

THE IMINOXYL BIRADICAL WITH UNUSUAL SPIN-EXCHANGE

PROPERTIES

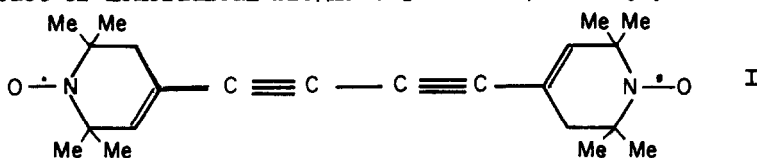
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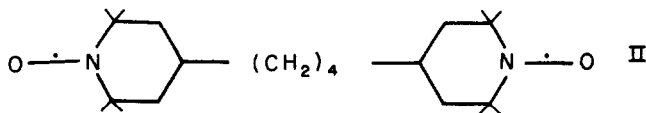
The criteria for characterising conjugation and delocalisation effects have been extensively discussed in theoretical chemistry. It was suggested that the reactivity of two distant atomic groups can be mutually influenced even when the optical spectra, dipole moments and bond lengths show no deviation from additivity, because the energy involved in these weak interactions is several order less than that of the chemical bond (1). However, these interactions are detectable by radiospectroscopic methods, sensitive to such low energetic "dynamic" conjugation. The stable iminoxyl biradicals (2) may provide an appropriate model for studying these weak interactions. The identity of the two free monoradical groups ensures weak spin exchange with an energy only slightly exceeding that of hyperfine interaction. The spin exchange results in the appearance of components additional to the basic triplet ESR spectrum of a monoradical iminoxyl. It has been shown however that in most cases the exchange interaction in these compounds, if observed, was time-modulated by the conformational motion of the connecting chain, providing direct overlap of unpaired electron orbitals. Time modulation results in alternation of the hyperfine linewidths, and this can be used for exchange energy evaluation. These phenomena usually reveal considerable and characteristic temperature and solvent dependence (2). There are also some indications that spin exchange may be realized through the connecting chain, but to our knowledge, in the iminoxyl biradicals for which this "indirect" exchange was assumed the exchanging free radical fragments were quite close to each other (2), or were connected by a highly conjugated chain (3), or the chain was not rigid enough completely to prevent direct

contact of monoradical fragments. A new species (I)



exhibiting unusual exchange properties will be described here. The structure of the connecting chain evidently rules out conformational motion with direct contact between exchanging monoradicals. I was obtained by condensation of triacetonamine with diacetylene in THF in the presence of solid KOH(-15°), followed by dehydration of the butadiyne-glycol with 65% H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>WO<sub>4</sub> - catalyzed oxidation with H<sub>2</sub>O<sub>2</sub>. Orange crystals, m.p. 208°. The sample contained 12.10<sup>23</sup> spin/mol.

The ESR spectra of I in dilute solutions showed 5 hyperfine lines, corresponding to the 5 allowed values of nitrogen nuclear spin projection onto the magnetic field direction (fig.1). This is typical of radicals in which the energy of the exchange interaction is comparable with that of the hyperfine interaction. But in contrast to the ESR spectra of other known iminoxyl biradicals, the parameters of exchange (e.g. the ratio I<sub>+2</sub>/I<sub>+1</sub> of ESR line amplitudes (fig.1,3), are nearly independent of temperature (-120 - +160°) and of the solvent (C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, C<sub>5</sub>H<sub>12</sub>, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>5</sub>OH). This is consistent only with the intramolecular indirect exchange and spin density propagation through the bond system not conjugated in the stationary, but conjugated in the dynamic sense (to see (1)). Fig.2,3 and Table 1 show for comparison typical temperature and solvent dependence for II. This species (orange crystals, m.p. 110° \*) was obtained by the same procedure of oxidation of bis-(2,2,6,6-tetramethyl-4-piperidyl) butane.



The closest analogue of II synthesized hitherto the biradical 1,4-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)butadiyne (III) (3) showed

a triplet ESR spectra in polar solvents at room temperature but decomposed on heating.

