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PROBING THE NATURE OF POLYCYCLIC CONJUGATED DIANIONS: FROM CARBOCYCLIC TO HETEROCYCLIC DIANIONS: NMR STUDIES, π-DELOCALIZATION AND ELECTRONIC STRUCTURE

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CONTENTS

1. INTRODUCTION

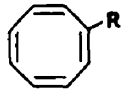
1.1. *General*

The carbanions represent one of the most important groups of reactive intermediates known in organic chemistry.[1-3] A group of major importance in the carbanion chemistry consists of π-conjugated anions known since Thiele's study of the cyclopentadienyl anion (**1**$^-$) in 1900.[4] Constant

efforts were made throughout the years[5-7] to elucidate the structure and nature of these intriguing and yet most important species. Monoanions, radical anions as well as dianions and even polyanions of π-conjugated systems were prepared and characterized by different spectroscopic methods.[2,3,7,8] Katz's pioneering work on the reduction of cyclooctatetraene (**2**)[7a] represents a landmark in the chemistry of charged π-conjugated systems for several reasons. First, it demonstrated that such systems can serve as good model compounds for the clarification of the notion of aromaticity[9] and it represents one of the most important successes of Hückel's rule.[10] Secondly, it was realized that doubly charged organic molecules can be relatively stable and easy to prepare. Recently, there has been a growing interest in the potential application of these multicharged systems in synthesis especially in the field of reductive alkylation.[11] The study of π-conjugated charged systems allows confrontation of theory and experiment and is therefore of interest to the spectroscopists as well as theoretical and synthetic chemists. Therefore, our discussion will concentrate mainly on π-conjugated polyanions of polycyclic systems.[12] We choose to focus mainly on the 'missing link' in the chemistry of doubly charged series, i.e. the polyheterocyclic $4n\pi$-electron dianions. The NMR characterization of these species and the comparison of their magnetic properties with those of the carbocyclic series is emphasized. In view of the numerous spectroscopic studies concerning carbocyclic dianions, the large number of commercially available polyheterocyclic compounds which can serve as starting materials, and the theoretical importance of $4n\pi$ systems, it is surprising that only recently such polyheterocyclic dianions were characterized by NMR techniques.[13,14] In this report, efforts will be made to clarify this finding through the establishment of the structure–stability relationships of $4n\pi$-polyheterocyclic dianions. Dianions obtained by the reduction of $[4n+2]\pi$ electron compounds have a $4n\pi$ array of electrons and can therefore serve as model compounds for antiaromatic species, thus enabling discussion of the notion of antiaromaticity. On these grounds the effect of the heteroatom on the main characteristics of these charged systems such as their paratropicity, charge delocalization and ion-pairing, seems interesting. The introduction of a heteroatom into the path of the electron delocalization of the charged system may increase the regioselectivity of their reactions (such as alkylation), and even change their chemistry. The preparation of charged systems of the same structure which differ only in the heteroatom, may enable an insight into the effect of the heteroatom on the charge delocalization pattern. These issues are discussed in Sections 3, 4 and 5 while in Section 6 several selected examples of the application of the charge alternation concept (see below) to π-conjugated doubly charged systems is demonstrated.

Before embarking on the description of these new families of charged systems, we shall discuss and review some general topics concerning the preparation and characterization of π-conjugated carbanions.

1 $^-$



2 a, R=H
b, R=OCH_3

1.2. *Methods of preparation of π-conjugated anions*

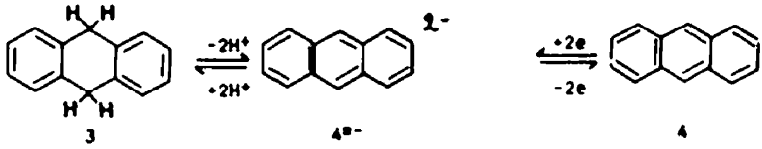
The two effective ways to prepare such negatively charged systems are deprotonation and electron transfer reactions. The electron transfer reaction can be carried out by alkali metal reduction or by electrochemical reduction techniques such as cyclic voltammetry (C.V.).[15,16] These are equilibria processes as shown in equation 1. Recently the analogous reverse process was accomplished in the NMR tube by the photochemical ejection of an electron from a dianion to form the radical anion (eq. 2).[17,18]

(eq. 1) $$A \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} A^{\cdot-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} A^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} A^{3\cdot-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} A^{4-} \qquad (1)$$

(eq. 2) $$A^{2-} \xrightarrow{h} A^{\cdot-} + e. \qquad (2)$$

The metal reduction of polycyclic systems for spectroscopic studies is usually carried out in ether solvents in an extended NMR tube or ESR cavity at low temperature (−78°C) using potassium mirror or sodium or lithium wire. It must be emphasized that accurate reaction rates are difficult to measure and are therefore difficult to compare. Nevertheless, it has recently been found that the application of ultrasonic bath facilitates and accelerates the reactions and can avoid side reactions.[18b]

Polycyclic dianions can also be prepared by deprotonation as demonstrated by the double deprotonation of 9,10-dihydroanthracene (3) to form the anthracene dianion[19] (4^{2-}) (eq. 3).



3 4^{2-} 4 (3)

The most commonly used bases are alkyllithium derivatives such as methyllithium or butyllithium. When polyanions are prepared, the addition of a complexing agent such as tetramethylethylenediamine (TMEDA) to the alkyllithium is required. One may also use the Lochmann reagent[20] which is a very strong base.

1.3. *Methods of study of π-conjugated anions*

The main methods used to study charged systems include reaction with electrophiles, electrochemical[15,16] and calorimetric[21] studies as well as different spectroscopic techniques such as UV-Visible spectroscopy,[22] electron spin resonance (ESR),[4d,23] NMR[7,8] and X-ray diffraction.[24,25]

The X-ray study is a powerful tool for the investigation of carbanions and yet difficult to obtain[26,27] due to the difficulties in obtaining suitable crystals of such reactive compounds. Recently, there has been a growing interest in the X-ray structure of charged ions but the major interest has been focused on the field of organolithium compounds and to date the number of X-ray structures of π-delocalized carbanions is rather limited.[26,27] Therefore, only a few X-ray structures of π-delocalized dianions have been reported most of which are due to the pioneering work of Stucky and coworkers.[26,27] They reported, for example, the X-ray structure of the salts of naphthalene dianion (5^{2-}),[26a] anthracene dianion (4^{2-})[26b] and of acenapathylene dianion (6^{2-}).[27a] Stucky has demonstrated that in these cases the lithium cations occupy opposite faces of the organic framework which is nearly planar. These structures, together with the structure of 9,9′-bifluorene dianion (7^{2-})[27b] were one of the corner-stones on which the ion-triplet model, introduced later by Streitwieser,[28] is based. These lithium salts are stabilized by complexing agents like *N,N,N′,N′*-tetramethylethylenediamine (TMEDA). For example, in $C_{10}H_8^{2-}$ $(Li^+\text{-TMEDA})_2$, each lithium cation is coordinated to two nitrogen atoms of the TMEDA and six carbons of one 6-membered ring moiety in the naphthalene molecule.[26a]

Early electrochemical studies were aimed mainly to evaluate thermodynamic parameters but recent progress in cyclic voltammetry (C.V.) techniques enable the study of the kinetics of electrode reactions.[15,16] Cyclic voltammetry can provide meaningful information concerning the electron affinity of neutral compounds by recording their half-wave potential ($E^0_{1/2}$). This parameter is a very important one as it reflects, amongst other things, the relative thermodynamic stability of the charged system as compared with its neutral precursor. It should be noted that one of the early successes of Hückel's theory was the correlation between the energies of Hückel's LUMOs with the first half-wave potential of polycyclic systems.[29] The power of electrochemical methods in the study of multistep one electron reductions and oxidation of polycyclic systems was demonstrated recently by Heinze[16] and others.[30] Evans and his coworkers have shown that, in certain cases, detailed cyclic voltammetry may enable detection of changes in structure and conformations in the course of electrochemical reactions.[31] Nevertheless, the structural information that one can get from electrochemical studies is by far less detailed than that obtained by NMR, for example.

Calorimetric measurements aimed at obtaining the heat of formation and other thermodynamic parameters of $4n\pi$ polycyclic dianions were accomplished only recently by Stevenson *et al.*[21] The importance of such a study is that it enables the estimation of the relative stability of the charged system which is the most direct criterion for aromaticity. It was found that in general the generation processes for the organic dianions given in eq. 4 and eq. 5 are much more exothermic for $(4n+2)\pi$

Table 1. Heats of generation of solid and solvated organic dianions, hydrocarbons and solid metal in Kcal/mol

Reaction	ΔH° for formation of A^{2-} [a]							
	A = AN	TE	PT	PY	PE	BPY	COT	[16]ANNULENE
$2Na_{(s)} + A_{(s)} \rightleftharpoons 2Na^+A^{2-}$	−26.1[b]	−25.1[b]	−34.5[b]	−47.7[b]	−36.4[b]	−20.3[b]	−80.5[b]	−105[c]
$2Na_{(s)} + A(THF) \rightleftharpoons A^{2-}, 2Na^+(THF)$	−40.3[d]	−37.8[d]	−40.3[d]	−40.2[d]	−46.1[d]	−44.5[d]	−90.2[e]	—

[a] Abbreviations: AN = anthracene, TE = tetracene, PT = pentacene, PY = pyrene, PE = perylene, BPY = benzo[a]-pyrene, COT = cyclooctatetraene.
[b] Data from ref. 21b.
[c] Data from ref. 21a.
[d] Data from ref. 21d.
[e] Data from ref. 21c.

electron dianions, thus reflecting their enhanced stability ascribed to the aromatic nature (Table 1).[21]

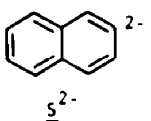
$$2Na_{(s)} + A_{(s)} \rightleftharpoons 2Na^+A^{2-} \tag{4}$$

$$2Na_{(s)} + A(THF) \rightleftharpoons A^{2-}, 2Na^+(THF). \tag{5}$$

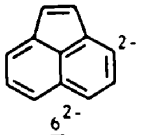
This result is expected according to Hückel's rule. The huge enthalpy of −177 Kcal/mol calculated for the hypothetical reaction, of transferring two electrons from the benzene dianion to the anti-aromatic (planar) cyclooctatetraene also corroborates this result.[21b] It was suggested that the aromatic character is not the only factor controlling the thermodynamic stabilities of these salts and that entropy considerations precludes the preparation of small organic dianions such as benzene and naphthalene dianions.[21d]

UV-Visible spectroscopy seems to be, at first sight, an attractive method for the study of π-conjugated anions. Although many of the early studies concerning ion-pairing in organic chemistry[22,32] were performed by UV-Visible spectroscopy, this technique gives only limited structural information. The large peak line width makes it difficult to assign the different bands of the spectra—a problem which may become even more serious when several species are present in the solution. Moreover, the very high extinction coefficients of these charged systems pose some technical problems.

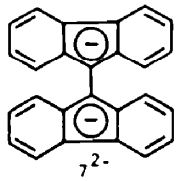
The first electron reduction of π-conjugated molecules affords a radical anion which can be characterized by ESR.[8d,23] The hyperfine proton splitting constant (A_H) can be used to estimate the local spin densities (McConnell's equation[33]) which in turn can be related to the square of the specific atomic orbital coefficient of the HOMO of the radical anion.[34] Therefore, one can use hyperfine proton couplings to determine the spin densities and the symmetry of the Singly Occupied Molecular Orbital (SOMO) of the paramagnetic system[35] and confront it with theoretical predictions. The application of ESR to the study of radical anions of π-conjugated systems is quite extensive[8c,d,17] and recently it has been shown that by using the ENDOR technique[36] in combination with classical ESR spectroscopy, one can characterize even highly charged systems, e.g. trianion radicals,[35c,d,e] quite satisfactorily—a subject which has been reviewed only very recently.[8d]



5^{2-}



6^{2-}



7^{2-}

2. NMR—THE METHOD OF CHOICE FOR THE INVESTIGATION OF ORGANIC ANIONS IN SOLUTION

2.1. *General*

NMR is the most popular method for the study of diamagnetic anions and for several good reasons. First, the combination of a multinuclear study (^1H, ^{13}C, ^{15}N, ^7Li, etc.) and 2D-NMR

techniques[37] enables a complete and unambiguous structure elucidation of the charged system. Second, from the carbon NMR parameters one can estimate the experimental charge densities.[38,39] Moreover, the proton chemical shifts in the NMR spectra can be related to the diatropicity and paratropicity of the system[8b,c,40] and hence can serve as a criterion for the assessment of their aromatic nature.[41] On the one hand, unlike the X-ray diffraction studies of solid state complexed structures, NMR enables the study of such reactive intermediates in solution and their ion-pair equilibria.[32,22] These equilibria were found to influence the chemistry of the charged system. Dynamic NMR[42] (DNMR) enables indentification of dynamic processes which are otherwise difficult to detect. On the other hand, calorimetric and electrochemical studies, which can be related to the thermodynamic stability of the charged systems, give very limited, if any, structural information. Therefore, NMR became the method of choice for the investigation of multicharged systems.

2.2. *Proton chemical shifts and anisotropic effects—a criterion for the aromatic character of the system*

The shielding constant (σ_{total}) is given by the combination of three different terms in the expression known as the Ramsey equation (eq. 6):[43a,b]

$$\sigma_{total} = \sigma_{dia} + \sigma_{para} + \sigma'. \tag{6}$$

The first term is the diamagnetic term (σ_{dia}) which is the result of electron shielding and is responsible for a diamagnetic shift (eq. 7) which increases as the electron density increases:[43d]

$$\sigma_{dia} = \frac{e^2}{3mC^2}\sum_i \langle r_i^{-1}\rangle. \tag{7}$$

$\langle r_i\rangle$ is the average distance of the ith electron from the observed nucleus and m, e are the mass and charge of an electron respectively. This term is the one which reflects the influence of electron density on the observed chemical shift.

The second term in the Ramsey equation is the paramagnetic term (σ_{para}) which is more complicated as shown by eq. 8:[43c]

$$\sigma_{para} = \frac{-e^2h^2}{2m^2C^2\Delta E}\langle r^{-3}\rangle_{2p}\sum_B Q_{AB}. \tag{8}$$

The main parameters which influence this term are the mean average excitation energy (ΔE), the dimensions of the $2p$ orbitals and the term reflecting changes in the bond order of the nucleus and adjacent atoms (Q_{AB}). From eq. 8 it can be seen that σ_{para} increases as ΔE decreases. The σ_{para} term is responsible for the down-field shift of the proton's chemical shift.[44a]

The third term of the Ramsey equation is σ' which reflects the influence of neighbouring atoms, molecular structure, solvent effects and is constituted of several factors. It was found that in aromatic systems the anisotropic effect attributed to the "ring current effect"[44b] is the most important one in σ'.

The ring current model, first proposed by Pauling,[45] was formulated quantitively to the proton chemical shifts by Pople only in 1956.[46] According to this model the benzene ring is looked upon as a conducting loop in which the π-electrons circulate perpendicularly to the direction of the external magnetic field B_0. A secondary magnetic field is being induced opposing the external one. The point dipole model approximates this property of the ring as a dipole moment (μ) placed in the center of the ring, the magnitude of which is given by:

$$\mu = I \cdot A = I \cdot \pi a^2 \tag{9}$$

when A is the area of the ring, a is its radius, and I is the current produced by the six electrons (eq. 10):

$$I = \frac{\mu_0}{4\pi} \cdot \frac{3e^2B_0}{2\pi m}. \tag{10}$$

μ_0 is the permeability of the free space, m, e are the mass and the charge of an electron respectively, and A is the area of the ring. The secondary induced magnetic field (B') at a proton located at a

distance R from the center of the ring is μ/R^3 according to eq. 11:

$$B' = -B_0\sigma = \frac{\mu_0}{4\pi}\cdot\frac{3e^2a^2}{2m}\frac{1}{R^3}\cdot B_0. \tag{11}$$

Therefore, the contribution to the shielding constant after introducing the statistical factor 1/3 and generalizing the equation to polycyclic systems, is shown below (eq. 12):

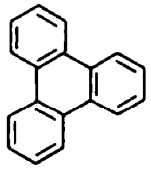
$$\sigma_i = \frac{\mu_0}{4\pi}\cdot\frac{e^2a^2}{2m}\sum_i\frac{1}{R_i^3}. \tag{12}$$

By introducing the known constants (μ_0, m, e) and assuming $a = 1.4\ A^0$ for the radius of the benzene ring and $2.5\ A^0$ for the distance of the benzene proton from the center of the ring, the calculated value is 1.77 ppm which slightly overestimates the experimental value (≈ 1.5 ppm).[47] A more successful model is the one in which the point dipole is replaced by two loops, one below and one above the σ skeleton.

