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Studies on Stable Free Radicals. XI. ESR Spectra of Stable Nitroxide Biradicals

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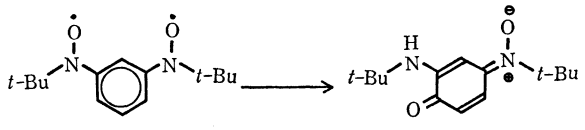
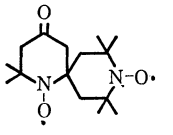
The ESR spectra of the triplet state of stable nitroxide biradicals, 1,9-diaza-2,2,8,8,10,10-hexamethyl-4-oxo-spiro[5.5]-undecane-1,9-dioxyl (III), cyclohexane-1-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (IV) and cyclohexane-1-spiro-2′-(3′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,-6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (V) have been observed in a frozen MTHF glass. The biradicals have $2\mathbf{D}\simeq 500$ and $\mathbf{E}\simeq 0$ gauss. The distance ($r\simeq 5$ Å) between the two radical sites in these biradicals indicates that one piperidine ring can exist in chair form and the other in twisted form in III, and both in the twisted form in IV and V. The biradical, 2,2,6,6-tetramethylpiperidine-4-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,-6″,6″-tetramethylpiperidine)-1,1″-dioxyl (VI) in a MTHF frozen glass shows no spectrum corresponding to a triplet state.

The electron spin resonance spectra of the stable biradicals and in particular nitroxide biradicals[2] with a small scalar electron spin-spin interaction are well known. However, cases of very large interaction are less common.[3] Calder and his co-workers[4] reported on the ESR spectrum of the nitroxide biradical (I) of this type. The crystalline samples of the triplet I undergoes a spontaneous topochemical change to the aminoquinone imine *N*-oxide (II).



(I) (II)

We have isolated four stable nitroxide biradicals, III–VI.[5,6] They are very stable and no change have taken place on standing at room teaperature over several years.



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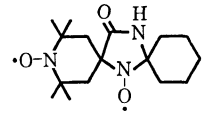

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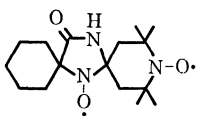

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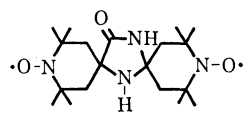

(VI)

1) Part X: T. Toda, E. Mori, H. Horiuchi, and K. Murayama, This Bulletin, **45**, 1802 (1972).

2) a) R. Briere, R. M. Dupeyre, H. Lamaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, **1966**, 3290. b) E. G. Rozantsev, V. A. Golubev, V. I. Suskina, and M. B. Neiman, *Izv. Akad. Nauk SSSR, Ser, Khim.*, **1966**, 2192.

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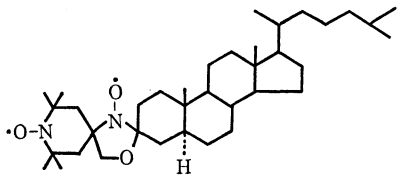
Since the molecular models of these nitroxide biradicals indicate that the two radical sites in the molecule can approach each other closely, and the molecules are relatively rigid, the direct intramolecular interactions of the two radical sites are expected to be larger than those of the nitroxide biradicals in which the two nitroxide radical subunits are connected to each other by flexible chains.[2a,7]

In this paper, we wish to report on the ESR spectra of the nitroxide biradicals III—VI.

After our work had been completed, Keana and Dinerstein[8] published a report on the ESR spectrum of stable nitroxide biradical (VII), which is compatible with ours.



(VII)

Results and Discussion

The nitroxide biradical, 1,9-diaza-2,2,8,8,10,10-hexamethyl-4-oxo-spiro[5.5]undecane-1,9-dioxyl (III) in solution and frozen 2-methyltetrahydrofuran (MTHF) gave the spectra shown in Fig. 1. Since the spectrum in the transition of $\Delta m=\pm 2$ could be observed in a rigid glass state, the spectrum in Fig. 1-b gives a typical triplet state in a randomly oriented molecule.[9]

