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New Polyheterocyclic 4$n\pi$-Electron Dianions: Paratropicity, Charge Delocalization, and Reactions

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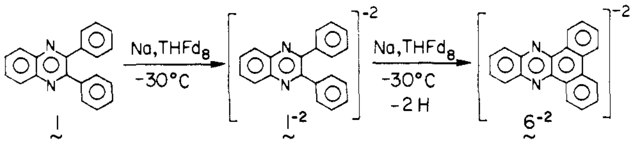
Abstract: A novel class of anions, namely, nitrogen-containing polyheterocyclic dianions, is described. These species show a very interesting spectral and chemical behavior. 2,3-Diphenylquinoxaline (**1**), 1,4-diphenylphthalazine (**2**), 2,3,7,8-tetraphenylpyrzo[2,3-*g*]quinoxaline (**3**), tribenzo[*a*,*c*,*i*]phenazine (**4**), and 2,3-diphenyldibenzo[*f*,*h*]quinoxaline (**5**) were reduced by alkali metals to the corresponding 4$n\pi$ conjugated dianions. The ^{1}H and ^{13}C NMR spectra as well as theoretical calculations ($\omega\beta$) are reported and discussed in terms of the mode of charge delocalization and its relevance to paratropicity in these systems. The proton NMR line shapes of these charged species correlate with the energy difference calculated between their ground and first excited states. The striking differences in the ^{1}H and ^{13}C spectra of the two apparently similar dianions **1**$^{2-}$ and **2**$^{2-}$ are rationalized by the calculated HOMO-LUMO energy gaps. A very unusual mode of charge delocalization is detected in the NMR spectrum of the doubly charged system **4**$^{2-}$, rationalized by a partitioning of the conjugated system into an uncharged phenanthrene-like moiety and a benzo[*g*]quinoxaline dianion moiety. A thermal ring closure reaction of **1**$^{2-}$ and **5**$^{2-}$ has been observed, forming dibenzo[*a*,*c*]phenazine dianion **6**$^{2-}$ and phenanthrazine dianion **7**$^{2-}$, respectively. This reaction opens up a new pathway to synthetic transformations of heterocycles.

"Actually, the inherent assumptions of the method (HMO) are so unrealistic we marvel that the theory finds use at all!"[1] And yet, an outstanding achievement of the HMO theory is the prediction by Hückel's rule[2] that $(4n + 2)\pi$-electron systems are conjugatively stabilized. In 1965 Breslow coined the term antiaromaticity[3] to emphasize the fact that 4$n\pi$-conjugated monocycles are destabilized by conjugation. Ever since, difficulties inherent in the concept of aromatic or antiaromatic character burden experimentalists and theoreticians. Yet, these concepts are invoked to interpret variegated structural, physical, and chemical phenomena.[4] The most comprehensive definition of aromatic nature is the energy content of cyclic conjugated systems relative to a relevant model compound devoid of such cyclic delocalization.[5]

The major criteria, ensuing for aromaticity and antiaromaticity from theoretical concepts, are Hückel's rule, Platt's peripheral model[6] (which is an extension of the Hückel rule to polycyclic hydrocarbons), and Randić's conjugated circuits.[7a-c] The latter criterion has been extended recently to encompass polycyclic aza compounds.[7d] Among the observable phenomena, the most useful definition of aromatic character is based on magnetic anisotropy.[8] A system is considered aromatic if it sustains a diamagnetic ring current and shows consequently a total diatropic (downfield) ^{1}H NMR chemical shift relative to vinylic protons. However, 4$n\pi$ antiaromatic systems are expected to show a paratropic (upfield) shift in ^{1}H NMR.[9] Recently, a link between a computational descriptor and a physical observation, viz., the HOMO-LUMO energy gap and the paratropic shift in the ^{1}H NMR, was demonstrated. In the polycyclic 4$n\pi$ conjugated anions, the HOMO-LUMO gap was proposed as a criterion for antiaromaticity.[9b] These systems are stable enough to be investigated by chemical and spectroscopic methods and thus allow the study of the link between paratropicity and 4$n\pi$ conjugated arrays of electrons. Now, contrary to the comprehensive studies of charged carbocyclic systems,[10] information concerning heterocyclic 4$n\pi$ dianions is rather limited.[11] The supposition that the presence of a heteroatom may affect the pattern of charge delocalization

Scheme I



Scheme II

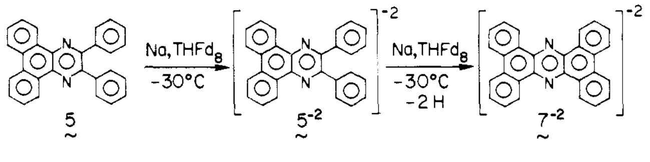


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Table I. ^{1}H NMR Parameters of Doubly Charged Heterocyclic System of **1–4** and **7** in THF-d_8

