Reactions of Radical Anions. Part XIV.[1] An Electron Spin Resonance Study of the Radical Anions of 9,9'-Azophenanthrene and 9,9'-Azoanthracene

By Alwyn G. Evans,* Jeffrey C. Evans, and Peter J. Pomery, University College, Cardiff, P.O. Box 78, Cardiff

The effect of temperature on the disproportionation equilibrium of the radical anions of 9,9'-azophenanthrene and 9,9'-azoanthracene in tetrahydrofuran, with various alkali metals as gegenions, has been determined by measurement of the radical-anion concentration at different temperatures, using electron spin resonance spectroscopy. The e.s.r. spectra were also obtained and analysed for these radical anions and the splitting constants assigned, using simple Hückel and McLachlan molecular orbital theory.

WE have previously studied[2] the disproportionation of the radical anions of azobenzene, naphthalene-1-azobenzene, 1,1'-azonaphthalene, and 2,2'-azonaphthalene in tetrahydrofuran as solvent with Li^+, Na^+, K^+, Rb^+, and Cs^+ as gegenion. The e.s.r. spectra were analysed and the various splitting constants assigned, using a simple Hückel molecular orbital theory.

In this paper the work has been extended to an e.s.r. study of tetrahydrofuran solutions of the radical anions of 9,9'-azophenanthrene and 9,9'-azoanthracene, using Li^+, Na^+, K^+, Rb^+, and Cs^+ as gegenions.

The complicated e.s.r. spectra were analysed on a JEOL R.A.1 spectrum accumulator and the splitting constants were assigned by using simple Hückel and McLachlan molecular orbital theory. The disproportionation equilibria of these radical anions were examined and the thermodynamic constants determined.

EXPERIMENTAL

Materials.—9,9'-Azophenanthrene was prepared by the method of Nystron and Brown,[3] in which 9-nitrophenanthrene (prepared by the method of Schmidt and Strobel[4]) was reduced and coupled using $LiAlH_4$ at -80 °C. The 9,9'-azophenanthrene was purified by passage through an activated alumina column using light petroleum (b.p. 40—60°) as solvent, recrystallisation from the same solvent, and drying *in vacuo*, m.p. 269 °C (lit.,[4] 270 °C).

Azoanthracene was prepared and purified similarly, to give violet crystals, m.p. 345 °C (lit.,[5] 347 °C).

Tetrahydrofuran (THF) (B.D.H.) was purified and dried as previously described.[2,6] Lithium, sodium, potassium, rubidium, and caesium metals (B.D.H.) were purified and transformed into mirrors as described earlier.[2,7]

Procedure.—Solutions of 9,9'-azoanthracene or 9,9'-azophenanthrene in THF were made and passed over the appropriate alkali metal film under high vacuum using techniques previously described.[8] The concentration of gegenion was determined by flame photometry. The concentration of radical anion was determined as previously[2,6,7] on a Hilger–Watts Microspin e.s.r. spectrometer which had a facility for double integration. This spectrometer was fitted with a Varian temperature control which was used over a temperature range $+20$ to -80 °C. Analysis was done from e.s.r. spectra using a Varian E3

spectrometer fitted with a temperature control. Simulated e.s.r. spectra were obtained using a JEOL R.A.1 spectrum accumulator.

RESULTS AND DISCUSSION

Dianions.—9,9'-*Azophenanthrene.* When a solution of 9,9'-azophenanthrene in THF ($3\cdot87 \times 10^{-3}$ mol l⁻¹) was in prolonged contact with a metal film, a purple solution developed with sodium, potassium, and caesium and a dark brown solution with lithium. These solutions had an [alkali metal] : [9,9'-azophenanthrene] ratio of 2 : 1 and no e.s.r. spectra showing that the solutions contained only the dianions. The optical absorptions and extinction coefficients are given in Table 1. On addition of air or water the THF solutions gave the

TABLE 1

Optical absorptions and extinction coefficients of radical anions and dianions at room temperature

Azo-compound	Gegenion	Dianion $\lambda_{max.}/nm$	Dianion $10^{-4}\varepsilon$	Radical anion $\lambda_{max.}/nm$	Radical anion $10^{-4}\varepsilon$
	Li⁺	460	0·17	424	1·22
	Na⁺	518	0·17	430	1·92
9,9'-Azophenanthrene	K⁺	532	0·12	432	1·58
	Rb⁺	535	0·08	434	2·05
	Cs⁺	540	0·11	437	3·28
	Li⁺	—	—	—	—
	Na⁺	716	0·10	370	2·6
9,9'-Azoanthracene	K⁺	718	0·12	388	10·2
	Rb⁺	721	0·09	390	12·1
	Cs⁺	723	0·11	394	13·4

original azophenanthrene identified by t.l.c., u.v., and i.r. spectra, and the appropriate alkali metal hydroxide.

