Nitroxides. LXIX. 1,4-Bis(4′,4′-dimethyloxazolidine-3′-oxyl)cyclohexane Structure Determination by Electron Spin Resonance and Nuclear Magnetic Resonance

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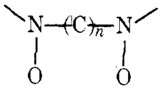
Abstract: The title biradical is obtained by condensation of cyclohexane-1,4-dione with 2-amino-2-methylpropan-1-ol, followed by *m*-chloroperbenzoic acid oxidation. Fluid isotropic solution esr spectrum shows that exchange interaction J is much larger than hyperfine splitting a_N. Dipolar interaction D = 121 G can be measured in frozen solution esr spectrum. This shows that only one isomer exists in which the two C–N bonds are both equatorial relative to the chair cyclohexane ring. Detailed analysis of the frozen solution esr spectrum is consistent with C_{2h} symmetry of the molecule. Landé (**g**), dipolar (**D**), and hyperfine (**A**) tensors are determined. Proton hyperfine splittings have been measured by nmr at room temperature. The nmr results are also consistent with C_{2h} symmetry of this biradical.

Electron spin resonance (esr) spectrum of biradicals[1-5] depends on various second-rank tensors (Landé (**g**) factor, dipolar (**D**) interaction between unpaired electrons, and hyperfine (**A**) electron-nuclei interaction) as well as scalar exchange interaction J.[5-7] For this reason, they are potentially useful spin probes.[8-14]

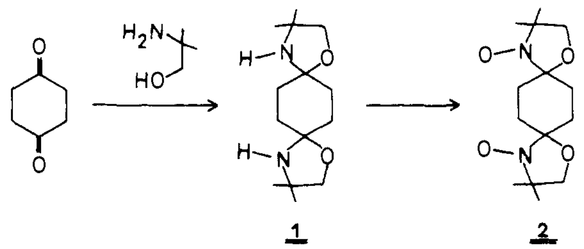
In the course of a study of rigid biradicals with large dipolar splitting, we have prepared various stable biradicals of general formula


$$\underset{\mathrm{O}}{\underset{|}{\diagdown\mathrm{N}}}-(\mathrm{C})_n-\underset{\mathrm{O}}{\underset{|}{\mathrm{N}\diagup}}$$

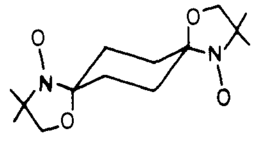
n = 3[14-16] and n = 5.[17,18] In this paper, we shall describe the synthesis of 1,4-bis(4′,4′-dimethyloxazolidine-3′-oxyl)cyclohexane (**2**), in which the two nitrogen atoms are separated by four carbons (n = 4). Some properties of this biradical have already been reported.[18,19]

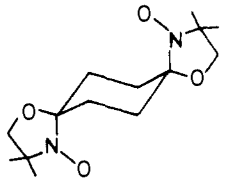
Synthesis

2-Amino-2-methylpropan-1-ol-was condensed, according to Keana,[20] with cyclohexane-1,4-dione to give diamine **1**. When this compound was oxidized with *m*-chloroperbenzoic acid,[21] a yellow-red compound (mp 189–190°) was obtained, which was homogeneous to recrystallization and thin-layer chromatography. Its formula **2** is in agreement with mass spectra, microanalysis, and ultraviolet (uv) spectroscopy (data: at 400 nm, ϵ = 15.6, twice the value of oxazolidinoxy monoradical for which 8.5 < ϵ < 9.9[22]). Structural formula **2** corresponds to two possible isomers, in which the two CN bonds are cis or trans relative to the cyclohexane ring.


1 **2**

Trans isomer may exist in several conformations. For a chair cyclohexane ring, CN bonds may be equatorial or axial (**2a** or **2b**); both conformations belong to the C_{2h} point group (C_{2h} symmetry). For a twist cyclohexane ring, the molecule **2c** has C_2 symmetry.


