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Low field photo-CIDNP in the intramolecular electron transfer in naproxen-pyrrolidine dyads.

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Photoinduced processes with partial (exciplex) and full charge transfer in donor–acceptor systems are of interest due to they are frequently used for modeling drug – protein binding. Low field photo CIDNP (chemically induced dynamic nuclear polarization) for these processes in dyads including drug - (S) and (R) naproxen and (S) N-methyl pyrrolidine in solutions with strong and weak permittivity has been measured. The dramatic influence of solvent permittivity on the field dependences of the N-methyl pyrrolidine ^{1}H CIDNP effects has been found. The field dependences of both R,S- and S,S-dyads in polar medium are the curves with a single extremum in the area of the S-T_+ terms intersection. Meanwhile, the CIDNP field dependences of the same protons measured in low polar medium present curves with several extrema. The shapes of experimental CIDNP field dependences with two extrema have been described using the Green function approach for the calculations of CIDNP effects in the system without electron exchange interaction. The article discusses the possible causes of the difference between the CIDNP field dependences detected in low-permittivity solvent with the strong Coulomb interaction and in a polar solvent.

Introducton

Electron transfer (ET) is the most widespread and universal chemical process, therefore ET attracts the permanent interest of researchers [1]. This interest extends in particular on the photoinduced electron transfer (PET). PET processes in linked systems, dyads and triads, are often used as a model of enzyme-substrate interaction, as well as an individual stages of photosynthesis [2, 3]. Dyads are also utilized for the simulation of binding between the medicine molecules and various transport proteins, since it is known that these processes often include donor-acceptor interaction [4]. The main attention in such studies is paid to the detection of the short-lived particles with partial and full charge transfer, namely exciplexes and radical ion pairs (RIP) and the clarification of these particles role [5, 6, 7].What is the first step in the chromophore excited state quenching: the formation of the exciplex, electron transfer or these processes occur simultaneously; is also widely discussed issue [2, 6, 7]. This is important because binding processes in biological systems involve the formation of intermediates with partial and full charge-transfer: charge-transfer complexes, ion pairs [1, 8]. Using photoinduced processes to simulate drug/receptor or drug/enzyme binding is based on the assumption that the donor-acceptor properties of paramagnetic particles would not be highly dependent on their generation pathway: photoirradiation or thermal electron transfer [9].

One of the ways to study the connection between exciplex and RIP is to analyze the effect of an external magnetic field (MFE) on time-resolved pulse photolysis or fluorescence [2, 10].

Another promising approach has been applied in the study of photoinduced processes involving partial (exciplex) and full (biradical ion) charge transfer in the dyad NPX-PYR ((*S*)-*N*-methyl-2-pyrrolidinemethyl 2 (*R*) or (*S*)-(6-methoxy-2-naphthylpropanoate – Chart 1) containing a widely studied anti-inflammatory drug naproxen and N-methyl pyrrolidine using CIDNP and time-resolved fluorescence techniques [11, 12].

The established reaction scheme includes the following short-lived intermediates: naproxen in local excited state, exciplex and biradical ion (Scheme1).

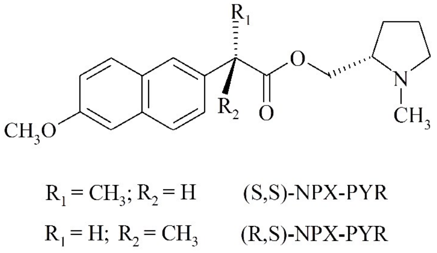

***Chart 1**. R,S and S,S Naproxen-pyrrolidine dyads.*

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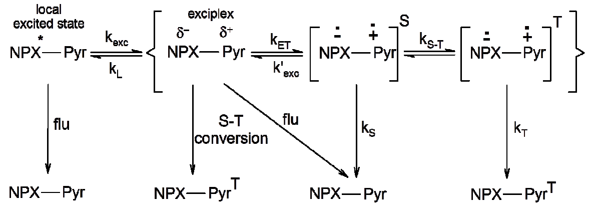

Scheme 1 Quenching of the excited singlet state of the NPX-Pyr dyad. The following symbols are used to describe the rate constants of separate stages: k_{exc} – local excited state transfer to exciplex; k_L – transfer of exciplex to local excited state; k_{ET} – electron transfer; k'_{exc} – transfer from biradical ion to exciplex; $k_{S\text{-}T}$ – singlet-triplet conversion in biradical ion; *flu* – fluorescence quenching; k_S and k_T – back electron transfer from the singlet and triplet spin state of biradical ion.

