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MAGNETIC FIELD DEPENDENT BIRADICAL CIDNP AS A TOOL FOR THE STUDY OF CONFORMATIONS OF POLYMETHYLENE CHAINS

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A theory is presented for the interpretation of the magnetic field dependence of CIDNP from polymethylene biradicals. It is shown that the field dependence curves give information about the conformational behaviour of biradicals.

1. Introduction

Experimental information on the conformations and dynamical behaviour of short flexible polymethylene chains is not easily accessible. In this paper we wish to show that biradical CIDNP, and specifically its magnetic field dependence, constitutes a useful tool for the study of the behaviour of chain molecules in solution. In particular it will be shown that the field dependence is related to the end-to-end distance distribution of the biradicals.

A few other approaches to this problem, which had similar but somewhat more limited aim, have been reported. Thus Brady et al. [1] determined the most probable end-to-end distance of α,ω -dibromo- and α,ω -diiodo-*n*-alkanes by means of X-ray diffraction. Shimada and Szwarc [2] studied the intramolecular electron transfer reaction $N-(CH_2)_n-N^\cdot \rightleftharpoons \cdot N-(CH_2)_n-N$ ($N = \alpha$ -naphthyl) by electron spin resonance. By computer simulation of the ESR spec-

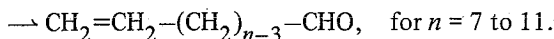
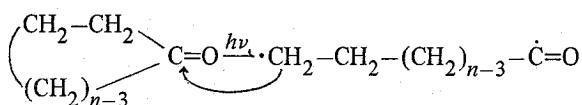
tra they were able to calculate the effective concentration of the acceptor α -naphthyl group. Winnik et al. [3] investigated the intramolecular phosphorescence quenching of the carbonyl oxygen of a number of *n*-alkyl esters of benzophenone-4-carboxylic acid. The quenching rate constant is proportional to the ratio of reactive conformations/total conformations, i.e. the probability that any methylene group in the alkyl chain occupies the reactive volume about the ketone oxygen. Using a Monte Carlo computer program [4] based on a diamond lattice walk model these probabilities were calculated. From these methods only an average distance or a reactive volume as fraction of the total space is obtained.

CIDNP from biradicals has been interpreted qualitatively by assuming that $S-T_-$ [5] or $S-T_+$ [6] evolution is important, whereas $S-T_0$ mixing plays an important role for radical pairs. In biradicals the residual exchange interaction (J) can match the electronic Zeeman interaction in a magnetic field H_0 :

$$2|J| = g\beta H_0. \quad (1)$$

When the S and T₋ levels are degenerated, the hyperfine interactions are able to induce S-T₋ transitions which are accompanied with nuclear spin flips. Generation of the biradicals from a triplet state, while intramolecular disproportionation or recombination occurs from the singlet state, gives rise to emissive CIDNP spectra of the products.

Closs and Doubleday [7] have studied the magnetic field dependence of CIDNP of the emission signal of the aldehydes, formed during the photolysis of cyclic ketones:



These authors reported that for each of the aldehyde signals a maximum emission occurred at a certain magnetic field strength. For larger ketones (i.e. larger biradical intermediates) this maximum appeared at a lower magnetic field, which was related to a decrease of the average exchange interaction with increasing chain length. The decrease of the width of the field dependence curve with increasing chain length was interpreted [8] by a chemical lifetime of the singlet state of the biradical. Another description of the field dependence was given by Atkins and Evans [9]. They proposed a two-jump model, which limits the biradicals to two distinct conformations, each with a given lifetime and exchange interaction. A correlation was then made between the length of the biradical and the lineshape of the magnetic field dependence. In both models an ad hoc value of the exchange interaction has to be assumed. However making use of a functional form of $J(r)$, valid for the whole series of biradicals, a relation can be established between the end-to-end distribution and the maximum and shape of the field dependence curves.

2. Theory

We assume that the exchange interaction for a biradical is only a function of the end-to-end distance r . In this paper we assume an exponential dependence:

$$J(r) = J_0 e^{-\alpha r}. \quad (2)$$

Other forms of $J(r)$ can however be used in our model.

An exponential behaviour has been found for the interaction between two hydrogen atoms [10]. For π -radicals the situation is more complicated as the exchange interaction is also orientation dependent [11], but we will neglect this orientation dependence. As the terminating radical site of a methylene chain has a very short rotational correlation time around the C-C single bond, this simplification seems justified.

