

## ANIONIC PRODUCTS OF THE TWO-ELECTRON REDUCTION OF AROMATIC NITRILES IN LIQUID AMMONIA\*

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The reduction of 9-cyanoanthracene by two equivalents of potassium in liquid ammonia was shown to yield the 9-cyanoanthracene dianion, whereas 1-naphtho- and benzonitrile gave the cyanodihydroaryl anions corresponding to the protonation of nitrile dianions at a position *para* to the cyano group. The 9-cyanoanthracene dianion underwent the same transformation in the presence of a stronger protonating agent, methanol. According to <sup>13</sup>C NMR spectral data of the generated species, the cyano group extracts the negative charge from the  $\pi$ -electronic system: *ca* 0.20:0.25 e in the case of the 9-cyanoanthracene dianion and *ca* 0.14:0.17 e in the case of cyanodihydroaryl anions. These estimations and the general NMR pattern of  $\pi$ -charge distribution in all the anionic species under investigation are in accordance with data from quantum molecular orbital calculations at the PM3 and INDO levels, being reflected by the fairly good linear relationships between the changes of ring carbon chemical shifts on going to the anionic species from the respective neutral precursors on the one hand and the calculated  $\pi$ -charges on the other. The *para*-orienting effect of the cyano group in the protonation of nitrile dianions is discussed in terms of the  $\pi$ -charge distribution in the starting dianion and the tendency to form a most stable cyanodihydroaryl anion isomer.

### INTRODUCTION

The reduction of arenes by alkali metals in liquid ammonia followed by the protonation or alkylation of the reduced anionic form of an arene is a general method for the preparation of dihydro- and alkylidihydroaromatic compounds.<sup>3-5</sup> For long time the aromatic nitriles were not involved in these reactions, probably because they were thought to be inclined to react at the cyano group rather than the aromatic ring.<sup>3</sup> However, recently it has been shown independently by two groups<sup>5,6</sup> that in fact the products of the two-electron reduction of aromatic nitriles in liquid ammonia are alkylated in the ring, providing results of synthetic value. The potential use of reductive nitrile activation towards electrophilic attack demands a knowledge of the nature of the anionic species produced by the reduction of substrates with alkali metals in liquid ammonia and the regularities governing the interaction of these anionic intermediates with alkylating reagents.<sup>7</sup> In turn, this makes it necessary to study their electronic structures.

Depending on degree of charge delocalization and the nature of the counter ion or substituents, the dianions

formed due to two-electron reduction of arenes in liquid ammonia are known to be stable in this medium or, being basic, to undergo protonation by ammonia to form cyclohexadienyl (dihydroaryl) anions. The latter in turn may be converted into dihydroarenes.<sup>3</sup> Usually, the conclusions about the nature of anionic precursors of the final products rely on indirect evidence. Direct NMR and ESR observations of the formation of the anionic products as a result of substrate reduction in liquid ammonia have been performed only for a few polynuclear aromatic hydrocarbons.<sup>7</sup>

In this connection, we now report the results of a <sup>13</sup>C NMR study of 9-cyanoanthracene (1), 1-naphthonitrile (2) and benzonitrile (3) reduction products by two equivalents of potassium metal in liquid ammonia. The choice of potassium was dictated by the better chance of avoiding protonation of the dianions formed than with other alkali metals.<sup>7</sup>

### RESULTS

The reduction was performed just before recording NMR spectra by adding two equivalents of potassium

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metal to a solution or suspension of substrate in liquid ammonia under an argon atmosphere at  $-65^{\circ}\text{C}$ .  $^{13}\text{C}$  NMR measurements were carried out by pulse recording with subsequent Fourier transformation. To facilitate signal assignment, the spectra of  $^{13}\text{C}$  and  $^1\text{H}$  mono-resonances,  $^{13}\text{C}$ - $^1\text{H}$  double resonance with broadband decoupling and proton off-resonance saturation were recorded. The spectral data are presented in Table 1.

The solutions of the reduction products of nitriles **1** and **2** are fairly stable and do not visibly change during the NMR recording time. However, the solution obtained as a result of the reduction of nitrile **3** was unstable, as indicated by the colour change and precipitation. According to these observations, the resonance assignments in NMR spectra of the reduction products of **1** and **2** are unequivocal, whereas with **3** the spectrum confirms the complexity of the transformations.

Two sets of signals were observed in the spectrum of an ammonia solution of the reduction products of **1** owing to their very different intensities. The more intense signals were assigned to the dianion ( $1^{2-}$ ) based on the chemical shifts and splittings in the off-resonance spectra in comparison with the analogous characteristics of the anthracene dianion ( $4^{2-}$ )<sup>8</sup> (see Table 1; cf. Ref. 11). On this basis, the doublet at  $\delta_{\text{C}}$  77.2 ppm was assigned to C-10 and two most downfield signals were assigned to C-11,14 and C-12,13. The assignment of the absorption at 141.6 ppm to the former pair of nodal carbons is justified by the fact that this signal shows one doublet splitting with  $J_{\text{CH}}^{\text{trans}} \approx 7$  Hz more than the signal at 148.9 ppm. It is reasonable to ascribe the group of doublets in the range 105–122 ppm to the carbons of lateral benzene rings. Similarly to the dianion  $4^{2-}$ , two low-field resonances of this group are assigned to  $\beta$ -carbons and two high-field resonances to  $\alpha$ -carbons of the anthracene framework. The assumptions about the more distinct assignment of these signals could be made by considering the chemical shift changes on passing from the precursors to the corresponding anionic species ( $\Delta\delta$  values; see below). The singlet at 55.8 ppm was assigned to C-9 since its upfield shift on going from  $4^{2-}$  to  $1^{2-}$  is an expected result of hydrogen substitution by the cyano group at C-9, as indicated by the comparison of  $^{13}\text{C}$  NMR data for anthracene and **1** (see Table 1). The singlet at  $\delta_{\text{C}}$  136.5 ppm was ascribed to a carbon of this group as it has no counterpart in the spectrum of  $4^{2-}$ .

