

# Novel Polycyclic Dianions: Metal Reduction of Nitrogen Heterocycles

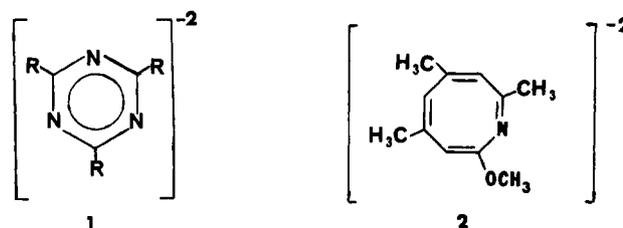
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**Abstract:** Fused benzenoid heterocyclic systems, i.e., benzo[*c*]cinnoline (3), dibenzo[*a,c*]phenazine (4), and quinoxaline derivatives 5 and 6, were reduced with lithium and sodium in ether solvents to the corresponding antiaromatic doubly charged species. These dianions represent a new class of charged species, i.e., nitrogen-containing polycyclic anions. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra as well as theoretical calculations are reported and discussed in terms of antiaromatic contributions as well as the modes of interaction between the organic moiety and the cations. In view of the strong dependency of the  $^1\text{H}$  NMR spectra on the counteraction and temperature, an equilibrium between ionic and covalent structure is suggested.

Experimental and theoretical studies of neutral and charged  $\pi$ -conjugated polycyclic hydrocarbons are quite extensive.<sup>1</sup> Parameters such as degree of charging, different modes of charge delocalization and its distribution over the  $\pi$ -framework, states of solvation of the counterions, and the aromatic (or antiaromatic) contributions sustained as a result of the charging processes attracted much interest and are well documented.<sup>2-4</sup> The factors which govern these parameters were studied with the aid of various chemical and physical methods including quenching experiments, UV, ESR, and NMR spectroscopies.<sup>5</sup> Theoretical approaches, aimed to interpret these experimental findings such as Platt's peripheral method,<sup>6a</sup> the conjugated circuits theory suggested by Randić,<sup>6b,c</sup> the Hess and Schaad semiempirical model<sup>6d,e</sup> as well as theories concerned with ion-solvation equilibria are generally found to nicely correlate with the experimental results.

In view of these considerations, the scarcity of information related to heteropolycyclic anions seems quite startling. In fact, the only reported  $\pi$ -conjugated dianions which contain heteroatoms in their path of conjugation are those derived from 2,4,6-triphenyl-*sym*-triazine (1a), its *p*-tolyl analogue (1b), and the substituted azocine system, i.e., 2. The dianions, 1a and 1b, are characterized by a singlet ground state and a low-lying thermally excited triplet state,<sup>7</sup> and detection of their NMR characteristics is therefore precluded. This result presents a major drawback,



1a, R = Ph  
1b, R = *p*-tolyl

as the assembly of  $^1\text{H}$ ,  $^{13}\text{C}$ , and counteraction NMR patterns usually affords a powerful tool for the investigation of charged systems. However, Paquette's monocyclic azocine dianion (2)<sup>8a</sup> could be studied by NMR spectroscopy and revealed the expected diamagnetic NMR features. This anion was reexamined recently by Stevenson.<sup>8b</sup>

This contribution is concerned with the preparation and characterization of a new class of doubly charged systems, i.e., those derived from nitrogen-containing benzenoid polycycles. The studied dianions were found, in most cases, to be relatively stable and to sustain only minor, if any, line broadening due to paramagnetic contributions. Thus, their NMR patterns can be thoroughly studied. The results are discussed in terms of the antiaromatic contributions revealed by these dianions, as well as in terms of the interactions between the organic moieties and the counteractions. These interactions are found to be substantially different from those exhibited by the carbopolycyclic dianions.

## Results and Discussion

It is well established that polycyclic compounds which contain heteroatoms and an array of  $(4n + 2)$   $\pi$  electrons in their conjugated periphery are considered aromatic in the same sense as the carbocycles are. A host of spectroscopic studies have been reported on these systems.<sup>9,10</sup> Hückel MO  $\pi$ -resonance energies were estimated on systems containing amine nitrogen, sulfur, and oxygen.<sup>11</sup> In view of our interest in polycyclic  $4n$   $\pi$  paratropic dianions and dication, we undertook an investigation of heteropolycyclic dianions containing two nitrogen atoms, i.e., benzo[*c*]cinnoline (3), dibenzo[*a,c*]phenazine (4), 2,3-di-*p*-tolylbenzo[*g*]quinoxaline (5), and 2,3-di-*p*-tolylquinoxaline (6). The reduction of these systems was carried out by sodium or lithium

