that, as expected,[3] the transformation of **1** into **2** involves an inversion of configuration at C_6.

The conversion of **3c** into **4c** is quenched by addition of isoprene. Our evidence suggests that the mechanism of the transformations of the hydroquinones parallels that of the hydrocarbons[7] with the difference that the hydroquinones do not need sensitizers to enter the triplet state.

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Correlation between Conformation and Pairwise Spin Exchange in Flexible Biradicals in Solution. Control of Conformation by pH-Dependent Ionic Forces

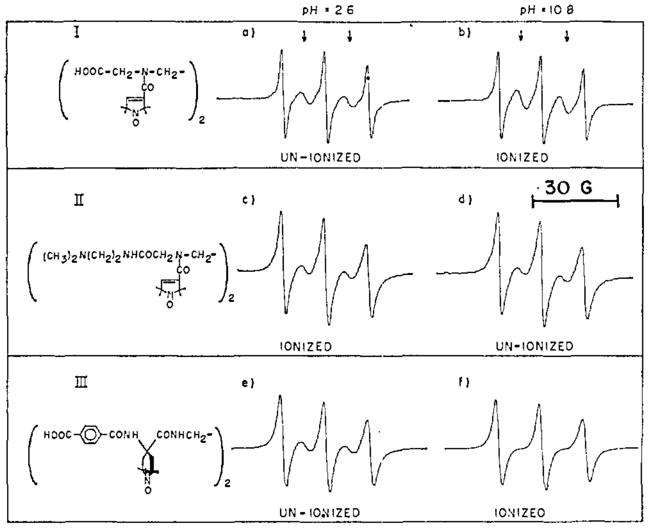

Figure 1. The formulas of the three flexible bielectrolyte biradical molecules (I–III) and their respective esr spectra in $\sim 10^{-4}$ *M* aqueous solutions at pH values of 2.6 and 10.8, at 24°. The spectra are distinguished by the presence of the two interpolating lines (marked by arrows at the top), the intensities of which are a measure of the intramolecular spin exchange. The molecules stretch at pH values in which fully ionized $-COO^-$ or $-NH^+(CH_3)_2$ groups are formed. Under similar conditions the behavior of III is opposite to that of I.

Sir:

Pairwise spin exchange between the free-radical subunits of *flexible* biradicals is manifest in the esr spectra of these molecules in dilute solutions.[1-10] The spin-containing subunits of the biradicals of interest here are attached *via* amide or ester bonds to the interconnecting *saturated* hydrocarbon chain. Two principal mechanisms enabling spin exchange have been discussed.[6] In the *indirect* process, spin density propagates through the molecular backbone. The alternative mechanism of spin exchange by the *direct* overlap of the singly occupied orbitals of the subunits requires the biradical to assume conformations favoring this overlap. Indirect exchange is expected to be no more sensitive to temperature or solvents than is the distribution of spin density.[6] The observations that exchange can be suppressed by cooling[6] or by the proper choice of solvents[2,10] have been interpreted to indicate the relative weakness of the indirect mechanism and the conformational parentage of the direct process.

Lack of methods for the on–off switching of the interaction other than by solvent or thermal treatment[2-10] has precluded the conclusive verification of the plausible direct exchange model.

We report here the introduction of a switchable ionic interaction between the biradical subunits. This has been achieved in three biradical molecules[11] (Figure 1, I–III) in which each subunit contains a nitroxide radical and an ionizable functional group. Electrostatic repulsion between the subunits, and hence conformational modification, can be turned on and off by ionizing or neutralizing the polar groups *without necessitating a change of solvent or temperature.*

Each of the biradicals[11] (Figure 1) (the preparation and characterization of which will be reported elsewhere[12,13]) consists of two identical subunits connected by a flexible hydrocarbon chain. The subunit contains one heterocycle ring which incorporates a nitroxide group[14-17] and one ionizable function, *e.g.*, $-COOH$ or $-N(CH_3)_2$. The bonding of the radical-carrying rings in I and II has much in common with the majority of nitroxide biradicals under study, whereas the spirane-

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(11) The compounds are I, N,N′-bis(1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxy)ethylenediamine-N,N′-diacetic acid; II, N,N′ bis(2-dimethylamino)ethyldiamide of I; III, N,N′-bis[2,2,6,6-tetramethyl-4-(*p*-carboxybenzoyl)amino-4-carboxypiperidine]ethylenediamine.