Taking into account the location of the remaining signals of lower intensity observed in the spectrum along with the resonances attributed to  $1^{2-}$ , they could be ascribed tentatively to the 9-cyano-9, 10-dihydro-9-anthryl anion ( $1\text{-H}^-$ ) possibly resulting in a small amount from the interaction of  $1^{2-}$  with residual moisture absorbed when the NMR ampoule is being filled. To confirm this suggestion, **1** was reduced in the presence of methanol as a protonating reagent.

The  $^{13}\text{C}$  NMR spectrum of the resulting solution appeared to show all the signals mentioned above as attributed presumably to  $1\text{-H}^-$  being entirely similar to the spectrum of the 9,10-dihydro-9-anthryl anion ( $4\text{-H}^-$ )<sup>7,8</sup> (see Table 1). Based on this similarity, the triplet in the highest field was assigned to the  $\text{sp}^3$ -hybridized C-10. The singlet at  $\delta_{\text{C}}$  55.4 was ascribed to C-9 bearing the cyano group for the same reasons as considered above for  $1^{2-}$ . The doublets in the range 116–127 ppm were assigned to the carbons of lateral rings, with those at higher field being attributed to C-3, 6 and C-1, 8. The  $J_{\text{CH}}$  values in the off-resonance spectrum were also taken into account. In contrast, the discrimination between signals of C-2,7,4,5 was impossible. Finally, for the same reasons as considered below for  $4\text{-H}^-$ , the singlets at  $\delta_{\text{C}}$  123.9 and 141.2 ppm were assigned to C-12,13 and C-11,14, respectively, and the singlet at  $\delta_{\text{C}}$  132.7 ppm, analogously to the interpretation of the  $1^{2-}$  spectrum, was ascribed to the cyano carbon.

Hence the data considered above allow us to conclude that the two-electron reduction of **1** yields its dianion  $1^{2-}$ , which is fairly stable in liquid ammonia but is protonated in the presence of stronger acids of the ROH type (water, alcohols) to form the dihydroaryl anion  $1\text{-H}^-$ .

In contrast to the results for the reduction of **1**, treatment of **2** with two equivalents of potassium metal in liquid ammonia leads, as revealed by  $^{13}\text{C}$  NMR spectrum of the resulting solution (see Table 1), only to the formation of the protonation product of dianion  $2^{2-}$ , i.e. the 1-cyano-1,4-dihydro-1-naphthyl anion  $2\text{-H}^-$ . To facilitate the rationalization of  $^{13}\text{C}$  NMR spectra and elucidate the effect of the cyano group on the charge distribution in the framework, the 1,4-dihydro-1-naphthyl anion  $5\text{-H}^-$  was generated by treatment of naphthalene (**5**) under the same conditions. Analogously to the interpretation of the spectrum of  $1\text{-H}^-$  (see above), the triplet at  $\delta_{\text{C}}$  35.2 ppm was assigned to the  $\text{sp}^3$ -hybridized C-4 and the singlets at  $\delta_{\text{C}}$  117.4 and 145.6 ppm to C-10 and C-9, respectively. The assignment of the remaining doublets was confirmed by comparison of the experimental  $\delta_{\text{C}}$  values with the estimated values using the spectral data for **5** and 1,4-dihydronaphthalene ( $5\text{-H}_2$ )<sup>12</sup> and taking into account the chemical shift changes on going from **4** or 9,10-dihydronaphthalene ( $4\text{-H}_2$ )<sup>12</sup> to the anion  $4\text{-H}^-$ , from toluene<sup>14</sup> to the benzyl anion (**6**)<sup>13</sup> and from benzene and cyclohexa-1,4- and -1,3-diene<sup>14</sup> to the cyclohexadienyl anion (**7**) (see Table 1), with respect to the  $\delta_{\text{C}}$  values of allyl and 1-phenylallyl anions.<sup>13</sup> Further, the signal assignment in the spectrum of  $5\text{-H}^-$  corresponds to the expected pattern of negative charge distribution in this anion (see below).

Based on this assignment, the spectrum of  $2\text{-H}^-$  was rationalized taking into account the expected change in  $\delta_{\text{C}}$  values due to hydrogen replacement by the cyano group, as revealed on passing from **6** to the  $\alpha$ -cyano-

Table 1. <sup>13</sup>C NMR characteristics of arenes and their two-electron reduction products