9,9'-*Azoanthracene.* When a solution of 9,9'-azoanthracene in THF ($3\cdot52 \times 10^{-3}$ mol l⁻¹) was in contact with a metal film for *ca.* 30 min a purple solution developed with sodium, potassium, rubidium, and caesium. These solutions had an [alkali metal] : [9,9'-azoanthracene] ratio of 2 : 1 and no e.s.r. spectra showing that the solutions contained only the dianions. The optical absorptions and extinction coefficients are given in Table 1. Treatment of the dianion system with air or water gave only the azoanthracene, identified by t.l.c.

[1] Part XIII, A. G. Evans, J. C. Evans, and C. Bevan, *J.C.S. Perkin II*, 1974, 1220.

[2] A. G. Evans, J. C. Evans, C. L. James, and P. J. Pomery, *J. Chem. Soc. (B)*, 1971, 1484.

[3] R. F. Nystron and W. G. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738.

[4] J. Schmidt and M. Strobel, *Ber.*, 1903, **36**, 2508.

[5] J. Rigaudy and J. Barcelo, *Compt. rend.*, 1964, **258**(19), 4799.

[6] J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

[7] A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

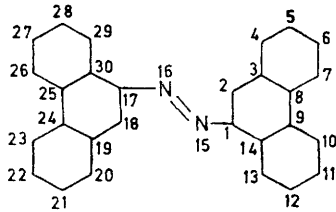[8] A. G. Evans, J. C. Evans, and E. H. Godden, *Trans. Faraday Soc.*, 1967, **63**, 136.

and u.v. and i.r. spectra, and the appropriate alkali metal hydroxide.

No dianion solution was obtained when lithium metal was used. On prolonged contact of a THF solution of azoanthracene with a lithium film, a bright blue solution was obtained which had an e.s.r. spectrum identical with that of the anthracene radical anion.

Radical Anions.—9,9'-Azophenanthrene. The radical anions were formed by brief contact of THF solutions of azophenanthrene $(3 \cdot 97 \times 10^{-3}$ mol $l^{-1})$ with the various alkali metals. The solutions were green-brown and had an e.s.r. absorption which changed reversibly in intensity with change in temperature. Highly resolved e.s.r. spectra were difficult to obtain and because of the many lines expected, analysis of the spectra could not be done with any degree of certainty. No gegenion splitting could be assigned even on comparing the spectra of the electrolytically reduced solutions (using tetraphenyl-ammonium iodide as supporting electrolyte in dimethyl-formamide as solvent) with those obtained from the metal film. The splitting constants are shown in Table 2, and were arrived at and assigned with the help

TABLE 2

9,9'-Azophenanthrene

Molecular orbital parameters

$\alpha_N = \alpha_C + (0 \cdot 75 + 1 \cdot 18)\beta_{CC}, \delta = 0 \cdot 25$
$\beta_{NN} = 1 \cdot 1\beta_{CC}$
$\beta_{CN} = \beta_{CC}$
$\left.\begin{array}{l} \alpha_2 = \alpha_C + \delta\beta_{CC} \\ \alpha_{18} = \alpha_C + \delta\beta_{CC} \end{array}\right\} \delta = -0 \cdot 2$

Position	Hückel spin density	McLachlan spin density	Observed spin density	Observed splitting constant at 0 °C (mT)
2, 18	0·1565	0·2375	0·142 a	0·354
4, 20	0·0428	0·0677	0·044 a	0·110
5, 21	0·0069	−0·0152		
6, 22	0·0384	0·0524	0·044 a	0·110
7, 23	0·0119	−0·0037	0·013 a	~0·033
10, 26	0·0112	−0·0010	0·013 a	~0·033
11, 27	0·0412	0·0439	0·044 a	0·110
12, 28	0·0064	−0·0123		
13, 29	0·0455	0·0570	0·044 a	0·110
(N) 15, 16	0·2100	0·2595	0·209 b	0·440

*a* Calculated using $Q = 2 \cdot 5$ mT.   *b* Calculated using $Q = 2 \cdot 11$ mT.

of Hückel MO Theory. The optical results and extinction coefficients are given in Table 1. Treatment of the system with air or water gave only the neutral azo-compound, identified by t.l.c. and u.v. and i.r. spectra, and the corresponding alkali metal hydroxide.

9,9'-Azoanthracene. Similar results were obtained when a THF solution of 9,9'-azoanthracene $(3 \cdot 52 \times 10^{-3}$ mol $l^{-1})$ was brought into contact with a sodium, potassium, rubidium, or caesium metal film for a short time.