The "ring current effect" was adopted by the organic chemists as a criterion for aromaticity in the early days of NMR.[48] The simple "ring current" model implies that inner protons will suffer an opposite effect and exhibit a high-field shift. This prediction was verified by the inner protons of porphyrins[49] and the inner methylene protons of 1,4-polymethylene benzene.[50] But the best examples were the annulenes, and the planar dehydroannulenes whose inner and outer protons resonate at very different chemical shifts.[51]

Experiments showed that $[4n]\pi$ annulenes exhibit a dramatic reversal effect in which the outer protons reveal a high-field shift while the inner protons are shifted down-field. These systems were called paratropic[52] and their behavior was at first, erroneously, attributed to a "paramagnetic ring current" effect. It should be noted, however, that according to this model this reversal effect on the chemical shift was described in terms of a reversed direction of the circulation of the electron in the ring which seems an inadequate explanation.[44b]

A better description of the opposite anisotropy revealed by $[4n]\pi$ annulenes relative to that of $[4n+2]\pi$ annulenes, is given by the quantum-mechanical models of the "ring current effect". The quantum-mechanical theories of the "ring current concept" introduced by London[53a] and applied later to proton chemical shifts by Pople[53b] and McWeeny[53c] is based on the influence of an external magnetic field on the "field free" Hückel-type molecular orbitals and consequently on their energy. It was found that the external magnetic field influences only non-diagonal terms in the Hückel secular determinant which are absent in linear π-conjugated molecules. If follows from this approach that the total magnetic energy in the presence of a magnetic dipole, depends on two terms σ_1 and σ_2, which arise from first-order and second-order perturbation theories and therefore must have opposite signs.[44b] In most cases, although there is indeed a considerable cancellation, the sign is determined by σ_1 which results in the well known diatropic shift of the outside protons. The σ_2 which is the second term resulting from perturbation theory has a denominator that contains the energy difference (ΔE) between the highest occupied and the lowest unoccupied molecular orbitals (HOMO–LUMO energy gap). In the [4] annulene which has D_4h symmetry, the highest occupied molecular orbitals are degenerate and contain two electrons. For such systems, Hund's rule predicts a triplet ground state which is seldom observed [i.e. triphenylene dianion (8^2)],[54] because any factor which reduces the symmetry can eliminate this degeneracy. In any case, the HOMO–LUMO energy gap of the $4n\pi$ system will be small and this has been found to be one of the main characteristics of $4n\pi$ conjugated systems even of low symmetry.[40c,d] In such cases the term σ_2 becomes much larger than σ_1 and it determines the sign of the total anisotropic effect thus giving the reversal effect on the proton's chemical shift. These reversed effects are illustrated by the proton's chemical shifts of two structurally related systems **9**[55a] and **10**.[55b] The best examples to demonstrate the different



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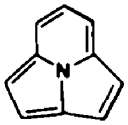

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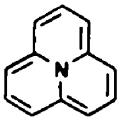

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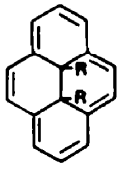

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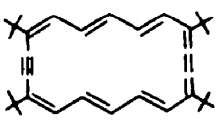
anisotropies of [4n] and [4n+2]π electron systems are the dihydropyrene derivatives, e.g. (**11**) and their dianions, e.g. (11^{2-})[56] and the series of dehydroannulenes (**12, 13, 14**) prepared by Iyoda and Nakagawa[51] and their respective dianions and tetraanions prepared by Müllen.[57] The neutral systems (**12, 13, 14**) which contain [4n+2]π electrons exhibit a down-field shift for the outer protons and a high-field shift for the inner proton (the so-called "diamagnetic ring current effect") while the respective dianions 12^{2-}, 13^{2-} and 14^{2-}, which contain 4nπ-electrons, showed the reversal effect. The further reduction of the dianions to tetraanions, which contain [4n+2]π electrons, brought about a second reversal of the anisotropic effect, thus showing the same effect as exhibited by the neutral systems.[57]

On these grounds it seems logical to suggest these magnetic properties as possible criteria for aromaticity. Although the direct link between "ring current effect" and aromaticity is by no means simple,[41] the former gained an important role among the various criteria suggested for the assessment of the system's aromaticity.[44b] Several review articles[41a,b] devoted to this subject left the problem unsettled although some progress has been made recently.[41c] However, it seems that the paratropic shift of protons can be linked to antiaromaticity in the same sense as the diatropic shift is linked to aromaticity.



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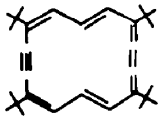

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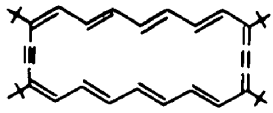

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2.3. *Chemical shift as a probe for charge density*

Another important feature in characterizing charged systems is their charge distribution. Already in the early stages of the NMR study of charged systems, it was pointed out that there is a correlation between the changes in the π electron density (Δq^{π}) and the changes in the proton[38] or carbon[39] chemical shift ($\Delta\delta^{1}$H and $\Delta\delta^{13}$C, eq. 13):

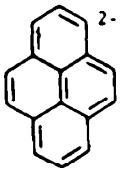
$$\Delta\delta_N = K_N \Delta q^{\pi}, \quad K_H = 10.7\,\text{ppm}/e, \quad K_c = 160\,\text{ppm}/e. \tag{13}$$

K_H and K_c are the proportionality constant indicating the expected shift observed for each electron.

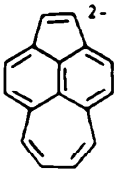
The influence of the charge density on the proton chemical shift seems to be through the σ_{dia} term which was shown to be governed by electron density.[39c] The correlation between charge density and the proton chemical shift was derived from monocyclic classical diatropic systems and it was fairly good.[38b] As already mentioned, in the case of protons, the σ_{para} term has only negligible contribution to σ_{total} so it is nearly equal to $\sigma_{dia}+\sigma'$. For diatropic systems one can assume that σ' is nearly the same, thus enabling determination of the influence of charge on the protons' chemical shift. For this reason the proportionality constant found for this series of compounds (K_H = 10.7 ppm/e) can be regarded as nearly a pure charge effect.

Carbon chemical shift was believed to be a better probe for charge density in the early stages of the ^{13}C NMR study of charged systems. First, σ' for carbon chemical shift, is believed to be small, and second, the range of the carbon chemical shift is twenty times larger than that of protons. Another reason for preferring carbon chemical shifts is that it is the carbon which bears the charge and not the proton connected to it. The value of 160 ppm/e has been found for [4n+2]π electron systems,[39b] but the more data collected, the worse was the agreement between the different correlations.[39,59] For different classes of compounds, different K_c values were found in the range of 152[59a] to 306[59b] ppm per electron. Only recently, it was demonstrated by Müllen, Edlund and Eliasson that for a series of 4nπ dianions, K_c decreases as the paratropicity of the charged system increases.[60] In some paratropic systems, like pyrene dianion (15^{2-}) and acepleiadylene dianion (16^{2-}), K_c was shown to be as low as a few ppm only.[39c] They were able to show that all the different K_c values can be expressed by single correlation, if charge density effects, as well as paratropicity, are taken into account.[60] The paratropicity of the system was reflected by the excess high-field exhibited by the proton NMR spectra of the charged systems (X_H).[40c,d,60,61] According to this correlation, K_c values that contain only charge effects will amount to 134 ppm per electron.[60]

In conclusion it seems that by applying the above correlations and being aware of this limitation and the various terms affecting the shielding constant one can get useful data concerning the important characteristics of the charged system under investigation, from their ^1H and ^{13}C NMR spectra.



15^{2-}



16^{2-}

3. HETEROCYCLIC ANIONS

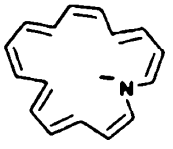
3.1. *NMR study of anions derived from heterocyclic compounds—the beginning*

The pioneering NMR investigations of Anastassiou[62] and Oth[63] concerning heterocyclic charged systems and their relevance to aromaticity, dates from the early seventies. The azoninyl anion (**17a**$^-$)[62a] which is the heterocyclic analogue of cyclononatetraenyl anion (**17b**$^-$)[62d] and therefore isoelectronic with the cyclooctatetraene dianion (**2**$^{2-}$),[7a] was found to be diatropic, and based on this criterion, it was described as "aromatic". Later, the aza[13] and aza[17] annulenyl anions (**18**$^-$,[62b] **19**$^-$,[63] respectively), were prepared and found to be, as expected, diatropic, sustaining considerable diamagnetic ring current, as deduced from the large difference in the chemical shifts of their inner and outer protons (*ca* 14 ppm). Interestingly, it was shown that the diatropicity of the heterocyclic systems (**17a**$^-$) is quenched much more drastically by benzannelation than in the case of benzocyclononatetraenyl anion (**20**$^-$). In contrast to the benzocyclononatetraenyl anion (**20**$^-$) which exhibits a pronounced diamagnetic ring current,[64] the 3-benzazoninyl anion (**21**$^-$) has a proton spectrum characteristic of a benzopolyene system.[62c] The aromaticity of the heteronins was correlated with the extent of the lone pair delocalization of the heteroatom as could be gathered from the ^{13}C NMR chemical shifts by comparison with suitable reference molecules.[65]

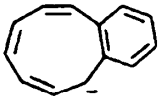
The monoanions of the polyheterocyclic systems (**22**$^-$, **23**$^-$ and **24**$^-$)[66] were prepared *via deprotonation* and were found to be stable. These charged systems which contain $4n\pi$-electrons, were claimed to be paratropic, and it has been pointed out that the anion of the sulphur heterocycle (**23**$^-$) exhibits the least pronounced effect.[66b]

17a$^-$ X=N
17b$^-$ X=CH

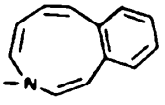
18$^-$



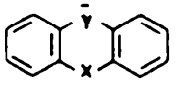
19$^-$



20$^-$



21$^-$



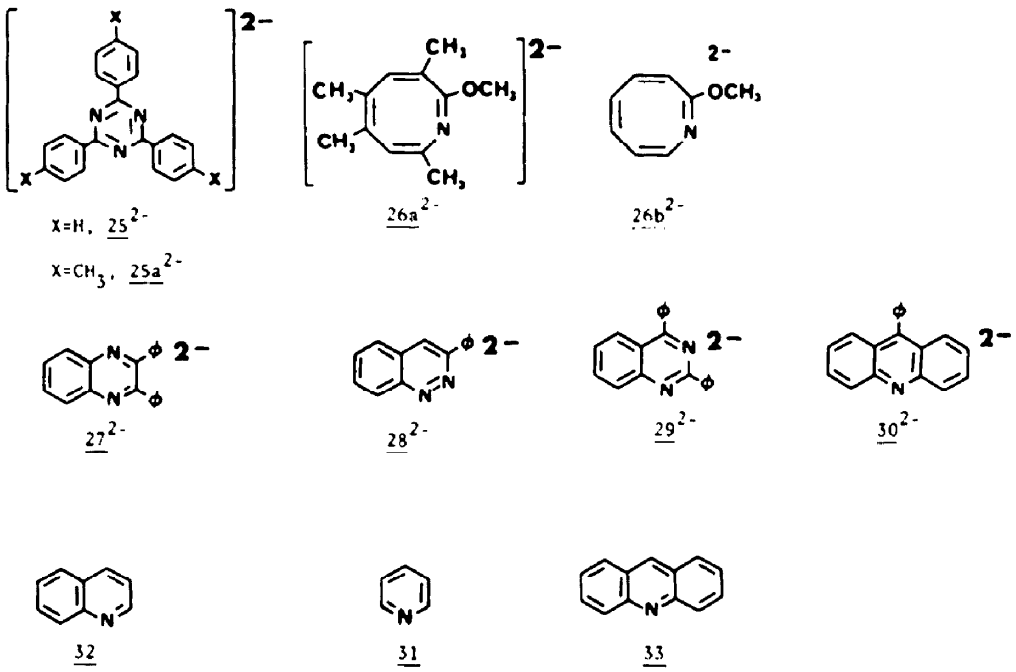
22$^-$ Y=CH, X=O
22a$^-$ Y=N, X=O
23$^-$ Y=N, X=S
24$^-$ Y=N, X=N-CH$_3$

3.2. *Heterocyclic dianions—The missing link*

The preparation of charged heterocyclic systems via metal reduction seems to be more complex.[67] Although many carbocyclic systems were reduced by alkali metals to form their respective

dianions,[7,8,11] most of which were stable enough to be characterized by NMR, only few heterocyclic dianions are known.[68] Even more so, only two dianions which contain the heteroatom in their path of delocalization, were characterized by magnetic resonance techniques.[69,70] These systems are the dianions of 2,4,6-triphenyl-syntriazine (25^{2-}), its *p*-tolyl analogue ($25a^{2-}$)[69] and the dianion of the substituted azocine ($26a^{2-}$) prepared by Paquette.[70a] The dianion $26a^{2-}$, which has recently been investigated by Stevenson,[70b] is a $[4n+2]\pi$ electron system and was found to be diatropic[70a] as Katz's cyclooctatetraene dianion (2^{2-}).[7a]

The other systems, 25^{2-} and $25a^{2-}$, being $4n\pi$ systems, are more interesting but have a singlet ground state with a low-lying thermally accessible triplet state which precluded their characterization by NMR.[69] In the field of polyheterocyclic dianions containing $4n\pi$-electrons, the situation was even more puzzling. The growing amount of chemical evidence[71] concerning polyheterocyclic $4n\pi$-dianions and the lack of spectroscopic information on these series of charged systems prompted us to investigate these systems. On the one hand, in a 1981 paper Lebedev and Sidorov, who tried to characterize such charged systems by spectroscopic methods, commented that "these species tend to be extremely reactive and even unstable...",[72] which is in line with the findings of Szwarc and coworkers who showed that radical anions of pyridine ($31^{\cdot-}$), quinoline ($32^{\cdot-}$), acridine ($33^{\cdot-}$) and related systems tend to dimerize thus preventing the formation of doubly charged systems.[2,73] On the other hand, Smith provided chemical evidence during the last two decades of $4n\pi$-polyheterocyclic dianions, such as 27^{2-},[68a] 28^{2-},[68c] 29^{2-}[68b] and 30^{2-}.[71] Nevertheless, the first NMR investigation of such charged systems appeared only in 1985.[13]



4. $4n\pi$-ELECTRON POLYHETEROCYCLIC DIANIONS CONTAINING PYRIDINE TYPE NITROGEN ATOM

4.1. *General*

Heterocyclic $4n\pi$ dianions, which were prepared and characterized are shown in Scheme 1 (34^{2-}-46^{2-}).[13] But before embarking on the description of the main characteristic of these new series of $4n\pi$-charged systems, the preparation, as well as the determination of the degree of charging of the systems will be demonstrated for the benzo[*c*]cinnoline (**34**) case (Fig. 1). An extended NMR tube containing the solution of the heterocycle in THF-d_8 and the alkali metal is sealed under vacuum. In the benzo[*c*]cinnoline (**34**) case contact between the solution and the sodium metal, affords a dark green color, followed by the disappearance of the NMR spectrum due to the formation of $34^{\cdot-}$ which is a paramagnetic species. After several days a change in color of the solution to a magenta-

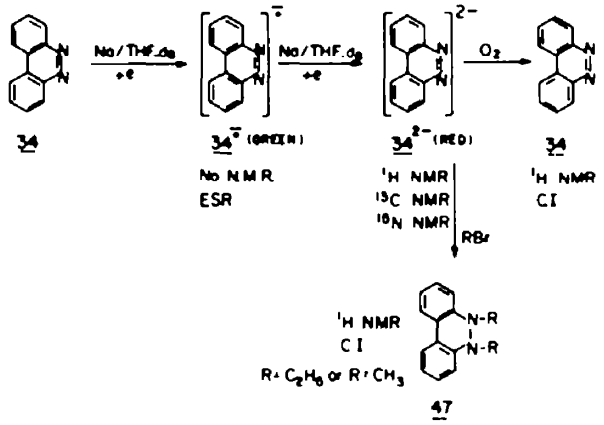


Fig. 1. The steps involved in determination of the degree of charging of anionic species obtained in the course of electron transfer reaction, as demonstrated by reactions of **34**.

red color is observed, accompanied by the appearance of a well resolved NMR spectrum (Fig. 2) as a result of the formation of the diamagnetic species 34^{2-}. The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded, assigned and analysed, and the colored solution was quenched by dry oxygen. The fact that the starting material **34** is the only product, suggests that we have been observing an electron transfer process in which no skeletal change occurred. The quenching of the recorded solution of 34^{2} with an electrophile, afforded **47** as a major product, accompanied by 5% of benzo[*c*]cinnoline (**34**) obtained presumably by partial oxidation of the dianion 34^{2-}.[73e] Product **47** has two alkyl groups, thus corroborating the assumption that the recorded species is a dianion. The

