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Novel Carbocyclic Dianions: NMR Study of Charge Delocalization, Paratropicity, and Structure in the Dianions of Acephenanthrylene and Aceanthrylene

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The mode of electron delocalization of novel polycyclic dianions, viz. acephenanthrylene dianion ($\mathbf{2}^{2-}$) and aceanthrylene dianion ($\mathbf{3}^{2-}$), is deduced from their ^{1}H and ^{13}C NMR parameters (1D and 2D NMR). While the reduction of acephenanthrylene (**2**) afforded only the respective dianion ($\mathbf{2}^{2-}$), the reduction of aceanthrylene (**3**) afforded dianion ($\mathbf{3}^{2-}$) followed by monoanion (**4**). The electron delocalization of the neutral systems (**2**, **3**) as well as the respective dianions ($\mathbf{2}^{2-}$, $\mathbf{3}^{2-}$) is discussed. It is concluded that there exists a preferred path of electron delocalization which dominates. Interestingly, the paths of electron delocalization of the charged systems differ from those of the neutral systems. In the neutral systems **1**, **2**, and **3** the "aromatic" structures that dominate are **1b**, **2b**, and **3b**, respectively, whereas the bridge double bond represents only a small perturbation. On the other hand in the dianions $\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, and $\mathbf{3}^{2-}$ the bridges are part of the path of the electron delocalization. These differences of the paths of electron delocalization are accompanied by structural changes as manifested by the X-ray structures and by the coupling constants of the bridge protons and corroborated by calculations. It is demonstrated that in each case the path of electron delocalization that dominates is the one which has the minimum paratropic contribution.

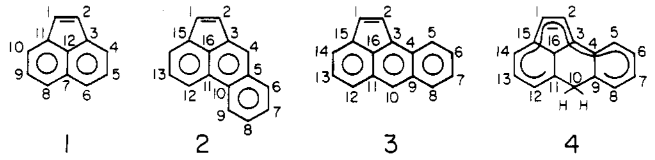
Introduction

An elegant demonstration of the tendency of systems to sustain aromatic character[1] is manifested in the charge density distribution of charged derivatives of $4n\pi$ and $(4n + 2)\pi$ electron systems. In principle, nonalternant conjugated pericondensed polycycles such as **1**, **2**, and **3** can accommodate more than one mode of electron delocalization over the π framework (Figures 1 and 2).

Acenaphthylene dianion[2] ($\mathbf{1}^{2-}$) has been reexamined recently and its charge delocalization was discussed.[3] Although it seems, at first sight, that there is no reason to assume or expect a larger contribution of one conjugated path of delocalization over the others, it has been demonstrated unequivocally for acenaphthylene (**1**) and its dianion $\mathbf{1}^{2-}$ that there is a preferred pattern of electron delocalization which dominates.[3a] Some plausible paths of electron delocalization for acenaphthylene (**1**) and its doubly charged derivative $\mathbf{1}^{2-}$ are shown in Figures 1 and 2, respectively. It has been suggested that the charge delocalization in $\mathbf{1}^{2-}$ is best described by formula $\mathbf{1}^{2-}\mathbf{a}$ (Figure 2) while that of the neutral system agrees with structure **1b**[3a] (Figure 1). It should be noted here that upon reduction a change in the pattern of electron delocalization emerges. In the neutral system **1** the aromatic structure **1b** is preferred over the nonaromatic "annulenic type" **1a** which has a perimeter of 11 π electrons over 11 carbons [$11\pi e$; 11C] (Figure 1). However, dianion $\mathbf{1}^{2-}$ is best described by structure $\mathbf{1}^{2-}\mathbf{a}$ which can be described as "nonaromatic", resulting in the least destabilized structure in which two negative charges are delocalized in its periphery. In the other possible paths of delocalization of $\mathbf{1}^{2-}$ there are more destabilizing circuits of $4n\pi$ electrons, thus rendering them energetically less favorable.

The recent convenient synthesis of the two title compounds, viz. acephenanthrylene[4] (**2**) and aceanthrylene (**3**), enabled us to undertake a detailed investigation of the metal reduction of these two intriguing compounds and to explore their patterns of delocalization. Metal reduction of acephenanthrylene (**2**) and aceanthrylene (**3**) to the corresponding, so far undocumented, $(4n + 2)\pi$ electron dianions in THF and their characterization by NMR techniques is reported. For reasons discussed below, we applied recently developed two-dimensional NMR techniques (2D NMR).[5] Acephenanthrylene (**2**) gave the expected doubly charged anion $\mathbf{2}^{2-}$ while aceanthylene (**3**) gave a mixture of $\mathbf{3}^{2-}$ as a major product and monoanion **4** which is the protonation product of $\mathbf{3}^{2-}$ (Chart I). Calculations ($\omega\beta$) were performed on neutral **2** and **3** as well as on the corresponding dianions.[6] The results are discussed with respect to the charge delocalization and the magnetic properties of the systems. It seems that the pattern of electron delocalization is reflected by their structural parameters (vide supra). The various modes of conjugation in these complex polycyclic systems (**2**, **3**, $\mathbf{2}^{2-}$, and $\mathbf{3}^{2-}$, see Figures 1 and 2) are compared with those in

Chart I



1 2 3 4

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[‡] University of Nevada.