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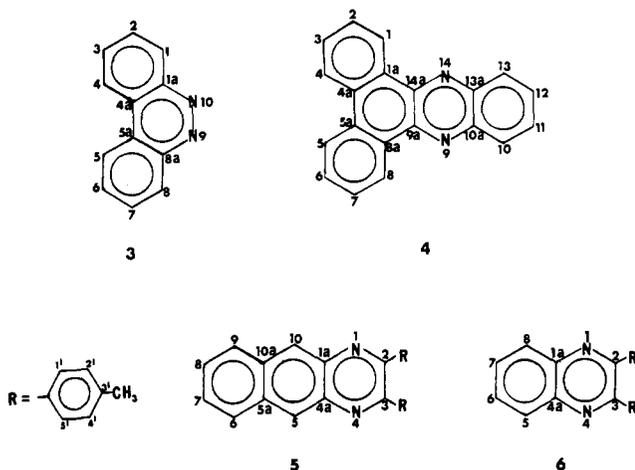
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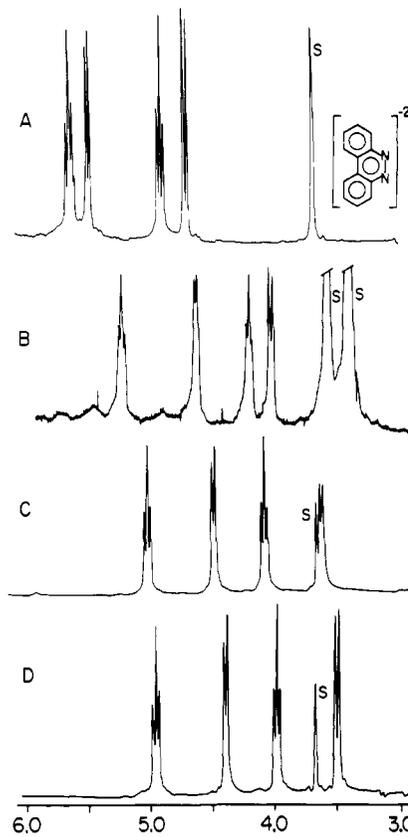
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metals.<sup>12</sup> Although it has been commented in the literature that polyheterocyclic anions are unstable,<sup>13</sup> we observe that the corresponding disodium and, in some cases, dilithium salts are stable enough to enable a study of their NMR parameters.

The dianionic nature of the charged systems was deduced from <sup>13</sup>C NMR and <sup>1</sup>H NMR charge density correlations<sup>14</sup> and quenching experiments (see Experimental Section). Reduction of **3** with lithium and sodium metals was carried out in ether solvents (Tables I and II). The proton chemical shifts exhibit a strong dependency upon the reduction conditions (reducing metal, solvent, and temperature). The orange solution of the dilithium salt of **3**<sup>2-</sup> (THF-*d*<sub>8</sub>, 293 K) shows a nearly first-order pattern (Figure 1, Table I) in the range 5.66–4.68 ppm, with a center of gravity at 5.18 ppm. The reduction product of **3** with lithium metal in DME-*d*<sub>10</sub> showed a similar pattern at 243 K in the range 5.18–3.94 ppm (center of gravity at 4.45 ppm). Sodium reduction of **3** in THF-*d*<sub>8</sub> afforded a magenta colored solution, and the proton spectrum (at 293 K) appears in the range 5.07–3.61 ppm (center of gravity 4.32 ppm). However, decreasing the sample's temperature afforded a spectrum which is shifted to a higher field (4.95–3.49 ppm, center of gravity 4.20 ppm). Contrary to the proton spectra, the carbon spectra did not reveal significant changes as the conditions (reducing metal and temperature) were varied. The six expected <sup>13</sup>C bands appear in the range 169–104 ppm (Table II).

At first sight there seems to be a basic discrepancy between the charge density calculated for the organic moiety using the charge–chemical shift empirical correlations.<sup>14</sup> From the <sup>1</sup>H NMR chemical shifts on the one hand it seems as if a net charge of more than two units resides on the organic moiety; on the other hand, the charge density, calculated by <sup>13</sup>C NMR chemical shifts is estimated to be less than one unit of charge. This discrepancy is only apparent, as this phenomenon is observed in paratropic systems.<sup>4c,15a,c</sup> While <sup>13</sup>C chemical shifts are very sensitive to charge density and to a much lesser extent to the diatropicity or paratropicity of the system, proton chemical shifts are sensitive to both charge density and to the anisotropy effects. Consequently, it is expected that a  $4n\pi$  paratropic system would reveal an enhancement of the proton high-field shifts. Hückel MO calculations ( $\omega\beta$  technique) were carried out on the neutral as well as on the doubly charged systems.<sup>16</sup> These calculations show that in



**Figure 1.** <sup>1</sup>H NMR spectra of benzo[*c*]cinnoline dianion **3**<sup>2-</sup>: (A) **3**<sup>2-</sup>/2Li<sup>+</sup>, THF, 293 K; (B) **3**<sup>2-</sup>/2Li<sup>+</sup>, DME, 243 K; (C) **3**<sup>2-</sup>/2Na<sup>+</sup>, THF, 293 K; (D) **3**<sup>2-</sup>/2Na<sup>+</sup>, THF, 220 K.

benzo[*c*]cinnoline dianion (**3**<sup>2-</sup>) as well as in the other members of this series much of the net charge (nearly one unit) is located on the nitrogen atoms (Table III). The effect of the charge that resides on the nitrogen atoms is not manifested in the <sup>13</sup>C NMR chemical shifts, consequently, the deviation from the Spiesscke and Schneider correlation<sup>14c</sup> is clear.

