Electronic and Ring Current Structure of Phenalenyl Ions

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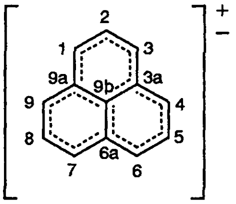
Based on ^1H, ^7Li, and ^{13}C NMR chemical shifts of phenalenyl ions, it is argued that the observed diamagnetism of the systems is due to the diatropic benzene and naphthalene subcircuits. MNDO and graph theoretical calculations support this observation.

Odd-alternant polycyclic hydrocarbons, where all π-electrons can be found in closed circuits, are rather unique and have been of special interest theoretically for many years.[1] The phenalenyl or perinaphthenyl system constitutes a basic model for such systems. It readily forms a cation, a radical, and an anion of considerable stability in comparison with the corresponding triphenylmethyl species. Like all odd-alternant systems of this type, the phenalenyl system has a non-bonding orbital (NBMO), which accordingly will be unoccupied, singly occupied, or doubly occupied for these three species. The charges or spin density will be located on the six equivalent CH positions since the LCAO coefficients are non-zero only at these positions. Recent all-valence-electron SCF (MNDO) calculations did show that there exists a truly non-bonding orbital based on the finding that bond lengths and bond orders are equal for the three species.[2] Hence, the Hückel $4n + 2$ rule is argued to have no general applicability in the total phenalenyl system in this case.

In spite of the mass of theoretical work, the electronic structure of the phenalenyl systems remains unclear. It has recently been stated that the phenalenyl anion is a 'non-aromatic, tricyclic anion system'[3] or 'is best represented as having a 12 π-electron periphery with the charge on the central carbon atom'.[4] Using Hückel MO resonance energy as an aromatic criterion one notices that the phenalenyl ions have a large resonance energy per atom (REPA) of 0.073.[5] Randic also classified, using the conjugated circuits approach, the phenalenyl ions to be mainly aromatic.[6]

Surprisingly, based on the stability of the ionic forms, the spectroscopic support for the quoted structures has been meagre. The proton NMR data of both cation and anion were previously reported, but the data were not interpreted in terms of delocalization or ring currents.[7] A structural position of special interest would be the central carbon atom, but carbon shift data have not been reported so far. The scatter in MO calculated data could indirectly be a reason why almost no experimental data have been reported in connection with the theoretical efforts. The calculated magnetic properties of non-benzenoid compounds are very sensitive to the level of sophistication of the MO method, a condition which has been a burden to the whole aromaticity or ring-current concept.[8]

In this study a complete NMR investigation of the phenalenyl cation and anion is reported, including the NMR shift of the lithium counterion. The concept of circuit current as introduced by Aihara[8] will be used as a comparison for NMR aromaticity criterion. In this approach, the bond current in the phenalenyl system is treated as a superposition of the individual currents in all possible π-bond circuits in the polycycle.[8] MNDO calculated energies for species with various lithium positions are also used as an aid in the understanding of the observed data.



Scheme 1.

Results and Discussion

The proton chemical shifts of the phenalenyl anion and cation are given in Table 1. The reported values are in good agreement with earlier published data for the two ions.[7] Moreover, there are no significant shift changes in the proton spectra caused by solvent changes or by changing the alkali counter-ion. As expected most of the charge is located on the six equivalent positions, but the 2,5,8 positions are also significantly shielded ($\Delta\delta = -2.5$ ppm) when the system is reduced from a cation to an anion. A comparison with the dication of the (3,3,3) cyclazine is very helpful in the understanding of these shift changes in terms of charge distribution and ring-current effects. The NMR spectrum of the *N*-bridged annulene dication shows the effect of the central carbon being replaced by a nitrogen atom and the addition of one positive charge to the system.[9] Such a comparison shows that the alpha and beta positions in the cyclazine dication are both shifted downfield by *ca.* 1.2 ppm, relative to the equivalent positions in the phenalenyl cation. This provides a total downfield shift of 10.8 ppm per electron which corresponds well with the widely accepted shift charge correlation factor for protons. The comparison strongly supports a molecular structure for the phenalenyl cation where the periphery contains 11 π-electrons. The phenalenyl cation is also of comparable diatropicity to the 10-π *N*-bridged cyclazine. The observed shielding of the 2,5,8-positions by the two-electron reduction of the phenalene system is approximately twice ($\Delta\delta = -2.5$ ppm) that noticed for the same positions by changing from the diatropic cyclazine dication to the phenalene cation. A charge effect is, therefore, a likely factor. MNDO calculations also support this view as the charge difference of the H-2 proton is 0.1 electron on changing from the phenalenyl cation to the anion. This carbon to proton charge transfer could also explain why the total proton spectrum of phenalenyl lithium appears at somewhat higher field (*ca.* 1 ppm) than expected. But proton shift changes of this magnitude are too small to be interpreted safely. Regardless, the observation that both proton signals of the negatively charged phenalenyl system are displaced by more than 2 ppm *low-field* relative to the *neutral* paratropic

Table 1. ^{1}H and ^{13}C NMR chemical shifts of phenalenyl ions ($Ph^{-}M^{+}/Ph^{+}M^{-}$).

