distribution of the extra charge on C-1 and C-2′ cannot be ascertained on the basis of the current data.

Carbon atoms with a *peri* acetylenic substituent are shifted upfield by approximately 1.7 ppm.[18] Therefore, a lower actual charge density is assumed at C-9 of **3**$^{-}$ than is suggested by its chemical shift. The highest charge density on the tertiary positions in **3**$^{-}$ is therefore assumed to be located at position 3.

On going from C-1 of the phenalenyl anion to C-1 of **4**$^{-}$, an upfield shift of 28.65 ppm is observed, which is significantly larger than the 17.1 ppm[16] upfield shift observed for the same substitution on C-1 of naphthalene. The tertiary carbon atoms of **4**$^{-}$ are also shifted downfield compared to the tertiary positions of the phenalenyl anion (**1**$^{-}$), indicating that charge has moved from these positions to C-1, the nitrogen atom or, more likely, both of these atoms. In this case, the average downfield shift of C-3–C-9 and the upfield shift of C-1 are larger than in **3**$^{-}$. This indicates that more charge has shifted from the phenalenyl moiety to positions 1 and 2′ of **4**$^{-}$ than to the corresponding positions in **3**$^{-}$.

In the case of 1-cyanonaphthalene, the carbon atom *peri* with respect to the cyano substituent is shifted upfield by 2.4 ppm relative to unsubstituted naphthalene. This suggests that, although C-9 in **4**$^{-}$ is the tertiary position at the highest field, position 3 bears slightly more charge.

NMR spectroscopy and semiempirical calculations show a shift of negative charge from positions 3–9 to C-1 in **2**$^{-}$. Many examples of stabilization of negative charge by silyl substituents have been reported.[15,19] The nature of this stabilization has been attributed to (p–d)π bonding, although the inclusion of d-functions on silicon had little effect on the proton affinity of the anions in high-level *ab initio* calculations.[15] A second rationalization of the stabilization of negative charge by silicon suggested by different kinds of calculations is a hyperconjugative interaction between anion and trimethylsilyl group.[19,20] As a consequence of this, higher electron densities at the three methyl groups are expected. However, the chemical shift of the methyl carbons in tetramethylsilane, 1-(trimethylsilyl)naphthalene and **2**$^{-}$ do not differ very much, suggesting no significant extra electron density at these atoms and thus that hyperconjugation only plays a minor role in the interaction of the trimethylsilyl substituent with the π-electrons of **2**$^{-}$. If conjugative interactions are indeed less important in this effect, another rationalization of the observed polarization of the charge distribution may arise from the positive charge on silicon. This charge is induced by the more electronegative carbon atoms and results in an electrostatic perturbation of the adjacent π-electron cloud.[16]

The ability of the trimethylsilyl group to attract negative charge to the adjacent carbon atom is illustrated by the observation that in 1-methyl-4-(trimethylsilyl)-naphthalene the substituted ring is reduced, whereas reduction of 1-methylnaphthalene occurs in the unsubstituted ring.[10] The TMS substituent in the 1-methyl-4-(trimethylsilyl)naphthalene dianion, draws negative charge to the substituted ring, causing protonation and thus reduction to occur in this ring. A second illustration of the attraction of charge by the trimethylsilyl group is reaction of the trimethylsilylcyclopentadienyl anion with dimethyldichlorosilane, which, despite of steric hindrance, only occurs at C-1.[21]

According to NMR spectroscopy, the acetylenic substituent has little effect on the charge distribution in the anion. The 8.1 ppm upfield shift of the β-acetylenic carbon on going from 1-(3,3-dimethylbutynyl)naphthalene to **3**$^-$ is significantly less than the 23.3 ppm upfield shift of the β-vinylic carbon on going from 1-vinylnaphthalene[22] to the 1-vinylphenalenyl anion.[4] This indicates that much less negative charge is located in the triple bond of **3**$^-$ than in the double bond of the 1-vinylphenalenyl anion. This is in accordance with the slight perturbation of the charge distribution in the rest of the phenalenyl moiety of **3**$^-$. These findings are not in accordance with the results of the semiempirical calculations, which predict a high negative charge at the β-carbon atom of the triple bond. In the case of **3**$^-$, a large HOMO coefficient is calculated at C-1. This may suggest that the π-electrons compensate for a perturbation of the underlying σ-framework as observed with the aid of NMR spectroscopy in the case of the substituted naphthalenes. However, it is uncertain if the charge density of C-1 of **3**$^-$ is correctly predicted by the calculations. A more precise estimation of the charge density at C-1 is not possible with the current data.