The analysis of the kinetics of fluorescence quenching allows one to get the rate constant of separated stages. So, in the solution with ε = 8.1 k'_{exc} =2.0 10^8 s^{-1} and 1.2 10^8 s^{-1}; k_{ET} =0.23 10^8 s^{-1} and 0.34 10^8 s^{-1} for (R,S) and (S,S) enantiomers of NPX–Pyr dyad, respectively. In polar solvent (ε = 37.5) k'_{exc} =2.6 10^8 s^{-1} and 2.0 10^8 s^{-1}; k_{ET} =1.29 10^8 s^{-1} and 1.62 10^8 s^{-1} for (R,S) and (S,S) enantiomers.

The states with partial (exciplex) and full charge transfer are, according to CIDNP data, in a rapid dynamic equilibrium that is in the nanosecond range [12].

It seems interesting to study the CIDNP effects in NPX-PYR dyads in low magnetic fields. Since the chemical polarization is a differential effect, unlike the integral MFE, one would expect a significant diversity in the CIDNP field dependences in the media with different permittivity due to the change in the exciplex/biradical ion ratio, as well as in the Coulomb interaction. Besides that, the abovementioned fast balance between the states with partial and full charge transfer in the naproxen-pyrrolidine dyad lets us expect the possibility of the impact of the rapid exchange between the exciplex and biradical ion on the spin evolution.

It should be noted that the influence of exciplex/biradical ion balance on the recombination probability of radical ion pair in the external magnetic field has been considered recently by G. Grampp with coworkers [2]. The authors take this into account as a reduction in the concentration of the radical ion pairs all along the transfer of the system to the exciplex's state.

We can expect the sensitivity of low field CIDNP to the Coulomb interaction strength due to the dependence of CIDNP intensity on the paramagnetic precursors lifetime in the zone of proximity between paramagnetic centers, where S and $T_{+,-}$ terms intercross.

The influence of these parameters on the width and location of the extremum on the field dependence of the biradical recombination probability has been shown earlier theoretically by using density matrix formalism [13]. In the present study this theoretical approach has been applied for the discussion of key factors which affect the CIDNP of the NPX-PYR dyad in low magnetic field.

Experimental section

The *R,S*- and S,S-NPX-PYR dyads have been synthesized as described elsewhere [4]. Naphthalene (Aldrich) has been sublimated prior to using. Triethylamine (TEA) has been distilled under zinc powder. Acetonitrile-d_3 (ACN, D99.9%) and benzene-d_6 (BZ, D99.8%) (both from Sigma-Aldrich) have been used in NMR and CIDNP experiments. Solvent permittivity has been varied by changing the proportion of the BZ/ACN mixture. The mixture of 0.7 ml of ACN (ε=37.5) and 2.4 ml of BZ (ε=2.3) has a dielectric constant about 10 [14, 15]. All samples were bubbled with N_2 for 15 min to remove dissolved oxygen just before photolysis. The concentration of the dyad has been varied from 0.2 to 2 mM.

The ^{1}H NMR and CIDNP spectra have been recorded at room temperature on homemade NMR spectrometer (300 MHz ^{1}H operating frequency, ($\tau(90^\circ)$ = 3.5 μs) with Oxford 7 T cryomagnet) [16]. The samples in 5 mm quartz tubes have been irradiated directly in the probe of an NMR spectrometer via flexible liquid optical light guide with a 90° prism on the top (20 pulses, 50 Hz, 308 nm).

