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REGULATION BY POTASSIUM IONS OF SPIN EXCHANGE AND DIPOLAR SPLITTING IN A BIRADICAL. A SIMPLE ALLOSTERIC SYSTEM

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ABSTRACT : An acyclic glycol ether ligand with two nitroxide groups shows in frozen solution a dipole-dipole interaction only in the presence of potassium ions. At room temperature the spin-spin exchange is still observed, but it is amplified in presence of K^+. The results are discussed in terms of conformational effects that mimic allosteric effects.

Synthetic models which mimic allosteric effects have been described (1) by some authors. The regulation of catalytic activity of enzymes can be accomplished by the reversible binding of some agents. These enzymes possess in addition to the active sites, one or several allosteric (remote) sites for binding of a specific modulator (2). Conformational changes induced by binding give rise to allosteric behaviour. In a previous paper (3), we have described a model in which the formation of an intramolecular charge-transfer complex was regulated by potassium ions.

In the course of our studies on synthetic allosteric systems, we have prepared a model in which the intramolecular spin exchange is regulated by potassium ions, via an induced conformational modification.

Biradical **R** (Fig. I) was obtained by treatment of 4-hydroxy 2,2,6,6 tetramethyl piperidinyl-1 oxyl (4) and tetraethylene glycol ditosylate with sodium hydride in refluxing tetrahydrofuran. Purification by column chromatography (alumina ; Et_2O) affords the biradical that is identified by satisfactory spectral data : mass spectra (m/e 502 for $C_{26}H_{50}O_7N_2$ and 334 for 2,2,6,6 tetramethyl piperidinyl-1-oxyl fragment) ; electronic spectrum ($\lambda_{max.}$(EtOH) : 230 nm. (4000) and 410 nm. (17) ; ESR spectrum (Fig. I) (Varian E_{112}, X band, 100 KHz modulation).

At room temperature, the ESR spectrum of a freshly prepared dilute solution (0.001M) of biradical **R** in various solvents exhibits always a five line spectrum (5). The hyperfine interaction tends to increase with increasing solvent polarity (a_N = 15.9 G (EtOH) ; 15.37 G (Et_2O) ; 15.68 G (CH_2Cl_2) and 14.76 G (Toluene)).

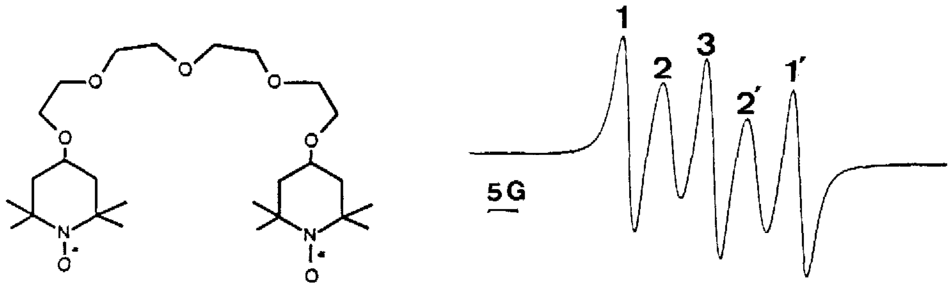

FIGURE I : ESR Spectrum of **R**, 0.001 M (EtOH), 25°C.

As reported by Parmon and coll. (6), this spectrum (Fig.I) displays the ESR features of a long chain ω,ω–dinitroxide biradical that are typical both for the spectrum of the "elongated" conformation, (with $J = 0$: 3 line spectrum) and for those of all possible folded conformations, in which the radical fragments are drawn near together, ($J > a_N$: 5 line spectrum). On addition of one equivalent of alkali ion M^+, a modification in the linewidth 2,2' (Fig.1) was readily detected : by example, the difference between the widths ΔH_2 of the ± 2 lines, and the widths ΔH_1 of the ± 1 lines (0.8 G in ethanol) increase to 1.37 G by adding potassium ions. Indeed, broadening of linewidth 2,2, with increasing alkali cation radius indicates a modification in the relaxation process that modulates the exchange interaction **J**, (since the positions of the lines are strongly dependent on **J** value (7)). The maximal spectral change is obtained with K^+.