The solutions were red-brown and had e.s.r. absorption. A change of temperature caused the intensity of the e.s.r. spectra to change and this change was reversible. It was difficult to obtain good e.s.r. spectra for the radical anions. The spectra showed alkali metal hyperfine splitting, the values of which could be determined by comparison of the spectra with those obtained from electrochemical reduction of the solution. The splitting constants are given in Table 3 and they were assigned by

TABLE 3

9,9'-Azoanthracene
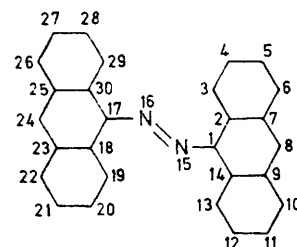
Molecular orbital parameters

$\alpha_N = \alpha_C + (0 \cdot 75 + 1 \cdot 18)\beta_{CC}, \delta = 0 \cdot 25$
$\beta_{NN} = 1 \cdot 1\beta_{CC}$
$\beta_{CN} = \beta_{CC}$

Position	Hückel spin density	McLachlan spin density	Observed spin density	Observed splitting constant at 0 °C (mT)
3, 19	0·00013	−0·02595		
4, 20	0·03570	0·04968	0·0380 a	0·095
5, 21	0·0006	−0·02439		
6, 22	0·03577	0·05549	0·0380 a	0·095
8, 24	0·1428	0·21320	0·148 a	0·370
10, 26	0·03577	0·05549	0·0380 a	0·095
11, 27	0·0006	−0·02439		
12, 28	0·03757	0·04968	0·0380 a	0·095
13, 29	0·00013	−0·02596		
(N) 15, 16	0·1420	0·1864	0·154 b	0·320

a Calculated using $Q = 2 \cdot 5$ mT.   *b* Calculated using $Q = 2 \cdot 11$ mT.

Gegenion splitting constants at 0 °C (mT) Na+ 0·03, Rb+ 0·035, Cs+ 0·055.

using the Hückel MO theory. The optical results and extinction coefficients are given in Table 1. On opening to air or on adding water the neutral azo-compound was obtained together with the appropriate alkali metal hydroxide. When a THF solution of 9,9'-azoanthracene was passed over a lithium film there was no build up of colour and no e.s.r. signal detected. On prolonged standing over the film, however, a bright blue solution developed which had an e.s.r. signal identical with that of the anthracene radical anion. On exposure to air or water the solution yielded anthracene (identified by t.l.c. and u.v. and i.r. spectra) and lithium hydroxide.

Disproportionation Equilibria.—The e.s.r. spectra of the radical anion solutions were stable with time and the change in their intensity with change of temperature was completely reversible. The fact that after opening to air only the original azo-compound could be recovered means that the radical anions do not dimerise. Furthermore, in all cases, the system obeyed Beer's Law at room temperature over some three-fold dilution, confirming that no dimerisation occurs and showing

that the ions exist wholly as ion-pairs or as free ions. Since the equilibria are affected by the nature of the gegenion we assume that the ions exist wholly as ion-pairs. The Warhurst type [9] plots of $1/(r_c + 2)$ against $\tilde{v}$ (r_c being the cationic radius) for the radical anions are reasonably linear, which means that at room temperature ' contact ' ion-pairs must be involved. This is supported in the case of 9,9'-azoanthracene by the observation of alkali metal hyperfine splitting in the e.s.r. spectra. In these systems, therefore, equilibrium (1) exists where R is 9-phenanthryl or 9-anthryl.

$$2(RN=NR)^{-\cdot}M^+ \xrightleftharpoons{K} (RN=NR)^{2-}2M^+ + RN=NR \quad (1)$$

The disproportionation equilibrium constant

$$K = \frac{[(RN=NR)^{2-}2M^+][RN=NR]}{[(RN=NR)^{-\cdot}M^+]^2}$$

can be determined by knowing the total radical-anion concentration from e.s.r. measurements, the total gegenion concentration from flame photometry, and the total azo-compound concentration. The temperature dependence of K for various gegenions is shown in Figures 1 and 2, and the thermodynamic constants for the equilibria are given in Table 4.