Molecule or ion	Solvent, counter ion, temperature	<sup>13</sup> C-chemical shifts, $\delta$ [ppm from tetramethylsilane (TMS)] <sup>a</sup>												$\sum \Delta \delta_c$	Ref.
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11,14	C-12,13		
4	CDCl <sub>3</sub>	128.1	125.3	125.3	128.1	128.1	125.3	125.3	128.1	126.2	126.2	131.8	131.8	131.8	8
4 <sup>b</sup>	Li <sup>+</sup> , DME, 25 °C	102.8	115.7	115.7	102.8	102.8	115.7	115.7	102.8	76.4	76.4	151.7	151.7	151.7	8
	(a)	25.3	-9.6	-9.6	-25.3	-25.3	-9.6	-9.6	-25.3	-49.8	-49.8	19.9	19.9	19.9	-159.6
	(b)	147.0	147.9	147.9	147.0	147.0	147.9	147.9	147.0	147.0	147.0	147.9	147.9	147.0	8
4-H <sup>-</sup>	Li <sup>+</sup> , DME, 25 °C	114.6	126.0	109.3	126.3	126.3	109.3	126.0	114.6	77.5	40.2	146.5	120.1	120.1	8
	(a)	13.5	0.7	-16.0	-1.8	-1.8	-16.0	0.7	-13.5	-48.7	14.7	14.7	-11.7	-11.7	-103.9
	(b)	151.0	151.5	152.0	151.5	151.5	152.0	151.5	151.0	150.0	123.0	123.0	119.1	119.1	7
4-H <sup>-</sup>	Li <sup>+</sup> , NH <sub>3</sub> , -65 °C	111.6	126.1	107.1	126.1	126.1	107.1	126.1	111.6	79.0	39.8	145.6	119.1	119.1	7
	(a)	16.5	0.8	-17.7	-2.0	-2.0	-17.7	0.8	-16.5	-47.2	13.8	13.8	-12.7	-12.7	-115.8
1	CDCl <sub>3</sub>	128.9	125.2	126.3	128.9	128.9	126.3	125.2	128.9	105.4	132.6	133.2	130.6	117.1	9
1 <sup>b</sup> -b	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	110.5	111.6	121.4	105.6	105.6	121.4	111.6	110.5	55.8	77.2	141.6	148.9	136.5	9
	(a)	18.4	-13.6	-4.9	-23.3	-23.3	-4.9	-13.6	-18.4	-49.6	-55.4	8.4	18.3	19.4	-172.0
	(b)	152.0	158.0	153.0	152.0	152.0	153.0	158.0	152.0	149.0	149.0	141.2	123.9	132.7	9
1-H <sup>-c,d</sup>	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	117.0	126.4	116.1	126.9	126.9	116.1	126.4	117.1	55.4	36.5	141.2	123.9	132.7	9
	(a)	11.9	1.2	-10.2	-2.0	-2.0	-10.2	1.2	-11.9	-50.0	8.0	8.0	-6.7	15.6	-93.2
5	CDCl <sub>3</sub>	127.8	125.8	125.8	127.8	127.8	125.8	127.8	127.8	133.6	133.6	133.6	133.6	133.6	9
5-H <sup>-e</sup>	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	78.5	132.3	77.0	35.2	35.2	77.0	132.3	109.5	145.6	117.4	145.6	117.4	117.4	9
	(a)	49.3	6.5	-48.8	-0.8	-0.8	-48.8	6.5	-18.3	12.0	-16.2	-16.2	-16.2	-16.2	-127.1
	(b)	155.6	141.7	151.6	131.9	148.8	148.8	152.1	155.8	152.1	155.8	152.1	155.8	155.8	9
2	CDCl <sub>3</sub>	109.3	131.7	124.2	132.6	128.0	126.7	127.6	124.2	131.4	132.1	117.2	117.2	117.2	9
2-H <sup>-</sup>	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	53.2	129.9	94.8	33.0	33.0	126.1	116.7	117.8	142.1	123.6	135.8	135.8	135.8	9
	(a)	56.1	-1.8	-29.4	-1.9	-1.9	-29.4	0.3	-6.4	10.7	-8.5	18.6	18.6	18.6	-103.1
Benzene	CDCl <sub>3</sub>	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	128.5	9
7	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	78.0	131.8	75.8	30.0	30.0	75.8	131.8	75.8	131.8	131.8	118.8	118.8	118.8	10
	(a)	50.5	3.3	-52.7	3.3	3.3	-52.7	3.3	-52.7	3.3	3.3	139.5	139.5	139.5	9
3	CDCl <sub>3</sub>	112.4	132.1	129.2	132.8	132.8	129.2	132.1	112.4	118.8	118.8	118.8	118.8	118.8	9
3-H <sup>-f</sup>	K <sup>+</sup> , NH <sub>3</sub> , -65 °C	51.5	130.1	96.8	28.3	28.3	96.8	130.1	96.8	28.3	28.3	20.7	20.7	20.7	-129.7
	(a)	60.9	-2.0	-32.4	-2.0	-2.0	-32.4	-2.0	-32.4	-2.0	-2.0	20.7	20.7	20.7	-129.7
	(b)	150.8	150.8	154.4	154.4	154.4	154.4	154.4	154.4	154.4	154.4	154.4	154.4	154.4	154.4

<sup>a</sup> Substituted and nodal atoms have a singlet form of signal in monoresonance spectra and geminal group atoms, a triplet form; assignments are uncertain for chemical shift values marked by the same superscript symbol.

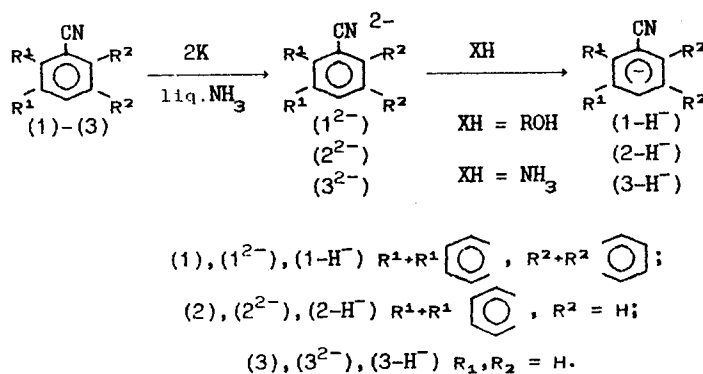
<sup>b</sup> PMR spectrum, NH<sub>3</sub>,  $\delta$  [ppm from tetramethylsilane (TMS)]: 1.60 s (1H, H-10), 3.21 d (2H, H-4,5), 3.69 d (2H, H-1,8), 4.0 m (2H, H-2,7), 4.26 m (2H, H-3,6).

<sup>c</sup> Reduction was carried out in the presence of an equimolar amount of methanol.

