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ESR Studies of Radicals Generated by the PbO_2 Oxidation of Some Mono- and Bis-formazans

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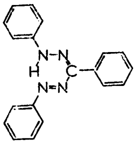
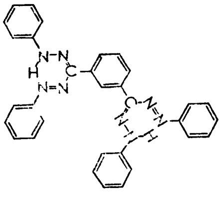
Several investigators[1–3] have reported that the air oxidation of formazans or the reduction of tetrazolium salts gives rise to a paramagnetic product whose ESR spectrum generally shows 9 lines easily explained by two pairs of equivalent nitrogens, and have proposed two structures for the radical, that is, (a) the openchain formazyl radical and (b) the cyclic tetrazolinyl radical. Neugebauer and Russel[4] obtained much better resolved spectra due to four nitrogens and further phenyl ring protons in a benzene solution by the



I



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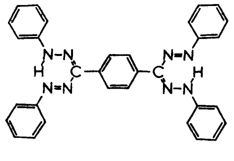

III

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1) R. T. Lofbert, *Nature*, **206**, 503 (1965).

2) O. W. Maender and G. A. Russell, *J. Org. Chem.*, **31**, 442 (1966).

3) Y. Deguchi and Y. Takagi, *Tetrahedron Lett.*, 3179 (1967).

4) F. A. Neugebauer and G. A. Russell, *J. Org. Chem.*, **33**, 2744 (1968).

abstraction of a hydrogen atom formazans by di(p-tolyl)nitrogen. They attributed these spectra to a cyclic structure, based on McLachlan molecular orbital calculations performed for the above two structures. Moreover, from the fact that the ESR spectrum of the radical derived from *N,N′* diphenyl-C-benzeneazoformazan shows 9 groups easily interpreted by only four nitrogen atoms, Neugebauer[5] concluded that the radical has the cyclic structure.

We with to report here the ESR spectra observed when the mono- or bis-formazans I-III are oxidized with lead dioxide in 2-methyltetrahydrofuran (2-MeTHF) under a vacuum.

Experimental

The formazans I—III (I, mp 177.2—178.0°C, II, mp 204.6—205.0°C, III, mp 222.5—222.8°C), were prepared following the method of Kuhn, Neugebauer and Trischmann[6] and were recrystallized, from alcohol for I, from aceton for II, and from DMF for III, as dark red crystals. All the ESR measurements were carried out using a JES-3BX spectrometer equipped with 100 Kc/sec field modulation.

Results and Discussion

Powder samples of the I-III formazans do not show any ESR spectra in 2-MeTHF at room temperature. An initial slight oxidation of the I-III formazans with PbO_2 gives the ESR spectra shown in Fig. 1(a), indicating an interaction with four equivalent nitrogens. We assign the spectra to the corresponding tetrazolinyl monoradicals (I(M), $a_N=6.2$ G; II(M), $a_N=6.1$ G; III(M), $a_N=6.2$ G), which have tetrazolinyl ring. There is no apparent interaction with the protons in the conjugated phynyl rings. Further oxidation of the monoformazan solution causes a marked decrease in the intensity of the ESR spectrum. However, in the case of the II and III bisformazans, as the oxidation proceeds the nine-line spectra of the monoradicals begin to overlap with each other and, finally, are completely altered to the spectra shown in Fig. 1(b). These spectra, which consist of nine considerably overlapped lines, were unchanged at the lowest concentration at which they could be detected; thus they are thought to be due to tetrazolinyl biradicals (II(B), $a_N=6.3$ G; III(B), $a_N=6.5$ G). These facts show that the broadening of lines in the ESR spectra of the tetrazolinyl biradicals can be attributed mainly to electron-electron interaction, and not to slow molecular tumbling motion as a consequence of the large molecular size. These circumstances are very similar to those of verdazyl radicals, which have a π-electron system closely related to that of tetrazolinyl radicals.[6-8]