system[a]	temp, K	^{1}H NMR pattern[a,b]	neutral system center of gravity	charged system center of gravity	calcd high field[e]
$\mathbf{1}^{2-}/2Na^+$	292	6.88 (d, J = 7.5, 4 H, $H_{2',6'}$), 6.76 (t, J = 7.6, 4 H, $H_{3',5'}$), 6.58 (t, J = 7.0, 2 H, $H_{4'}$), 4.67 (br s, 2 H, $H_{6,7}$), 4.13 (br s, 2 H, $H_{5,8}$)	7.64	6.09	2.03
$\mathbf{1}^{2-}/2Na^+$	203	6.75 (d, J = 7.4, 4 H, $H_{2',6'}$), 6.67 (t, J = 7.1, 4 H, $H_{3',5'}$), 6.52 (t, J = 6.8, 2 H, $H_{4'}$), 4.44 (br s, 2 H, $H_{6,7}$), 3.62 (br s, 2 H, $H_{5,8}$)	7.64	5.92	2.25
$\mathbf{2}^{2-}/2Na^+$	300	7.21 (d, J = 8.1, 4 H, $H_{2',6'}$), 6.71 (t, J = 7.1, 4 H, $H_{3',5'}$), 6.33, 5.84 (AA′BB′, 4 H, $H_{6,7}$, $H_{5,8}$), 5.96 (t, J = 7.1, 2 H, $H_{4'}$)	7.86	6.57	1.69
$\mathbf{2}^{2-}/2Na^+$	213	7.20 (d, J = 8.1, 4 H, $H_{2',6'}$), 6.70 (t, J = 7.6, 4 H, $H_{3',5'}$), 6.31, 5.78 (AA′BB′, 4 H, $H_{6,7,5,8}$), 5.91 (t, J = 7.1, 2 H, $H_{4'}$)	7.86	6.54	1.73
$\mathbf{3}^{2-}/2Na^+$	298	7.12 (d, J = 7.2, 8 H, $H_{2',6'}$), 6.95 (t, J = 7.6, 8 H, $H_{3',5'}$), 6.85 (t, J = 6.9, 4 H, $H_{4'}$), 4.48 (s, 2 H, $H_{5,10}$)	7.69	6.77	1.89
$\mathbf{4}^{2-}/2Li^+$	295	8.09 (d, J = 8.0, 2 H, $H_{4,5}$), 7.71 (d, J = 6.8, 2 H, $H_{1,8}$), 7.00 (t, J = 6.9, 2 H, $H_{2,7}$), 6.81 (t, J = 7.3, 2 H, $H_{3,6}$), 5.93 (br s, 4 H, $H_{11,12,13,14}$), 4.70 (s, 2 H, $H_{10,15}$)	8.43	6.60	2.39
$\mathbf{4}^{2-}/2Na^+$	293	8.04 (d, J = 7.9, 2 H, $H_{4,5}$), 7.76 (d, J = 8.2, 2 H, $H_{1,8}$), 7.01 (t, J = 7.0, 2 H, $H_{2,7}$), 6.75 (t, J = 7.5, 2 H, $H_{3,6}$), 5.71 (br s, 4 H, $H_{11,12,13,14}$), 4.49 (s, 2 H, $H_{10,15}$)	8.43	6.50	2.53
$\mathbf{4}^{2-}/2Na^+$	203	8.01 (d, J = 8.1, 2 H, $H_{4,5}$), 7.62 (d, J = 8.6, 2 H, $H_{1,8}$), 6.95 (t, J = 7.7, 2 H, $H_{2,7}$), 6.73 (t, J = 7.6, 2 H, $H_{3,6}$), 5.58 (AA′BB′, 4 H, $H_{11,12,13,14}$), 4.27 (s, 2 H, $H_{10,15}$)	8.43	6.25	2.85
$\mathbf{7}^{2-}/2Na^+$	213	7.55 (d, J = 8.3, 4 H, $H_{4,5,13,14}$), 6.80 (d, J = 8.3, 4 H, $H_{1,8,10,17}$), *d* 6.71 (t, J = 7.3, 4 H, $H_{2,7,11,16}$), 6.39 (t, J = 6.7, 4 H, $H_{3,6,12,15}$)	*d*	6.86	*d*

[a] For numbering, see Chart I. [b] Chemical shifts are given in ppm referenced to Me_4Si (for numbering see the chart and schemes; coupling constants are given in Hz). [c] Abbreviations: s = singlet, d = doublet, t = triplet, br = broad bands. [d] No ^{1}H spectrum could be observed for **7** in THF. [e] In units of charge; calculated according to the chemical shifts charge density correlations for carbocyclic systems.[15a,b]

Table II. ^{13}C NMR Parameters of the Doubly Charged Heterocyclic Systems of **1–4** and **7** in THF

system[a]	temp, K	NMR chemical shift, ppm[b]	neutral system center-of gravity	charged system center of gravity	$\Delta\delta(^{13}C)$
$\mathbf{1}^{2-}/2Na^+$	213	163.6, 145.6, 139.2, 126.8, 126.3, 120.6, 116.4, 100.3	133.6	129.2	88
$\mathbf{2}^{2-}/2Na^+$	213	140.9, 138.7, 127.7, 121.2, 120.8, 115.2, 109.5, 107.9	132.6	122.5	202
$\mathbf{2}^{2-}/2Na^+$	273	140.6, 138.9, 127.9, 121.5, 120.5, 115.5, 110.3, 108.9	132.6	122.7	198
$\mathbf{3}^{2-}/2Na^+$	293	157.2, 144.7, 138.2, 128.8, 127.6, 124.3, 93.8	134.8	132.2	88.4
$\mathbf{4}^{2-}/2Na^+$	293	159.9, 139.7, 139.0, 128.2, 125.5, 123.9, 121.8, 120.0, 118.3, 118.1, 117.9, 96.8	129.3	125.8	84
$\mathbf{7}^{2-}/2Na^+$	213	151.1, 126.4, 124.2, 123.3, 121.7, 119.1, 116.2	*c*	126.0	*c*

[a] For numbering, see Chart I. [b] Chemical shifts are given in ppm referenced to Me_4Si. [c] These data could not be obtained because of the limited solubility of **7** in THF.

in the charged systems, as well as their chemical behavior, motivated us to study the preparation and the spectroscopic properties of this intriguing class of anions. Although a recent publication claimed that heterocyclic anions are extremely unstable,[12a] the chemistry of such systems has been reported.[12b,c] We report the spectroscopy and the chemical properties of nitrogen-containing polycyclic dianions. The results are discussed in terms of charge delocalization and the antiaromatic contribution to paratropicity. ^{1}H NMR line broadening is rationalized by a narrow HOMO–LUMO gap, which is manifested by a thermal equilibrium between the singlet and the triplet states.[13] This phenomenon will be demonstrated by systems $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$. The system $\mathbf{4}^{2-}$ shows a peculiar mode of charge delocalization as deduced from its NMR spectra. This phenomenon is rationalized by the pictorial statement that even an alternant charged conjugated system would adopt a pattern of charge delocalization that minimizes the antiaromatic contribution. In dianions $\mathbf{1}^{2-}$ and $\mathbf{5}^{2-}$, we encountered a thermal ring-closure reaction which forms a new carbon–carbon bond.[12b] This reaction is reminiscent of the photochemical transformation of stilbene to phenanthrene.[14]