2a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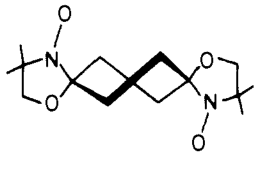
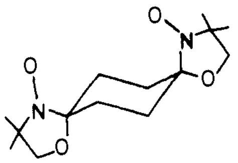
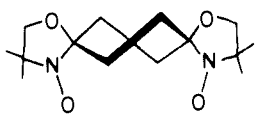

2c

Similarly, the cis isomer has various conformations: for a chair cyclohexane ring, there is one conformation **2d** only of C_s symmetry; for a twist cyclohexane ring, the molecule **2e** has now no symmetry element (C_1).


2d


2e

Previous studies[16,23] have shown that the magnetic resonance spectra are strongly dependent on the symmetry of the molecule;[24-26] we shall show here that these spectra are consistent with structure **2a**. While this paper was being prepared for publication, these predictions[18,19] have recently been confirmed by a totally independent X-ray study.[27]

Esr Study

Crystalline pure biradical **2**, at room temperature, displays a single broad line of *ca.* 12 G width. Dilute (M/1000) chloroform solution, at 23°, shows (Figure 1) five equally space lines, separated by 7.25 G, the peak-to-peak intensity being in a 1:1.8:2.6:1.8:1 ratio. This is in agreement with the 1:2:3:2:1 spectrum[28] of a biradical with a large exchange interaction J ($|J| \gg |a_N|$ = 14.5 G).[29]

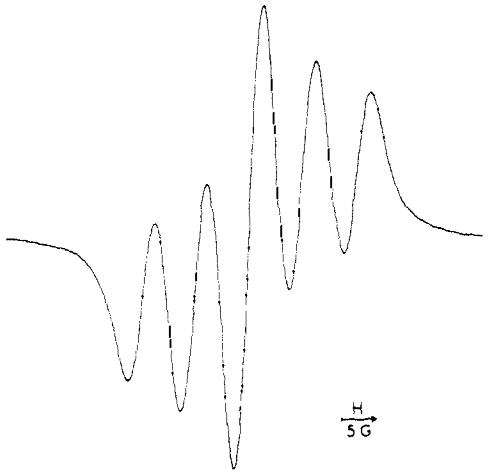


Figure 1. Esr spectrum of biradical **2** in chloroform solution at room temperature.

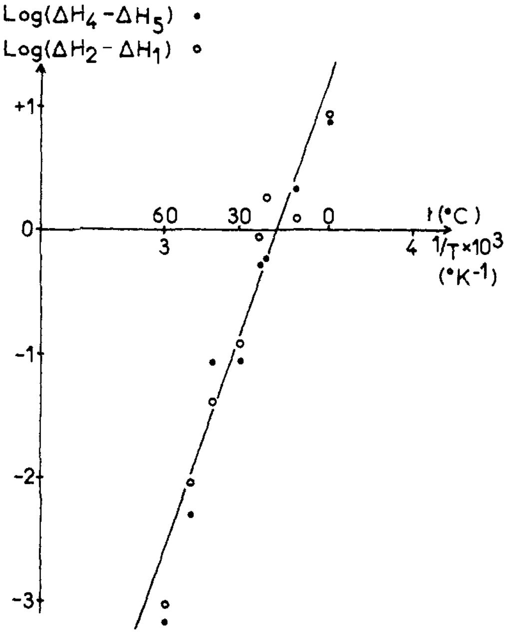


Figure 2. Variation of log ($\Delta H_2 - \Delta H_1$) and log ($\Delta H_4 - \Delta H_5$) as a function of $1/T$ in ethanol. (ΔH_i is the width of the i line.)

Internal Motion of Biradical. In a "fast-exchange" biradical, the broadening of the second and fourth lines is attributed to modulation of the exchange interaction by internal motion.[30-33] A simplified analysis can be given as follows: if ΔH_1 and ΔH_2 are the peak-to-peak line widths of the first and second lines of the biradical isotropic solution spectrum, due to overlapping of the lines, the second-line broadening is approximately $\Delta H_2 - \Delta H_1$. With simplifying assumptions, this can be written as $\log(\Delta H_2 - \Delta H_1) = A + \Delta E/RT$. In this case, it seems reasonable to identify ΔE to the activation enthalpy for internal motion of the cyclohexane ring.

