182. The Radical Anions of *N,N'*-Dicyanoquinone Diimines, a New Class of Electron Acceptors

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The radical anions of 12 *N,N'*-dicyanoquinone diimines, a new class of electron acceptors, have been characterized by their hyperfine data with the use of ESR and ENDOR spectroscopy. The largest coupling constant (0.30–0.45 mT), due to the two ^{14}N nuclei in the exocyclic positions, gives rise to a conspicuous broadening of the peripheral ESR lines by an incomplete averaging of the hyperfine anisotropy. The most plausible interpretation of the experimental results for the radical anions of *N,N'*-dicyano-1,4-benzoquinone diimine (**1**) and *N,N'*-dicyano-9,10-anthraquinone diimine (**9**) is in terms of both *'syn'*- and *'anti'*-configurations contributing to the ESR and ENDOR spectra and having equal proton- and ^{14}N-coupling constants. The π-spin distribution in the radical anions of *N,N'*-dicyanoquinone diimines is compared with those in the analogous ions of tetracyanoquinodimethanes and quinones.

Introduction. – Owing to a one-step synthesis from the corresponding quinones [1–3], *N,N'*-dicyanoquinone diimines have become readily available in the last few years. These compounds represent a new class of electron acceptors which exhibit two reduction waves at potentials similar to those of analogous tetracyanoquinodimethanes [4]. They are also capable of forming electrically conducting CT complexes with strong electron donors such as 1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene (= 2-(1,3-dithiol-2-ylidene)-1,3-dithiole; TTF) [3] [5] [6]. Of particular interest are their highly conducting radical-anion salts formed with inorganic cations [7–9].

The formulas **1**–**12** specify those dicyanoquinone diimines of which the radical anions are dealt with in the present work.

The two CN groups in **1**–**12** are coplanar with the quinone-diimine π-systems and adopt the *'syn'*- or *'anti'*-configuration. The planar geometry has been verified by X-ray crystallography for *N,N'*-dicyano-1,4-naphthoquinone diimine (**8**) in its TTF complex [5] and for the 2,3-dimethyl derivative, **10**, of *N,N'*-dicyano-9,10-anthraquinone diimine (**9**) [10]. The CN groups in both **8** and **10** are *'syn'*-configurated in the solid state. Planarity and *'anti'*-configuration of the CN groups have been observed for the crystalline *N,N'*-dicyano-1,4-benzoquinone diimine (**1**) [6] and for its 2,5-disubstituted derivatives **4** [7],

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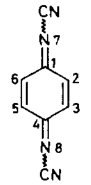

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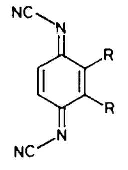
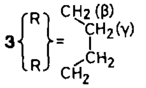


2 R = Me



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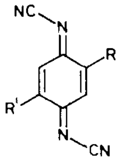
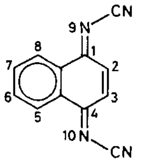


4 R = R' = Me
5 R = R' = *t*-Bu
6 R = R' = Cl
7 R = Cl, R' = Me



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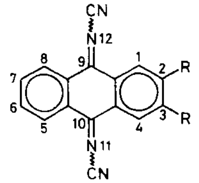
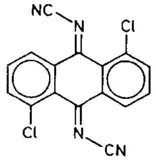


9 R = H
10 R = Me



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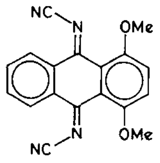

12

6 [11], and **7** [12] in the solid radical-anion salts. According to ^{1}H- and ^{13}C-NMR spectroscopic evidence, the *'syn'*-configuration is preferred in solution by the 2,3-substituted derivatives, **2** and **3**, of **1**, as well as by **8** and the 1,4-dimethoxy derivative, **12**, of **9** [2] [13]. By contrast, the *'anti'*-configuration is favoured in solution by the 2,5-disubstituted derivatives, **4**–**7**, of **1** and also by the 1,5-dichloro derivative, **11**, of **9** [2] [13]. For the parent diimine **1** in solution, a 43:57 population ratio of the *'syn'*- and *'anti'*-configurations is indicated by recent NMR studies [14] and, likewise, a configurational equilibrium prevails in the unsubstituted compound **9** [1] [2] [13]. However, contrary to **1**, the *'syn'* ⇄ *'anti'* isomerization in **9** must be fast on the time-scale of the NMR-chemical shifts, so that a higher effective symmetry D_{2h} is apparent [13]. An interchange between the *'syn'*- and *'anti'*-configurations has also recently been observed for the 2,3-dimethyl derivative **10** in solution [15].