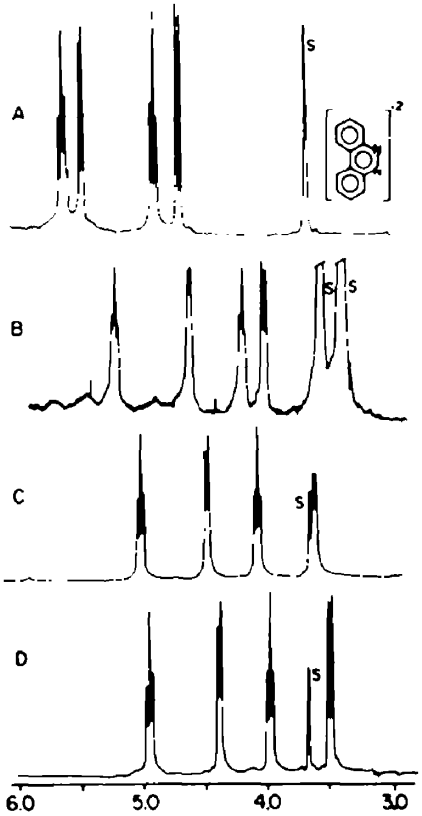
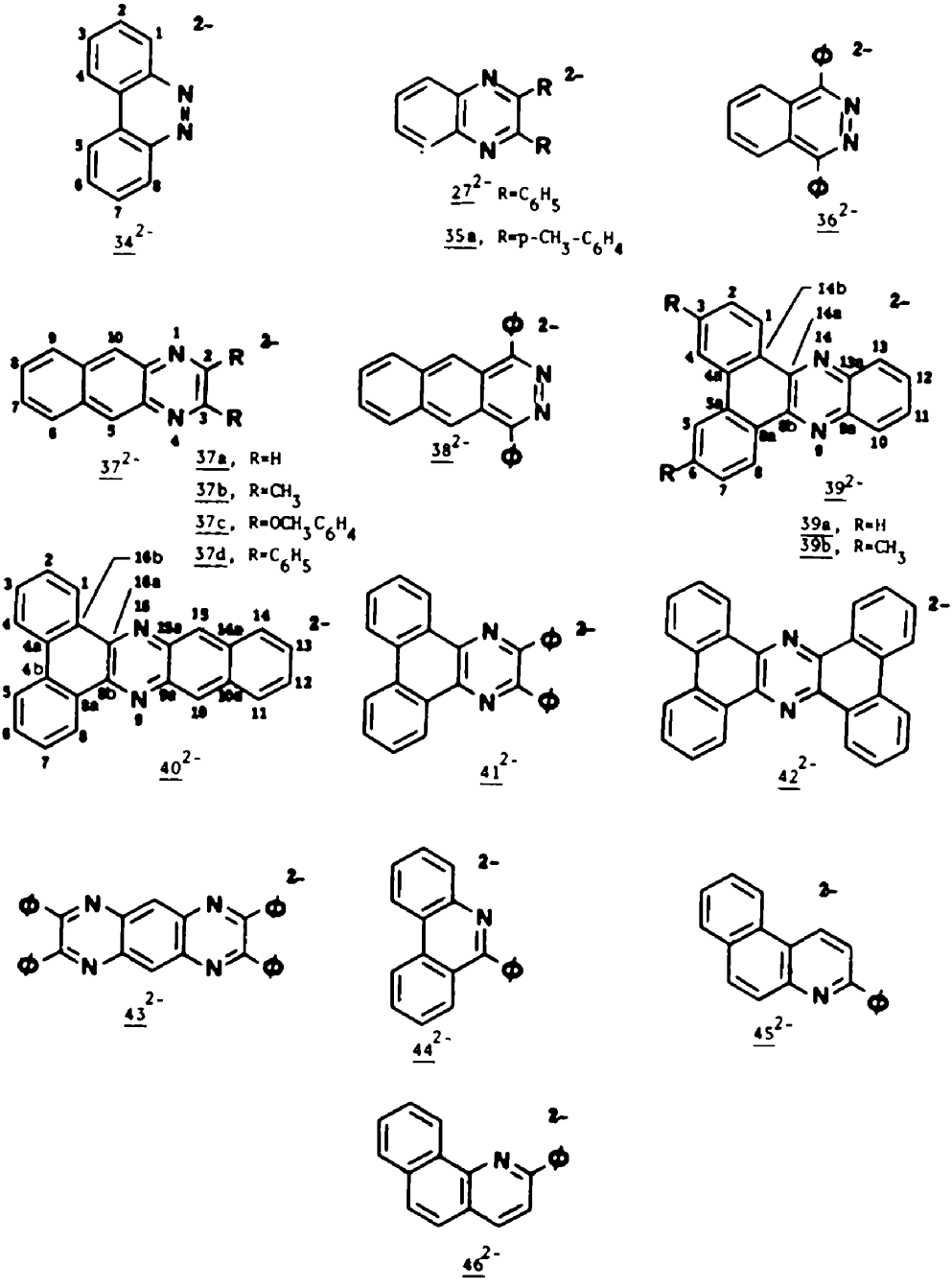


Fig. 2. 300 MHz ^{1}H NMR spectra of benzo[*c*]cinnoline dianion; (34^{2-}): A $34^{2-}/2Li^{+}$, THF, 293°K. (B) $34^{2-}/2Li^{+}$, DME, 243°K. (C) $34^{2-}/2Na^{+}$, THF, 293°K. (D) $34^{-2}/2Na^{+}$, THF, 220°K.

fact that the quenching experiment is regioselective and that only the N-alkylated product is formed hints that a relatively high charge density is residing on the nitrogen atoms of 34^{2-}. It has been commented that reactions of electrophiles with dianions are kinetically controlled and in general reflect the charge density distribution of the charged systems.[11a,b,74] This conclusion is supported by calculated charge density and the significant high-field shifts of nitrogens' chemical shift ($\Delta\delta^{15}N$) in the course of the reduction reaction. The value of $\Delta\delta^{15}N$ for the benzo[*c*]cinnoline system (**34**) and its respective dianion (34^{2-}) amounts to 236 ppm.[73b]

4.2. *The paratropicity of 4nπ-polyheterocyclic dianions containing nitrogen*

4.2.1. *The* ^{1}H *NMR paratropic shift.* As stated in the introduction, $4n\pi$ systems tend to exist as ground state triplets or as ground state singlets with a low lying triplet state.[75] Recently, the HOMO–LUMO energy gap was suggested as an index for the paratropicity and hence the antiaromaticity



Scheme 1.

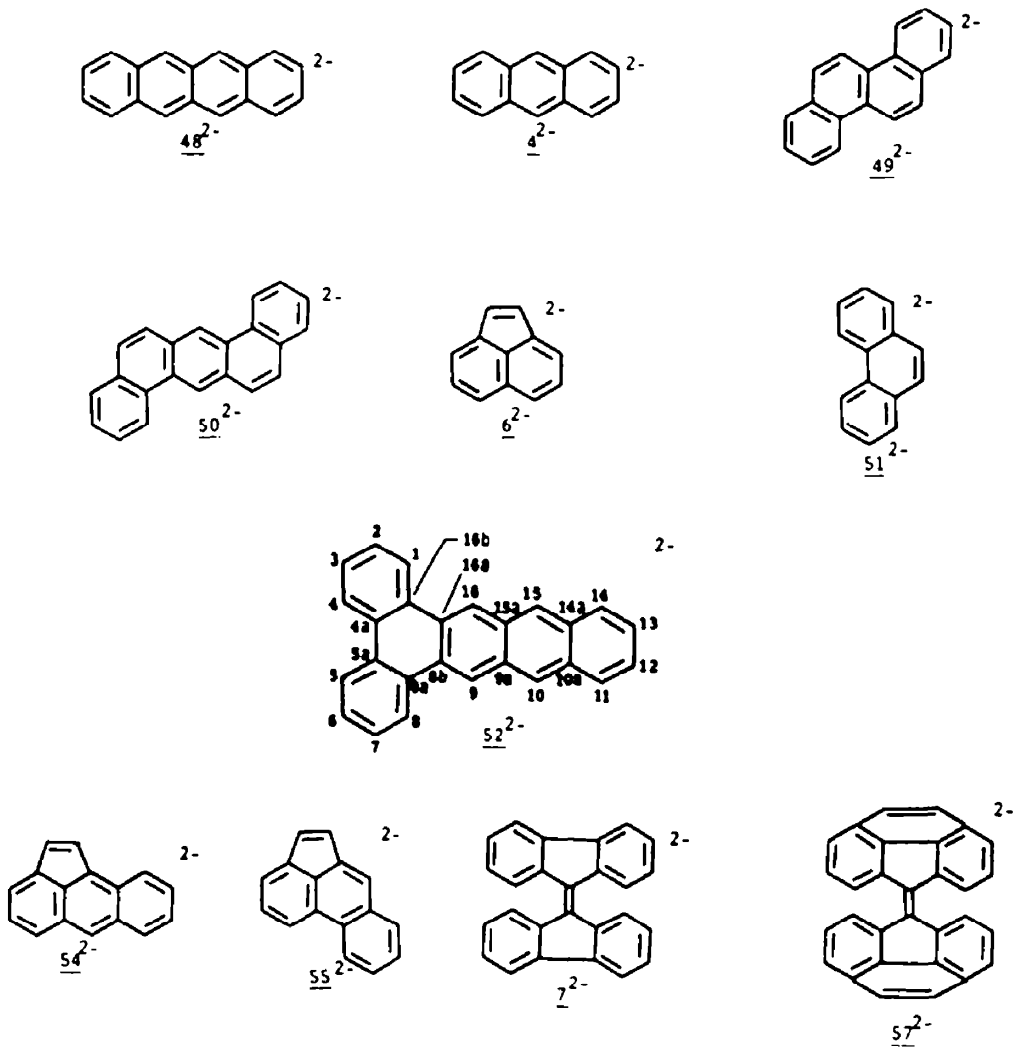
Table 2. Spectral parameters, calculated paratropic shifts, charge density on the heteroatom and K_c of polycyclic dianions

System	^{1}H center of gravity of the neutral system	^{1}H center of gravity of the charged system	X_H	$\Delta\sigma_N^{para}$	$\Sigma\Delta\delta^{13}C$	K_c^{exp}	$K_c^{calc}C$	ΔK
48^{2-}	—	4.13[a]	−2.55[a]	—	—	—	—	—
4^{2-}	—	3.06[b]	−2.93[a]	—	178[b]	89[b]	83.8	−4.2
49^{2-}	—	2.42[a]	−4.06[a]	—	—	—	—	—
50^{2-}	—	1.78[a]	−5.18[a]	—	—	—	—	—
51^{2-}	7.68[b]	0.80[c]	−5.33[a]	—	103[a]	51.5[a]	44.6	−6.9
34^{2-}	8.41[c]	4.32[c]	−2.80	−0.68[c]	43.2[c]	21.6	93.7	72.1
35^{2-}	7.64[d]	6.09[d]	−0.94	−0.84[d]	88.0[d]	44.0	111.2	67.2
36^{2-}	7.86[d]	6.57[d]	−0.59	−0.42[d]	198.0[d]	99.0	119.8	20.8
37^{2-}	7.75[c]	5.95[c]	−1.14	−0.64[c]	120.0[c]	60.0	101.2	41.2
38^{2-}	7.99	5.82	−1.47	−0.38	175.2	87.6	91.7	4.1
39^{2-}	8.26[d]	6.31[d]	−1.16	−0.72[d]	90.0[d]	45.0	106.2	61.2
40^{2-}	8.43[d]	6.50[d]	−1.33	−0.64[d]	84.0[d]	42.0	98.0	56.0
52^{2-}	—	—	—	—	192.4	—	—	—
6	7.56[f]	4.53[f]	−1.07[f]	—	238.8	119.4[f]	118	−1.4
54^{2-}	7.89[g]	5.27[g]	−1.13[g]	—	228.8[h]	114.4	112.3[h]	−2.1[h]
55^{2-}	7.88[g]	5.09[g]	−1.47[g]	—	225.6[h]	112.8[h]	105.8[h]	−7.0[h]
56^{2}	7.75[i]	7.28[i]	0.31[i]	—	358.8[i]	179.9	143.7	−36.2
57^{2}	8.12[i]	7.81[i]	0.33[i]	—	338.8[i]	169.0	145.9	−23.1

All numbers are given in ppm and ^{1}H centers of gravity are reported down-field to TMS.
K values are given in ppm per electron (ppm/e).
Data taken from references: [a]40c; [b]7g; [c]13a; [d]13b; [e]114c; [f]77; [g]61; [h]14b; [i]78; [j]$\omega\beta$ calculations.

of $4n\pi$-polybenzenoid dianions.[40c,d] The HOMO–LUMO gap was shown to govern both the line shape[76] and to correlate with the excess high-field shift (X_H)[60b] known as the paratropic shift,[40c,d,60a,61] of their ^{1}H NMR spectra. The relationship between these different parameters seems by no means obvious at first glance. But recalling the discussion, concerning the Ramsey equation and the factors governing the proton shielding constant, clarifies this relationship (Section 2.2). As already mentioned, in cyclic conjugated systems σ_{total} for protons is governed by σ_{dia} and σ' with the latter being governed by the anisotropic effect and the former mainly governed by the charge density. Following this argument, by excluding the high-field shift caused by the introduction of charge, one can isolate the influence of the anisotropic effect on the proton chemical shift, thus probing its diatropicity or paratropicity. X_H Values for diatropic systems are positive[60] and become negative as the paratropicity of the charged system increases. An excessive high-field shift which exceeds 1.5 ppm ($X < -1.5$ ppm *vide infra*) indicates a paratropic contribution in the resulting charged system. The X_H value of $4n\pi$-polyheterocyclic and carbocyclic dianions are shown in Table 2. The differences between the values of X_H of these two series of $4n\pi$-dianions are large. The data in Table 2 show that the values for the heterocyclic dianions ($\mathbf{34}^{2-}$–$\mathbf{40}^{2-}$) are much smaller than those of the $4n\pi$-polybenzenoid dianions ($\mathbf{48}^{2-}$–$\mathbf{52}^{2-}$). While the absolute values of X_H for the polybenzenoid dianions are larger than 2.50 ppm, the values for the heterocyclic dianions are around 1 ppm. It can therefore be concluded that these heterocyclic dianions ($\mathbf{34}^{2-}$–$\mathbf{40}^{2-}$) despite having $4n\pi$ electrons, show only minor, if any, paratropic contributions, as compared with the polybenzenoid anions. As mentioned, the experimental diamagnetic shift of the protons of benzene is *ca* 1.5 ppm.[47] Therefore, values of X_H that are in the range of −1.5 ppm represent a loss of the diatropicity of the parent compound rather than a partial gain of paratropicity by the respective dianion. It should be noted that the X_H's absolute values of the acenaphthylene dianion ($\mathbf{6}^{2-}$) and the related systems $\mathbf{54}^{2-}$, $\mathbf{55}^{2-}$ all of which were found to be non-aromatic by different criteria are in the range of 1.1–1.5 ppm.[61,77]

The only example in the heterocyclic dianion series that shows more pronounced paratropicity is the benzo[*c*]cinnoline dianion ($\mathbf{34}^{2-}$) (X_H = 2.80 ppm) which is the diaza analogue of the highly paratropic phenanthrene dianion ($\mathbf{51}^{2-}$).[40c,d] Here, again, the same trend emerges as the paratropicity of $\mathbf{34}^{2-}$ is by far less pronounced as compared with that of $\mathbf{51}^{2-}$ for which X_H is 5.33 ppm and it is found to be the highest value in these series of polybenzenoid carbocyclic dianions (Table 2). The fact that the benzo[*c*]cinnoline dianion ($\mathbf{34}^{2-}$) is much less paratropic than phenanthrene dianion ($\mathbf{51}^{2-}$) can be deduced by simply comparing their ^{1}H NMR spectra (Figs 2 and 3 respectively). These two spectra i.e. $\mathbf{34}^{2-}$ and $\mathbf{51}^{2-}$ differ considerably also in their line shape.



4.2.2. *The HOMO–LUMO energy gap* (ΔE) *and the* ^{1}H *NMR line shape.* As already stated, the $4n\pi$ systems are characterized by a narrow HOMO–LUMO energy gap (ΔE) which is responsible for the paratropic shift of their ^{1}H NMR spectra. It is obvious that in extreme cases one should find the influence of this energy gap on the line shape of the proton spectra of the $4n\pi$-dianion series. This observation was encountered in the series of $4n\pi$-electron polybenzenoid carbocyclic dianions and interpreted in terms of an involvement of the triplet state in the ground state, i.e. a possible singlet–triplet equilibrium.[76] According to this hypothesis the line broadening observed in this series of charged systems arises from an equilibrium between a singlet and a low lying thermally accessible triplet state. The narrower the HOMO–LUMO energy gap the higher is the population of the triplet state which results in a paramagnetic dilution which is responsible for the shortening of the T_2 relaxation time and hence for the line broadening. In extreme cases where the HOMO–LUMO energy gap is very narrow, the population equilibrium is shifted toward the triplet state which precludes monitoring of any NMR spectra.

There is a good correlation between the calculated HOMO-LUMO energy gap (ΔE) and the observed line broadening in the heterocyclic dianion series.[13,79] As expected in the heterocyclic dianions, the narrower this gap is, the broader is the ^{1}H NMR line shape (Table 3). These results are in agreement with the singlet- triplet hypothesis.[76]

It is difficult to estimate *a priori* the HOMO–LUMO energy gap, but generally in systems which are composed of few fused rings, one may expect narrow energy gaps. However, it turns out that the topology of the system has a major influence on the energy gap. This is exemplified by the two structurally related dianions **35a**$^{2-}$ and **36**$^{2-}$ which differ in their HOMO–LUMO energy gaps ($\Delta E = 0.19\ \beta$ and $0.29\ \beta$, respectively) and consequently in their ^{1}H NMR spectra (Fig. 4). On

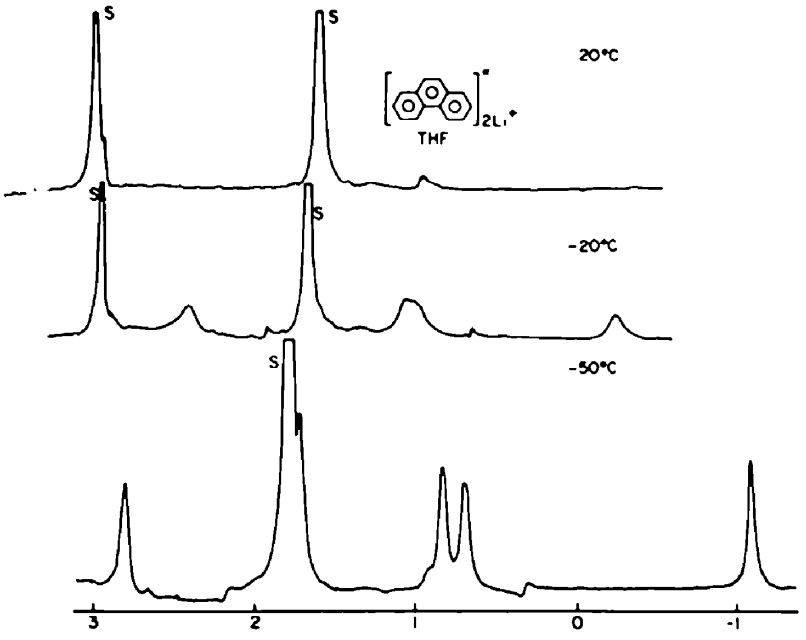


Fig. 3. 300 MHz ^{1}H NMR spectra of phenanthrene dianion (51^{2-}) at −20°C and −50°C.

these grounds, the phenanthrazine dianion (42^{2-}) presented a real challenge for the singlet–triplet hypothesis.[13b] Surprisingly, the ^{1}H NMR spectrum of this dianion, composed of seven fused rings, revealed considerable line broadening which seems, at first glance, to contradict the singlet–triplet hypothesis (Fig. 5). The very narrow HOMO–LUMO energy gap calculated for this charged system (0.11 β) supplies the explanation for this observation.[13b]

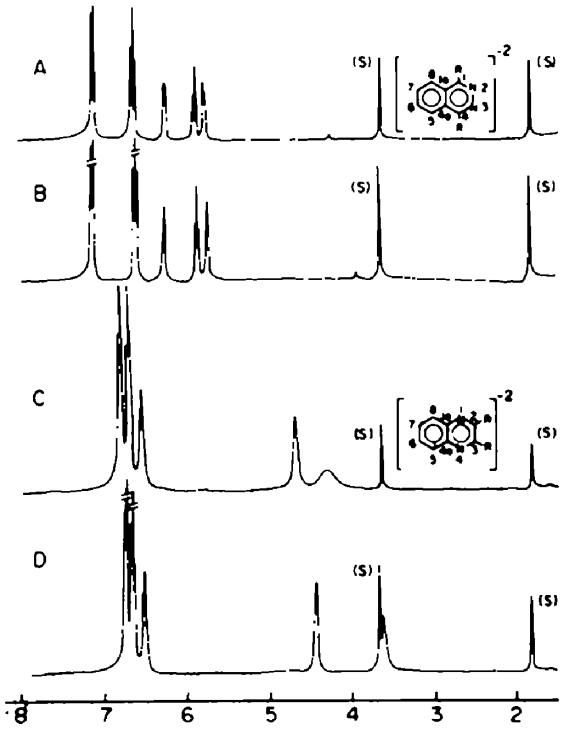


Fig. 4. 300 MHz ^{1}H NMR spectra of the two structurally related dianions, i.e. 2,3-diphenylquinoxaline ($35a^{2-}$) and 1,4-diphenylphthalazine (36^{2-}) in THF-d_8: (A) 36^{2-}/2Na$^+$, 300°K. (B) 36^{2-}/2Na$^+$, 213°K. (C) $35a^{2-}$/2Na$^+$, 292°K. (D) $35a^{2-}$/2Na$^+$, 203°K.