Field-cycling unit with the fast digital positioning of a high-resolution nuclear magnetic resonance probe in a spatially varying magnetic field [16] has been used to measure CIDNP spectra. Field-cycling setup allows to vary magnetic field between 0.1 mT and 7 T and detect NMR spectra under sample rotation keeping high resolution 0.5 Hz. It is based on the step-motor-driven transfer of the whole NMR probe along the bore axis of the 7 T cryomagnet of NMR spectrometer down to an electromagnet (Helmholtz pair) located in the stray field.

The CIDNP effects are the signals with increased absorption or emission in the NMR spectra of the products of radical reactions. An analysis of these effects, described elsewhere, provides information about paramagnetic precursors of the products [19]. CIDNP effects presented in Figures 1-3 are the difference of the intensity of the polarized lines, detected during UV irradiation of solutions of the dyad and a related system naphthalene/triethylamine (TEA), and the intensity of the lines in the NMR spectra taken without irradiation.

Results and Discussion

CIDNP field dependences in NPX-PYR dyad and related system: Naphthalene + Triethylamine.

CIDNP field dependences for R,S- and S,S- isomers of dyad (Chart 1) have been measured in the magnetic field from 0 to 100 mT at two different solvent permittivities (in acetonitrile, ε_1 = 37.5, and in ACN/BZ mixture, ε_2 = 10). These two different permittivity values have been specifically chosen based on the analysis of the high field CIDNP dependence on the solvent dielectric constant and the exciplex fluorescence quantum yields. They correspond to the maximum and minimum contribution of the exciplex in the chemical polarization of formed in a biradical ion [10, 11].

Strong polarization has been observed for CH, CH_2, and CH_3 protons of N-methyl-pyrrolidine fragment (emission), and very weak emission for aromatic protons. CIDNP field dependences for N-CH_3 protons of *R,S*-NPX-PYR dyad are shown in Figures 1 and 2. The CIDNP effects of CH and CH_2 protons have similar field dependences.

The CIDNP field dependence of N-CH_3 protons of the NPX–Pyr dyads in low permittivity region demonstrates changes of sign (Figure 2).

For comparison we have measured low field CIDNP in related system naphthalene/TEA. Note, that the donor and acceptor redox parameters in the quenching reaction of the naphthalene excited singlet state by TEA are similar to those in NPX-PYR dyad [17, 18].

The low field CIDNP dependence of N-CH_2 protons of TEA is shown in Figure 3. This dependence is almost a mirror image of that for the dyad protons in low polar environment (Figure 2). Both these dependences have maxima at about 5mT and 25mT.

Note that the chemical polarization for all these three field dependences is formed in the biradical ion or RIP, with similar magnetic resonance parameters (HFI constants of CH_2 and CH protons of the methyl-pyrrolidine radical cation are about 2.9 – 5.8 mT, for CH_3 protons it is about 2.9 mT, and HFI constants of CH_2 protons of TEA radical cation are 2.19 mT [19, 20]).

We can suggest that the different signs of the extrema in the CIDNP field dependence of the dyad protons at weak permittivity and of TEA CH_2 protons at high permittivity are a result of the difference in the ratio of the rate constants of back electron transfer (BET) from the singlet and triplet spin states of the RIP and biradical ion, k_S and k_T (see Scheme 1). There are reference data that k_T is higher than k_S in the act of BET in RIP "naphthalene/TEA" in the polar environment [21]. The prevalence of opposite sign of CIDNP in dyad NPX-Pyr has been explained previously by the contribution to the value of k_S from the additional channel of the dyad excitation quenching [12]. This channel is fast reversible transition between biradical ion and singlet exciplex.

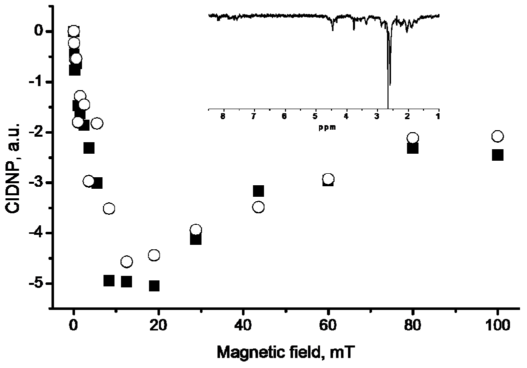

Figure 1. CIDNP field dependences (low field region) for N-CH_3 protons (2.6 ppm) measured after laser irradiation (308 nm) of 2 mM solutions *of R,S*- (■) and *S,S*-NPX-PYR (○) dyads in ACN (ε = 37.5). Insert shows the CIDNP effects of N-methyl pyrrolidine protons in *S,S*-NPX-PYR dyad detected in magnetic field 12.5mT.

