The Spectra of Ions of Phenanthrene and 9,10-Dihydrophenanthrene in Dioxan

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A comparison of the spectra of the ions produced by the action of metallic potassium on phenanthrene and 9,10-dihydrophenanthrene in dioxan in a high vacuum reveals that the spectrum of the dinegative ion of phenanthrene closely resembles the spectrum of the negative ion of dihydrophenanthrene. The spectrum of the mononegative ion of phenanthrene differs, however, clearly from these spectra. The ions with similar spectra have greatly different molar extinction coefficients at their common wavelength of maximum absorption (4200 Å).

Many aromatic hydrocarbons form negative ions when they react with alkali metals in ethers such as tetrahydrofuran, dioxan, and dimethoxyethane in a high vacuum.[1,2] Ions of phenanthrene have previously been produced by this technique in dioxan and tetrahydrofuran.[3,4] In the present study the equilibrium between the mono- and dinegative ions of phenanthrene and the formation of negative ions from 9,10-dihydrophenanthrene were investigated.

The solvent has a great influence on the formation of negative ions. The alkali metal does not necessarily have to dissolve readily in the solvent, for both the mono- and dinegative ions of naphthacene have been produced by the action of both sodium and potassium, although sodium is much more sparingly soluble than potassium in the tetrahydrofuran employed as solvent. If the same ion is produced from a hydrogenated aromatic hydrocarbon as from the aromatic hydrocarbon, it is possible that the dinegative ion is not produced from the latter but instead the mononegative ion of the hydrogenated hydrocarbon. The required hydrogen may be produced by the reaction of the alkali metal with moisture adhering to the walls of the container or dissolved in the solution. The existence of the dinegative ion of naphthacene [5] has, however, been established in flash photolysis experiments.

EXPERIMENTAL

Phenanthrene and dioxan (b.p. 101.5°) were purified and the samples were prepared as described previously.[4,5] The 9,10-dihydrophenanthrene was a product of L. Light & Co. for laboratory use. Its spectrum in dioxan revealed that it did not contain any phenanthrene, and gave absorption spectra agreeing with the literature.

The thermostat contained water and its temperature was maintained constant to ±0.02°C by an electric thermoregulator. The spectra were measured with a Beckman DU spectrophotometer manually and in some cases recorded with a recorder. The cells were 0.63 cm and 1 cm long glass cuvettes or 1 cm long quartz cuvettes. When the temperature was above room temperature (about 22°C) in the experiments, the samples were allowed to cool to room temperature before the spectra were recorded.

Phenanthrene. Cuvettes 0.63 cm long were employed in all studies (Table 1) of phenanthrene and its ions. Spectrum 1 is the spectrum of the phenanthrene solution before it had been in contact with the potassium mirror, *i.e.* before any reaction should have occurred. The reaction had, however, progressed to a slight extent owing to the entrance of some of the alkali metal into the solvent when the metal was distilled.

Spectrum 2 (Fig. 1, curve 2). The solution had been in contact with potassium for 10 min. The reaction began immediately, for the solution turned greenish yellow in the vicinity of the metal surface.

Spectrum 3. After spectrum 2 had been recorded, the solution was allowed to be in contact with the metallic mirror for another ten minutes before spectrum 3 was recorded.
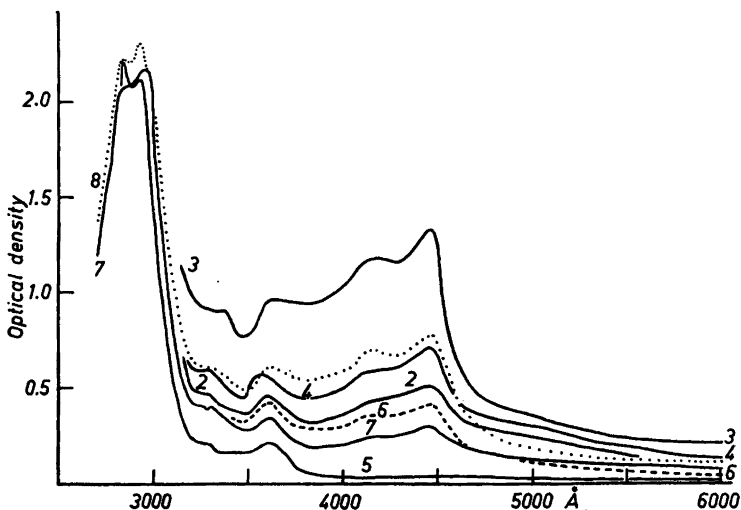