M	Solvent	δ C-1	 C-2	 C-3a	 C-9b
DSO_4^-	D_2SO_4	155.5[a] (9.2)[b]	133.7 (8.4)	132.9	123.7
$ClSO_3^-$	$ClSO_3H$	155.3 (9.3)	133.6 (8.5)	132.7	123.5
FSO_3^-	FSO_3D	155.5 (9.3)	133.6 (8.5)	133.1	123.8
Li^+	THF[c]	103.4 (5.1)	128.0 (5.9)	145.0	139.6
Li^+	DEE[c]	103.9 (5.4)	129.1 (6.1)	143.9	138.4
Li^+	DEE–solid	103.8	128.3	142.2	138.1
Na^+	THF	103.3 (5.3)	128.4 (6.0)	144.5	138.8
K^+	THF	103.7 (5.3)	128.8 (6.0)	144.7	138.8
$\Delta\delta(Ph^{-}_{av} - Ph^{+}_{av})$[d]		−51.8 (−4.0)	−5.0 (−2.5)	11.6	15.2
(β,ω',ω'')[e]		−0.30	−0.05	−0.04	0.16

[a] ^{13}C NMR chemical shifts relative to internal (anion) or external TMS. Carbon assignments were based on selective decoupling and/or relative intensities. [b] ^{1}H NMR chemical shifts relative to internal TMS except for the cation solutions where external referencing was used. [c] THF (tetrahydrofuran): δ (^{7}Li) −2.0 ppm, DEE (diethyl ether): δ (^{7}Li) −1.7 ppm with LiCl as external reference. [d] Average ^{13}C NMR chemical shift change by two-electron reduction (solid-state data not included). [e] π-Charge differences between Ph^- and Ph^+, using a self-consistent Hückel method.[8]

(3,3,3)cyclazine and that the phenalenyl cation and anion proton spectra are mirror images of each other centred on δ 7.2 strongly suggests that the anion should also be classified as diatropic/aromatic.

As can be deduced from the ^{13}C NMR chemical shifts listed in Table 1 most of the excessive charge is located on the six equivalent positions while, in contrast with the proton data, the 2,5, and 8 positions are only to a minor extent affected by a two-electron reduction. Interestingly, the central C-13 position is deshielded in the anion but this condition and the overall pattern are, as regards sign and magnitude, in reasonble agreement with the charge densities obtained by an iterative β,ω',ω'' method (Table 1). This method is claimed to be the most suitable for computing magnetic and electronic properties in non-benzenoid structures.[8,10] The observation that the central carbon is significantly *deshielded* in the anion relative to the cation excludes the possibilities that the phenalenyl ions should be treated as 12 π peripheral systems with the central carbon charged.[4]

In contrast with proton data there is a small but significant ion pairing effect in the carbon spectrum observed on changing the solvent or the counter-ion. Only minor effects are expected due to the D_{3h} symmetry of the system. An unsymmetrical position of the cation relative to the phenalenyl anion might cause a redistribution of charge but that will be unobservable on the whole since the shifts for the peripheral positions are averaged over all equivalent positions. However, by changing to contact-ion-pair conditions *i.e.* using less polar ethers or larger counter-ions, one could observe that the shift variance decreases, the charge is more evenly distributed over the 13 carbon skeleton. The C-9b position, but also the C-3a, -6a, -9a positions, gain some charge from the remaining ring carbons as reflected by a total upfield shift of 4.8 ppm of the non-proton-bearing carbons changing to a contact-ion-pair condition. Such a cation-induced polarization of excessive charge can be foreseen if the counter-ion is positioned over the central carbon atom.

A most interesting fact deduced from the carbon data is that the total induced carbon shifts per electron (K_C) is 139 ppm/e, *i.e.* only slightly smaller than the 'true' charge factor previously suggested by us. Hence, no major differences in anisotropy effects of the two ions such as ring currents are indicated although the information gathered from ^{1}H and ^{13}C shifts so far might indicate that the diatropicity is slightly reduced in the anion. O'Brien[11] did point out that there is a linear relationship between the average ^{13}C shifts, δ_{av}, and the average π-electron

$$\delta_{av} = -156.8\,\rho_{av} + 289.9 \qquad (1)$$

densities at carbon according to, equation (1). Using equation (1), the calculated value for the phenalenyl cation is given as 145.2 ppm [$\delta_{av}(\exp) = 142.6$] while for the anion a value of 121.1 ppm is obtained [$\delta_{av}(\exp) = 121.4$].

An MNDO study of phenalenyl lithium including lithium parametrization shows that the most favourable cation position is above one of the rings, *i.e.* an η^6 arrangement. This structure is 8.4 kcal mol^{-1} more stable than the η^3-edge lithiated arrangement ($\Delta H_f = 34.5$ kcal mol^{-1}). However, MNDO parametrization overestimates the C–Li bond energies and the suggested arrangement might be valid only under solid-state or extreme contact-ion-pair conditions. Solution data are expected to be better predicted if the counter-ion is handled as a sparkle excluding overlapping C–Li orbitals. In this case a slightly more stable structure is the arrangement in which the lithium cation is positioned over the central C-9b carbon although the energy surface is quite shallow.