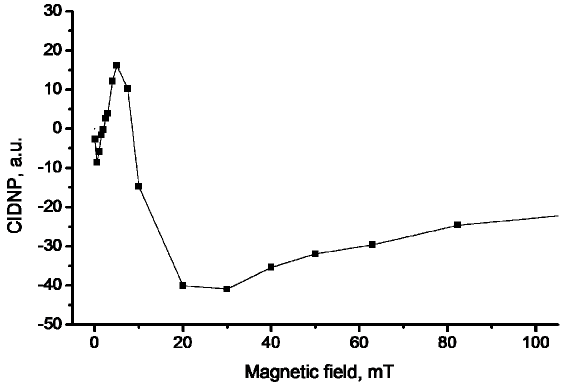

Figure 2. CIDNP field dependence for N-CH_3 protons measured after laser irradiation (308 nm) of 2 mM solution *R,S*-NPX-PYR dyad in ACN/BZ mixture at ε = 10.

The comparison of the field dependence extrema positions with the HFI constants values in the paramagnetic precursors of polarized products allows us to draw some conclusions. So, the CIDNP field dependence for the NPX–Pyr dyads in the ACN, which has one extremum whose position exceeds the magnitude of HFI constant twice, includes the contribution from electron exchange interaction (J). On the contrary, both dependences with several extrema (fig.2 -3) are similar to those which are usually observed for products of RP without sizeable J [19].

Next we provide the theoretical analysis of the field dependences to explain the dramatic difference between the dyads field dependences in the media of high and weak permittivity, and to explain why the CIDNP field dependence of the dyad in the conditions of strong Coulomb interaction (weak permittivity) is similar to that in the product of diffusive quenching in a polar solution which does not include electron exchange interaction.

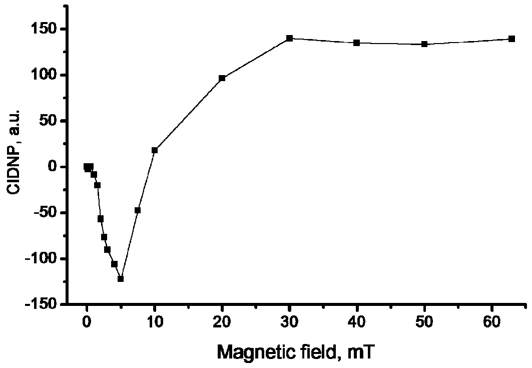

Figure 3 CIDNP field dependence (low field region) for N-CH_2 protons of TEA measured after laser irradiation (308 nm) of 2 mM solutions of naphthalene in the presence of 10 mM TEA in CD_3CN

CIDNP field dependence theoretical description.

For the theoretical description of the CIDNP effects in dyad we have been applied Green's functions method. This approach is widely used to describe the magnetic and spin effects in radical reactions [22, 23]. In a modified version it has been successfully used in particular for the theoretical description of the spin effects (CIDNP, magnetic effect) in biradical [18]. In this approach the recombination probability or CIDNP effects are described through the spin and molecular dynamics of the radical centers.

The recombination probability of pairs is given by a spin state vector $\hat{w}$:

$$\hat{w} = \hat{U}(1+\hat{g}\hat{U})^{-1}\hat{g}\rho_0 \qquad (1)$$

Matrix $\hat{U}$ describes the recombination rate constant of a particular spin state; the matrix $\hat{g}$ describes the spin dynamics of the radical centers averaged relative movement and the residence time of a pair in the reaction zone; ρ_0 – is the initial density matrix of the pair.