In the frozen matrix of an ethanolic dilute solution (0.001M) at 120°K, the ESR spectrum of **R**, as shown on Figure II_a , was obtained. This spectrum is the same that of the monoradical ; it is modified only in the presence of the potassium ions (Fig. II_b) (8), where the largest dipolar splitting mesured from the distance between the outer peaks (arrows) yields an approximate value : $2D_{ZZ} = 175$ G. According to the point-dipole approximation (9), ($D_{ZZ} = 27810/r^3$) ; the average distance r between the unpaired electron of each nitroxide group cannot be smaller than the value of 6.8 Å. The forbidden transition $\Delta M_S = 2$, observed in a field of 1665 G, only in the presence of one equivalent of K^+ (Fig. II_c), exhibits 5 lines ; this corresponds to the case of strong exchange. These spectral observations emphasize the crucial role played by the potassium ions that influence the distance between the two nitroxide groups. As reported by us (3), for similar case of molecule without terminal radical groups, the change in the conformation of the biradical **R** is correlated to the presence of K^+ ; this suggests a 1:1 stoechiometric complex between **R** and K^+, in which the arrangement of the ligand is favoured by coordination to K^+ and where the polyether chain is wrapped around the alkali cation.

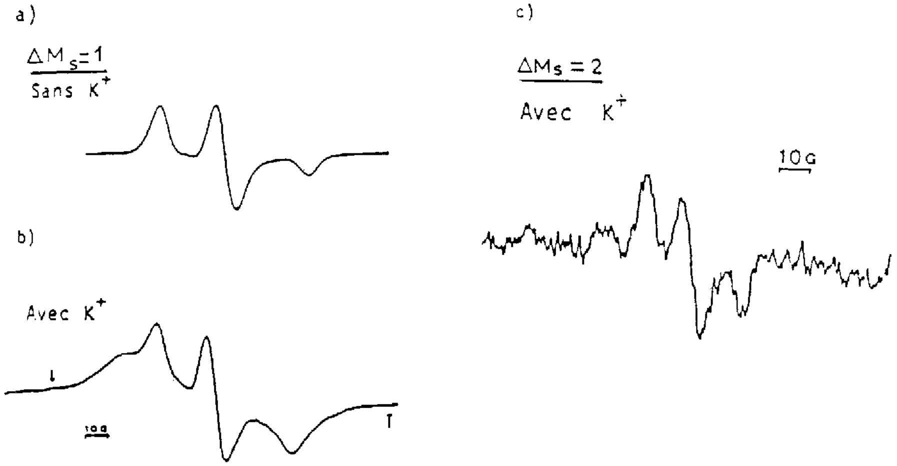

FIGURE II : ESR Spectrum in frozen solution (0.001M EtOH, 120°K)

The interpretation of these results is illustrated by the Figure III : the complexation with K+ induces and stabilises the conformation of biradical that allows the intramolecular spin exchange ; these conformational effects mimic an allosteric system (10) :

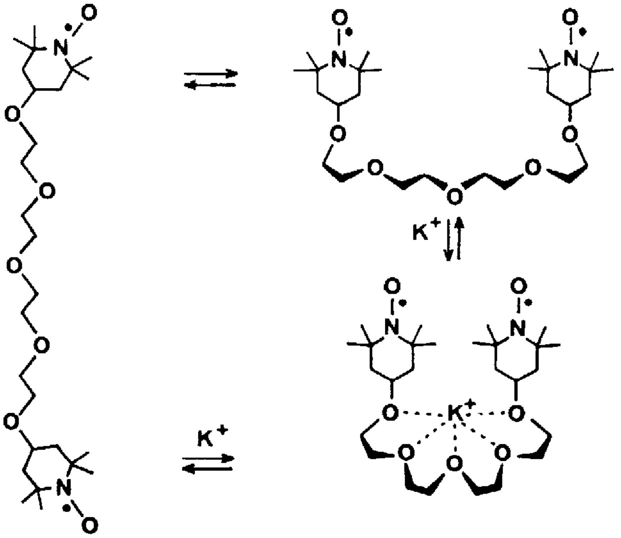

FIGURE III : Allosteric regulation of spin exchange in **R**.

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