The unusual spectral features and especially the significant changes in the protons chemical shifts that are exhibited by the dilithium vs. the disodium salts of **3**<sup>2-</sup> are meaningful. In principle, two interpretations of the <sup>1</sup>H NMR phenomena seem plausible at first sight. (a) The cation–anion interactions are purely ionic, the observed high-field shift of **3**<sup>2-</sup>/2Na<sup>+</sup> relative to **3**<sup>2-</sup>/2Li<sup>+</sup> is related only to those factors that govern ion solvation equilibrium. (b) These phenomena may be ascribed to an equilibrium which prevails between covalent and ionic contributions to the bonding mode. The first interpretation does not stand further examination. Singly charged  $\pi$ -systems evidence the existence of ion solvation equilibria as reflected by their proton and carbon spectra.<sup>3c,d</sup> The equilibria between contact and solvent-separated ion pairs are influenced by the nature of the alkali cation, temperature, solvent, and the charge density of the organic moiety. As the size of the cation increases, the equilibrium is shifted toward tight ion pairing. Increasing the temperature of the salt solution also favors contact ion pairing. A solvent of enhanced solvating power would favor solvent-separated ion pairs, and an increased charge density in the organic moiety will shift the equilibrium toward contact ion pairing. The charge density of the organic moiety is influenced by the size of the  $\pi$ -system, the number of charges and their distribution mode. The smaller lithium cation and reduced temperature favor solvent-separated ion pairs. Therefore, one would expect the <sup>1</sup>H NMR spectrum of the disodium salt at low temperature to resemble that of the lithium salt at elevated temperatures. However, our data (Table I, Figure 1) show the opposite trend. The second interpretation seems reasonable. When the bonding mode is of solely ionic nature, the small lithium cation favors solvent-separated ion pairs, whereas when covalent contributions occur, its tendency toward such an interaction is much

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**Table I.**  $^1\text{H}$  NMR Parameters of Doubly Charged Heterocyclic System of 3-6

| system                | solvent     | temp, K | $^1\text{H}$ NMR pattern <sup>a,b</sup>   | neutral system center of gravity <sup>c</sup> | charged systems center of gravity <sup>c</sup> |
|-----------------------|-------------|---------|---|---|--|
| $3^{2-}/2\text{Li}^+$ | THF         | 293     | 5.63 (t, $J = 7$ Hz, $\text{H}_{2,7}$ ), 5.84 (d, $J = 7$ Hz, $\text{H}_{4,5}$ ), 4.90 (t, $J = 7$ Hz, $\text{H}_{3,6}$ ), 4.69 (d, $J = 7$ Hz, $\text{H}_{1,8}$ )  | 8.41  | 5.18   |
| $3^{2-}/2\text{Li}^+$ | DME         | 243     | 5.14 (t, $J = 7$ Hz, $\text{H}_{2,7}$ ), 4.55 (d, $J = 6$ Hz, $\text{H}_{4,5}$ ), 4.12 (t, $J = 6$ Hz, $\text{H}_{3,6}$ ), 3.95 (d, $J = 8$ Hz, $\text{H}_{4,5}$ )  | 8.41  | 4.45   |
| $3^{2-}/2\text{Na}^+$ | THF         | 293     | 5.05 (t, $J = 7$ Hz, $\text{H}_{2,7}$ ), 4.51 (d, $J = 7$ Hz, $\text{H}_{4,5}$ ), 4.09 (t, $J = 6$ Hz, $\text{H}_{3,6}$ ), 3.62 (d, $J = 8$ Hz, $\text{H}_{4,5}$ )  | 8.41  | 4.32   |
| $3^{2-}/2\text{Na}^+$ | THF         | 220     | 4.95 (t, $J = 7$ Hz, $\text{H}_{2,7}$ ), 4.39 (d, $J = 7$ Hz, $\text{H}_{4,5}$ ), 3.98 (t, $J = 6$ Hz, $\text{H}_{3,6}$ ), 3.49 (d, $J = 8$ Hz, $\text{H}_{4,5}$ )  | 8.41  | 4.20   |
| $4^{2-}/2\text{Na}^+$ | THF         | 293     | 7.81 (d, $J = 8$ Hz, $\text{H}_{1,8}$ ), 7.37 (d, $J = 8$ Hz, $\text{H}_{4,5}$ ), 6.78 (t, $J = 7$ Hz, $\text{H}_{3,6}$ ), 6.51 (t, $J = 7$ Hz, $\text{H}_{2,9}$ ), 4.75 (bd, $J = 3$ Hz, $\text{H}_{12,11}$ ), 4.672 (s, b, $\text{H}_{13,10}$ ) | 8.26  | 6.31   |
| $4^{2-}/2\text{Na}^+$ | THF         | 211     | 7.73 (d, $J = 8$ Hz, $\text{H}_{1,8}$ ), 7.25 (d, $J = 8$ Hz, $\text{H}_{4,5}$ ), 6.74 (t, $J = 7$ Hz, $\text{H}_{3,6}$ ), 6.44 (t, $J = 7$ Hz, $\text{H}_{2,9}$ ), 4.67 (s, b, $\text{H}_{12,11}$ ), 4.37 (s, b, $\text{H}_{13,10}$ )            | 8.26  | 6.20   |
| $4^{2-}/2\text{Na}^+$ | THF/DME 1:1 | 300     | 7.76 (d, $J = 7$ Hz, $\text{H}_{1,8}$ ), 7.26 (d, $J = 7$ Hz, $\text{H}_{4,5}$ ), 6.73 (t, $J = 7$ Hz, $\text{H}_{3,6}$ ), 6.46 (b, $\text{H}_{2,9}$ ), 4.74 (s, b, $\text{H}_{12,11}$ ), 4.40 (s, b, $\text{H}_{13,10}$ )                        | 8.26  | 6.23   |
| $4^{2-}/2\text{Na}^+$ | THF/DME 1:1 | 200     | 7.70 (d, $J = 8$ Hz, $\text{H}_{1,8}$ ), 7.1 (d, $J = 8$ Hz, $\text{H}_{4,5}$ ), 6.69 (t, $J = 7$ Hz, $\text{H}_{3,6}$ ), 6.42 (t, $J = 7$ Hz, $\text{H}_{2,9}$ ), 4.60 (t, $J = 4$ Hz, $\text{H}_{12,11}$ ), 4.00 (s, b, $\text{H}_{13,10}$ )    | 8.26  | 6.08   |
| $5^{2-}/2\text{Li}^+$ | THF         | 294     | 6.77 (AB, H-tolyl), 5.58 (AA'BB', $\text{H}_{6,7,8,9}$ ), 3.93 (s, $\text{H}_{5,10}$ ), 2.18 (s, $p\text{-CH}_3$ )  | 7.75 <sup>d,e</sup>                           | 6.00 <sup>e</sup>                              |
| $5^{2-}/2\text{Na}^+$ | THF         | 294     | 6.77 (AB, H-tolyl), 5.37 (AA'BB', $\text{H}_{6,7,8,9}$ ), 3.86 (s, $\text{H}_{5,10}$ ), 2.17 (s, $p\text{-CH}_3$ )  | 7.75 <sup>d,e</sup>                           | 5.95 <sup>e</sup>                              |
| $5^{2-}/2\text{Na}^+$ | THF         | 203     | 6.72 (AB, H-tolyl), 5.14 (AA'BB', $\text{H}_{6,7,8,9}$ ), 3.57 (s, $\text{H}_{5,10}$ ), 2.17 (s, $p\text{-CH}_3$ )  | 7.75 <sup>e</sup>                             | 5.82 <sup>e</sup>                              |
| $6^{2-}/2\text{Na}^+$ | THF         | 293     | 6.70 (AB, H-tolyl), 4.76 (s, b, $\text{H}_{6,7}$ ), 4.34 (s, b, $\text{H}_{5,8}$ ), 2.11 (s, $p\text{-CH}_3$ )  | 7.58 <sup>e</sup>                             | 5.98 <sup>e</sup>                              |
| $6^{2-}/2\text{Na}^+$ | THF         | 213     | 6.65 (AB, H-tolyl), 4.50 (s, b, $\text{H}_{6,7}$ ), 3.76 (s, b, $\text{H}_{5,8}$ ), 2.11 (s, $p\text{-CH}_3$ )  | 7.58 <sup>e</sup>                             | 5.81 <sup>e</sup>                              |