Experimental. – *Syntheses of* **1**–**12** have been described elsewhere [1–3] [16].

Preparation of **1**$^{\cdot-}$–**12**$^{\cdot-}$. Because of their high electron affinities, **1**–**12** could readily be converted into the corresponding radical anions not only by the standard reaction with K in an ethereal solvent such as 1,2-dimethoxyethane (DME), THF, or 2-methyltetrahydrofuran (MTHF), but also by reduction with Hg or Zn in the more polar DMF. In the absence of air and humidity, **1**$^{\cdot-}$–**12**$^{\cdot-}$ were very persistent; their concentrations remained unchanged for weeks, even at r.t.

Instrumental. The ESR spectra were taken on the *Varian-E3* and *-E9* instruments, while the *Bruker-ESP-300* spectrometer system served for the ENDOR- and general TRIPLE-resonance studies.

Results. – The ESR spectra of **1**$^{\cdot-}$–**12**$^{\cdot-}$ are exemplified in *Fig. 1* by those of the three parent radical anions **1**$^{\cdot-}$, **8**$^{\cdot-}$, and **9**$^{\cdot-}$. In sharp contrast to the previously studied radical anions of tetracyanoquinodimethanes [17] [18] which exhibited extremely narrow linewidths (0.005–0.008 mT), only a moderate resolution could be achieved for **1**$^{\cdot-}$–**12**$^{\cdot-}$. A conspicuous line-broadening was observed on going from the centres of the spectra to their peripheries and, to a lesser extent, on passing from the low-to the high-field halves.

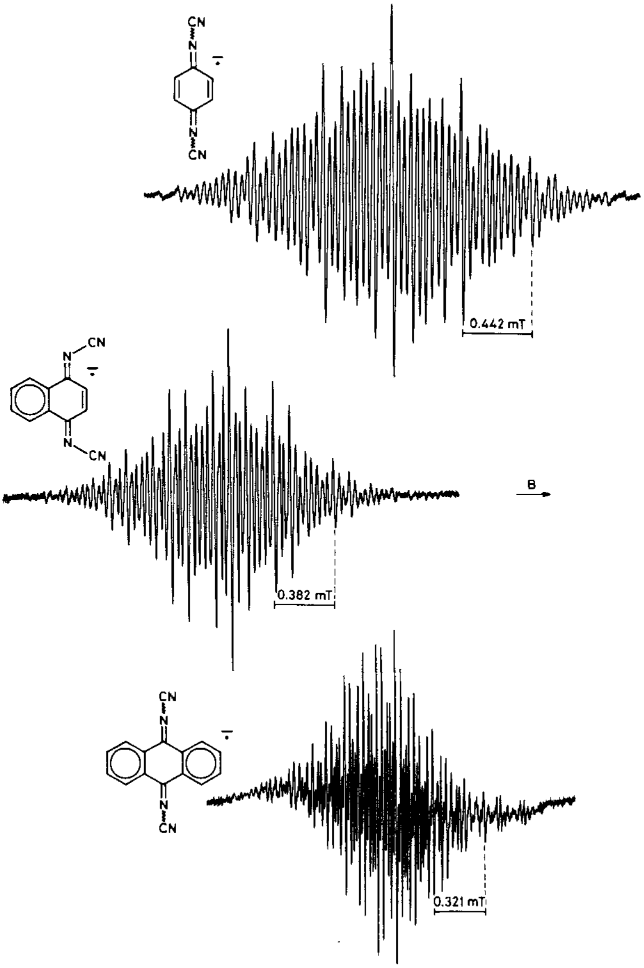

Fig. 1. *ESR spectra of* $\mathbf{1}^{\cdot -}$, $\mathbf{8}^{\cdot -}$, *and* $\mathbf{9}^{\cdot -}$. Solvent: DME ($\mathbf{1}^{\cdot -}$), DMF ($\mathbf{8}^{\cdot -}$), and MTHF ($\mathbf{9}^{\cdot -}$); counterion: K^+ ($\mathbf{1}^{\cdot -}$ and $\mathbf{9}^{\cdot -}$) and Hg_2^{2+} or Hg^{2+} ($\mathbf{8}^{\cdot -}$); temp.: 243 ($\mathbf{1}^{\cdot -}$), 263 ($\mathbf{8}^{\cdot -}$), and 233 K ($\mathbf{9}^{\cdot -}$).