Fig. 1. Spectra of phenanthrene and its ions in dioxan at the beginning of the reaction with potassium.
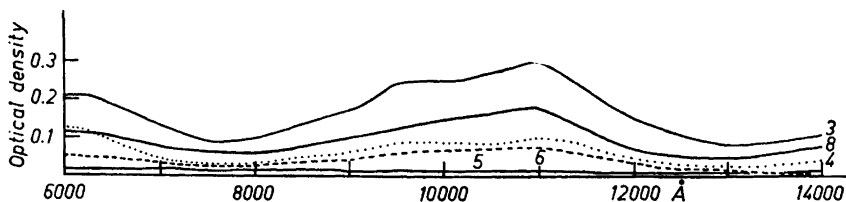

Fig. 2. Spectra of solvated electrons in dioxan.

Spectra 4 and 5. The sample had stood without touching the metallic surface for 18 h (spectrum 4) and 12 days (spectrum 5) from the preceding recording before these spectra were recorded.

Spectra 6 and 8. The solution had been in contact with the metal surface for 1 and 2 min, respectively, during which time the solution was shaken.

Spectra 7 and 9. The sample had stood unexposed to the metal for 22 h and 5 days, respectively, in the latter case at 40° in the thermostat.
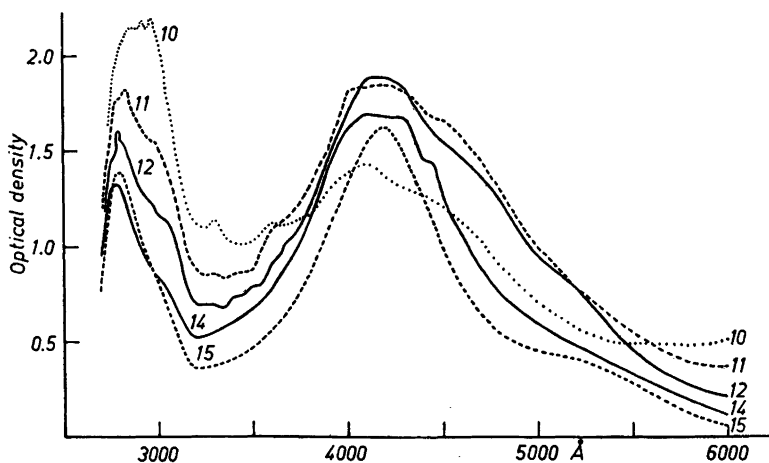

Fig. 3. Spectra of negative phenanthrene ions in dioxan.

Spectra 10, 11, 12, and 13, (Fig. 3). The sample had stood at room temperature in contact with the metal surface successively for 10 h, 3 days, 3 days and 25 days, respectively.

Spectra 14 and 15. The sample had been kept unexposed to the metal in the 40° thermostat for kinetic measurements.
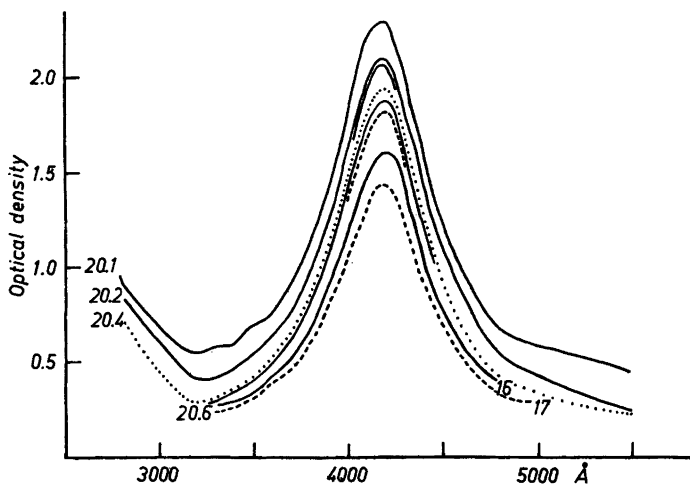

Fig. 4. Spectra of the dinegative phenanthrene ion in dioxan.