The cyano substituent clearly has a larger influence on the charge distribution of the phenalenyl anion than the acetylene substituent. With the aid of NMR spectroscopy, a shift of negative charge is observed from the phenalenyl moiety to C-1 and possibly to the nitrogen atom. Abbotto *et al.*[23] concluded on the basis of a ^{13}C NMR study of a wide variety of α-substituted acetonitrile and phenylacetonitrile anions that the cyano group has a mesomeric electron demand about equal to that of the phenyl substituent. This implies that only a small amount of charge is drawn to the nitrogen atom and most of the charge is localized at C-1. In contrast to what is predicted by the calculations, the charge on C-1 of **4**$^-$ may be equal to or even higher than that on the tertiary positions in the anion. The shift of charge will be mainly from the tertiary positions 3–9 to C-1 and only slightly to the nitrogen atom. The exact distribution of charge between C-1 and the nitrogen atom could not be determined. The localization of negative charge next to the cyano substituent may be due to several factors. First, it may be due to an electrostatic effect of the CN substituent, similar to that observed in the case of the 1-(trimethylsilyl)phenalenyl anion. Second, a compensation by the π-electrons for the polarization in the σ-electron skeleton is possible. Third, stabilization of negative charge by a strong π-interaction with the cyano carbon atom, resulting in a high double bond character between C-1 and the CN group, as suggested by Abbotto *et al.*,[23] is possible. The exact mechanism of the polarization of negative charge by the cyano substituent is uncertain. Most likely it is a combination of the factors mentioned above.

EXPERIMENTAL

1*H*-Phenalene (**1**) and 2,3-dihydro-1*H*-phenalen-1-one (**5**) were prepared according to the procedure of Hempenius *et al.*[11] *n*-Butyllithium (1.6 M in hexane) was purchased from Janssen Chimica (Beese, Belgium). Trimethylsilyl chloride, *tert*-butylacetylene, diethylaluminum cyanide (1.0 M in toluene) and methyllithium (1.0 M in diethyl ether) were obtained from Aldrich. 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 NMR samples of the anions were prepared in a glove-bag under an atmosphere of argon. The 300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR, H–H COSY, NOE difference and ^{13}C–^{1}H correlated spectra were recorded on a Bruker WM-300 spectrometer. The 200 MHz ^{1}H NMR spectra were recorded on a Jeol JNM-FX-200 spectrometer. All chemical shifts (δ) of the neutral compounds are given in ppm relative to tetramethylsilane (TMS); the chemical shifts of the ^{1}H 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 hertz. Observed NOE effects from NOE difference experiments are printed as NOE: irradiated proton (observed correlation proton).

*1-TMS-1H-phenalene (**2**).* To a solution of **1**$^-$ in THF, prepared from 429 mg (2.36 mmol) of 2,3-dihydro-1-hydroxy-1*H*-phenalene according to the method of Hempenius *et al.*,[24] 327 µl (2.60 mmol) of trimethylsilyl chloride were added at −15 °C. The solution turned yellow within 15 min. Addition of water and diethyl ether, extraction, drying of the organic layer over magnesium sulfate, filtration and concentration under reduced pressure resulted in 454 mg (1.67 mmol, 70.7%) of 1-trimethylsilyl-1*H*-phenalene (**2**) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): −0.02 (9H, s, 1-TMS), 3.64 (1H, dd, $J = 1.6$, 6.3 Hz, H-1), 6.10 (1H, dd, $J = 6.3$, 9.4 Hz, H-2), 6.49 (1H, dd, $J = 1.6$, 9.4 Hz, H-3), 6.87 (1H, d, $J = 7.0$ Hz, 4-H), 6.93 (1H, d, $J = 7.0$ Hz, 9-H), 7.17–7.32 (2H, m, H-5 + H-8), 7.40–7.47 (2H, m, H-6 + H-7).

*Preparation of the 1-TMS-phenalenyl anion (**2**$^-$) in an NMR tube.* In a glove-bag under an atmosphere of dry argon, a solution of **2** (54.8 mg, 0.23 mmol) in a 1:1 mixture of THF-d_8 and diglyme-d_{14} (total volume 1 ml) was transferred to an NMR tube. With a long needle, the solution was purged with dry argon. After this, the solution was cooled to −130 °C in a hexane bath. A 1.0 M solution (generated by addition of 2.0 ml of n-butyllithium to a solution of 418 μl of diisopropylamine in 1.2 ml of THF) of lithium diisopropylamide (0.22 ml, 0.22 mmol) in dry diethyl ether was added by means of a syringe. The NMR tube was connected to a vacuum line in the glove-bag, submitted to three freeze–pump–thaw cycles, sealed under vacuum and separated from the vacuum line. In this way, a moisture- and oxygen-free sample was prepared. The colour changed from yellow to deep orange. ^{1}H NMR (300 MHz, THF-d_8, diglyme-d_{14}), δ (ppm): 0.01 (9H, s, 1-TMS), 5.18 (1H, d, $J = 7.9$ Hz, H-3), 5.21 (1H, d, $J = 7.7$ Hz, H-4), 5.36 (2H, d, $J = 7.7$ Hz, H-6 + H-7), 5.46 (1H, d, $J = 7.8$ Hz, H-9), 5.95 (1H, t, $J = 7.7$ Hz, H-5), 6.00 (1H, dd, $J = 7.7$, 7.8 Hz, H-8), 6.08 (1H, d, $J = 7.9$ Hz, H-2).