These findings point to a considerable hyperfine anisotropy associated with the larger ^{14}N-coupling constant (0.30 to 0.45 mT). Expectedly, the line-broadening became more pronounced with the lengthening of the rotational correlation time, *i.e.* with an enhanced viscosity of the solvent and an increase in the size of the radical anion (see *e.g.* [19] [20a]). The ESR lines of $\mathbf{1}^{\cdot -}$–$\mathbf{12}^{\cdot -}$ were also much more difficult to saturate than the hyperfine components of the radical anions of tetracyanoquinodimethanes, so that the ENDOR signals were not as readily observable for the former as for the latter. Nevertheless, proton-ENDOR spectra could be obtained for all radical anions $\mathbf{1}^{\cdot -}$–$\mathbf{12}^{\cdot -}$ and, thus, the analysis of the ESR-hyperfine patterns was both facilitated and ensured.

The coupling constants of the ^{1}H and ^{14}N nuclei in $\mathbf{1}^{\cdot -}$ did not markedly depend on the temperature (203–298 K), the solvent (DME, THF, MTHF, DMF), and the counterion

Table 1. *^{1}H- and ^{14}N-Coupling Constants* [mT] *and g Factors for* **1**$^{\cdot-}$–**12**$^{\cdot-}$ [a])

1$^{\cdot-}$	Position
0.442(2N)	7,8
0.121(2N)	CN
0.201(2H)	2,3,5,6
0.163(2H)	
g = 2.0034	

2$^{\cdot-}$	Position
0.417(2N)	7,8
0.115(2N)	CN
0.221(2H)	5,6
0.107(6H)	2,3-Me
g = 2.0035	

3$^{\cdot-}$	Position
0.416(2N)	7,8
0.114(2N)	CN
0.224(2H)	5,6
0.148(4H)	2,3-CH$_2$(β)
< 0.010(4H)	2,3-CH$_2$(γ)
g = 2.0034	

4$^{\cdot-}$	Position
0.405(2N)	7,8
0.119(2N)	CN
0.167(6H)	2,5-Me
0.138(2H)	3,6
g = 2.0035	

5$^{\cdot-}$	Position
0.406(2N)	7,8
0.118(2N)	CN
0.165(2H)	3,6
< 0.010(18H)	2,5-(*t*-Bu)
g = 2.0035	

6$^{\cdot-}$	Position
0.444(2N)	7,8
0.121(2N)	CN
0.154(2H)	3,6
< 0.010(2Cl)	2,5-Cl
g = 2.0036	

7$^{\cdot-}$	Position
0.424(2N)	7,8
0.120(2N)	CN
0.177(1H)	3,6
0.120(1H)	
0.150(3H)	5-Me
< 0.010(1Cl)	2-Cl
g = 2.0036	

8$^{\cdot-}$	Position
0.382(2N)	9,10
0.103(2N)	CN
0.278(2H)	2,3
0.040(2H)	5,8
0.040(2H)	6,7
g = 2.0034	

9$^{\cdot-}$	Position
0.321(2N)	11,12
0.119(2N)	CN
0.085(2H)	2,3,6,7
0.064(2H)	
0.052(2H)	1,4,5,8
0.040(2H)	
g = 2.0034	

10$^{\cdot-}$	Position
0.309(2N)	11,12
0.115(2N)	CN
0.088(3H)	2,3-Me
0.067(3H)	
0.088(1H)	6,7
0.064(1H)	
0.053(2H)	1,4,5,8
0.040(2H)	
g = 2.0034	

11$^{\cdot-}$	Position
0.317(2N)	11,12
0.105(2N)	CN
0.094(2H)	2, 3, 6, 7
0.072(2H)	
0.037(2H)	4,8
< 0.010(2Cl)	1,5-Cl
g = 2.0035	

12$^{\cdot-}$	Position
0.298(2N)	11,12
0.103(2N)	CN
0.127(2H)	2,3
0.061(2H)	6,7
0.029(2H)	5,8
0.009(6H)	1,4-OMe
g = 2.0034	

[a]) Experimental error ± 0.002 mT and ± 0.001 mT in the coupling constants larger and smaller than 0.1 mT, respectively; g factors accurate to ± 0.0001.