Table I. ^{1}H NMR Parameters of the Charged Systems 2^{2-}, 3^{2-}, and 4^- in THF-d_8

system^a	temp, K	^{1}H NMR pattern^{a,b}	neutral systems center of gravity^c	charged systems center of gravity^c
$2^{2-}/2Na^+$	293	6.02 (d, J = 7.6, H9), 5.69 (t, J = 7.5, H7), 5.47 (d, J = 8.5, H6), 5.40 (t, J = 8.4, H13), 5.29 (d, J = 8.1, H14), 4.88 (t, J = 7.3, H8), 4.78 (d, J = 2.1, H2), 4.72 (d, J = 2.0, H1), 4.42 (d, J = 6.6, H12), 4.27 (s, H4)	7.88	5.09
$2^{2-}/2Na^+$	213	6.04 (d, J = 7.4, H9), 5.68 (t, J = 7.1, H7), 5.46 (d, J = 8.0, H6), 5.41 (t, J = 6.8, H13), 5.28 (d, J = 8.1, H14), 4.88 (t, J = 6.8, H8), 4.74 (d, J = 2.4, H2), 4.68 (d, J = 2.2, H1), 4.45 (d, J = 6.7, H12), 4.31 (s, H4)	7.88	5.09
$2^{2-}/2Li^+$	293	6.32 (d, J = 7.9, H9), 5.88 (t, J = 7.3, H7), 5.70 (d, J = 8.5, H6), 5.62 (t, J = 7.5, H13), 5.43 (d, J = 8.2, H9), 5.17 (t, J = 6.6, H8), 4.78 (d, J = 6.7, H12), 4.63 (d, J = 1.8, H2), 4.56 (d, J = 1.8, H9), 4.31 (s, H 4)	7.88	5.24
$2^{2-}/2Li^+$	213	6.36 (d, J = 7.4, H9), 5.86 (t, J = 6.4, H7), 5.66 (m, H6, H13), 5.42 (d, J = 7.6, H9), 5.10 (t, J = 6.6, H8), 4.81 (d, J = 6.6, H12), 4.58 (s, H2), 4.54 (s, H1), 4.44 (s, H4)	7.88	5.24
$3^{2-}/2Li^+$	293	6.32 (d, J = 6.9, H5), 5.96 (t, J = 8.2, H7), 5.72 (d, J = 8.7, H8), 5.55 (d, J = 2.3, H1), 5.52 (t, J = 6.9, H6), 5.50 (t, J = 8.4, H13), 5.09 (d, J = 8.1, H14), 5.02 (d, J = 3.0, H2), 4.14 (d, J = 6.5, H12), 3.85 (s, H10)	7.89	5.27
$4^-/Li^{+\,d}$	293	7.10 (d, J = 7.3), 6.89 (d, J = 7.8), 6.79 (d, J = 7.2), 6.77 (t, J = 7.5), 6.66 (d, J = 3.2), 6.40 (t, J = 8.0), 6.32 (t, J = 7.5), 6.13 (d, J = 6.9), 5.78 (d, J = 3.2), 4.36 (s, 2 H)		6.54^e

[a] For numbering see Chart I. [b] Chemical shifts are given in ppm downfield from external TMS with δ = 3.67 ppm for THF-d_8. The spin–spin couplings are given in hertz. [c] Center of gravity in THF-d_8. [d] No assignment is given for the monoanion 4^-. [e] Center of gravity calculated by excluding the singlet absorption at 4.36 ppm.

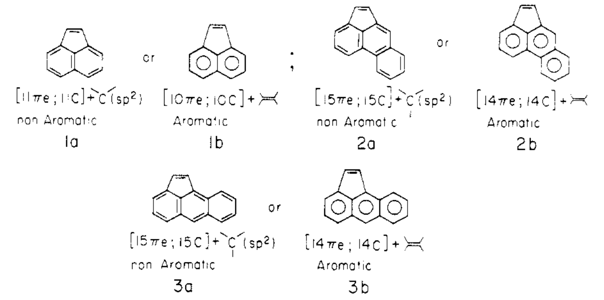

Figure 1. Possible patterns of electron delocalization of the neutral systems **1**, **2**, and **3**.

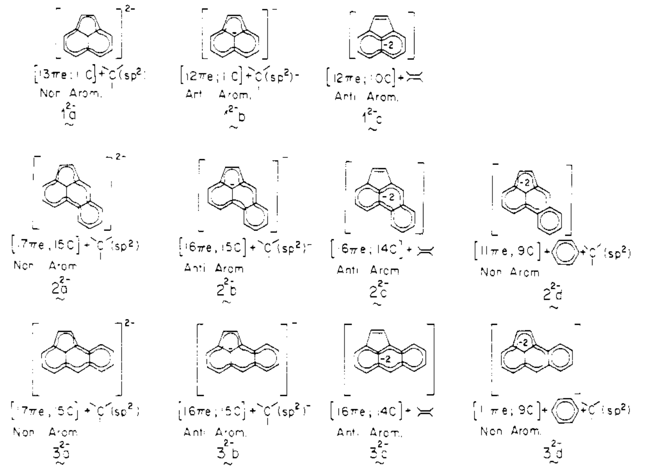

Figure 2. Possible patterns of charge delocalization of the respective dianions 1^{2-}, 2^{2-}, and 3^{2-}.

the acenaphthylene case. We arrive at the conclusion that in the different systems there are paths of delocalization which are clearly preferred over the others and that this discrimination is based on the energy content of the structures. Therefore, the structures which best represent anions 2^{2-} and 3^{2-} are the ones in which the π-electrons are delocalized over the entire periphery (Structures 2^{2-}**a** and 3^{2-}**a**). However, in the neutral systems the bridge double bond represents only a minor perturbation and is not strongly conjugated to the aromatic skeleton, as exemplified by structures **1b**, **2b**, and **3b** in Figure 1. It will be demonstrated that the discussed variations of the patterns of electron delocalization represent an elegant manifestation of the tendency of polycyclic conjugated π systems to minimize paratropic contributions and to gain maximum aromatic character.[3a]

Results

The ^{1}H and ^{13}C NMR parameters of acephenanthrylene (**2**) and aceanthrylene (**3**) are given in the Experimental Section. The center of gravity of the ^{1}H NMR spectra of **2** and **3** are 7.88 and 7.89 ppm, respectively, a typical value for aromatic diatropic systems (vide infra). The center of gravity of the ^{13}C NMR spectra of acephenanthrylene (**2**) and aceanthrylene (**3**) are 128.6 and 128.3 ppm, respectively. The reductions of acephenanthrylene (**2**) and aceanthrylene (**3**) were carried out in THF-d_8 by alkali metals (lithium, sodium, and potassium), yielding 2^{2-}, 3^{2-}, and 4^-, respectively. The dianionic nature of the charged systems was deduced from their proton and carbon NMR spectra, the respective chemical shift–charge density correlations,[8] and quenching experiments.