Results

The reduction of the parent systems 2,3-diphenylquinoxaline (**1**), 1,4-diphenylphthalazine (**2**), 2,3,7,8-tetraphenylpyrazo[2,3-*g*]quinoxaline (**3**), tribenzo[*a*,*c*,*i*]phenazine (**4**), and 2,3-diphenyldibenzo[*f*,*h*]quinoxaline **5** (Chart I) was carried out in THF-d_8 as solvent with sodium or lithium wire. In each case, the spectrum of the parent system disappears, due to the formation of a paramagnetic species in the first one-electron reduction step. Following the second one-electron reduction, a new spectrum appears at high field, which is attributed to the diamagnetic dianion. The proton and carbon NMR parameters of the charged systems are reported in Tables I and II. The dianionic nature was deduced from their carbon and proton spectra[15] and quenching

Chart I

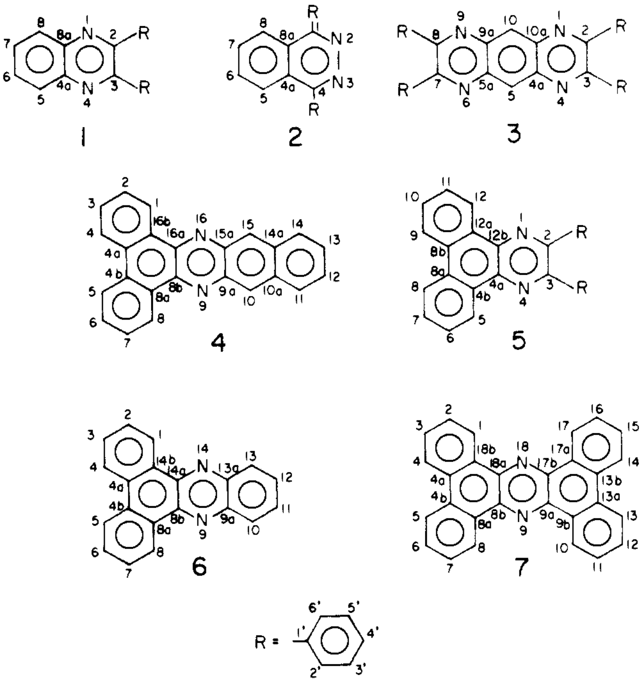

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Table III. HOMO-LUMO Energy Gap, Line Broadening, and Charge Density of the Heterocyclic Dianions[a]

HOMO-LUMO energy gap[b,c]	$\mathbf{3}^{2-\,d}$	$\mathbf{4}^{2-}$	$\mathbf{2}^{2-\,d}$	$\mathbf{1}^{2-\,d}$	$\mathbf{7}^{2-\,e}$	$\mathbf{5}^{2-\,d,e}$
HOMO-LUMO energy gap[b,c]	0.38	0.31	0.29	0.19	0.11	0.11
detectable line broadening				+	+	*f*
net charge on nitrogen	-0.265	-0.321	-0.205	-0.418	-0.372	-0.364
maximum net charge on carbon	-0.219	-0.192	-0.241	-0.221	-0.079	-0.132

[a] For numbering, see Chart I. [b] As obtained by $\omega\beta$ calculation.[16] [c] The HOMO-LUMO energy gaps are given in β units. [d] The calculations were carried out assuming β as 0.5 for the bond between the phenyl groups and the aromatic skeleton. [e] Calculations were run for these systems with ω = 1.0 (see text).[16c] [f] No spectrum could be recorded at all.

experiments. The sodium reduction products of **2**, **4**, **6**, and **7** showed ^{1}H and ^{13}C NMR spectra which persisted under refrigeration for months. The reduction process of **3** seems to proceed beyond the formation of the dianion $\mathbf{3}^{2-}$. After 2 days, the well-resolved spectrum of $\mathbf{3}^{2-}/2\mathrm{Na}^+$ broadened, and after 3 days no NMR signal could be detected. Lithium salts were found to be less stable and could be observed only in the case of the process $\mathbf{4} \rightarrow \mathbf{4}^{2-}$.

In the course of the reduction of $\mathbf{1}^{2-}$ and $\mathbf{5}^{2-}$, we encountered an interesting process: ring closure to dianions $\mathbf{6}^{2-}$ and $\mathbf{7}^{2-}$, respectively (Schemes I and II). The structure of the product from **1** was deduced from the identity of its spectrum with the spectrum of an independently prepared dianion from dibenzo[*a*,*c*]phenazine (**6**).[11b] Dianion $\mathbf{7}^{2-}$ could not be prepared from the neutral heterocycle **7** due to the insolubility of the latter. However, the structural parameters of the product from **5** (^{1}H and ^{13}C) are in line with a symmetrical species.

HOMO-LUMO energy gaps and charge distribution in the doubly charged species are reported in Tables III and IV. As in the case of the carbocycles, the MO technique was "$\omega\beta$", this time amplified[16a] by parameters[16b] for =N— and the aromatic C—N bonds: $\alpha(\mathrm{N}) = \alpha(\mathrm{C}) + 0.4\beta(\mathrm{CC})$, $\beta(\mathrm{CN}) = \beta(\mathrm{CC})$, $\beta(\mathrm{NN}) = \beta(\mathrm{CC})$. In cases **1**–**4** and **6**, the habitual position was used, ω = 1.4. For **5** and **7** we used a narrower step,[16c] ω = 1.0, since $\mathbf{5}^{2-}$ and $\mathbf{7}^{2-}$ could not be converged with ω = 1.4. A check showed that switching to ω = 1.0 affects only insignificantly the results for **1**–**4**.