When calculating the CIDNP effects we restrict one flip flop transition of electron and nuclear spins. The recombination probability of the singlet state at the start from the singlet in this case is described by formula (2):

$$w^S = \frac{U_0\tau_S}{1+U_0\tau_S} \qquad (2)$$

Here U_0 is a quasi-monomolecular constant of recombination rate, and τ_s – the residence time of a pair in the reaction zone in the singlet state. The recombination probability in the singlet state at an initial triplet state can be written as (3):

$$w^T = \frac{1}{3}\frac{U_0(\tau_r-\tau_S)}{1+U_0\tau_S} \qquad (3)$$

Here τ_r – is total residence time of the pair in the reaction zone.

It is known that the change of the reaction state from singlet to the triplet state results in the changing of only the sign of CIDNP but not the shape of the field dependence [24]. For the purposes of this study this fact is crucial since, as described above, both the singlet and triplet spin states of biradical ion participate in the quenching of dyad's excited state [11].

Below the calculated CIDNP field dependences in the case when recombination proceeds simultaneously from the singlet and triplet spin states of radical pair (RP) are presented. Here the electron exchange interaction is not included in the calculation (Figure 4).

As it can be seen from Figure 4, the position of the extremum in the field dependence of the CIDNP practically does not shift, and contributions of recombination channels can be considered as additive. So, in further calculations we will consider that the reaction proceeds only from any one state.

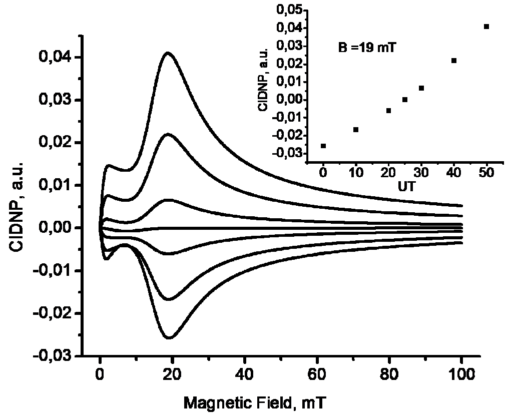

Figure 4. Calculated CIDNP field dependence for RP with one magnetic nucleus with arbitrary spin at the different contributions of the recombination from the singlet and triplet states. I = 3/2, (U_S + U_T)τ_r =0.5. From the bottom to up – $U_T\tau_r$ =0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5. In the inset – the value for CIDNP at the magnetic field 19 mT from the contribution of the triplet recombination channel ($U_T\tau_r$).

In order to simulate the experimental field dependences shown in Figures 2 and 3, we have used the following simplification: instead of biradical ion containing many magnetic nuclei, we have calculated a radical pair with one nucleus with spin **I**.

The calculations in Figure 5 have been made for the diffusion motion of the radicals. The initial spin state of the RP and the reaction state have been assumed as a singlet. Note that CIDNP sign alterations are characteristic for RP with $I \geq 3/2$. A similar pattern has been obtained for the exponential model of radicals relative motion under the condition that RP's lifetime is large enough [25].

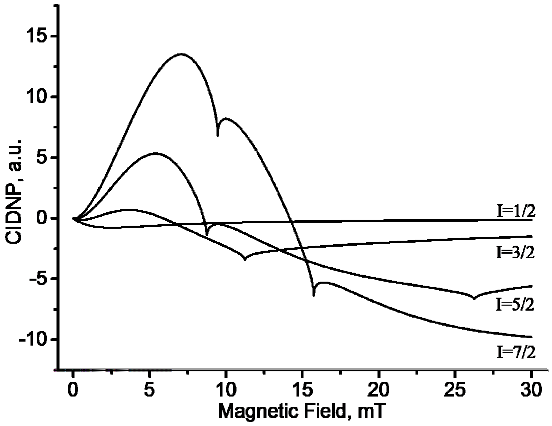

Figure 5. Calculated dependence of CIDNP of product from RPs with different values of the nuclear spin **I** on the magnetic field strength for HFI constant a=3 mT.

Similar field dependences can be obtained also under the following assumptions. An ensemble of RP containing six equivalent protons is equivalent to 4 subensambles of RP, which have magnetic nuclei with spins I = 3, 2, 1, 0. Figure 6 shows the field dependence of the CIDNP for RP containing 6 equivalent protons.