If we assume that the smaller the spin density on the nitrogen atom of the radical anion as measured by e.s.r., the greater the electron delocalisation by the aromatic groups, we see that, as regards electron delocalising power, 9,9'-azophenanthrene < 9,9'-azoanthracene.
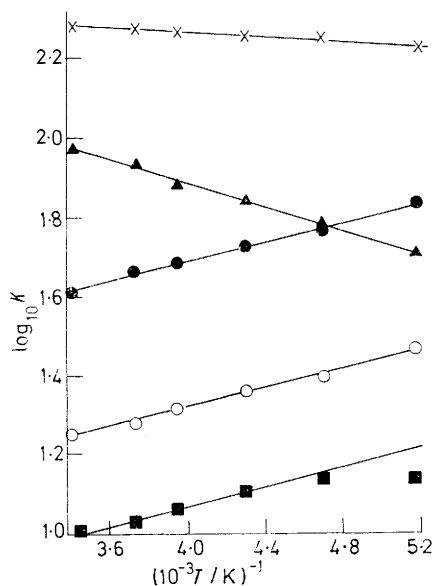

FIGURE 1   Temperature dependence of the disproportionation equilibrium constant (K) for the radical anion of 9,9'-azophenanthrene in THF with Li+ (●), Na+ (■), K+ (○), Rb+ (▲), and Cs+ (×), as gegenion

The change from 9,9'-azophenanthrene to 9,9'-azoanthracene will not only involve an increase in electron delocalisation but also an increase in steric restriction around the nitrogen atoms which will operate in both the radical anion and in the dianion. Thus it is not

surprising that the effect on the disproportionation equilibrium in changing from 9,9'-azophenanthrene to 9,9'-azoanthracene is dependent on gegenion.
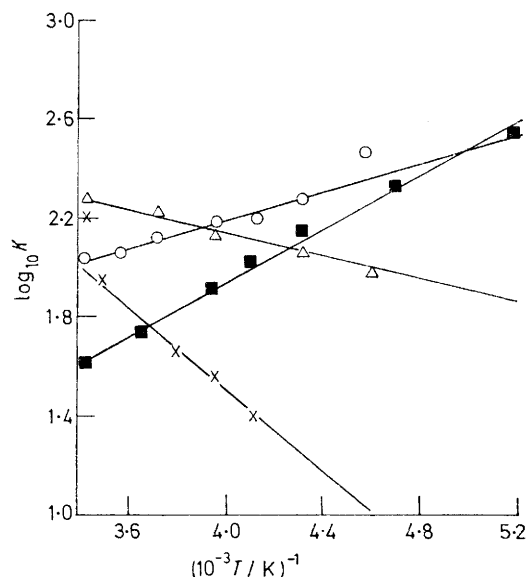

FIGURE 2   Temperature dependence of the disproportionation equilibrium constant (K) for the radical anion of 9,9'-azoanthracene in THF with Na+ (■), K+ (○), Rb+ (▲), and Cs+ (×), as gegenion

For Na+ there is an increase in K involving a greater solvation and a greater exothermicity, whereas for K+ there is an increase in K involving a greater desolvation and a greater exothermicity. For Rb+ there is also an increase in K, together with a greater desolvation but a greater endothermicity. For Cs+ on the other hand, there is a decrease in K involving an increase in desolvation and an increase in endothermicity.

In Table 5 we give the values of K, ΔS° and ΔH° for the disproportionation reaction of tetraphenylethylene,[6] 2,2'-azonaphthalene,[2] 1,1'-azonaphthalene,[2] naphthalene-1-azobenzene,[2] azobenzene,[2] N-diphenylmethyleneaniline,[10] 9,9'-azophenanthrene, and 9,9'-azoanthracene, with sodium as gegenion at 0° C. (We have the values of K for tetraphenylethylene and N-diphenylmethyleneaniline only in the case of Na+ as gegenion.)   In the case of the tetraphenylethylene radical anion the equilibrium lies well on the dianion side at room temperature with a large value of K, and the electron transfer from one radical anion to the other is associated with desolvation (increase of entropy) and is endothermic. On replacing a carbon atom by nitrogen, as in the case of the N-diphenylmethyleneaniline radical anion, the opposite occurs; the equilibrium lies well on the radical anion side at room temperature with a very small value of K and the electron transfer from one radical anion to the other is associated with an increase in solvation (decrease in entropy) and is exothermic.

[9] H. V. Carter, B. J. McClelland, and E. Warhurst, Trans. Faraday Soc., 1960, 56, 455.
[10] A. G. Evans and J. C. Evans, J. Chem. Soc. (B), 1966, 271.