We have studied the biradical **2** spectrum temperature variation between 0 and 70° in dilute ($M/1000$) ethanol solution. A plot of log ($\Delta H_2 - \Delta H_1$) and log ($\Delta H_4 - \Delta H_5$) *vs.* $1/T$ can be represented by a straight line (Figure 2), for which $\Delta E = 11 \pm 3$ kcal/mol. Because of the small temperature range and the approximation on the line-broadening measurement, this value is probably not very accurate. However, similar values have been found for interconversion of chair cyclohexane.[34,35]

Frozen Solution Spectra. In dilute ($M/1000$) n-butyl alcohol solution at −115°, the esr spectrum of biradical **2** is characteristic of a triplet without axial symmetry. Working at X band, $|\Delta M_s| = 1$ and $|\Delta M_s| = 2$ transitions are observed (Figures 3 and 4) at 3350 and 1670 G. Identical spectra were obtained in frozen toluene, ethanol, or dimethylformamide solution.

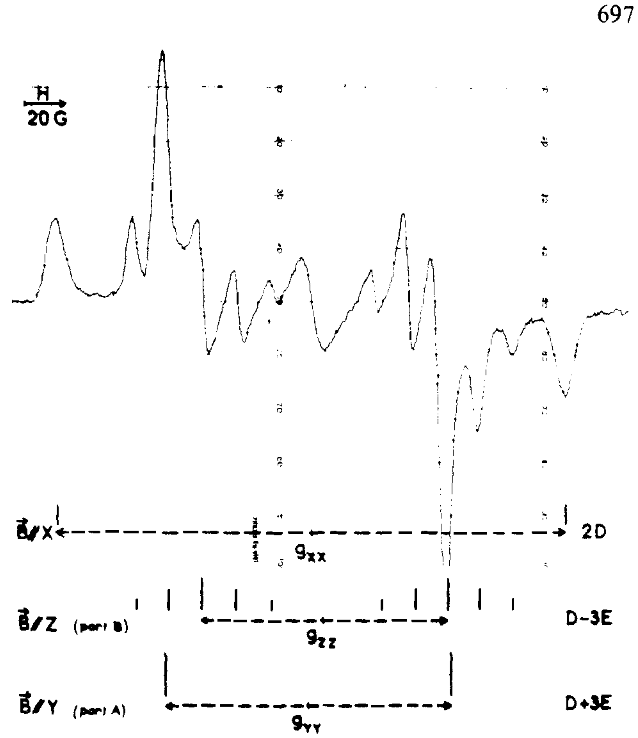


Figure 3. $\Delta M_s = \pm 1$ transition of biradical **2** in n-butyl alcohol at −115°. X, Y, and Z refer to the principal axes of the **D** tensor (Figure 7).

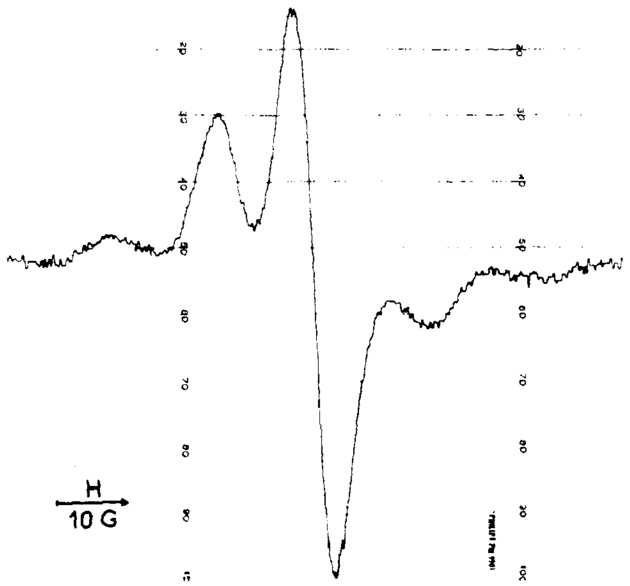


Figure 4. $\Delta M_s = 2$ transition of biradical **2** in n-butyl alcohol at −115°.

(I) $\Delta M_s = \pm 1$ Transitions. It is well known that the frozen solution spectrum is obtained as a superposition of single crystal spectra for all possible orientations of the magnetic field.[23,36-41]

Fine structure can be observed at the turning point of the magnetic field **B**, *i.e.*, when **B** is parallel to the principal axis of the dipolar second-rank tensor.