(K$^+$, Hg$_2^{2+}$ or Hg^{2+}, Zn$^+$), and only a moderate dependence of these values on the temperature and environments was found in the ESR and ENDOR spectra of the remaining radical anions. The hyperfine data for **1**$^{\cdot-}$–**12**$^{\cdot-}$ are compiled in *Table 1*, together with the corresponding g factors[4]).

The assignments of the coupling constants to protons in the individual positions of **8**$^{\cdot-}$–**12**$^{\cdot-}$ have been based on MO calculations by the *McLachlan* procedure [22] and on

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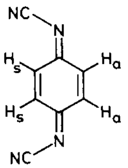
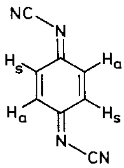
[4]) An ESR spectrum of **1**$^{\cdot-}$ was observed previously [21]. The coupling constants reported in that paper are throughout 8 ± 2% smaller than the values given in *Table 1*. This difference is presumably due to an error in the calibration of the magnetic field.

comparison with the analogous values for the radical anions of tetracyanoquinodimethanes and quinones (see *Discussion*). Theory requires a negative sign for the coupling constants of the ring protons (α) and a positive one for those of the CH_2 and CH_3 protons (β) at the sp^3-hybridized C-atoms adjacent to the π-system. The opposite signs of these values have been confirmed for **3**$^{\cdot-}$ by a general TRIPLE-resonance experiment (for an introduction to ENDOR- and TRIPLE-resonance spectroscopy, see [23]). MO models and analogy with structurally related radical anions have also served for the assignments of the coupling constants to the two pairs of ^{14}N nuclei. They clearly indicate that the larger value (0.30–0.45 mT) should be assigned to the ^{14}N nuclei in the exocyclic positions (7,8 in **1**$^{\cdot-}$–**7**$^{\cdot-}$, 9,10 in **8**$^{\cdot-}$, 11,12 in **9**$^{\cdot-}$–**12**$^{\cdot-}$). Both coupling constants are predicted to be positive. For the larger value, this prediction is in accordance with the observation that the above-mentioned broadening of the ESR lines is more pronounced in the high- than in the low-field halves of the spectra (see, *e.g.* [20a] for the underlying theory).

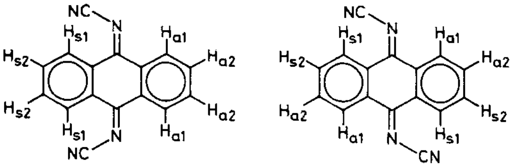
Discussion. – *Configuration of* **1**$^{\cdot-}$ *and* **9**$^{\cdot-}$. The hyperfine data for **1**$^{\cdot-}$ *(Table 1)* indicate the presence of *two pairs* of equivalent protons. They are diagnostic of either C_{2v} or C_{2h} symmetry which characterize the *'syn'*- and *'anti'*-configurations, respectively. However, an obvious interpretation of the results in terms of a *single* configuration does not seem realistic, since the two isomers coexist on an almost equal footing in solutions of the neutral compound **1** (see *Introduction*). The slight difference in the energies of the two configurations should not drastically increase on passing from **1** to **1**$^{\cdot-}$, unless one isomer is favoured by a strong association of the radical anion with its counterion. Tight ion pairs of this kind seem, however, not to be formed by **1**$^{\cdot-}$, as revealed by the relative lack of sensitivity of its ESR spectra to changes of temperature and environment (see *Results*). An alternative rationalization of the experimental findings implies the assumption that ESR and ENDOR spectra of **1**$^{\cdot-}$ arise from *both 'syn'*- and *'anti'*-configurated radical anions which have essentially *identical* ^1H- and ^{14}N-coupling constants. Equal hyperfine splittings can be expected for those protons (H_s) which, in each isomer, are *'syn'* to the near CN substituent, and an analogous statement should hold for the protons (H_a) *'anti'* to such a group.