The shape of the CIDNP field dependences in Figures 5 and 6 is in a qualitative agreement with the experimental dependence, registered for the protons of dyad in solvent with weak permittivity (Figure 2), as well as for CIDNP detected in the diffusion quenching of excitation in the related system (Figure 3). For RPs which contain one magnetic nuclei with I = 3 (or six equivalent protons) the first extremum is predicted in the fields B ≈ 2a, and the second one with the opposite sign in the field B ≈ 6a. Experimental field dependences show extrema located at 5 mT and 25 – 30 mT (Figures 2 and 3).

The same field dependence is also predicted by the well known semiclassical approximation for these radical pairs [26]. This is the case when the effective constant HFI (a_{eff}) of the detected radical exceeds significantly a_{eff} of the partner radical. Polarized NMR signal in the studied interval of magnetic fields involves all of alpha CH_3, CH_2 and CH protons from the N-methyl pyrrolidine radical cation in which HFI constants vary in the range 2.9 – 5.8 mT [19], and the partner radical, which is the substituted naphthalene radical anion, has a_{eff} ~ 0.5mT [27].

Thus, the comparison of the theory with our experimental data shows that CIDNP in the linked system in low-polar medium (Figure 2) can be described under the assumption of strong electron exchange interaction during contact and zero electron exchange interaction between contacts, as in the case of separated radical pair in high-polar media (Figure 3). To understand why in the linked system, in low-polar solvent where the Coulomb interaction might play an essential role, the contribution from the electron exchange interaction does not manifest itself, we consider two specific regions where the singlet–triplet transitions take place in low magnetic field (Figure 7).

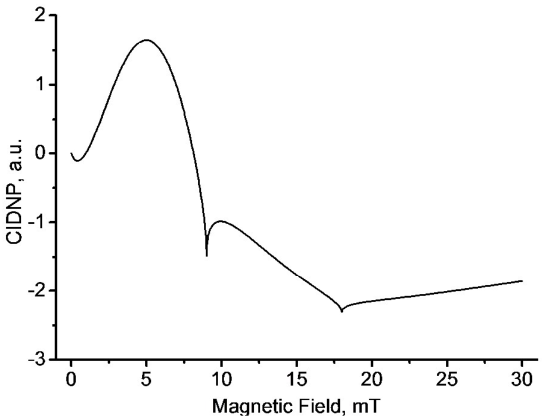

Figure 6. Calculated dependence of CIDNP of product form RP containing 6 equivalent protons on the magnetic field strength for HFI constant a=3 mT.

As is well known these two regions play key roles in the CIDNP formation (Figure 7). In region (1) singlet and triplet terms are close to each other, and electronic exchange interaction is usually insignificant. In region (2) the intersection of the singlet with one of the triplet terms (T_+ or T_- depending on the sign of the exchange interaction) is situated. In separated radical pairs the formation of chemical polarization usually occurs in region (1). In region (2) these pairs are typically located for a very short time therefore this region has no contribution to the CIDNP. Nevertheless, there are many systems where the main contribution to the polarization comes from region (2). Among them a typical example is the biradicals derived from the cyclic ketones [28, 29]. The relative motion of the radical centers in these biradicals is determined by the dynamic behavior of the polymethylene chain, namely its conformational transitions. The S–T transition probabilities and the distance distribution between the radical centers in different conformations are determined by the corresponding potential barriers and the changes of total energy. When the centers are very close, the probability is small, further it grows and reaches a maximum at relatively large distances, and then decreases again. The qualitative shape, of the dependence is shown in Figure 7.