The assignment of the ^{13}C NMR spectra is of utmost value in the investigation of charged systems as it reflects the distribution of charge. Therefore, efforts were made to assign unambiguously the ^{1}H and ^{13}C NMR spectra of the dianions 2^{2-} and 3^{2-}. In addition to the 1D ^{1}H and ^{13}C spectra, recently developed two-dimensional NMR techniques (2D NMR) were used to minimize chemical shift arguments as far as possible and to avoid circular reasonings in the discussion. In this way one can be more confident when comparing the calculated and experimental charged density (as deduced from the ^{13}C chemical shifts). The two-dimensional ^{1}H/^{1}H chemical shift correlation spectrum (2D-COSY)[7a] in its version that emphasizes long-range couplings (2D-COSYLR)[7b] of the acephenanthrylene dianion (2^{2-}) is shown in Figure 3. In these experiments we applied high digital resolution in order to preserve the information of the spin–spin coupling constants. We chose the COSY-45 and COSYLR-45 as they are more suitable pulse sequences for non-first-order spectra.[7b] The long-range "cross peaks" of the singlet attributed to H_4 of 2^{2-} with several peaks and the relative strong "cross peak" of only one of the bridge protons with only one triplet attributed to H_{13}) enabled a full unam-

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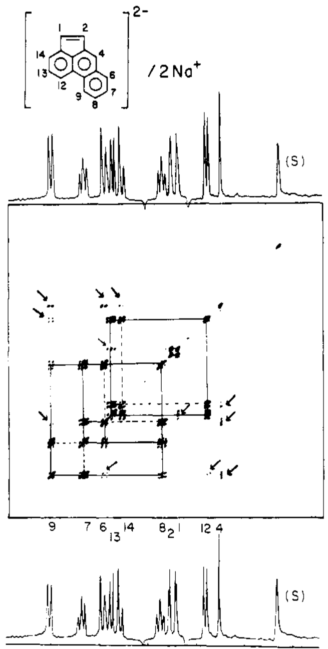

Figure 3. 2D-COSYLR-45 NMR spectrum of acephenanthrylene dianion (2^{2-}) as disodium salt in THF-d_8: — indicates $^3J_{HH}$; - - - indicates meta coupling, and long-range coupling is indicated by arrows.

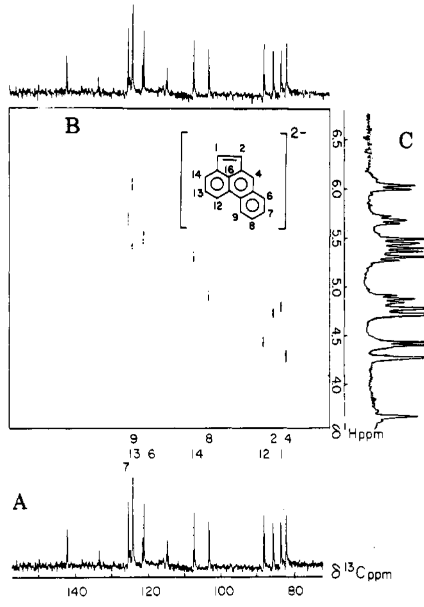

Figure 4. 2D-$^{13}C/^1H$ chemical shift correlation NMR spectrum of acephenanthrylene dianion (2^{2-}) as disodium salt in THF-d_8. (A) Normal 1D-^{13}C spectrum; (B) correlation spectrum; (C) normal 1D-^1H spectrum.

biguous assignment of the proton spectrum (Table I). The assignment was assisted by T_1 (inversion–recovery) experiments.[19c] As expected, the "bay" protons, i.e., H_9 and H_{12}, showed the shortest relaxation time.

The carbon-13 NMR spectra could not be assigned by conventional methods such as selective decoupling. Therefore we recorded the 2D $^{13}C/^1H$ chemical shift correlation[9a] (Figure 4, Table II) optimized for $^1J_{CH}$ of 150 Hz. The total high field shifts of the ^{13}C bands of 2^{2-} (Table II) amount to 112.8 and 114.4 ppm per e for the disodium and dilithium salts, respectively. These values are in good agreement with the value found for acenaphthylene dianion (1^{2-}) prepared under various reduction conditions (112.9 to 124.3 ppm per e).[3b]

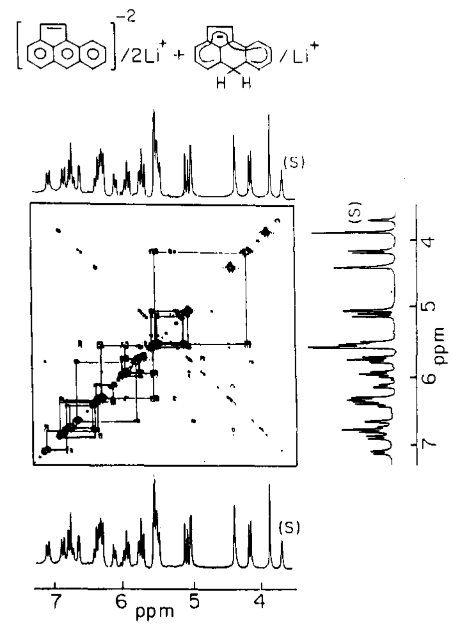

Figure 5. 2D-COSY-45 NMR spectrum of the lithium reduction products of aceanthrylene (3) in THF-d_8: — indicates $^3J_{HH}$.

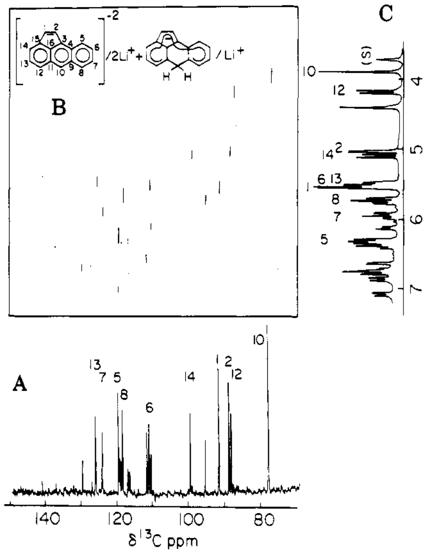

Figure 6. 2D-$^{13}C/^1H$ chemical shifts correlation NMR spectrum of $3^{2-}/2Li^+$ and $4/Li^+$ in THF-d_8. (A) ^{13}C projection spectrum; (B) correlation spectrum; (C) normal 1D-^1H spectrum.