Specific assignments of the observed values (0.201 and 0.163 mT) to pairs of H_s and H_a in **1**$^{\cdot-}$ are not feasible without further information. Unfortunately, the hyperfine data for the disubstituted radical anions **2**$^{\cdot-}$–**7**$^{\cdot-}$, which all should occur in a single configuration, fail to provide such an information. This is because the substitution changes the pertinent coupling constants by an amount comparable to the difference (0.038 mT) in the values of H_s and H_a.

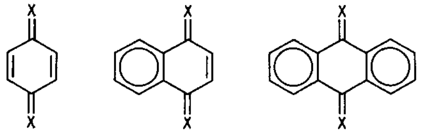
Arguments similar to those presented above for **1**$^{\cdot-}$ can be used in the discussion of the configuration of **9**$^{\cdot-}$. The observed hyperfine interaction with *four pairs* of equivalent protons *(Table 1)* is compatible with either the C_{2v} or C_{2h} symmetry, of the *'syn'*- and *'anti'*-configurations, respectively. However, also in the case of **9**$^{\cdot-}$, occurrence of only one configuration is at variance with the NMR-spectroscopic evidence for the neutral compound **9** which exhibits an effective D_{2h} symmetry in solution, as a consequence of a fast *'syn'*$\rightleftarrows$*'anti'* isomerization (see *Introduction*). Evidently, the rate of such an interconversion in **9** must be high relative to the difference in the relevant NMR-chemical shifts (10–100 MHz), but it needs not be so in **9**$^{\cdot-}$ on the hyperfine time-scale (10^6–10^7 Hz). Thus, for **9**$^{\cdot-}$ as well, the assumption seems reasonable that the ESR and ENDOR spectra arise from *both* configurations and that those protons (H_{s1}, H_{s2}, H_{a1}, and H_{a2}) which are similarly located relative to the near CN substituents have equal coupling constants.



Comparison of the hyperfine data for **9**$^{\cdot-}$ with those for **10**$^{\cdot-}$ and **11**$^{\cdot-}$ *(Table 1)* show that, unlike **1**$^{\cdot-}$, dimethyl and dichloro substitution on **9**$^{\cdot-}$ does not greatly change the coupling constants of H_{s1}, H_{s2}, H_{a1}, and H_{a2}. In the case of **11**$^{\cdot-}$, which exists exclusively in the *'anti'*-configuration, such a comparison strongly suggests that the *smaller* (0.037 mT) of the two coupling constants assigned to the protons at C(1), C(4), C(5), and C(8) of **9**$^{\cdot-}$ should belong to the pair of H_{s1}; this choice leaves the larger value (0.052 mT) for the pair of H_{a1}. An analogous information with respect to the coupling constants of the protons at C(2), C(3), C(6), and C(7) is, however, not available from the hyperfine data for **10**$^{\cdot-}$, since, in this case, both *'anti-* and *'syn'*-configurated radical anions contribute to the ESR and ENDOR spectra.

Spin Distribution. In *Table 2,* the coupling constants for **1**$^{\cdot-}$, **8**$^{\cdot-}$, and **9**$^{\cdot-}$ are presented along with those for the radical anions of the analogous tetracyanoquinodimethanes (**1** (TCNQ), **8** (TCNQ), and **9** (TCNQ)) and quinones (**1** (Q), **8** (Q), and **9** (Q)).

A general pattern of the π-spin distribution in the radical anions of all these electron acceptors is provided by the LUMO's of 1,4-quinodimethane (= cyclohexa-2,5-diene-1,4-dimethylidene) and its benzo and dibenzo derivatives. *Fig. 2* shows the diagrams of these MO's in the *Hückel* approximation. Their prominent features are the large LCAO coefficients at the exocyclic centres which point to high π-spin populations at the corresponding atoms in the radical anions. The following trends in the π-spin distribution are predicted by *McLachlan*-type calculations [22], using appropriate *Hückel* parameters for the heteroatoms (see, *e.g.* [20b]).



