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THE CONSTITUTION OF THE RADICAL INTERMEDIATE BETWEEN FORMAZAN AND TETRAZOLIUMSALT

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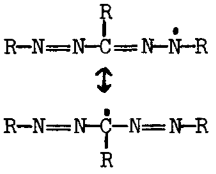
The reduction of 2,3,5-triphenyltetrazolium salts[1,2,3] the oxydation of N,N′, C-triphenylformazan by air[2] or the disproportionation of formazan-tetrazolium salt in the presence of base[2] gives rise to a paramagnetic species. The esr spectrum shows 9 lines easily explained by two pairs of equivalent nitrogens.[1,2,3]

The radical can be represented either as an open chain 1 or as a cyclic tetrazolinyl structure 2 related to the verdazyls (R = C_6H_5).



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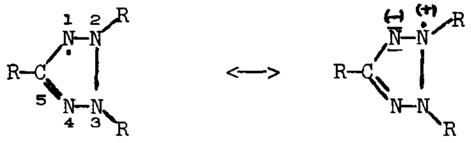

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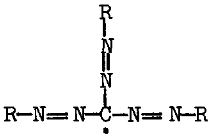
A very convenient new method to prepare this radical is the dehydrogenation of formazans by di(p-tolyl)nitrogen in benzene or other solvents.

The esr spectrum of the radical derived from N,N′-diphenyl-C-benzeneazoformazan should determine whether 3 or 4 is the true representation of the radical intermediate. Structure 3 demands two sets of 3 equivalent nitrogens.



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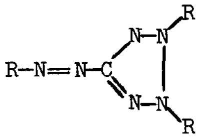

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The esr spectrum obtained (Figure 1) shows 9 groups easily interpreted by two pairs of equivalent nitrogens and excludes the open structure 3.

This result is in agreement with McLachlan calculations of the π-radicals 1 and 2. They show for 1 high spin densities in N-1, N-5 and C-3 and considerably smaller spin densities in N-2 and N-4. Structure 2 yields high spin densities of the same order in all four nitrogens, a small negative spin density in C-5 and very small spin densities in the substituent of C-5.

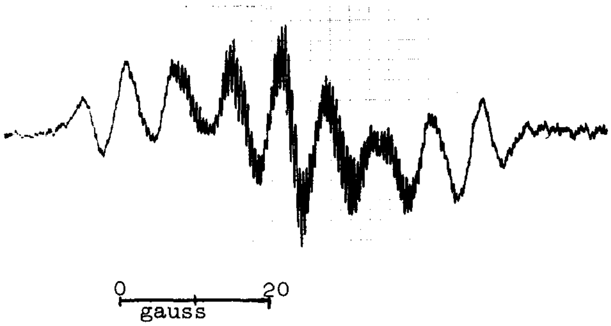
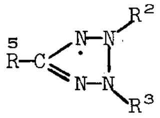


Figure 1.- First-derivative esr spectrum observed for the radical produced by dehydrogenation of N,N′-diphenyl-C-benzeneazoformazan in benzene.

The N-2, N-3 nitrogen splitting of the tetrazolinyl radicals should be sensitive to different substitution in the p-positions of the N-phenyl rings. Table 1 indicates that the larger nitrogen splitting is changed in a Hammett relationship ($OCH_3 > H > NO_2$). This assignment will be verified by N^{15} labelling.

TABLE 1

The HFSC of 2,3,5-Substituted Tetrazolinyl Radicals in Benzene



$R^2 = R^3$	R^5	a_1^N	a_2^N	$a^H_o = a^H_p$ (R^2,R^3)
C_6H_5-	C_6H_5-	5.6	7.5	---
C_6H_5-	C_6H_5–N=N–	5.8	7.5	---
4-$O_2NC_6H_4$-	C_6H_5-	5.6	6.5	---
4-$CH_3OC_6H_4$-	C_6H_5-	5.5	8.0	---
3,5-$Cl_2C_6H_3$-	4-$O_2NC_6H_4$-	5.7	7.5	0.9

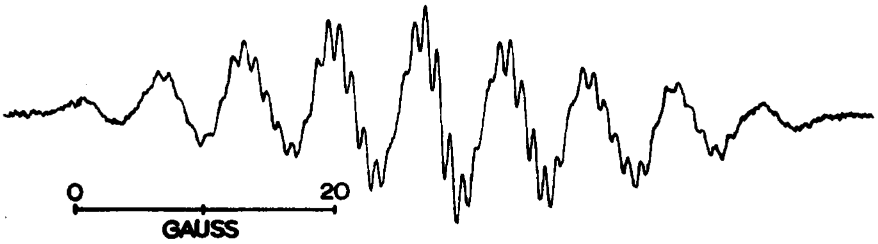
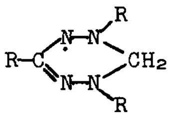


Figure 2.- First-derivative esr spectrum of 2,3-bis-(3,5-dichlorophenyl)-5-(4-nitrophenyl)-tetrazolinyl in benzene.

The selective substitution of the m-Hydrogens in the N-phenyl rings by chlorine yields a further resolved esr spectrum (Figure 2). Besides the nitrogen splittings a septet of 6 protons is obtained, which is attributed (based on the McLachlan calculations) to the protons in o- and p-positions of the N-phenyl rings.

The cyclic 7 π-electron system of the tetrazolinyl radicals 2 is closely related to the 7 π-electron system of the verdazyls 5 and tetraazapentenyls 6.4) Compounds 5 and 6 represent also the paramagnetic intermediate between a cation and a leuco stage.



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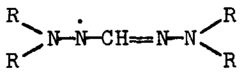

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