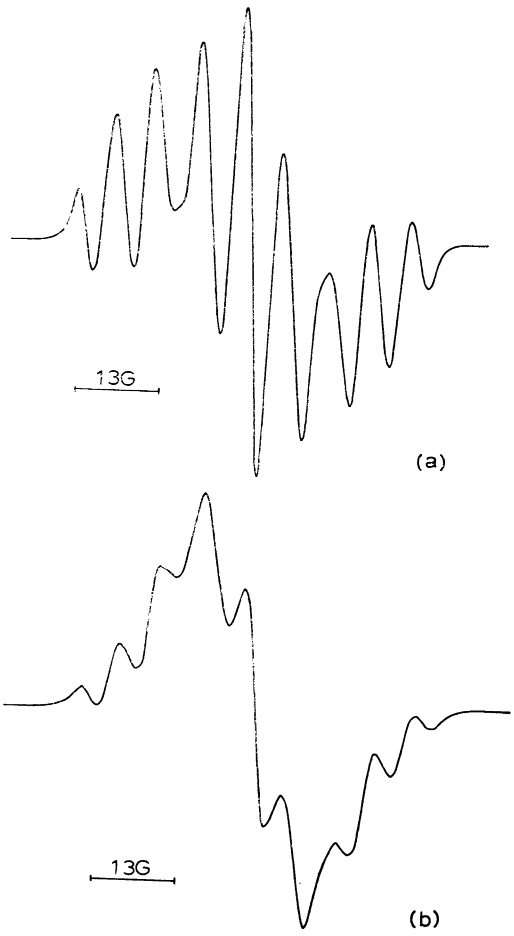
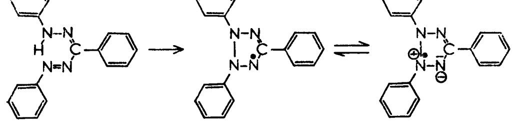


Fig. 1(a). First-derivative ESR spectrum observed for the II(M) monoradical, produced by the PbO_2 oxidation of formazan II in 2-MeTHF.
(b). ESR spectrum observed for the II(B) biradical, produced by the further oxidation of the II(M) monoradical in 2-MeTHF.



I I(M) I(M)

When the reddish-purple solution containing the II(B) biradical is frozen into a rigid glass (77°K),

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5) F. A. Neugebauer, *Tetrahedron Lett.*, 2129 (1968).

6) R. Kuhn, F. A. Neugebauer and H. Trischmann, *Mh. Chem.*, **97**, 525 (1966).

7) P. H. H. Fischer, *Tetrahedron*, **23**, 1939 (1967).

8) K. Mukai, N, Azuma, H. Shikata and K. Ishizu, This Bulletin, **43**, 3958 (1970).

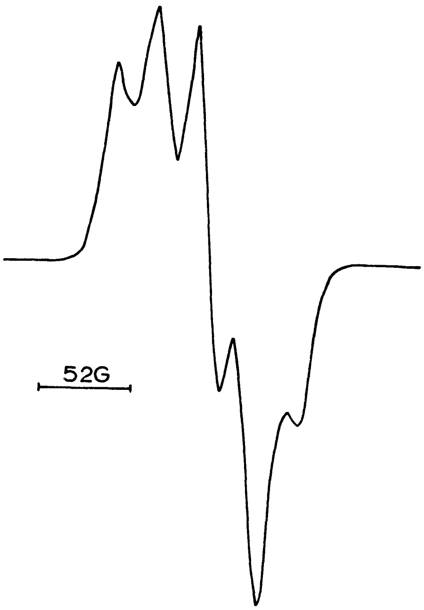

Fig. 2. ESR spectrum of the II(B) biradical in 2-MeTHF at 77°K.

one can observe dipolar splitting, as is shown in Fig. 2. The spectrum remained unchanged after a period of a few hours at 77°K. Upon annealing at room temperature, however, the reddish-purple color disappeared along with the ESR spectrum. The III (B) biradical gave similar, less resolved spectrum. No triplet signal could be observed from I(M) at 77°K.

The assignment of the observed peaks to the usual triplet-state spin Hamiltonian gave the zero-field splitting parameters, $D=51.2$ G for II(B) and $D=37.9$ G for III(B). These small splittings may be explained by the large separtion between the two tetrazolinyl rings and the small unpaired spin density on the centered phynylene ring and two carbon atoms bonded to the ring.[4,7)] The dipolar splittings, $D=51.2$ G and 37.9 G, obtained using a model of two-point dipoles, indicate that the average interelectronic distances in II(B) and III(B) are about 8.2 and 9.0 Å respectively. The observed increase in splitting constants, $D(\mathrm{II}) > D(\mathrm{III})$, is consistent with the structure.