A Polarographic Study of Aryl-substituted Tetra-aza- and Hexa-aza-pentalenes in Dimethylformamide

Akira Matsumoto, Joung Hee Lee, Masayuki Yoshida, and Osamu Simamura
Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo 113

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The polarographic reduction potentials of aryl-substituted 1,2,4,5-tetra-aza- and 1,2,3,4,5,6-hexa-aza-pentalenes were shown to be approximately governed by the numbers of nitrogen atoms and aryl-substituents. Such effect of nitrogen atoms was discussed in terms of the orbital energies of parent azapentalenes obtained by HMO calculations.

The preparations and properties of aryl-substituted 1,2,4,5-tetra-aza- (I) as well as 1,2,3,4,5,6-hexa-aza- (V–X) pentalenes were described previously,[1,2] and these compounds were shown to be very stable. In the present work the polarographic reduction of a number of 1,2,4,5-tetra-aza- and 1,2,3,4,5,6-hexa-aza-pentalenes (including compounds I and V–X) has been studied to examine any correlation between the half-wave reduction potentials and the chemical properties.

Results and Discussion

Polarograms of polyazapentalenes in dimethylformamide containing tetra-*n*-butylammonium iodide (0.155 M) as supporting electrolyte showed two well-defined reduction waves; polarographic data are given in Table 1. Plots of polarographic potential E *versus* $\log [(i_d - i)/i]$ give straight lines with a slope in good agreement with the theoretical value of 0.0585 V at 22 °C according to Heyrovsky and Ilkovic's derivation.[3] This result, therefore, indicates that these reduction waves correspond to reversible one-electron reduction of polyazapentalenes to radical anions.

A plot of the potentials for the first reduction waves ($E_{1/2}$) against the number (N) of aryl-substituents in each molecule (Fig. 1) gives two parallel straight lines, one ($E_{1/2}=0.36\,N-2.60$ (V)) for tetra-aza- and the other ($E_{1/2}=0.36\,N-1.32$(V)) for hexa-aza-pentalenes. These correlations clearly show that the number of nitrogen atoms in the azapentalene nucleus is important in determining the reduction potential. On the other hand, the fact that the slopes of the straight lines are found identical shows that the effect of an aryl substituent on the potential is additive and the same, giving rise to an elevation by 0.36 V for one substituent, irrespective of the nature of the nucleus. The effects of other factors such as the orientation of substituents or the replacement of a phenyl with a *p*-chlorophenyl group (V–VI) are small in comparison with the above major effects.

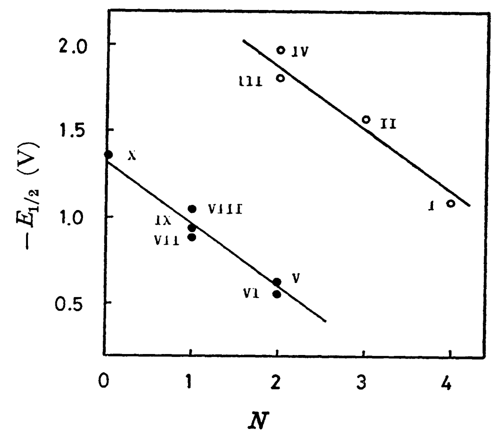
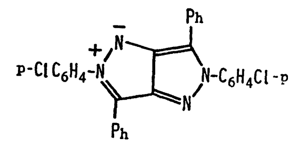


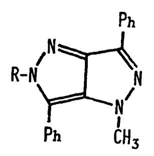
Fig. 1. Plot of the half-wave reduction potentials of the tetra-aza- and hexa-aza-pentalenes against the number (N) of aryl-substituents.
—○— Tetra-azapentalenes
—●— Hexa-azapentalenes

The plot corresponding to compound VIII does not fall on the straight line for hexa-azapentalenes; the reason is obviously the difference in the type of electronic structure, because compound VIII is not mesoionic, carrying a methyl and a phenyl group at positions 1 and 5, respectively, while the other hexa-azapentalenes examined are mesoionic carrying substituents at positions 2 and 5.