X =			
C(CN)$_2$	**1** (TCNQ)	**8** (TCNQ)	**9** (TCNQ)
N–CN	**1**	**8**	**9**
O	**1** (Q)	**8** (Q)	**9** (Q)

Table 2. *Comparison of the Coupling Constants* [mT][a]) *for* $\mathbf{1}^{\cdot-}$, $\mathbf{8}^{\cdot-}$, *and* $\mathbf{9}^{\cdot-}$ *with the Corresponding Values for* $\mathbf{1}\,(\mathrm{TCNQ})^{\cdot-}$, $\mathbf{8}\,(\mathrm{TCNQ})^{\cdot-}$, $\mathbf{9}\,(\mathrm{TCNQ})^{\cdot-}$, $\mathbf{1}\,(\mathrm{Q})^{\cdot-}$, $\mathbf{8}\,(\mathrm{Q})^{\cdot-}$, *and* $\mathbf{9}\,(\mathrm{Q})^{\cdot-}$ *in the Tetracyanoquinodimethane (TCNQ) and Quinone (Q) Series*

Position	$\mathbf{1}\,(\mathrm{TCNQ})^{\cdot-}$ [b])	$\mathbf{1}^{\cdot-}$ [c])	$\mathbf{1}\,(\mathrm{Q})^{\cdot-}$ [d])
2,3,5,6	– 0.142(4H)	– 0.182(2H + 2H)[e])	– 0.237(4H)
7,8	+ 0.718(2C)[f])	+ 0.442(2N)	– 0.953(2O)[g])
CN	+ 0.099(4N)	+ 0.121(2N)	

Position	$\mathbf{8}\,(\mathrm{TCNQ})^{\cdot-}$ [b])	$\mathbf{8}^{\cdot-}$ [c])	$\mathbf{8}\,(\mathrm{Q})^{\cdot-}$ [d])
2,3	– 0.182(2H)	– 0.278(2H)	– 0.323(2H)
5,8	– 0.040(2H)	– 0.040(2H)	– 0.051(2H)
6,7	– 0.040(2H)	– 0.040(2H)	– 0.066(2H)
9,10	[h])	+ 0.382(2N)	– 0.858(2O)[g])
CN	+ 0.095(2N + 2N)[e])	+ 0.103(2N)	

Position	$\mathbf{9}\,(\mathrm{TCNQ})^{\cdot-}$ [i])	$\mathbf{9}^{\cdot-}$ [c])	$\mathbf{9}\,(\mathrm{Q})^{\cdot-}$ [d])
1,4,5,8	– 0.042(4H)	– 0.046(2H + 2H)[e])	+ 0.055(4H)
2,3,6,7	– 0.070(4H)	– 0.075(2H + 2H)[e])	+ 0.096(4H)
11,12	[h])	+ 0.321(2N)	– 0.753(2O)[g])
CN	+ 0.081(2N)	+ 0.119(2N)	

[a]) Signs required by theory and confirmed, in part, by experiment. [b]) [17]. [c]) This work. [d]) [24]. [e]) Averaged value. [f]) ^{13}C-coupling constant [25]. [g]) ^{17}O-coupling constant [26]. [h]) ^{13}C-coupling constant not reported. [i]) [18].

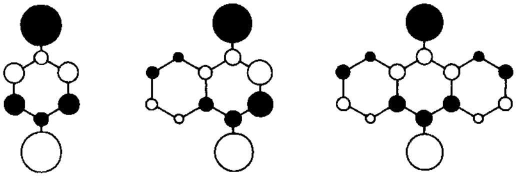


Fig. 2. *Diagrams of the LUMO's of 1,4-quinodimethane and its benzo and dibenzo derivatives*

i) Ongoing from tetracyanoquinodimethanes (X = C(CN)$_2$) to dicyanoquinone diimines (X = N–CN) to quinones (X = O), the π-spin populations in the arenediylidene moieties should be enhanced at the expense of those in the electron-attracting groups or atoms X. This prediction is confirmed experimentally by the absolute values of the ring-proton coupling constants increasing in the same order *(Table 2)*.

ii) Within each of three series, the extension of the π-system by a successive fusion of the benzene rings is also expected to lower the π-spin populations in X. This expectation is borne out by the parallel decrease in the absolute values of the ^{14}N- and ^{17}O-coupling constants observed for the magnetic nuclei in the exocyclic atoms of $\mathbf{1}^{\cdot-}$, $\mathbf{8}^{\cdot-}$, and $\mathbf{9}^{\cdot-}$ and in their quinone counterparts, respectively *(Table 2)*.

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