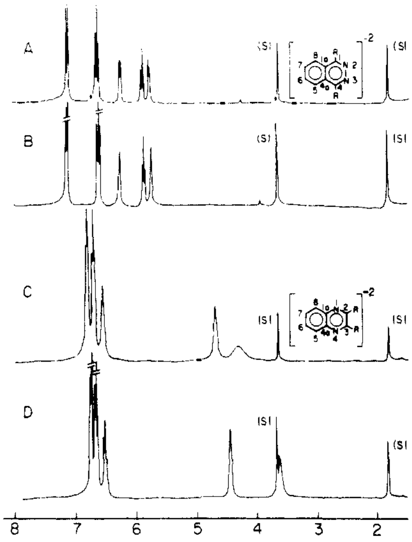

Figure 1. ^{1}H NMR spectra of 1,4-diphenylphthalazine dianion ($\mathbf{2}^{2-}$) and 2,3-diphenylquinoxaline dianion ($\mathbf{1}^{2-}$) in THF-d_8. (A) $\mathbf{2}^{2-}/2\mathrm{Na}^+$, 300 K; (B) $\mathbf{2}^{2-}/2\mathrm{Na}^+$, 213 K; (C) $\mathbf{1}^{2-}/2\mathrm{Na}^+$, 292 K; (D) $\mathbf{1}^{2-}/2\mathrm{Na}^+$, 203 K.

Discussion

The 4*n*π-electron systems are intriguing in view of their paratropicity and tendency to exist at least to some extent as ground-state triplets.[17] There is some parallelism between the conjugated 4*n*π series derived from the polycyclic hydrocarbon dianions and the respective aza derivatives. The calculated HOMO-LUMO gap is narrow in both series, as expected for 4*n*π conjugated systems. This narrow gap influences the line shape and the degree of the paratropicity of the dianions. The presence of a heteroatom influences the charge densities and, to some extent, the HOMO-LUMO gap, so that proton and carbon NMR parameters of the dianions containing even two fused rings can be studied.[18] The paratropicity of the systems arises from an effective delocalization of 4*n*π electrons. The introduction of electronegative nitrogen atoms into the path of conjugation may quench this electron distribution and hence the systems' paratropicity. This can be demonstrated by comparing the HOMO-LUMO energy gap and the ^{1}H NMR line shape of phenanthrene dianion[13] with those of benzo[*c*]cinnoline dianion[11b] and of 1,2,3,4-dibenzoanthracene[13] dianion with those of dibenzo[*a*,*c*]phenazine dianion[11b] ($\mathbf{6}^{2-}$).[11b] The fact that we were able to monitor and study heterocyclic dianions with only two fused rings (naphthalene skeleton) is another manifestation of the partial quenching of the paratropicity of the system.[19]

Although **1** and **2** are related compounds, the solution of $\mathbf{1}^{2-}$ and the solution of $\mathbf{2}^{2-}$ revealed entirely different ^{1}H NMR spectra (Figure 1). The main differences are (i) the ^{1}H NMR spectrum of $\mathbf{1}^{2-}$ shows line broadening while that of $\mathbf{2}^{2-}$ does not; (ii) the spectrum of $\mathbf{2}^{2-}$ is almost unaffected by temperature while $\mathbf{1}^{2-}$ shows a strong temperature dependence; and (iii) in 2,3-diphenylquinoxaline dianion ($\mathbf{1}^{2-}$), only a small portion of the negative charge is located on the phenyl moieties. This is deduced from calculations and from the proton absorption of the para hydrogen of the phenyl group. The band attributed to the para hydrogen appears at 6.58 in $\mathbf{1}^{2-}$, vs. 5.91 in $\mathbf{2}^{2-}$.

As previously mentioned, 4*n*π-electron systems tend to exist as ground-state triplets.[17] It was construed that line-broadening and, in extreme cases, disappearance of the spectrum of doubly charged 4*n*π-electrons carbocyclic dianions arise from paramagnetic dilution due to thermal equilibrium between the ground state and a low-lying triplet.[13] A correlation was demonstrated between the extent of line broadening and the HOMO-LUMO energy gap, as given by $\omega\beta$. The calculated gaps for $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ are 0.19β and 0.29β, respectively (Table III). In $\mathbf{2}^{2-}$, the gap is relatively high, predicting negligible concentration of the triplet and therefore no line broadening is expected. The high-field shift of the para hydrogen of the phenyls in $\mathbf{2}^{2-}$, relative to those of $\mathbf{1}^{2-}$, can be understood in terms of charge delocalization. In $\mathbf{2}^{2-}$ the phenyl rings are less hindered sterically and can attain better coplanarity and orbital overlap with the polycyclic backbone. Even if the same extent of coplanarity is assumed in $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$, as was done in calculating these two dianions, a higher charge density is predicted at the phenyl moiety of $\mathbf{2}^{2-}$ than in $\mathbf{1}^{2-}$: -0.226 vs. -0.092 electron units, respectively (Table IV). The better overlapping between the aromatic moiety and the phenyl groups in the 1,4-diphenyl-

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(18) Interestingly, the NMR spectrum of naphthalene dianion has never been reported. However, Gerson et al. have recently reported the preparation and ESR observation of 1,8-diphenylnaphthalene trianion radical. See: Gerson, F.; Heckendorn, R.; Mockel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 689; *Helv. Chim. Acta* **1985**, *68*, 1923.

(19) As the referee suggested, another explanation for the partial quenching of the paratropicity of heterocyclic dianions compared with the analogous carbocyclic ones may be the partial deviation from coplanarity at the nitrogen atoms. This explanation cannot be ruled out as no X-ray data for such a dianion are available.

