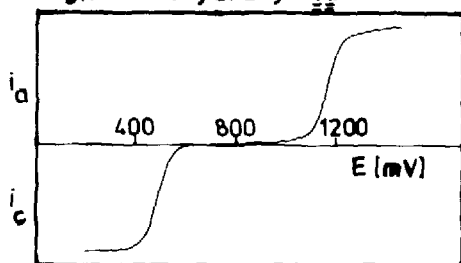
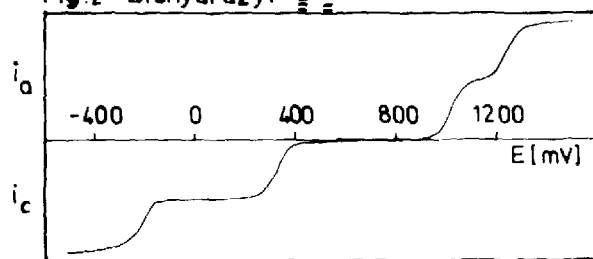


ELECTROCHEMICAL OXIDATION AND REDUCTION OF DIFFERENT SUBSTITUTED MONO- AND BISHYDRAZYLs OF THE CYANO BENZENE SERIES

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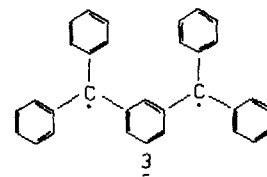
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The electrochemical behaviour of *N,N*-diphenyl-*N'*-picrylhydrazyl (DPPH) is well-known¹). In this paper we describe the cathodic reduction and anodic oxidation of mono- and bishydrazyls of the *N,N*-diphenyl-*N'*-(2,4,6-tricyanophenyl)hydrazyl-type. Recent reports have dealt with preparation of the hydrazyls 1b, 2a, 2b and 2d-k²⁻⁴). The nucleophilic substitution of one fluorine atom in 1,3,5-tricyano-2,4,6-trifluorobenzene by *N,N*-diphenylhydrazine in benzene at 15°C leads to the formation of 3,5-difluoro-2,4,6-tricyanophenyl(*N',N'*-diphenylhydrazine) (m.p. 153-155°C) and the substitution of the chlorine atom in 5-chloro-2,4,6-tricyano-1,3-phenylenebis(*N,N*-diphenylhydrazine) by sodium phenoxide in ethanol at 78°C under nitrogen gives 5-phenoxy-2,4,6-tricyano-1,3-phenylenebis(*N',N'*-diphenylhydrazine) (m.p. 205-207°C). 1a and 2c were obtained in nearly quantitative yields by treatment of these two hydrazine derivatives with lead dioxide²⁻⁴). The electrochemical measurements were carried out in dry benzonitrile with tetra-*n*-butylammonium perchlorate as supporting electrolyte, using a platinum rotating disc electrode, a platinum wire counter electrode and Ag/AgCl (benzonitrile, N(CH₃)₄Cl sat.) as reference electrode. The redox potential of cobaltocinium/cobaltocene against this reference electrode was -743 mV⁵). The concentration of depolarizer was 10⁻³ mol/l. Fig. 1 and 2 show typical current-potential curves for the voltammetric oxidation and reduction of monohydrazyl 1a and bishydrazyl 2a.

Fig.1 Monohydrazyl 1aFig.2 Bishydrazyl 2a

The polarographic curves of the monohydrazyls 1a, 1b and DPPH in benzonitrile show a single reversible one-electron anodic wave and a single reversible one-electron cathodic wave of equal height. Plots of potential vs. $\log [i/(i_d - i)]$ according to Tomeš ⁶⁾ are linear. S-values between 53-61 mV for both waves are obtained.

The D.C.-voltammograms of the bishydrazyls 2a-k give four waves of equal height, which are clearly separate from each other. This is in contrast to the behaviour of Schlenk's Diradical 3, where two one-electron waves overlap both in oxidation and reduction ⁷⁾.



The oxidation of the bishydrazyls occurs in two reversible one-electron waves. The first reduction wave is reversible, the second one pseudo-reversible ⁸⁾, each corresponding to one-electron addition.

According to the following schemes the hydrazyls 1 and 2 are oxidized and reduced in one-electron steps.