<sup>d</sup> PMR spectrum, NH<sub>3</sub>,  $\delta$  (ppm from NH<sub>3</sub>),  $\delta$  0.34): 3.3 s (2H, C<sup>10</sup>H<sub>2</sub>), 5.9 t (2H, H-3,6), 6.2 m (6H, H-1,2,4,5,7,8).

<sup>e</sup> PMR spectrum, NH<sub>3</sub>,  $\delta$  (ppm from NH<sub>3</sub>),  $\delta$  0.34): 2.9 m (3H, C<sup>4</sup>H<sub>2</sub>, H-1), 3.5 d (1H, H-3), 5.4 m (3H, H-2,6,8), 5.9 m (2H, H-5,7).

<sup>f</sup> Full <sup>13</sup>C NMR spectrum of the products of two-electron reduction of benzonitrile with potassium in liquid NH<sub>3</sub>,  $\delta$  (ppm from TMS): 25.4, 28.3 t, 29.9 d, 45.6, 51.5, 87.2 d, 96.8 d, 126.5 d, 127.1 d, 128.5 d, 129.7 d, 130.1 d, 139.5.



Scheme 1

benzyl anion (**8**)<sup>15</sup> and corresponding to the transfer of some portion of negative charge from the framework to the cyano group. However, this approach does not allow us to discriminate reliably the C-6 and C-8 from C-5 and C-7 signals.

Judging from the <sup>13</sup>C NMR spectrum of the product mixture obtained in the reduction of **3**, the result of this reaction was not as pronounced as for those of **1** and **2**. This agrees with the visual observations cited above. A set of signals was recognized as belonging to the 1-cyanocyclohexa-2,5-dien-1-yl anion (**3-H<sup>-</sup>**), according to their location, chemical shift changes accompanying insertion of the cyano group in the anion **7** and the splitting pattern in the monoresonance spectrum (see Table 1). However, along with these signals, doublets of approximately the same intensity were present at  $\delta_C$  29.9, 87.2 and 129.7 ppm, which were tentatively assigned to some other cyclohexadienyl anion, and absorptions of lower intensity at  $\delta_C$  126.5, 127.1 and 128.5 ppm, possibly arising from the interaction of **3-H<sup>-</sup>** with some of the cyclohexadiene products of its protonation.

Hence the results presented above show that the two-electron reduction of nitriles **1-3** by two equivalents of potassium metal in liquid ammonia forms the corresponding dianions **1<sup>2-</sup>-3<sup>2-</sup>**, followed in the cases of **2<sup>2-</sup>** and **3<sup>2-</sup>** by protonation by ammonia at a position *para* to the cyano group and the formation of the anions **2-H<sup>-</sup>** and **3-H<sup>-</sup>**, respectively. In contrast, the protonation of dianion **1<sup>2-</sup>** occurs only on treatment with protonating reagents stronger than ammonia, such as water or an alcohol (see Scheme 1).

#### DISCUSSION

The <sup>13</sup>C NMR spectroscopy of charged  $\pi$ -systems is widely used as an efficient method for the investigation of the relationships between structure and charge distribution on  $sp^2$ -hybridized carbons, since the corresponding  $\delta_C$  values are directly related to the  $\pi$ -electron

densities on these atoms. It seems reasonable to consider the variation of  $\delta_C$  values ( $\Delta \delta_C$ ) on passing to anions from their structurally related neutral compounds (precursors), rather than the  $\delta_C$  values themselves. Hence the contributions of the factors other than the character of  $\pi$ -electron charge distribution are minimized. For instance, such contributions apparently dominate in the change in the  $\delta_C$  value of the *ipso*-carbon resulting from substitution of the cyano group for hydrogen. All the  $\delta_C$  and  $\Delta \delta_C$  values under consideration are presented in Table 1.

#### 9-Cyanoanthracene dianion (**1<sup>2-</sup>**)

The effective attraction of the negative charge by CN in **1<sup>2-</sup>** is probably reflected by the value  $\Delta \delta_C = +19.4$  ppm for the carbon of this group, which is close to the analogous values for cyclohexadienyl anions. In addition, the  $\delta_C$  values themselves are close to those for the cyano groups of dianion **1<sup>2-</sup>** and the latter ions, as well as anion **8**.<sup>15</sup> Taking into account the absence of any significant charge on the carbon of the cyano group, the downfield shift of its signal on passing from **1** to **1<sup>2-</sup>** is akin to the same signal shift of nodal carbons and the carbons of dihydroaryl anions not participating efficiently in negative charge delocalization (see below). Moreover, this charge delocalization on to the cyano group changes the acetylenic character of its carbon to an allenic character (see the resonance structures **A** and **B**), which may be one of the reasons for the signal downfield shifts under discussion (cf. typical  $\delta_C$  values for the corresponding carbons in alkynes and allenes<sup>16</sup>).



The correlations of  $\delta_C$  or  $\Delta \delta_C$  values for certain carbons in dianions **1<sup>2-</sup>** and **4<sup>2-</sup>** are similar to each