The largest splitting 2D is observed for **B** parallel to the principal axis X of the dipolar tensor which connects the two NO groups. The distance between the spectrum exter-

Table I

Conformation	NN′	NO′	OO′	MM′
	$R \pm 0.1$,[a] Å			
2a	5.9	6.3	7.0	6.2
2b	4.5	4.7	5.1	4.7
2c	5.4	5.6	6.0	5.6
2d	4.6	4.2 and 4.8	4.1	4.5
2e	5.5	5.8	5.9	5.7

[a] Distances between the two N and N′ nitrogens, the two O and O′ oxygens, NO′ and N′O, and the middles M and M′ of two NO bonds.

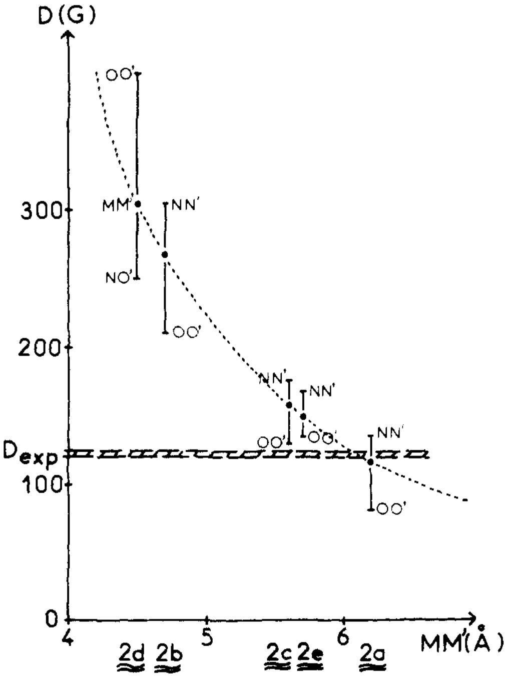
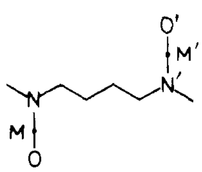


Figure 5. Variation of dipolar splitting D (in the point dipole approximation) as a function of the distance MM′ between the middles of the two NO bonds.

nal lines (Figure 3) being 242 ± 2 G, $D = 121 \pm 1$ G. In the point dipole approximation,[6,42] $D(\text{G}) = 27810/R^3$, R (in Å unit) being the average distance between the unpaired electrons. Protons and ^{13}C hyperfine coupling constants[43,44] in nitroxide indicate that the unpaired electron is mainly located on the NO group. R should be close to one of the distances between NN′, NO′, and OO′ and between the middles M and M′ of the NO and N′O′ bonds. These distances, measured on molecular models, are given in Table I for various conformations. Figure 5 gives calculated D values in the point dipole approximation for the different values of Table I, plotted as a function of distance MM′; it is seen that the experimental D value ($D = 121$ G, $R = 6.12$ Å) is consistent with conformation **2a** only. Since no other spectrum was observed in other solvents, we must conclude that other possible isomers or conformers are not detectable.[45]



Hyperfine structure can be seen when the magnetic field is parallel to the principal axes X, Y, and Z of the **D** tensor.[16,23,39-41] For a planar nitroxide group, the principal axes of the Landé (**g**) and hyperfine (**A**) tensors are parallel to the symmetry axes x, y, z (Figure 6) of the C_2NO group.[46-51]

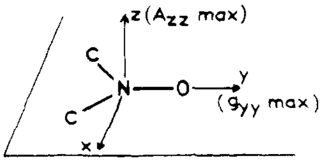


Figure 6. Principal axes of the Landé (g) and hyperfine (A) tensors for a planar nitroxide radical.

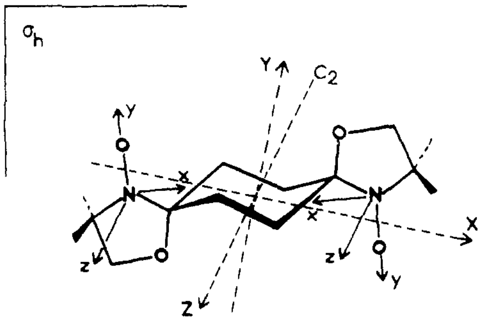


Figure 7. Principal axes X, Y, and Z of the **D** tensor for biradical **2a**.