Spectrum 16 and 17 (Fig. 4). The sample had stood unexposed to the metal at room temperature for 13 and 4 days, respectively.

Spectra 18, 19, and 20. The sample had stood in contact with the metallic mirror at room temperature for 5, 10, and 30 days.

Spectra 20_2, 20_3, 20_4, 20_5, 20_6, and 20_7. The sample had stood unexposed to the metal in the 45° thermostat for increasing periods of time.

9,10-Dihydrophenanthrene. The 1-cm glass cuvette was employed when the spectra of 9,10-dihydrophenanthrene and its ions were recorded (Table 3).
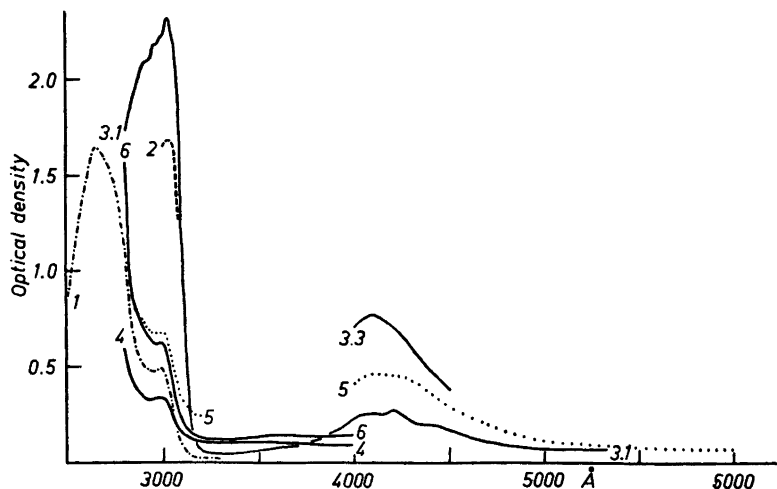

Fig. 5. Spectra of 9,10-dihydrophenanthrene and its ions in dioxan at the beginning of the reaction with potassium.

Spectrum 1 (Fig. 5) is the standard spectrum for dihydrophenanthrene at a concentration of 1.08×10^{-4} M.

Spectrum 2 was recorded for the sample solution before any reaction had occurred.

Spectrum 3. The sample was vigorously shaken so that it came into contact with the metal surface, whereupon an intense deep green colour developed in the solution. This colour disappeared so rapidly that there was not time to measure the whole spectrum reliably after one shaking.

Spectra 3_2, 3_3, and 3_4 represent only a small part of the spectrum near the absorption maximum. The shaking was repeated between the recordings to reproduce the green colour.

Spectrum 4. The solution had stood for 10 h without being in contact with the metal surface.

Spectrum 5 was measured after the sample had been vigorously shaken.

Spectrum 6. The sample had stood 22 h without being exposed to the potassium.

Spectrum 7 (Fig. 6). The sample was shaken before this spectrum was measured.

Spectrum 8. The sample had been in contact with the metal surface for 2 days.

Spectrum 9 was recorded after shaking the sample.

Spectra 10, 11, 12, and 13. The sample had stood unexposed to the metal for 1, 3, 2, and 1 day, respectively, at room temperature.

Spectra 14, 15, and 16. The sample was shaken before each recording and had been in contact with the metal 2 and 1 days after the preceding spectra had been recorded.

Spectra 17—23. The sample had been in the 45° thermostat unexposed to the metal.

Spectra 24. The container was opened and its contents transferred to the quartz before this spectrum was recorded. The colour disappeared from the solution immediately after the container was opened.
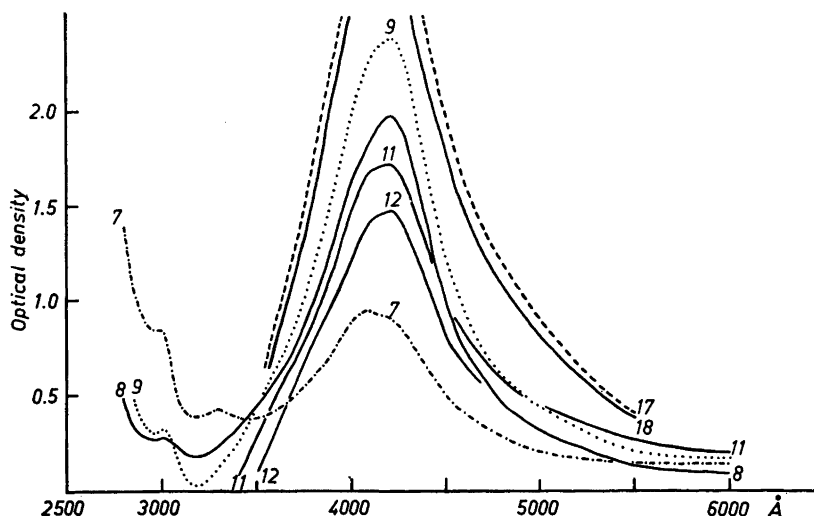
Fig. 6. Spectra of the negative 9,10-dihydrophenanthrene ion in dioxan.