It is possible that the large change from $(Ph_2C=CPh_2)^{-•}$ Na^+ to $(Ph_2C=NPh)^{-•}$ Na^+ is due to the restricting effect of the nitrogen atom on the electron distribution throughout the radical anion. A study of the azo-compounds, in Table 5, shows that in general as the groups attached to the nitrogen atoms increase in delocalising power (as shown by the general decrease in splitting constant A_N) the greater is the value of K and (with the exception of azophenanthrene and azoanthracene), the more positive is $\Delta S°$ (increase in solvation) and the more positive is $\Delta H°$ (increase in endothermicity). This might be

π-electron spin densities by the standard methods.[11] The Hückel molecular method together with McLachlan's [12] SCF approximation ($\lambda = 1.2$) was used to calculate the spin populations which were converted into splitting constants by the use of the McConnell [13] relation, $\alpha_H = Q\rho$. An average value of $|Q| = 2.5$ mT was used when considering the proton splittings and a value of $|Q| = 2.11$ mT [14] when considering the nitrogen atoms.

Good agreement was obtained between the calculated and observed splitting constants (Tables 2 and 3) for

TABLE 4

Thermodynamic constants for disproportionation equilibria at 0 °C

Azo-compound	Gegenion	K	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
	Li$^+$	46.5	−7.30	−2.42	17.9
	Na$^+$	10.2	−5.30	−2.38	10.4
9,9'-Azophenanthrene	K$^+$	19.1	−6.69	−2.29	16.1
	Rb$^+$	86.1	−10.16	2.88	47.6
	Cs$^+$	195	−11.95	0.58	45.9
	Na$^+$	13.0	−5.97	−21.3	−55.1
9,9'-Azoanthracene	K$^+$	114	−10.74	−4.89	21.4
	Rb$^+$	170	−11.74	4.47	59.3
	Cs$^+$	73.3	−9.73	17.8	101

TABLE 5

Thermodynamic constants for the disproportionation equilibria in THF at 0 °C, with Na^+ as gegenion

Compound	A_N/mT	K	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
Tetraphenylethylene [a]		3.8×10^2	−13.4	+46	+217
9,9'-Azoanthracene	0.32	13.0	−5.98	−21.3	−55.2
9,9'-Azophenanthrene	0.44	10.2	−5.3	−2.38	+10.4
2,2'-Azonaphthalene [b]	0.485	3.8	−3.00	−2.17	+19.0
1,1'-Azonaphthalene [b]	0.444	2.6	−2.17	+2.76	+18.1
Naphthalene-1-azobenzene [b]	0.53	0.12	+4.80	−6.30	−40.9
Azobenzene [b]	0.52	0.10	+5.40	−17.8	−84.8
N-Diphenylmethyleneaniline [c]		2.02×10^{-3}	+14.0	−53.5	−247

[a] See ref. 6.   [b] See ref. 2.   [c] See ref. 10.

expected since, other things being equal, the solvation of the dianion will be sterically more difficult than for the radical anions.

In the cases of 9,9'-azophenanthrene and 9,9'-azoanthracene, in addition to the large electron delocalisation effect as shown by the A_N values (Table 5), the steric hindrance of the bulky phenanthrene and anthracene groups must be considered. Courtauld models of these molecules show that the steric environment of the nitrogen atoms is markedly affected by the large phenanthrene and anthracene groups. In addition these two systems possess positions of high electron density other than the N atom, i.e. positions 8 and 24 in azoanthracene (0.370 mT) and 2 and 18 in azophenanthrene (0.354 mT) (the numbering system is shown in Tables 2 and 3). It is therefore not surprising that the $\Delta H°$ and $\Delta S°$ values in these cases are out of sequence.

Theoretical Calculations.—The observed proton hyperfine coupling constants have been related to calculated

9,9'-azophenanthrene and 9,9'-azoanthracene. In the case of 9,9'-azophenanthrene some interaction was assumed between atoms at the 2 and 18 positions. This is taken into account in the calculations by varying the coulomb integral for the respective carbon atoms at these positions, by using $\alpha_i = \alpha_c + \delta\beta_{CC}$ ($i = 2$ or 18) and a value of $\delta = -0.2$. The molecular orbital parameters used for the nitrogen atoms were similar to those used in our previous paper [2] and those used by Atherton et al.[15] in the case of azobenzene, i.e. $\alpha_N = \alpha_C + (0.75 + 1.18)\beta_{CC}$, $\beta_{CN} = \beta_{CC}$, $\beta_{NN} = 1.1\beta_{CC}$. A value of $\delta = +0.25$ gave good agreement.

The experimental results agree better with the Hückel than with the McLachlan calculated spin densities.

[11] A. Carrington, *Quart. Rev.*, 1963, **17**, 67.
[12] A. D. McLachlan, *Mol. Phys.*, 1969, **3**, 233.
[13] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764.
[14] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **37**, 1326.
[15] N. M. Atherton, F. Gerson, and J. N. Ockwell, *J. Chem. Soc.* (A), 1966, 109.