The very slight differences in the rate of exchange in I which can still be observed with solvent and temperature variations (though these can hardly be seen in table I) are not surprising. The coincidence of energy levels of electrons in both paramagnetic sites is known to be a strict requirement for spin exchange (both "direct" and "indirect"). The energy levels are but slightly affected by solvation, and hence by temperature variations. However these effects are not predictable at the present state of knowledge.

The rigid structure of I results in a lower rate or (and) a greater anisotropy of molecular tumbling, as compared with other iminoxyl bi- and monoradicals with flexible chains in nonviscous media such as hydrocarbons. This feature is clearly seen from comparison of the anisotropy of ESR signals (ratio  $I_{+2}/I_{-2}$ ) for I or  $I_{+1}/I_{-1}$  for II (fig.3). Thus biradical I is believed to be an appropriate spin-probe (2) of molecular motion in nonviscous matrices in which other iminoxyls show isotropic ESR spectra.

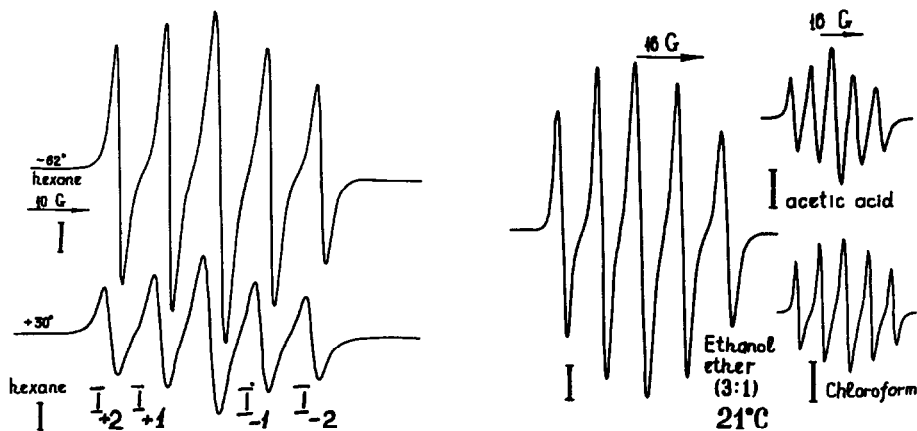


fig.1

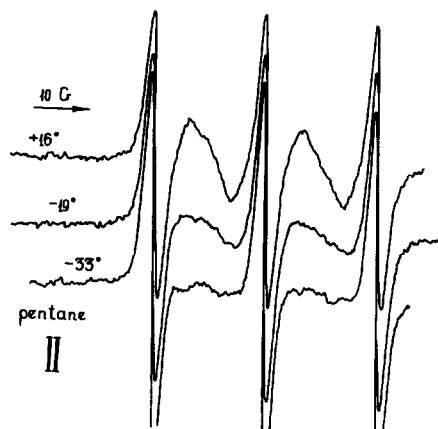


fig. 2

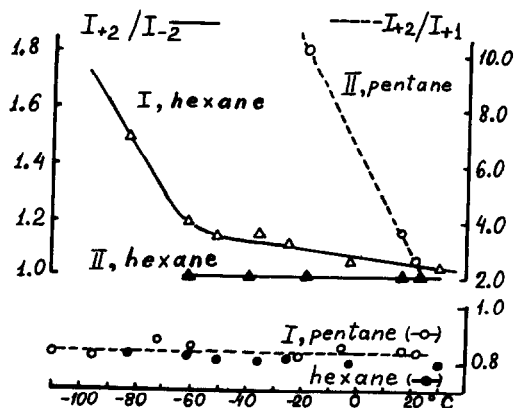


fig. 3

Table I.  $I_{+2}/I_{+1}$  and  $I_{+2}/I_{-2}$  for I and II in different solvents (21°).

	I		II	
	$I_{+2}/I_{+1}$	$I_{+2}/I_{-2}$	$I_{+2}/I_{+1}$	$I_{+2}/I_{-2}$
Pentane	0.83	1.08	2.59	1.00
Ethanol	0.76	1.16		
Benzene	0.84	1.10	5.25	1.00
Acetic acid	0.76	1.16	triplet	1.00
Chloroform	0.73	1.14	signal	1.00 ( $I_{+1}/I_{-1}$ )

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\* Satisfactory analytical data, and consistent I.R. and mass-spectra were obtained for these compounds.