RESULTS AND DISCUSSION

Phenanthrene

The concentration of phenanthrene in the sample solution was 2.30×10^{-3} M as determined from its absorption at 3300 Å (Table 1, spectrum 1) before the reaction and its concentration c_{21} after the container had been opened 1.87×10^{-3} M. The amount corresponding to the difference had evidently been reduced completely. After the reaction began, absorption peaks appeared at the wavelengths 4460 and 3600 Å. These are evidently due to the mononegative ion of phenanthrene (Fig. 1, curve 2). Also traces of phenanthrene were present in view of the absorption band at 3300 Å. The absorption of the dinegative ion is seen in the range 4100—4200 Å. According to curve 3, the reaction (P = phenanthrene)

$$P^- + e^- \rightleftharpoons P^{2-} \tag{1}$$

had clearly taken place as an absorption peak is evident at 4100—4200 Å. Very little absorption by phenanthrene is revealed by this spectrum, but the mononegative ion was present in relatively high concentration as shown by the absorption at 4460 Å. The absorption weakens when the sample solution is not in contact with the metal as shown by curves 4 and 5. The ratio of the mononegative to the dinegative ion has increased, which means that equilibrium (1) has shifted to the left. Absorption by phenanthrene is again evident at the wavelengths 3800 and 2950 Å. If we compare the spectrum with the standard, it is obvious that the mononegative ion has a strong absorption band in the region 2700—3100 Å. The influence of the metal surface is seen in Fig. 1,

Table 1. Phenanthrene and potassium in dioxan.

Spectrum	Optical density				
	3300 Å	3600 Å	4200 Å	4460 Å	11 000 Å
1	0.289	0.138	0	0	0
2	0.455	0.458	0.445	0.514	0.082
3	0.914	0.959	1.180	1.326	0.301
4	0.600	0.569	0.604	0.721	0.102
5	0.200	0.208	0.029	0.032	0.011
6	0.398	0.423	0.362	0.418	0.076
7	0.399	0.349	0.246	0.300	0.045
8	0.602	0.613	0.682	0.775	0.177
9	0.155	0.206	0.090	0.120	0.004
10	1.149	1.131	1.365	1.231	0.071
11	0.857	1.092	1.836	1.664	0.032
12	0.703	0.921	1.886	1.580	0.011
13	0.580	0.830	1.703	1.325	0.017
14	0.554	0.775	1.678	1.415	0.010
15	0.369	0.567	1.611	1.085	0.000
16	0.277	0.440	1.618	0.832	—
17	0.243	0.400	1.444	0.772	0.057
18	0.420	0.613	2.046	1.326	0.057
19	0.466	0.638	2.108	1.268	0.057
20_1	0.582	0.145	2.301	1.383	0.181
20_2	0.426	0.638	2.108	1.214	0.061
20_3	0.375	0.633	2.071	1.186	0.119
20_4	0.320	0.524	1.943	1.044	0.019
20_5	0.319	0.503	1.939	1.062	0.042
20_6	0.290	0.491	1.876	1.034	0.075
20_7	0.276	0.467	1.813	0.955	0.060

Table 2.

D (optical density)	time, s	$k \times 10^8$, s^{-1}
2.301	0	—
2.108	3 600	2430
2.071	7 200	1470
1.943	81 960	205
1.939	85 560	199
1.876	149 160	137
1.813	233 160	103

curve 8; the equilibrium (1) has shifted to the right. At the same time an absorption band at 11 000 Å reveals the absorption of solvated electrons (Fig. 2). The absorption band of these solvated electrons lies at longer wavelengths in dioxan than in tetrahydrofuran and dimethoxyethane.[5,6] The band lies at 7200 Å in dimethoxyethane and at 9000 Å in tetrahydrofuran.[5,8] When the flash photolysis technique has been employed, the change $e_2 \rightleftharpoons 2e$ has been observed in the spectra of solvated electrons; the absorption band of the singlet is located

at longer wavelengths (beyond 10 000 Å).[5],[10] The solvent evidently influences the equilibrium as also the solubility of the alkali metals.[6-9] The phenanthrene ions do not absorb in this region.