Table 3. The relationship between the calculated HOMO-LUMO energy gap ΔE and the line shape of the ^{1}H NMR spectra of heterocyclic dianions

System	ΔE Energy gap E_{HOMO}-E_{LUMO}[a] (β units)	Detectable line broadening[c]
43^{2-}	0.38	–
38^{2-}	0.36	–
37d^{2-}	0.34	–
40^{2-}	0.31	–
34^{2-}	0.29	–
36^{2-}	0.29	–
39a^{2-}	0.22	+
35a^{2-}	0.19	+ +
42^{2-}	0.11[b]	+ + +
41^{2-}	0.11[b]	no spectrum

[a] As obtained by $\omega\beta$ calculations using ω = 1.4.

[b] The same calculation using ω = 1.0 because no energy convergence could be obtained using the habitual value (i.e. ω = 1.4).

[c] The sign (–) indicates no line broadening while (+) designates detectable line broadening. All data correspond to the ^{1}H NMR spectra of the disodium salts of the respective dianion measured in THF-d_8 at room temperature.

As in the case of the paratropic shift the extent of the line broadening revealed by the polyheterocyclic 4$n\pi$-dianions is also much less pronounced than that of the polybenzenoid carbocyclic series. This characteristic is manifested by the ^{1}H NMR spectra of benzo[*c*]cinnoline and phenanthrene dianions (**34**$^{2-}$, **51**$^{2-}$) (Figs 1 and 3, respectively). It was also found that dibenzo[*a*,*c*]phenazine dianion (**39**$^{2-}$) prepared in THF-d_8 shows only minor line broadening in its 300 MHz proton spectrum (Fig. 6) while its carbocyclic analogue, i.e. dibenzo[*a*,*c*]anthracene (**58**$^{2-}$), prepared in THF-d_8 could not be observed as disodium salt at the same magnetic field even at low temperature,[76] in agreement with the very narrow HOMO–LUMO energy gap (0.157 β). Therefore, it seems according to these two criteria, that the series of the polyheterocyclic dianions is less

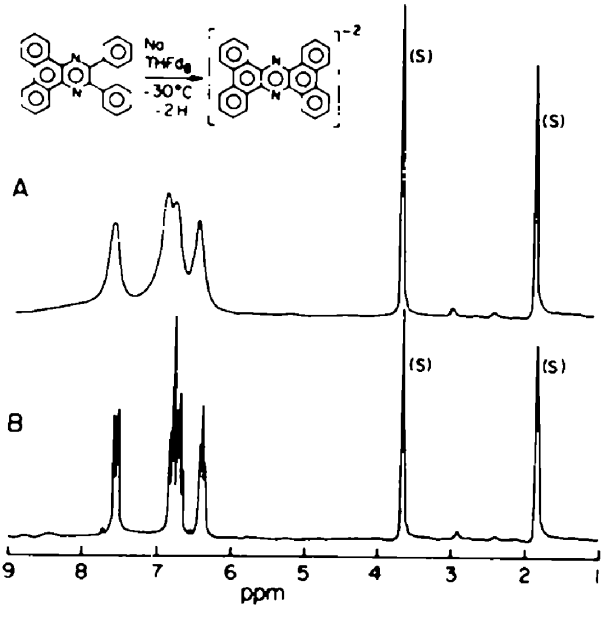


Fig. 5. 200 MHz ^{1}H NMR spectra of phenanthrazine dianion (**42**$^{2-}$) as disodium salt in THF-d_8. (A) 293°K, (B) 213°K.

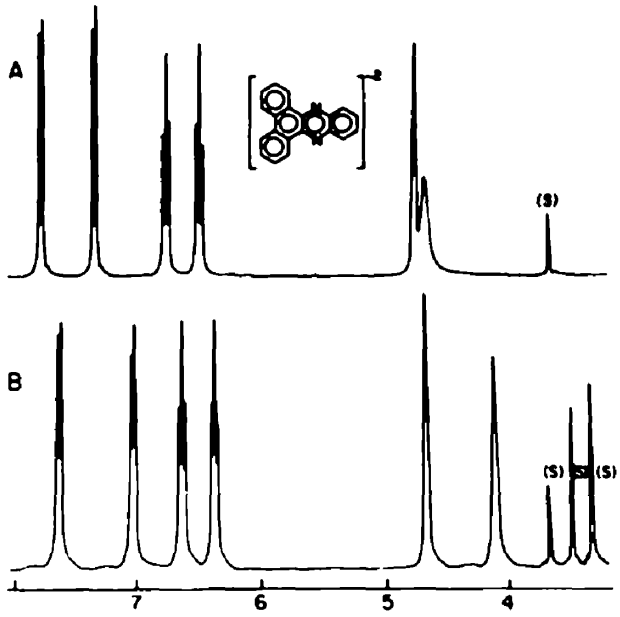


Fig. 6. 300 MHz ^{1}H NMR spectra of dibenzo[*a*,*c*]phenazine dianion (**39a**$^{2-}$): (A) **39a**$^{2-}$/2Na$^+$, THF at 293°K. (B) **39a**$^{2-}$/2Na$^+$ in 1 : 1 solution of THF-d_8/DME-d_{10} at 220°K.

paratropic than the corresponding carbocyclic dianions thus suggesting the former's unpronounced antiaromaticity.

4.2.3. *Electrochemical study of heterocycles and possible explanations for the quenched paratropicity of heterocyclic anions.* The quenched antiaromaticity of polyheterocyclic dianions can be challenged by other criteria for aromaticity, as aromatic or antiaromatic molecules were defined as species in which the π-electron delocalization reduces or increases respectively the energy content of the cyclic molecule relative to a model compound without such cyclic delocalization. Therefore, the most direct criterion of the aromatic nature is based on the energy content of the system under consideration. Some insight into the thermodynamics of the electron transfer process can be obtained from electrochemical studies, especially by the C.V. experiments. Thus, for example, the first electron reduction of quinoline (**32**) and naphthalene (**5**) are -1.14 and -2.5 V respectively.[80] These values demonstrate that the heterocyclic system is reduced much more easily. Recently a C.V. study of the reduction of polyheterocyclic and carbocyclic substrates was performed in THF by Laviron[81a] and Heinze.[81b] In each case the reduction potential of the two electron reductions to the corresponding dianions were measured. The main observation is that the heterocyclic systems are much more easily reduced to the respective dianions. For example the first half-wave reduction of phenanthrene[81b] (**51**) appears at a more negative potential than that of the second electron reduction of **44** and **45** and in *ca* 1 eV more negative potential than the potential of the first electron reduction of benzo[*c*]cinnoline (**34**).[81a] Another example is that the radical anion of pyridine (**31**$^{\cdot-}$)[80] can be formed much more easily than the radical anion of benzene.[82] It has been commented that nitrogen-containing polyheterocyclic molecules are reduced more easily than their carbocyclic analogues as the nitrogen atom behaves as an electron-withdrawing substituent on an aromatic molecule.[81c] But it seems that the large differences found in the first and the second electron reduction of these two series reflects also the difference in the stability of the resulting dianions. Paquette and coworkers demonstrated that $E^0_{1,2}$ for methoxycyclooctatetraene (**2a**) and methoxyazocine (**26b**) in THF are nearly the same (-1.87 and -1.84 respectively).[70c] These two systems form diatropic dianions and even the second electron reduction appears nearly in the same potential. Thus assuming that the difference between the ground state stabilities of the neutral systems is not very pronounced, the fact that the heterocyclic radical anions and dianions can be prepared much more easily probably reflects, besides the effect of the inductive effect of the nitrogen, the lower energy content of these species as compared to the *more paratropic antiaromatic* $4n\pi$-polybenzenoid carbocyclic dianions. It appears that the conclusion from the *electrochemical study lends strength* to the conclusion reached

from NMR spectroscopy. We conclude, therefore, that the polyheterocyclic dianions (34^{2-}–46^{2-}) although being $4n\pi$ systems, are much less antiaromatic than their carbocyclic analogues and possess nearly negligible paratropicity.

The reason for the quenched antiaromaticity as manifested by the quenched paratropicity of the $4n\pi$-heterocyclic dianions may be questioned. As already mentioned, antiaromaticity results from an effective cyclic delocalization of $4n\pi$-electrons. Therefore, the two possible explanations for this observation are deviation from planarity of the π-system and the high charge density on the nitrogen. The calculated charge densities and the low values of the total carbon chemical displacements ($\Sigma\Delta\delta^{13}C$) of the heterocyclic dianions (Table 2) indicate a relatively high degree of charge localization on their nitrogen atoms. According to Müllen and Edlund[60a] one should expect for the polyheterocyclic dianions, which possess only negligible paratropicity, higher $\Sigma\Delta\delta^{13}C$ values than that of the polybenzenoid carbocyclic dianions. This is in contrast with experimental data. Therefore, it happens that the localization of charge causes an ineffective delocalization of the $4n\pi$-electrons of the charged systems thus resulting in quenched paratropicity. The second possible explanation, namely the deviation from planarity of the π-system, cannot be excluded. This deviation may hamper the effective delocalization of the $4n\pi$-electrons of the system.

As no X-ray structures of such heterocyclic dianions have yet been reported, one can assume that both effects contribute to the quenching of the paratropicity of this series of $4n\pi$-dianions and it seems reasonable that the relative importance of these two effects varies from system to system according to its nitrogens' location and structure. These issues need more studies before any decisive conclusion can be made.

Generally, it seems that the HOMO–LUMO energy gap (ΔE) may indicate the diatropicity or the paratropicity of the system, thus probing its aromatic character. Therefore it seems that the HOMO–LUMO energy gap can be used as an index for the aromaticity or the antiaromaticity of the investigated systems. The data in Table 4 show that for the neutral polycyclic systems the HOMO–LUMO energy gap are of the order of 1 β unit, while for the respective dianions there is a pronounced decrease in these calculated values. An instructive example is the calculated HOMO–LUMO energy gap of the pentalene (**61**) and its respective dianion ($\mathbf{61}^{2-}$). The pentalene (**61**) being a $4n\pi$-antiaromatic system is the only example in which the calculated HOMO- LUMO energy gap (0.61 β) is smaller for the parent neutral system as compared with its respective dianion ($\mathbf{61}^{2-}$). The very wide HOMO–LUMO gap calculated for the pentalene dianion ($\mathbf{61}^{2-}$) (1.35 β), which is in the order of the HOMO–LUMO gap calculated for neutral polybenzenoid systems (i.e. 0.91 and 1.28 β for anthracene and phenanthrene, respectively) clearly correlate with the experiment. The pentalene dianion ($\mathbf{61}^{2-}$) was found to be diatropic[83] and exhibits no line broadening. It is much more stable both thermodynamically and kinetically than the parent compound. The calculated HOMO–LUMO energy gap of the dianions derived from dibenzo[*a*,*c*]cyclooctatetraene ($\mathbf{60}^{2-}$) or $\mathbf{59}^{2-}$ as well as that derived from overcrowded ethylenes ($\mathbf{7}^{2-}$, $\mathbf{57}^{2-}$) are relatively high. The ^{1}H NMR spectra of these dianions showed pronounced diatropicity and no line broadening as expected from charged systems in which only conjugated circuits of $(4n+2)\pi$ electrons prevail. The relatively large HOMO–LUMO energy gap found for biphenylene dianion ($\mathbf{62}^{2-}$) prepared recently[84] is in accord with the diatropicity and the well resolved ^{1}H NMR spectrum obtained even in a 400 MHz instrument. For the non-aromatic dianions $\mathbf{6}^{2-}$,[77] $\mathbf{54}^{2-}$ and $\mathbf{55}^{2-}$ [61] one finds intermediate values while for the highly paratropic $4n\pi$-electron polybenzenoid dianions the value decreases from *ca* 0.4 β for tetracene dianion ($\mathbf{48}^{2-}$) down to 0.11 β for benzo[*c*]phenanthrene dianion ($\mathbf{64}^{2-}$) (Table 4).

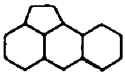
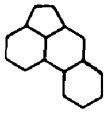
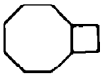
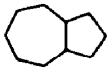
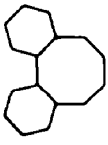
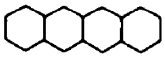
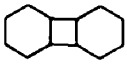
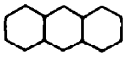
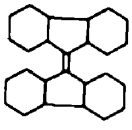
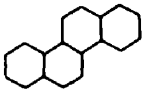
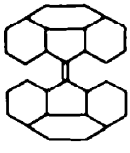
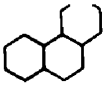
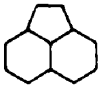
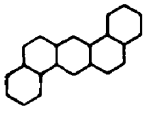
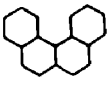
4.3. *Anion–cation interactions and ion-pairing equilibria of* 4nπ-*polyheterocyclic dianions*

Carbanion chemistry has been found to depend on the interactions between the anion, the alkali metal and the solvent molecules. Winstein[85] proposed an ion-pair model according to which ionic species exist as thermodynamically discrete species coined as "free ions", contact ion-pairs (C.I.P.) and solvent separated ion-pairs (S.S.I.P.) as shown in equation 14:[2,85]

$$\underset{\substack{\text{contact ion-pair}\\(C.I.P.)}}{M^+\,R^-} \rightleftharpoons \underset{\substack{\text{solvent separated}\\\text{ion-pairs (S.S.I.P.)}}}{M^+\,\|\,R^-} \rightleftharpoons \underset{\text{"free ions"}}{M^+ + R^-} \qquad (14)$$

It should be noted that for doubly charged systems the situation may be even more complex. Structures in which one cation appears in a solvent separated mode and the other participating in a contact ion pair ($M^+R^{2-}\,\|\,M^+$) as well as triplet ions ($M^+R^{2-}M^+$) were claimed.[28,86] The ion

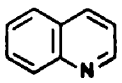
Table 4. The calculated HOMO–LUMO energy gap (ΔE, β units) of carbocyclic systems and their respective dianions as obtained by $\omega\beta$ calculations[a]

System		ΔE Neutral	ΔE Dianion	System		ΔE Neutral	ΔE Dianion
	61	0.61[b]	1.35		54	0.79	0.66
	66	1.06	0.87		55	1.04	0.46
	59	0.82	0.55		65	0.78	0.43
	60	0.84	0.56		48	0.72	0.41
	62	1.13	0.54		4	0.91	0.41
	7	0.82	0.66		49	1.15	0.27
	57	0.71	0.46		51	1.28	0.23
	6	1.08	0.65		50	1.07	0.16
					64	1.13	0.11
					5	1.36	0.11

[a] All calculations were done using the habitual position for ω (i.e. $\omega = 1.4$).
[b] The same calculations with $\omega = 1.0$ because no energy convergence could be obtained using the habitual value ω (i.e. $\omega = 1.4$).

triplet model introduced by Streitwieser[28] to explain the small differences in the first and second pKa of some delocalized carbanions has been suggested as a stabilizing effect and was found to explain several X-ray structures of such systems. In solution, the systems are quite labile, and it is difficult to obtain the exact location of the cation.[88,89] Moreover, some averaging is likely to occur on the time scale of the NMR measurements.