*2,3-Dihydro-1-hydroxy-1-(3,3-dimethyl-1-butynyl)-1H-phenalene (**6**).* To a solution of 420 mg (4.12 mmol) of *tert*-butylacetylene in 20 ml of THF, 2.19 ml (3.50 mmol) of *n*-butyllithium were added at −50 °C. After the addition, the temperature was raised to 0 °C and stirring was continued for 15 min. Subsequently, 500 mg (2.75 mmol) of 2,3-dihydro-1*H*-phenalen-1-one (**5**) in 8 ml of THF were added to the reaction mixture, resulting in a black solution. The temperature was raised to room temperature and the mixture was stirred for 1 h when TLC (CH_2Cl_2) indicated completion of the reaction. Addition of CH_2Cl_2 and water, washing the organic layer with water until neutral, drying over magnesium sulfate and column chromatography (50% CH_2Cl_2–hexanes) resulted in the isolation of 590 mg (2.08 mmol, 77%) of 2,3-dihydro-1-hydroxy-1-(3,3-dimethyl-1-butynyl)-1*H*-phenalene (**6**). ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.24 (9H, s, *t*Bu), 2.32 (2H, m, 2-CH_2), 3.13 (1H, dt, $J = 5.2$, 16.4 Hz, H-3a), 3.37 (1H, ddd, $J = 5.1$, 9.8, 16.4 Hz, H-3b), 7.28 (1H, d, $J = 7.2$ Hz, arom. H), 7.39 (1H, dd, $J = 7.2$, 8.2 Hz, arom. H), 7.48 (1H, dd, $J = 6.7$, 8.2 Hz, arom H), 7.68 (1H, d, $J = 8.2$ Hz, arom. H), 7.78 (1H, d, $J = 8.2$ Hz, arom. H), 7.94 (1H, d, $J = 6.7$ Hz, arom. H).

*Preparation of the 1-(3,3-dimethyl-1-butynyl)phenalenyl anion (**3**$^-$) in an NMR tube.* A mixture of 190 mg (0.72 mmol) of alcohol **6** and a catalytic amount of *p*-toluenesulfonic acid in 15 ml of toluene were refluxed for 1 h when TLC indicated completion of the reaction. Cooling and addition of hexanes caused the sulfonic acid to crystallize. Filtration over Hyflo and column chromatography resulted in the isolation of a fraction of pure **3**. A 50 mg amount of **3** was quickly converted into an anion according to the method as described for **2**$^-$, this time using a 1.0 M solution of methyllithium as the base. ^{1}H NMR (300 MHz, THF-d_8, diglyme-d_{14}), δ (ppm): 1.20 (9H, s, *t*Bu), 5.17 (H, d, $J = 7.8$ Hz, H-3), 5.34 (H, d, $J = 7.1$ Hz, H-4), 5.47 (H, d, $J = 7.7$ Hz, H-7), 5.49 (H, d, $J = 8.0$ Hz, H-6), 5.68 (H, d, $J = 7.4$ Hz, H-9), 6.04 (H, d, $J = 7.8$ Hz, H-2), 6.05 (1H, dd, $J = 7.1$, 8.0 Hz, H-5), 6.15 (H, dd, $J = 7.4$, 7.7 Hz, H-8).