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Table IV. Charge Density of the Heterocyclic Dianions[a,b]

system	net charge calcd by the $\omega\beta$ technique
$\mathbf{1}^{2-d}$	$N_{1,4} = -0.418$; $C_{2,3} = -0.117$; $C_{5,8} = -0.221$; $C_{6,3} = -0.116$; $C_{4a,8a} = -0.048$; $C_{1'} = -0.018$; $C_{2',6'} = -0.014$; $C_{3',5'} = -0.008$; $C_{4'} = -0.020$
$\mathbf{2}^{2-d}$	$C_{1,4} = -0.241$; $N_{2,3} = -0.205$; $C_{5,8} = -0.186$; $C_{6,7} = -0.098$; $C_{4a,8a} = -0.043$; $C_{1'} = -0.051$; $C_{2',6'} = -0.038$; $C_{3',5'} = -0.021$; $C_{4'} = -0.057$
$\mathbf{3}^{2-d}$	$N_{1,4,6,9} = -0.265$; $C_{2,3,7,8} = -0.074$; $C_{4a,5a,9a,10a} = -0.030$; $C_{5,10} = -0.219$; $C_{1'} = -0.004$; $C_{2',6'} = -0.005$; $C_{3',5'} = -0.002$; $C_{4'} = -0.005$
$\mathbf{4}^{2-}$	$C_{1,8} = -0.019$; $C_{2,7} = -0.031$; $C_{3,6} = -0.032$; $C_{4,5} = -0.018$; $C_{4a,5a} = -0.050$; $C_{8a,16b} = -0.049$; $C_{8b,16a} = -0.057$; $N_{9,16} = -0.321$; $C_{9a,15a} = -0.033$; $C_{10,15} = -0.192$; $C_{10a,14a} = -0.046$; $C_{11,14} = -0.088$; $C_{12,13} = -0.065$
$\mathbf{7}^{2-c}$	$C_{1,8,10,17} = -0.017$; $C_{2,7,11,16} = -0.054$; $C_{3,5,12,15} = -0.037$; $C_{4,5,13,14} = -0.024$; $C_{4a,4b,13a,13b} = -0.073$; $C_{8a,9b,17a,18b} = -0.079$; $C_{8b,9a,17b,18a} = -0.03$; $N_{9,18} = -0.372$

[a] For numbering, see Chart I. [b] As deduced from $\omega\beta$ calculations.[16] The calculations were run assuming $\omega = 1.4$, unless otherwise cited. [c] $\omega = 1.0$ because convergence could not be obtained for $\mathbf{7}^{-2}$ using the ordinary value of ω, i.e., 1.4. [d] Assuming β as 0.5 for the bond between the phenyl group and the aromatic skeleton.

phthalazine dianion $\mathbf{2}^{2-}$ than that in $\mathbf{1}^{2-}$ is also manifested by the variations in the bond lengths, as derived from the calculations. The bond length of C2–C1′ in the neutral molecule **1** is 1.495 Å and that of C1–C1′ in **2** is 1.495 Å. The corresponding bond lengths in the dianions are 1.484 Å for $\mathbf{1}^{2-}$ and 1.462 Å for $\mathbf{2}^{2-}$. The calculations show a higher bond contraction as a result of the reduction process of **2** relative to **1**.

On the basis of the ^{1}H NMR spectra of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ it seems that the charge density on the diazanaphthalene nucleus in $\mathbf{1}^{2-}$ is higher and shows a more pronounced paratropicity (line broadening and a higher field shift). This conclusion is supported by the differences in the chemical shifts of the various hydrogens, and carbons in the NMR spectra which are by far more pronounced in the dianion derived from the quinoxaline system (Table I and II). The range of the ^{1}H and ^{13}C NMR bands of $\mathbf{1}^{2-}$ is 3.1 and 63.3 ppm, respectively, while that of $\mathbf{2}^{2-}$ is much narrower, 1.4 for ^{1}H and 33.0 for the ^{13}C spectrum. Such a nonuniform charge distribution, as in $\mathbf{1}^{2-}$, is characteristic of paratropic $4n\pi$-electron antiaromatic systems. Noteworthy is the difference in the net charges between the two doubly charged systems. The charge densities from calculation and from carbon chemical shifts are in good agreement. $\omega\beta$ shows that the π-charge density on the nitrogens in the 2,3-diphenylquinoxaline dianion ($\mathbf{1}^{2-}$) is –0.926 while only –0.410 units reside on the nitrogens of $\mathbf{2}^{2-}$. Carbon chemical shifts are very sensitive to charge density and only feebly sensitive to the diatropicity or the paratropicity of the system. Thus, relative to the uncharged starting materials, one would expect to find a larger total high-field shift of the ^{13}C bands of the dianion $\mathbf{2}^{2-}$ relative to that of $\mathbf{1}^{2-}$. Indeed, chemical shift differences ($\Delta\delta^{13}$C) are 202 ppm for the phthalazine but only 88 ppm for the quinoxaline derivative.

Apart from its spectroscopic properties, 2,3-diphenylquinoxaline dianion ($\mathbf{1}^{2-}$) shows a very interesting ring closure to the dibenzo[*a*,*c*]phenazine dianion ($\mathbf{6}^{2-}$) (Figure 2, Scheme I).[12b] The deep purple solution of $\mathbf{1}^{2-}$ turned red, and changes in the ^{1}H and ^{13}C spectra were recorded. The new absorption bands of the ^{1}H and ^{13}C NMR which appeared after 1 week are identical with those of $\mathbf{6}^{2-}$ which was prepared and characterized separately.[11b] The transformation of $\mathbf{1}^{2-}$ to $\mathbf{6}^{2-}$ requires a formal loss of H_2, a rather strange event under the reductive reaction conditions. It is well-known that in the photocyclization of stilbene and its derivatives an oxidant is employed in order to push the dehydrogenation to the final aromatized product.[14] The closure seems to constitute a good synthetic route to polyheterocyclic systems.[12b] It should be noted that, in this case, a photochemical route from neutral **1** to neutral **6** is unattainable.[21] The lengthy reaction time is overcome by employing C_8K as a reagent.[22] A possible mechanism involves an electrocyclic conversion of the dianion (Scheme III). Yet, the only species which could be observed in the course of the reaction is the starting material $\mathbf{1}^{2-}$ and the final product $\mathbf{6}^{2-}$ (Figure 2).