From various spectroscopic studies on different series of monoanions, the influence of several factors on the ion-solvation equilibria has been deduced as follows.[86,87,90,91]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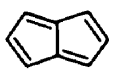
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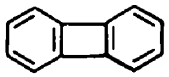
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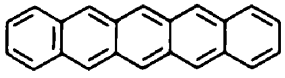
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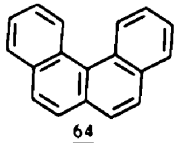
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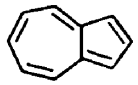
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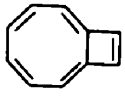
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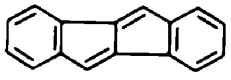

67

Table 5. ^1H and ^{13}C NMR parameters of selected heterocyclic dianions 34^{2-}, $37d^{2-}$, 40^{2-} [3a,b]

System	Temp. °K	Solvent	NMR parameters[a]	Center of gravity
$34^{2-}/2Li^+$	293	THF	^1H: 5.63 (t, J = 7.1, $H_{2,7}$); 5.84 (d, J = 7.3, $H_{4,5}$); 4.90 (t, J = 7.2, $H_{3,6}$); 4.69 (d, J = 7.7, $H_{1,8}$).	5.18
$34^{2-}/2Li^+$	243	DME	^1H: 5.14 (t, J = 7.3, $H_{2,7}$); 4.55 (d, J = 5.7, $H_{4,5}$); 4.12 (t, J = 6.5, $H_{3,6}$); 3.95 (d, J = 8.1, $H_{1,8}$).	4.45
$34^{2-}/2Na^+$	293	THF	^1H: 5.05 (t, J = 7.1, $H_{2,7}$); 4.51 (d, J = 6.7, $H_{4,5}$); 4.09 (t, J = 6.7, $H_{3,6}$); 3.62 (d, J = 7.6, $H_{1,8}$).	4.32
$34^{2-}/2Na^+$	220	THF	^1H: 4.95 (t, J = 7.1, $H_{2,7}$); 4.39 (d, J = 6.7, $H_{4,5}$); 3.98 (t, J = 6.7, $H_{3,6}$); 3.49 (d, J = 8.1, $H_{1,8}$).	4.20
$34^{2-}/2Li^+$	293	THF	^{13}C: 166.7; 129.3; 124.4; 118.3; 110.6; 108.3	126.3
$34^{2-}/2Na^+$	293	THF	^{13}C: 168.7; 131.6; 125.1; 117.4; 107.0; 105.2	125.8
$34^{2-}/2Na^+$	220	THF	^{13}C: 168.7; 131.2; 125.0; 116.3; 107.3; 104.1	125.5
$37d^{2-}/2Li^+$	294	THF	^1H: 6.77 (AB, H-tolyl); 5.57; 5.46 (AA'BB', $H_{6,9}$); 3.93 (s, $H_{5,10}$); 2.18 (s, p-CH_3).	6.00[c]
$37d^{2-}/2Na^+$	294	THF	^1H: 6.77 (AB, H-tolyl); 5.42; 5.32 (AA'BB', $H_{6,9}$); 3.86 ($H_{5,10}$); 2.17 (s, p-CH_3).	5.95[c]
$37d^{2-}/2Na^+$	203	THF	^1H: 6.72 (AB, H-tolyl); 5.25; 5.03 (AA'BB', $H_{6,9}$); 3.57 (s, $H_{5,10}$); 2.17 (s, p-CH_3).	5.82[b]
$37d^{2-}/2Na^+$	300	THF	^{13}C: 159.9; 143.4; 141.9; 135.3; 130.9; 127.8; 127.8; 117.3; 115.6; 90.8; p-CH_3 20.7.	128.9[c]
$37d^{2-}/2Na^+$	223	THF	^{13}C: 160.1; 143.4; 142.7; 135.2; 130.2; 127.4; 127.4; 116.4; 114.4; 91.0; p-CH_3 20.7.	128.8[b]
$39a^{2-}/2Na^+$	293	THF	^1H: 7.81 (d, J = 8.1, $H_{4,5}$); 7.37 (d, J = 8.6, $H_{1,8}$); 6.78 (t, J = 7.2, $H_{3,6}$); 6.51 (t, J = 7.1, $H_{2,7}$); 4.75 (bd, J = 3.3, $H_{11,12}$); 4.67 (bs, $H_{13,10}$).	6.31
$39a^{2-}/2Na^+$	211	THF	^1H: 7.73 (d, J = 8.1, $H_{4,5}$); 7.25 (d, J = 7.6, $H_{1,8}$); 6.74 (t, J = 6.7, $H_{3,6}$); 6.44 (t, J = 6.7, $H_{2,7}$); 4.67 (bs, $H_{11,12}$); 4.37 (bs, $H_{13,10}$).	6.20
$39a^{2-}/2Na^+$	220	THF/DME 1:1	^1H: 7.70 (d, J = 8.1, $H_{4,5}$); 7.10 (d, J = 8.1, $H_{1,8}$); 6.69 (t, J = 7.7, $H_{3,6}$); 6.42 (t, J = 7.1, $H_{2,7}$); 4.60 (t, J = 3.8, $H_{11,12}$); 4.00 (bs, $H_{13,10}$).	6.08
$39a^{2-}/2Na^+$	300	THF	^{13}C: 162.7; 144.2; 125.5; 123.7; 121.7; 119.3; 117.7; 125.5; 116.5; 107.4.	126.4
$40^{2-}/2Li^+$	295	THF	^1H: 8.09 (d, J = 8.0, $H_{4,5}$); 7.71 (d, J = 6.8, $H_{1,8}$); 7.00 (t, J = 6.9, $H_{2,7}$); 6.81 (t, J = 7.3, $H_{3,6}$); 5.93 (bs, H_{11-14}); 4.70 (s, $H_{10,15}$).	6.60
$40^{2-}/2Na^+$	293	THF	^1H: 8.04 (d, J = 7.9, $H_{4,5}$); 7.76 (d, J = 8.2, $H_{1,8}$); 7.01 (t, J = 7.0, $H_{2,7}$); 6.74 (t, J = 7.5, $H_{3,6}$); 5.71 (bs, H_{11-14}); 4.49 (s, $H_{10,15}$).	6.50
$40^{2-}/2Na^+$	203	THF	^1H: 8.01 (d, J = 8.1, $H_{4,5}$); 7.62 (d, J = 8.6, $H_{1,8}$); 6.95 (t, J = 7.7, $H_{2,7}$); 6.73 (t, J = 7.6, $H_{3,6}$); 5.58 (AA'BB'; H_{11-14}); 4.27 (s, $H_{10,15}$).	6.25
$40^{2-}/2Na^+$	300	THF	^{13}C: 159.9; 139.7; 137.0; 128.2; 125.5; 123.9; 121.8; 120.8; 118.3; 118.1; 117.9; 96.8.	125.8[c]

[a] All chemical shifts (δ) are reported in ppm down-field to external TMS, and spin-spin couplings (J) are given in Herz.
[b] Center of gravity calculated excluding the absorption bands of the p-CH_3 groups.

(a) The nature of the cation—smaller cations ($Li^+ < Na^+$ $K^+ < Rb^+ < Cs^+$) shift the equilibrium towards solvent separated ion-pairs.

(b) Temperature—lowering the temperature shifts the equilibrium to the solvent separated end.

(c) The solvating power of the solvent—as expected the better the solvating power of the solvent, the higher is the extent of the solvent separated ion-pair.

(d) The organic anion—the higher the charge density in a certain position of the organic anions, the higher is the concentration of the contact ion-pairs. It is obvious that the charge density in the various positions of the organic ion depends on the degree of charging and on its delocalization pattern.[88,92]

Therefore it is expected that lowering the temperature of a sodium salt of an organic anion, will shift the ion-pair equilibrium towards the solvent separated ion-pair resulting in a spectrum reminiscent of its lithium salt. The same effect is to be expected when the sodium salt of an organic ion is prepared in a solvent with a higher solvating power. This trend, which is generally observed in the carbocyclic dianions,[7,8,93,94] opposes the trend found for the $4n\pi$-polyheterocyclic dianions (Table 5) as demonstrated by the benzo[*c*]cinnoline dianion ($\mathbf{34}^{2-}$) (Fig. 2).[13a] In this case cooling the dilithium salt of $\mathbf{34}^{2-}$ or preparing it in dimethoxyethane (DME) shifts the spectrum to high-field which is the range of the bands of $\mathbf{34}^{2-}/2Na^+$. Cooling of the solution of $\mathbf{34}^{2-}/2Na^+$ shifted the ^1H NMR spectrum further to high-field (Fig. 2, Table 5). The explanation to these observations seems to be that although the lithium cation is believed to favor solvent separated ion-pairs over the sodium cation, the opposite trend prevails in the heterocyclic dianions. It seems that in the lithium salts of heterocyclic dianions the ion solvation equilibrium is shifted toward contact ion-pairs. Therefore, one needs to cool the solution or to use a solvent of higher solvating power in order to pull the lithium cation away from the nitrogen of the charged heterocycle, thus resulting in a shift of the ion solvation equilibrium towards the solvent separated ion-pair mode. The data in Table 5 show that this is a general characteristic of the heterocyclic dianions.

The differences between the chemical shifts of the lithium and sodium salts of $\mathbf{34}^{2-}$, $\mathbf{37d}^{2-}$ and $\mathbf{40}^{2-}$ are relatively large and the most pronounced effect is found for the most paratropic heterocyclic system, i.e. benzo[*c*]cinnoline dianion ($\mathbf{34}^{2-}$). For $\mathbf{34}^{2-}$ the variations of the ^1H NMR parameters are significant and the difference between the center of gravity of $\mathbf{34}^{2-}/2Li^+$ at 293°K and $\mathbf{34}^{2-}/2Na^+$ at 203°K is *ca* 0.9 ppm. It should be noted that these differences are in the range of the changes found for paratropic carbocyclic dianions.[92] These dianions were found to be much more sensitive to factors governing the ion solvation equilibria than those of diatropic carbocyclic dianions. It is interesting that one finds large differences in the ^1H NMR spectra of the various salts of the same charged systems, while their carbon spectra appear to be relatively insensitive to the nature of the cation, temperature and solvent (Table 5). This discrepancy is only apparent because these facts result from the influence of the ion-pairing equilibria on the paratropicity of the system. The lithium cation which is very close to the nitrogen in the contact ion mode, may increase the charge localization on the latter, reduce the effective delocalization in $\mathbf{34}^{2-}$ and in turn quench its paratropicity. It is also possible that the lithium cation coordinates to the nitrogen. Thus a deviation from planarity may occur in such a way that it reduces the effectiveness of the delocalization of the $4n\pi$-electrons of the benzo[*c*]cinnoline dianion ($\mathbf{34}^{2-}$).

A puzzling characteristic of these polyheterocyclic dianions i.e., $\mathbf{34}^{2-}$–$\mathbf{46}^{2-}$ is the very significant difference in the kinetic stability of the various salts. In contrast to the observed trend in the carbocyclic charged series the dilithium salts of the heterocyclic dianions are kinetically much less stable than the respective disodium salts. For example, dianions $\mathbf{35}^{2-}$, $\mathbf{36}^{2-}$ and $\mathbf{43}^{2-}$ could be prepared only as disodium salts and in the case of $\mathbf{34}^{2-}$ and $\mathbf{39}^{2-}$ in which the disodium salts were stable for several weeks (−30°C, under vacuum), the respective dilithium salts were stable only for several hours. This observation is puzzling as the polybenzenoid dianions do not show such differences in the relative stability of their various salts and on the contrary, many of the carbocyclic tetraanions prepared were prepared as lithium salts.[95] This difference in stability lends strength to the assumption that the various salts differ not only in the ion-pairing equilibrium, but also in their mode of bonding. It seems that the lithium cation is so close to the nitrogen that one can think of some covalent contribution to their bonding mode. Such tight ion-pairing may result in an attack of the cation on the organic ion. The authors are aware of the fact that this covalency is not easy to accept in view of the ionic character attributed to the carbon–lithium bond.[28a] Nevertheless, the

growing number of cases in which a carbon–lithium spin coupling is observed, suggesting some covalent contribution to the carbon–lithium bond has to be taken into account.[96,97] The strong affinity of the lithium cation to the negatively charged nitrogen is manifested by the products of the addition of alkyllithium to pyridine and other heterocyclics.[98]

4.4. *Stability involved in different arrays of* 4nπ*-electrons—The charge distribution in dibenzo- and tribenzophenazine dianions* (**39a**$^{2-}$, **40**$^{2-}$)

One of the most important characteristics of an aromatic system is its tendency to remain so or to "avoid" as much as possible antiaromatic contributions. *For this very reason* a π-conjugated system will prefer to avoid as much as possible paratropic contributions resulting from delocalization of 4nπ-electrons. Such phenomena have been observed to be a general property of the nonalternant systems acenaphthylene (**6**),[77] acephenanthrylene (**54**) and aceanthrylene (**55**)[61] and their respective dianions (**6**$^{2-}$, **54**$^{2-}$ and **55**$^{2-}$),[61] and even more so in the case of the alternant system dibenzo[*a*,*c*]tetracene dianion (**52**$^{2-}$).[99]

The ^{1}H NMR spectra of dibenzo[*a*,*c*]phenazine dianion (**39**$^{2-}$) and tribenzo[*a*,*c*,*i*]phenazine dianion (**40**$^{2-}$) are shown in Figs 6 and 7 respectively.[13] Each one of these two ^{1}H NMR spectra seems to be constituted of two distinct regions. Although it seems bizarre to divide fully conjugated systems into sub-systems, the ^{1}H NMR spectra of **39a**$^{2-}$ and **40**$^{2-}$ clearly indicate such a behavior. In both cases it appears that most of the charge is directed towards the linear part of the molecules, leaving the angular part virtually uncharged. The data show that the protons attributed to the angular part of **39a**$^{2-}$ ($H_{1,8}$) appear at a low-field (7.8 6.5 ppm) while the signal attributed to the proton of its linear part (H_{10-13}) appears at higher field ($\approx$4.7 ppm). This phenomenon of partitioning of charge is even more pronounced for tribenzo[*a*,*c*,*i*]phenazine dianion (**40**$^{2-}$). It should be noted that the absorptions of H_{1-8} of **40**$^{2-}$ (8.0–6.8 ppm) are close to those of the protons of the neutral phenanthrene (**51**) (8.6–7.2 ppm). The phenanthrene dianion (**51**$^{2-}$) shows a center of gravity at a much higher field ($\approx$1 ppm, Fig. 3). By simply comparing the chemical shifts of H_{10-15} and H_{11-14} of **40**$^{2-}$ (Fig. 7) with those of 2,3-di-*p*-tolylbenzo[*g*]quinoxaline (**37d**$^{2-}$) (Fig. 8), one is convinced that most of the charge is located on the benzo[*g*]quinoxaline moiety of **40**$^{2-}$. Based on these arguments, it seems that the proton spectrum of tribenzo[*a*,*c*,*i*]phenazine dianion (**40**$^{2-}$) which can be regarded as benzo[*g*]quinoxalino-phenanthrene, is best described as a superposition of virtually "uncharged phenanthrene" and "benzo[*g*]quinoxaline dianion" moieties. This observation seems to be a general characteristic of systems with such a topology, as already mentioned, the partitioning of the charge delocalization was also observed in **52**$^{2-}$ [99] the carbocyclic analogue of **40**$^{2-}$. These assumptions are corroborated by the carbon spectra of **39a**$^{2-}$ and **40**$^{2-}$ and the calculated charge densities as obtained by $\omega\beta$ calculations (Table 6). Both the spectrum and the calculations predict higher charge densities on the carbons of the linear part of these charged systems.

The question which now arises is what is the cause of these bizarre electron delocalization patterns. In a naive way, it can be assumed that the best pattern of electron delocalization is the one in which the charges are spread uniformly on the entire system, thus reducing the Coulombic repulsions. The rationale for the special pattern of charge delocalization encountered in **40**$^{2-}$ and

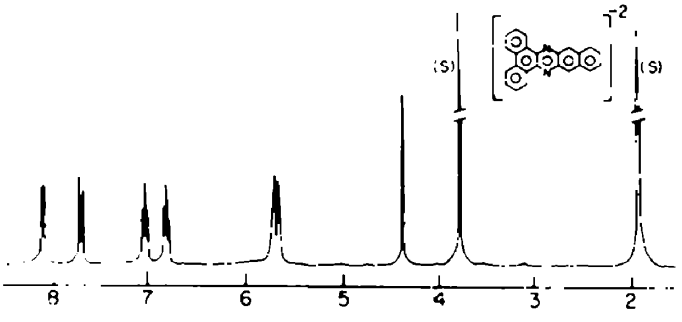


Fig. 7. 300 MHz ^{1}H NMR spectrum of tribenzo[*a*,*c*,*i*]phenazine (**40**$^{2-}$) in THF-d_8 at 203°K.

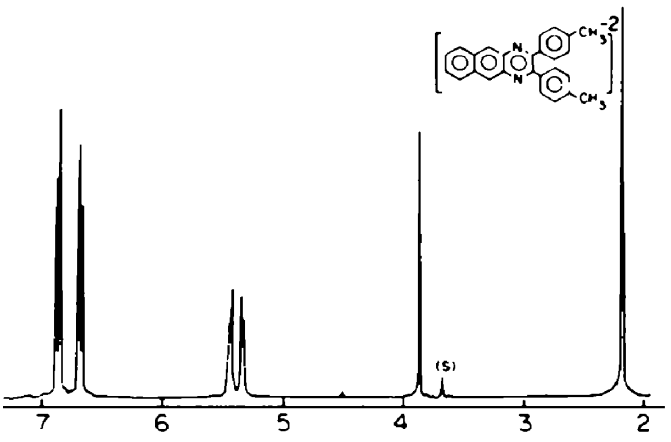


Fig. 8. 300 MHz ^{1}H NMR spectrum of 2,3 di-*p*-tolybenzo[*g*]quinoxaline dianion ($37d^{2-}$) in THF-d_8 at 294°K.