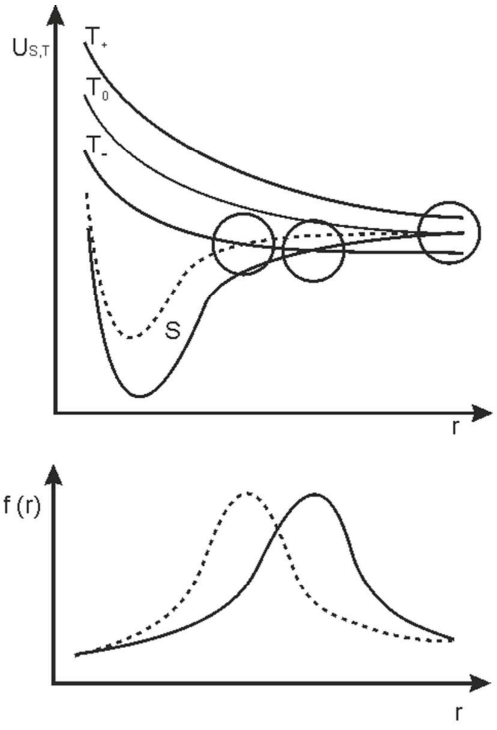

Figure 7. At the top - the dependence of the singlet and triplet energy levels of biradical on the distance between radical centers. Two transition zones 1 and 2 correspond to the area of weak and the strong exchange interaction. At the bottom – the probability of the distance distribution between radical centers in the biradical at different permittivities: the solid line corresponds to high permittivity and dotted line refers to low permittivity.

The CIDNP would have the maximum in a magnetic field, where the intersection of S and $T_\pm$ terms coincides with the maximum of the distribution function (f_r). Region (1), where the singlet and triplet terms are close to each other, usually makes a small contribution to the biradical polarization. But in some cases the situation may be changed dramatically. For example, in the study of the CIDNP in a strong magnetic field (4.7 T) region "1", on the contrary, is the main source of the polarization, since the effective transition in the area of terms intersection becomes small due to the strong increase in the slope of terms intersection [30].

The change between the contribution to the CIDNP from regions 1 and 2 in the biradical ion can also occur in the presence of acceptors [31].The influence of acceptor on the S-T evolution is described in detail in the RP theory and has been studied experimentally [32, 33]. Basically it comes down to a reduction in the lifetime of RP. In the case of biradicals the acceptors action leads to a reduction in the residence time of the biradical in both regions 1 and 2. In accordance with the general consideration the prevailing influence of acceptors on region 1 would be expected: it is known that in free radical reactions a decrease of CIDNP from distant trajectories occurs primarily. However, the experimentally observed shift of field dependence extremum to the strong field shows that in the case of biradicals the situation is different. This fact can be explained if we take into account that the residence times of biradical in regions 1 and 2 are different. In the region of intersection of the terms (2) the system is spent less time than in region (1) where the exchange interaction is much smaller than the HFI. The CIDNP effects in region 1 for long lived RP, to which most biradicals belong, are often averaged: case ($A\cdot\tau \geq 1$). In this case, shortening the lifetime can lead to growth of the CIDNP due to the decrease in the ($A\cdot\tau$) value. At the same time chemical polarization arising in region 2 can only decrease. Thus, the result of the acceptor influence on the field dependence of biradical described in [26] is a manifestation of the CIDNP formed in region 1, where electron exchange interaction is negligible.

Some insight into the contribution to the observed CIDNP from regions 1 and 2 can be obtained on the example of the CIDNP on protons of the NPX-PYR dyad (Figure 8). This figure compares the scale of effects in weak and strong fields (4.7 T) in the solution with high and low dielectric constant. The figure shows that for field dependence obtained in solution with high ε the region of $S–T_+$ crossing indeed makes a significant contribution to CIDNP, while in the field dependence for weak permittivity the contribution from region 1 prevails.

It is worth noting that a similar situation also occurs in the optically detected EPR spectroscopy and MARY spectroscopy in non-polar systems [34]. In this case for the theoretical description of the magnetic field influence on the recombination of charged particles generated by radiolysis in the Coulomb field hyperfine interaction is always sufficient, i.e., the exchange interaction does not manifest itself, due to the short time that the system spends in the term crossing region 2.