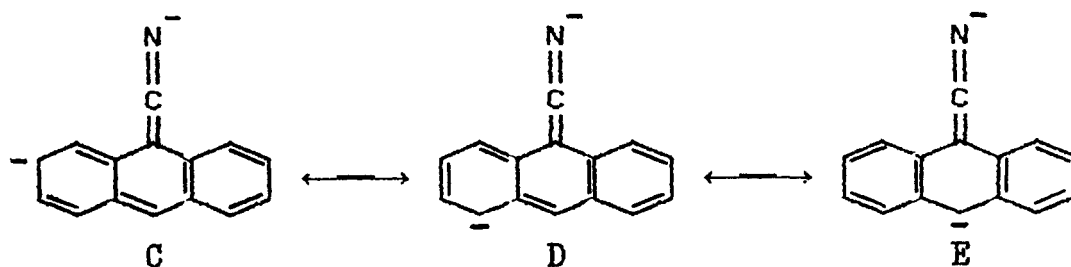
other, demonstrating that the extraction of some portion of negative charge by the cyano group from the framework does not alter significantly the electron density distribution among the ring carbons. Judging from the relationships of both the  $\delta_C$  and  $\Delta \delta_C$  values in the dianions under consideration, this distribution is in accord with the sequence  $C-10 \geq C-9 > C-4,5 \geq C-1,8 > C-2,7 > C-3,6$ . At the same time, the passage from  $4^{2-}$  to  $1^{2-}$  gives rise to asymmetry of charge distribution among two sets of carbons of the anthracene framework: the charge densities on C-1,3,6,8,9 conjugated to the cyano group decrease, whereas those on C-2,4,5,7,10 even increased. Accordingly, the sum of  $\Delta \delta_C$  values ( $\Sigma \Delta \delta_C$ ) for C-2,4,5,7,10,11,14 is  $-112.4$  ppm, whereas for C-1,3,6,8,9,12,13 this sum is only  $-59.6$  ppm. The former  $\Sigma \Delta \delta_C$  value is greater and the latter value is smaller than the  $\Sigma \Delta \delta_C/2$  value for  $4^{2-}$ . These correlations reflect the polarization of the  $\pi$ -electronic system of the anthracene dianion arising from the cyano group impacement and resulting in its splitting into two subsystems. The first consists of carbons not conjugated with the cyano group over which nearly unit or larger negative charge is distributed. The second, consisting of carbons conjugated with the cyano group, contains significantly less charge, which is apparently due to both the electron-accepting effect of the cyano group and the polarization of the  $\pi$ -system mentioned above. Thus, on going from  $4^{2-}$  to  $1^{2-}$  the  $\pi$ -electron density distribution is altered, approaching the state represented by the set of structures C–E with increasing contributions in the sequence  $C < D < E$ .

The  $\Sigma \Delta \delta_C$  value corresponding to the formation of  $2^{2-}$  from 2 is  $-171.6$  ppm, which is significantly smaller than the expected value of  $-270$  to  $-320$  ppm, in accordance with the well known relationships between chemical shift and  $\pi$ -charge,<sup>8,10,13,17</sup> on passing from the neutral to dianionic  $\pi$ -system. In this regard, the dianion  $1^{2-}$  is similar to  $4^{2-}$ , the  $\Sigma \Delta \delta_C$  value of which is  $-159.6$  ppm for the lithium salt in THF<sup>8</sup> (according to Ref. 11,  $\Sigma \Delta \delta_C$  for  $4^{2-}$  is  $-170.4$  ppm). As can be seen from the data for  $4^{2-}$  in Table 1, the passage from this system to the solution in liquid ammonia brings about an average upfield shift of

individual signals in the  $^{13}C$  NMR spectrum of ca 1 ppm. Taking this into account, a  $\Sigma \Delta \delta_C$  value of  $-173.6$  ppm was accepted for  $4^{2-}$ .

Such a difference between the experimental  $\Sigma \Delta \delta_C$  value and the value predicted by the aforementioned relationships suggests the coincidence of two effects accompanying the passage from 4 to  $4^{2-}$ : increased  $\pi$ -electron density and the exchange of the diatropic anisotropy in 4 for the paratropic anisotropy in  $4^{2-}$ . The latter effect may be quantitatively considered<sup>8</sup> by using the ring current approximation.<sup>18</sup> In this connection, it is worth noting that the absolute  $\Sigma \Delta \delta_C$  value for  $4^{2-}$  is at least not less than that for  $1^{2-}$ . At the same time, if one assumes that the cyano group participates efficiently in charge delocalization, the absolute  $\Sigma \Delta \delta_C$  value for  $4^{2-}$  is expected to be less than that for  $1^{2-}$ . Hence one may suggest that the electron-withdrawing effect of the cyano group manifests itself in a decreased paratropic influence of ring current due to the decreased electron density in the framework  $\pi$ -system on going from  $4^{2-}$  to  $1^{2-}$ . The similar decrease in paratropicity due to the electron-withdrawing effect of structure fragments has been observed for dianions of certain nitrogen heterocycles.<sup>19</sup>

In view of the above considerations, the corrections were assessed analogously<sup>13</sup> to the observed  $\Delta \delta_C$  values of  $1^{2-}$  making use of the Coulomb and resonance parameters for the cyano group recommended in Ref. 20. These corrections were found to be  $+0.4$  ppm for  $\alpha$ - and  $\beta$ -carbons,  $-3.1$  ppm for *meso*-carbons and  $-2.7$  ppm for the nodal carbons of the anthracenic framework. Thus, in accordance with the above expectation, the  $\Sigma \Delta \delta_C$  value of  $-42.6$  ppm observed for  $4^{2-}$  (Ref. 8) changes to  $-13.8$  ppm on going to  $1^{2-}$ . In contrast, close values of the total anisotropic corrections have been found for ring carbons of the precursors of these dianions, i.e. 4 ( $+85.8$  ppm<sup>8</sup>) and 1 ( $+82.4$  ppm). Hence the aggregation of all the anisotropic corrections leads to a change of 34 ppm for the  $\Sigma \Delta \delta_C$  value on going from  $4^{2-}$  to  $1^{2-}$ . If one accepts a  $\Sigma \Delta \delta_C$  value of  $-145$  ppm as equivalent to the appearance of unit negative charge in the  $\pi$ -electronic system,<sup>8</sup> this change corresponds to the location of



0.23 e on the cyano group ( $q_{\text{CN}}^-$ ) in  $1^{2-}$ . In view of the considerable amount of corrections, a range of 0.20–0.25 e should be accepted for this  $q_{\text{CN}}^-$  value.