52^{2-} is the energy destabilization involved in the different patterns of charge delocalization.[79,99] It was proposed that the charged systems have much more "to lose" if most of the charge will be directed towards their angular components, thus resulting in the case of 40^{2-} in "phenanthrene dianion" and an uncharged benzo[*g*]quinoxaline moiety.[79] Such a delocalization pattern is much less favorable because it involves more pronounced paratropic contributions. Figure 3 illustrates the enhanced paratropicity of phenanthrene dianion (51^{2-}) compared with that of the dianion of the benzo[*g*] quinoxaline derivative (37^{2-}) (Fig. 8).

4.5. 4nπ-*Electron polyheterocyclic dianions—Structure–stability relationships*

As already pointed out, it was claimed in the literature that reduction of polyheterocyclic systems affords very reactive and even unstable products,[72] although Smith *et al.* provided chemical evidence for the existence of some polyheterocyclic dianions.[68,71] In our previous studies it was found that most of the disodium salts of dianions 34^{2-}–43^{2-} (Scheme 1) are stable enough to be characterized by NMR. All these systems have *three* common structural features: (a) they all have two nitrogen atoms, (b) they have no neighboring α-hydrogens, and (c) they all have relatively high steric hindrance in the vicinity of their nitrogen atoms. In order to establish the structural requirements which enable the

Table 6. Unsymmetrical charge distribution between linear and angular components of polycyclic dianions: calculated charge densities of dianions 39^{2-}, 40^{2-} and 52^{2-}

System[a]	Charge density[b]	
	"Angular" component	"Linear" component
52^{2-}	$C_{1,8} = -0.018$; $C_{2,7} = -0.033$; $C_{3,6} = -0.033$; $C_{4,5} = -0.018$; $C_{4a,4b} = -0.053$; $C_{8a,16b} = -0.049$; Total: -0.408	$C_{9,16} = -0.200$; $C_{8a,15a} = -0.043$; $C_{10,15} = -0.239$; $C_{10a,16a} = -0.046$; $C_{11,14} = -0.120$; $C_{12,13} = -0.079$; $C_{8b,16a} = -0.069$ Total: -1.592
$39a^{2-}$	$C_{1,8} = -0.085$; $C_{2,7} = -0.060$; $C_{3,6} = -0.045$; $C_{4,5} = -0.031$; $C_{4a,4b} = -0.081$; $C_{8a,16b} = -0.084$; Total: -0.772	$C_{8b,16a} = -0.052$; $C_{9,16} = -0.363$; $C_{8a,15a} = -0.036$; $C_{13,10} = -0.140$; $C_{11,12} = -0.080$. Total: -1.228
40^{2-}	$C_{1,8} = -0.019$; $C_{2,7} = -0.031$; $C_{3,6} = -0.032$; $C_{4,5} = -0.018$; $C_{4a,5a} = -0.050$; $C_{8a,16b} = -0.049$. Total: -0.398	$C_{8b,16a} = -0.057$; $N_{9,16} = -0.321$; $C_{8a,15a} = -0.033$; $C_{10,15} = -0.192$; $C_{10a,16a} = -0.046$; $C_{11,14} = -0.088$; $C_{12,13} = -0.064$. Total: -1.602

[a] For numbering of carbons of **39** and **40** see Scheme 1; the numbering of carbons of **52** follows that of **40**.

[b] As obtained from $\omega\beta$ calculations.

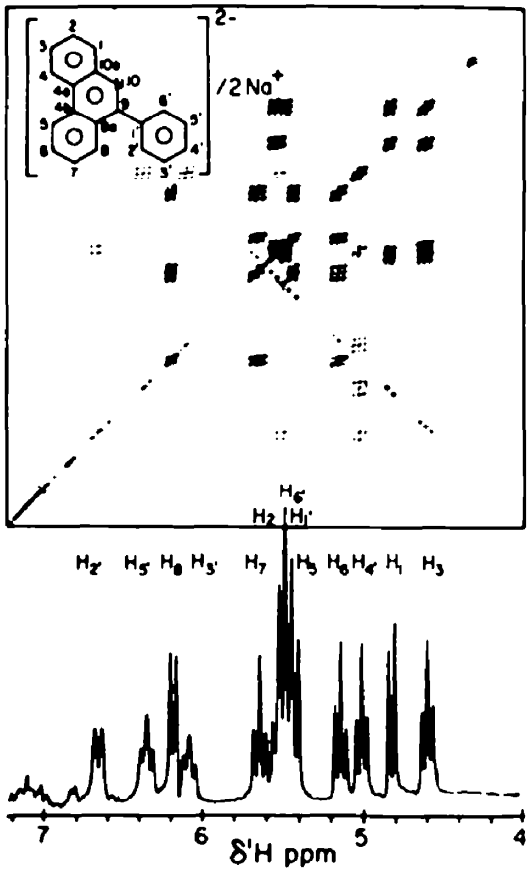


Fig. 9. 200 MHz 2D-COSY ^{1}H NMR spectrum of 68^{2-} in THF-d_8 at 253°K.

preparation of stable polyheterocyclic dianions, we investigated the metal reduction of phenanthridine (**68**), benzo[*f*]quinoline (**69**), and benzo[*h*]quinoline (**70**), all of which have hydrogens in the α-position to the nitrogens.[100] In all three cases a color change was observed, followed by precipitation of solid material and no ^{1}H NMR spectrum could be recorded. After quenching the solution of the reduction products of **68**, **69** and **70** with oxygen, we could not identify the starting material. Following this observation, the α-position of **68**–**70** was blocked by phenyl groups and the products **44**–**46** (Scheme 1) were reduced by sodium in THF-d_8. In these cases we could characterize the respective dianions (44^{2-}–46^{2-}) which exhibit moderate stability. (For example, see the COSY spectrum of 68^{2-} given in Fig. 9). Quenching of the anion solutions with oxygen afforded quantitively in all cases only the starting material. These results show the importance of blocking the α-position to the nitrogen and demonstrate that the number of nitrogen atoms is not crucial for obtaining stable heterocyclic dianions.[100] In all the heterocyclic dianions prepared, there is a steric hindrance on the nitrogen atoms which may prevent dimerization in the stage of the radical anion. Such a dimerization is one of the most important side reactions in the metal reduction of heterocycles.[101,102]

The reduction of phenazine (**71**) afforded a red colored solution, accompanied by a red precipitate which gave no ^{1}H NMR signals. In the quenching of this solution with oxygen, phenazine was recovered as a sole product. It seems that although no decomposition had occurred, the resulting charged system forms a rather insoluble product. The calculated charge density on the nitrogen atoms of phenazine dianion (71^{2-}) is high (0.82 units of charge), therefore it is possible that its sodium salt exists as a very tight ion-pair which precipitates from THF, resulting in a low effective concentration of $71^{2-}/2Na^+$ which precludes its observation by NMR. Another possibility is that the phenazine radical anion ($71^{\cdot-}$) forms a dimer which is relatively insoluble in THF in the same way as the acridine radical anion ($72^{\cdot-}$) does.[56] Thus, it seems that in order to form stable heterocyclic dianions, the neutral parent system must not have any α-hydrogen and it is preferable to have

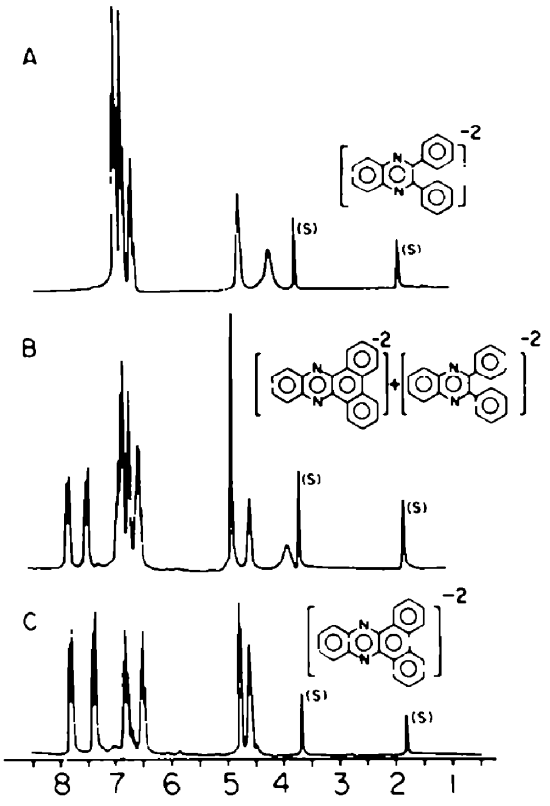
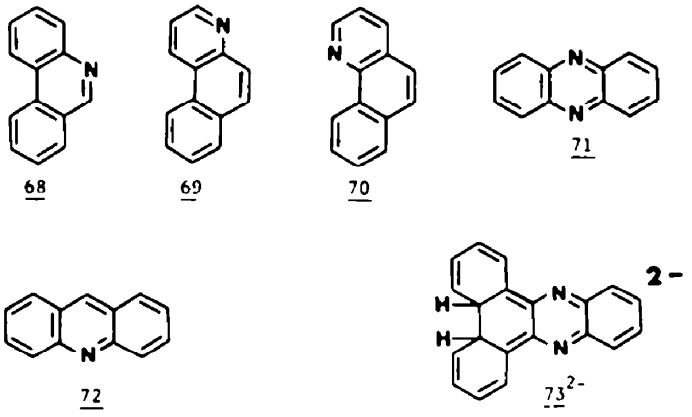


Fig. 10. The ^{1}H NMR spectra evolution in the course of the ring closure reaction of $35a^{2-}$ to $39a^{2-}$ in THF-d_8.

systems in which there is a relatively high steric hindrance around the nitrogen region of the molecule. This steric hindrance may reduce the probability of dimerization and the formation of very tight ion-pairs reminiscent of inorganic salts which are insoluble even in polar organic solvents.



4.6. *The ring closure reaction of* 4n*π-heterocyclic dianions—Mechanism and application*

In the course of the spectroscopic study of these series of charged systems, we encountered their ring closure reaction first described by Smith[68a] as demonstrated in Scheme 2. The progression of this reaction for $35a^{2-}$ is shown in Fig. 10 and demonstrates two important features of this reaction: First, there is no line broadening throughout the synthetic transformation of $35a^{2-}$ to 39^{2-}—a fact which does not support the trianion radical as a long living intermediate in this reaction. This observation favors the electrocyclic mechanism over the trianion mechanism suggested by Smith *et al.*[68a] Second, it appears that there are no other long living intermediates in this reaction. Therefore, we prefer the electrocyclic mechanism shown in Fig. 11 in which the dihydro product, *viz* 73^{2-}, must be a short living intermediate.

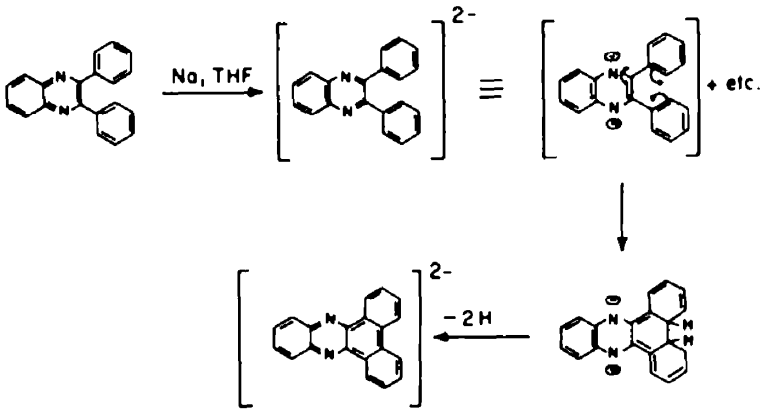
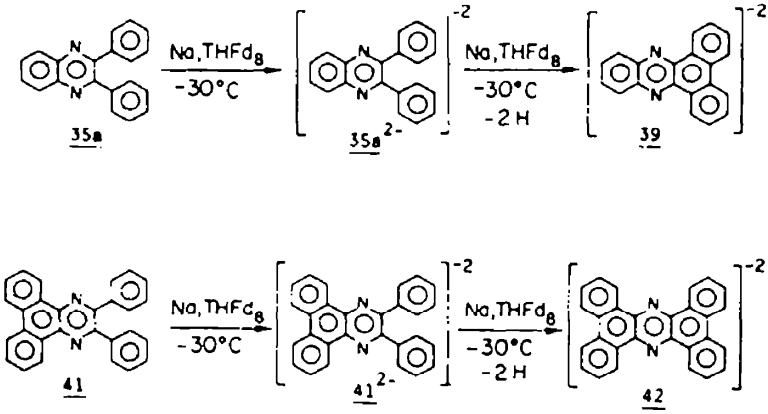


Fig. 11. Suggested mechanism for the ring closure reaction of polyheterocyclic $4n\pi$-dianions ($35a^{2-} \rightarrow 39a^{2-}$)

From the synthetic point of view, it was found that the reaction rate is relatively slow when the reaction is carried out with sodium metal. It was found that this drawback can be easily overcome by using the potassium graphite intercalate C_8K as the reducing agent.[103] Several examples of the application of C_8K to this reaction are presented in Table 7 and it can be seen that despite the short reaction time the yields are relatively high. This reaction seems to afford the possibility of preparing similar heterocycles with specific substituents in specific positions.

Table 7. Ring closure products of dianions $35a^{2-}$, $35b^{2-}$ and $37d^{2-}$ [103]

Substrate	Product	Yield %	^{1}H NMR (THF-d_8) δ ppm
35a	39a	70 (THF)	9.37 (dd, 2H, J = 8.3 Hz); 8.53 (dd, J = 7.7 1.5 Hz); 8.38, 7.84 (AA'BB', 4H); 7.75 (m, 4H).
35b	39b	65 (DME)	9.32 (d, J = 8.1 Hz, 2H); 8.55 (s, 2H); 8.35; 7.93 (AA'BB';
		90 (THF)	4H); 7.63 (dd, 2H, J = 8.5 Hz, 1.4 Hz); 2.71 (s, 6H).
37d	40	85 (DME)	9.52 (d, 2H, J = 6.6 Hz); 9.05 (s, 2H); 8.75 (2H, J = 8.1 Hz);
		60 (THF)	8.33; 7.69 (AA'BB', 4H); 7.83 (m, 4H).

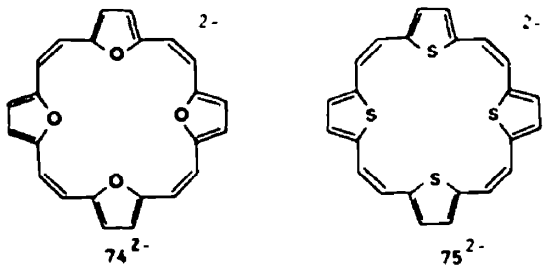


Scheme 2.

5. $4n\pi$-HETEROCYCLIC DIANIONS CONTAINING 5-MEMBERED RINGS: FURAN AND THIOPHENE DOUBLY CHARGED DERIVATIVES

5.1. *Background*

As mentioned previously, the spectroscopic information concerning $4n\pi$-polycyclic dianions is scarce. This scarcity is even more pronounced when oxygen and sulfur doubly charged heterocycles



74^{2-} 75^{2-}

are involved. Two interesting known examples are 74^{2-} and 75^{2-} which were prepared by Müllen and Wennerström and were shown to be diatropic, a fact which led the authors to the conclusion that in these two systems the heteroatoms do not belong to the path of the charge delocalization.[95] In a 1980 paper, Smith and McCall provided chemical information and evidence for the existence of 1,3-diphenylbenzo[*c*]furan dianion (76^{2-}).[104] They stated that it seems that this dianion is stable for 24 hours and they were even successful in studying the stereoselectivity of the alkylation of its different salts. This dianion was re-examined recently by NMR spectroscopy[14b] (*vide infra*).

The information concerning sulfur containing $4n\pi$-electrons was also limited. The dianion derived of dibenzothiophene (77^{2-}) prepared by Ito *et al.* had a structure in which the carbon–sulfur bond was cleaved.[105] In the following section we shall concentrate on some recent developments and findings in the preparation and spectroscopic characterization of oxygen and sulfur containing $4n\pi$-polycyclic dianions.[14,78]

5.2. *The* 1,3-*diphenylbenzo*[c]*furan dianion* (76^{2-}): *A* $4n\pi$-*electron polyheterocyclic dianion containing oxygen*

The 1,3-diphenylbenzo[*c*]furan dianion (76^{2-}) was prepared as lithium, sodium and potassium salts[14b] and it was found that $76^{2-}/2Na^{+}$ is much more stable than its other salts (Fig. 12).

The parent compound benzo[*c*]furan (**78**), despite its containing a $[4n+2]$ electron, has a low calculated resonance energy and low thermodynamic stability, and cannot be classified as a classical aromatic system.[106] Therefore, it is expected that its doubly charged derivative which contains $4n\pi$-electrons will exhibit only quenched paratropicity. This expectation is realised as dianion 76^{2-} shows a very small excessive high-field shift ($X_H = -0.95$ ppm, Table 8) indicating its quenched paratropicity.