<sup>a</sup>Chemical shifts are given in ppm referenced to  $\text{Me}_4\text{Si}$  (for numbering see the schemes; coupling constants are given in Hz units). <sup>b</sup>Abbreviations: s = singlet, d = doublet, t = triplet, b = broad bands. <sup>c</sup>Center of gravity calculated in the same solvent for the neutral and charged systems unless otherwise indicated. <sup>d</sup>Center of gravity calculated in  $\text{CDCl}_3$ . <sup>e</sup>Center of gravity calculated excluding the  $p\text{-CH}_3$  band.

**Table II.**  $^{13}\text{C}$  NMR Chemical Shifts of the Doubly Charged Heterocycles 3-6

| system                | solvent | temp, K | NMR chemical shift, ppm <sup>a</sup>  | neutral system center of gravity <sup>b</sup> | charged system center of gravity <sup>b</sup> |
|-----------------------|---------|---------|---|---|---|
| $3^{2-}/2\text{Li}^+$ | THF     | 293     | 166.7, 129.3, 124.4, 118.3, 110.6, 108.3  | 129.4   | 126.3   |
| $3^{2-}/2\text{Na}^+$ | THF     | 293     | 168.7, 131.6, 125.1, 117.4, 107.0, 105.2  | 129.4   | 125.8   |
| $3^{2-}/2\text{Na}^+$ | THF     | 220     | 168.7, 131.2, 125.0, 116.8, 107.3, 104.1  | 129.4   | 125.5   |
| $4^{2-}/2\text{Na}^+$ | THF     | 300     | 162.7, 144.2, 125.5, 123.7, 121.7, 119.3, 117.7, 125.5, 116.5, 107.4                      | 130.9   | 126.4   |
| $5^{2-}/2\text{Na}^+$ | THF     | 300     | 159.9, 143.4, 141.9, 135.3, 130.9, 127.8, 127.8, 117.3, 115.6, 90.8, $p\text{-CH}_3$ 20.7 | 133.9 <sup>c</sup>                            | 128.9 <sup>c</sup>                            |
| $5^{2-}/2\text{Na}^+$ | THF     | 223     | 160.1, 143.4, 142.7, 135.2, 130.2, 127.4, 127.4, 116.4, 91.0, $p\text{-CH}_3$ 20.9        | 133.9 <sup>c</sup>                            | 128.6 <sup>c</sup>                            |
| $6^{2-}/2\text{Na}^+$ | THF     | 278     | 163.6, 142.9, 137.4, 129.9, 128.0, 126.9, 116.7, 101.2, $p\text{-CH}_3$ 20.8              | 134.1 <sup>c</sup>                            | 130.1 <sup>c</sup>                            |
| $6^{2-}/2\text{Na}^+$ | THF     | 220     | 163.8, 143.1, 137.8, 129.2, 127.0, 126.0, 116.2, 99.9, $p\text{-CH}_3$ 20.8               | 134.1 <sup>c</sup>                            | 129.6 <sup>c</sup>                            |

<sup>a</sup>Chemical shifts are given in ppm referenced to  $\text{Me}_4\text{Si}$ . <sup>b</sup>Center of gravity calculated in THF for the neutral and charged systems. <sup>c</sup>Center of gravity calculated excluding the  $p\text{-CH}_3$  band.