### 9-Cyano-9,10-dihydro-9-anthryl anion ( $1\text{-H}^-$ )

By analogy with the above consideration of the cyano group effect in  $1^{2-}$ , let us compare the values of  $\Delta \delta_{\text{C}}$  and  $\Sigma \Delta \delta_{\text{C}}$  for the anions  $1\text{-H}^-$  and  $4\text{-H}^-$ . Attention should be paid to the closeness of  $\Delta \delta_{\text{C}}$  values for the latter and the diphenylmethyl anion.<sup>13</sup> On the other hand, considering  $4\text{-H}^-$  as bring of the dibenzocyclohexadienyl type, the similarity between the  $\Delta \delta_{\text{C}}$  values for the lateral rings induced by passing to this anion from both **4** and **4-H<sub>2</sub>** seems meaningful. According to Ref. 8, only C-9 in the anion  $4\text{-H}^-$  retains a small residual paratropic shift (+1.3 ppm, whereas the other sp<sup>2</sup>-carbons reveal diatropic shifts which are close to those in **4**. We believe on this basis that in this case and the cases to follow, anisotropic effects can be neglected.

The  $\Sigma \Delta \delta_{\text{C}}$  value of –45 ppm observed for carbons C-9,11,12,13,14 corresponds to ca 0.3 e negative charge dispersed among carbons in the cyclohexadienyl fragment of  $4\text{-H}^-$ . The effect of cyano group insertion at C-9 on going from  $4\text{-H}^-$  to  $1\text{-H}^-$  is displayed in the 22.6 ppm decrease in the absolute  $\Sigma \Delta \delta_{\text{C}}$  value for carbons of the framework. This quantity is equivalent to the extraction of  $q_{\text{CN}}^- = 0.16$  e by the cyano group. However, it is easily seen that charge redistribution really involves only lateral benzene rings whereas the total charge density in the cyclohexadienyl ring remains unchanged.

### 1-Cyano-1,4-dihydro-1-naphthyl anion ( $2\text{-H}^-$ )

Similarly to the findings from the comparison of  $\delta_{\text{C}}$  values for anion  $1\text{-H}^-$  and the related neutral compounds, the  $\delta_{\text{C}}$  values of  $5\text{-H}^-$  are close to those of the 1-phenylallyl anion.<sup>13</sup> Further, the  $\Delta \delta_{\text{C}}$  values are almost equal on going to  $5\text{-H}^-$  from both **5** and **5-H<sub>2</sub>**.<sup>12</sup> Of the  $\Sigma \Delta \delta_{\text{C}}$  value of –127 ppm observed for this anion, the portion of approximately –96 ppm belongs to C-1,2,3,9,10 displaying the location in the cyclohexadienyl fragment of 0.66 unit negative charge. Thus, on passing from  $4\text{-H}^-$  to  $5\text{-H}^-$ , the charge from the eliminated benzene ring is almost entirely transferred into the cyclohexadienyl fragment. The change in the  $\Sigma \Delta \delta_{\text{C}}$  value concomitant with insertion of a cyano group into the C-1 position on going from  $5\text{-H}^-$  to  $2\text{-H}^-$  corresponds to the total framework charge decreased by  $q_{\text{CN}}^- = 0.17$  e. However, unlike the dihydroaryl anions considered above, in this case the total charge is extracted in nearly equal portions from both benzene and cyclohexadienyl moieties. Furthermore, polarization of the cyclohexadienyl  $\pi$ -system takes place, consisting in the shift of electron density from C-3,10 to C-1. As a result, whereas the negative

charges on C-1 and C-3 in  $5\text{-H}^-$  are almost identical, C-1 in  $2\text{-H}^-$  carries approximately twice as large a negative charge as C-3.

### 1-Cyanocyclohexa-2,5-dien-1-yl anion ( $3\text{-H}^-$ )

Judging from the  $\Delta \delta_{\text{C}}$  values of anions **7** and  $3\text{-H}^-$ , the insertion of a cyano group brings about a change in the correlation of charge densities on C-1 and C-3,5 which is analogous to that considered above for the passage from  $5\text{-H}^-$  to  $2\text{-H}^-$ . The  $\Sigma \Delta \delta_{\text{C}}$  value for anion **7** is –149 ppm, which is close to the –145 ppm equivalent of the unit negative  $\pi$ -charge.<sup>8</sup> For  $3\text{-H}^-$ , the  $\Sigma \Delta \delta_{\text{C}}$  value is –130 ppm, being 19 ppm smaller in absolute value and corresponding to the absorbance of  $q_{\text{CN}}^- = 0.14$  e by the cyano group. It seems that this estimation, being anisotropically affected to a smaller extent among the cases under consideration, was close to the values obtained for the anions  $1\text{-H}^-$  and  $2\text{-H}^-$ . This finding supports the possibility of neglecting anisotropic effects for all the cyclohexadienyl anionic systems in the framework of the analysis performed.

Thus, from all the above results, it can be concluded that the involvement of the cyano group in the  $\pi$ -charge delocalization in the anionic systems under consideration brings about the absorbance of  $q_{\text{CN}}^-$  densities of 0.20–0.25 e in dianion  $1^{2-}$  and 0.14–0.17 e in anions  $1\text{-H}^-$ ,  $2\text{-H}^-$  and  $3\text{-H}^-$  (Table 2). However, it is noteworthy that these quantities comprise the ion association effect, which is capable of strengthening the electron-withdrawing influence of the cyano group if tight counter-ion association with the nitrogen anionic centre takes place.<sup>21</sup> Evaluating the portion of negative charge located on nitrogen, the polarization within the cyano group itself must be taken into account.