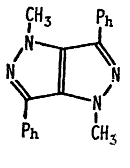
As regards the regression line for tetra-azapentalenes,



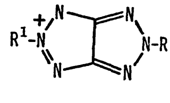
I



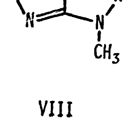
II: R= Ph
III: R= CH_3



IV



V: R^1= R^2= Ph
VI: R^1= Ph, R^2= p-ClC_6H_4
VII: R^1= Ph, R^2= CH_3
IX: R^1= Ph, R^2= cyclo-C_6H_{11}
X: R^1= R^2= cyclo-C_6H_{11}



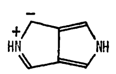
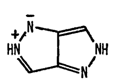
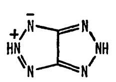
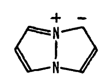
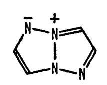
VIII

TABLE 1. POLAROGRAPHIC DATA OF POLY-AZAPENTALENES IN DIMETHYLFORMAMIDE CONTAINING TETRA-n-BUTYLAMMONIUM IODIDE AT 22 °C

Compound	$E_{1/2}$	i_d/c	Slope × 10^2	$E'_{1/2}$	i'_d/c
I	−1.10	3.4	6.4		
II	−1.58	4.6	5.2		
III	−1.82	4.6	5.2		
IV	−1.98	4.1	5.6		
V	−0.62	3.2	6.5	−1.37	3.0
VI	−0.57	2.4	6.2	−1.27	2.4
VII	−0.90	3.4	5.8	−1.5	5
VIII	−1.06	4.3	5.3	−1.88	6.7
IX	−0.94	2.7	6.4	−1.47	3.5
X	−1.32	2.7	6.1	−1.7	6

$E_{1/2}$: Half-wave potential (V) *vs.* mercury pool for the first reduction wave.
Slope: Slope from plot of E *vs.* $\log[(i_d-i)/i]$.
i_d: Diffusion current in μA.
c: Concentration (mmol/l).
$E'_{1/2}$, i'_d: Half-wave potential and diffusion current for the second reduction wave, respectively.

TABLE 2. ENERGY LEVELS ($E_m=\alpha+k_m\beta$) AND TOTAL ENERGY OF π-ELECTRONS[a)] OF SOME AZAPENTALENES CALCULATED BY HMO METHOD[7)]

k_m[b)]	 XI	 XIII	 XV	 XII	 XIV
k_8	−2.00	−1.93	−1.85	−1.67	−1.54
k_7	−1.48	−1.35	−1.17	−1.41	−1.34
k_6	−0.85	−0.68	−0.50	−1.19	−1.05
k_5	0.00	0.25	0.50	0.00	0.25
k_4	1.00	1.18	1.24	0.92	0.98
k_3	1.23	1.24	1.35	1.41	1.59
k_2	2.35	2.43	2.50	1.69	1.80
k_1	2.75	2.84	2.90	3.26	3.31
$\sum_m^{\text{occ}} k_m$	14.66	15.90	16.98	14.55	15.86

a) Values of only k_m's are shown. b) Occupied levels are distinguished from unoccupied ones by underline.

the correlation can not be regarded as excellent, as is apparent, for example, from the discrepancy between the plots for compounds III and IV. This is probably because the type of electronic structure may be slightly different in the compounds examined, the orientations of the four substituent groups being different except between compounds II and III, and furthermore, compound I is mesoionic.

If a straight line is drawn through the two points representing compounds II and III, the slope will be decreased to 0.24 V/N, indicating thus a weaker effect of the aryl substituent in this type of compounds. The reason may be attributable to non-coplanarity of the phenyl group with the azapentalene nucleus owing to the juxtaposition of substituent groups.[4)]

The polarographic reduction potentials of aromatic hydrocarbons are known to be correlated linearly with the energy of their lowest vacant molecular orbitals as calculated by the simple HMO method.[5)] This is found to be the case also with 2,5-disubstituted hexa-azapentalenes as is shown in Fig. 2. In the present calculations, aryl substituents were thought