*Preparation of the 1-cyanophenalenyl anion (**4**$^-$) in an NMR tube.* To a solution of 300 mg (1.65 mmol) of 2,3-dihydro-1*H*-phenalen-1-one (**5**) in 30 ml of dry toluene, 1.65 ml (1.65 mmol) of a 1.0 M solution of Et_2AlCN in toluene was added at −25 °C. After stirring at −25 °C for 4 h, the reaction mixture was added to a solution of 30 ml of dry methanol and 20 ml of concentrated HCl at −70 °C. After stirring for 1 h the reaction mixture was poured into a mixture of ice–water and HCl. Extraction with CH_2Cl_2 and washing with water until neutral resulted in the crude product, which was purified by means of column chromatography. Elution was started with CH_2Cl_2. After all the phenalenone had been isolated, elution was continued with 2% CH_2Cl_2–hexanes, which resulted in the isolation of a small amount of highly unstable cyanohydrin **7**, which was immediately transformed into the phenalene derivative **4** according to the procedure described for the conversion of **6** to **3**. This phenalene derivative was immediately transformed into its anion (**4**$^-$) according to the procedure described above. ^{1}H NMR (300 MHz, THF-d_8, diglyme-d_{14}), δ (ppm): 5.26 (1H, d, $J = 8.6$ Hz, H-3), 5.65 (1H, d, $J = 7.6$ Hz, H-4), 5.88 (1H, d, $J = 7.6$ Hz, H-9), 5.91 (1H, d, $J = 7.6$ Hz, H-7), 6.00 (1H, d, $J = 8.1$ Hz, H-6), 6.10 (1H, d, $J = 8.6$ Hz, H-2), 6.34 (1H, dd, $J = 7.6$, 8.1 Hz, H-5), 6.40 (1H, t, $J = 7.6$ Hz, H-8).

Acknowledgements

This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

REFERENCES

1. P. W. Rabideau and Z. Marcinow, *Org. React. (NY)* **42**, 1–334 (1992).
2. R. G. Harvey, Polycyclic Aromatic Hydrocarbons. Cambridge Monographs on Cancer Research, Cambridge University Press, Cambridge (1991).
3. J. T. M. van Dijk, A. Hartwijk, A. C. Bleeker, J. Lugtenburg and J. Cornelisse, *J. Org. Chem.* **61**, 1136–1139 (1996).

4. M. A. Hempenius, C. Erkelens, P. P. J. Mulder, H. Zuilhof, W. Heinen, J. Lugtenburg and J. Cornelisse, *J. Org. Chem.* **58**, 3076–3084 (1993).
5. K. Müllen, *Angew. Chem., Int. Ed. Engl.* **26**, 204–217 (1987).
6. B. C. Becker, W. Huber, C. Schnieders and K. Müllen, *Chem. Ber.* **116**, 1573–1594 (1983).
7. R. G. Harvey, *Synthesis* 161–172 (1970).
8. H. E. Zimmerman and P. A. Wang, *J. Am. Chem. Soc.* **115**, 2205–2216 (1993).
9. (a) P. W. Rabideau and G. L. Karrick, *Tetrahedron Lett.* **28**, 2481–2484 (1987); (b) P. W. Rabideau and Z. Marcinow, *Tetrahedron Lett.* **29**, 3761–3764 (1988).
10. Z. Marcinow, D. K. Clawson and P. W. Rabideau, *Tetrahedron* **45**, 5441–5448 (1989).
11. M. A. Hempenius, W. Heinen, P. P. J. Mulder, C. Erkelens, H. Zuilhof, J. Lugtenburg and J. Cornelisse, *J. Phys. Org. Chem.* **7**, 296–302 (1994).
12. A. G. Schultz and M. Macielag, *J. Org. Chem.* **51**, 4983–4987 (1986).
13. I. I. Bilkis, T. A. Vaganova, E. V. Panteleeva, G. E. Salnikov, A. P. Tananakin, V. I. Mamatyuk and V. D. Shteingarts, *J. Phys. Org. Chem.* **7**, 153–161 (1994).
14. M. A. Hempenius, Thesis, Leiden University (1992).
15. A. R. Bassindale and P. G. Taylor, The Chemistry of Organic Silicon Compounds, edited by S. Patai and Z. Rappoport, Chapt 14, pp. 893–963. Wiley, New York (1989), and references cited therein.
16. P. E. Hansen, *Org. Magn. Reson.* **12**, 109–142 (1979).
17. H.-O. Kalinowski, S. Berger and S. Braun, ^{13}C-NMR-Spektroskopie. Georg Thieme, Stuttgart (1984).
18. P. A. A. Klusener, J. C. Hanekamp, L. Brandsma and P. von Ragué Schleyer, *J. Org. Chem.* **55**, 1311–1321 (1990).
19. E. A. Brinkman, S. Berger and J. I. Brauman, *J. Am. Chem. Soc.* **116**, 8304–8310 (1994).
20. D. M. Wetzel and J. I. Brauman, *J. Am. Chem. Soc.* **110**, 8333–8336 (1988).
21. T. J. Barton, G. T. Burns, E. V. Arnold and J. Clardy, *Tetrahedron Lett.* **22**, 7–10 (1981).
22. G. T. Crisp and S. Papadopoulos, *Aust. J. Chem.* **41**, 1711–1715 (1988).
23. A. Abbotto, S. Bradamante and G. A. Pagani, *J. Org. Chem.* **58**, 449–455 (1993).
24. M. A. Hempenius, J. Lugtenburg and J. Cornelisse, *Recl. Trav. Chim. Pays-Bas* **109**, 403–409 (1990).