Reduction of 2,3,7,8-tetraphenylpyrazo[2,3-*g*]quinoxaline dianion ($\mathbf{3}^{2-}$) was performed in THF-d_8 by both sodium and lithium, and only with sodium could we detect a spectrum. After an initial yellowish color, the solution turned blue, and a sharp, well-resolved spectrum appeared (Figure 3). The center of gravity of the ^{1}H NMR of **3** is at 7.69, while that of the charged system is at 6.77 ppm (Figure 3, Tables I and II). According to the charge shift correlation for protons[15a,b] in carbocyclic systems, this shift corresponds to 1.89 units of charge. Despite the high degree of charging of the nitrogen atoms (1.058 units of charge according to $\omega\beta$ calculation, Table IV) there is still a high charge density left at positions C-5 and C-10 (–0.438). These calculated numbers are corroborated by the ^{1}H and ^{13}C NMR spectra. Relative to **3**, the singlet assigned to H-5 and H-10 is shifted by 4.5 ppm to high field. The band attributed by selective decoupling experiments to C-5 and C-10 (Table II) appears at a field relatively high, i.e., 93.8 ppm.

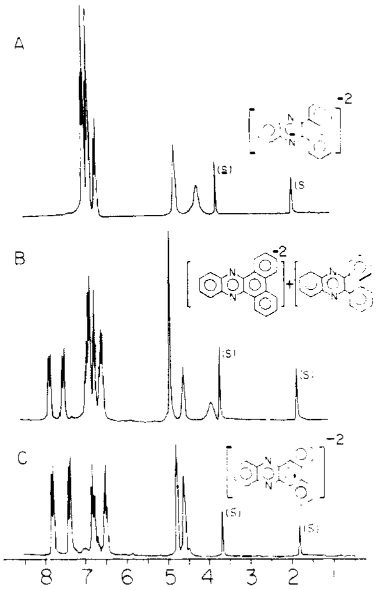
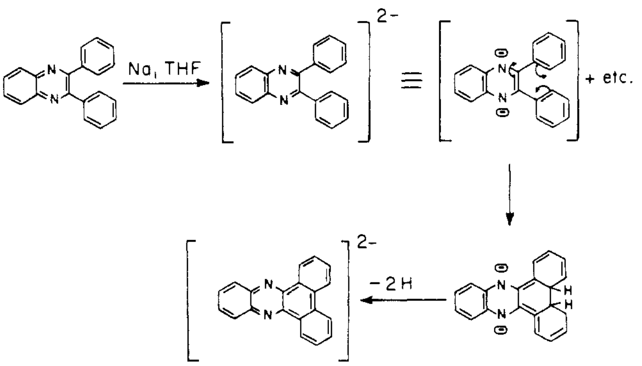


Figure 2. ^{1}H NMR spectra of the ring-closure process of $\mathbf{1}^{2-} \rightarrow \mathbf{6}^{2-}$ in THF-d_8 at room temperature.

Scheme III



As expected from the relatively wide HOMO–LUMO energy gap (0.38β units in $\mathbf{3}^{2-}$, Table III) no line broadening was observed in the ^{1}H NMR spectrum even at room temperature (Figure 3). From the disappearance of the signals of $\mathbf{3}^{2-}$, we assume that a

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[21] Several experiments to carry out this ring-closure reaction via a photochemical process on the neutral compound **1** failed. Compound **1** was recovered (≈100%).

[22] Tamarkin, D.; Cohen, Y.; Rabinovitz, M. *Synthesis*, in press.

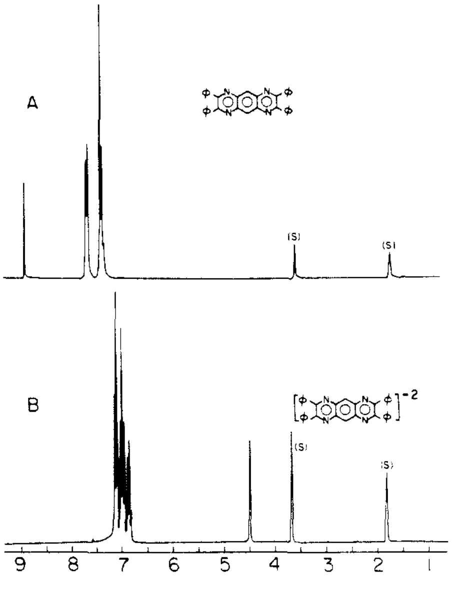

Figure 3. (A) ^1H NMR spectra of 2,3,7,8-tetraphenylpyrazo[2,3-*g*]-quinoxaline (3) and (B) its doubly charged system 3^{2-} in THF-d_8 as the disodium salt.

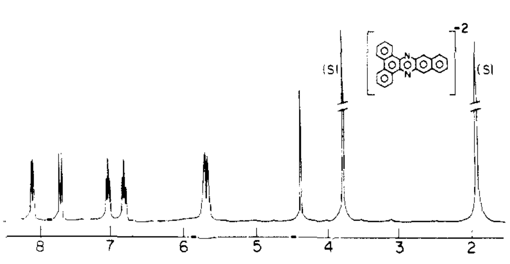

Figure 4. ^1H NMR spectrum of tribenzo[*a,c,i*]phenazine dianion 4^{2-} as the disodium salt in THF-d_8 at 203 K.

reduction to the corresponding trianion radical ($3^{\cdot 3-}$) or the tetraanion (3^{4-}) occurred. The tetraanion cannot be ruled out in view of the narrow HOMO–LUMO energy gap (0.06β units) calculated for 3^{4-}. This value implies that no NMR signals would be obtained for this tetraanion.