**Table III.** Charge Density of the Heterocyclic Dianions<sup>a-c</sup>

| system    | net charge calculated by the $\omega\beta$ technique |                     |                      |                       |                       |
|-----------|--|---------------------|----------------------|-----------------------|-----------------------|
| $3^{2-}$  | $C_{1a,8a} = 0.063$                                  | $C_{1,8} = 0.166$   | $C_{2,7} = 0.055$    | $C_{3,6} = 0.167$     | $C_{4,5} = 0.094$     |
|           |  | $C_{4a,5a} = 0.090$ | $N_{9,10} = 0.366$   |                       |                       |
| $4^{2-}$  | $C_{1a,8a} = 0.084$                                  | $C_{1,8} = 0.085$   | $C_{2,7} = 0.060$    | $C_{3,6} = 0.045$     |                       |
|           | $C_{4,5} = 0.031$                                    | $C_{4a,5a} = 0.081$ | $C_{14a,9a} = 0.052$ | $N_{9,14} = 0.363$    | $C_{13a,10a} = 0.036$ |
|           |  | $C_{13,10} = 0.140$ | $C_{11,12} = 0.084$  |                       |                       |
| $5^{2-d}$ | $C_{1a,4a} = 0.041$                                  | $N_{1,4} = 0.320$   | $C_{2,3} = 0.097$    | $C_{2a',3a'} = 0.006$ | $C_{1',5'} = 0.007$   |
|           |  | $C_{2',4'} = 0.003$ | $C_{3'} = 0.008$     | $C_{5,10} = 0.241$    | $C_{5a,10a} = 0.054$  |
|           |  | $C_{9,6} = 0.127$   | $C_{7,8} = 0.086$    |                       |                       |
| $6^{2-d}$ | $C_{1a,4a} = 0.048$                                  | $N_{1,4} = 0.418$   | $C_{2,3} = 0.117$    | $C_{2a',3a'} = 0.018$ | $C_{1',5'} = 0.014$   |
|           |  | $C_{2',4'} = 0.008$ | $C_{3'} = 0.020$     | $C_{5,8} = 0.221$     | $C_{7,6} = 0.116$     |

<sup>a</sup>Reference 16. <sup>b</sup>Calculations were performed on the phenyl-substituted benzoquinoxaline and quinoxaline and not on the  $p\text{-tolyl}$  substituted benzoquinoxaline and quinoxaline. <sup>c</sup>For numbering see schemes. <sup>d</sup>Assuming  $\beta$  as 0.5 for the bond between the phenyl group and the aromatic skeleton.

more conspicuous than that of the sodium cation.<sup>17</sup> This tendency should be emphasized in those systems where a high portion of the net charge is localized over a small part of the entire system, e.g., the nitrogen atoms of  $3^{2-}$ .

This type of bonding may rationalize the unexpected difference in the stability of the salts. Lithium salts, in ionic systems, should

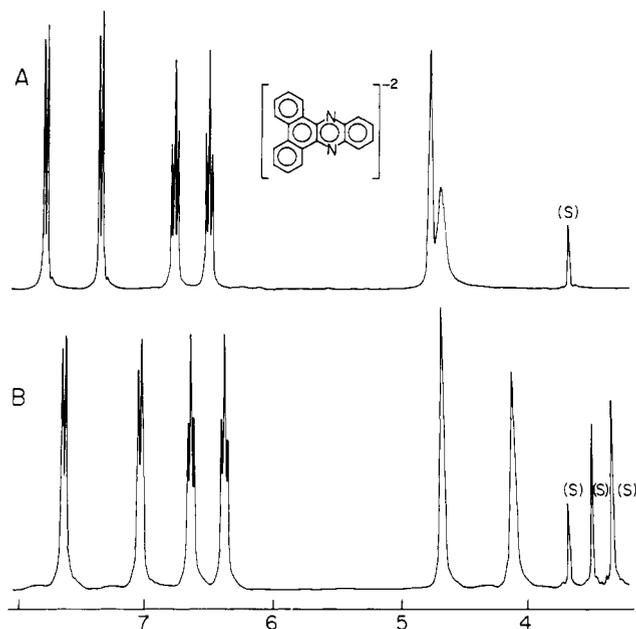
**Table IV.** HOMO-LUMO Energy Gap and Charge Density of the Heterocyclic Dianions

|                              | $3^{2-}$ | $5^{2-}$          | $4^{2-}$ | $6^{2-}$            |
|------------------------------|----------|-------------------|----------|---------------------|
| HOMO-LUMO <sup>a,d</sup> gap | 0.29     | 0.34 <sup>b</sup> | 0.21     | 0.18 <sup>b,c</sup> |
| detectable line broadening   | -        | -                 | +        | +                   |
| net charge on nitrogen       | 0.336    | 0.320             | 0.363    | 0.418               |
| maximum net charge on carbon | 0.166    | 0.241             | 0.140    | 0.221               |

<sup>a</sup>As obtained by  $\omega\beta$  calculations, ref 16. <sup>b</sup>The calculations were done on  $4^{2-}$  and  $6^{2-}$  when R = phenyl and not  $p\text{-tolyl}$  as the systems that were reduced, assuming  $\beta$  as 0.5 for the bond between the phenyl group and the aromatic skeleton. <sup>c</sup>On this system calculations were made also for cases when  $\beta$  has the values of 0.2 and 0.8 for the bond between the phenyl group and the aromatic skeleton. The HOMO-LUMO energy gaps were 0.23 and 0.12  $\beta$  unit, respectively. <sup>d</sup>Given in  $\beta$  units.

be stabilized due to an effective ion solvation interaction. However, we observe a very significant difference between the stability of the lithium and the sodium salts of  $3^{2-}$ . While  $3^{2-}/2\text{Li}^+$  decomposes within several hours,  $3^{2-}/2\text{Na}^+$  is stable under the same conditions (at  $-18^\circ\text{C}$ ) for months. This trend is found to be general for heteropolycyclic dianions. A difference which results from simple ion-solvation behavior cannot account for such an effect. The covalent lithium bonding may reduce its solvation and consequently its stability.

