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ESR Studies on 2,3,5-Triphenyltetrazolyl and 2,3-(2,2′-Biphenylylene)-5-phenyltetrazolyl Radicals

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Synopsis. 2,3-(2,2′-Biphenylylene)-5-phenyltetrazolium chloride has been prepared. The ESR spectra of 2,3,5-triphenyltetrazolyl and 2,3-(2,2′-biphenylylene)-5-phenyltetrazolyl have been measured and their ESR coupling constants determined.

Since Deguchi and Takagi reported that 2,3,5-triphenyltetrazolium chloride with silver amalgam in 1,2-dimethoxyethane (DME) shows an ESR spectrum consisting of nine broad lines due to the hyperfine coupling of four equivalent N^{14} nuclei,1) a few papers have been published concerning radicals of this type.2)

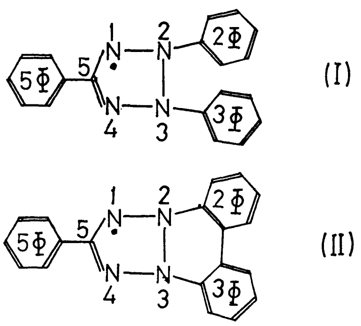

Fig. 1. Moleculer structure of 2,3,5-triphenyltetrazolyl radical (I) and 2,3-(2,2′-biphenylylene)-5-phenyltetrazolyl radical (II).

In this paper we will report the more detailed analyses of ESR spectra of radicals produced by alkali metal reduction from 2,3,5-triphenyltetrazolium chloride (TTC) and its photo-illuminated derivative; 2,3-(2,2′-biphenylylene)-5-phenyltetrazolium chloride (Photo-TTC).

Experimental

Commercial TTC was recrystallized from absolute ethanol by addition of dried ether. Photo-TTC was synthesized from the purified TTC following the photo-illumination method of Kuhn *et al.*3) and the elementary analyses of carbon, hydrogen, nitrogen, and chlorine agreed with the values of the literature.

Found: H, 3.79; C, 68.38; N, 16.59; Cl, 10.56%. Calcd for $C_{19}H_{13}N_4Cl$: H, 3.91; C, 68.57; N, 16.84; Cl, 10.67%.

Each free radical was prepared *in vacuo* by contact reduction with alkali metal at -30—-40 °C, the contact time being 1—2 s.

ESR spectra were observed using a X-band ESR apparatus equipped with 100 kHz field modulation.

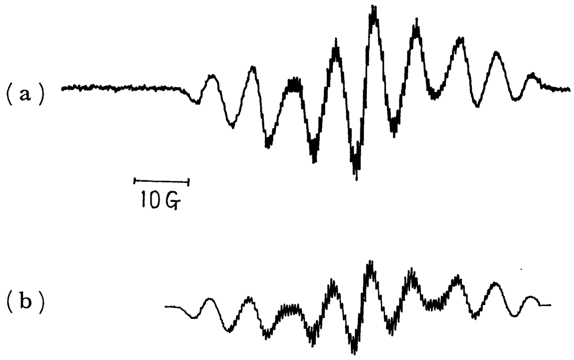

Fig. 2. ESR spectrum of radical (I) (2a) and its simulation (2b).

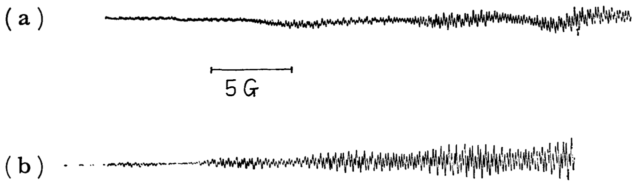

Fig. 3. Slightly more than one-half of ESR spectrum of radical (I) (better resolved than Fig. 2a) (3a) and its simulation (3b).

Results and Discussion

2,3,5-Triphenyltetrazolyl (I). The ESR spectrum of 2,3,5-triphenyltetrazolyl obtained by reduction with potassium in DME is shown in Fig. 2a. In this spectrum the third line from the center is slightly flat and broader than the others. Thus the spectrum is satisfactorily analyzed if we assume the presence of two unequivalent pairs of N^{14} nuclei summarized in Table 1 from which the simulated spectrum (Fig. 2b) was calculated.