Reduction of tribenzo[*a,c,i*]phenazine (4) was accomplished by both sodium and lithium metals. The first stage of the process, that is, the one-electron reduction, afforded a green solution showing no NMR signals. The green solution turns to deep purple, whereupon a well-resolved spectrum emerges (Figure 4). As expected, dianion 4^{2-} showed paratropicity, being a 4*n*π-electron system. No line broadening was observed, in line with the relatively wide HOMO–LUMO gap (0.31β). A very interesting phenomenon ensues, as can be gathered from the ^1H NMR spectrum of 4^{2-} (Figure 4). The spectrum is composed of two distinct components. The first group, attributable to H_{1-8} appears in the range 8.1–6.7 ppm, a very low field for a charged system. The second group appears in the high-field range 5.6–4.3 ppm and consists of an AA′BB′ pattern and a singlet. The latter bands are attributed to H_{11-14} and $H_{10,15}$, respectively. A strange mode of charge delocalization is thus suggested, i.e., formal segregation of the charged conjugated system into two components: (a) a "phenanthrene"-like moiety which accomodates only a minor fraction of the negative charge; (b) a benzo[*g*]qunioxaline-like moiety which accommodates the major part of negative charge. This mode of delocalization is quite unusual, since the system is alternant while such a phenomenon is characteristic of nonalternant systems. The partitioning is clearly corroborated by $\omega\beta$ calculations as can be gleaned from Table IV. Recall that a similar partitioning has been reported for tribenzo[*a,c,i*]anthracene dianion.[23] The interpretation given there seems to apply here as well. Tribenzo[*a,c,i*]phenazine (4) can be regarded as built up

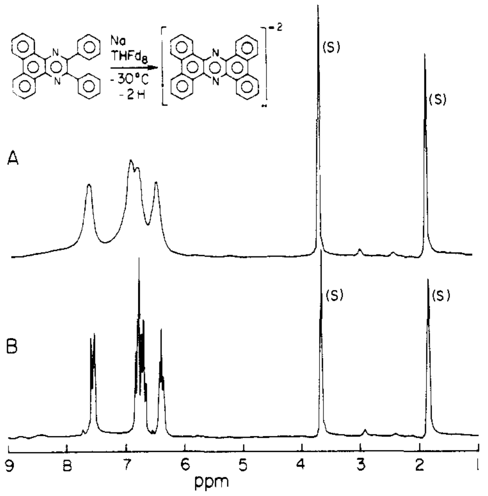

Figure 5. ^1H NMR spectra of phenanthrazine dianion (7^{2-}), obtained by the sodium reduction of 2,3-diphenyldibenzo[*f,h*]quinoxaline (5) in THF-d_8. (A) 293 K; (B) 213 K.

formally of benzo[*g*]quinoxaline and phenanthrene-like components. Phenanthrene dianion is rather antiaromatic, as shown by its very pronounced paratropicity as well as by the calculated HOMO–LUMO energy gap which is relatively low. Benzo[*g*]-quinoxaline dianion, which is the heterocyclic analogue of anthracene dianion, is "much less antiaromatic" than phenanthrene dianion. This comes out both from the ^1H NMR spectrum of 2,3-di-*p*-tolylbenzo[*g*]quinoxaline dianion and from the computed HOMO–LUMO gap, 0.34β.[11b] It seems that when 4 is charged to form 4^{2-} it would "lose" more if the major part of the negative charge were directed to the phenanthrene moiety. Therefore, the alternative pathway is preferred, resulting in a formal benzo-[*g*]quinoxaline dianion-like moiety and a virtually uncharged phenanthrene. In an alternant system it is reasonable, even though somewhat unexpected, that a molecule will choose a delocalization path that minimizes antiaromatic contributions. This observation strengthens the viewpoint that phenanthrene dianion is a highly paratropic antiaromatic system.[9] In our opinion, it also reflects the tendency of an aromatic system to remain so.[10f]

Reduction of 2,3-diphenyldibenzo[*f,h*]quinoxaline (5) with metallic sodium afforded an initially red solution which turned after several days to blue. No NMR signals could be detected in this solution. It was gratifying to find that the HOMO–LUMO energy gap for 5^{2-} is only 0.11β units, a very low value indeed. This should account for the absence of any NMR signal due to the paramagnetic nature of the system.

A color change to a shade slightly more purple occurred after several weeks of contact between 5 and the metal. At this stage we could detect very broad signals at room temperature (Figure 5). Cooling led to a well resolved ^1H NMR spectrum composed of two doublets and two triplets which cannot be attributed to the dianion 5^{2-}. In view of the ring closure, viz., $1^{2-} \rightarrow 6^{2-}$, we attribute the ^1H NMR spectrum to 7^{2-} (Scheme III). This assignment is confirmed by the ^{13}C NMR spectrum as recorded at 213 K, which revealed only seven bands in agreement with structure 7^{2-} (Tables I and II). The fact that the spectrum was well-resolved only at a very low temperature provides another confirmation of the singlet–triplet hypothesis. According to this hypothesis, the width of the HOMO–LUMO energy gap affects the thermal equilibrium between the singlet ground state and the low-lying triplet state. The low value computed for 7^{2-}, 0.11β units, is entirely in line with experiment (Table III).

Conclusions

Introduction of nitrogen atoms into a polycyclic skeleton brings about novel spectroscopic phenomena in the respective 4*n*π dianions. ^1H NMR line broadening correlates well with the HOMO–LUMO energy gap, as deduced from $\omega\beta$ calculations. The two heterocyclic analogues of substituted naphthalene dianion 1^{2-} and 2^{2-} were shown to differ significantly by ^1H and ^{13}C NMR

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[23] Minsky, A.; Rabinovitz, M. *J. Am. Chem. Soc.* **1984**, *106*, 6755.

spectra, charge delocalization, and ^{1}H NMR line shape. These unexpected differences were predicted by computation. A perculiar mode of charge delocalization was observed in tribenzo[*a*,*c*,*i*]phenazine dianion $\mathbf{4}^{2-}$ and rationalized as a manifestation of a $4n\pi$-electron system which adopts such a path of delocalization to minimize the antiaromatic contribution. A very interesting ring closure reaction, viz., $\mathbf{1}^{2-} \rightarrow \mathbf{6}^{2-}$ and $\mathbf{5}^{2-} \rightarrow \mathbf{7}^{2-}$, was encountered. This reaction proceeds via dianionic intermediates as concluded from Figure 2. It is interesting to note that there is partial quenching of the paratropicity of $4n\pi$-electron heterocyclic dianions compared with the analogous carbocyclic ones. This observation can be rationalized by partial localization of electron density or some extent of distortion from coplanarity of $4n\pi$ heterocyclic dianions.