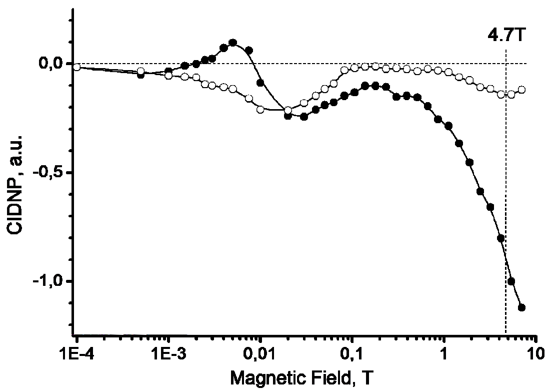

Figure 8. CIDNP field dependence of N-CH_3 protons measured after laser irradiation (308 nm) of 2 mM solution *R,S*-NPX-PYR dyad in ACN (○, ε=37.5) and ACN/BZ mixture (●, ε = 10) on external magnetic field strength (*B*). The ratio of field dependences at 4.7 T corresponds to the literature values from CIDNP dependence on solvent permittivity [11].

In accordance with the picture considered above, it seems to us that the appearance of the CIDNP from zone “1” in the field dependence of NPX-PYR dyad in low polar solvent is also possible for several reasons. This is due to the Coulomb attraction between the paramagnetic centers of the dyad and the fast exchange of biradical ion with exciplex. It is also possible to expect that this exchange will be manifested in low polar environment, where the contribution from exciplex is maximal [12].

So, with decreasing the permittivity the strength of the Coulomb attraction, which strongly influences the position of the maximum of the distribution function, will increase and the maximum of the distribution function in Figure 7 has to be shifted to shorter distances between the radical centers. It would result in the shift of the extremum in the CIDNP field dependence to higher magnetic fields.

Besides that the slope of the intersection of the terms is increased at shorter distances and, therefore, the probability of transitions in the area of intersection of the terms decreases (Figure 7). The CIDNP intensity in this case can be significantly reduced.

Even more important is the increase in the probability of the BET with decreasing distance between the radical centers. The acceleration of BET can lead to the destruction or the severe reduction of the CIDNP due to the decrease of S-T evolution time. It was shown that in the NPX-Pyr dyads the dynamic equilibrium between biradical ion and exciplex significantly accelerates BET from its singlet spin state [12].

According to the work [10] it occurs due to the decay of the exciplex through fluorescence, intrinsic singlet – triplet conversion and the transfer to the local excited state. All these processes also accelerate the biradical ion decay (scheme 1).

Since the rates of transitions between the states with partial and full charge transfer are in the nanosecond range, one can expect that the fast exchange between the exciplex and the biradical ion would influence the S-T evolution. In this case the transfer of the system into exciplex and its return to biradical ion would be accompanied by the loss of spin correlation in the state with full charge transfer [32, 33, 35]. This results in a reduction of the contribution to CIDNP from the near trajectories (region 2, Figure 7) and leads to the predominance of the CIDNP from region 1 formed at long distances.

These considerations are fully confirmed by the theoretical description of the experimental field dependence of CIDNP in the NPX-Pyr dyad in low-polar solvent (Figure 2) which did not take into account the electron exchange interaction.

And finally, the CIDNP field dependences for the R,S and S,S diastereoisomers of NPX-PYR dyad in polar medium (ACN, Figure 1) contain only one extremum with the negative sign.

The origin of the CIDNP extremum for S,S and R,S diastereomers are located at magnetic fields 12– 20 mT (Figure 1), which are several times greater than the HFI. It can be explained by the intersection of S and T_+ terms with a moderate electron exchange interaction between paramagnetic centers in biradical ion. According to Kaptein rules [24], the negative sign of CIDNP with the singlet precursor multiplicity will be correspond to the positive sign of electron exchange interaction.

Thus, it has been demonstrated that the low field CIDNP dependence on the magnetic field strength varies greatly depending on solvent permittivity and the exciplex quantum yields.

Conclusions

This study shows that the difference in molecular and spin dynamics in a linked system in the media of strong and weak permittivity leads to dramatic differences in the CIDNP field dependences in low magnetic fields. The CIDNP effects in these fields demonstrate high sensitivity to the Coulomb interaction and the rapid dynamic equilibrium between states with partial (exciplex) and complete charge transfer (biradical ion).

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