The assignment of the NMR spectra of the lithium reduction products of 3 was more difficult in view of the low effective concentration of the charged species and its complexity. A 2D-homonuclear J-resolved experiment[7a,10] was carried out first, followed by a 2D COSY-45[7b] chemical shift correlation which is shown in Figure 5. From the complexity of the spectra we conclude that the reduction process afforded a mixture of two products. The $^{13}C\{H\}$ NMR spectrum consisted of 32 peaks including one line in the aliphatic region that was found to be a triplet with J_{CH} = 125 Hz, characteristic of an sp^3 carbon, thus proving that the products are 3^{2-} and monoanion 4. The assignment of the ^{13}C absorption bands was carried out by a $^{13}C/^1H$ 2D chemical shift correlation[9] experiment using the $^1J_{CH}$ coupling constant (average value $^1J_{CH}$ = 150 Hz)

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Table II. ^{13}C NMR Chemical Shifts and Calculated Charged Densities of 2^{2-}, 3^{2-}, and 4^{-}[a]

system[a]	temp, K	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	$\Delta\delta^{15}$C, ppm/e
$2^{2-}/2Na^+$	293	85.4 (−0.21)	83.3 (−0.21)	122.2[b] (−0.17)	81.8 (−0.23)	143.2[b] (−0.08)	121.8 (−0.10)	125.0 (−0.04)	103.5 (−0.13)	126.1 (−0.05)	115.2[b] (−0.12)	143.4[b] (−0.05)	88.1 (−0.16)	125.0 (−0.07)	107.7 (−0.10)	125.6[b] (−0.15)	134.4[b] (−0.12)	112.8
$2^{2-}/2Li^+$	293	80.8 (−0.21)	79.8 (−0.21)	123.8 (−0.17)	78.4 (−0.23)	142.9 (−0.08)	121.8 (−0.10)	125.9 (−0.04)	105.2 (−0.13)	127.0 (−0.05)	116.7 (−0.12)	144.2 (−0.05)	90.5 (−0.16)	126.0 (−0.07)	107.4 (−0.10)	124.5 (−0.15)	134.5 (−0.12)	114.4
$3^{2-}/2Li^+$	293	91.5 (−0.21)	88.8 (−0.18)	129.8[b] (−0.18)	166.6[b] (−0.07)	119.1 (−0.06)	110.7 (−0.10)	123.6 (−0.04)	118.0 (−0.10)	145.9[b] (−0.04)	78.0 (−0.27)	146.5[b] (−0.05)	88.2 (−0.21)	125.4 (−0.07)	99.3 (−0.15)	132.0[b] (−0.15)	124.1[b] (−0.12)	108.0
$4^-/Li^+$[c]	293[c]	140.6	131.7	130.0	129.0	127.2	126.4	126.4	118.7	118.3	116.4	115.9	111.4	110.0	106.8	95.5	36.1	(t, J = 125 Hz)

[a] For numbering see Chart I. All spectra were recorded in THF as solvent, and the ^{13}C chemical shifts are given in ppm downfield from TMS. Charge densities as obtained by the $\omega\beta$ calculations are given in parentheses. [b] Tentative assignment of quaternary carbon atoms not using 2D heteronuclear ^{13}C/^{1}H chemical shift correlation. [c] No assignment of the carbon resonances is given for $4^-/Li^+$.

(Table II, Figure 6). The center of gravity of the proton spectrum of $3^{2-}/2Li^+$ is 5.27 ppm, which corresponds to a high field shift caused by approximately 2.4 units of charge relative to neutral 3[8] (Table I).

The total high field shift of the ^{13}C bands of 3^{2-} with respect to neutral **3** is 108 ppm per electron (Table II). The ^{1}H and ^{13}C NMR parameters of $4/Li^+$ are summarized in Tables I and II. It is interesting to note that the protonation of the aceanthrylene dianion 3^{2-} that afforded **4** takes place selectively at C_{10}—a carbon with the highest charge density. However, this result is not surprising in view of a recent report of Müllen et al.[11] on the protonation of the acenaphthylene dianion (1^{2-}).

Calculations ($\omega\beta$)[6] were performed on the neutral as well as on the charged systems. The calculated charge densities for 2^{2-} and 3^{2-} are given in Table II. As expected for such aromatic molecules, the calculated HOMO–LUMO energy gaps for **2** and **3** are 1.040 and 0.793 β units, respectively. The calculated HOMO–LUMO gaps of the two dianions, i.e., 2^{2-} and 3^{2-}, are smaller than those of the neutral systems (0.455 for 2^{2-} and 0.657 β for 3^{2-}) but higher than that found for $4n\pi$ dianion[12,13] (Table III).

Calculated bond lengths for the neutral and the charged systems of the five-membered rings are reported in Table IV together with experimental and calculated $^3J_{HH}$ coupling constants. All $\omega\beta$ calculations[6] were performed with the habitual position, ω = 1.4; the tolerance in energy was at least 1×10^{-5} β unit.

Discussion

The Neutral Systems: Electron Delocalization, Diatropicity, and Structure. The acephenanthrylene (**2**) and aceanthrylene (**3**) are both 16π electron systems and should be classified merely on these grounds as paratropic "antiaromatic".[14] However, this classification contradicts their relative stability and pronounced diatropicity as deduced from their ^{1}H NMR spectra.

Platt's perimeter model[15] ascribes aromatic character to a system according to the number of π electrons in its periphery. The total number of π electrons in the peripheries of acephenanthrylene (**2**) and aceanthrylene (**3**) is 15. According to this model these two molecules are expected to be "nonaromatic" vinylic systems which is in contrast with experiment. The conjugated circuits model introduced by Randić[16] seems to be a real challenge for the peripheral model and it appears that this model affords the best description of the electronic structure of **2** and **3**. Referring to the conjugated circuits approach, acephenanthrylene (**2**) and aceanthrylene (**3**) can be regarded as composed of either phenanthrene or anthracene moieties linked to a virtually isolated double bond (Figure 1). The phenanthrene and anthracene moieties contain only conjugated circuits of $(4n + 2)\pi$ electrons and are therefore assigned as "pure" diatropic/aromatic molecules with Randić's A and even B factors equal to 1.[17] The conclusion based on this model correlates well with experiment. First,

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(14) (a) Breslow, R. *Chem. Eng. News* **1965**, *43*, 90. (b) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(15) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448.