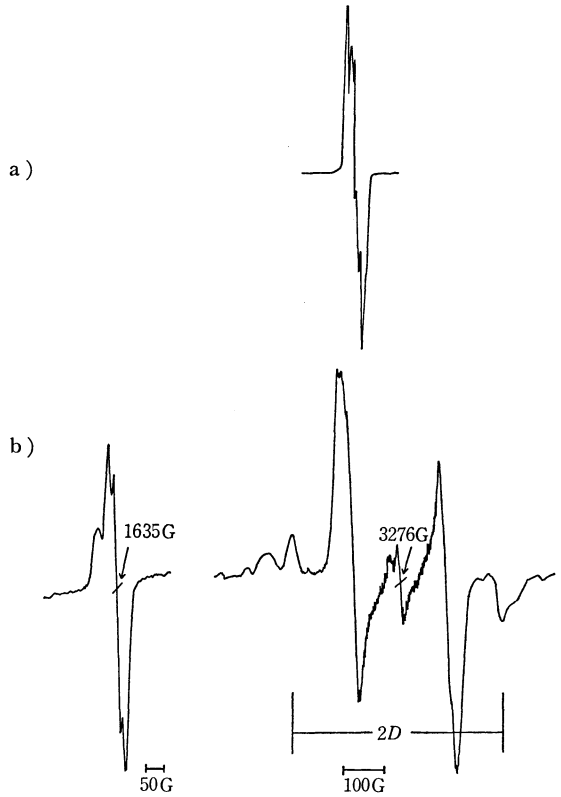


Fig. 1. ESR Spectra of III in 10^{-3} mol/l MTHF solution. a): at room temperature and b): at −196°C (measured in liquid nitrogen Dewar vessel).

The Hamiltonian for a biradical is

$$H = H_{\text{Zeeman}} + H_{\text{hyperfine}} + H_{\text{exchange}} + H_{\text{dipolar}}$$

The anisotropic effect observed in Fig. 1 is due to H_{dipolar}, where $H_{\text{dipolar}}=\mathbf{D}(S_z^2-1/3\cdot S^2)+\mathbf{E}(S_x^2-S_y^2)$. The zero field splitting parameter **D** can be estimated from the rigid glass spectrum as shown in Fig. 1, in which the separation between the outermost of lines in the spectrum is 2**D**.

The frozen MTHF glass spectrum of cyclohexane-1-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (IV) is given in Fig. 2.

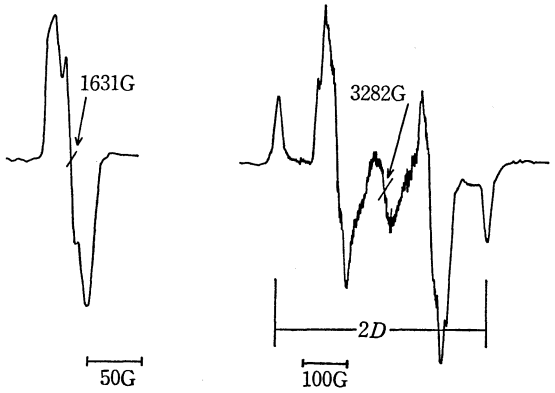


Fig. 2. ESR spectrum of IV in MTHF rigid glass at −196°C.

The spectrum of cyclohexane-1-spiro-2′-(3′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (V) in a rigid glass of MTHF (not shown) exhibited a shape similar to the spectrum of IV.

The parameter **D** for the biradicals IV and V can also be estimated from these spectra. The exact calculations of **E** for the nitroxide biradicals III, IV and V are not possible from our data, but it is clear that $|\mathbf{E}|\ll|\mathbf{D}|$ in each of the biradicals.

In the point dipole approximation, 2**D** is related to the distance r between the >N–O· groups by the equation.[10]

$$2\mathbf{D} = 55600 \times r^{-3} \qquad (1)$$

The zero field splitting parameter **D** and the distance r for the nitroxide biradicals are given in Table 1.

Table 1. The values of zero field parameter **D** and distance between two >N–O· groups r

Biradical	2·**D** (gauss)[a]	r (Å)[b]
III	532	4.72
IV	487	4.85
V	530	4.71

a) accuracy ±7 gauss.
b) accuracy ±0.02Å, from calculation by equation (1).