If biradical **2** has structure **2a**, it belongs to the C_{2h} point group. In this case, individual **A** and **g** tensors of each NO group are all parallel. Due to symmetry, the C_2 rotation axis is the principal Z axis of the **D** tensor. It is parallel to the z axis of **g** and **A** tensors (Figure 7). Due to the localization of each unpaired electron on its NO group, the principal X axis of the **D** tensor, corresponding to the maximum value $2D$, is probably situated between the line connecting NN′ and OO′. On molecular models the angle between these two lines is *ca.* 20°. The angle between X and x is then probably smaller than 20°. There is the same angle between Y and y. The principal axes of the fine and hyperfine tensors (**D, g,** and **A**) are nearly parallel; this is a favorable situation to detect resolved hyperfine structure.[16,23]

(a) **B Parallel to** X. When the magnetic field is parallel to X, it gives rise to two external lines separated by 242 G. The frequency center of these lines gives $g_{XX} = 2.0063 \pm 0.0002$. This value is close to monoradical g_{xx} values,[46,51] thus confirming the X parallel to x orientation of **D** and **g** tensors.

(b) **B Parallel to** Y **and** Z. The rest of the hyperfine structure comes from the **B** ∥ Y and **B** ∥ Z turning points. The spectrum is analyzed as originating from two turning points spectra (Figure 3): (A) two strong lines of *ca.* 8 G width, separated by 134 G; (B) five less intense lines on each side of the spectrum, of *ca.* 5 G line width. The central lines of the (B) multiplicity are separated by 112 G.

This is characteristic of a nonaxially symmetrical triplet ($E \neq 0$). These two turning points give $(D + 3E) = 134 \pm 2$ G, $(D - 3E) = 112 \pm 2$ G, *i.e.*, $2D = 246 \pm 4$ G, equal to the value from **B** ∥ X, and $E = 3.5 \pm 1$ G.

The g values from these two (A) and (B) subspectra are $g_A = 2.0085 \pm 0.0002$ and $g_B = 2.0026 \pm 0.0002$.

The average $g_{av} = \frac{1}{3}(g_{XX} + g_{YY} + g_{ZZ}) = 2.0058 \pm 0.0002$ is in agreement with the isotropic $g_{iso} = 2.0061 \pm 0.0002$ value measured at room temperature. By comparison of the known g_{yy} and g_{zz} values for monoradicals ($g_{yy} = 2.0089 \pm 0.0001$, $g_{zz} = 2.0021 \pm 0.0001$[47]), the (A) subspectrum can be attributed to the **B** ∥ Y turning point and (**B**) subspectrum to the **B** ∥ Z.

Hyperfine Structure. At each turning point **B** ∥ K ($K \equiv X$, Y, or Z), the expected hyperfine structure should be made of five lines separated by $A_{KK}/2$ for strong exchange, or three lines separated by A_{KK} for weak exchange.

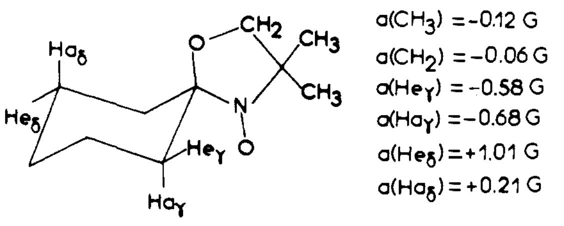


Figure 8. Nmr hyperfine coupling constants for the spirooxazolidinoxy radical.

For **B** ∥ Z, the experimental (**B**) subspectrum shows five lines separated by 16 G; this is evidence of strong exchange for biradical **2** and $A_{ZZ}/2$ = 16 G.

Since in isotropic solution a_{iso} = 14.5 G, A_{XX} and A_{YY} are expected to be of *ca.* 6 G ($A_{XX} \simeq A_{YY} = (3a_{\text{iso}} - A_{zz})/2$, the **B** ∥ X or **B** ∥ Y turning points should display five lines separated by *ca.* 3 G. At both turning points, a simple line of *ca.* 9 G width is observed, without hyperfine structure. This is in agreement with expectations, the line width preventing the observation of hyperfine structure.