(16) (a) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68. (b) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444. (c) Randić, M. *Tetrahedron* **1977**, *33*, 1905.

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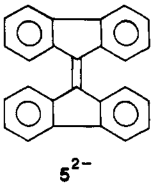
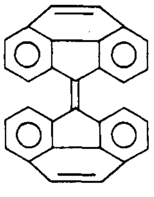
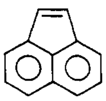
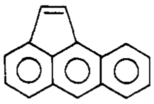
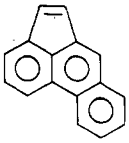
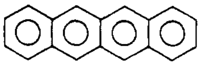
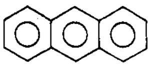
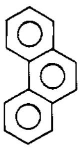
Table III. HOMO-LUMO Energy Gap of Selected Dianions and the Extra High Field Shift of Their ^{1}H NMR Spectral Data[a]

system	HOMO-LUMO energy gap (β units)	$\delta_c{}^t$ = theor ctr of gravity using only charge effects (ppm)	$\delta_c{}^{ex}$ = exptl ctr of gravity (ppm)	$\Delta\delta = \delta_M{}^t - \delta_M{}^{ex}$, (ppm)
 **5**$^{2-}$	0.568[b]	7.21	7.40	−0.19
 **6**$^{2-}$	0.463[b]	7.62	7.81	−0.19
 **1**$^{2-}$	0.653[c]	5.57[c]	4.53[c]	+1.07[c]
 **3**$^{2-}$	0.657	6.40	5.27	+1.13
 **2**$^{2-}$	0.455	6.56	5.09	+1.47
 **7**$^{2-}$	0.414[d]	6.68[d]	4.13[d]	+2.55[d]
 **8**$^{2-}$	0.310[d]	5.96[d]	3.06[d]	+2.90[d]
 **9**$^{2-}$	0.231[d]	6.13[d]	0.80[d]	+5.33[d]

[a] For details of method of calculations, see text. The HOMO-LUMO energy gap as deduced from $\omega\beta$ calculations. [b] Data obtained from ref 22. [c] Data obtained from ref 3a. [d] Data obtained from ref 12.

these two systems are stable compounds and, second, their ^{1}H NMR spectra show a pronounced downfield shift originating from a "diamagnetic ring current effect",[18] very characteristic of aromatic systems. For example, the ^{1}H NMR spectrum of acephenanthrylene (**2**), neglecting the AB pattern attributed to the bridge protons, appears in the range of 8.80–7.63 ppm which is typical for polybenzenoid molecules. The ^{1}H NMR spectrum supports structure **3b** for aceanthrylene (Figure 1). In addition to the low field absorptions of the protons of the aromatic nucleus of the molecule, one of the bridge protons (H_1) absorbs at 7.19 ppm while the other (H_2) absorbs at a relatively low field, viz, 7.88 ppm. Proton H_2 of **3** is subject to a more pronounced secondary "ring current effect" endowed by the proximity of a neighboring ring of the "anthracene moiety", while the secondary "ring current effect" in the "phenanthrene moiety" of **2** is very small.

Another line of support for describing **2** and **3** as polybenzenoid skeletons connected with virtually an isolated double bond (Figure 1, structures **2b** and **3b**) is reached

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(18) For a general review of the "ring current" concept in NMR, see: Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *12*, 303. For a critical discussion of the "ring current" concept and its relationship to "aromaticity", see: Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541 and references cited therein.

Table IV. Theoretical and Experimental Parameters of the Bridge Double Bonds of 2, 3, 2^{2-}, and 3^{2-}[a]

system	$\omega\beta$ calcd bond lengths for C15–C1 (Å)	$\omega\beta$ calcd bond lengths for C_2–C3 (Å)	$\omega\beta$ calcd bond lengths for C1–C2 (Å)	calcd bond lengths for C1–C2 using eq 1 (Å)	exptl $^3J_{HH}$ of the bridges' protons (Hz)	$^3J_{HH}$ expected using the $\omega\beta$ calcd bond lengths for C1–C2 (Hz)
2	1.452	1.452	1.356	1.341	5.2	4.71
$2^{2-}/2Na^+$	1.404	1.404	1.403	1.431	2.3	3.19
3	1.451	1.447	1.359	1.344	5.1	4.61
$3^{2-}/2Li^+$	1.409	1.405	1.398	1.415	2.8	3.35

[a] For numbering see Chart I.

from the spin–spin coupling constants of the bridge protons. The vicinal coupling constants of the bridge protons of **2** and **3** are 5.3 and 5.2 Hz, respectively, very similar to vicinal coupling constants of the vinylic protons of substituted cyclopentene (5.1–7.0 Hz).[19a]

Interestingly, $\omega\beta$ calculations based only on connectivity also favors this description of the electronic structure of acephenanthrylene (**2**) and aceanthrylene (**3**). In the neutral systems the C_1–C_2 bonds are very short indeed (1.356 Å for **2** and 1.359 Å for **3**) while the bonds that connect the bridge carbons to the aromatic skeleton are very long (see Table IV), a general property of this type of compounds. The X-ray structure of the acenaphthylene molecule (**1**)[20] lends strength to this description. The bridge double bond is very short (1.283 Å for C_1–C_2), while the connecting bonds between the naphthalenic skeleton and the double bond are long and can be regarded as virtually single bonds (C_1–C_{11} and C_2–C_3 1.516 Å!).

The Anions: Charge Delocalization and Its Relationship to Diatropicity and Structure. The two-electron reduction of polycyclic molecules results in a pronounced modification in their electronic structures. In systems **1**–**3** the polybenzenoid skeleton of the molecule is relatively rigid and limits the possibilities of bond-length alternation and the extent of deviation from planarity. Therefore, it is expected that the five-membered rings will be vulnerable to structural changes if any such changes have to occur.