This phenomenon, i.e., the high-field shift of  $3^{2-}/2\text{Na}^+$  vs. the relative low-field shift of  $3^{2-}/2\text{Li}^+$  imposes the questions of its origin and its relationship to the paratropic character of the system.

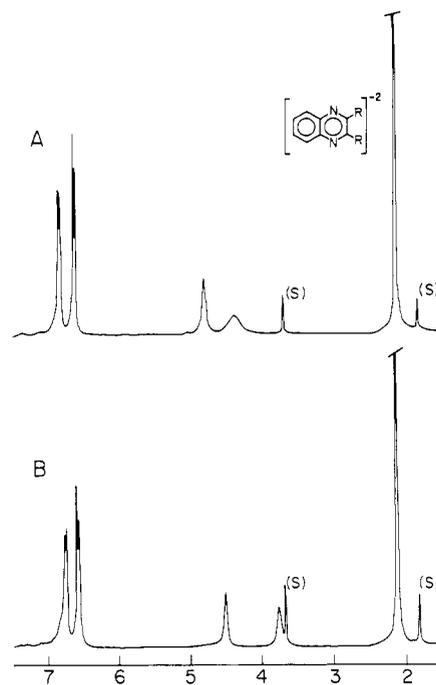


**Figure 2.**  $^1\text{H}$  NMR spectra of dibenzo[*a,c*]phenazine dianion  $4^{2-}$ : (A)  $4^{2-}/2\text{Na}^+$ , THF at 293 K; (B)  $4^{2-}/2\text{Na}^+$  in 1:1 solution of THF/DME at 220 K.

The HOMO–LUMO energy gap derived from  $\omega\beta$  calculations performed on the neutral and the doubly charged analogues revealed the following feature. The HOMO–LUMO energy gap of the neutral species is found to be of the order of one  $\beta$  unit which is in line with their aromatic character. In the corresponding dianions the HOMO–LUMO energy gap is significantly lower as rationalized by the paratropic nature of these  $4n\pi$  electron systems. Benzo[*c*]cinnoline dianion  $3^{2-}$  shows such a gap of  $0.29\beta$  (Table IV). Ion solvation equilibria of these systems should affect the HOMO–LUMO energy gap and hence its paratropicity.<sup>15b</sup> A possible covalent contribution of the lithium salts may quench the antiaromatic contribution due to a higher degree of charge localization followed by a lesser degree of the  $4n\pi$  delocalization. Such a covalent contribution may also perturb the system's symmetry and consequently its antiaromaticity.<sup>18</sup>

In conclusion, the proton chemical shifts of the lithium salt are not only deshielded relative to the disodium salt but also afford a spectrum that resembles that of the sodium salt at low temperature which cannot be accounted for by ion–solvation equilibria. Lowering of the temperature and a smaller cation should afford a high degree of solvation and hence an opposite trend. Therefore, this behavior is rationalized in terms of substantial covalent contributions to the lithium–nitrogen bonding mode. It should be noted that no detectable line broadening was observed in any of the dianions derived from benzo[*c*]cinnoline (**3**) (Figure 1) as expected from the relatively large HOMO–LUMO gap (vide supra).

**Dibenzo[*a,c*]phenazine Dianion ( $4^{2-}$ ).** Reduction of dibenzo[*a,c*]phenazine with sodium gave a red solution of a dianion which could be detected by NMR. Lithium and potassium gave an unstable species which could not be recorded. The spectrum of the disodium salt  $4^{2-}$  exhibited, like the other dianions of this new class, a strong dependency on the reduction conditions. The  $^1\text{H}$  NMR of  $4^{2-}/2\text{Na}^+$  at 293 K in THF revealed the expected pattern (Table I, Figure 2). The center of gravity of  $4^{2-}/2\text{Na}^+$  in THF at 293 K and in 1:1 THF/DME at 220 K is observed at 6.31 and 6.08 ppm, respectively, a smaller change than that observed in  $3^{2-}$ . Here again conditions that favor solvent-separated ion pairs (solvent of high solvating power, e.g., DME) and low temperature shifted the spectrum to higher field. It should be noted that this dianion exhibited a detectable line broadening of the proton bands of the high-field part of the spectrum.



**Figure 3.**  $^1\text{H}$  NMR spectra of 2,3-di-*p*-tolylquinoxaline dianion  $6^{2-}$  with sodium metal, in THF at: (A) 293 K; (B) 213 K.

The HOMO–LUMO energy gap estimated for  $4^{2-}$  is  $0.21\beta$ , a smaller gap than that of  $3^{2-}$  (Table IV). We have previously shown that such a line broadening can be accounted for by a thermally accessible low lying triplet state due to a small HOMO–LUMO gap.<sup>15b</sup> This effect should be more pronounced in that part of the molecule which bears a higher charge density. Indeed, such a line broadening is observed in those bands which are attributed to the protons on the more highly charged region of the molecule, i.e., near the nitrogen atoms (Figure 2). The carbon spectral parameters appear in Table II.