The absorption of the mononegative ion is stronger than that of the dinegative ion in spectra 1—8 (Fig. 1). When the solution is in contact with the metal surface for a longer time, the absorption of the dinegative ion (Table 1 and Fig. 3) becomes stronger than that of the mononegative ions with a reversion of the heights of the bands at 4200 and 4460 Å. The absorption by the mononegative ion is still clearly seen in spectra 10—14, but no longer in spectrum 15 and later spectra in Fig. 4. The absorption bands of these ions overlap so much, however, that it is not possible to conclude that the mononegative ion has disappeared completely. There is a weak band at 6200 Å which is evidently due to the dinegative ion.

If the molar extinction coefficient of the dinegative ion is computed from the absorption band at 4200 Å in spectrum 20, assuming that only this ion is present, it is found that

$$\varepsilon = \frac{2 \times 30}{2.3 \times 10^{-3} \times 0.63} = 1600$$

The reaction (1) from the right to the left should be a homogeneous one. It would be possible to follow the rate if the spectra of the ions were not superimposed. First-order rate constants computed from the variation of the absorption at 4200 Å for the reaction to the left at 45.0°C are given in Table 2.

The decrease in the value of the first-order rate constant shows that the absorption at 4200 Å diminishes much less rapidly than expected. This means that the mononegative ion is formed and that it absorbs in this region. The absorption band at 11 000 Å diminishes in height much more rapidly than the preceding band immediately after shaking the solution but later begins to diminish at the same rate as the absorption band at 4200 Å.

9,10- D i h y d r o p h e n a n t h r e n e

The bond joining carbon atoms 9 and 10 in phenanthrene closely resembles a double bond. It would therefore be expected that negative ions would be formed as intermediates when phenanthrene is reduced to dihydrophenanthrene even when the reduction does not take place in a high vacuum.[11],[12] It was noted that the concentrations before (c_2) and after (c_{24}) the opening of the container did not differ from each other within the limits of experimental error.

$c_2 = (1.67/1.485)\ 1.08 \times 10^{-4}\ \text{M} = 3.7 \times 10^{-4}\ \text{M}$

$c_{24} = (1.64/0.488)\ 1.08 \times 10^{-4}\ \text{M} = 3.6 \times 10^{-4}\ \text{M}$

This clearly differs from the results for phenanthrene the concentration of which decreased by 4×10^{-4} M. Dihydrophenanthrene reacts less readily than phenanthrene, for although its solution was in contact with the metal surface, the reaction did not begin before the container was shaken. Absorption bands

Table 3. 9,10-Dihydrophenanthrene and potassium in dioxan.

Spectrum	Optical density 3000 Å	4200 Å	11 000 Å
1	0.488	—	—
2	1.670	0.003	0.001
3_1	2.244	0.270	—
3_2	—	0.103	—
3_3	—	0.712	—
3_4	2.276	—	—
4	0.336	—	—
5	0.676	0.455	0.013
6	0.622	—	—
7	0.848	0.910	0.020
8	0.283	1.963	0.010
9	0.323	2.377	0.009
10	0.215	2.337	0.018
11	—	1.726	0.026
12	—	1.466	0.011
13	—	1.674	0.017
14	—	> 3.0	0.095
15	—	> 3.0	0.114
16	—	> 3.0	0.144
17	—	3.0	0.029
18	—	2.9	0.022
19	—	1.587	0.010
20	—	1.125	0.000
21	—	1.401	0.012
22	—	0.845	0.005
23	—	0.757	0.002
24	1.638	—	—

Table 4.