The question that now arises is whether the change in the electronic structure is accompanied by a modification of the pattern of electron delocalization which in turn influences its structure. There is a correlation between calculated charge densities and ^{13}C chemical shifts of the dianions (2^{2-} and 3^{2-}) (Table II). According to the ^{13}C NMR spectrum of acephenanthrylene dianion (2^{2-}) it seems that a significant portion of charge density resides on carbons that are located on the entire periphery (see, for example, the chemical shifts of $C_{1,4,8,12}$ of 2^{2-} in Table II). Therefore, 2^{2-} is the best represented by structure 2^{2-}**a** (Figure 2) in which a [17πe;15C] nonaromatic annulenic type path of delocalization prevails. The direct introduction of two electrons into the path of delocalization of **2** would have afforded a [16πe;14C] antiaromatic structure 2^{2-}**c** (Figure 2), which is less favored as it represents an increase in the system's energy content. Therefore, it appears that upon reduction the dianion "prefers" a modified path of electron delocalization which leads to a minimization of the paratropic contribution. The argument concerning the structure of 3^{2-} follows the same rationale. Charge delocalization patterns for the aceanthrylene dianion (3^{2-}) are shown in Figure 2. There are two possible antiaromatic paths of charge delocalization (structures 3^{2-}**b** and 3^{2-}**c** in Figure 2) and two nonaromatic ones, viz. 3^{2-}**a** and 3^{2-}**d** (Figure 2). The results given in Table III show clearly that the charges are distributed over the entire perimeter. There is no evidence for a high electron density at any of the quaternary carbons; therefore, the antiaromatic structure 3^{2-}**b** is ruled out. In structure 3^{2-}**c** only a minor charge density would have been expected on C_1 and C_2 (bridge carbon atoms). From the data in Table II it follows that such a formulation can be excluded. It therefore appears that upon a two-electron reduction of the aromatic neutral systems (**2** and **3**) the resulting dianions differ in their path of delocalization from the parent hydrocarbons. In the dianions, nonaromatic conjugated circuits rather than antiaromatic ones prevail.

The latter conclusion can be challenged by other criteria for the estimation of the degree of paratropicity and diatropicity of these dianions. These criteria are the excessive high field shift experienced by their ^1H NMR spectra and the calculated HOMO–LUMO energy gap of the charged systems.[12,13,21b] As mentioned previously, the ^1H NMR chemical shifts are affected by both anisotropy and charge density effects. In order to get an estimation of the "real" diatropicity or the paratropicity of the dianions, one can try to eliminate the charge density effect from the experimental chemical shifts. Neglecting charge effects, diatropic dianions would show down field shifts due to the "diamagnetic ring current effect".[18] Paratropic anions are expected to show an extra high field shift resulting from the pronounced contribution of the paramagnetic effect on the anisotropy term of the proton shielding constant.[21] The method of differentiation between these two effects was as follows: First, calculations were performed to get the theoretical charge density on the protonated carbons. These theoretical charges were then summed up and this sum was multiplied by the constant of 10.7 ppm per electron.[8b] The result was divided by the number of protons and subtracted from the experimental center of gravity of the neutral system. A theoretical center of gravity is thus obtained for the dianions neglecting anisotropic effect ($\delta_c{}^t$, Table III). This deviation, viz. $\Delta\delta = \delta_c{}^t - \delta c^{ex}$ (Table III) of the experimental center of gravity ($\delta_c{}^{ex}$) from the above-mentioned calculated value ($\delta_c{}^t$) can serve as a measure of the degree of diatropicity or paratropicity. If the experimental center of gravity appears at high field relative to the theoretical center of gravity (i.e., $\Delta\delta > 0$), it implies that the system is paratropic, while the dianion is considered as diatropic when $\Delta\delta < 0$ (Table III). The data presented in Table III enable one to distinguish between representatives of three different groups of dianions. The first group represents dianions derived from overcrowded ethylenes, viz. **5** and **6**, in which $\Delta\delta$ is negative and are therefore classified as diatropic systems.[22] As expected, these dianions do not exhibit an extra high field shift of the experimental center of gravity. They can be regarded as being composed of two substructures in

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(19) (a) Günther, H. *NMR Spectroscopy*; John Wiley and Sons: New York, 1980; (a) p 110; (b) p 109; (c) p 225.

(20) Cser, F. *Acta Chim. Hung.* **1974**, *80*, 317.

(21) (a) Pople, J.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811. (b) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785.

(22) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1071.

which only Hückeloid conjugated circuits of $(4n + 2)\pi$ electrons prevail. Thus, the diamagnetic "ring current" compensates partially the proton high field shift caused by the negative charges. The second group consists of polybenzenoid dianions in which an effective delocalization of $4n\pi$ electrons prevails. This group shows significant proton high field shift relative to the calculated center of gravity which takes into account charge effect only. These values are $\Delta\delta = +2.55$, $+2.90$, $+5.33$ ppm for tetracene dianion (**7**), anthracene dianion (**8**), and phenanthrene dianion (**9**), respectively, as expected for $4n\pi$ electrons paratropic dianions.[12] In between these two groups we find the third family of dianions, all of which are structurally related. The aceanthrylene dianion ($\mathbf{3}^{2-}$) as well as the acephenanthrylene dianion ($\mathbf{2}^{2-}$) reveals a relatively small anisotropic effect. The deviations of the experimental center of gravity are small ($\Delta\delta = 1.13$ ppm for $\mathbf{3}^{2-}$ and 1.47 ppm for $\mathbf{2}^{2-}$). These deviations indicate that these dianions are neither paratropic nor diatropic, in accord with their nonaromatic path of charge delocalization as deduced from their ^{13}C NMR spectra. The diamagnetic "ring current effect" of the protons of benzene is of the order of ca. 1.5 ppm.[23] It follows that the small anisotropic effect found here originates from the loss of the diatropicity of the aromatic netural systems, viz. **2** and **3**, rather than from a partial gain of paratropicity of the respective dianions (viz. $\mathbf{2}^{2-}$ and $\mathbf{3}^{2-}$).