Interestingly, $\omega\beta$ calculations predict only a small degree of charge on the oxygen atom of 76^{2-} (0.11 units of charge). This prediction is in line with the high value of $\Sigma\Delta\delta^{13}C$ upon reduction of **76** to 76^{2-} which amounts to 232.4 ppm. Table 8 demonstrates the role played by the different heteroatoms in maintaining charge of disodium salts in THF-d_8. The proportionality constant (K_c) is defined as the sum of the changes in the carbons' chemical shift, as a result of the electron transfer reaction ($\Sigma\Delta\delta^{13}C$), divided by n, the number of electrons participating in the process. Following the correlation presented by Eliasson, Edlund and Müllen,[60a] one can formulate eq. 15 to predict

Table 8. The dependence of the difference between the experimental and calculated K_c (ΔK) on the charge density of heterocyclic dianions[14b]

Systems	$\Sigma\Delta\delta^{13}C$[a]	X_H[d]	K_c^{exp}[b]	$K_c^{cal\,b,c}$	ΔK_c[b] $= K_c^{cal} - K_c^{exp}$	Total π-charge on heteroatoms
$35a^{2-}$	88.0	−0.95	44.0	111.2	67.2	−0.84
34^{2-}	43.2	−2.80	21.6	93.7	72.1	−0.68
43^{2-}	88.4	−0.67	44.2	109.9	65.7	−1.06
40^{2-}	84.0	−1.25	42.0	98.0	56.0	−0.64
36^{2-}	198.0	−0.59	99.0	119.8	20.8	−0.41
54^{2-}	228.8[e]	−1.13[e]	114.4[e]	112.3[e]	2.1[e]	—
55^{2-}	225.6	−1.47	112.8	105.8	7.0	—
76^{2-}	232.4	−0.95	116.2	111.2	5.0	−0.11

[a] In ppm units.
[b] The units are ppm per electron (ppm/*e*).
[c] As obtained from eq. (1). See also ref. 60.
[d] For details of calculations of X_H see text and ref. 60.
[e] Data of $54^{2-}/2Li^{+}$.

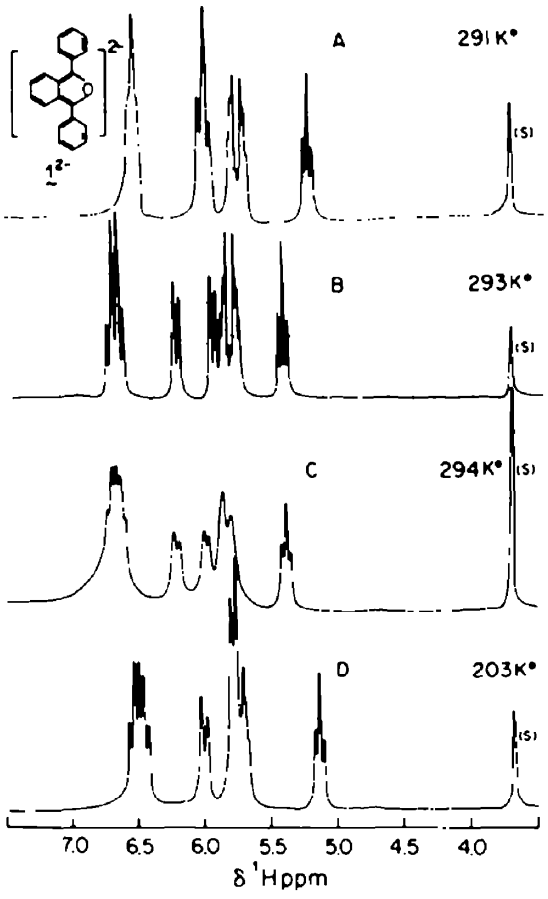


Fig. 12. 200 MHz ^{1}H NMR spectra of 1,3-diphenylbenzo[*c*]furan dianion (76^{2-}) in THF-d_8. (A) $76^{2-}/2Li^+$, 291°K. (B) $76^{2-}/2Na^+$, 293°K. (C) $76^{2-}/2K^+$, 294°K. (D) $76^{2-}/2Na^+$, 203°K.

the proportionality constant for dianions (K_c^{cal}):

$$K_c^{cal} = 134 + 1.2\, n_c X_H. \tag{15}$$

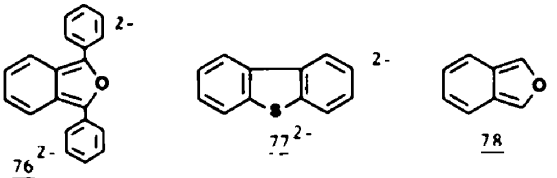
n_c is the number of carbon atoms of the system;
X_H is the excess high-field shift of the center of gravity of the proton spectrum.

It is expected that in heterocyclic dianions the differences between the predicted values using eq. 15 for the proportionality constant (K_c^{cal}) and the experimental one (K_c^{exp}) will be more significant as the charge density on the heteroatom increases.[146] It is found that this is indeed the case (Table 8) and in the new carbocyclic dianions 54^{2-} and 55^{2-} the deviations are small while in the diaza dianions 43^{2-}, 35^{2-}, 40^{2-} and 34^{2-} the deviation exceeds 50 ppm/*e*. In 1,4-diphenylphthalazine dianion (36^{2-}) for which calculations predict only 0.42 units of charge on the nitrogen atoms, the deviation is only 20.8 ppm/*e*. Therefore, the value obtained for 76^{2-} ($\Delta K = 5.0$ ppm/*e*) clearly corroborate the low π-charge density found for the oxygen atom of 76^{2-} by calculation.

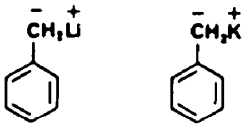
The sodium and potassium salts of 76^{2-} show nearly identical spectra which differ from that of $76^{2-}/2Li^+$. Smith and McCall suggested that, based on quenching experiments, 76^{2-} can be regarded as two isolated benzylic anions with carbon atoms $C_{1,3}$ at the α-position to the oxygen as the benzylic carbons.[104] The comparison of the proton and carbon spectra of $76^{2-}/2Li^+$ and $76^{2-}/2K^+$ with those of benzyllithium (**79**)[107] and benzylpotassium (**80**)[108] is shown in Scheme 3. It has been pointed out that both **79** and **80** exist as contact ion-pairs in THF. The smaller lithium cation polarizes better the charge toward the α-carbon atom and consequently less charge is delocalized into the benzene ring. For this very reason the *para* carbon of benzylpotassium (**80**) appears at 95.7 ppm while that of benzyllithium (**79**) appears at significantly lower field (104.4 ppm). However, the observed trend for $76^{2-}/2Li^+$ and $76^{2-}/2K^+$ is the opposite one.[146] Assuming that both salts of

76^{2-} form contact ion-pairs, one should expect an enhanced polarization of charge towards $C_{1,3}$ for $76^{2-}/2Li^+$ as in the case of benzyl anions. Therefore, it was concluded that while potassium and sodium salts of 76^{2-} exist predominantly as contact ion-pairs, the small lithium cation shifts the equilibrium towards solvent separated ion-pairs, thus resulting in a solvated lithium cation which can hardly polarize the charge towards $C_{1,3}$.

This ion solvation equilibrium may shed light on the differences encountered in the stereoselectivity of the alkylation reaction of the various salts of 76^{2-}. It has been reported that the alkylation reactions of $76^{2-}/2Na^+$ and $76^{2-}/2K^+$ in THF are much more stereoselective than that of $76^{2-}/2Li^+$.[104] It seems logical to assume that as the metal cation is removed from the carbanionic center, it enhances the chances for planarization of this center, thus rendering the reaction less stereoselective. Moreover, it is reasonable that when the metal cation is remote from the carbanionic center (as in the case of $76^{2-}/2Li^+$) the alkylation reaction will be less stereoselective. The stereoselectivity of the alkylation is determined by the structure of the monoanion. The fact that 76^{2-} can be regarded mainly as composed of two isolated benzylic anions, implies that it is reasonable to assume that the ion solvation pattern of the dianion 76^{2-} correlates with the situation in the monanion. It is therefore suggested that the similarity of the spectra of $76^{2-}/2Na^+$ and $76^{2-}/2K^+$ indicates similarity of their ion solvation states which rationalizes their observed stereoselectivity in the alkylation reaction.



76 77^{2-} 78

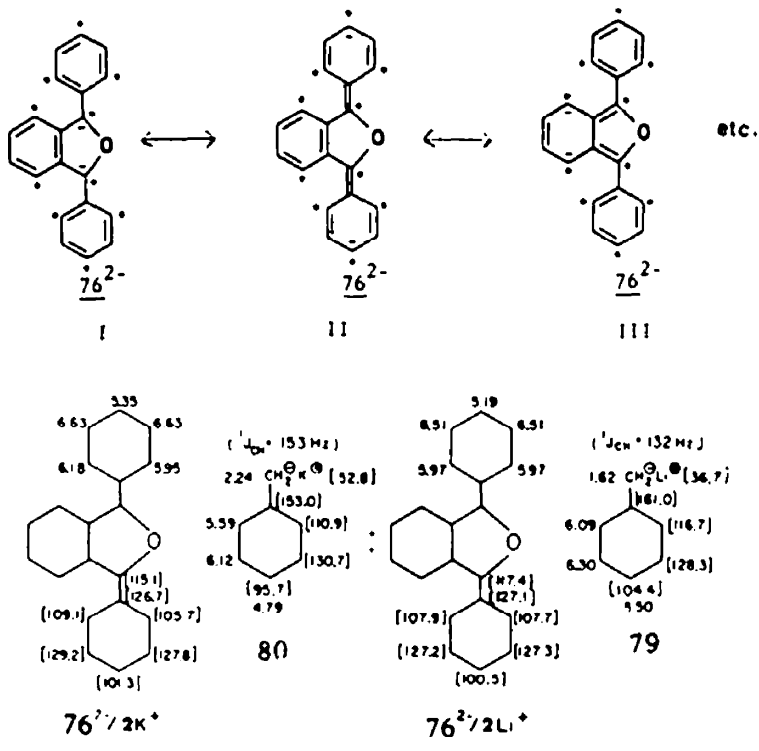


79 80

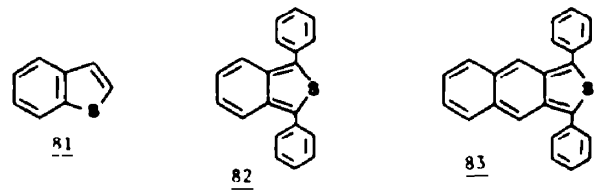
5.3. *Sulfur containing* $4n\pi$*-polyheterocyclic dianions*

Benzo[*b*]thiophene dianion (81^{2-}) is the first characterized $4n\pi$-electron dianion containing sulfur in its path of electron delocalization.[14a] Benzo[*b*]thiophene dianion (81^{2-}) having an α-hydrogen could be prepared only as disodium salt and showed only limited stability. It was found that the reaction path depends on the reaction conditions (cation, temperature) as demonstrated in Scheme 4.

The evolution of the ^1H NMR spectra as a result of the sodium reduction of benzo[*b*]thiophene (81^{2-}) is shown in Fig. 13. At first the spectrum of the starting material disappeared followed by the appearance of very broad signals accompanied by a well resolved spectrum of a diamagnetic species. This spectrum has been attributed to the *ortho*-metalation product of benzo[*b*]thiophene (**81a**). Five days later at −78°C the broad signal starts to split into several broad lines which after several more days rendered into a well resolved spectrum. The assignment of the minor product to the *ortho*-metalation product (**81a**) is corroborated by the absorption band at 189.1 ppm, characteristic of a carbon–lithium bond.[109] The final proof of this assignment was obtained from the comparison of this spectrum (Fig. 13) with the spectrum of the product obtained by the addition of butyllithium to benzo[*b*]thiophene (**81**) (Fig. 14). Benzo[*b*]thiophene dianion (81^{2-}) could not be prepared by lithium reduction because the metalation reaction dominates even at low temperature. An interesting characteristic of the ^{13}C NMR spectra of benzo[*b*]thiophene dianion (81^{2-}) is the existence of one absorption band which appears at a much higher field than all its other bands (*vide infra*).



Scheme 3. Proton (top) and carbon (bottom, parenthesis) NMR data of $76^{2-}/2K^+$ and $76^{2-}/2Li^+$ as compared with benzyllithium (79) and benzylpotassium (80).



The 1,3-diphenylbenzo[*c*]thiophene (82^{2-})[14c] and 1,3-diphenylnaphtho[*c*]thiophene (83^{2-})[14d] dianions were prepared recently and showed enhanced kinetic stability compared with 81^{2-}. This enhanced kinetic stability is to be expected as these two systems have no hydrogens at the α-positions to the sulfur atoms. These dianions show some common spectral characteristics:

(a) The centers of gravity of their ^1H NMR spectra appear in a relatively low-field which indicates a low paratropicity.

(b) The total change in carbon chemical shift ($\Sigma\Delta\delta^{13}C$) upon the two electron reduction of **82** and **83** to their respective dianions is high (278 and 261 ppm respectively). These large values which are larger even than those found for the reduction of **76** to 76^{2-} indicate, *inter alia*, the low π-charge density on the sulfur atoms.

(c) Both dianions (82^{2-}, 83^{2-}) show ^1H line broadening and ^{13}C NMR spectra which show that there is no free rotation about the C_1-C_1', and C_3-C_1', bonds (Figs 15 and 16). It should be noted that such a phenomenon was also observed in 76^{2-} (Fig. 12). In all three dianions (82^{2-}, 83^{2-} and 76^{2-}) there is a "flow" of charge into the phenyl substituents thus increasing to energy barrier for these rotations.

(d) Dianions 82^{2-} and 83^{2-} have ^{13}C spectra in which one band appears at high-field with respect to all other bands. It should be noted that this was also the case of benzo[*b*]thiophene dianion (81^{2-}) and reflects the effect of sulfur atom on the charge distribution in the charged systems.

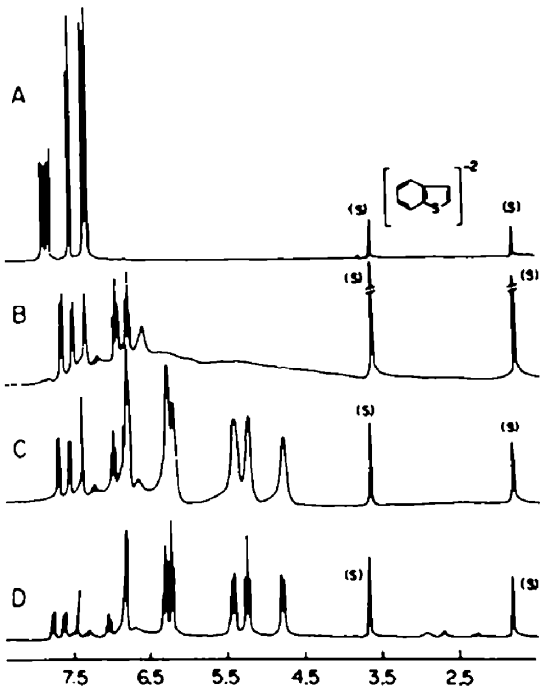


Fig. 13. The evolution of the 300 MHz ^{1}H NMR spectra of the sodium reduction of benzo[*b*]thiophene (**81**) in THF-d_8. (A) Starting material. (B) After two days. (C) After one week. (D) After ten days.

5.4. *The effect of the nature of the heteroatoms on the charge distribution of structurally related dianions*

It seems that the oxygen and the sulfur atoms of heterocyclic dianions, accommodate, in general, less charge than the pyridine-type nitrogen of heterocyclic dianions. The calculated charge densities of the nitrogen atoms of a series of dianions **34**$^{2-}$–**46**$^{2-}$ ranges between 0.21–0.84 units of charge per nitrogen, while the value obtained for 1,3-diphenylbenzo[*c*]furan dianions (**76**$^{2-}$) is only 0.11 units of charge. This is also partially the reason for the much smaller K_r values obtained for the pyridine type nitrogen containing dianions (Table 2) as compared with the oxygen and sulfur charged systems. The question which now arises is how the rest of the charge is delocalized on the other part of the molecule?

As stated before, in all the sulfur containing dianions prepared so far, one finds one carbon atom which is shifted to high-field more than the others. In the case of **82**$^{2-}$ and **83**$^{2-}$ we could show

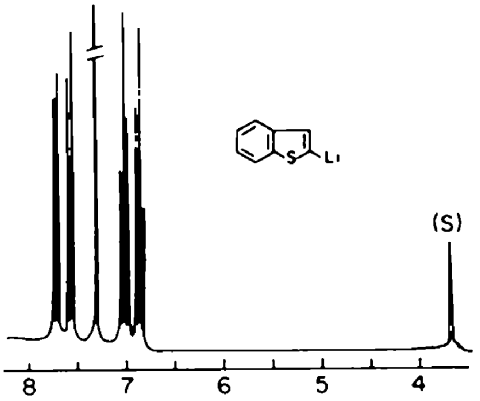


Fig. 14. 200 MHz ^{1}H NMR spectrum of the addition product **81a** of benzo[*b*]thiophene (**81**) and butyllithium in THF-d_8 at room temperature.