D	Time, s	$k \times 10^8$, s^{-1}
1.587 1.125	75 120	457
1.401 0.845 0.757	112 680 156 600	450 393 Mean 433
2.337 1.726 1.466	275 300 437 700	110 107 Mean 109

are seen at 3020 Å and 4100—4200 Å in spectrum 3 in Fig. 5, but there is practically no absorption in the region 6000—14 000 Å. A notable decrease in the absorption is noted in curve 4. The absorption by dihydrophenanthrene at 3000 Å is weaker than in spectrum 2 and the concentration of the ion is very low. The influence of shaking is seen in spectrum 5 where the absorption at 4200 Å has increased. The absorption in the visible region in spectrum 6 has decreased from that observed earlier and the concentration of dihydrophenanthrene is higher than that of its ion. It may be concluded from Fig. 6 that equilibrium prevails between dihydrophenanthrene and its ion. If we assume that $\Delta c_{DP} = \Delta c_{DF^-}$ (DF = dihydrophenanthrene), the molar extinction coefficient of the ion at 4200 Å is found to be 8400. The value of the extinction coefficient at 4200 Å estimated from spectra 15 and 16 exceeds 8100. The equilibrium is then greatly in favour of the ion. Before spectrum 17 and the next spectra (Table 3) were recorded, the solution was held at 45.0°C. Values of the first-order rate constant for the reaction

$$DP^{2-} \rightarrow [DP^-] \rightarrow DP \quad \text{or} \quad DP^- \rightarrow DP \tag{2}$$
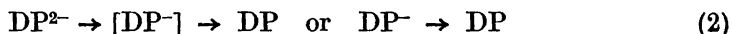
at 45.0 and 22°C computed from the absorption at 4200 Å are given in Table 4.

The rate constants are clearly better than in the case of phenanthrene owing to the fact that dihydrophenanthrene forms only one ion in dioxan and the absorption bands of two ions are not superimposed. Values of the first-order rate constants computed from absorption data at different wavelengths and 45° are the following.

Å	$k \times 10^8$, s^{-1}	Å	$k \times 10^8$, s^{-1}
6200	448	4000	435
4300	466	3800	535
4300	418	3800	478
4000	507		

The rate of decrease of the absorption in the visible region is kinetically of the same order. The activation energy estimated from the data at the two temperatures is 11 kcal/mole. When the optical density at 4200 Å is high, a weak band is noted also in the region 6100—6200 Å as in the case of the dinegative ion of phenanthrene.

Both mononegative and dinegative ions are produced from phenanthrene in dioxan. The relative magnitudes of the absorptions (optical densities) at 4200 and 4460 Å are seen in Table 1. The former band is due to the dinegative ion and the latter to the mononegative ion. The kinetic data for phenanthrene indicate that two different species absorb in the same spectral region.

Only one ion is produced from dihydrophenanthrene as shown by spectra 5 and 6 and Table 3. The absorption band of the negative dihydrophenanthrene ion coincides with the band of the dinegative phenanthrene ion and also otherwise the spectra of these two ions are closely similar at 6200 Å. The spectrum of the mononegative phenanthrene ion differs, however, clearly from the spectra of these two ions.

The initial and final concentrations of phenanthrene differed by 4×10^{-4} mole/l, which amount had evidently been reduced to stable reduction products.

There was not enough water in the sample to react with potassium to give this amount of reduction products. On the other hand, employing the highest value (8400) of the extinction coefficient computed at 4200 Å and the highest value of the optical density for the dinegative phenanthrene ion, the concentration of this ion is found to have been $c = 2.30/(8400 \times 0.63) = 4.3 \times 10^{-4}$ M.

This concentration of the dinegative ion is equivalent to the concentration decrease of phenanthrene, although the employed value of the extinction coefficient was that found for dihydrophenanthrene. Despite the similarity of the spectra, it cannot be concluded with certainty that the dinegative phenanthrene ion is the same as the negative ion of dihydrophenanthrene because the extinction coefficients of the ions at 4200 Å differ greatly (1600 and 8400). Suhrmann and Matejec[3] have similarly interpreted the absorptions of the two phenanthrene ions (at 4200 Å for the dinegative and at 4460 Å for the mononegative ion). If these two absorption bands were assigned differently, it would explain why the spectrum of the negative ion of dihydrophenanthrene resembles the spectrum of the dinegative ion of phenanthrene. The other possibility is that dihydrophenanthrene does not form a stable mononegative ion, but only the dinegative ion in high vacuum.[11,12] In order to effect a different equilibrium between the ions, it is necessary to employ another solvent. This is under investigation.

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