The calculated HOMO–LUMO energy gap was found to correlate with the paratropicity of the $4n\pi$ electron dianions and dications.[12,13,21b] The smaller the HOMO–LUMO energy gap the more pronounced is its paratropicity as reflected by its proton NMR spectra (both chemical shifts and line shapes).[13,21b] The calculated HOMO–LUMO energy gaps for several dianions are given in Table III. The energy gaps for acephenanthrylene dianion ($\mathbf{2}^{2-}$) and aceanthrylene dianion ($\mathbf{3}^{2-}$) are 0.455 and 0.657 β units, respectively. These values are relatively high and according to this criterion they cannot be classified as classical paratropic species.

Calculations of $\mathbf{1}^{2-}$, $\mathbf{2}^{2-}$, and $\mathbf{3}^{2-}$ indicate that the five-membered ring double bond is part of their path of electron delocalization, in contrast to the respective neutral systems. Upon charging of **2** and **3**, the bridge double bonds become longer while the virtual single bonds, which connect the bridge with the aromatic skeleton of the dianions, become much shorter (Table IV). In the acephenanthrylene and aceanthrylene cases, we can use the $^3J_{HH}$ coupling constants of the bridge protons as a probe for C_1–C_2 bond lengths. There is a correlation between the bond length of a C–C double bond in a five-membered ring and the spin coupling constant of the vicinal protons as shown in eq 1.[19b] The data in Table IV show that there

$$^3J_{HH} = -32.26R_{\mu v} + 48.45 \qquad (1)$$

$$^3J_{HH} = \text{vicinal coupling constant (Hz)}$$

$$R_{\mu v} = \text{length of } C_\mu\text{–}C_v \text{ double bond (Å)}$$

are drastic differences between the $^3J_{HH}$ coupling constants of the neutral molecules and the corresponding dianions. The spin–spin coupling constant of the bridge protons in acephenanthrylene and aceanthrylene are 5.2 and 5.1 Hz, respectively, which correspond (eq 1) to short bonds of 1.341 and 1.344 Å, respectively. The calculated values from $\omega\beta$ calculations for the acephenanthrylene and aceanthrylene are 1.356 and 1.359 Å, respectively. Our dianions show a drastic decrease in the spin–spin coupling constants of the bridge protons originating from the increase in the C_1–C_2 bond length in the dianions. The calculated bond lengths (eq 1) using the experimental spin–spin coupling in dianions $\mathbf{2}^{2-}$ and $\mathbf{3}^{2-}$ are 1.431 and 1.415 Å, respectively, while the predicted values by $\omega\beta$ calculation are 1.403 and 1.398 Å, respectively. Although the correlation is not a quantitative one, the trend is obvious. It can therefore be concluded that the decrease in the spin–spin couplings of the bridge protons reflects the geometrical changes taking place in the course of the reduction processes, so that a new pattern of charge delocalization could prevail. This conclusion is strengthened by the crystal structure of the acenaphthylene dianion. The X-ray structure of $\mathbf{1}^{2-}/2Li^+\cdot 2TMEDA$ was reported by Stucky et al.[24] Although dianion $\mathbf{1}^{2-}/2Li^+$ lost its C_{2h} symmetry in the solid state in contrast to the situation in solution, the geometrical changes in the five-membered ring of $\mathbf{1}^{2-}$, namely the lengthening of the bridge double bond C_1–C_2 and the shortening of C_2–C_3 and C_{11}–C_1, are very pronounced.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The 1D and 2D NMR spectra were recorded on a Bruker SY-200 pulsed FT spectrometer equipped with a pulse programmer operating at 200.133 and 50.32 MHz for ^{1}H and ^{13}C NMR, respectively. Field/frequency regulations were maintained by ^{2}H locking. The free induction decay (FID) signals were digitized and accumulated in as Aspect-2000 computer. All 2D NMR experiments were carried out by using standard pulse sequences as they appear in the microprogrammes supplied by Bruker (DISN 85 Version). The metal reduction of the solutions of acephenanthrylene (**2**) and aceanthrylene (**3**) (ca. 10^{-2} M) was carried out by lithium, sodium, and potassium metals as described before.[3a,12b] Quenching of the anion solutions was carried out by bubbling oxygen via a syringe into the solutions of the anions at a slow rate at −78 °C.

Compounds. For the synthesis of acephenanthrylene (**2**), see ref 4. The synthesis of aceanthrylene (**3**) is outlined below.

ω-Bromo-9-acetylanthracene (11). To a 0 °C solution of 9-acetylanthracene[25] (**10**) (5 g, 22.7 mmol) in 50 mL of dry ether was added bromine (1.1 mL, 43.2 mmol) dropwise over a 1-h period. Upon completion of addition, the mixture was stirred for 5 h. A yellow precipitate was collected by suction filtration. The filtrate was concentrated to 10 mL and mixed with 10 mL of pentane to give a second crop of precipitate. The combined solids were recrystallized from hexane to yield 3.8 g (56%) of **11** as yellow plates: mp 107–108 °C (lit.[26] mp 107–108.5 °C).

1-Aceanthrenone (12). To a 25 °C slurry of $AlCl_3$ (10 g, 75 mmol) in 250 mL of CS_2 was added a solution of ω-bromo-9-acetylanthracene (**11**) (9.8 g, 32.6 mmol) in 250 mL of CS_2 over a 1-h period. Upon completion of addition, the mixture was stirred for an additional 2 h. The solution was then added to a mixture of 100 mL of 10% HCl and 50 g of ice. The aqueous solution was extracted with CH_2Cl_2 (4 × 100 mL), and the combined organic layers were washed with saturated $NaHCO_3$ solution (2 × 150 mL) and water (1 × 150 mL), dried over $MgSO_4$, and concentrated. Chromatography on a 3 × 25 cm silica gel column with benzene afforded 4.31 g (60%) of **12** as yellow needles: mp 154 °C.

1-Aceanthrenol (13). A solution of 1-aceanthrenone (**12**) (600 mg, 2.75 mmol) in a mixture of 50 mL of tetrahydrofuran and 25 mL of methanol was cooled to 0 °C. To this dark yellow solution was added $NaBH_4$ (300 mg, 8.3 mmol) in several portions over a 1-h period. The solution was allowed to warm to room temperature while being stirred over a 2-h period and was then poured onto 100 g of ice and extracted with CH_2Cl_2 (3 × 50 mL).