Hyperfine structure analysis of the frozen solution spectrum confirms that biradical **2** exists in the symmetrical **2a** conformation.

(II) ΔM_s = 2 Transition and Singlet–Triplet Separation J. The "forbidden" ΔM_s = 2 transition at 1670 G[52] displays a five-line hyperfine structure (Figure 4). A detailed analysis of the ΔM_s = 2 transition in triplet species has been published.[53] Since the ΔM_s = 2 occurs only in the triplet state, the variation of its intensity I with temperature is related to the singlet–triplet splitting J by

$$C/I = T(3 + \exp(J/T)) \qquad (1)$$

where C is a constant depending, among other things, on the spectrometer. We have studied this temperature dependence in various solvents (dimethylformamide, *o*-terphenyl, and *n*-butyl alcohol) for 123°K < T < 233°K. The results are consistent with formula 1 with $J = 0 \pm 20$°K; it is well known that when J is weak, too high temperature measurements prevent precise determination of J.[45]

This value is in agreement with a calculation using a simple model of nitroxide biradical:[54] when nitrogen groups are separated by 6.12 Å, depending on their relative orientations, this calculation predicts $-10°\text{K} < J < +0.5°\text{K}$.

Nmr Study

Proton–electron hyperfine coupling in nitroxide monoradicals can be measured in magnitude and sign by nuclear magnetic resonance.[22,55-66] Nmr spectra of biradicals have been studied.[67-69] When proton hyperfine coupling constants are appreciable with one unpaired electron only, the biradical nmr spectrum is identical with the corresponding monoradical spectrum. When one proton is appreciably coupled with both unpaired electrons and if $kT \gg |J| \gg |a_{\text{N}}|$, its nmr shift is the sum of the corresponding shifts in monoradical.

All proton hyperfine coupling constants with the unpaired electron have been determined in spirooxazolidinoxy radicals[22] (Figure 8).

Biradical **2** nmr spectrum will be strongly dependent on its symmetry and will provide an independent proof of its structure. If biradical **2** has structure **2a** of C_{2h} symmetry, hyperfine interactions (J and a_{H}) between electrons and protons can be represented by diagram 1. For such a coupling diagram, four types of paramagnetic shift Δbi are predicted: oxazolidine methyl and methylene protons are expected to undergo the same paramagnetic shift as in monoradicals Δmono, while cyclohexane equatorial (H$_\text{e}$) and axial (H$_\text{a}$) protons are expected to undergo shifts Δ(H$_\text{e}$)bi and Δ(H$_\text{a}$)bi. The sums of the corresponding monoradicals shifts are: Δ(H$_\text{e}$)bi = Δ(H$_{\text{e}\gamma}$)mono + Δ(H$_{\text{e}\delta}$)mono and Δ(H$_\text{a}$)bi = Δ(H$_{\text{a}\gamma}$)mono + Δ(H$_{\text{a}\delta}$)mono. If biradical **2** has structure **2b,** four types of paramagnetic shifts will also be observed, but the cyclohexane proton shifts will be different.

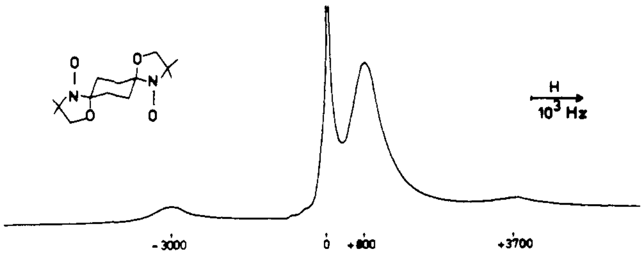


Figure 9. Nmr spectrum of biradical **2** in CDCl$_3$ solution at room temperature.

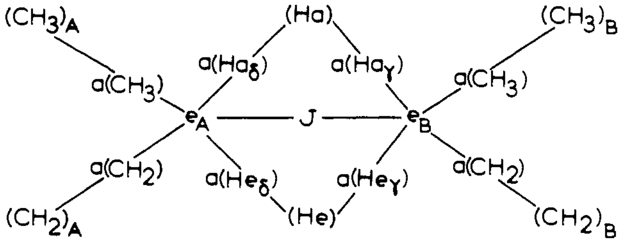


diagram 1

For isomers of lower symmetry (**2c, 2d** and **2e**), a large number of nmr lines will be observed.