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like bonding of the piperidine-derived radicals in III is somewhat exceptional.[18]

Trace quantities of the three compounds were dissolved in aqueous glycine–hydrochloric acid or glycine–NaOH buffers (ionic strength 0.1, pH values of 2.6 and 10.8, respectively). Although we report here on spectra from two carefully prepared aqueous buffered solutions, other spectra showed no sensitivity to buffers of different composition, ionic strength, or to the absence of buffer in solutions of reasonable acidic or basic pH. The carboxyl groups of biradicals I and III ionize completely ($-COO^-$) at basic pH but not at acid pH. Conversely, the dimethylamine group of II is ionized at acid pH.

First-derivative esr spectra (Figure 1) were taken in a Varian E-3 spectrometer equipped with temperature controller. The esr spectra of mononitroxide radicals exhibit three lines which arise through hyperfine interaction with the abundant ^{14}N nuclei.[14–17] For short correlation times, $\tau_c \sim 10^{-11}$ sec, the lines have equal peak heights, while longer correlation times bring about departures from equality.[16,17] Nitroxide biradicals exhibit a five-line esr spectrum with relative intensity 1:2:3:2:1 when the spin–spin exchange interaction (measured in frequency units) is large in comparison with the hyperfine frequency. Intermediate strengths of exchange interaction lead to spectra intermediate between these limiting cases.[1,8] Thus the esr spectra reflect intramolecular pairwise spin exchange by the presence of the second and fourth weaker, broader lines. Our findings may be summarized by the following statement: *ionization augments the spin exchange in biradicals I and II, but decreases the exchange in biradical III.*

Examination of CPK space-filling models of biradicals I–III, with particular attention to the conformational changes which may accompany electrostatic repulsion of the ionic charges, suggests the probabilities of the conformations favoring direct overlap and provides the basis for the following interpretation of our findings.

When biradicals I and II are predominantly un-ionized, spin exchange is partly hindered because conformations in which the ionizable groups are proximal, and the nitroxide groups are distal, contribute appreciably to the partition function. In doubly ionized biradicals I and II, where the charged groups are mutually repelled, the aforementioned conformations become less likely, and thus the probability of spin exchange encounters of the nitroxide subunits increases. The pH effect is smaller in II than in I because the separation between the ionizable extremities of II is larger than between those of I.

The mutual repulsion of the *ionized* carboxylic groups of III constrains the planes of the nitroxide-bearing piperidine rings to be parallel, at a distance of 7.6 Å. Under this condition of constraint, only the *cis* conformation, in which parallel planes of the rings are juxtaposed, may give rise to exchange. The observation of no exchange (Figure 1f) indicates to us that at the 7.6-Å distance the overlap of the peak radial densities of the unpaired π orbitals is too small to permit observable spin exchange. At acid pH, when III is predominantly un-ionized, the rings are no longer constrained to be parallel and conformations in which the nitroxide-bearing extremities of the rings are in close contact become likely (Figure 1e).

Deeper understanding of the relation between direct exchange and molecular geometry would be achieved by computer simulation of biradical conformations in the spirit of the work of Levinthal, *et al.*[19]

We have in progress measurements to determine the electrostatic energy of the doubly ionized biradicals by determining the temperature dependence of the spin exchange.

With this information it should be possible to use appropriately constructed biradicals to measure conformational changes of molecules and membranes to which they are suitably coupled.[10,17]

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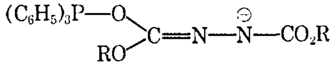
Structure and Cycloaddition of a Quasi 1,3 Dipole from Triphenylphosphine and 4-Chlorobenzene Diazocyanide

Sir:

Structures **1**[1–3] and **2**[4] have been proposed for the betaine derived from triphenylphosphine and azodicarboxylic ester. Recently we found the cycloaddition reactions of this quasi 1,3 dipole to be reconcilable only with **2**.[5] We now demonstrate structure **3** for an analogous, somewhat more stable, betaine from triphenylphosphine and 4-chlorobenzene *anti*-diazocyanide.

Combination of the components in dry ether led to the precipitation of pale yellow crystals (93%, decomposes above 80°) which analyzed correctly for **3**. The stretching frequency of the cyanamide anion was found at 2098 cm^{-1} (KBr); the ^{31}P chemical shift, −32.2 ppm (benzene; 85% H_3PO_4 external standard), suggests a phosphonium ion. The betaine **3** is stable for a few hours at 20° in the crystalline state; in solution it deteriorates rapidly.



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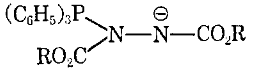

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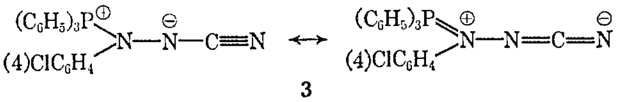

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