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[23] O'Brien, D. H. In *Comprehensive Carbanion Chemistry*; Buncel, F., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Chapter 6, pp 300–301.

[24] Rhine, W. E.; Davis, J. H.; Stucky, G. *J. Organomet. Chem.* **1977**, *134*, 139.

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[26] May, E. L.; Mosettig, E. *J. Am. Chem. Soc.* **1948**, *70*, 686.

The combined organic layers were washed with water (2 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was recrystallized from 1:1 CH_2Cl_2/hexane to yield 576 mg (95%) of **13** as pale yellow crystals: mp 177-179 °C dec.

Aceanthrylene (3). To a slurry of 1-aceanthrenol (**13**) (380 mg, 1.72 mmol) in 50 mL of dry toluene was added Al_2O_3 (5 g, neutral, dried 8 h at 180 °C/0.1 mm). This solution was refluxed for 10 min, cooled to room temperature, and filtered. The Al_2O_3 was washed in toluene (2 × 20 mL), and the combined organic layers were concentrated to yield 317 mg (93%) of **3** as bright red crystals, mp 103-104 °C (lit.[27] mp 95.0-96.0 °C, lit.[28] mp 103-104 °C, lit.[29] mp 94-95 °C).

NMR parameters of acephenanthrylene (**2**) in THF-d_8. δ ^{1}H: 8.80 (d, J = 8.0 Hz, 1 H); 8.53 (dd, J_1 = 6.8 Hz, J_2 = 1.9 Hz, 1 H); 8.11 (s, H_4); 8.10 (dd, J_1 = 7.4 Hz, J_2 = 1.5 Hz, 1 H); 7.70 (m, 4 H); 7.28 (d, J = 5.2 Hz, H_2); 7.17 (d, J = 5.2 Hz, H_1). δ ^{13}C: 139.4, 138.0, 134.0, 131.7, 130.8, 130.2, 128.5, 127.9, 127.5, 127.0, 126.2, 125.7, 125.6, 122.8, 121.9, 121.0.

NMR parameters of aceanthrylene (**3**) in THF-d_8. δ ^{1}H: 8.58 (s, H_{10}); 8.40 (d, J = 8.4, 1 H); 8.20 (d, J = 8.5 Hz, 1 H); 8.08 (d, J = 7.4 Hz, 1 H); 7.88 (d, J = 6.8 Hz, 1 H); 7.72 (d, J = 5.2 Hz, H_2); 7.65 (m, 3 H); 7.54 (dd, J_1 = 8.6 Hz; J_2 = 1.4 Hz, 1 H); 7.19 (d, J = 5.1 Hz, H_1). δ ^{13}C: 139.9, 134.9, 133.8, 129.6, 128.7, 127.3, 127.3, 127.0, 127.0, 126.8, 126.7, 126.1, 126.0, 124.9, 124.0, 123.4.

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Registry No. 2, 201-06-9; 2^{2-}, 109669-63-8; $2^{2-}/2Na^+$, 109669-59-2; $2^{2-}/2Li^+$, 109669-61-6; 3, 202-03-9; 3^{2-}, 109669-62-7; $3^{2-}/2Li^+$, 109686-30-8; $4^{1-}/Li^+$, 109686-31-9.

Supplementary Material Available: A more detailed report that includes spectroscopic data and elemental analyses for the synthetic compounds as well as acquisitions and processing parameters of the 2D NMR experiments and figures of the ^{1}H NMR 2D COSY spectra of **2** and **3**, the T_1 inversion-recovery spectrum of 2^{2-}, and the ^{1}H NMR 2D J-resolved spectra of 3^{2-} and 4^- (38 pages). Ordering information is given on any current masthead page.

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Photosubstitution of 1-Methoxy-4-nitronaphthalene with Amine Nucleophiles: Dual Pathways[†]

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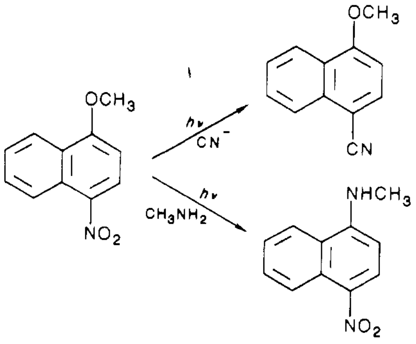
The photosubstitution of 1-methoxy-4-nitronaphthalene (MNN) with amines has been investigated by a combination of continuous and time-resolved experiments. Primary amines cause replacement of the nitro group, while secondary amines displace the methoxy substituent. Both reactions involve attack of the amine upon the triplet excited state of MNN. Spectroscopic evidence for the radical anion $MNN^{\bullet-}$ has been obtained; the yield of this species depends upon the structure of the amine in the order $RNH_2 < R_2NH < R_3N$. It is concluded that the reaction with secondary amines is an electron-transfer process leading to $MNN^{\bullet-}$, but that the reaction with primary amines is most probably an example of an S_N2 Ar* process. The results for MNN and related compounds are discussed in the context of the orientation rules proposed by Mutai et al.

Nucleophilic photochemical substitutions have been a subject of intense research activity since their first discovery in 1956. The scope of these reactions,[1] empirical rules for product predictions,[2] and possible mechanisms[3] have all been reviewed. Of considerable importance in developing our ideas about the scope and mechanisms of these photosubstitutions have been reactions carried out on methoxy nitro compounds as substrates, notably with 3- and 4-nitroanisoles and 4-nitroveratrole.

The subject of experimentation in the present work is the nucleophilic photosubstitution of 1-methoxy-4-nitronaphthalene (MNN). Letsinger and Hautala[4] found that when MNN was irradiated with aqueous cyanide ion the nitro group was displaced, while Havinga and Cornelisse[1] reported that the corresponding reaction with methylamine led to the replacement of the methoxy substituent (Scheme I). This example was used by Havinga and Cornelisse as the basis of the empirical "merging resonance stabilization" rule for product prediction.[2] Cyanation was interpreted as leading to the replacement of one electron-attracting substituent (NO_2) by another (CN), while the reaction with

Scheme I



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