To test the latter hypothesis, a CP/MAS NMR spectrum of the crystalline state was obtained. From the red–orange phenalenyl lithium–diethylether complex only one set of signals was observed with almost identical shift values as those found in solution (Table 1, Figure 1). No specific line-broadening could be observed owing to dipolar coupling to the quadrupolar ^{7}Li nucleus. Together with the MNDO data and the shift differences induced by ion-pairing, this strongly suggests a symmetrical ionic arrangement with the lithium cation above the C-9b position.

The possibility of using CP/MAS ^{13}C NMR to study solid organolithium compounds, such as fluorenyl-lithium–diethyl ether (DEE) complex, has recently been suggested by us. By changing to the solid state it is possible, at room temperature,

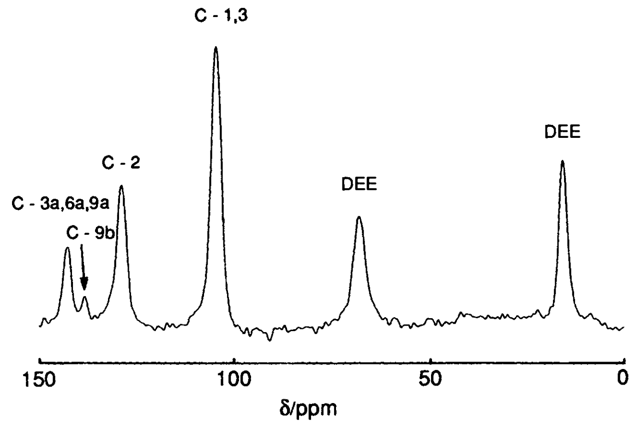
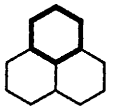
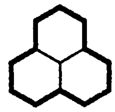


Figure 1. ^{13}C CP/MAS NMR spectrum of diethyl ether complexed phenalenyl lithium. Red–orange crystals obtained from a hexane solution. A pulse repetition rate of 2.5 s and a contact time of 1 ms was used at a frequency of 25.178 MHz (Bruker MSL-100).

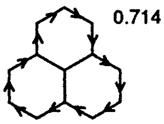
Table 2. Ring currents and susceptibilities of phenalenyl ions.

			
I_0[a]	0.350	0.218	−0.072
χ_0[b]	0.350	0.437	−0.217

London susceptibility: 2.141 χ_0

Resonance energy: 0:301 β

Bond current (I_0):



[a] I_0 = ring current of benzene. [b] χ_0 = magnetic susceptibility of benzene.

to confirm the existence of an unsymmetrical structure.[12] Using other complexation agents, a symmetrical structure was revealed.

Due to the possible involvement of ring currents from substructures, it may be of interest to see whether a graph theoretical analysis of the phenalenyl ions could increase our understanding in terms of resonance energy, ring currents, and magnetic susceptibility. We have adopted the formalism of Aihara[8] to obtain a theoretical estimation of these effects and the results are summarized in Table 2. Data are identical for both anion and cation as expected. The resonance energy of 0.301 β suggests that the ions are stable aromatic entities comparable to other peripheral tricyclic 14π systems. However, in contradiction to these peripheral systems, the main contribution to the magnetic effect stems from benzene and naphthalene sub-units having circuit currents of 0.350 I_0 and 0.218 I_0, respectively. The peripheral circuit only affords a minor paramagnetic contribution to the structure. So the diatropic bond current, 0.714 as compared with the benzene value of 1.000, originates entirely from the smaller sub-circuits. A most interesting NMR observation in this context is the very minor downfield shift noted for the ^7Li counter-ion using contact-ion-pair conditions. A shift of 1.8 ppm upfield from the LiCl signal indicates only minor ring current anisotropy effects on the lithium ion similar to those found in non-aromatic ion pairs. Lithium shifts in systems having diatropic peripheral carbanions are normally found in the range 6–8 ppm downfield of LiCl.[13] This shift value strengthens our suggestion that the peripheral ring current is unimportant. The most attractive model based on the data presented herein is a solution structure where the counterion has a symmetrical position above the central position and that the observed diatropicity stems from the remaining benzene/naphthalene subunits.

Experimental

General.—Phenalene was prepared as previously described[14] by reduction of commercially available phenalenone (Aldrich) using di-isobutylaluminium hydride (DIBAL-H). The anion solution was generated by dissolving the light-yellow crystals of phenalene (54 mg) in dry [$^2H_8$]THF (1 cm^3). BuLi (6.5 mol dm^{-3} in hexane; 0.65 cm^3) was added under an argon atmosphere whereby a deep-red solution was formed. The anion solution was then transferred to a 5 mm NMR tube using a syringe.

MNDO calculations.—The MNDO calculations were performed using the MNDOC[15] or MOPAC[16] program package. The lithium parameters of Thiel and Clark available in MNDOC were used. It has been shown that these parameters closely reproduce the MNDO results obtained with an unpublished, refined set of parameters used by Schleyer's group.[17]

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