We consider only T₋-S mixing. From eqs. (1) and (2), crossing of these two levels occurs at a distance

$$r_c = \alpha^{-1} \ln(|2J_0|/\omega_0), \quad \omega_0 = g\beta H_0. \quad (3)$$

The transition probability W between both levels is directly related to the CIDNP intensities. W is calculated with Aleksandrov's [12] theory for non-adiabatic transitions between linear intersecting energy levels. Although the relative motion of the radical centres of a biradical cannot be described by a uniform free diffusive motion, we assume that Aleksandrov's theory can still be applied to the present problem. When we take into account only one nucleus with spin $I = \frac{1}{2}$ and hyperfine coupling constant A ,

$$W = \pi^2 A^2 r_c^2 C(r_c) / \alpha \omega_0. \quad (4)$$

$C(r_c)$ is the concentration of biradicals at r_c , i.e. the end-to-end distance distribution. Interestingly the diffusion coefficient D does not enter in the result of eq. (4). This is due to the fact that the transition probability is inversely related to the rate of passage through the point of intersection, i.e. inversely related to D , but on the other hand the number of passages is directly proportional to D .

We assume that the biradicals from cyclic ketone photolysis are well defined by polymethylene chains. A number of distribution functions has been proposed for the characterization of polymethylene chains [13]. First we have tried Treloar's [14] radial distribution function for a freely jointed chain:

$$C(r) = (r/2l^2)^{(n-1)(n-2)} \times \sum_{t=0}^{\tau} \frac{(-1)^t}{t!(n-1-t)!} \left[\frac{1}{2}(n-1-r/l-2t) \right]^{n-3}, \quad (5)$$

where τ is an integer specified by

$$\frac{1}{2}(n-1-r/l)-1 < \tau < \frac{1}{2}(n-1-r/l),$$

with n the number of methylene groups and l the bond length. For large n the distribution of eq. (5) is close to a gaussian distribution, which is valid for large chains. The results will be discussed in the next section.

A second more realistic distribution function has been obtained from a Monte Carlo computer simulation of n -alkanes as described by Lal and Spencer [15].

The computer program calculates conformational energies, consisting of the bond rotation energies and the energies due to the interaction of nonbonded atoms in the molecule. The short range interatomic interactions (between the C and H atoms of segments separated by four or less bonds) are calculated using the Buckingham potential; the long range interatomic interactions between CH_2 segments, assumed to be spherical, by a Lennard-Jones potential. No distinction was made between CH_2 and CH_3 segments. When for a large number of random conformations the energy U_i and the end-to-end distance r_i are calculated, a distribution function of discrete distances is obtained:

$$C(r) = \frac{\sum_i \exp(-U_i/kT)}{\sum_j \exp(-U_j/kT)}. \quad (6)$$

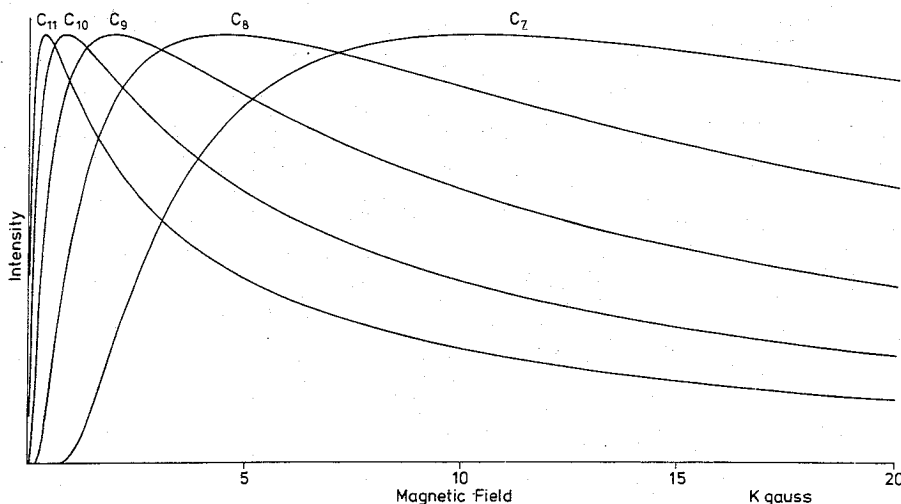


Fig. 1. CIDNP emission intensities from biradicals (C_7 – C_{11}) as function of the magnetic field, calculated according to eqs. (4) and (5). Intensities are in arbitrary units.

Σ_i' is the summation over the conformations for which $r < r_i < r + \Delta r$ while Σ_j is the summation over all conformations.

3. Results and discussion

Fig. 1 shows the field dependence curves calculated according to eqs. (4) and (5) for freely jointed chains. α and J_0 were adjusted to obtain the best agreement between the calculated maxima and the experimental maxima reported by Closs and Doubleday [7]. The best values were found to be $\alpha = 1.32 \text{ \AA}^{-1}$ and $J_0 = -0.11 \times 10^{15} \text{ rad/s}$. The value of $l = 1.25 \text{ \AA}$ was chosen so that $nl = r_{\text{max}}$, with r_{max} the maximum end-to-end distance of a polymethylene chain. The maxima of the different curves were scaled to the same value. In spite of the crudeness of the model, it appears that with an exponential behaviour of J the maxima of the whole series fit reasonably well (table 1). The decay of the curves for increasing magnetic field is however too slow, resulting in too large widths of the curves.