Biradical 2 in concentrated (3 M) deuterated chloroform solution displays a four-line nmr spectrum (Figure 9). This is consistent with the C_{2h} symmetry of biradical. The high- and low-field lines have an apparently similar intensity, while one of the central line has a much higher intensity.

In order to calculate the biradical **2** hyperfine coupling constants, diamagnetic shifts must be estimated. We have taken the corresponding diamine **1** values. Table II gives the hyperfine coupling constants thus calculated compared with the coupling constants expected for structure **2a.** The experimental results are in full agreement with this expectation, thus providing an independent proof for structure **2a.**

Conclusion

Esr and nmr studies of biradical **2** have provided two independent and consistent proofs of its structure.

Experimental Section

For general indications see ref 22.

The esr spectra were taken on a Varian E3 esr spectrometer or Varian V 4501 A esr spectrometer equipped with a variable-temperature accessory.

Table II

Protons	δ_{para} ± 100, Hz	δ_{dia}, Hz	$\Delta H = \delta_{\text{para}} - \delta_{\text{dia}}$, Hz	a_{H} ± 0.02,[a] G	a_{H} expected for structure **2a**, G
CH$_3$	+756	−125	+881	−0.12	−0.12[b]
CH$_2$	0	−358	+358	−0.06	−0.06[b]
H$_\text{e}$	−3088	−180	−2908	+0.39	+0.43[c]
H$_\text{a}$	+3680	−180	+3860	−0.52	−0.47[c]

[a] $a_{\text{H}} = -[g_{\text{H}}\beta_{\text{H}}/(g_{\text{e}}\beta_{\text{e}})2](4kT/H_0)\,\Delta H$ or[22] $a_{\text{H}}(\text{G}) = -1.35 \times 10^{-4}\,\Delta H$ (Hz). [b] Monoradical value. [c] Sum of monoradical values.

The temperature was measured with a copper–constantan thermocouple to ±1°K.

The intensities I of $\Delta M = 2$ transitions were obtained after a double integration using an Adler OTT Integraph.

The nmr spectra were taken on Varian A 60 (diamagnetic molecules) or HA 100 (paramagnetic molecules) nmr spectrometers.

1,4-Bis(4′,4′-dimethyloxazolidine)cyclohexane (1). Cyclohexane-1,4-dione (5.6 g) and 2-amino-2-methylpropan-1-ol (9 g) were boiled for 2 days in a benzene solution (100 ml) containing 10 mg of *p*-toluenesulfonic acid. Water was removed by azeotropic distillation.

After extraction with ether and recrystallization in benzene, white crystals were obtained (7.6 g, yield 60%): mp 104–105°; ir (Nujol) ν_{N-H} 3300 cm^{-1}; nmr ($CDCl_3$) 1.25 ($CH_3(4')$), 3.58 ($CH_2(5')$), 1.8 (CH_2(cyclohexyl)), ~1.66 ppm (NH).

Anal. Calcd for $C_{14}H_{26}N_2O_2$: C, 66.10; H, 10.30; O, 12.58; N, 11.01. Found: C, 66.35; H, 10.33; O, 12.61; N, 11.13.

1,4-Bis(4′,4′-dimethyloxazolidine-3′-oxyl)cyclohexane (2). The amine **1** (1 g) in ether solution was oxidized by *m*-chloroperbenzoic acid (2.04 g) at room temperature. After 24 hr, this was washed with a 5% sodium bicarbonate solution and dried over sodium sulfate. After recrystallization in ether, yellow-red crystals were obtained (0.56 g, yield 50%), mp 189–190°.

By thin-layer chromatography (silica gel, 50% pentane–50% ether) only one spot was detected. The eluted compound had the same melting point: esr ($CHCl_3$) five lines separated by $a_N/2$ = 7.25 G; uv (methanol) λ 230 (ε 6100), 400 nm (ε 15.6).

Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.13; H, 8.51; O, 22.51; N, 9.85. Found: C, 59.23; H, 8.36; O, 22.52; N, 9.72.

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