7) P. Ferruti, D. Gill, M. P. Klein, H. H. Wang, G. Entin, and M. Calvin, *J. Amer. Chem. Soc.*, **92**, 3704 (1970).
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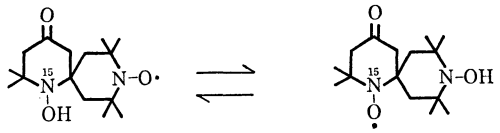
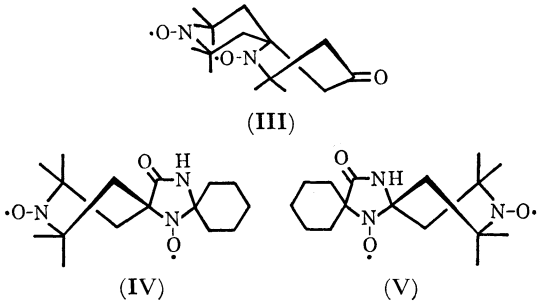
Measurements on molecular models of III with various conformations for two piperidine rings provide values of 4—6 Å for r which is the distance between each oxygen of two >N–O· groups. It was reported[11] distribution of spin density of unpaired electron is 73% on oxygen atom and 27% on nitrogen atom in the nitroxide radical, 2,2,6,6-tetramethylpiperidine-1-oxyl. When one piperidine ring is in a twisted form[11] and the other in a chair form[12] in III, as shown in Fig. 3, r is about 5 Å, in agreement with the value estimated from its ESR spectrum. When two piperidine rings are in boat forms in III, r is about 6 Å and 2**D** is 257 gauss; in chair forms, 4 Å and 869 gauss.

We reported on the intramolecular hydrogen transfer between the >N–OH and >N–O· groups in 1,9-diaza-(1-^{15}N)-2,2,8,8,10,10-hexamethyl-4-oxo-spiro[5.5]undecane-1-hydroxy-9-oxyl (VIII) corresponding to the precursor of the nitroxide biradical, III.[13] This was found from the ESR spectrum of VIII in toluene solution in which the intensity of the doublet lines resulting from a ^{15}N nucleus increased at high temperatures and decreased at low temperatures.



(VIIIa) (VIIIb)

From the intramolecular hydrogen transfer in VIII, it seems that the distance between two radical sites in III is 4.8 Å, because the distance between the hydrogen of >N–OH group and the oxygen of >N–O· group in VIII could approach that of van der Waals radius if the conformation of VIII corresponds to that of III. On the other hand, the values of r obtained for IV and V from these spectra in a MTHF frozen glass are in agreement with those measured from their molecular models in which the conformation of each



(III)

(IV) (V)

Fig. 3. Conformation of biradicals III, IV, and V.

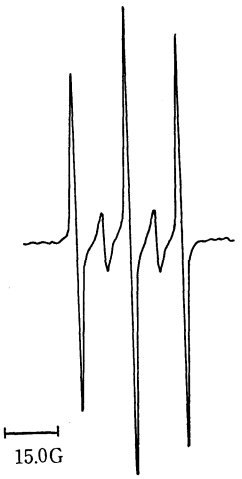


Fig. 4. ESR spectrum of VI in 10^{-3} mol/l toluene solution at room temperature.

piperidine ring is in a twisted form as shown in Fig. 3.

The spectrum of 2,2,6,6-tetramethylpiperidine-4-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″6″6″-tetramethylpiperidine)-1,1″-dioxyl (VI) in toluene solution at room temperature give quintet lines just like the spectrum of the carbonate diester of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl[2a] as shown in Fig. 4.

The frozen glass spectrum of VI does not correspond to that of a crystalline triplet. The distance between the two radical sites in VI may be longer than those of the other nitroxide biradicals III—V. The molecular model of VI indicates that two radical sites can approach each other in the molecule when both piperidine rings exist in boat form. However, such a conformation would not be predominant in VI.

Experiments for estimating the values of the triplet-singlet separation **J** in these nitroxide biradicals were not successful since there is no suitable solvent to measure the signal intensity of these solid state spectra at various temperatures.

Experimental

ESR measurements. The spectra were recorded with a Hitachi MES 4001 type X-band spectrometer equipped with the cavity of TE_{011} mode employing 100 kc modulation. The magnetic field was monitored by a Hitachi M 4704 digital gauss meter using a Hall element.

Materials. The nitroxide biradicals were prepared by oxidation of amines with hydrogen peroxide or *m*-chloroperbenzoic acid.[5,6,13]

We would like to thank Dr. Genshun Sunagawa, the director, for his encouragement.

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