Accordingly the value of $C(r)$ for small distances, as given by eq. (5), is too large. Smaller widths are obtained using the r -distribution functions from Monte Carlo calculations [eq. (6)]. These distribu-

Table 1
Experimental ^{a)} and calculated maxima and widths of the field dependence CIDNP curves (in gauss)

Number of C atoms	Experimental maxima	Maxima according to		Experimental widths	Widths according to	
		eqs. (4) + (5)	eqs. (4) + (6)		eqs. (4) + (5)	eqs. (4) + (6)
7	20000 ± 3000	10280	17920	24492 ± 5346	—	—
8	4000 ± 400	4480	5160	5634 ± 320	—	14541
9	2096 ± 96	1960	2200	2747 ± 114	14970	5030
10	913 ± 32	840	920	479 ± 32	7330	1945
11	279 ± 53	360	280	325 ± 53	3812	609

^{a)} From ref. [7].

tion functions have however, particularly for small chains, a number of peaks corresponding to distinct conformations. These peaks appear in the field dependence curves because the dynamical behaviour (jumps between various conformations) was not taken into account properly. Eq. (4) is only valid for not too rapid diffusive motions. Faster motions will cause smoothing of the field dependence curves. Also fluctuations in J due to its orientation dependence, which is not included, will cause smoothing. We simulated smoothing by a gaussian function with half width δ over $C(r)$.

Figs. 2 and 3 show the field dependence curves calculated according to eqs. (4) and (6) with δ equal to 0.3 and 0.7 Å respectively. For both figures the parameters are $\alpha = 1.06 \text{ \AA}^{-1}$ and $J_0 = -0.25 \times 10^{15}$

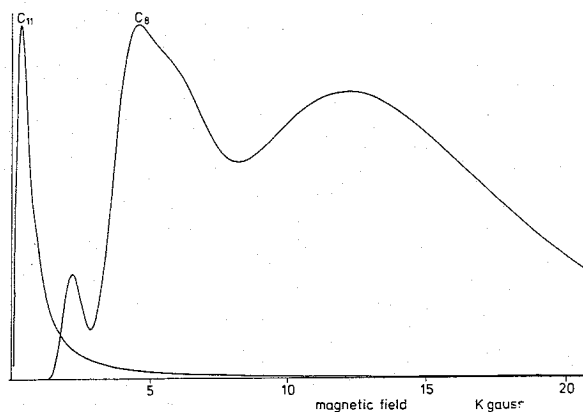


Fig. 2. CIDNP emission intensities from biradicals (C_8 and C_{11}) as function of the magnetic field, calculated according to eqs. (4) and (6) for $\delta = 0.3 \text{ \AA}$. Intensities are in arbitrary units.

rad/s, which give the best agreement between calculated and experimental maxima (table 1).

4. Conclusion

From our results it appears that the field dependence of biradical CIDNP can be related to the end-to-end distance distribution. With a model based on an exponential exchange interaction we simulated both the maximum and the general shape of the curves. Although the calculated widths are somewhat too large it appears that they may not be solely determined by the lifetime of the singlet state. Our model has a few shortcomings:

- (i) The dynamical behaviour of the biradicals is not described properly and we have to use a smoothing function.
- (ii) Electron spin relaxation and T_0-S and T_+-S mixing are neglected.

A model including all these effects, will be published later.

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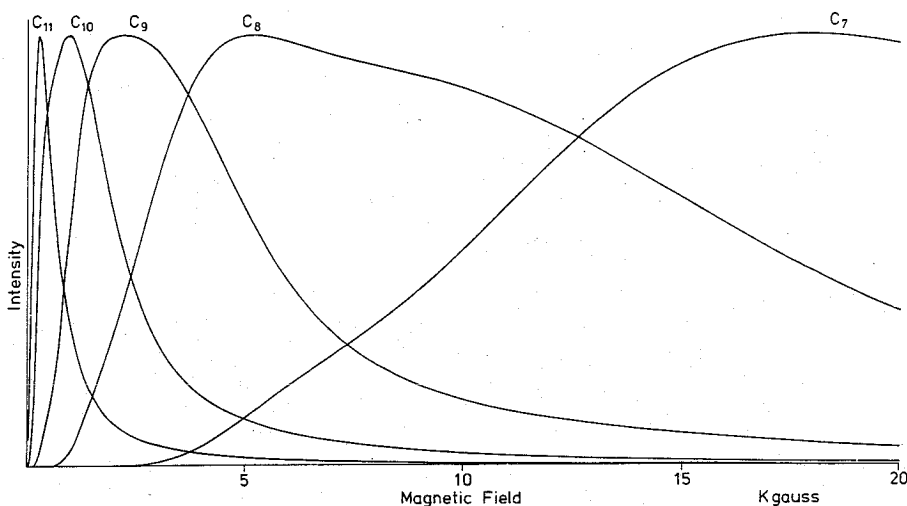


Fig. 3. CIDNP emission intensities from biradicals (C_7 – C_{11}) as function of the magnetic field, calculated according to eqs. (4) and (6) for $\delta = 0.7$ Å. Intensities are in arbitrary units.

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