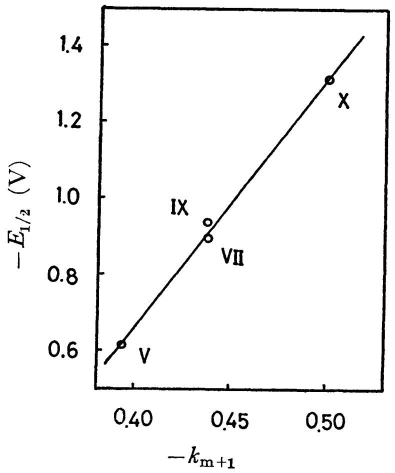


Fig. 2. Half-wave reduction potentials for hexa-azapentalenes in dimethylformamide *versus* energies of lowest vacant orbitals.
The axis of abscissa shows energy in terms of coefficient k_{m+1} in energy expression $E_{m+1}=\alpha+k_{m+1}\beta$ of lowest vacant orbital.[7)]

to be coplanar with the hexa-azapentalene nucleus, as is supported by UV and NMR spectroscopic measurements.[6]

Hückel molecular orbital calculations were also carried out for some mesoionic azapentalene parent rings[7] in order to compare the effect of the number and positions of nitrogen atoms on the π-electron energy with that on the chemical behaviour. The results are summarized in Table 2. 2,5-Diaza- (XI) and 3a,6a-diaza- (XII)[8] pentalenes have an occupied non-bonding orbital, and the total π-electron energy is nearly the same for the two rings, but the lowest vacant orbital lies lower in ring XI than in ring XII. Introduction of two nitrogen atoms into these diazapentalenes to give 1,2,4,5-tetra-aza-(XIII) and 1,3a,4,6a-tetra-aza-(XIV) pentalenes results in lowering of the energies of all the orbitals, but again the energy of the highest occupied orbital and the total π-electron energy are nearly the same for (XIII) and (XIV), and the energy of the lowest vacant orbital of (XIII) is lower than that of (XIV). Introduction of two more nitrogen atoms into XIII to give 1,2,3,4,5,6-hexa-azapentalene (XV) causes further decrease in the energy of each of the molecular orbitals and hence in the total energy.

Thus, in the series of the azapentalenes, XI, XIII, and XV, the effect of the number of nitrogen atoms on the energy of the lowest vacant orbital, to which the polarographic reduction potential should be related, is in harmony with the earlier mentioned result that introduction of two more nitrogen atoms into positions 3 and 6 of the 1,2,4,5-tetra-azapentalene nucleus causes elevation of the reduction potentials by 2.60—1.32=1.28 V.

The HMO calculations also show that the energy of the highest occupied orbital and the stability of azapentalenes as judged by the total π-electron energy seem to be approximately governed by the number of nitrogen atoms, their position in the nucleus exerting insignificant influence.

Irrelevance of the position of nitrogen atoms appears to be the case also with the chemical behaviour relating to the highest occupied orbital; the reactivity of 2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalene in reaction such as electrophilic substitution and oxidation parallels closely that reported for dibenzo-1,3a,4,6a-tetra-aza- and dibenzo-1,3a,6,6a-tetra-aza-pentalenes.[4,9]

Comparison of the energy values shown in Table 2 predicts that 1,2,3,4,5,6-hexa-azapentalene (XV) should be subjected to more facile reduction, but not to more facile oxidation than 1,2,4,5-tetra-azapentalene (XIII). This view is supported by the finding that 2,5-diphenyl-1,2,3,4,5,6-hexa-azapentalene (V) is easily reduced by sodium to the corresponding anion radical, but does not undergo any oxidation with potassium permanganate in boiling pyridine, whereas the reverse is the case with the tetra-azapentalene (I).[10]

Experimental

The syntheses of compounds I and V—X were reported previously.[1,2] Non-mesoionic tetra-azapentalenes II—IV are new compounds and their syntheses were reported in a separate paper.[4] Commercial tetra-*n*-butylammonium iodide was twice recrystallized from a mixture of ethanol and ethyl acetate and stored under nitrogen. Dimethylformamide was boiled under reflux with calcium hydride and distilled under nitrogen.

Polarographic measurements were carried out with a Yanagimoto Model P-8 apparatus. The dropping mercury electrode was operated at 60 cm pressure and had a drop-time of 4.36 sec in dimethylformamide (open circuit).

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7) The following parameters were used for the calculation: $\alpha_N = \alpha_C + 1.5\beta$ (pyrrole-like N), $\alpha_N = \alpha_C + 0.5\beta$ (pyridine-like N), and all $\beta = \beta_{CC}$ (*cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y. (1961), p. 135).

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