**2,3-Di-*p*-tolylbenzo[*g*]quinoxaline Dianion ( $5^{2-}$ ).** This dianion was prepared by sodium and lithium metal reduction. The proton and carbon NMR parameters are given in Tables I and II, respectively. The dianionic nature was deduced from its high-field shift by the charge–chemical shift empirical correlation. It should, however, be noted that in the  $^1\text{H}$  NMR spectrum there is an excessive high-field shift due to the paratropicity of these dianions. A significant portion of the charge density resides on the two nitrogen atoms (Tables III and IV). Therefore, the charge density calculated from the total shift of the carbon atoms is rather low, i.e., less than one unit of charge is residing on the carbon atoms. The chemical shift variations due to the sample's temperature were less significant than those observed in  $3^{2-}$ . Like  $3^{2-}$  also  $5^{2-}$  revealed no detectable line broadening. This phenomenon is in good agreement with the relatively wide HOMO–LUMO energy gap ( $0.34\beta$ , Table IV).

**2,3-Di-*p*-tolylquinoxaline Dianion ( $6^{2-}$ ).** A one-electron reduction of naphthalene by an alkali metal yields the corresponding radical anion and therefore no detectable NMR bands are reported for the metal reduction product of naphthalene.<sup>19</sup> Sodium reduction of **6**, a two nitrogen heterocyclic analogue of a substituted naphthalene, afforded the corresponding dianion. Dianion  $6^{2-}$  shows only moderate stability but could be detected by the NMR technique. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $6^{2-}/2\text{Na}^+$  are summarized in Tables I and II (Figure 3).

The  $^1\text{H}$  NMR of the disodium salt in THF shows temperature dependency. The band attributed to  $\text{H}_{5,8}$  appears at 4.34 and 3.76 ppm at 293 and 213 K, respectively. The changes in the  $^{13}\text{C}$  chemical shifts are less significant when the energy scale is con-

(18) Longuet-Higgins. *Spec. Publ.-Chem. Soc.* 1967, No. 21, 110.

(19) There are quite few publications which show that this dianion exists. To the best of our knowledge there is no NMR evidence for its existence. Ebert, L., private communication.

sidered (Table II). It should be noted that although the AB pattern of the *p*-tolyl ring is highly resolved, the lines attributed to H<sub>5,8</sub> and H<sub>6,7</sub> are rather broad and did not show any fine structure (Figure 3). These phenomena are in good agreement with the small HOMO-LUMO energy gap of this dianion (0.18 eV (Table IV)). This relatively narrow energy gap is also manifested in the <sup>13</sup>C NMR of 6<sup>2-</sup>/2Na<sup>+</sup>. The <sup>13</sup>C NMR of 6<sup>2-</sup>/2Na<sup>+</sup> at 213 K in THF-*d*<sub>8</sub> gave the expected eight bands in the range of 164–100 ppm. At 273 K only seven bands were detected after a short accumulation. Accumulation of 1000–2000 scans enabled us to observe the eight lines which appear as broad ones. These phenomena can be rationalized in terms of local paramagnetic contributions in the region of the high charge density. Such a contribution may cause line broadening of <sup>1</sup>H and <sup>13</sup>C NMR bands and in extreme cases may even lead to a total disappearance of these lines.

## Conclusions

A new class of dianions derived from polycyclic systems containing two nitrogen atoms has been prepared and its NMR parameters were determined. The resulting dianions are, as expected, paratropic and show moderate stability. From calculations and carbon NMR spectroscopy it is concluded that a significant portion of the charge resides on the nitrogen atoms. The charging experiments were carried out with sodium and lithium, and the spectra were measured at various temperatures. The temperature-dependent spectra of the lithium and the sodium salts contradict the trend expected due to the ion-solvation equilibrium. A different mode of bonding is suggested for the lithium and the sodium salts, viz., a covalent contribution to the structure of the lithium salts vs. an ionic nature of the sodium salts.

## Experimental Section

**Materials.** The benzo[*c*]cinnoline **3** was purchased from Aldrich Co. and used without further purification. Dibenzo[*a,c*]phenazine (**4**) and the quinoxaline derivatives **5** and **6** were prepared from the corresponding diamine and dicarbonyl compounds according to the following general procedure (as demonstrated for dibenzo[*a,c*]phenazine (**4**)): A mixture of 1 mmol of 9,10-phenanthrenequinone, 1 mmol of orthophenylenediamine, and a catalytic amount of HCl in 20 mL of ethanol was placed in a 50-mL flask equipped with a reflux condenser. The mixture was heated to reflux for 2 h with magnetic stirring. The precipitate was collected on a Büchner funnel. The resulting solid was crystallized from EtOH/CHCl<sub>3</sub>.

**Dibenzo[*a,c*]phenazine (4):** light brown needles, mp 223–224 °C (lit.<sup>20</sup> 227–228 °C); <sup>1</sup>H NMR (THF-*d*<sub>6</sub>) δ 8.21, 7.62 (*J*<sub>1</sub> = 7.8, *J*<sub>2</sub> = 1.5, 2 H), 8.53 (dd, *J*<sub>1</sub> = 7.7, *J*<sub>2</sub> = 1.5, 2 H), 8.38, 7.84 (AA'BB', 4 H), 7.75 (m, 4 H); <sup>13</sup>C NMR (THF) δ 141.9, 141.8, 131.7, 130.0, 129.8, 129.2, 129.0, 127.6, 125.7, 122.5. Anal. Calcd for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>: C, 85.69; H, 4.31; N, 10.0. Found: C, 85.93; H, 4.24; N, 10.16.