The better resolved spectrum is shown in Fig. 3a, and the simulated one using the coupling constant in the Table in Fig. 3b.

When the solution is kept in contact with alkali metal further, the color turns red and the ESR signal disappears. This suggests the formation of formazane in the solution, since formazane treated with alkali metal in the etheric solvent such as DME gives no ESR signal.

2,3-(2,2′-Biphenylylene)-5-phenyltetrazolyl (II). This radical was obtained by the same procedure as that for radical (I). The ESR spectrum of radical (II) (Fig. 4a) consists of twenty nine absorption lines were observed. Figure 4b shows the better resolved spectrum of radical (II) and Fig. 4c its simulated one calculated by the data in Table 1. The result reveals that *o,o′*-bridging between the two phenyl rings attached to the nitrogens at 2- and 3-positions of tetrazolium ring causes more conjugation of the two phenyl rings than in the case of TTC. The unpaired electron is, however,

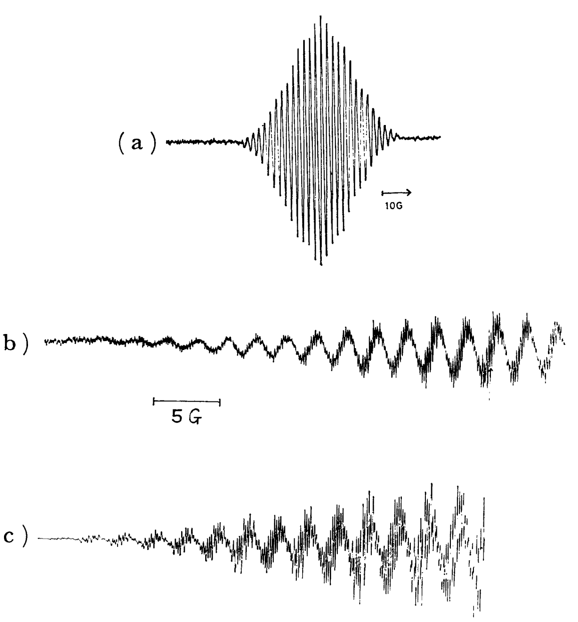

Fig. 4. ESR spectrum of radical (II) (4a), slightly more than one-half of ESR spectrum of radical (II) (better resolved than Fig. 4a) (4b), and its simulation (4c).

distributed to a greater extent to the tetrazolium ring rather than to the biphenylene ring. Both the results of Neugebauer[4] and the present MO calculation show that the distribution of the unpaired electron on the nitrogens does not differ remarkably between radicals (I) and (II).

Long contact of the solution with alkali metal, however, gives rise to the spectrum of benzo[*c*]cinnoline radical anion, the overall-width of which is about a half of that of radical (II). This result offers another evidence for the moleculer structure of Photo-TTC.[5]

Table 1. Hyperfine spllitting constants of radical (I) and radical (II)

	Radical (I)		Radical (II)	
	Found[a]	Calcd[b]	Found[a]	Calcd[b]
a_1^N	5.25^G	4.61^G	4.03^G	4.00^G
a_2^N	7.35	7.97	7.80	7.94
$a_{2\phi.o}^H$	0.90	1.63	1.95	1.74
$a_{2\phi.p}^H$	0.90	1.58	1.95	1.46
$a_{2\phi\ m}^H$	0.45	(−)0.63	0.39	(−)0.38
$a_{5\phi.o}^H$	0.30	(−)0.12	0.26	(−)0.11
$a_{5\phi.p}^H$	0.30	(−)0.10	0.26	(−)0.09
$a_{5\phi.m}^H$	—	0.0043	—	0.004

a) The values were determined by the analyses of the observed spectra referring to the simulated spectra. b) The values were estimated with the relations: $a_N=32.0\cdot|\rho_N^\pi|$ and $a_H=22.5|\rho_C^\pi|$. c) Parameters used in MO calculations are $h_{N1}=1.20$, $h_{N2}=1.50$, $k_{CN}=1.20$ and $k_{NN}=1.0$.

The spectra of both radicals (I) and (II) do not change from 20 to −50 °C during observation. The same is true for those produced by sodium metal. Both experimental and calculated (by McLachlan method) data for radicals (I) and (II) are summarized in Table 1.

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