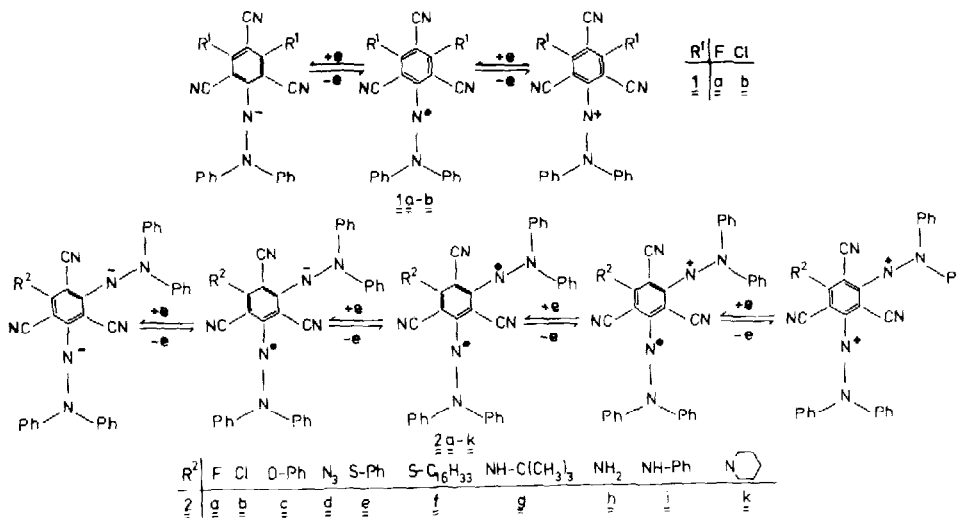


Table 1 Electrochemical data of monohydrazyls

comp.	$E_{1/2}^1$ a) S^1 b)		$E_{1/2}^2$ a) S^2 b)		$\Delta E_{1/2}^{(2-1)}$	log K c)
	[mV]		[mV]			
<u>1a</u>	530	58	1200	55	670	11.4
<u>2a</u>	489	57	1180	55	691	11.7
DPPH	397	61	972	53	575	9.7

Table 2 Electrochemical data of bishydrazyls

comp.	$E_{1/2}^1$ a)	$E_{1/2}^2$ a)	S^2 b)	$\Delta E_{1/2}^{(2-1)}$	$E_{1/2}^3$ a)	S^3 b)	$E_{1/2}^4$ a)	S^4 b)	$\Delta E_{1/2}^{(4-3)}$	log K c)
	[mV]				[mV]					
<u>a</u>	-225	350	59	575	1028	55	1248	58	220	11.4
<u>b</u>	-260	330	66	590	1010	55	1230	57	220	11.5
<u>c</u>	-279	300	65	579	988	54	1202	52	214	11.7
<u>d</u>	-292	289	60	581	976	53	1180	64	204	11.5
<u>e</u>	-330	270	66	600	968	57	1179	59	211	11.7
<u>f</u>	-381	258	59	639	968	53	1179	63	211	12.1
<u>g</u>	-406	205	66	611	912	60	1146	62	234	11.9
<u>h</u>	-427	184	66	611	905	54	1122	56	217	12.1
<u>i</u>	-431	179	60	610	896	54	1111	60	215	12.1
<u>k</u>	-478	158	60	636	890	55	1100	59	210	12.4

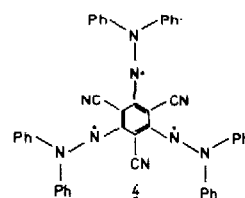
a) Half-wave potentials vs. Ag/AgCl (benzonitrile, $N(CH_3)_4Cl$ sat.)

b) Slopes of the logarithmic analyses curves, $S = dE/d\log(i/i_d - i)$ ⁶⁾

c) Semiquinone stability constant ⁹⁾.

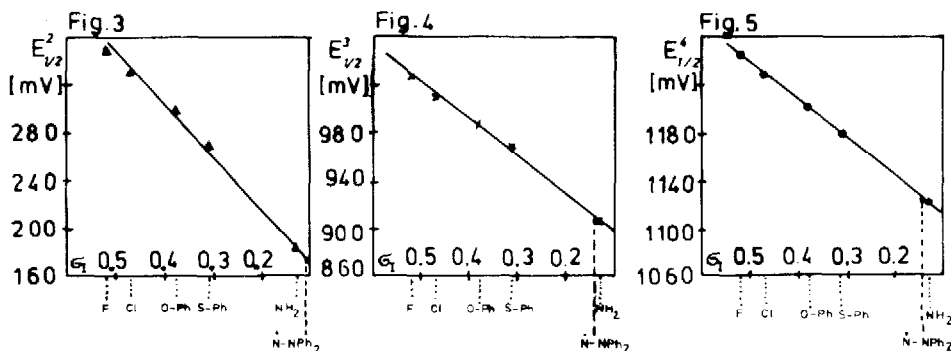
The results of measurements show that the electrochemical oxidation and reduction of the hydrazyls 1 and 2 are strongly influenced by the substituents of the tri-cyanobenzene ring. Hydrazyls with electron-withdrawing groups are difficult to oxidize and easy to reduce. This becomes clear with the bishydrazyls 2a-k which differ only on the substituents R^2 . A successive shift of half-wave potentials is obtained going from hydrazyl 2a with fluorine to hydrazyl 2k with a piperidine substituent.

The comparison of the half-wave potentials of the first oxidation and reduction waves in the series 1a \rightarrow 2a \rightarrow 4, where stepwise replacements of fluorine substituents by N,N-diphenyl hydrazyl groups $-\dot{N}-NPh_2$ take place, indicate that the oxidation of 2a becomes easier with 172 mV, that of 4 easier with



291 mV than that of 1a; the reduction is more difficult with 180 and 355 mV respectively.

Fig. 3-5 show that a linear relationship exists between the half-wave potentials (table 2) and the inductive effect of the substituents R^2 , represented by the σ_r values ¹⁰. By applying the corresponding values of the trishydrazyl 4 (the electrochemical behaviour of which will soon be published) on the curves the σ_r value of a *N,N*-diphenylhydrazyl group was found to be between 0.11 and 0.14. The inductive effect is therefore similar to that of a NH_2 -substituent.



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