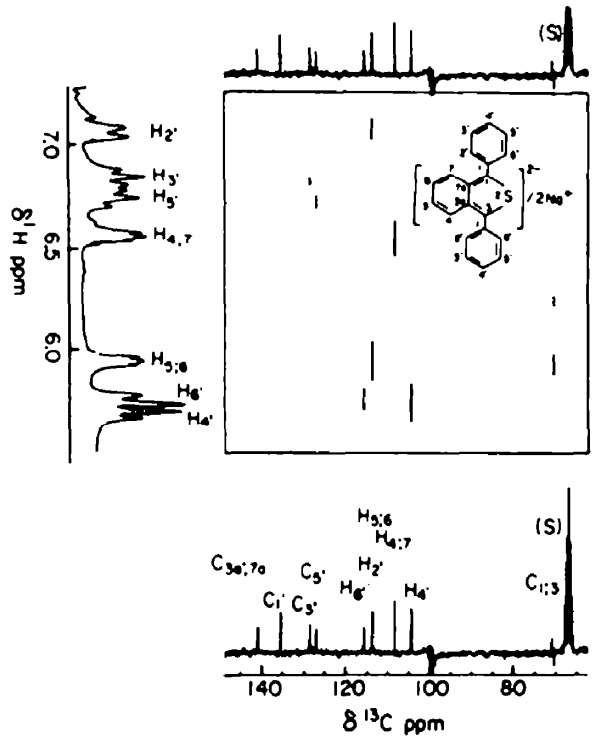


Fig. 15. 2D-NMR C/H correlation spectrum of 1,3-diphenylbenzo[*c*]thiophene dianion ($\mathbf{82}^{2-}$) as disodium salt in THF-d_8 at 253°K.

that these are the carbons which occupy the α-position to the sulfur. It therefore seems that the sulfur atoms polarize better the charge. The best two examples for assessment of the role played by the heteroatoms on the charge distribution are the two structurally related dianions $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$. For these two systems a complete analysis of the carbon spectra of the starting materials as well as of the dianions were carried out and afforded the estimation of the $\Delta\delta^{13}C$ values for each carbon of

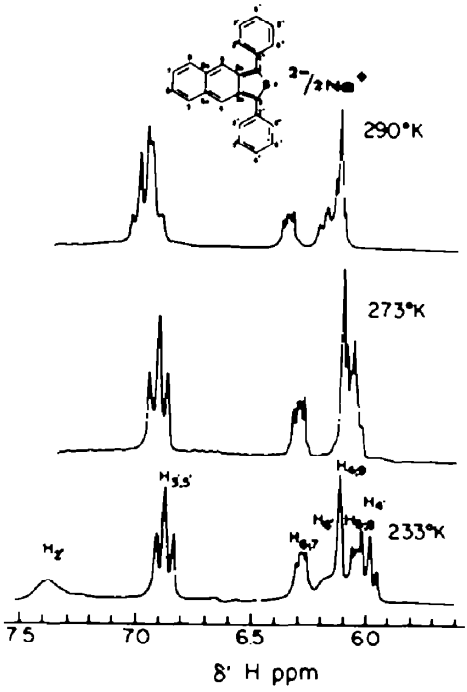
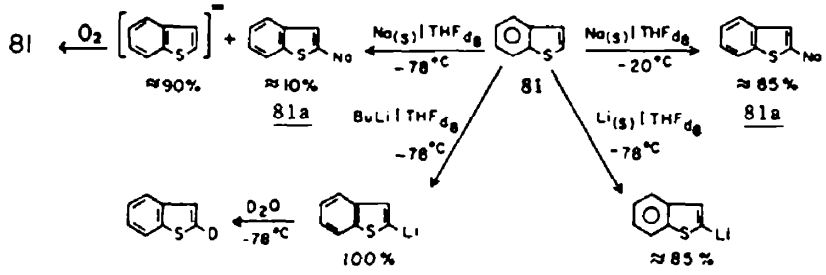


Fig. 16. 200 MHz ^{1}H NMR spectra of 1,3-diphenylnaphtho[*c*]thiophene dianion ($\mathbf{83}^{2-}$) as disodium salt in THF-d_8 at various temperatures.

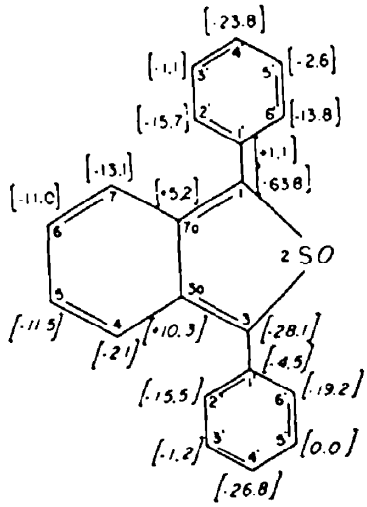


Scheme 4.

these two systems. Although it has been commented recently that carbon chemical shifts of doubly charged systems are influenced by anisotropic effects, the $\Delta\delta^{13}C$ of the specific carbon in the course of an electron transfer reaction is still one of the best indirect measures for charge density. This parameter is even more reliable when dealing with charged systems which exhibit only quenched paratropicity like $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$, provided that no change in the hybridization of the carbon occurs in the course of the reduction.

The $\Delta\delta^{13}C$ data for $\mathbf{82}^{2-}$ and $\mathbf{76}^{2-}$ are shown in Scheme 5 and demonstrate clearly that there is a much more pronounced polarization of charge towards the α-position in $\mathbf{82}^{2-}$ as compared with its oxa analogue $\mathbf{76}^{2-}$. The effect is quite pronounced as can be judged from the very significant difference between the $\Delta\delta^{13}C$ values of $C_{1,3}$ in $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$ (28.1 *vs* 63.4 ppm). One cannot, however, be sure that the $\Delta\delta^{13}C$ values are entirely due to charge density effect as a change in the hybridization of $C_{1,3}$ in $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$ may also contribute. There is no simple spectroscopic solution to this problem as $C_{1,3}$ are quaternary carbons.

The data presented in Scheme 5 demonstrate that much of the charge is located on $C_{1,3}$, on the *ortho* and *para* carbons ($C_{2,6,4}$) and on carbons $C_{4,7}$. Therefore, it seems that the best representation for $\mathbf{76}^{2-}$ and its sulfur analogue $\mathbf{82}^{2-}$ is the resonance hybrid of structures I, II and III (Scheme 3). Structure I is reminiscent of Smith and McCall's suggestion that $\mathbf{76}^{2-}$ can be regarded as two isolated benzylic anions.[104] The contribution of structure II is manifested by the high energy barrier observed for the rotation about C_1–$C_{1'}$ and C_3–$C_{1'}$ bonds both in $\mathbf{76}^{2-}$[14b] and $\mathbf{82}^{2-}$.[14c] It is interesting to note that the charges of 1,3-diphenylbenzo[*c*]furan and 1,3-diphenylbenzo[*c*]thiophene dianions ($\mathbf{76}^{2-}$, $\mathbf{82}^{2-}$) are by no means distributed uniformly and that the quaternary carbons $C_{3a,7a}$ exhibit down-field shift although $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$ are negatively charged systems. Moreover, it seems that the charges are distributed only on parts of the molecules in an alternating mode (*vide infra*).



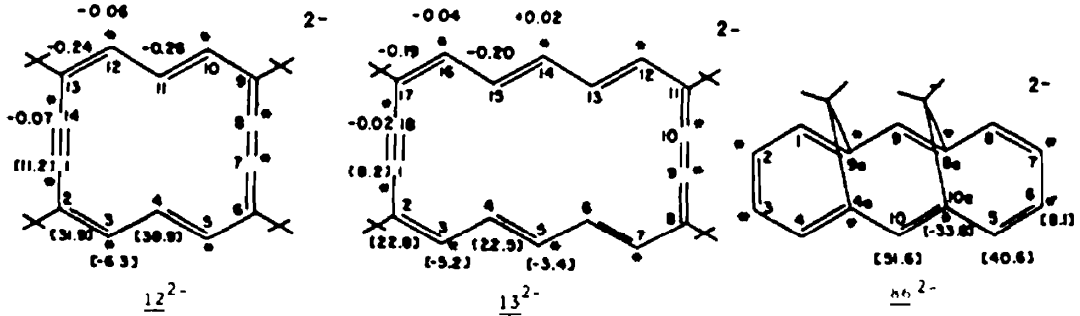
Scheme 5. Values of $\Delta\delta^{13}C$ for $\mathbf{76}^{2-}$ and $\mathbf{82}^{2-}$. Numbers in parentheses: for $\mathbf{82}^{2-}$ (upper part), for $\mathbf{76}^{2-}$ in the lower part of the formula.

6. THE APPLICATION OF THE CHARGE ALTERNATION CONCEPT TO π-CONJUGATED DOUBLY CHARGED SYSTEMS: SELECTED EXAMPLES

The two main models for predicting and explaining the electron delocalization pattern of π-conjugated systems and assigning their aromatic character are Platt's peripheral model[110] and the conjugated circuits approach of Randić.[111] While the former emphasizes the importance of the largest conjugated circuit in the molecule, the latter stresses the importance of the smaller conjugated circuits. These two opposite models were confronted and several systems were prepared and characterized by NMR in order to verify which of the two models describe better their π-electron delocalization patterns. Some selected recent examples are the diindeno[*cd,lm*]perylene (**84**) and acenaphthylene (**6**) and their respective dianions $\mathbf{84}^{2-}$ and $\mathbf{6}^{2-}$,[61,77,112] as well as the [14]-annuleno[14]annulene (**85**) and its di- and tetraanions ($\mathbf{85}^{2-}$ and $\mathbf{85}^{4-}$).[95] Recalling the charge distribution of 1,3-diphenylbenzo[*c*]furan dianion ($\mathbf{76}^{2-}$) (Scheme 3), that of 1,3-diphenylbenzo[*c*]thiophene dianion ($\mathbf{82}^{2-}$) (Scheme 5) and the charge alternation concept (see below), it seems that a basic characteristic of polycharged systems, namely, their mode of charge distribution has been neglected.

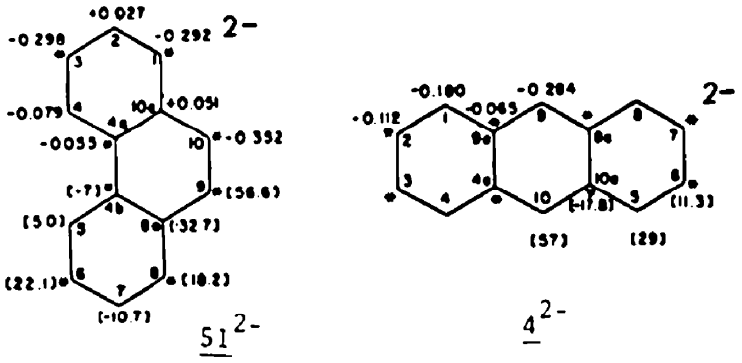
The charge alternation concept originally introduced by Klein as a directive effect of polymetalations,[113,114] states that in a charged molecule, the charge is distributed non-uniformly in an alternating mode. This charge alternation results in donor–acceptor interactions which stabilize the charged system. It is understandable that in the annulene series with D_{nh} symmetry, one should not expect a full charge alternation due to symmetry reasons. In the case of π-conjugated cyclic systems one has to divide the systems into various subsystems according to their symmetry.[115a] The subsystems are divided into starred and nonstarred sets of atoms in a way that the starred set is the longest. The charge alternation concept predicts that in general the charge will be distributed on the starred set. In those cases where the starred set is constituted of a relatively large number of quaternary carbons or brings about severe Coulombic repulsions, the charge will be distributed in an alternating mode but on the nonstarred set of atoms. Coulombic repulsions may arise when several starred atoms from the different subsystems are adjacent atoms. This concept which was tested on 25 doubly charged systems from different families of charged systems seems to predict the charge distribution quite nicely.[115a] The charge distribution has been tested in two levels, computationally and experimentally[115a] and therefore each carbon atom is characterized by two numbers. One is the calculated charge density difference between the neutral and the charged system or the charge density of the charged system (Δq^{π} or q^{π}) and the other is the change in the carbon chemical shift ($\Delta\delta^{13}C$) or the actual chemical shift of the charged system which is taken as an experimental measure of charge density.

The charge distribution of the annulenes shown in Scheme 6 is in total agreement with the prediction of the charge alternation concept. For example, bisecting $\mathbf{12}^{2-}$ through the C_1–C_{14} and C_7–C_8 bonds results in two subsystems in which the charge alternation prevails. As an example, compare the data for the nonstarred atoms C_2 and C_4 ($\Delta q^{\pi} = -0.24$ and -0.26, $\Delta\delta^{13}C = 31.9$ and 38.9 ppm) with that of their neighbors C_1 and C_3 ($\Delta q^{\pi} = -0.07$ and -0.06; $\Delta\delta^{13}C = 11.2$ and -6.3 ppm). It should be noted that C_3 which is in between C_2 and C_4 which are the most negatively charged atoms of $\mathbf{12}^{2-}$, is shifted down-field by the amount of 6.3 ppm ($\Delta\delta^{13}C = -6.3$ ppm) although $\mathbf{12}^{2-}$ is a dianion in which one expects high-field shifts. Bisection of $\mathbf{13}^{2-}$ through C_1–C_{18} and C_9–C_{10} reveals the same charge distribution. In these annulene dianions ($\mathbf{12}^{2-}$, $\mathbf{13}^{2-}$ and



$\underline{12}^{2-}$ $\underline{13}^{2-}$ $\underline{86}^{2-}$

Scheme 6. Charge distribution on annulene dianions: numbers on top represent the charge on each carbon atom (Δq^{π}), numbers in parentheses represent the ^{13}C chemical shift $\Delta\delta^{13}C$ between the neutral and the charged system (positive values represent a high-field shift).



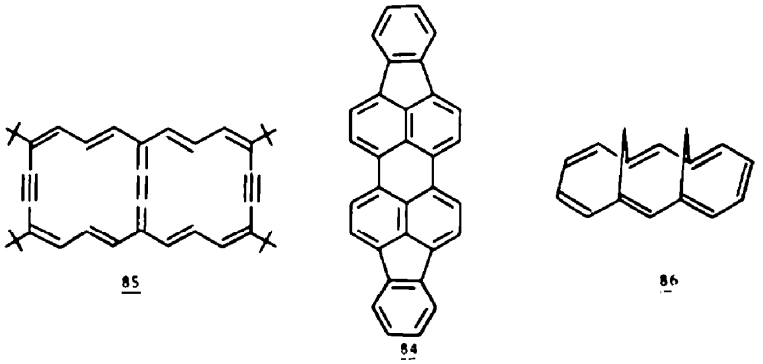
Scheme 7.

86^{2-})[57,116] a small perturbation in the symmetry of the systems imposes pronounced charge alternation.

The phenanthrene dianion (51^{2-}) and anthracene dianion (4^{2-}) exemplify the application of this concept to polycyclic dianions (Scheme 7). Bisecting 51^{2-} with the plane of symmetry across the C_9–C_{10} and C_{4a}–C_{4b} bonds gives two benzylic fragments. In each of these fragments the charge alternation is like that in the benzylic anion except on C_{4a} and C_{4b} where charge repulsion leads to a relatively low negative charge. Compare, for example, the differences in the chemical shift and the calculated charge density of the starred atoms $C_{9,10}$, $C_{1,8}$ and $C_{3,6}$ with the nonstarred carbons $C_{2,7}$, $C_{4,5}$ and $C_{8a,10a}$ in the phenanthrene dianion 51^{2-}. It is interesting to note that for the nonstarred carbons $C_{2,7}$ of 51^{2-} calculation predicts a small *positive* charge in contrast to the high negative charge of their starred neighbors ($C_{1,3}$ and $C_{6,8}$). This calculation is corroborated by the unusual down-field shift (10.7 ppm) of the $C_{2,7}$ absorption band in the phenanthrene dianion (51^{2-}). Quaternary carbons of *anions* prefer to accommodate *positive* charges. From the two types of quaternary carbons of phenanthrene dianion (51^{2-}) the nonstarred atoms $C_{4a,4b}$ ($\Delta\delta^{13}C = -7$ ppm) behave as charge acceptors as compared to the nonstarred $C_{10a,8a}$ ($\Delta\delta^{13}C = -32.7$ ppm, see Scheme 7).

In the anthracene dianion (4^{2-}) bisection across the C_2–C_3, C_{4a}–C_{9a}, C_{8a}–C_{10a}, and C_6–C_7 bonds leads again to two subsystems. The main charge in 4^{2-} is not located on the starred set because such a contribution will result in a pronounced Coulombic repulsion. The starred set has also the disadvantage of including quaternary carbons which accommodate negative charges with difficulty. Still, the amount of charge in the case of anthracene dianions 4^{2-} is distributed in an alternating mode.

In view of the above discussion it appears that the charge density is not uniformly distributed, but appears in an alternating mode.



SUMMARY AND OUTLOOK

The easy preparation and stability of polycarbocyclic and polyheterocyclic dianions affords systems which enable an insight and a better understanding of the paratropicity of π-conjugated

charged systems as related to their total number of π-electrons. NMR studies (proton and carbon) afford an experimental tool for the evaluation of the patterns of charge delocalization and charge distribution in π-conjugated polycyclic dianions. It has been shown that the topology of the system plays a decisive role in its electronic structure. In several cases a partitioning of charge could be observed (as well as a segregation of M.O.s), a situation unprecedented in π-conjugated systems. This charge partitioning is rationalized by the relative paratropicities of the charged and uncharged components.

More specific points to be raised are the following:

(a) The ^1H line shapes of polycarbocyclic and polyheterocyclic dianions depend on the HOMO–LUMO energy gap (ΔE). The narrower is the gap the more paratropic is the dianion as manifested by the high-field shift and broad lines.

(b) Heteroatoms quench the paratropicity of $4n\pi$-polycyclic dianions. In the nitrogen heterocycles there is a relatively high charge density on the nitrogen atom.

(c) Factors which govern the ion-solvation equilibrium can not account for the stability of the dianions as well as the ^1H NMR lineshapes.

(d) In the case of the nitrogen heterocyclic dianions, sodium cations are the preferred ones. Lithium as counter cation tends to destabilize the system.

(e) The requirements for stable nitrogen containing dianions are: no α-hydrogens and steric hindrance at the nitrogen atoms.

(f) Sulfur and oxygen containing polyheterocyclic dianions can indeed be prepared. Sulfur tends to polarize the charge more than oxygen. These systems are even less paratropic than dianions of the nitrogen series.

A more elaborate theoretical study is required in order to establish the exact relationships between paratropicity and the detailed electronic structure. In the polycyclic anions the charge alternation concept applies, and enables us to arrive at the particular charge distribution on the various carbon atoms. The charge tends to arrange in an alternating fashion. The possibility of applying such dianions in synthesis on the one hand, and in photophysics on the other, may open new avenues in the research of polycarbocyclic and polyheterocyclic dianions.

Acknowledgement—We gratefully acknowledge support from the U.S. Israel Binational Science Foundation.

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