Table 2.  $\pi$ -Electron charges ( $q$ ) on the cyano group in the two-electron reduction products of aromatic nitriles

Ion Method <sup>a</sup>	$q_{\text{C}}$	$q_{\text{N}}$	$q_{\text{CN}}$
$1^{2-}$ a	+0.12	–0.35	–0.23
	+0.11	–0.32	–0.21
	+0.13	–0.36	–0.23
$1\text{-H}^-$ a	+0.11	–0.25	–0.13
	+0.10	–0.24	–0.14
	+0.11	–0.27	–0.16
$2\text{-H}^-$ a	+0.12	–0.26	–0.14
	+0.11	–0.25	–0.15
	+0.13	–0.30	–0.17
$3\text{-H}^-$ a	+0.12	–0.29	–0.17
	+0.11	–0.27	–0.16
	+0.14	–0.28	–0.14

(a) From PM3 calculations; (b) from INDO calculations; (c) from <sup>13</sup>C NMR data ( $\Delta \delta_{\text{C}}/145.0$ ).

Assuming that the downfield shift of *ca* 20 ppm observed for the cyano group carbon on passing from precursors to anions is a measure of the electron deficiency induced at this site and ascribing equivalent electron density to nitrogen, it is concluded that the latter carries the negative charge of 0.3 e. However, this obviously overestimated quantity is not sufficient to consider nitrogen as the most preferred site for the location of the counter ion, since in all anionic species under consideration, judging from their  $\Delta \delta_C$  values, even larger negative charges are located on *ipso*-carbons and, in  $1^{2-}$ , on C-10. Further, according to Ref. 22, in liquid ammonia ion association is unlikely to make a significant contribution to charge delocalization in the anionic species under consideration.

The value found of negative charge absorption by the cyano group in anions  $1-H^-$ ,  $2-H^-$  and  $3-H^-$  ( $q_{CN} \approx 0.15$  e) is in line with the finding by Olah and Mayer<sup>10</sup> that three *ortho-para*-located nitro groups in the anionic cyclohexadienyl system absorb *ca* 0.6 e. Assuming one third of this quantity to be the average measure of negative charge absorbed by a single nitro group ( $q_{NO_2} = 0.2$  e), one obtains the ratio  $q_{NO_2}/q_{CN} \approx 1.3$ , which almost coincides with the ratio of  $\sigma^-$  constants of these substituents (1.27 for  $NO_2$  and 1.00 for  $CN$ <sup>21</sup>). Further, it is worth emphasizing that the ratio  $q^-/\sigma^- \approx 0.15$  for these two substituents can turn out to be universal for a wider range of substituents. However, it cannot be ruled out that  $q_{NO_2} = 0.2$  is an underestimated value because of the possible saturation of the single nitro group effect in the trinitro-cyclohexadienyl system. If so, one should expect the real  $q_{NO_2}/q_{CN}$  ratio to approximate the ratio  $\sigma_R^-(NO_2)/\sigma_R^-(CN) = 1.8$ .<sup>23</sup> Disregarding this uncertainty, the value  $q_{CN} \approx 1.15$  e seems reliable.

We believed it important to test the pattern of  $\pi$ -charge distribution in the anionic species derived above

by means of molecular orbital calculations. In the initial step, geometry optimization was performed using the version<sup>24</sup> of the valence approximation PM3. All the  $\pi$ -electronic systems were assumed to be planar with  $D_{2h}$  symmetry for the dianion  $4^{2-}$ ,  $C_{2v}$  for the dianion  $1^{2-}$  and the anions  $1-H^-$  and  $3-H^-$  and  $C_s$  for the anion  $2-H^-$ . Thereafter, the optimized geometric structures were applied to perform two procedures of calculating  $\pi$ -charge distribution: the first in the PM3 and the other in the INDO approximation. The results are presented in Table 3. It is easily seen that fairly good agreement is observed, which is supported by the fairly good linear correlations expressed by equations (1) and (2) for the dianions  $1^{2-}$  and  $4^{2-}$  and equations (3) and (4) for the anions  $1-H^-$ ,  $2-H^-$  and  $3-H^-$ :

$$\Delta \delta_C^i = 117.7 q_C^i (\text{PM3}) - 5.0 \quad (r = 0.98) \quad (1)$$

$$\Delta \delta_C^i = 121.6 q_C^i (\text{INDO}) - 4.1 \quad (r = 0.99) \quad (2)$$

$$\Delta \delta_C^i = 120.9 q_C^i (\text{PM3}) - 1.7 \quad (r = 0.97) \quad (3)$$

$$\Delta \delta_C^i = 131.9 q_C^i (\text{INDO}) - 1.8 \quad (r = 0.96) \quad (4)$$

These relationships appeared to be close to those derived previously for the dianion  $4^{2-}$ , the anion  $4-H^-$  and their cationic counterparts on the basis of CNDO/2 calculations.<sup>8</sup> Further, the closeness of the experimentally estimated  $q_C$  values located on the cyano carbon to the calculated values, and also the corresponding charge distributions within the cyano group (Table 2), is noteworthy.