**2,3-Di-*p*-tolylbenzo[*g*]quinoxaline (5):** yellow needles, mp 197–198 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.76 (s, 2 H), 8.21, 7.62 (AA'BB', 4 H), 7.60, 7.23 (AB, 8 H), 2.44 (s, 6 H); <sup>13</sup>C NMR (THF) δ 154.4, 139.2, 138.7, 137.6, 134.6, 130.4, 129.0, 129.0, 127.7, 126.8, 20.9. Anal. Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.35; H, 5.98; N, 7.47.

**2,3-Di-*p*-tolylquinoxaline (6):** light brown needles, mp 145–146 °C; <sup>1</sup>H NMR (THF-*d*<sub>6</sub>) δ 8.16, 7.82 (AA'BB', 4 H), 7.54, 7.21 (AB, 8 H), 2.42 (s, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.5, 141.2, 138.7, 136.5, 129.7, 129.6, 129.2, 129.0, 21.3. Anal. Calcd for C<sub>22</sub>N<sub>18</sub>N<sub>2</sub>: C, 85.1; H, 5.84; N, 9.02. Found: C, 84.84; H, 5.54; N, 9.23.

**General Procedure for Metal Reduction Process.** Lithium, sodium wire, or potassium chips are introduced to the upper part of an extended NMR tube containing the polyheterocyclic compound, dissolved in THF-*d*<sub>8</sub> or DME-*d*<sub>10</sub> (Aldrich). The frozen solution was degassed and sealed under vacuum. The solution was brought into contact with the metal solution by turning the tube upside down.

**Quenching of the Anions.** All anions were quenched with oxygen. The quenching experiments were carried out by bubbling oxygen gas into the NMR sample under anhydrous conditions. Oxygen gas is bubbled via a syringe into the anion solution at a slow rate at -78 °C. The deep color disappears and the <sup>1</sup>H NMR of the solution is then recorded. In each case the only product observed was the starting material.

In one case a quench experiment was carried out with methyl bromide. To the anion of **3** was bubbled methyl bromide at -78 °C. The product was analyzed by CI mass spectrometry. The appearance of the *m/e* 211 is a proof of the dianionic nature of 3<sup>2-</sup>.

The NMR spectra were obtained on Bruker WH-300 pulsed FT spectrometer operating at 300.133 and 75.46 MHz for <sup>1</sup>H and <sup>13</sup>C NMR, respectively. The field/frequency regulations were maintained by <sup>2</sup>H locking. The free induction decay signals were digitalized and accumulated on an Aspect-2000 computer (32K).

**Registry No.** **3**, 230-17-1; 3<sup>2-</sup>, 94370-25-9; 3·2Li, 94370-20-4; 3·2Na, 94404-04-3; **4**, 215-64-5; 4<sup>2-</sup>, 94370-26-0; 4·2Na, 94370-21-5; **5**, 94370-19-1; 5<sup>2-</sup>, 94404-05-4; 5·2Li, 94370-22-6; 5·2Na, 94370-23-7; **6**, 3719-84-4; 6<sup>2-</sup>, 94370-27-1; 6·2Na, 94370-24-8; 9,10-phenanthrenequinone, 84-11-7; *o*-phenylenediamine, 95-54-5; lithium, 7439-93-2; sodium, 7440-23-5; oxygen, 7782-44-7; methyl bromide, 74-83-9; potassium, 7440-09-7.

(20) Hall, D. M.; Huaun-Yong, H.; Bhanthumnavin, B. *J. Chem. Soc. Perkin Trans. 2* 1973, 2131.

# Mn(CNR)<sub>6</sub><sup>+2+</sup> Electron Self-Exchange in Acetonitrile. A Possible Distance Dependence for a Bimolecular Electron-Transfer Reaction in Solution

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**Abstract:** The electron self-exchange of Mn(CNR)<sub>6</sub><sup>+2+</sup> has been measured, for five alkyl R groups by <sup>55</sup>Mn NMR, as a function of concentration, temperature, and added *n*-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>. The results (0.1 M *n*-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub>, 26 °C) are the following: R = CH<sub>3</sub>, *k* (M<sup>-1</sup> s<sup>-1</sup>) = 2.06 × 10<sup>7</sup>, Δ*H*<sup>\*</sup> (kcal/mol) = 1.79, Δ*S*<sup>\*</sup> = -19.5 cal/mol-deg; CH<sub>3</sub>CH<sub>2</sub>, 1.97 × 10<sup>6</sup>, 3.61, -17.7; (CH<sub>3</sub>)<sub>2</sub>CH, 2.61 × 10<sup>5</sup>, 4.85, -17.7; (CH<sub>3</sub>)<sub>3</sub>C, 6.51 × 10<sup>4</sup>, 5.38, -18.5; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 1.30 × 10<sup>6</sup>, 1.97, -24.0. All rate constants increase with ionic strength. The data are analyzed in terms of a current semiclassical theory of electron transfer by estimating precursor complex formation constants and inner-sphere and outer-sphere reorganization energies. It is concluded that, within the assumptions, the rate variation is due to a decrease in electron-transfer rate constant with distance. The possibility, more consistent with the activation parameters, that the rate variation arises from a decrease in the precursor complex stability due to a requirement to attain a common, short electron-transfer distance, is also discussed.

The study of the electron-transfer reactions of transition metal complexes has been an especially active field in recent years

because improved theoretical treatments and refined experimental work have developed cooperatively.<sup>1-4</sup> This is especially apparent