Experimental Section

2,3-Diphenylquinoxaline (**1**), 1,4-diphenylphthalazine (**2**), tribenzo[*a*,*c*,*i*]phenazine (**4**), and 2,3-diphenyldibenzo[*g*,*h*]quinoxaline (**5**) were prepared from the corresponding diamine and dicarbonyl compounds according to the following general procedure. Tetraphenylpyrazo[2,3-*g*]quinoxaline (**3**) was prepared by a different procedure (vide infra).

General Procedure. A mixture of 1 mmol of *o*-phenylenediamine, 1.1 mmol of benzil, and a catalytic amount of HCl in 30 mL of ethanol was placed in a 50-mL flask equipped with a reflux condenser. The mixture was heated to reflux for 24 h with magnetic stirring. The mixture was cooled down and then concentrated with the aid of a rotatory evaporator and the product was allowed to precipitate. The precipitate was collected on a Buchner funnel. The resulting solid was crystallized from EtOH.

2,3-Diphenylquinoxaline (1): colorless needles, mp 122–124 °C (lit.[24] 126 °C); ^{1}H NMR δ 8.20, 7.85 (AA′BB′, 4 H), 7.63 (m, 4 H), 7.40 (m, 6 H); ^{13}C NMR (THF) δ 153.1, 141.0, 139.1, 129.8, 129.6, 129.0, 128.5, 127.8. Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.90; H, 4.94; N, 10.27.

1,4-Diphenylphthalazine (2): colorless needles, mp 196 °C (lit.[25] 194 °C); ^{1}H NMR (THF-d_8) δ 8.23, 7.97 (AA′BB′, 4 H), 7.90 (m, 4 H), 7.62 (m, 6 H); ^{13}C NMR (THF) δ 151.6, 133.1, 131.9, 130.2, 129.0, 128.4, 126.4, 125.7. Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.37; H, 5.30; N, 10.00.

Tribenzo[*a*,*c*,*i*]phenazine (4): yellow-orange colored solid, mp 292–293 °C; ^{1}H NMR (THF-d_8) δ 9.52 (d, J = 6.6 Hz, 2 H), 9.05 (s, 2 H), 8.75 (d, J = 8.1 Hz, 2 H), 8.33, 7.69 (AA′BB′, 4 H), 7.83 (m, 4 H); ^{13}C NMR (THF) δ 133.9, 133.4, 132.5, 132.1, 131.1, 130.3, 128.0, 127.5, 127.0, 126.4, 126.0, 122.8. Anal. Calcd for $C_{24}H_{14}N_2$: C, 87.25; H, 4.27; N, 8.48. Found: C, 87.01; H, 4.46; N, 8.45.

2,3-Diphenyldibenzo[*g*,*h*]quinoxaline (5): pale yellow solid, mp 267–269 °C; ^{1}H NMR (DME-d_{10}) δ 9.30 (dd, J_1 = 7.2, J_2 = 2.0 Hz, 2 H), 8.77 (dd, J_1 = 7.4, J_2 = 2.0 Hz, 2 H), 7.79 (m, 4 H), 7.69 (m, 4 H), 7.28 (m, 6 H). Anal. Calcd for $C_{28}H_{18}N_2$: C, 87.93; H, 4.74; N, 7.32. Found: C, 87.91; H, 4.88; N, 7.28.

Tetraphenylpyrazo[2,3-*g*]quinoxaline (3): To a solution of 6 mmol of benzil and 2 mmol of sodium acetate placed in a 500-mL flask equipped with a reflux condenser and a magnetic stirrer was added 30 mL of EtOH. The mixture was brought to reflux and 1 mmol of 1,2,4,5-tetraaminobenzene hydrochloride in EtOH was added within 3 h to the refluxed mixture (the total volume was 200 mL). A yellow solid precipitated. The mixture was refluxed for 24 h and the solid collected on a Buchner funnel and crystallized from toluene. Mp 292–293 °C; ^{1}H NMR (THF-d_8) δ 8.98 (s, 2 H), 7.74 (m, 8 H), 7.45 (m, 12 H); ^{13}C NMR (THF) δ 155.3, 140.5, 139.4, 130.3, 129.3, 128.5, 128.2.

General Procedure for Metal Reduction Process. Lithium or sodium wire were introduced to the upper part of an extended NMR tube contaning the solution (ca. 10^{-2} M) of the diaza hydrocarbon in THF-d_8. The solution was frozen and degassed and the tube sealed under vacuum. Solutions were brought to contact with the metal by turning the tube upside down. All solutions showed bright colors.

Quenching of the Anions. All dianions were quenched by bubbling oxygen via syringe into the solutions at a slow rate at −78 °C. The deep color disappeared and the ^{1}H NMR spectrum was recorded. In each case the only product observed was the starting material.

NMR spectra were obtained on Bruker SY-200 pulsed FT spectrometer operating at 200.132 and 50.323 MHz for ^{1}H and ^{13}C NMR, respectively, equipped with a pulse programmer and an Aspect-2000 computer (32 K). Field/frequency regulations were maintained by ^{2}H locking.

Acknowledgment. The financial support from the Fund of Basic Research, administered by the Israel Academy of Science and Humanities, is gratefully acknowledged.

Registry No. 1, 1684-14-6; $\mathbf{1}^{2-}$/2Na$^+$, 104266-49-1; **2**, 10132-05-5; $\mathbf{2}^{2-}$/2Na$^+$, 104240-10-0; **3**, 80829-03-4; $\mathbf{3}^{2-}$/2Na$^+$, 104240-11-1; **4**, 216-01-3; $\mathbf{4}^{2-}$/2Li$^+$, 104240-12-2; **5**, 103307-09-1; $\mathbf{5}^{2-}$/2Na$^+$, 104240-14-4; $\mathbf{6}^{2-}$/2Na$^+$, 94370-21-5; $\mathbf{7}^{2-}$/2Na$^+$, 104240-13-3.

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(24) Lanquist, J. K. *J. Chem. Soc.* **1953**, 2828.

(25) Mustafa, M.; Harhash, A. H.; Salem, A. A. S. *J. Am. Chem. Soc.* **1960**, *82*, 2738.