The pattern of negative charge distribution revealed in the anionic reduction products of aromatic nitriles in liquid ammonia allows one to establish how the cyano group affects the relative basicity and protonation regioselectivity of nitrile dianions. It seems obvious that the insertion of the cyano group renders all the anionic

Table 3. Calculated  $\pi$ -electron charges ( $-q$ ) in the two-electron reduction products of aromatic nitriles by (a) PM3 and (b) INDO methods

Ion Method	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11,14	C-12,13
$1^{2-}$ a	0.153	0.151	0.087	0.227	0.227	0.087	0.151	0.153	0.443	0.409	-0.061	-0.099
b	0.163	0.132	0.069	0.218	0.218	0.069	0.132	0.163	0.432	0.432	-0.039	-0.078
$2^{2-}$ a	0.432	0.106	0.103	0.407	0.343	0.054	0.218	0.197	-0.064	-0.113		
b	0.428	0.119	0.094	0.424	0.344	0.039	0.196	0.227	-0.047	-0.093		
$3^{2-}$ a	0.407	0.190	0.048	0.552	0.048	0.190						
b	0.455	0.206	0.031	0.581	0.031	0.206						
$4^{2-}$ a	0.254	0.132	0.132	0.254	0.254	0.132	0.132	0.254	0.417	0.417	-0.095	-0.095
b	0.242	0.110	0.110	0.242	0.242	0.110	0.110	0.242	0.436	0.436	-0.070	-0.070
$1-H^-$ a	0.093	0.006	0.129	0.012	0.012	0.129	0.006	0.093	0.427		-0.106	-0.090
b	0.103	-0.011	0.120	-0.010	-0.010	0.120	-0.011	0.103	0.399		-0.088	0.099
$2-H^-$ a	0.431	-0.064	0.237		0.015	0.143	0.009	0.108	-0.111	0.082		
b	0.390	-0.067	0.241		-0.010	0.125	-0.009	0.108	-0.085	0.093		
$3-H^-$ a	0.440	-0.059	0.243		0.243	-0.059						
b	0.379	-0.057	0.234		0.234	-0.057						

systems in question more stable. The fact that the dianion  $1^{2-}$ , unlike  $4^{2-}$ , is not protonated by liquid ammonia suggests more effective stabilization by the cyano group substituted in the C-9 position for the anthracene dianionic system compared with the mono-anionic 9,10-dihydro-9-anthryl system. This difference could be attributed to the dramatic decrease in acidity on going from  $1-H^-$  to  $4-H^-$ .<sup>25</sup> A similar conclusion can be inferred for the difference in the benzoannulation stabilizing effect on the dianionic systems  $2^{2-}$  and  $3^{2-}$  on the one hand, and the cyclohexadienyl anion systems  $2-H^-$  and  $3-H^-$  on the other since, unlike  $1^{2-}$ , the dianions  $2^{2-}$  and  $3^{2-}$  are protonated in liquid ammonia, whose  $pK_a$  value is ca 34.<sup>26</sup>

It seems obvious that when discussing the origins of the protonation regioselectivity of  $1^{2-}$ ,  $2^{2-}$  and  $3^{2-}$ , one should first consider the relative stabilities of isomeric cyanodihydroaryl anions resulting from the protonation of the dianions in question and the charge distribution in the starting dianions. Assuming that the greater stabilizing effect is associated with the cyano group substitution in those sites of  $4-H^-$  and  $5-H^-$  which carry a larger negative charge, the formation of  $1-H^-$  and  $2-H^-$  containing the cyano group in the cyclohexadienyl ring as a result of protonation of  $1^{2-}$  and  $2^{2-}$  seems to be understandable. However, this argument cannot justify the preferred protonation just at the position *para* to the cyano group, but this regioselectivity is in line with the calculated relative stabilities of isomeric cyanocyclohexadienyl anions.<sup>27</sup> At the same time, the protonation regioselectivity of  $1^{2-}$  can be considered to correspond also to the  $\pi$ -charge distribution in this dianion since, according to the correlation of the  $\Delta\delta_c$  values (see Table 1), the larger charge density is located on C-10. However, the latter conclusion is not clearly supported by the calculation of the electron density distribution in  $1^{2-}$  (Table 3), with INDO results being closer to the correlation of C-9 and C-10  $\pi$ -charge densities as reflected by the corresponding  $\Delta\delta_c$  values than PM3 results. Taking this into account, one should assume the principal  $\pi$ -charge density to be located at a position *para* to the cyano group in dianions  $2^{2-}$  and  $3^{2-}$ , which is clearly supported by the calculated pattern of charge distribution in  $3^{2-}$ . Hence the regioselectivity of the protonation of aromatic nitrile dianions can be recognized to correspond with both the concept of kinetic control in carbanion reactions with electrophiles<sup>11,28</sup> and the relative stabilities of the resulting isomeric cyclohexadienyl anions.<sup>27</sup>

## EXPERIMENTAL

**Materials.** All the materials were commercially available. Tetrahydrofuran was purified according to a previously reported procedure<sup>19</sup> and redistilled from

disodium benzophenone solution under atmospheric pressure immediately into the reaction flask. Liquid ammonia was purified by dissolving sodium metal successive redistillation under an argon atmosphere into the reaction flask at  $-70^\circ\text{C}$ . Argon was purified by passing it through two flasks containing THF solution of disodium benzophenone. Benzonitrile was purified as described.<sup>30</sup> 1-Naphthonitrile and 9-cyanoanthracene were prepared according to previously reported procedures.<sup>31,32</sup>

**Preparation of carbanions.** Potassium metal (1.2 mmol) was added to a solution or suspension of an arene (0.6 mmol) in  $\text{NH}_3$  (1.2 ml) in an NMR ampoule under an argon atmosphere immediately before recording the NMR spectrum.

**Nuclear magnetic resonance spectra.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of precursor solutions in  $(\text{CD}_3)_2\text{CO}$  or  $\text{CDCl}_3$  (5% by weight) were obtained with internal  $\text{Me}_4\text{Si}$  as reference using a Bruker AC-200 or Bruker WP-200 SY spectrometer.  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the products of the two-electron reduction of arenes were obtained at  $-65^\circ\text{C}$  using a Bruker WP-200 SY spectrometer equipped with a broadband decoupler and Fourier transform accessory. A mixture of  $(\text{CD}_3)_2\text{CO}$  and  $\text{Me}_4\text{Si}$  (1:1, v/v) was used as an external (capillary) reference.

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